THE FORMS OF COMBINATION OF CU, NI AND ZN IN ANAEROBIC SEWAGE SLUDGE

Thesis submitted for the degree of Doctor of Philosophy.

Roger MacNicol

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Department of Plant Science

University of Oxford

ABSTRACT

Roger D MacNicol
Exeter College

DPhil
Trinity 89

The forms of combination of Cu, Ni and Zn in anaerobic sewage sludge

As a first step in understanding the chemistry of toxic elements in sludged soil, this thesis presents a comprehensive model of their chemistry in the digester.

A review of the literature had shown that heavy metals were likely to be held in 3 pools: as precipitated and detrital mineral phases 'Particulate'; as complexes with the flocculated biomass 'Biofloc'; and as complexes in solution 'Soluble'.

A simple pragmatic fractionation procedure has been offered to separate these 3 pools based on their physical properties in water. A mass-balance between the pools showed that the 'Particulate' fraction held only 5-16% of the heavy metals but contained them in the highest concentration. The 'Biofloc' held 82-94% of the heavy metals.

The 'Particulate' material was subdivided by density separation and examined by a combination of analytical SEM and XRD. Thirty-four minerals were identified by XRD, many of which were detrital. Secondary precipitates on the surface of detrital minerals were revealed by the SEM; of these only the sulphides were found to contain detectable levels of heavy metals. Eleven minerals were identified in the 'Biofloc', of which most were clays.

The fractionation scheme defined 2 fractions that could hold heavy metals by complexation. The 'Soluble' had a CEC of 8.8 meq/gm and the 'Biofloc' 4 meq/gm. Complexation by the heavy metals and a few other important cations was measured.

A thermodynamic model was built which describes the possible solution species, mineral phases and complexation by the biomass in terms of a set of 33 primary components. This model was solved by computer for an 'average' sludge based on published analyses, and considered 313 solution species, 42 exchange reactions and 129 possible minerals. The predicted speciation was broadly in line with observations and suggested that the majority of the heavy metals separating with the 'Biofloc' would have been held as fine enmeshed sulphide precipitates.

The model may be used with existing programs such as MINEQL and GEOCHEM. Preliminary studies have shown that with a few additions the model may be used to describe the heavy metals in sludged soil.

ACKNOWLEDGMENTS

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Several people provided technical help with complicated equipment. Dr M Wilson from Macaulay did the powder X-ray diffractometry of the clay minerals in the finer fractions, Dr Juan Cegarra did the IR analyses of the 'Biofloc' and 'Colloid', and Dr Duncan Campbell did the ICP analyses for me.

Work with two people was of a more collaborative nature. Dr Barbara Cressey helped with the use of the analytical scanning electron microscope, and did the Guinier X-ray diffractometry for me.

I worked with Dr Philip Fletcher of Schlumberger Cambridge Research on the development of the techniques used for measuring complexation by the organic fractions. Dr Fletcher measured the complexation of the 'Soluble' fraction by ISE for me. I also thank him for making the program SCRAM available to run the model.

Alex
PEATTIE+TAYLOR

ALEX, DID YOU KNOW THAT IN SOME PLACES IN THE BRITISH ISLES THEY PUMP UP TO 40 MILLION GALLONS OF UNTREATED HUMAN SEWAGE INTO THE SEA EVERY DAY?

NEWS

ASTOUNDING, ISN'T IT?

FACTS LIKE THAT SHOULD BE BETTER PUBLICISED...

...IF WE WANT OUR CHILDREN TO GROW UP HEALTHY AND NORMAL.

...WHEN I THINK HOW RACKED WITH GUILT I WAS FOR YEARS BECAUSE I ONCE SECRETLY WEE'D IN THE SEA AT MARGATE...

A DROP IN THE OCEAN, CLIVE.

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Units used in this Thesis

Concentrations of heavy metals in dry solids are given as mg kg^{-1}

(milligrams per kilogram)

Concentrations of heavy metals in wet sludge are given as mg $litre^{-1}$

(milligrams per litre)

Total quantities of heavy metals are given as mg

(milligrams)

Densities of minerals are given as gm cm^{-3}

(grams per cubic centimetre)

Sludge applications on land are given as tonnes ha^{-1}

(tonnes per hectare)

Heavy Metals

Where the phrase 'heavy metals' is used in this thesis it means Copper, Nickel and Zinc only, unless otherwise stated.

List of abbreviations used

Methods and technical terms:

SEM	-	Analytical Scanning Electron Microscope
XRD	-	X-Ray Diffraction
IR	-	Infrared spectroscopy
BOD	-	Biological Oxygen Demand
SOM	-	Soluble Organic Matter
OM	-	Organic Matter
CEC	-	Cation exchange capacity
AA	-	Atomic Absorption Spectroscopy
ICP	-	Inductively Coupled Plasma Spectroscopy
ISE	-	Ion-selective Electrode
ASV	-	Anode Stripping Voltametry
USD	-	Ultrasonic dispersion
ESCA	-	Electron spectroscopy for chemical analysis
IAP	-	ion activity product

Organisations:

TWA	-	Thames Water Authority
NWC	-	National Water Centre
DoE	-	Department of the Environment
ADAS	-	Agricultural Development and Advisory Service
NAAS	-	National Agricultural Advisory Service
CAB	-	Commonwealth Agricultural Bureau
BGS	-	British Geological Survey
EHS	-	Experimental Horticultural Station

SETTING THE SCENE

The water industry currently supplies 15,000 million litres of water per day, of which 40% is taken for domestic use by the 99% of dwellings in England and Wales that have a piped supply (National Water Council, 1978). Of these, 95% are connected to the public sewers; this is a high proportion when compared with 88% of dwellings in the Netherlands, 80% in Germany and 75% in the USA. A total of 4,440 sewage works provide secondary treatment for 80% of the catchment and remove 77% of the total polluting load, measured as tonnes biological oxygen demand (BOD).

Sewage treatment involves settling out the suspended solids as a slurry, which must then be disposed of. The quantity involved has been estimated as 1,100,000 tonnes dry solids per annum of primary sludge, or 26 kg per head per annum for the 95% of the population served by the public sewers.

After settlement of the solids, the remaining water (confusingly known as settled sewage) must be treated to reduce its potential environmental impact, and to meet the Royal Commission standard of 20 mg litre^{-1} BOD. The putrescible content can be reduced by the use of micro-organisms which consume it. In the smaller works the most common method of secondary treatment is the use of percolating filters, while in larger works a simplified form of the activated sludge process is used. Finally, where the output of a treatment works forms a large part of the flow of water-supply rivers, the quality of the water being returned can be improved by tertiary treatments, such as sand filters and microstrainers.

The raw slurry from settlement must also be treated before disposal. Again, the putrescible content is reduced by digestion with micro-organisms. The most common method is the activated sludge process, but since the 1950s larger works have started to use anaerobic digestion. These processes produce a more concentrated sludge, with a lower environmental impact.

There are four main options open to the water authorities for the disposal of the concentrated digested sludge. It can be spread on farmland as a fertilizer, dumped for landfill and reclamation, dumped at sea, or incinerated. Of these, incineration has proved too costly for all except the most heavily contaminated industrial sludges. Disposal to land and sea are being controlled by ever stricter EEC regulations, and there is a shortage of suitable landfill sites. The national breakdown for sludge disposal is given below:

Table 1.1 National sludge disposal (1975)

Method	percent
Spreading on farmland	46
Dumping as landfill	31
Dumping at sea	20
Incineration	3

(DoE, 1978)

The proportions for each water authority vary considerably, with geographical location and other factors. In 1975, the figures for Thames Water Authority (TWA), were:

Table 1.2 Sludge disposal by TWA (1975)

Method	Dry solids (tonnes)	Percent
Spreading on farmland	125,000	47
Dumping as landfill	40,000	15
Dumping at sea	99,000	37
Incineration	2,000	1

(ibid)

Faced with increasing environmental concern from within the authorities, from pressure groups, and from legislation, the authorities are facing an increasing problem. This particular thesis forms part of a continuing project, which has been funded by TWA, to look specifically at the problem of the disposal of anaerobically digested sludge onto farmland.

Anaerobic digestion

Briefly, the incoming raw sewage flows over a grit trap to stop large mineral fragments from soil run-off and industrial sources; these are removed and used for landfill. It is then screened to remove rags and other large organic particles which are removed, comminuted, and returned to the main flow. The raw sewage is then sedimented on a continuous flow basis, with a typical minimum retention time of 2 hours. This removes 50-70% of the suspended solids, and a travelling scraper periodically removes the settled matter to a hopper from which it can be drawn off. This primary sludge is usually a yellowish-grey colour and has a characteristic, sour, objectionable odour.

Treatment of the primary sludge is based on the use of micro-organisms to consume the bulk of the putrescible organic pollutants, converting them to CO_2 and water. It is the putrescible material which imposes the main biological load on the environment, and which causes the objectionable odours.

At Beckton, sewage is treated by anaerobic digestion (although the activated sludge process is used for secondary treatment of settled sewage). The activated sludge process depends upon the forced aeration of the settled sewage together with a seed of activated sludge. The product of this is a flocculated biomass which readily settles out. Some of the activated sludge is returned upstream to act as a seed for the next cycle, while the surplus activated sludge is mixed with primary sludge to form the raw feed for the anaerobic digesters.

If faecal matter is left to decompose in a stagnant pool, an anaerobic fermentation sets in, producing H_2, CO_2 and volatile acids; digestion will proceed until all the decomposable matter has been converted. This leaves a thick, viscous, evil-smelling sludge with a pH of 4-5. The sludge is not easily dewatered and therefore offers little reduction in volume; it is also difficult to dispose of. This process is termed 'acid fermentation'.

In contrast, if the sludge is seeded with a suitable quantity of methanogenic micro-organisms under conditions where it can become and remain anaerobic, a two-stage fermentation will set in. The methanogenic biomass utilizes the volatile acids and H_2 produced during acid fermentation to produce CO_2 and CH_4. This leaves a dark sludge which does not smell offensive; it is readily dewatered and therefore more easily disposed of. The sludge has a final pH of

7-7.6, and the process is termed 'alkaline fermentation'. Acid fermentation is used for only a few industrial wastes, while it is alkaline fermentation that is used for the treatment of normal domestic sewage (Imhoff et al, 1971).

Digested sludge is a complex mixture of a wide variety of components, and the heavy metal content can vary over several orders of magnitude. In addition to its detrital content of minerals from soil and industry, and organic residues like paint, plastics, plant residues and hair, it contains many secondary components added by the digestion process, such as precipitated minerals, amorphous degraded plant matter and the digester biomass.

Sludge disposal to land

Anaerobic digestion produces a sludge particularly suitable for disposal onto agricultural land: because of the reduction in unacceptable odours, because many potential pathogens which could cause environmental health problems have been killed off, and because of its useful content of N, P and organic matter. However, sludge may contain several potentially phytotoxic elements: B, Mo, the heavy metals, Cd, and N when in excess (Johnston, 1981). Of these, B, Mo and N are mobile and soon washed out of the soil. Therefore, the amount of digested sludge that may be spread onto agricultural land depends, in the short term, on the immediate phytotoxicity of any elements in the sludge, and potential contamination of groundwater by mobile elements. In the long term it will depend on whether, and how rapidly, the non-mobile heavy metals in the sludge will revert to the non-toxic forms in which they usually occur in soil. This is not known. The aim of this

project was to ascertain, directly or indirectly, whether official guidelines should or should not make allowance for the reversion of heavy metals from sludge to immobile, non-toxic forms.

Guidelines for sludge disposal

Adequate guidelines are needed to allay farmers' fears about possible ill-effects of the sludge they are using. Since the report of the working party on Sewage Disposal (Jeger Report, 1971), three sets of guidelines have been published. These are ADAS-10 (Chumbley G C, 1971) and the DoE/NWC Standing Technical Committee Reports No 5 (DoE, 1977) and No 20 (DoE, 1981).

ADAS-10 was concerned solely with the problems of B, Zn, Ni and Cu phytotoxicity, and made only brief mention of dangers to grazing livestock.

The 'Working Party Report' (1977) widened the recommendations to cover other elements, and offered a comprehensive discussion of environmental problems such as water-pollution, public nuisance and the heavy metal build-up in the human food chain. The discussion was widened still further in the 'Report of the Sub-committee on the Disposal of Sewage Sludge to Land' (1981). This report changed few recommendations but shifted its emphasis towards problems of the environment and human food chains, and in particular to the accumulation of cadmium.

The three sets of guidelines drew on the information available at the time. ADAS/NAAS provided the results of advisory experience, pot-trials using inorganic metal salts, and work with mixed sludges at the Lee Valley and Luddington Experimental Horticulture Stations (EHS).

ADAS-10 was based solely on the first two sources. The pot-trials were carried out by NAAS at Wolverhampton and other centres (Webber, 1972), and used to set the levels initially recommended. Between 1971 and 1974 ADAS carried out further pot-trials with inorganic metal salts to investigate the interactions when more than one metal was present (Davies, 1980). However, the 1977 Report points out that trials with inorganic salts may not be applicable to sewage sludge (para 3.2.28) since the form of the metals in sewage was unknown and was unlikely to be that of a simple salt. Work in the USA has also used sludges spiked with metal salts, but there is the same uncertainty. It was in answer to this problem that a far-sighted set of trials at Lee Valley and Luddington EHS was carried out between 1968 and 1973. Its first results were available for the 1977 Report. The results of a continuation study in 1976-77 on the long-term effects in these trials were available for the 1981 Report. The importance of these trials lay in their use of sludges from industrial areas, each heavily contaminated with one metal, blended with a relatively uncontaminated rural sludge, to give various natural levels of heavy metals. This met the criticism of earlier trials. The trials suggested that crop yields might be reduced by heavy metal loads lower than the level set by ADAS-10, but the interpolation of toxicity thresholds is difficult.

The limit to the amount of heavy metals that may be added to the soil was defined in terms of a 'zinc equivalent'. This is the sum of Cu, Ni and Zn each weighted by their relative toxicities, as inferred from the pot-trials. The permissible zinc equivalent of 250 ppm has remained unchanged throughout successive guidelines, but the interpretation of what it means has varied. Appendix 2 compares

the guidelines, and the implications of the changes in interpretation are discussed.

So far the results of short-term field trials (2-4 years) on the immobilization of sludge heavy metals in soil have been too inconsistent to justify extrapolation to periods 50-100 years ahead. The inconsistencies suggest that the early stages of sludge-soil interaction are mainly microbial. It does seem, however, that though a heavy metal may occur in different forms of combination in different sludges, it will end up in the same form of combination after the sludges have interacted with the soil for 2-4 years (Beckett et al, 1983), and that the character of this does not depend very much on the nature of the soil. It does not follow that the compounds produced by this stage will not be transformed further over longer periods.

There are a few long-term field trials still active but all of them lack some part of the data required. It is unfortunate that the best of them, the Lee Valley and Luddington trials, are apparently being allowed to lapse after 20 years.

The potential of data from so called historic sites (usually 'sewage farms'), that have received very large quantities of heavy metals over long periods, has not yet been fully exploited. The data may be difficult to interpret because details of the quantities and analyses of the sludges applied may not have been recorded. But the toxicity of the heavy metals could reasonably be compared with similar native levels of heavy metals and with those from recently applied sludge.

Rationale behind this thesis

The guidelines for sludge disposal provide a reasonable degree of protection against short-term hazards, for both the farmer and the environment. The re-interpretation of results in terms of total levels of heavy metals in the soil to extractable levels (see Appendix 2) provides some allowance for differences in soil chemistry. But we are no nearer understanding the long-term (50-100 years) hazards from sludge in soil.

The problem of short-term hazards has been adequately solved by empirical research. However, we do not have 50-100 years to solve the long-term problem on this basis, and in the meantime the water industry is being squeezed between costs and guidelines. The simplest case would be to assume that there will be no decrease in heavy metal toxicity. If this were so, all the sludge that could be spread on a given field could be added in a single application (while bearing B and N toxicity in mind!). This would result in considerable savings for the industry in transport costs. But we have already seen evidence against this assumption. Heavy metals native to the soil are less toxic to plants than added forms, and may also be less 'available', as measured by extractants. Is it unreasonable to assume that heavy metals added to the soil in sludge may, in time, revert to these less toxic forms? If this is the case, it would be better to apply sludge in small regular quantities, resulting in the end in far higher total sludge additions. This would prove valuable where land for sludge dumping was at a premium. Meanwhile, those of a more cautious nature are suggesting that toxicity and 'availability' may increase with time, presenting future generations with infertile soil and reduced crop

yields. This could occur if the pH of the soil were allowed to fall through bad management, because of acid-rain, or because of unforeseen long-term chemical processes. An intermediate problem could also arise when a large proportion of a toxic element had been added to the soil in organic complexes, and subsequent oxidation of the organic matter released the element, causing crop-yield depression.

Clearly, the chemistry of the processes involved must be elucidated. It is likely that the chemistry may be affected by the forms of combination of the heavy metals added to the soil, both because of kinetic factors and because of the other elements added to the soil with the sludge. Therefore, we also need to understand the forms of combination of the heavy metals in sludge before it is added to the soil, and this in turn will entail an understanding of the chemical processes occuring in the digester.

If we follow the genesis of the heavy metal compounds from the raw sludge, through the digester, via lagooning, drying and transport until the sludge is ploughed into a field with soil of arbitrary composition, it is clear that the place in the system with the fewest variables is the digester. The digester serves to dampen out daily fluctuations in the composition of the raw sewage, and to release many of the cations from their initial forms of combination. It is logical to start by attempting to understand the chemistry of the heavy metals in the digester, and their forms of combination as they leave the digester. An ideal sequence of events would be:

1) Identify the forms of combination of heavy metals in the digester, and the factors controlling them.
2) Follow the changes to these forms as the sludge leaves the

anaerobic environment of the digester, and becomes oxidised on contact with air.

3) Follow the changes to these forms as they interact with the soil environment; first with single soil components and then together.

4) Compile the understanding gained from steps 1-3, to form a coherent chemical model of sludge in soil, sufficiently comprehensive to provide a base for long-term predictions.

In view of the complexity of the system and the multiplicity of ions present, such a model would have to be created on a computer. The number of simultaneous equilibria to be calculated would be beyond the use of hand-held calculators. More importantly, a model must be able to answer 'What if?' questions, for example, 'What would be the effect of allowing the pH of the soil to rise by 0.5 pH units?', or 'What would happen if a field became water-logged and anaerobic?'. Computers offer the ability to recalculate a problem quickly with chosen variations in the data. Similar computer models that attempt to solve the simpler problems of the soil solution already exist, although they still have limitations, particularly in their inability to consider kinetic factors. A good example of this kind of program is GEOCHEM (Sposito, 1980).

The results of such a model could be compared with data from the 'historic sites'. If the results were a close fit, the final logical extension would be to incorporate information on 'availability' and plant uptake, together with information on critical tissue concentrations for yield-depression (MacNicol and Beckett, 1985). If the model still gave a close fit to reality, it

would be an invaluable aid for agricultural advisory workers, and for those with responsibility to draw up the guidelines for sludge disposal.

This thesis

The first of the above objectives (ie the elucidation of heavy metal chemistry in the digester) seemed sufficient for one D Phil project (though this thesis will present some preliminary exploration of points 2 and 3). It can be broken down into several further steps:

1 Review information already known about heavy metal chemistry in the digester

2 Develop suitable procedures for separating the different components of sludge, whilst causing the minimum change to the separated fractions

3 Describe the separated fractions, and identify the forms of combination of the heavy metals associated with them

4 Identify the solid phases that might exert their solubility products on the system

5 Describe phases that could hold heavy metals by complexation, detailing their behaviour

6 Assemble a model of the fractions in terms of equilibrium constants describing the interactions of their components

8 Use the model to predict the speciation of the heavy metals in the digester and compare the predictions with the observations

Again, the complexity of this objective is such that only a computer model could bring all the information together

simultaneously. Therefore, the work must be planned from the beginning with the model in mind; each phase must be described in terms that are both suitable for incorporation in a computer model, and compatible with the descriptions of other parts of the system.

Synopsis of the chapters

This section details how the above scheme has worked out in practice, and how the results are presented in the following chapters.

Chapter	Contents
2	Review of the literature. A brief summary of the composition of raw and primary sludge is followed by as complete a survey as possible of the composition of digester sludge and the digester solution in equilibrium with the sludge.
3	Separation of the principal fractions of sludge. The problems of separation are discussed and a scheme of separation proposed. Further purification of the defined fractions is considered together with checks on any changes which separation may have wrought. The mass balance of the heavy metals between the fractions is presented.
4	Analysis of the 'Particulate' fraction I. The use of the analytical scanning electron microscope and X-ray diffraction camera is discussed, as are the limitations of these techniques.
5	Analysis of the 'Particulate' fraction II. Results of the use of the techniques described in chapter 4. A complete list of all the mineral phases identified in sludge is

given and their significance discussed.

6 Analysis of the organic fractions I. The methods for available for describing organic complexation are considered, and complexation by the 'Soluble' fraction is described.

7 Analysis of the organic fractions II. The method used and the results obtained for the 'Biofloc' and 'Colloid' are presented.

8 Computer modelling I. The problems and limitations of computer modelling are discussed, together with descriptions of six of the currently available programs.

9 Computer modelling II. The results of using the model to speciate an 'average' sludge are presented.

10 Computer modelling III. Further parameters are explored using the model.

11 The final conclusion. The results are summarised.

Reference sources which might help the reader understand the text are presented in 5 appendixes:

Appendix	Contents
1	Detailed description of methods to which reference has been made.
2	Comparison of the successive guidelines for sludge disposal together with a discussion of the changes in interpretation.
3	Table of equilibrium constants used in the model, 'the database'
4	Results of speciating systems using the model.

5 Table of the SEM and the XRD studies, which were used to draw the conclusions in chapter 5.

The SEM and XRD results produced from the studies listed in appendix 5 are indexed and described in a document held in the Library of the Department of Plant Sciences in Oxford. They run to over 50 pages and were felt to be too bulky to incorporate directly into the thesis. They may be consulted in the Library by anyone interested.

THE STATE OF THE ART

The literature was searched for information on sludge analyses, heavy metal compounds in the digester, and models of heavy metal chemistry in the digester.

In addition to searching reference lists of known papers, conference proceedings and books, material was gleaned from 2 other sources:

1) Water Pollution Control abstracts. These were searched on the Aqualine on-line database; references before 1971 are not held on the database, and these were checked by manual searching.
2) CAB abstracts and Pollution abstracts were briefly searched on the Lockheed DIALOG database, but gave little that Aqualine had not already covered.

The paucity of relevant information was surprising. Most published work has been on analytical techniques, on sludge in soil, or on the practical problems of heavy metal toxicity in working anaerobic digesters. There is a much larger body of information on the activated sludge process.

This chapter presents the results of the survey in 5 parts: sludge production, organic components, inorganic components, fractionation by extractants and total analyses.

I SLUDGE PRODUCTION

Raw or crude sewage

Raw sewage is a mixture of soil components, particulate industrial wastes, particulate vegetable wastes, suspended or colloidal organic matter and inorganic sediments, and soluble compounds of major and minor elements. Some ions of the elements in these materials remain in solution as single or complex ions: many of them are absorbed onto ionised groups, complexing ligands or charged surfaces in the particulate or colloidal matter. Some reduction occurs in the sewers, which is instanced by the occurrence of precipitated sulphides in the raw sewage.

The major sources of industrial metal contamination are diverse, for example the petroleum and metallurgical industries may contribute arsenic, zinc, mercury and chromium, the paint industry may contribute barium, chromium, titanium, zinc and lead, the photographic industry cadmium, silver, lead, molybdenum and selenium, the textile industry silver, barium, copper, tellurium, mercury, nickel and lead. The chloride-alkali industry is the major contributor of mercury to the environment (Hao, 1979).

However, analysis of effluents in the New York sewerage system revealed that overall the major source of heavy metals entering the sewage works was from domestic (residential) origins:

Table 2.1 Sources of Heavy metals in raw sludge

Source	Cu	Cr	Ni	Zn	Cd
Water supply	20	0	0	7	0
Electroplaters	12	43	62	13	33
Other Industry	7	9	3	7	6
Runoff	14	9	10	31	12
Residential	47	28	25	42	49
Unknown	0	11	0	0	0

% Total weight contributed to plant influent

Range of total analyses for above table:

Cu	0.11 - 0.33	mg litre^{-1} wet weight
Cr	0.003 - 0.15	
Ni	0.01 - 0.15	
Zn	0.13 - 0.37	
Cd	0.001 - 0.007	

Analysis of the variation in heavy metal content of sewage entering one works (Beckett, 1980) showed a log-normal distribution skewed in favour of lower concentrations, whilst similar analyses of digested sludge were skewed in favour of higher concentrations. Weekends and holidays gave clear reductions in the heavy metal concentrations of the raw sewage, but a proportionately smaller reduction was observed for Cu, Pb and Zn, where domestic sources make a greater contribution, than for Cd, Ni or Cr.

The total concentration of heavy metals in raw sewage has been reported by various workers over the years:

Table 2.2 Heavy metal analyses of raw sewage

Author	Stones	Klein	Perry	Stoveland	Beckton**
Date	1955-59	1974	1975	1980	1983-84
Fe	5.04				
Cr	0.71	0.16		0.06	0.02 (mg litre^{-1})
Cu	0.56	0.27	0.32	0.25	0.02
Ni	0.19	0.11		0.04	0.01
Zn	0.91	0.41		1.6	0.17
Pb	0.62		0.2	0.16	0.02
Cd		0.16	0.006	0.006	0.001

** Current figures from TWA Beckton works (see table 2.14)

The general decrease in the heavy metal content of raw sewage demonstrates the effects of increasing trade effluent control.

The average phosphorus content of raw sewage at one works has been reported as 340 mg litre^{-1} (Perry, 1975). This comprised 154 mg litre^{-1} orthophosphate, 3.3 mg litre^{-1} pyrophosphate, 12.7 mg litre^{-1} tripolyphosphate and 170 mg litre^{-1} 'soluble phosphate', using the procedure of Lewin (1973). Of this 65% (200 mg litre^{-1}) would have entered the system as tripolyphosphates from synthetic detergent builders, and 35% from faeces, urine, and waste-food disposal (Tomson and Vignona, 1984). A high percentage of which, had already been hydrolysed by the time they reached the works and would then have to be removed by precipitation in the works to meet water standards.

Primary sludge

Primary sludge retains approximately 20% of the Ni, 30% of the Cr, 40% of the Fe and Zn, and 50% of the Cu, Pb and Cd of the total load in the raw sewage (Stones, 1977; Perry, 1975). A typical primary sludge, from co-settled raw sewage and surplus activated sludge, analysed as:

Table 2.3 Heavy metal analyses of primary (crude) sewage

Author	Perry	Stoveland	Beckton**	
Date	1975	1980	1983-84	
Cr		13	7	(mg litre^{-1})
Cu	2.9	19	14	
Ni		10	17	
Zn		140	65	
Pb	20	21	19	
Cd	0.58	0.55	0.47	

** Current figures from TWA Beckton works

The contribution of various fractions to the organic content of primary sludge has been reported as:

Table 2.4 Total analysis of primary sludge

Fraction	Percent dry matter
Suspended solids	95
Organic carbon	40
Organic matter	60 - 80

Greases and fats	7 - 35
Cellulose	4
Hemicellulose	3
Lignin	6
Protein	22 - 28
Anionic detergents	0.5 - 1.5
Total nitrogen	2.5 - 4.5

(Mosey, 1980)

Anaerobic digestion

The main features of the processes of anaerobic digestion are well known. Briefly, on charging the digester with primary sludge, bacterial organisms consume first the oxygen present and then other hydrogen acceptors, and the redox potential of the digester contents falls:

i) denitrification

ii) hydrolysis of organic polymers (carbohydrates, lipids, proteins) to H_2, CO_2, alcohols and acetic (mainly), propionic and butyric acids

iii) sulphate reduction

iv) methanogenesis from (mainly) acetate and also H_2 and CO_2, at redox potentials (Eh) of -265 to -300 mV (or Ec, relative to the calomel electrode, of -524 to -560 mV)

The production of acids in stage (ii) reduces the pH, but stage (iv) degrades the acids formed and allows the pH to rise: pH 7 to 7.5 and a redox potential of -265 mV are characteristic of a healthy

digester.

The process is operated by regular additions of primary sewage and withdrawals of sludge rather than as a batch process. The digester is kept around 35°C, with a retention time of 20 to 30 days. Under these conditions some 45% of the total combustible solids, and 70% of the fats and greases (Mosey, 1980) may be degraded to produce a mixture of 70% methane and 30% carbon dioxide with a trace of hydrogen sulphide. The gas composition does not vary significantly with digester conditions.

Methanogenesis is sensitive to the concentration of heavy metals, with both excess and deficient concentrations inhibiting fermentation (Callander, 1983). If it is inhibited, organic acids accumulate and the pH may fall to 6.5, and the redox potential (Eh) may rise to -170 mV (Mosey, 1975 & 1976).

The degradation of labile organic matter releases NH_4^+, HPO_4^{2-}, S^{2-}, and any bound cations. Some organic materials in the raw sewage, and particularly those that include lignin and cutin, remain unchanged in the digester, except they are freed from less resistant components. Concurrently, new biomass and bacterial detritus accumulate along with microbial exudates (mainly polysaccharides). Parts of these are easily decomposed but some components are surprisingly resistant (Degens et al, 1970).

Some inorganic components of the raw sewage, particularly mineral grains from soil, and comminuted fragments of industrial wastes such as plastics and titanium dioxide, remain unchanged. Other components (particularly reducible compounds of Fe and Mn) dissolve or decompose to release Cl^-, HPO_4^{2-}, HCO_3^-, S^{2-} and silica, with Ca^{2+}, Na^+, K^+, Mg^{2+}, Fe^{2+}, Ba^{2+} and cations or anions of minor

elements. If the solubility products of any compounds are exceeded, these are likely to be precipitated as 'secondary' nodules or crystals, or as coatings on and around organic and inorganic particulate material.

In principle the contents of the digester are well stirred, but in practice local micro-environments exist where a variety of different chemical forms may precipitate. Also, mineral grains and crystalline precipitates, possibly with amorphous coatings, sink and accumulate at the bottom.

In discussing these processes further it will be necessary to draw upon data for the composition of digested sludge (ie sludge which has finished being digested, and collected from the outlet of the digester). This is assumed to correspond fairly closely to that of digester sludge (ie sludge still being digested) except for those components that are easily oxidised.

II ORGANIC COMPONENTS OF DIGESTER SLUDGE

Nitrogen

The organic-carbon fraction of 8 digested sludges in the USA was found to vary between 19 and 27% dry matter (Sommers et al, 1976). This roughly corresponds to 30-45% organic matter. They found 1.3-4.3% organic-nitrogen, and 0.2-9.4% inorganic nitrogen, (table 2.5). These figures depend on the extent of mineralisation of organic-nitrogen after the sludge left the digester, and of losses of NO_3^- by leaching or denitrification. The total nitrogen can be divided into the following components:

Table 2.5 Nitrogen components of a digested sludge

	In dry matter	In wet sludge
Total N	11.9 (percent)	2,300 (mg litre^{-1})
Inorganic N	4.7	950
Hexosamine	0.38	75
Amino-acids	1.3	250

(Ryan et al, 1973)

Phosphorus

The organic-phosphorus content of digested sludges has been found to vary between 0.15 and 1.1% of the dry matter (Sommers et al, 1976), and the inorganic-phosphorus between 1.1 and 2.4% dry matter. It has been suggested that the soluble phosphorus is virtually all in the orthophosphate form (Marson, 1971).

Sulphur

The total sulphur content of 11 sludges from the USA was found to vary between 0.7 and 2.1% of the dry matter. It comprised:

Table 2.6 Sulphur components in digested sludge

Sulphide	1 - 35	(percent total S)
Inorganic and ester sulphate	0 - 35	
Inorganic non-sulphate	18 - 35	
Carbon-bonded sulphur	18 - 56	
Unidentified	0 - 42	

(Sommers et al, 1977)

The range of proportions of sulphide, and of intermediate oxidation states, suggests that when sampled the sludges had become oxidised to different degrees after removal from the digester.

Carbon

Baldwin et al (1982) separated digested sludge from the TWA Sandford works by elutriation into fractions that settled 10 cm in 5, 15, 180 or more than 180 minutes. Quartz grains in these fractions would have had diameters of >0.12, 0.12-0.02, 0.02-0.0035 and <0.0035 mm: their organic particles were somewhat larger. The coarser material could be seen to comprise mineral grains and plant structures such as fibres and cuticle. The organic structures found in a range of digested sludges from TWA have been listed and illustrated (Rodkiewicz, 1981). Bacterial detritus comprised much of the matrix in which the mineral grains and organic fragments were embedded. The embedded material could be dislodged from the matrix by sonication (Baldwin et al, 1982). Together, the matrix of detritus and fine organic colloids (3-10 μm) comprised up to half of the total sludge.

Bergman et al (1979) separated sludge into 6 fractions according to their density, and found appreciable organic matter (of low density) in all density fractions, which suggested that there were organic coatings on mineral grains. Except for quartz and feldspar many of the minerals were found in fractions of less than their true density, which seems to confirm that they were embedded in or coated by amorphous precipitates and organic matter.

Baldwin et al (1982) presented the results from 'forage fibre analysis' on the organic content of different sludge fractions

(table 2.7). This revealed that much of the cellulose in sludge has been degraded into finer fractions, while the majority of the undegraded cellulose is found in the coarsest fraction.

Table 2.7 Analysis of digested sludge by 'forage fibre analysis'

Fraction	Soluble and hemicellulose	Cellulose	Cutin	Lignin	Ash
5 min	50	19	3	13	15
15 min	65	7	2	10	16
180 min	78	3	2	6	11
>180 min	(97)*	(1)	(1)	(1)	(11)
Whole	65	15		9	12
compare with:					
Filter paper	14	77		9	0
Well-rotted mixture of straw and farmyard manure	52	31		15	2

* by difference (percent dry matter)

Baham and Sposito (1983) found that 8% of the total carbon in a digested sludge occurred in the finest (colloidal or soluble) fraction. Of this at least half had a molecular weight of 1,500 or less. It comprised 25% of amino-acids, 12% polysaccharides, 9% hexosamines and 8% aliphatic acids, and showed similar complexing properties to fulvic acid, with Zn being taken up in the largest quantity of all the heavy metals.

Newland et al (1976) separated a digested sludge into

conventional humic fractions by solution in strong alkali and precipitation by strong acid, and analysed the fractions for heavy metals:

Table 2.8 Separation of digested sludge into humic fractions

Fraction	% of organic matter	Cd	Ni	Mn	Zn	Cu	
Humin*	75	50	50	400	525	250	(mg kg^{-1})
Fulvic acid	10	15	50	40	80	95	
b-humus	7	1	5	1	50	50	
Humic acid	8	0.5	7	0	4	10	

* Humin is usually a mixture of unhumified and highly humified organic matter.

Since the sample was first treated with strong alkali, and then with strong acid, it is not clear how closely these analyses correspond to those for the sludge in its original state, though the progressive decrease in heavy metal content with degree of humification may be significant.

Baldwin et al (1982) showed that 60% of the Cu and Zn in digested sludges was held in predominantly organic fractions that took more than 5 minutes to settle through 10 cm of water. The coarse fractions of particulate inorganic and organic matter contained lower concentrations of Cu and Zn than the fine fractions. Significant proportions of the total Cu and Zn in a sludge were transferred from the coarsest fraction to the finest fraction by ultrasonic dispersion which removed a matrix of fine colloids and

bacterial detritus from the plant fragments. In their finer fractions, 60-70% of the Cu and 50-70% of the Zn were solubilised by treatment with H_2O_2, 70-95% of the Zn was displaced by 0.005 M $CuSO_4$, and 80-95% of the Zn and 30-70% of the Cu were displaced by 0.005 M $CaCl_2$ and 0.01 M HCl, (subsequent work would suggest that H^+ was the main agent).

Hayes and Theis (1978) fractionated anaerobic sludge from a laboratory digester 20 days after dosing with heavy metals. Their procedure involved elutriation, sieving and clarification. They defined a 'biomass' fraction, removed by flocculation, which they believed to contain 75% of the total biomass from the anaerobic sludge. The mass balance of heavy metals between their different fractions is presented in table 2.9:

Table 2.9 Proportions of total heavy metals held in different fractions of anaerobic sludge

Metal	Biomass	Particulate	Other	
Cr	55	35	10	(percent)
Ni	20	70	10	
Pb	25	65	10	
Cd	25	65	10	
Zn	25	70	5	
Cu	25	65	10	

(Hayes and Theis, 1978)

Similarly Fristoe and Nelson (1983) showed that 30% of the total Cd in a sludge was associated with a biomass fraction. This figure was raised to as much as 90% by addition of lime, apparently because this reduced the competition of protons for retention sites in the biomass.

Hayes and Theis (1978) have suggested that the greater part of the metals in the biomass is held intracellularly rather than by complexation on the outside of the cell walls. They deduced this from the observation that only 1% of the total heavy metals in sludge may be removed from the reflocculated biomass by EDTA, and the supposition that EDTA has a stronger affinity for the heavy metals than the bacterial exopolymers from activated sludge (Cheng et al, 1975). They did not show that their data were relevant to the very different bacterial flora in digester sludge. Other workers have shown that bacterial exudates and cell wall polymers from activated sludge bind heavy metals very strongly (Stoveland and Lester, 1980).

The forms of combination of the heavy metals separating with the organic fraction can only be defined by detailed measurements of the stability constants involved. Most work to date has involved activated sludge where heavy metal retention depends on chelation by bacterial extracellular polymers to a greater extent than in anaerobic sludge digesters where sulphide is available for metal precipitation. While much of the work on activated sludge has involved the use of purified polymers from bacteria such as Klebsiella aerogenes (capsule forming, gram-negative) and Zoogloea ramigera (gelatinous matrix forming, gram-negative), most work on digester sludge has used unseparated sludge, without any control on

its subsequent oxidation during the experiment.

Gould and Genetelli (1978) modelled heavy metal binding in unseparated digested sludge and found that there is competition between heavy metal ions and hydrogen, suggesting an ion-exchange mechanism whose behaviour is consistent with that of soil organic matter, and confirmed it by demonstrating reversible competition for binding sites between the different heavy metals (Gould and Genetelli, 1984). Their Freundlich isotherms suggest that Cd, Ni and Zn each displace one proton while Cu displaces 2, for each complex formed.

Stability constants do not identify the nature of the cation-ligand interaction uniquely; they only describe its strength and characteristics. Several groups have used infra-red analysis to look at the functional groups on the ligands responsible for complexation. The involvement of hydroxyl and carboxyl groups (Tan et al, 1971), thiol groups (Baham et al, 1978) and protein amide bonds (Boyd et al, 1979) has been reported.

The nature of the ligands involved in binding has also been examined by ESCA, which has a resolution of 1 part in 10^3-10^4. Cotherne et al (1977) found that both copper and zinc gave a similar shift in binding energy, indicating that both cations exist in a similar environment. The electron negativity of the ligand suggested that binding was through an oxygen atom, therefore possible ligands include: carbonate, carboxylate, phosphate, nitrate, sulphate or silicate. When carboxylate and phenolic functional groups were methylated with dimethyl sulphate, there was a decrease in heavy metal binding capacity (Gould and Genetelli, 1978).

A preliminary C^{13} solid-state NMR study provided general information on 4 carbon types in composted sludges and an anaerobic tannery waste (Piotrowski et al, 1984). The complex spectra could be resolved into carbonyl, aromatic, aliphatic and O- and N-bonded carbon atoms. While little additional information could be derived, the authors believed that the technique seemed promising for future clarification of the groups involved in binding.

Bacterial cell walls holding complexed heavy metals can in turn nucleate the precipitation of crystalline phosphates and sulphides under anaerobic conditions (Beveridge et al, 1983); Bacillus subtilis incubated with a sand/calcite sediment and with a 5 mM supplement of heavy metals in the growth medium, precipitated calcium and iron phosphates, and copper and zinc sulphides in intimate association with their cell walls. Other widely occurring groups of bacteria have been shown to precipitate metallic iron on their cell walls (Ghiorse, 1984), and octacalcium-phosphate precipitation has been implicated in the flocculation of algal biomass under alkaline conditions (Sukenik et al, 1985).

If such secondary precipitates were attached to the digester biomass, this may account for the high proportion of the total heavy metal associated with the 'Biofloc' fraction of digester sludge (see mass balance p 80 ff).

III INORGANIC COMPONENTS

Identification of mineral phases

Several workers have examined the mineral grains in the coarser fractions of digested sludge, usually by X-ray diffraction (Seitz et al, 1973; Levi-Minzi et al, 1981; Bergman et al, 1979).

Levi-Minzi et al (1981) destroyed the organic content of sludge with peroxide and found quartz, calcite, gypsum, dolomite, feldspars, kaolinite, micas and chlorite and smaller amounts of halite, talc, opal and montmorillonite remaining. The gypsum may have resulted from the oxidation treatment. Sommers (1977) reported quartz, calcite, dolomite, feldspars and clay minerals.

Bergman et al (1979) reported several minerals in fractions of digested sludge separated non-destructively on their density (table 2.10) together with borickite (calcium-iron phosphate), pyrite, chalcopyrite and sphalerite (sulphides of iron, copper and zinc) and goethite (secondary iron oxide) probably formed as secondary precipitates. Seitz et al (1973) concentrated vivianite (ferrous phosphate) by magnetic separation and reported that it accounted for 1% of a dried secondary sludge. G Brown (pers comm) found kaolinite, talc, lepidocrocite (secondary iron oxide) and calcite, with a little mica, quartz and feldspar, and a very little anatase in the finest (180 min) fraction of a digested sludge. Baldwin et al (1982) reported grains of what appeared to be calcium phosphate, and of calcite and quartz with coatings of calcium phosphate, and of mixed iron oxide and iron sulphide that also contained Cu and Zn.

Table 2.10 Density separates from digested sludge

Density range	% of total sludge	% organic matter in fraction	XRD patterns observed
1.75 - 2.01	0.4	99	None observed
2.01 - 2.05	19	90	amesite*, corundum (Al_2O_3)
2.05 - 2.35	7.4	80	borickite
2.35 - 2.61	0.4	35	quartz, feldspar amesite, borickite boracite, gypsum garnet, corundum illite
2.61 - 2.89	3.2	10	quartz, feldspar illite, magnetite corundum, garnet haematite, pyrite boracite
> 2.89	0.02	10	magnetite, corundum garnet, haematite boracite, gypsum amesite, goethite pyrite, chalcopyrite sphalerite

(Bergman et al, 1972)

* amesite is $(Mg_4Al_2)(Si_2Al_2)O_{10}OH_8$

Carbonates

It is clear that calcium carbonate is precipitated in the digester, and probably during primary treatment as well. The activity of CO_2 in the digester solution is controlled by the reaction:

$$CO_2^{2-} + H_2O = CO_3^{2-} + 2H^+$$

Typically at 35°C the digester gas contains 30% CO_2, so:

$$pCO_3^{2-} = 18.6 - 2pH$$

On this basis Mosey and Hughes (1975) suggested that, unless the digester pH rose to inordinately high levels, the normal concentrations of heavy metals in the digester would be insufficient to precipitate their carbonates except possibly $CdCO_3$, $BaCO_3$, and $FeCO_3$. They suggest that these carbonates may play a role in buffering the solution concentrations of Cd and Fe. If the solution pH is greater than 7.2-7.4 then $CdCO_3$ will hold the Cd concentration below 180 mg litre^{-1}, the upper sub-toxic limit. However, Sposito (1983) suggests that $CdCO_3$ might be precipitated in solid solution with $CaCO_3$ since their crystal structures are the same. Mosey and Hughes showed that even when they increased the total Fe content of the digester, the S^{2-} concentration in the solution remained constant. This seemed to imply that the added Fe was being precipitated as the carbonate, since they thought that ferrous hydroxide was too soluble to precipitate and no S was being removed from the solution. pH 6.4 is the lower limit for $FeCO_3$ precipitation. Groundwaters are often supersaturated by up to 10-fold with respect to siderite (Postma, 1981, 1982), but it does not precipitate. This has been explained in terms of slow precipitation rates, discrepancies between the solubility product

and the solubility of small crystals and the effects of organic complexing agents.

Wajon et al (1985) examined the precipitation of siderite from iron(II)-rich waste-waters and calcite but with no organic matter present; they found that several months would be needed for the system to come to equilibrium with respect to siderite at neutral pH, and that calcium siderites of variable composition could be precipitated.

Patterson et al (1977) examined the precipitation of heavy metal carbonates as a possible way of controlling metal levels in waste-waters. Their calculations showed that the heavy metal carbonates should be precipitated at lower pH than their hydroxides. The addition of sodium carbonate to achieve the necessary high levels of CO_3^{2-} precipitated heavy metal carbonates only rather slowly, even from supersaturated solutions. However, their 4 experiments were much shorter than the normal 20-30 days in the digester, and so slow precipitation may not be a problem in the digester. It is not clear whether the dolomite reported (above) in digested sludge is primary or secondary.

Phosphates

There have been several reports of phosphate precipitates in sludge, particularly after addition of lime: in these circumstances they may form up to 30% of the mineral fraction.

Zoltek (1974, 1976) reported octacalcium-phosphate (OCP); Moreno et al (1960) found that the stoichiometry of the calcium phosphate precipitated on the surface of particles lay in the range OCP to dicalcium phosphate (DCP), while Eanes (1965) found amorphous

forms corresponding to calcium-deficient apatite, tricalcium phosphate (TCP), and OCP. The Ostwald-Gay-Lussac step-rule states that the least insoluble form will probably crystallise first, and then later disproportionate to less soluble forms. Clark (1955) reported that the formation of apatite required raised temperatures and extended time. Mixed carbonate-phosphates with a wide range of composition have been reported, these might be able to incorporate minor elements into their crystal structure.

Borgerding (1972) reported deposits of magnesium ammonium phosphate in digester sludge in a variety of forms: large crystals, very small crystals, curds and as a gelatinous mass.

Sulphides

Sulphides seem to be the most important of the secondary deposits, and appear to exert the principal control over the concentrations of heavy metals in the digester solution. Thus Lawrence and McCarty (1965) found that, if sulphates of heavy metals were added to the digester, these were not toxic to digestion, but that their chlorides were. They concluded that the sulphate was reduced to sulphide, which precipitated heavy metals. Mosey (1971; 1976; 1980; Mosey and Hughes, 1975) concluded that the sulphide concentration in the digester solution is mainly controlled by the iron concentration. He suggested that as the load of other heavy metals increases, iron sulphide dissolves to release the sulphide necessary to precipitate the less soluble heavy metal sulphides, and the iron reprecipitates as the carbonate. As long as sufficient ferrous sulphide is present, heavy metal concentrations in the digester will be held below toxic levels. This mechanism will not

work for chromium which does not form an insoluble sulphide, and he had concluded that cadmium was controlled by the insolubility of the carbonate rather than the sulphide. Mosey and Hughes (1975) added doses of metal salts to model digesters and followed the sulphide and metal ion activities and their effects on gas production over the following 17 hours. The added metals were precipitated as sulphides, which reduced the sulphide concentration from its initial value around 10^{-10} M to between 10^{-12} M and 10^{-17} M. Over a second 17 hour period the metal ion concentrations fell towards their pre-dosing levels as the sulphide activity increased towards its pre-dosing level. They explained this in terms of the further reduction of sulphate to H_2S, and the release of sulphide from the least insoluble iron sulphides. In a later paper (Mosey, 1976) their figures were refined and pS values calculated for 50% toxicity:

Table 2.11 Sulphide levels in the digester (pS)

Cation	In equilibrium with the sulphide	For 50% heavy metal toxicity to the biomass
Fe	4	13.2
Zn	8	14.2
Cd	12	
Cu	17	13.8
Cu	21	

It is unlikely that the digester will achieve equilibrium within the short period of 17 hours. They presented the values of pS necessary to hold heavy metal concentrations down to a maximum tolerable level over a period of several days: for a single dose of a toxic heavy metal the corresponding pS value is 17. However, the extent to which sulphide can cope with toxic shock doses depends on the proportion of the total sulphur in the primary sludge that can be reduced to sulphide. Sulphide ions are themselves toxic to digestion at concentrations greater than 150 mg litre^{-1} (pS 2.5).

In their earlier papers Mosey and Hughes (1975) suggested that zinc was also buffered against toxicity by zinc carbonate, but they later showed that this was incorrect. At pS 14, the equilibrium pZn must be 7.1 which would require a pCO_2 of 3.5 to precipitate zinc carbonate, which can only be achieved with a pH of 7.6 or greater. In practice an average urban sludge has a pS of 12 rather than the pS 10 in these authors' work, because of the higher iron content of most urban sludges.

Mosey and Hughes also concluded that the redox potential of a healthy digester was -265 +/- 25 mV on the Eh scale, which decreased by 57 mV for each unit increase in pH. From this they argued that at equilibrium iron will be in the +2 oxidation state and that copper will be in the +1 oxidation state. Cotherne et al (1977) showed that the binding energy of the Cu $2p_{3/2}$ electron in sludge was characteristic of Cu in the +2 oxidation state, but they had air-dried their samples before grinding in a pestle and mortar and so these may have become oxidised in the process.

Bergman et al (1979) and Baldwin et al (1982) confirmed that sulphides of iron, copper and zinc were present in digester sludge.

Baldwin et al (1982) implied that they were mixed. The relatively high Fe/S ratio they observed suggested that much of the sulphide originally present had become oxidised during storage of the sludge (see figure 5.8). This is also suggested by the presence of sulphates and intermediate oxidation states of sulphur in the sludges analysed by Sommers et al (1977). Even in their finest fractions Baldwin et al (1982) recorded some S associated with Cu and Zn.

The crucial point is that whether or not the precipitated sulphides (and carbonates for iron and cadmium) contain the main or even a major part of the heavy metals in the digester, they do appear to control the concentrations of heavy metals in the digester solution.

Chlorides and hydroxides

There is no evidence for chloride or hydroxide precipitates in the digester sludge, but oxidised digested sludge is extensively permeated by iron oxides, probably due to the oxidation of iron sulphides, and to the precipitation of soluble iron II from solution when the anaerobic sludge is oxidised. A comparison of the solubilities of the heavy metal hydroxides in CO_2-free distilled water and Birmingham tap-water has been presented by Jenkins et al (1964). They concluded that at neutral pH the solubility of Ni was 1-7 ppm, Cu 0.2-0.3 ppm, Zn 1-2.5 ppm, Cr III 0.05-0.4 ppm and Cd 1-2 ppm in pure water.

IV FRACTIONATION BY CHEMICAL EXTRACTANTS

Various reagents have been used to extract particular groups of heavy metal components from sludge: acids, bases, salts and complexing agents. Thus McLaren and Crawford (1973) used different reagents in sequence to build up a picture of the different pools that hold copper in soils. It is hoped that each reagent extracts the same fraction of each of the heavy metals. Then from knowledge of its chemistry, and argument by analogy, each fraction is identified with a particular group of compounds.

The simplest form of fractionation is by water extraction. Jenkins and Cooper (1964) repeatedly percolated columns of dried digested sludge with distilled water, and found that a limit of 0.3% of the Cu, 14.3% of the Ni and 1.7% of the Zn could be extracted. Bloomfield and Pruden (1975) showed that the water-soluble fraction was significantly reduced by prior anaerobic incubation. Subsequent aeration increased the solubilities of Cr, Cu and Zn, but not of Cd, Ni and Pb. Cd and Ni are the most water-soluble of the heavy metals.

The sequential method of McLaren and Crawford (1973) has been adapted for sludge by Stover et al (1976). They use, in order:

1 M KNO_3 for 16 hr at 50:1;

0.5 M KF (pH 6.5) for 16 hr at 80:1;

0.1 M pyrophosphate for 16 hr at 80:1;

0.1 M EDTA (pH 6.5) for 8 hr at 80:1;

1 M HNO_3 for 16 hr at 50:1.

These are intended to extract:

KNO_3 : metals bound by exchange sites, by K^+ saturation.

KF: absorbed metals, by fluoride complexation.

Pyrophosphate: metals bound by organic matter, by complexation.

EDTA: metal carbonates by dissolution.

HNO_3 : metal sulphides and other mineral forms, by dissolution.

The relative proportions of each metal released by each reagent are deemed to indicate which forms of combination of the metal were dominant. Their results suggest:

Cu: sulphides >carbonates >organically bound =adsorbed =exchangeable

Zn: organically bound >carbonates >sulphides >adsorbed >exchangeable

Pb: carbonates >organically bound >sulphides >adsorbed >exchangeable

Ni: carbonates >organically bound >exchangeable >adsorbed >sulphides

Cd: carbonates >sulphides >organically bound >adsorbed =exchangeable

However, a similar sequence of reagents was used by Emmerich et al (1982). They gave the opposite sequence for Cu: organically bound>carbonate>sulphide/residual; Zn, Cd and Ni were found predominantly in the carbonate fraction.

Miller et al (1986) used a series of 9 extractants ranging from water to a HF-based triacid mixture to evaluate the solid phase forms of copper in copper-enriched pig manure. They concluded that most of the copper was held in organic forms, but that prior freeze-drying of the manure resulted in copper oxides and hydroxides becoming dominant. Extraction with 0.05 M $Pb(NO_3)_2$ failed to

solubilise significantly more Cu than water, suggesting that the stability constant for the Cu complexes greatly exceeded that for the Pb complexes. Only 2% of the Cu remained after extraction with pyrophosphate and then oxalate, suggesting that CuS was unlikely to have been present in significant quantities.

If valid these sequences would provide a good starting-point for studies in heavy metal chemistry in sludge, but clearly there are problems: analogies with pure systems may not hold in the complex environment of sludge. Even in the pure systems there are problems. Stover et al (1976) found that pyrophosphate, intended to extract organically bound forms, extracted 79% of $PbCO_3$ and 18% of PbS present, while Miller et al (1986) found that pyrophosphate extracted 21% of CuS, 21% $Cu_2(OH)_2CO_3$ and 13% of CuO present. The use of pyrophosphate to extract the organically held pool of heavy metals was proposed by McKeague et al (1971), who demonstrated only that it extracted Fe from synthetic Fe-fulvic acid complexes. They noted that it was not a good extractant for organically held Al, and that it extracted iron from gelatinous iron oxide. Stover et al (1976) also found that EDTA, intended to extract carbonates, extracted >90% of Cu, Pb and Zn carbonates but only extracted 68% of Cd carbonate. Most recently, Angelidis and Gibbs (1989) used extractants to distinguish heavy metals held as sulphide mineral forms from those held as organic complexes.

In general, it may be unwise to link the heavy metals extracted by one reagent to a particular group of compounds. The use of extractants on sludge and sludge-amended soils has been reviewed by Lake et al (1984) and more recently and critically by Beckett (1989).

V TOTAL ANALYSES OF SLUDGE

Any model of the chemistry of sludge and of the processes occurring in the digester has to account for the known total analyses, and to predict the distribution of the components between its different constituent fractions. The variability of the total analyses presents one of the major problems to understanding their chemistry. Typically, heavy metal contents may vary by 2 orders of magnitude between a domestic and an industrial sludge so the range of chemically stable species may vary considerably. The heavy metal content of sludge leaving the digester may have been concentrated by a factor of between 50- and 170-fold compared with raw sewage (Beckett, 1980).

A wide variety of analytical techniques has been used for analysing the levels of various cations in the sludge; many of these have been reviewed by Lim and Jackson (1982).

Williams (1975) surveyed sludges from 182 treatment plants in England and Wales, reporting the spread of analyses for Cu, Zn, Pb, Cr and Ni.

Berrow and Webber (1972) reported range, mean and median values of elements in 42 English sludges analysed in 1964. This was followed up by a similar comparison in 1979 (Sterritt and Lester, 1980), which showed reductions in the concentrations of Cd, Zn and Ni over that period, but no corresponding reduction in elements for which there had been little or no public concern.

Sommers et al (1976) summarised the analyses of a very large number of sludges from the USA, grouping them into sludge from aerobic and anaerobic digesters (table 2.12).

Beckett (1978) presented all-element analyses (excluding H, C, N, O) of digested sludge from the TWA Maple Lodge treatment works (table 2.13).

Table 2.14 presents analyses of sludges from the TWA Beckton treatment works, which was the source of most of the sludge used in the following experiments.

Table 2.15 presents a summary of sludge analyses from the literature compiled by Dr P Beckett. This table was used to help define an 'average' sludge as a starting-point for the model (see chapter 9).

Table 2.12. Summary of sludge analyses from the USA

	Aerobic		Anaerobic	
	Range	Media	Range	Media
	All in percent dry matter			
Organic C	27-37	29.5	18-39	26.8
Total N	0.5-7.6	4.8	0.5-17.6	4.2
Total P	1.1-5.5	2.7	0.5-14.3	3.0
Total S	0.6-1.1	0.8	0.8-1.5	1.1
	All in percent dry matter			
Ca	0.6-13.5	3.0	1.9-20	4.9
Fe	0.1-4.0	1.0	0.1-15.3	1.2
Na	0.03-3.1	0.77	0.01-2.2	0.73
Al	0.1-2.3	0.4	0.1-13.5	0.5
Mg	0.03-1.1	0.41	0.03-1.9	0.48
K	0.08-1.1	0.38	0.02-2.6	0.30
Ba	0.00-0.03	0.02	0.00-0.90	0.05
	All in mg/kg dry matter			
Cr	10-13,600	260	24-28,850	1,350
Zn	108-14,900	1,800	108-27,800	1,890
Cu	85-2,900	970	85-10,100	1,000
Pb	13-15,000	300	58-19,730	540
Mn	55-1,120	340	58-7,100	280
Ni	2-1,700	31	2-3,520	85
B	17-74	33	12-760	36
Cd	5-2,170	16	3-3,410	16
Hg	1.0-22	5	0.5-10,600	5

Table 2.13. All-element analysis of a digested sludge

2nd Row	
Li	3
Be	2
B	20
F	20

3rd Row	
Na	2,500
Mg	5,500
Al	23,000
P	20,000
S	6,000
Cl	700

4th Row	
K	3,500
Ca	35,000
Sc	2
Ti	1,400
Cr	550
Mn	750
Fe	9,000
Co	55
Ni	1,200
Cu	850
Zn	1,700
Ga	5
Ge	1
As	25
Se	1
Br	6

5th Row	
Rb	35
Sr	250
Y	3
Zr	45
Nb	2
Mo	8
Tc	-
Ru	1
Rh	1
Pd	5
Ag	200
Cd	40
In	1
Sn	80
Sb	15
Te	1
I	10

6th Row	
Cs	20
Ba	7,000
La	6
Hf	1
Ta	1
W	2
Re	1
Os	1
Ir	1
Pt	1
Au	1
Hg	6
Ti	1
Pb	400
Bi	7
Po	-
At	-

Lanthanides (>1 mg kg^{-1})	
Ce	30
Nd	6
Sm	20

Beckett, 1978

Table 2.14. Analyses of sewage, sludge and effluent from TWA Beckton treatment works (1983/84)

	Dry matter (percent liquid sludge)	Volatile matter (percent DM)	N (percent DM)	Cu	Ni	Zn	Cr	Pb	Cd	Ag
				(mg kg^{-1} dry matter)						
Crude sewage	0.024	-	0.13(3)	88	49	720	70	100	6	11
Primary sludge	2.6 (3.4)(1)	74.5 (75.1)(1)	-	530	66	2,500	270	720	18	69
Settled sewage	0.0083	-	0.33	-	-	-	-	-	-	-
Digested sludge	2.2	64.6	-	780	92	3,400	390	930	25	94
Surplus activated sludge	0.72(2) 0.7	-	-	620	89	2,450	350	580	22	106
Final effluent	-	-	-	12	32	200	18	4	6	1
Sludge to sea(4)	2.2	-	-	930	129	3,130	360	860	25	87

(1) After thickening

(2) New and old plant

(3) NH_4^+ and NO_3^-

(4) Includes Deephams and Riverside sludge

Table 2.15

Overall composition of anaerobically digested sludges, Europe and USA
(median values for each set of data: two significant figures)

	Percent DM (ref)
Volatile solids	40 (2), 43 (18a), 46 (7), 47 (6, 23), 51 (10, 18c)
Organic C	18 (5), 22 (6), 23 (1, 3), 26 (17), 27 (4), 28 (11)
Inorganic C	1.1 (5), 1.3 (3), 1.6 (1)
Total N	1.7 (18b), 1.9 (19), 2.0 (18d), 2.3 (14, 23), 2.4 (10, 20), 2.5 (17, 18c), 2.7 (18a), 3.0 (2), 3.1 (21), 4.2 (4), 11.8 (11)
Organic N	1.7 (5), 2.4 (1), 2.5 (3)
Inorganic N	0.75 (1), 0.48 (11)
Total P	0.01 (14), 0.24 (18d), 0.26 (18b), 0.33 (19), 0.35 (18c), 0.44 (18a), 0.59 (20), 0.81 (21), 0.85 (23), 1.1 (2), 1.5 (22), 1.6 (10, 17), 2 (8), 2.5 (11), 3 (4)
Organic P	0.3 (3), 0.6 (1), 1.1 (17)
Inorganic P	0.6 (17), 1.7 (1), 1.8 (3)
Total S	1.1 (4, 12), 1.2 (17), 1.6 (3)
Organic S	1.1 (3)
Inorganic S	0.5 (3)
Aluminium	0.4 (11), 0.5 (4), 1.5 (22), 1.6 (10), 2 (8)
Calcium	1.3 (11), 1.5 (21), 1.7 (14), 2.6 (10), 3.5 (8), 4.9 (4), 5.2 (22), 6.6 (13), 6.9 (1)
Iron	0.7 (24), 0.74 (11), 0.9 (8), 1.2 (4), 1.3 (14), 1.6 (22), 1.7 (25), 2.1 (9), 2.3 (13), 2.4 (3), 2.6 (10), 3 (1), 4 (2)
Magnesium	0.1 (21), 0.29 (14), 0.35 (22), 0.4 (13), 0.48 (4), 0.55 (8), 0.59 (10), 0.88 (11), 1.0 (1)
Potassium	0.07 (19), 0.08 (18d), 0.10 (19), 0.17 (21), 0.21 (13), 0.30 (4), 0.35 (1), 0.72 (10), 0.82 (2), 0.96 (11), 1.4 (22)
Sodium	0.03 (21), 0.12 (14), 0.20 (23), 0.24 (10), 0.25 (8), 0.44 (22), 0.73 (4), 1.0 (11)
Titanium	0.04 (22), 0.14 (8), 0.20 (9), 0.22 (10)

Table 2.15 (continued)

	mg kg^{-1} (ref)
Antimony	0.9 (22), 10 (10), 15 (8)
Arsenic	8 (16, 22), 10 (25), 25 (8), 116 (4)
Barium	89 (21), 500 (4), 540 (10), 1,100 (11, 22), 1,500 (9), 7,000 (8)
Boron	11 (21), 20 (8), 35 (4, 10), 50 (9), 250 (11)
Cadmium	6.7 (15), 10 (24, 25), 12 (16), 16 (4, 13), 26 (22), 40 (8), 45 (3), 57 (20), 65 (10), 87 (1)
Chlorine	700 (8), 2,900 (10), 7,100 (22)
Chromium	62 (14), 100 (9), 280 (13, 22), 380 (16), 500 (25), 550 (8), 870 (15), 1,300 (10), 1,400 (4), 2,900 (11), 4,300 (24)
Cobalt	7 (4, 22), 9 (10), 11 (15), 12 (9), 30 (25), 55 (8)
Copper	62 (14), 260 (13), 440 (18), 470 (21), 550 (26), 560 (15), 700 (16), 800 (9, 25), 850 (8, 22), 1,000 (1, 4), 1,100 (24), 1,200 (3, 10), 1,600 (20), 1,450 (11), 2,000 (23)
Fluorine	20 (8), 87 (10), 260 (25)
Lead	180 (15), 240 (24), 370 (13), 400 (8), 480 (16), 500 (25), 540 (4), 700 (9), 860 (20), 910 (3), 920 (22), 940 (1), 1,500 (10)
Manganese	110 (11), 130 (18), 140 (10), 190 (21), 220 (22), 260 (14, 25), 280 (4, 24), 390 (15), 400 (9), 750 (8), 3,400 (13)
Mercury	3 (16), 5 (4, 15), 6 (8, 13), 7 (10), 8 (22)
Molybdenum	4 (25), 5 (9), 8 (8), 9 (10), 12 (21), 13 (21), 30 (4), 85 (22)
Nickel	26 (21), 29 (14), 51 (15), 52 (16), 56 (13), 80 (9, 25), 85 (4), 94 (26), 120 (8, 24), 130 (3), 140 (20), 170 (10), 230 (1)
Silver	20 (9), 200 (8)
Strontium	210 (10), 250 (8), 300 (9)
Tin	14 (25), 80 (8), 90 (22), 120 (9), 190 (10)
Vanadium	15 (8), 20 (22), 36 (10), 60 (9)

Table 2.15 (continued)

	mg kg^{-1} (ref)
Zinc	980 (13), 1,300 (26), 1,600 (15), 1,700 (8, 22, 25), 1,800 (10), 1,900 (4, 20), 2,200 (16, 18), 2,500 (21), 3,000 (9, 12), 3,200 (14), 6,200 (3), 6,500 (1)
Zirconium	18 (10), 45 (8), 50 (23), 150 (9)

Source of values for Table 2.15

(1) 8 Indiana treatment works
(2) Generalised values, USA
(3) 10 Indiana works
(4) 20-80 works, north-east USA
(5) 13 US works
(6) 11 Indiana works
(7) 10 works, Italy
(8) One UK works, repeatedly sampled
(9) 42 UK works
(10) 16 US works
(11) One Wisconsin works
(12) Domestic sludges, Connecticut
(13) 3 W Virginia works
(14) Poland, 3 towns
(15) 93 works in Sweden
(16) 57 sludges from Michigan
(17) 9 sludges from Iowa
(18) (a) 7 works USA
(b) 12 works Ohio
(c) 9 works USA
(d) Average, USA
(19) Connecticut
(20) 8 works, Connecticut
(21) 2 works Georgia, repeatedly sampled
(22) One US works
(23) 12 works, Oklahoma
(24) 3 Canadian works
(25) General median values
(26) DoE

All references Dr P Beckett (pers comm)

SEPARATION OF THE PRINCIPAL COMPONENTS OF SLUDGE

In order to develop a model of heavy metal chemistry in the digester we must identify the major forms of combination and assess the proportion of each element held by each form. However, the complex nature of sludge means that it is virtually impossible to gain any useful information about its constituents without first separating them into defined uniform fractions.

Previous attempts by other workers to fractionate sludge have been described in the preceding chapter. The methods used have fallen into 3 broad categories. As sludge is a water-based suspension, most workers have started by fractionation in water, by settling or elutriation (Baldwin et al, 1982) or by flocculation (Hayes and Theis, 1978). Other workers have separated dried ground sludge on a density gradient (Bergman et al, 1979) or tried to concentrate particular fractions by the use of clearing agents to destroy organic matter (Levi-Minzi et al, 1981), or by magnetic separation to concentrate Fe-bearing grains (Seitz et al, 1973). 'Fractionation' by extractants cannot be regarded as a method of separation.

Density separation attempts to resolve the components of sludge into organic and inorganic fractions, and then to separate different mineral groups on their density. Bergman et al (1979) started by oven-drying their sludge, and then grinding it in a pestle and mortar; the powder was then placed on a density gradient and centrifuged. Many minerals were recovered in fractions far removed from their natural densities, and even the fraction of highest density contained an appreciable content of volatiles, which

suggests that the grains had been coated by organic materials. It is possible that the drying process used by Bergman et al had baked an amorphous organic layer onto the mineral grains. The blurring of fractions will be exacerbated if grains of different types of minerals are cemented into aggregates. Dried organic films may be hydrophobic and Bergman et al needed to use a surfactant to solubilise the dried material in the organic liquids. This problem had been encountered by previous workers (Greenland and Ford, 1964). Pilkington and Warren (1979) separated marine sediments and found a surfactant was needed only for particles finer than 10 μm.

Bergman et al (1979) divided the density range 1.75 to 2.85 gm cm^{-3} into 6 fractions. Fewer fractions within that range and extra fractions at higher densities would have been more useful, as many of the minerals relevant to heavy metal chemistry have densities higher than 2.85 gm cm^{-3} (table 5.2).

Levi-Minzi et al (1981) treated sludge with strong peroxide to produce a mineral sample sufficiently free from organic matter to give a clear X-ray pattern, but peroxide may dissolve some mineral types (eg sulphides) and cause artefacts by altering the oxidation state of cations such as Fe.

Before starting to develop a standard separation procedure we compiled a list of the major components to be expected in sludge, from the literature and from common sense, of which the most important categories are:

Detrital - minerals from soil and industrial sources

- organic detritus such as plant residues, hairs, plastics and paints

Secondary - precipitated minerals

- amorphous degraded organic matter

- digester biomass

From earlier work (Baldwin et al, 1982; Rodkiewicz, 1981) it is clear that secondary precipitates often form on the surface of other minerals. Secondary precipitates may then act as a cement to aggregate adjacent particles, both organic and inorganic. Particulate matter may be also coated with bacterial detritus and amorphous organic matter, and enmeshed in flocculated biomass.

In order to separate these components the flocs must first be dispersed. This may be achieved by dilution and agitation. At the beginning of this project I inherited the elutriator used by Baldwin et al (1982). This consisted of a series of 4 glass vessels connected in series (Fig 3.1A), each of which had a rotating bladed glass stirrer through the centre. Each successive vessel was wider than the previous one, and since the flow rate was constant, the flow velocity up through the main body of each vessel was successively less. This flow velocity had been related to the theoretical Stokes diameter of a particle that could fall faster than the upward velocity of the water and would therefore be trapped in the main body of the vessel.

There were a number of problems with the apparatus as it stood. It was slow because only as much sludge as could be diluted by the volume of the first flask could be added at a time, and the process had to be stopped when any one vessel reached too high a viscosity from the material accumulating in it. The sludge could not be pre-diluted because the particulates would settle out and block the inlet, and since sludge is a viscous mixture of granular and

fibrous material it could not be added continually by peristaltic pump; both of which I tried. The second and more important problem was that elutriation depends on a smooth flow to size the particles accurately, but the particles also needed to be shaken free of the embedding 'gunge'. The turbulence resulting from the stirrer caused more particles to end up in the wrong fractions than the right one.

After a period of experimenting with several different designs, I achieved a design that allowed a considerably greater volume of sludge to be separated (figure 3.1B). This allowed material, of too large a diameter to be held in suspension by the velocity of the flow, to fall out below the point of entry of the water. This apparatus was used to separate the fractions examined in the first exploratory series of SEM and XRD experiments (appendix 5, samples 1-5). Ultimately, I was unable to solve the problem of stirring.

However, the major weakness of this approach is that it attempts to separate sludge into physical rather than functional fractions. If such a model is to be used with any sludge people may wish, a functional fractionation that is pragmatic and easily repeatable is required. The literature review had shown that the heavy metals were likely to be held in three pools:

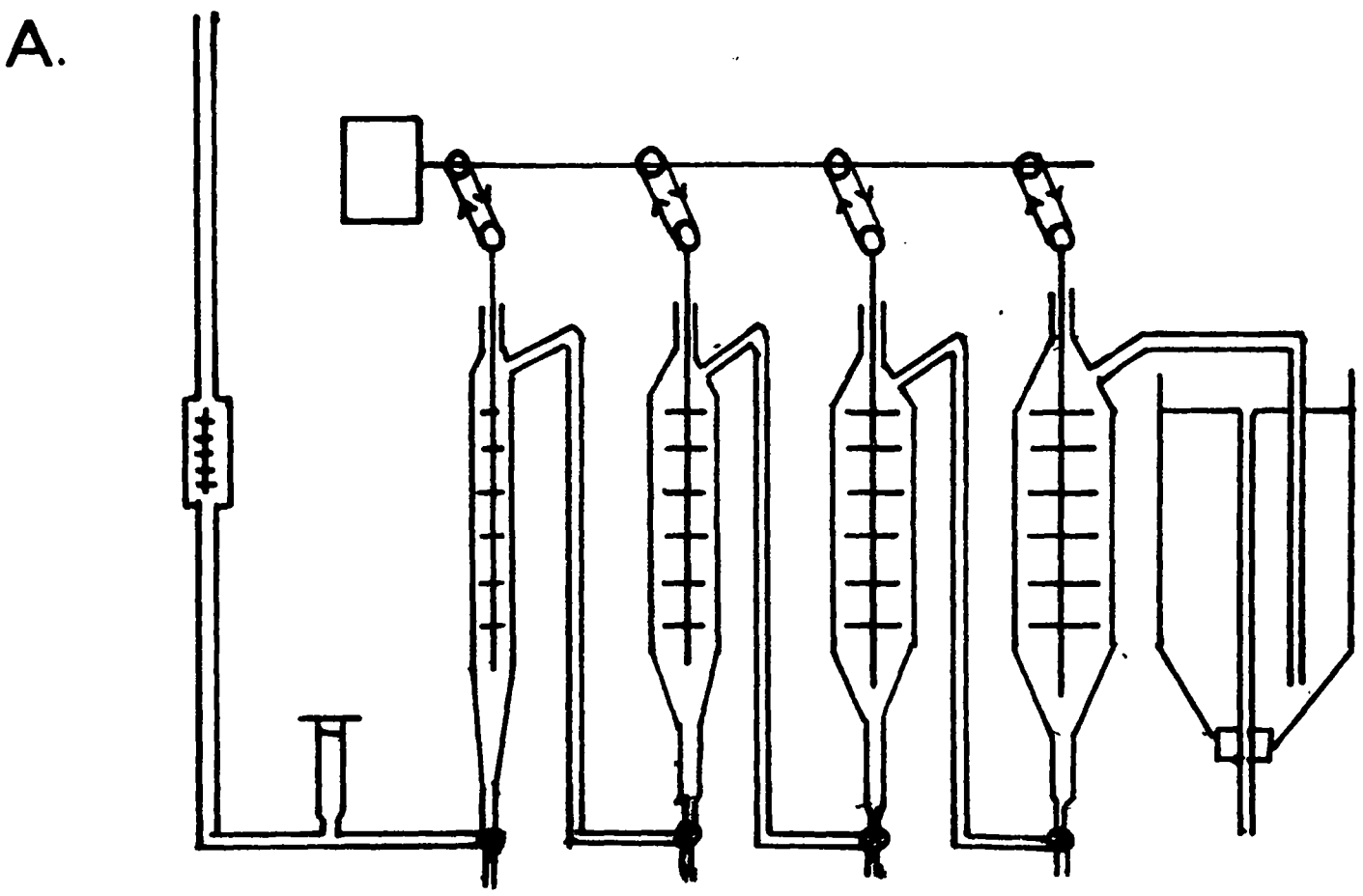
1 as precipitated and detrital mineral phases;

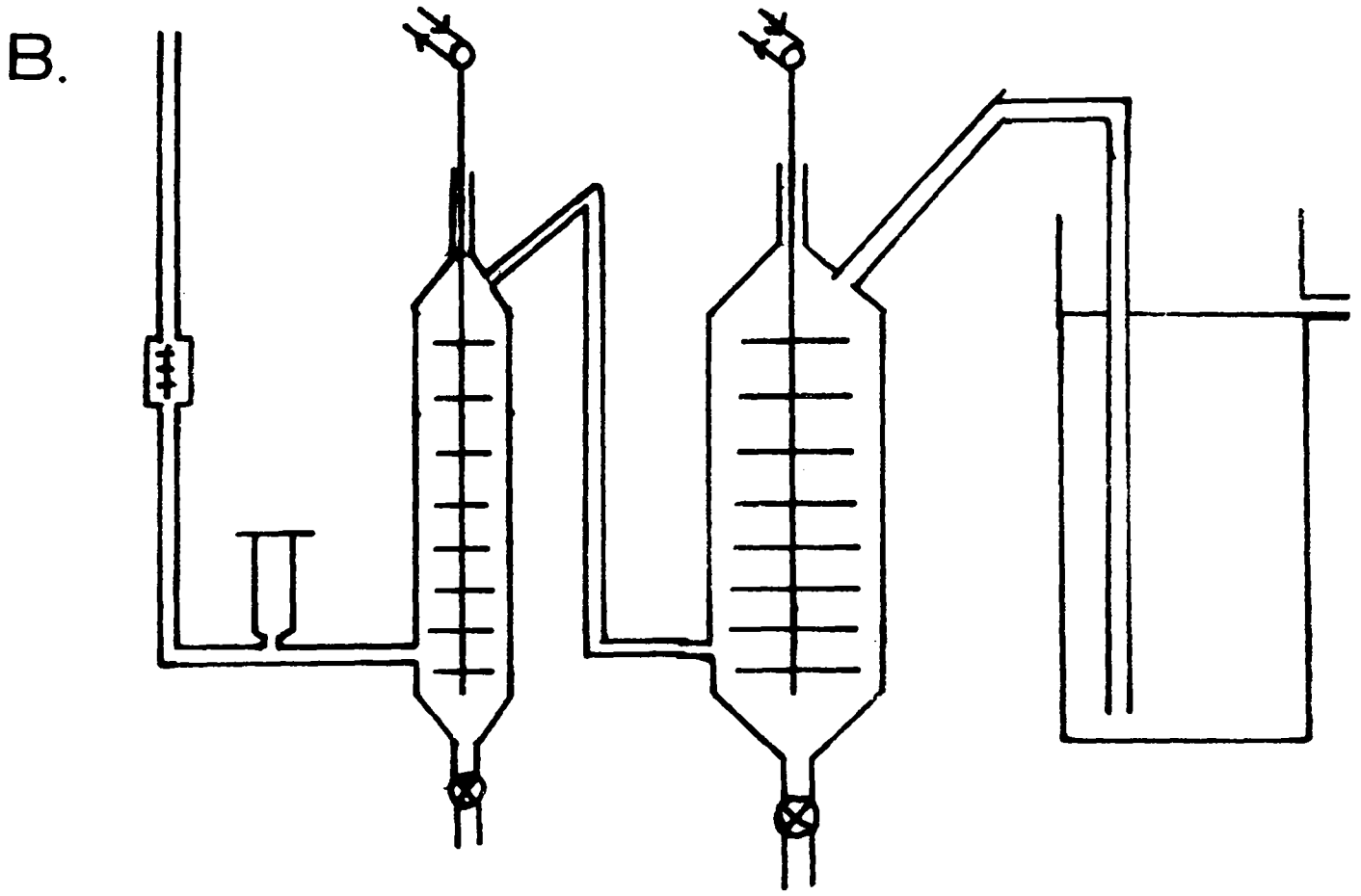
2 as complexes with the flocculated biomass;

3 as organic and inorganic complexes in solution.

Consequently, I switched to the simpler method of sedimentation. With this method, it seemed possible to define ideal fractions in sludge (table 3.1), according to a scheme of separation (table 3.2), as a starting-point for more detailed studies.

Figure 3.1 Elutriator designs





A. The top design was that used by Baldwin et al (1983), which I inherited at the start of this project.

B. The improved design which suffered less from the problems outlined in the text.

Table 3.1. Principal fractions of sewage sludge

Fraction	Definition	Composition	Heavy metal combinations
Particulate	Will settle 10 cm in water in less than one minute.	Mineral grains, plant fragments, hair, fibres, fragments of metal or plastic: these may be coated or cemented by secondary precipitates. If not cleared will be enmeshed in Biofloc.	In primary[(a)] particles: as amorphous or crystalline precipitates on grains or fragments; possibly exchangeable on inorganic surfaces.
Biofloc	Pelleted by centrifugation at 3,500 rpm for 30 mins, after elutriation of the Particulate material.	Flocculated bacteria, bacterial detritus and organic mucilage; also fine plant fragments, fine mineral grains and amorphous precipitates.	Organic complexes: intracellular and extracellular uptake; amorphous inorganic precipitates.
Colloid (gunge[(b)])	Pelleted by centrifugation at 12,000 rpm for 30 mins.	Colloidal organic matter, isolated bacteria, very fine plant fragments and clays.	Organic complexes: exchangeable on clays or amorphous precipitates on clays.
Soluble	Supernatant from centrifugation at 12,000 rpm for 30 mins.	Soluble and colloidal organic matter >100,000 MW but much of it <1,500 MW, inorganic ions.	Simple ions, complex ions, complexed organic matter.

(a) Where possible it is convenient to distinguish the grains, coating or precipitates known to have been formed in the digester from those present in Raw sewage.

(b) The 'gunge' of Baldwin et al (1983) contained variable and sometimes substantial proportions of Biofloc depending on how it was separated.

Table 3.2 Sludge fractionation

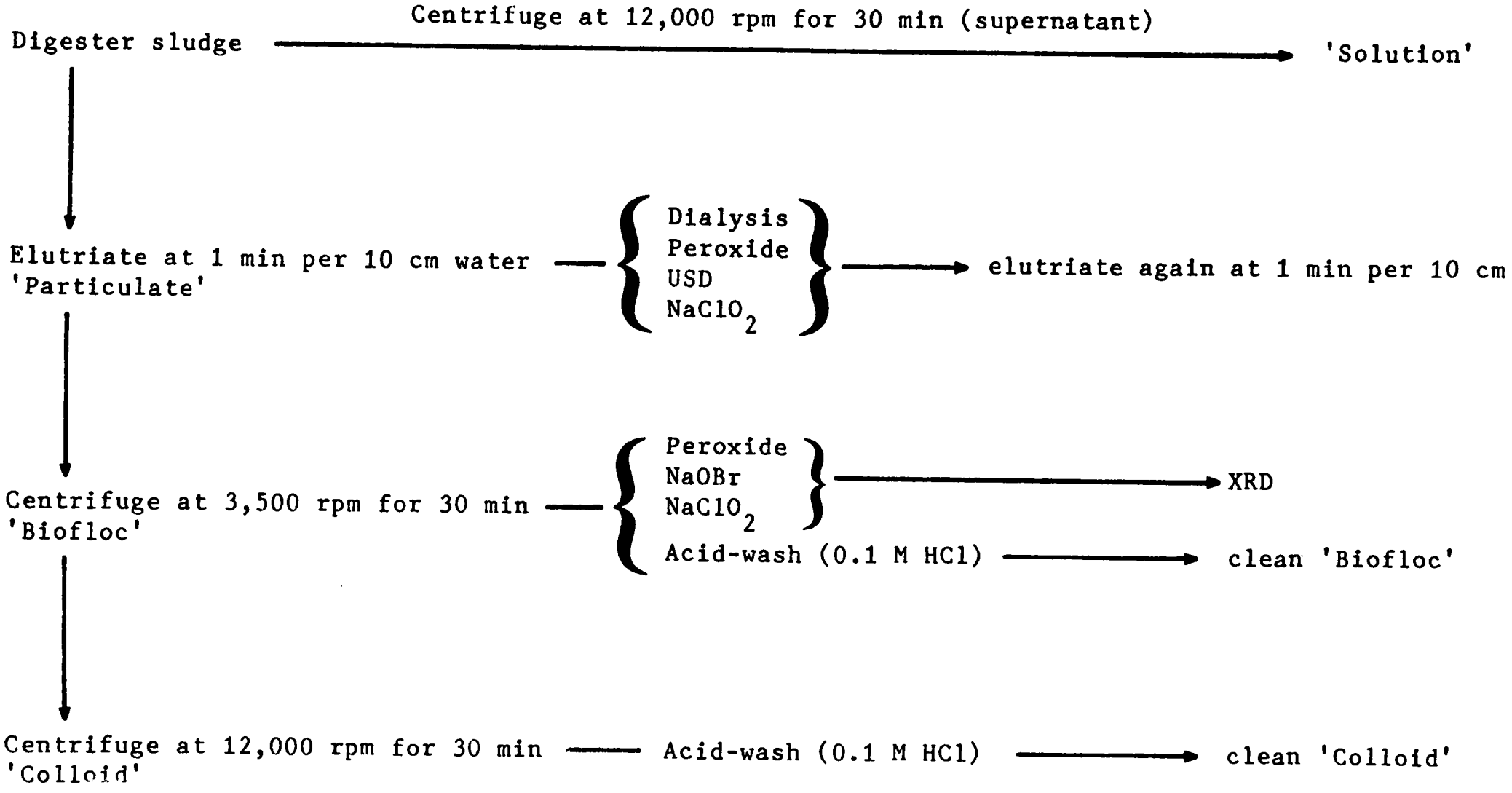


Table 3.3. Comparison of analyses of the solution after centrifugation and filtration

Treatment	Na	K	Ca	Mg	Li	Ba	Mn	Cu	Zn	Ni	Fe	S	P
12,000 rpm x 30 min	94	85	161	31	0.019	0.014	0.142	na	0.011	0.021	0.86	12.7	69
12,000 rpm x 60 min	95	84	158	31	0.02	0.008	0.123	0.52	0.013	0.025	0.31	13.7	67
0.3 μ filter	95	95	130	36	0.021	0.004	0.051	0.29	0.007	0.018	0.09	17.8	59
0.1 μ filter	126	101	101	19	0.022	0.002	0.001	0.51	0.018	0.022	0.06	23.5	31

Units: mg litre^{-1}

na - not available

Cadmium, vanadium and lead were below the limits of detection.

Analyses were done by ICP.

Definition of the fractions

The 'Particulate' fraction is functionally defined as the material that will settle through 10 cm water in less than one minute: this figure is chosen to include as much as possible of the mineral phases whilst excluding all of the biomass. A 50-fold dilution is needed to reduce the divalent cation concentration enough to deflocculate the biomass and release enmeshed material; 100-fold dilution is better. The purity of any fraction can be simply related to the number of times the material is resedimented. Sedimenting 3 times left very little visible organic matter on the surface of the particles.

There is a risk that secondary precipitates might dissolve during dilution. This was checked by comparing the 'Particulate' fraction sedimented in industrial methylated spirit (IMS) with a comparable fraction sedimented in water; allowance was made for the difference in densities between the two solvents (appendix 5, samples 14.2-14.4). There was no discernible difference between the 2 fractions under the SEM or XRD; however these techniques would not reveal the loss of small amorphous deposits (less than 1 μm).

The 'Biofloc' is defined as the material that pellets out when centrifuged at 3,500 rpm for 30 minutes after the 'Particulate' fraction has first been removed by dilution and settlement. As separated, this fraction will include all the bacterial biomass, but will also include those mineral grains and other particulate matter too fine to settle through 10 cm of water in one minute. It may also contain some enmeshed particulate material that was not released by dilution and stirring from the flocculated organic matter.

The supernatant from centrifuging whole sludge at 3500 rpm contains the 'Colloid' fraction and the 'Solution'. The division between these 2 is arbitrary, but the definition has been chosen so as to give an optically clear solution.

Several authors have standardised on the use of 0.45 µm filters to distinguish dissolved material in solution from particulate material. However, this has now been shown to be inadequate (Danielsson, 1982). Partitioning by filters depends on their loading, and the solutions can be modified by leaching and by adsorption. More importantly, it has been shown that particulate aluminium can pass through 0.45 µm filters (Hem and Robertson, 1967), some clay particles can pass through a 0.45 µm filter (Kennedy et al, 1974), and up to 80% of the 'dissolved' iron passing through 0.45 µm filters can be collected by 0.05 µm filters. Cameron and Liss (1984) showed that much of iron passing through 0.45 µm filters may be present as fine colloidal particles.

To try to avoid these problems, the use of centrifugation and the use of filtration to separate the 2 fractions were compared. Centrifugation gave more consistent results (table 3.3). Increasing the time of centrifugation to one hour had little effect apart from on the Fe concentration. Centrifugation offers the additional advantage of being independent of the volume separated. Filtration suffers because the filters clog rapidly even when glass fibre pre-filters have been used and frequent filter changes increase the chance of error in the small volume of liquid filtrate. This is shown by comparing the results of the 2 filter sizes (table 3.3). The finer filter gave a higher concentration than the coarser filter for some elements.

Further purification of the fractions

As indicated, several repetitions of sedimentation and centrifugation may be needed to free fractions from occluded finer material or enmeshed coarser material. Even so, there may remain fine mineral grains in the 'Biofloc', and organic matter coatings on the 'Particulate' grains. The possibility of further purifying the fractions by various pre-treatments and post-treatments was investigated; these are listed in appendix 1.I.

1) Particulate

With the 'Particulate' fraction it was important to identify the secondary precipitates that were commonly formed; the surface of detrital minerals seemed to be the best place to look for them. Therefore, it was necessary to clean the organic matter off the surface of the grains without disturbing the secondary precipitates. This might be done by using reagents that either dissolve or oxidise organics, or by shaking the organics off. The most effective treatment was found as a by-product of the method used to prepare the particulate matter for density separation. This involved washing the material successively in industrial methylated spirits (IMS), acetone and ether. These solvents dissolved much of the organic coating and released a proportion of the clays that had previously been held on the surfaces of the grains. As a result, fewer grains analysed as aggregates. Even this treatment left a residual carbon content of 2% (analysed by combustion and CO_2 analysis: see appendix 1.J), some of which may have been occluded in cemented aggregates.

Table 3.4 Reduction in background noise during separation

Elutriation	Drying	Study*	Background noise
Once in water	air	6	6.0
3 times in water	air	14.3	4.3
3 times in IMS	air	14.4	3.2
3 times in water	IMS/ acetone/ether	after 14	2.5

* see appendix 5

The effect of these treatments is shown by the reduction in background noise on the SEM micro-probe analyses. The background on different analyses can be compared by taking the height of the background when the plot is scaled to a standard size vertically after a specified counting period. This provides a very rough qualitative guide. The results (table 3.4) show that solvent drying reduced the background noise by around 40% while sedimenting in IMS reduced the background noise by around 25%.

Any organic matter remaining on the surface of the grains could potentially be removed by the use of clearing agents (appendix 1.I, and table 3.2). Four methods were compared (appendix 5, sample 32): ultrasonic dispersion, dialysis to remove small soluble components, and 2 oxidising agents - peroxide and chlorine dioxide.

Aliquots of the 'Particulate' fraction were treated with various clearing agents and post-treatments after separation, and the effects of these are given in table 3.6A-L.

The results are presented first as the effect of the treatment on the concentrations of the heavy metals in the different density cuts, and then as the percentage of the total heavy metals in the different density cuts. In each case the fraction labelled 'supernatant' is the material that the treatment removed from the fraction.

In order to obtain sufficient mineral material to work with, thicker sludge was obtained by auger from the bottom 4 feet of the digester. The weight distribution of this sludge is different from that of sludge removed from the top of the digester because of its high proportion of quartz and lower organic content. In order to make the figures comparable with normal sludge, they have been reworked using the standard weight distribution of table 3.8, and presented as percentages of total metal (table 3.6I-L). It was not possible to collect the material removed by dialysis because of the large quantity of water involved.

Table 3.5 Oxidation of samples by clearing treatments

Treatment	Average relative peak height					Number
	Fe	Cu	Zn	Ni	S	analysed
USD	13	1.2	4.3	0.7	16.4	14
Dialysis	37	0	0	0	8.4	11
ClO_2	17	0	0	0	1.3	11
Peroxide	19	0	0	0	1.1	11

Table 3.6. Effects of clearing agents on the 'Particulate' fraction

(A) Dialysis

Density	Fe	Cu	Zn	Ni	Cd
<1.6	8,400	92	520	80	2
1.6-2.2	19,000	290	1,600	100	10
2.2-2.9	13,000	110	860	40	2
2.9-3.3	130,000	3,200	7,100	130	13
>3.3	260,000	14,000	16,000	1,400	54

(B) Ultrasonic dispersion

Density	Fe	Cu	Zn	Ni	Cd
<1.6	6,800	120	410	56	1
1.6-2.2	16,000	280	1,700	92	9
2.2-2.9	11,000	110	920	37	2
2.9-3.3	140,000	4,200	10,000	400	7
>3.3	280,000	20,000	17,000	1,500	190

(C) Chlorine dioxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	3,000	67	170	20	-
1.6-2.2	10,000	150	640	38	-
2.2-2.9	11,000	180	1,100	45	-
2.9-3.3	98,000	1,800	1,700	210	-
>3.3	400,000	8,000	8,100	960	-

(D) Hydrogen peroxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	6,300	210	820	57	4
1.6-2.2	17,000	290	1,100	76	5
2.2-2.9	12,000	180	1,200	33	5
2.9-3.3	180,000	4,900	2,000	120	6
>3.3	260,000	17,000	7,400	1,100	-

Table 3.6 (continued)

Effects of clearing agents: Percentage of the total metal in each density cut

(E) Dialysis

Density	Fe	Cu	Zn	Ni	Cd
<1.6	2	2	2	6	3
1.6-2.2	4	4	4	6	12
2.2-2.9	76	44	76	67	67
2.9-3.3	7	12	6	2	5
>3.3	11	39	11	19	14
Supernatant	-	-	-	-	-

(F) Ultrasonic dispersion

Density	Fe	Cu	Zn	Ni	Cd
<1.6	2	2	2	5	1
1.6-2.2	5	4	6	6	8
2.2-2.9	65	32	65	55	33
2.9-3.3	7	10	6	5	1
>3.3	13	44	9	17	27
Supernatant	6	8	12	12	30

(G) Chlorine dioxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	1	1	1	1	-
1.6-2.2	1	1	1	1	-
2.2-2.9	63	56	86	65	-
2.9-3.3	6	7	2	3	-
>3.3	27	32	8	17	-
Supernatant	2	4	3	13	-

(H) Hydrogen peroxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	3	4	4	6	4
1.6-2.2	4	3	3	5	3
2.2-2.9	74	54	86	64	85
2.9-3.3	8	11	1	2	1
>3.3	7	25	3	10	0
Supernatant	4	3	5	14	6

Table 3.6 (continued)

Effects of clearing agents: Percentage of the total metal in each density cut*

(I) Dialysis

Density	Fe	Cu	Zn	Ni	Cd
<1.6	10	6	9	22	7
1.6-2.2	23	19	28	27	49
2.2-2.9	44	20	43	31	27
2.9-3.3	8	10	6	2	3
>3.3	15	45	14	19	13
Supernatant	-	-	-	-	-

(J) Ultrasonic dispersion

Density	Fe	Cu	Zn	Ni	Cd
<1.6	9	6	6	15	4
1.6-2.2	21	14	26	25	31
2.2-2.9	40	16	40	29	16
2.9-3.3	9	10	8	5	1
>3.3	18	50	13	20	32
Supernatant	4	4	7	6	15

(K) Chlorine dioxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	4	5	4	7	0
1.6-2.2	14	12	14	14	0
2.2-2.9	45	41	69	47	99
2.9-3.3	7	7	2	4	0
>3.3	28	31	9	18	0
Supernatant	1	3	2	10	1

(L) Hydrogen peroxide

Density	Fe	Cu	Zn	Ni	Cd
<1.6	8	10	14	17	17
1.6-2.2	21	14	18	25	21
2.2-2.9	42	24	57	31	56
2.9-3.3	11	11	2	2	1
>3.3	16	40	6	18	0
Supernatant	2	1	3	7	4

* These figures (I-L) are taken from analyses of the 'Particulate' fraction of sludge taken from the bottom 4 feet of the digester, and then adjusted for weights of different fractions in order to be comparable with the figures for sludge taken from the digester outlet.

Only small proportions of the heavy metals are released from the 'Particulate' fraction by the treatments, averaging 6% altogether. Comparison with the SEM studies on the effects of these treatments (appendix 5, sample 32) showed the treatments to have no discernible effect, except for the increasing oxidation of the sample with increasing severity of treatment. The average peak heights for Fe, Cu, Zn, Ni and S for each treatment are presented in table 3.5. These relative peak heights cannot be analysed statistically because the analyses are not taken from a random selection, but rather from points at which the grains looked interesting. However, they do reveal a general trend. In particular, the relative lability of Cu, Zn and Ni compared to that of Fe and S is striking (table 3.5).

It would seem that the 'Particulate' fraction, as defined, is largely free of contaminating organic matter, and not in need of any further purification. Hence, it is recommended that clearing agents are not used on this fraction, as they are more likely to cause artefacts than to purify the separates.

The combined 'Particulate' and 'Biofloc' fractions were treated with the 2 oxidising agents used above. When all the organic matter was destroyed by ClO_2 around half of the total heavy metals were released into the supernatant, except for the Fe which apparently precipitated out but without taking the other heavy metals with it. This further highlights the possible changes that may occur in the location of the heavy metals on oxidation of the sludge (see chapter 10, sections 4 and 5).

Even after the mineral grains had been cleaned there remained the problem that, though studies on mineral fractions had showed

that only the Fe oxides and the sulphides played an important role in heavy metal chemistry, the dominance of detrital mineral grains (quartz, feldspar, calcite) obliterated the fainter lines of the most relevant minerals on the X-ray pattern (the quartz pattern is particularly strong), and hid them under the SEM. It was therefore necessary to concentrate the relevant mineral fractions, and to this end density separation and magnetic separation were examined.

Magnetic separation had previously been used to concentrate and identify vivianite ($FePO_4$) in anaerobic sludge (Seitz et al, 1973). Magnetic grains were picked out of the 'Particulate' fraction by a simple hand magnet, and sellotape was then used to get them off the magnet. This method is simple but very effective because the sellotape preparation can be used directly for XRD analysis, while if double-sided sellotape is used, it may be directly mounted and coated for the SEM.

The density separation method used by Bergman et al (1979) had 2 weaknesses. It resulted in organic matter being baked onto the surface of the particles during oven-drying, and it could not easily be used to separate a sufficient quantity of material for both SEM and XRD. Their method was improved upon by drying the 'Particulate' fraction in organic solvents (appendix 1.C). This gave clean separate particles which no longer required the use of surfactants to give a clean separation in the high density liquids; indeed the surfactants tended to make things worse, causing severe flocculation. The quantity of material that could be separated was increased by using a 'float/sink' method, with density cut-off points chosen to cut between the major groups of minerals rather than a density gradient method. (This offers the advantage that the

float/sink separation can be easily repeated for any fraction to improve its purity).

The first density cut was chosen at 1.6 gm cm^{-3} to remove large organic fragments like tomato pips. The second was chosen at 2.2 gm cm^{-3} to remove the rest of the organics and bone fragments. These 2 fractions might then be combined for analysis, but their stepwise removal minimised losses of the heavier fractions. The third cut was chosen at 2.9 gm cm^{-3} to remove quartz, calcite and calcium phosphate, and the last was chosen at 3.3 gm cm^{-3} to remove aluminosilicates like feldspar and garnet. This leaves in the final fraction most of the iron oxides, iron carbonate, the sulphides and industrial abrasives with densities greater than 3.3 gm cm^{-3} (cf table 5.2 for mineral densities).

After comparing the spectra of grains after density separation in this way with those not separated, it was concluded that the procedure introduces no artefacts and effects no changes in the minerals. This conclusion was also reached by Essington (1983) who showed that heavy metals in soil samples are not solubilised in ethanol, and Pilkington and Warren (1979) who showed that Pb, Cd and Zn in marine sediments were not solubilised in the acetone/tetra-bromoethane mixture they used for density gradient separation. The concentrations of Pb, Cd and Zn in the mixture after separation were <0.01 ppm, <0.002 ppm and <0.1 ppm respectively.

In spite of this treatment some minerals still separated in the 'wrong' density fraction. In particular, many Fe-rich particles ended up in the 2.9-3.3 gm cm^{-3} fraction with the aluminosilicates. This was attributed either to the presence of lighter coatings and/or cemented aggregates reducing the density of iron-rich

particles, or to iron coatings or iron cements on lighter grains.

When large quantities of the denser fractions were needed, the time-honoured method of 'panning' was used to remove the worst of the large organic fragments before density separation. This cuts both the time and cost of sample preparation significantly.

2) Biofloc

The work on the 'Biofloc' fraction has concentrated on 2 aspects: fine minerals enmeshed in it, and the need for organic material free from contaminating cations for studies on equilibrium binding.

2.1) The organic part

The only published work on separation of the biomass is by Hayes and Theis (1978), who separated what they defined as 'biomass' on its ability to flocculate, but only claimed to recover 75% of it; the material recovered probably included a substantial degree of contamination. They used an elutriator but strangely assumed that the flocculated biomass would sink while the mineral grains would remain suspended. This is in direct contrast to my experience and to that of Baldwin et al (1982).

Previous workers who measured equilibrium binding of cations by anaerobic sludge did not appear to have cleaned their material before use (Gould and Genetelli, 1982; Hao, 1979). Consequently, the meaning of what they measured is unclear.

I attempted to clear the contaminating cations by repeatedly washing the 'Biofloc' with dilute HCl (appendix 1.I). The results of 3 successive washes are presented (table 3.4A-E), together with a comparison of the results from washing with HF. Although HF is

thought not to damage organic matter, it was felt to be inappropriate for use in large volumes for routine washing, where a safer reagent would do. After the third wash in HCl most of the Ca, Ni, Zn and Pb had been removed, but one third of the Fe and half the Cu still remained. HF was much more successful at removing Fe and Cu but less successful at removing Ni (table 3.4E). If the Fe and Cu remaining are not 'available' to 0.1 M HCl then they are most likely to be in the form of inert mineral grains.

On the basis of these results, 3 overnight washings in 0.1 M HCl on a magnetic stirrer were standardised upon. The material was diluted to 1 gm litre^{-1}. After cleaning, the 'Biofloc' was sieved with a 1.0 mm sieve to remove hairs and other large fragments. It was then elutriated again to remove any mineral grains that were not acid soluble and that were previously enmeshed and had been prevented from settling out with the 'Particulate' fraction. Finally, the 'Biofloc' was adjusted to pH 5 and freeze-dried to be stored for use. It is unlikely that this harsh treatment will structurally damage the methanogenic bacteria (Dr D Archer, pers comm) which are related to the acidophiles, but it might damage the partial anaerobes.

2.2) The mineral part

It was necessary to ascertain whether the minerals held in the 'Biofloc' fraction were essentially the same as those in the coarser 'Particulate' fraction or whether they were different kinds of mineral. If they are the same they can be catalogued in the 'Particulate' fraction, which is easier to handle, and allowance made in the mass balance for the presence of identical material with the same properties in the finer fraction.

I examined the use of reagents to dissolve organics (samples 11 and 12), and to oxidise organics (sample 28) in the 'Biofloc'. The reagents used to dissolve organics mostly work by complexing the divalent and trivalent cations that cross-link organic polymers; some work by breaking open the hydrogen-bonding of aggregated polymers. The reagents usually contain a small monovalent cation like sodium as the counter-ion to replace the divalent and trivalent cations.

All the reagents that were tried failed to clear a sufficient proportion of the organics for the fine mineral grains to be visible under the SEM or to give clear enough diffraction patterns on the XRD. Several of the reagents also created artefacts: pyrophosphate forced the precipitation of calcium phosphate, sodium carbonate forced the precipitation of calcite, and sodium oxalate forced the precipitation of calcium and ammonium oxalates. Reagents that oxidise organic matter were more successful, and peroxide and chlorine dioxide both produced minerals with clearer diffraction patterns and enabled more crystalline phases to be resolved than hyperbromite did. Results are given in the next section. All these reagents destroy sulphides, but these could have been recognised in untreated samples.

Table 3.7 Effects of acid-washing the organic fractions

A) Analysis of the 'Biofloc' solids after washing in 0.1 M HCl

	Fe	Cu	Zn	Ni	Ca	
Untreated	11,000	810	5,300	105	23,000	mg kg^{-1}
1st wash	4,800	740	1,200	39	1,600	
2nd wash	4,500	590	530	nd	1,500	
3rd wash	3,500	490	130	nd	1,000	

B) Concentrations in the acid wash

	Fe	Cu	Zn	Ni	Ca	
1st wash	7.1	-	5.7	0.14	18	mg $liter^{-1}$
2nd wash	1.1	0.3	0.9	nd	1.4	
3rd wash	0.5	0.1	0.1	nd	0.7	

C) Analysis of other elements in the acid-washed 'Biofloc'

By ICPOES

K - 1,500	Pb - 20	Mn - 19	mg kg^{-1}
Mg - 530	Ba - 20	V - 13	
Al - 7,100	Sr - 17	Co - 2.6	

D) Analysis of the 'Colloid' solids after washing in 0.1 M HCl

	Fe	Cu	Zn	Ni	Cd	
Untreated	3,200	200	1,700	120	-	mg kg^{-1}
1st wash	900	140	120	-	-	
2nd wash	810	43	36	22	-	

E) Analysis of the remaining 'Biofloc' solids

After washing three times in 48% HF, sat. HBO_3

	Fe	Cu	Zn	Ni	Cd	
Untreated	11,000	810	5,300	105	31	mg kg^{-1}
3rd wash	340	240	320	45	nd	

F) Analysis of the 'Solution' before and after cleaning

	Fe	Cu	Zn	Ni	Cd	
Untreated	5.67	5.10	6.27	nd	nd	pM
Cleaned	6.45	6.23	6.91	nd	nd	

	Pb	Mn	Na	Mg	K	Ca
Untreated	7.32	6.33	2.11	2.84	2.55	2.56
Cleaned	nd	7.12	3.08	3.93	3.41	3.6

3) Colloid

The 'Colloid' was found to have no discernible structure under the SEM and to be amorphous to X-rays. The relevance of the 'Colloid' to the model is its ability to complex heavy metal cations, so, in the interests of simplicity, a purification scheme similar to that for the 'Biofloc' was used. The results of the acid-washing to clean the fraction are presented in table 3.7D. The results present a similar pattern to that of the 'Biofloc' fraction; very little Ni and Zn remained but one quarter of the Fe and Cu remained. However, each acid wash resulted in the loss of 20% of the material, making this fraction laborious to collect. But as this material was cleaned more easily than the 'Biofloc', only 2 acid-washes were used.

4) Solution

The 'Solution' also needed to be freed from complexed cations before the complexation capacity of the soluble and suspended organic matter it contained could be determined. This was achieved by adjusting it to pH 2 with 60% SPECTROSOL perchloric acid, reacting it with amberlite MB-3 amphoteric exchange resin for one minute, and then filtering it through hardened ashless paper. This resulted in the total concentration of each of the cations being reduced by a factor of 10; no cations were removed significantly more or less than any others (see table 3.7F). However, there was a concomitant reduction in the organic content of the 'Solution' from around 1 gm litre^{-1} to between 0.6 and 0.3 gm litre^{-1} as measured by loss of weight on combustion after oven-drying at 105°C.

Table 3.8 Breakdown of the fractions by weight

One litre of Beckton sludge typically contains 2.5% dry solids, ie 25 gm dry solids. Of this 25gm, the 'Particulate' fraction typically accounts for 3.5 gm, and the 'Biofloc' for most of the rest.

Of the 3.5 gm 'Particulate' matter, density fractionation breaks it down typically as:

<1.6 gm cm^{-3}	0.7 gm	20% of the 'Particulate'
1.6-2.2	0.7 gm	20% "
2.2-2.9	2.0 gm	58% "
2.9-3.3	0.04 gm	1% "
>3.3	0.04 gm	1% "

Thus, for whole sludge:

'Particulate'	14%	<1.6	gm cm^{-3}	2.8%
		1.6-2.2	"	2.8%
		2.2-2.9	"	8.1%
		2.9-3.3	"	0.14%
		>3.3	"	0.14%
'Biofloc'	78%			
'Colloid'	4%			
'Solution'	4%			

Table 3.9 Volatile content of fractions of Beckton sludge

A) By combustion**

	Carbon Content
Whole sludge	35%
<2.2 gm cm^{-3} 'Particulate'	20-30%
2.2-2.9 " "	2%
2.9-3.3 " "	2%

B) By ashing**

	Volatile Content
Whole sludge	70%
Sludge from the bottom 4 feet of digester	65%
Sandy material off bottom of the digester floor	25%
<2.2 gm cm^{-3} 'Particulate'	55%
2.2-2.9 " "	10%
'Biofloc' (acid washed)	80%
'Colloid' (acid washed)	80%
'Solution' (freeze-dried solids)	50-55%
Sludge from landfill digester	20%
Scale from walls of landfill digester	10%

** see methods

This process resulted in an overall cleaning factor of betweeen 3 and 6 for the organics relative to the heavy metals. This treatment did not appear to affect the nature of the organic content as judged by the titration curve before and after cleaning, but appeared to have removed an equal proportion of all classes of organic constituents (see chapter 6).

Summary of fractionation

In concept, I have defined the fractions pragmatically - they correspond to useful distinctions. They have also been defined functionally. In practice, separation by the non-destructive procedures proposed will rarely be complete. The fractions can be purified by potentially more destructive procedures, but the further from the original environment a fraction is removed, the more likely it is to have been changed. Hence, there is a trade-off between the 'purity' of a fraction and the confidence that can be placed in the results. However, comparison of results from treated and untreated samples will often show when changes or artefacts have occurred.

Mass balance - the division of heavy metals between the fractions

Analyses of the fractions (separated as above) by XRD and SEM tell us which minerals are present, or at least which elements associate with which in the particulate material. However, these particulate components might account for only a small proportion of the sludge. In order to locate the remainder of the heavy metals in sludge, we also need to know the total elemental analysis of each fraction.

Each fraction has been analysed for Fe, Cu, Zn, Ni, and Cd by acid digestion and atomic absorption spectroscopy (appendix 1.F). Where analyses of other elements were required, the digests were analysed by Inductively-Coupled Plasma Spectroscopy (ICP). The results are presented in table 3.11A-N. All the sludge samples analysed were from the TWA Beckton works, except the old lagooned sludges (3.11M) and sludge from the soft-water Solihull works (3.11G-H).

3.11A - analysis of whole sludge presented as mg kg^{-1} dry weight and as mg $litre^{-1}$ wet weight. This is for digester sludge from Beckton taken from the normal outlet. The various fractions taken from this, as described in the section on separation, are presented in 3.11B to 3.11F.

3.11G - comparable figures for sludge taken from the Solihull works, a soft-water region, and 3.11H the 'Particulate' fraction separated from 3.11G.

3.11I - analysis of material taken by auger from the bottom 4 feet of the Beckton digester. Taken while the digester was being pumped out for cleaning, this thicker material contains 10% dry solids, but the high quartz content lowers the overall concentration of heavy metals. The analysis of the 'Particulate' fraction separated from this is presented in 3.11J.

3.11K - analysis of sandy material taken from the floor of a digester during cleaning. The material was partially aerobic, and had been partially washed during the cleaning process. The analysis of the 'Particulate' fraction separated from this is presented in 3.11L.

3.11M - analysis of various old lagooned sludges from various works in the TWA region. These were obtained in readiness for work on long-term changes in heavy metal chemistry and chosen to provide a good range of heavy metal concentrations and ages.

3.11N - analysis of sludge from a landfill digester, and of scale precipitated on the walls of that digester (which is mainly calcite). It can be seen that heavy metals have been excluded from the precipitate relative to Ca: the heavy metals it has incorporated may be largely accounted for by occlusion of iron-bearing compounds.

These results for the 'Particulate' fraction can be compared with the SEM analysis of the different density cuts (table 5.1), and with the list of minerals identified by XRD (table 5.4). The analysis of the density cuts shows the marked concentration of heavy metals in the fraction with density >3.3 gm cm^{-3} that would include the sulphides and the iron oxides. The heavy metal content of the lighter mineral fractions is probably mainly in the form of secondary precipitates of sulphides on the surface of lighter minerals grain (such as quartz - see figure 6.2) or occluded in aggregates of lighter minerals. Further evidence of this is given in chapter 5.

The acid digestion procedure often leaves a small undissolved residue. The results of analysis of the residue by XRD and SEM are presented in table 3.10.

Table 3.10 Minerals not dissolved by acid-digestion

Density cut	Mineral	Formula
2.2-2.9 gm cm^{-3}	Quartz	SiO_2
	Gypsum	$CaSO_4$
>3.3 gm cm^{-3}	Corundum	Al_2O_3
	Carborundum	SiC
	Anatase	TiO_2
	Rutile	TiO_2
	Anglesite	$PbSO_4$

The gypsum and the anglesite must have been precipitated by the sulphuric acid used in digestion since they are not normally present in anaerobic sludge, although oxidised sludge may contain gypsum (Bergman et al, 1979). There were no detectable levels of Fe, Cu, Zn, Ni or Cd in the undissolved residue. It is unlikely that the undissolved residue will have any effect on the heavy metal analyses.

There are problems in sampling material as heterogeneous as digester sludge, although it is buffered against the sharp variations in concentration in the incoming raw sewage by the process of continually removing some digested sludge and adding more raw sludge to the digester. In order to minimise variation, samples were finely ground before aliquots were taken, and where possible all analyses were performed in triplicate. Unfortunately, this was not always possible with the 2.9-3.3 gm cm^{-3} and >3.3 gm cm^{-3} density cuts, where it was laborious to separate sufficiently large quantities to work with.

Table 3.11. Elemental analysis of fractions

(A) Whole digester sludge (Beckton) (dry solids mg/kg; wet sludge mg/l)

	Fe	Cu	Zn	Ni	Cd
Dry solids	12,000	760	4,700	76	27
Wet sludge	300	19	118	1.9	0.7

(B) '3,500 rpm pellet' = 'Biofloc' + 'Particulate' taken from (A) (mg/kg)

Fe	Cu	Zn	Ni	Cd
11,000	770	5,300	80	26

(C) 'Biofloc' taken from (A) (mg/kg)

Fe	Cu	Zn	Ni	Cd
11,000	810	5,300	76	31

(D) 'Particulate' taken from (A) (mg/kg)

Density	Fe	Cu	Zn	Ni	Cd
<1.6	6,400	100	1,100	37	4
1.6-2.2	11,000	140	1,300	47	7
2.2-2.9	17,000	200	1,800	67	6
2.9-3.3	33,000	1,500	4,500	120	16
>3.3	260,000	22,300	14,000	2,300	97

(E) 'Colloid' taken from (A) (mg/kg)

Fe	Cu	Zn	Ni	Cd
3,200	91	380	nd	nd

(F) 'Soluble' taken from (A) (mg/l)

Fe	Cu	Zn	Ni	Cd
0.31	0.52	0.013	0.025	nd

Table 3.11 (continued)

(G) Whole digester sludge (Solihull) (dry solids mg/kg; wet sludge mg/l)

	Fe	Cu	Zn	Ni	Cd
Dry solids	12,000	680	1,300	65	5.5
Wet sludge	300	17	33	1.6	0.14

(H) 'Particulate' taken from (G) (mg/kg)

Density	Fe	Cu	Zn	Ni	Cd
<2.2	8,000	180	500	31	nd
2.2-2.9	13,000	240	550	51	nd
2.9-3.3	110,000	3,300	4,100	480	nd
>3.3	320,000	67,000	16,000	3,600	17

(I) Whole sludge from bottom four feet of the digester (Beckton) (mg/kg)

	Fe	Cu	Zn	Ni	Cd
Dry solids	16,000	420	2,600	110	11

(J) 'Particulate' taken from (I) (mg/kg)

Density	Fe	Cu	Zn	Ni	Cd
<2.2	12,000	130	980	14	8
2.2-2.9	13,000	240	1,200	70	10
2.9-3.3	190,000	5,600	15,000	640	23
>3.3	310,000	25,000	19,000	2,600	140

(K) Sandy material taken from bottom of the digester during cleaning (Beckton) (mg/kg)

	Fe	Cu	Zn	Ni	Cd
Dry solids	8,400	230	1,100	53	2.8

(L) 'Particulate' taken from (K) (mg/kg)

Density	Fe	Cu	Zn	Ni	Cd
<2.2	16,000	220	1,400	81	nd
2.2-2.9	13,000	130	1,300	39	nd
2.9-3.3	110,000	3,000	14,000	300	17
>3.3	100,000	19,000	20,000	1,900	77

Table 3.11 (continued)

(M) Whole old lagooned sludges, for historical comparison (mg/kg)

	Fe	Cu	Zn	Ni	Cd
Deep Hams 15 yr old	35,000	1,900	5,500	780	120
Slough 20 yr old	18,000	2,700	14,000	580	1,200
Ryemeads lagoon 4	24,000	1,200	3,000	450	100
Ryemeads v old dried	12,000	890	1,800	320	38
Perry Oaks lagoon	23,000	1,300	2,600	140	390

(N) Scale from the wall of a landfill digester (mg/kg)

	Fe	Cu	Zn	Ni	Cd
Sample 1	25,000	18	56	11	2
Sample 2	8,000	18	190	12	2
Sludge	25,000	48	920	25	1

Table 3.12. Mass balance for Beckton sludge, calculated on 2.5% dry solids

(A) Mass balance (as mg metal per litre wet sludge), using the average weight distribution from Table 3.9

Fraction	Fe	Cu	Zn	Ni	Cd
Particulate	58	1.5	6	0.29	0.024
Biofloc	215	15.8	103	1.5	0.6
Colloid	3	0.09	0.38	nd	nd
Soluble	0.31	0.52	0.013	0.025	nd
Whole	276	17.9	109	1.82	0.62

(B) Breakdown of the 'Particulate' fraction (as mg metal per litre), using the average weight distribution from Table 3.9

Density	Fe	Cu	Zn	Ni	Cd
<1.6	4.5	0.07	0.77	0.026	0.0028
1.6-2.2	7.7	0.10	0.91	0.033	0.0049
2.2-2.9	34.0	0.40	3.60	0.130	0.0120
2.9-3.3	1.3	0.06	0.18	0.005	0.0006
>3.3	10.4	0.89	0.56	0.092	0.0039

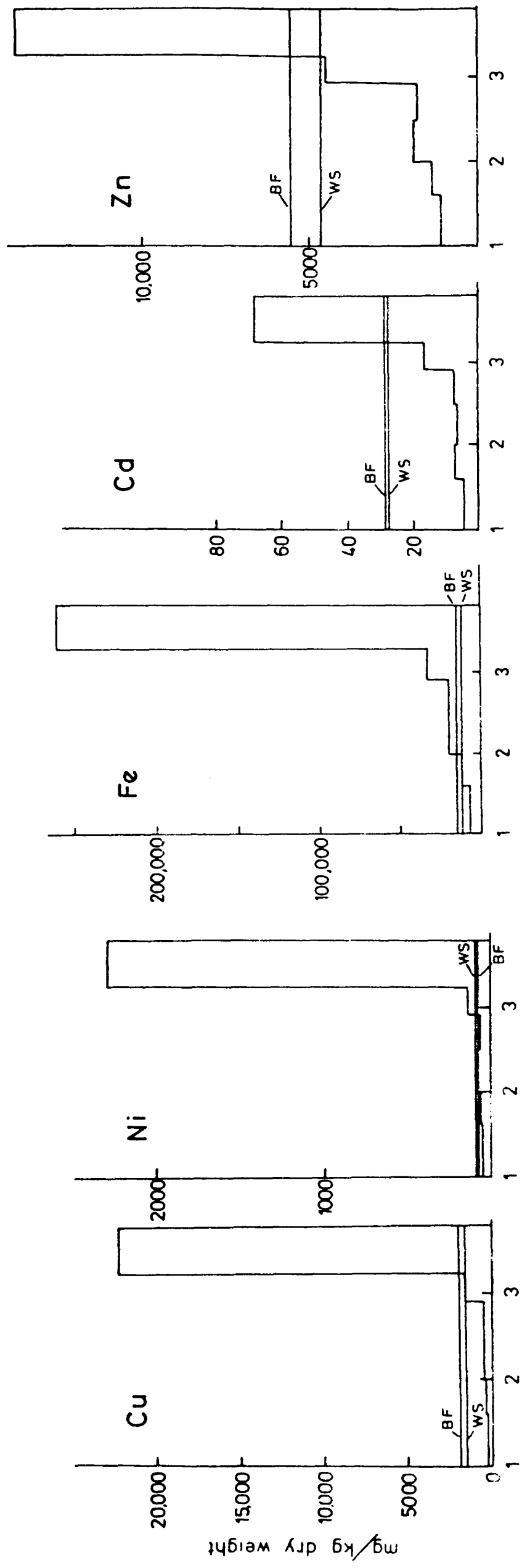
(C) Mass balance: (A) as % in each fraction

Fraction	Fe	Cu	Zn	Ni	Cd
Particulate	21	8.4	5.5	16	3.8
Biofloc	78	88	94	82	96
Colloid	1.1	0.5	0.35	-	-
Soluble	0.11	2.9	0.01	1.4	-

(D) The 'Particulate' fraction: (B) as % in each density cut

Density	Fe	Cu	Zn	Ni	Cd
<1.6	7.8	5.0	13	9.2	12
1.6-2.2	13	7.1	15	12	21
2.2-2.9	59	27	60	45	50
2.9-3.3	2.2	4	3	1.7	2.5
>3.3	18	59	9.3	32	16

Figure 3.2 Heavy metal content against density for the 'Particulate' fraction



The line 'WS' represents the concentration in whole sludge.
The line 'BF' represents the concentration in the 'Biofloc' fraction.

These figures are taken from table 3.11D

On average, a variation of around 5% between aliquots of the same sample was found. Variations of around 10% between successive samples from the same works were typical. This means that analyses can only be read to one or two significant figures.

The analyses for the heavy metals (table 3.11A) in whole sludge can be compared with the average figures for the Beckton works for the year 1983/84 (table 2.14). Unfortunately, the variance of the figures from TWA was not available. Nevertheless, for the relatively small samples I obtained, the figures for Cu and Cd were very close to those of the yearly average, while the analysis for Zn was 50% higher and the analysis for Ni was 20% lower.

In order to make the results from different samples and aliquots more easily comparable, the average proportions (by weight) of the sludge fractions were calculated (table 3.8). These proportions have then been used in all the calculations in this chapter, otherwise small differences in the proportions of fractions with very high concentrations of heavy metals (eg the >3.3 gm cm^{-3} fraction) would have affected the calculations of the mass balance disproportionately. The proportions of the density fractions in successive aliquots vary considerably more than the analyses of each fraction.

The 2 estimates of the total mass balance for sludge presented in tables 3.12A and 3.12B are calculated from these average proportions. The first (3.12A) is presented in terms of total mg metal in one litre sludge (mg $litre^{-1}$ wet weight). Tables 3.12A and 3.12C were calculated by multiplying the weight of each fraction or density cut in gm $litre^{-1}$ (taken from table 3.8) by the concentration of the cation in the fraction (taken from table 3.11).

Table 3.12C presents the information in table 3.12A as percentages of the total quantity of each element, to make the results easier to perceive. (The percentages do not always total exactly 100% in each column because the figures have been rounded off at various stages). It shows that the 'Biofloc' fraction holds 82-96% of the heavy metals and 78% of the Fe. However, the 'Biofloc' is likely to contain fine enmeshed mineral grains and aggregates including sulphides, so this fraction of the heavy metals cannot all be attributed to complexation by the biomass. Table 3.12C also shows that the 'Particulate' fraction accounts for 21% of the Fe, 16% of the Ni and less than 10% of the Zn, Cu and Cd. A higher proportion of the Fe than of the heavy metals separates with the 'Particulate' fraction which might suggest that more Fe enters the sewage in detrital mineral forms.

Table 3.12D shows the information in table 3.12B as percentages of the 'Particulate' fraction. It shows that the bulk of the heavy metals associated with the minerals of medium density, which might indicate that they were present as secondary deposits and crusts on lighter minerals. However, Cu is concentrated most strongly in the fraction of highest density which is interesting because it has the most insoluble sulphide.

The only metals present in significant quantities in the 'Soluble' are Cu and Ni. The Cu in the 'Soluble' is likely to be complexed entirely to soluble organic matter, while the Ni is likely to be largely uncomplexed (see chapter 9). Ni was the only metal in activated sludge reported in significant quantities in solution.

One sample of whole Beckton digester sludge was analysed for the minor elements by ICP as well as the elements of more direct

interest. These analyses are presented in table 3.13.

Table 3.13 Other elements in Beckton sludge

Element	Concentration
Li	6.4 mg kg^{-1} dry weight
Na	4,100
K	3,900
Mg	3,200
Mn	220
Co	8.3
V	38
Sr	200
Pb	380

Conclusion

A pragmatic separation of the principal components of sludge has been presented that offers fractions in a form suitable both for analysis of their role in heavy metal chemistry and for inclusion in a model of digester chemistry. A mass balance showing the distribution of the heavy metals between the fractions shows the 'Biofloc' holding the bulk of the heavy metals.

The next stage is to identify the forms of combination of the heavy metals in each fraction. The mineral forms present in each fraction need to be identified and the complexation capacity of the organic components needs to be measured.

IDENTIFICATION AND ANALYSIS OF SEPARATES

The previous chapter presented a pragmatic breakdown of sludge into various fractions. The next stage is to identify the forms of combination of the heavy metals in each fraction in a form suitable for inclusion in a model. This chapter and the next one deal with the 'Particulate' fraction.

The 'Particulate' fraction is made up of large organic fragments, mineral grains, and aggregates of these. These may be resolved into further fractions by density separation.

After treatment by chemical reagents and after magnetic or density separation, this fraction was examined by scanning electron microscopy with micro-probe analysis (SEM) and by X-ray diffraction (XRD). This chapter outlines the techniques and their limitations and the following chapter illustrates and discusses the results.

Bergman et al (1979), and Pilkington and Warren (1979) used XRD on density separates of sludge and marine sediments respectively, but neither combined analytical SEM and XRD analyses of the same fractions. Lee and Kittrick (1984) used an analytical SEM to look for Zn and Cu compounds in oxidising and anaerobic soil environments, having concluded that 'extractants may give clues to, but cannot identify, the specific minerals governing the solubilities of Zn^{2+} and Cu^{2+}'. The SEM has also been used to look at minerals (Rasmussen and Knezek, 1971; McHardy, 1977) and fulvic acid-metal complexes (Chen and Schnitzer, 1976) in soils. Baldwin et al (1982) have published preliminary SEM results on elutriated sludge minerals.

Analytical Scanning Electron Microscopy (SEM)

I The technique

In the SEM a finely focused primary electron beam scans the specimen surface and causes secondary electrons to be released at right angles to the surface. The secondary electrons detected are amplified and control the brightness of an image on a TV tube, or photographic plate. Because of the asymmetrical ray path to the detector, the intensity of the secondary electrons detected from a particular point will depend on local surface topography. Together with a very good depth of focus, this produces an apparently three-dimensional image.

The primary electron beam also generates X-rays whose energy is characteristic of the elements present in the specimen. The operator can chose whether these X-rays are excited from the whole area being scanned, or from a single spot on the surface whose diameter is related to the energy of the exciting beam. The spectrum of X-ray energy levels produced is detected by an energy-dispersive, solid-state X-ray detector. This X-ray detector is based on a crystal of lithium-drifted silicon whose response to each photon is proportional to its energy, and thus characteristic of the element that produced the photon. A histogram (spectrum) of the various X-ray energies arriving at the detector is built up by amplification and statistical processing.

The area under a peak in such a histogram is related to the amount of the element in the specimen producing it. However, the relationship between peak area and concentration is not simple, since it is affected by the efficiency of the detector, the accelerating voltage of the primary electron beam and the surface

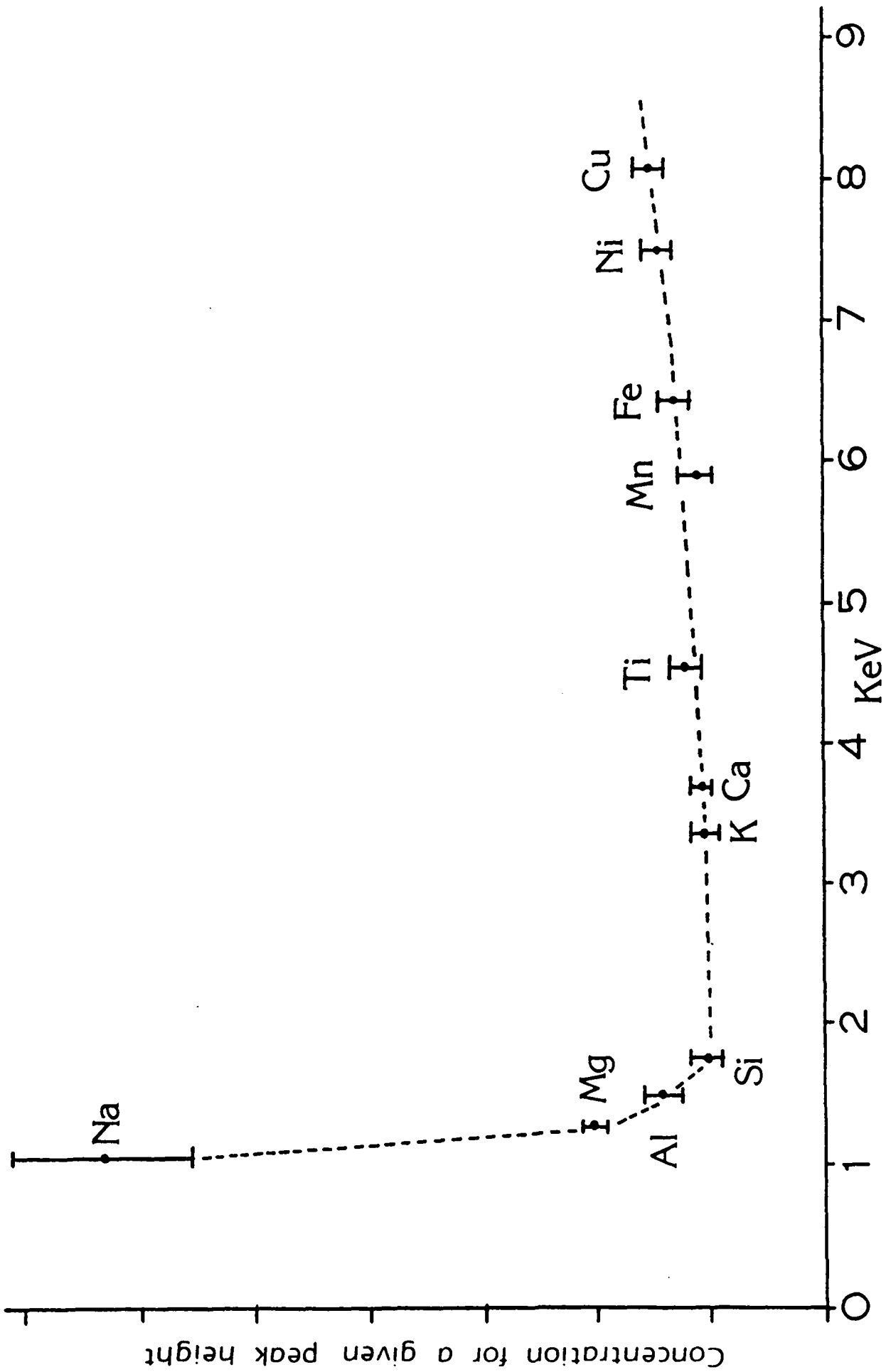
topography of the specimen.

The efficiency (ie peak height for a given percentage of the element) of K lines, which are used for elements with atomic number between 11 and 30, increases rapidly from very low for Na to a maximum for Si then decreases steadily to a moderate value by the end of the first transition series, at just below 10 keV. Elements lighter than Na cannot be detected. This variation of efficiency with atomic number is an inherent property of the detector, but it also depends on the accelerating voltage of the primary electron beam. The general trend that can be expected in the efficiency is shown in Fig 4.1.

At an accelerating voltage of 30 kV, which was the maximum available on the machine used, all elements heavier than Na will be excited and all lines in the range 0-20 keV will be generated. At this voltage the depth of penetration and the diameter of the analysis spot are typically around 6 μm, but the lighter elements, particularly Na, are so readily volatilised that analyses of Na, Mg and to a lesser extent Al are not very reliable.

At an accelerating voltage of 15 kV, only emission lines in the range 0-10 keV are excited. Although all elements have at least one line in this range, it is sometimes useful to employ additional lines in the range 10-20 keV for confirmation. At this voltage the heavier elements are not excited as efficiently as at 30 kV, but elements lighter than Si are excited more efficiently. The depth of penetration and the diameter of the analysis spot are typically around 1 μm.

Figure 4.1 Calibration curve for energy-dispersive analysis



At an accelerating voltage of 10 kV the depth of penetration and the diameter of the analysis spot are down to 0.25 μm, but for elements heavier than Si the efficiency falls off rapidly. This voltage cannot easily be used for analyses for the metals of the first transition series.

Surface topography is also an important factor affecting the peak sizes. Ideally the surface of the area to be analysed should be at a precise standard angle to the primary beam and the detector. However, this will not be possible for a specimen with a rough surface, and irregularities will affect some elements more than others. The apparent intensity of a peak is affected by the depth of penetration, and by absorption and fluorescence in the specimen, and these vary with the atomic numbers of the elements present and the nature and orientation of the specimen's surface.

Despite the many factors which affect peak size, it is possible to effect a quantitative analysis by means of a computer program which deconvolutes complex spectra, calculates corrections for atomic number (Z), absorption (A) and fluorescence (F) using a peak-to-background ratio (PB) method (the program is known as ZAF:PB) and calculates concentrations of the elements in the specimen by comparing the corrected intensity ratios with those of known standards. The accelerating voltage must be fixed (in this case the machine was calibrated for 15 kV) and best results are obtained if the surface being analyzed is set in roughly the right orientation. At best, detection limits are about 0.1% (depending on the nature of the sample): a relative accuracy of 10% can be expected routinely and as good as 0.2% under ideal conditions, depending on the nature of the sample. For the complex mixtures

with high levels of organic matter studied in this project, performance is likely to be somewhat poorer than ideal.

This study used an ISI 40 SEM to analyze samples of all the materials studied. Initially it was fitted with a Link Systems 860-200 energy dispersive X-ray analysis system, with an accelerating voltage of 30 kV (emission lines in the range 0-20 keV). This system permitted only qualitative (or semi-quantitative) analysis.

In May 1983 the facility was updated to the Link 860-500 system in order to obtain more quantitative analyses. The system was recalibrated to 15 kV (emission lines in the range 0-10 keV). At this voltage a maximum of 8 elements at a time can be measured quantitatively. If calibrated to 30 kV up to 30 elements at a time could be measured but Na and Mg would be unreliable.

In February 1984 the facility was further updated by the addition of the Digimap software, a system for the acquisition, display and processing of digitised X-ray element maps. Data are acquired by scanning the electron beam over a matrix of 128 by 128 pixels (ie 16,384 points) in a single frame. Data can be obtained for up to 18 elements simultaneously. Optimum results are obtained with a dwell time on each spot of 100-200 milliseconds. Using a dwell time of 100 ms, it takes about 45 minutes to produce the complete map. Digimap solves the problem of comparing spot analyses. It can be used to hunt through an area containing several hundred grains to look for potentially interesting ones, and used to answer questions such as the potential variation of Cu/Fe ratios in sulphides. However, for the reasons given above, it is obvious that it should only be used on polished surfaces.

II The method

Samples to be analyzed were air-dried from acetone (see methods, Appendix 1), and then about 20 mg was smeared onto double-sided sellotape on glass. This was glued to an aluminium stump and finally carbon-coated to minimise charging under the electron beam. Failure to coat with carbon does not affect the analysis but may result in the image becoming severely distorted. Statistical surveys of the mineral distribution in the sample were taken by counting 100 adjacent grains, without any selection. Although 100 grains are enough for any statistical confidence, the time taken to make the counts precluded a larger number being recorded. The results of these counts are presented in Table 5.1.

A representative selection of histogram analyses were printed for comparison and for the record. Those printed totalled over 1000 by the end.

Grains to be examined using Digimap were embedded in Araldite Ultra-Low Viscosity resin. Initial attempts to embed grains using normal resins supplied by the Department of Mineralogy failed because the grains were too fine and the polishing process ripped them from the surface of the resin, but the Ultra-Low Viscosity resin flowed round the grains better to hold them over a higher proportion of their surface. The resin was set under vacuum for 30 minutes to remove bubbles, then cured at 60°C for 4 hours. The block was polished with alumina paste to give the polished surface of a cross-section through the grains, and finally carbon-coated to minimise charging. (The accuracy of the results is directly linked to the quality of the polish achieved). Araldite does not interfere with the analysis (Lee and Kittrick, 1984).

The data acquired by Digimap are stored on floppy disk, and may then be loaded into an image buffer and manipulated in a variety of ways using an image-processing system, one element at a time. The data for an element may be plotted on the screen using a colour-coded scale for intensity, or presented as a histogram of intensity (vertical axis) against log frequency (horizontal axis). Examples of digimaps are given in figure 4.6. Maps of intensity for different elements from the same grain are not directly comparable because of variations in counting efficiency for different elements.

Since they are not directly comparable, the maps may be processed to extract the maximum information. The processing options available are:

1) smoothing, a 4:2:1 nearest neighbour 9 point smooth
2) scaling, adjusting the gain to expand or contract the spread of values
3) threshold, cutting off the bottom of the scale
4) moving, the dynamic colour-scale of the map may be moved relative to the actual spread of values

Moving the dynamic range of a map up and down, and contracting and expanding it over the available dynamic range, can be used to reveal high spots. Cutting off the bottom of the scale may be used to reduce background noise; this can be used progressively to remove slices off the bottom of the scale until a 'clear' image of the grains suddenly emerges from a confused picture. The problem is that the powerful facilities available can create very misleading pictures. Digimaps should be interpreted and compared with caution!

The finished maps can be dumped to a dot-matrix printer. These were ideal when used in comparison with the image on the SEM screen

to hunt for particular grains, but were often of little use when recording information about variation within a grain. The colour-scale runs black/pink/blue/green/yellow/red/white (see figure 4.6) but this is represented on the dot-matrix printer by three different lengths of horizontal, vertical and sloping lines for blue, yellow and red respectively, so the intensity of printing gave no indication of concentration and was very confusing to look at! Figure 5.8 presents a printed digimap of Ba content in a grain of galena - it was possible to get a particularly clear printout of this grain because of its large size and because it was clear of adjacent material. Where possible, photographs of the monitor screen provided a better record of results, but they too were limited by the low quality of the Link Systems monitor provided.

III Comments

Although the analyses obtained are not as accurate as can be obtained by other means, and elements lighter than Na cannot be detected, the method is non-destructive, it can analyze single grains down to about 1 μm, and photographic images can be obtained. Specimen preparation is quick and simple, and quantitative analyses of all elements heavier than atomic number 11 (except some rarer heavy elements for which standards are not yet available) can be obtained in minutes.

Typical energy-dispersive spectra from materials commonly found in sludge are presented for comparison (Figure 4.2). The first three are pure mineral phases with quantitative analyses as follows:

A) Feldspar $NaAlSi_3O_8$, weight %: Na_2O 11%, Al_2O_3 20%, SiO_2 68%

B) Pyrrhotite, approx FeS, weight %: Fe 61%, S 39%

C) Apatite, $Ca_5(PO_4)_3OH$, weight %: CaO 55%, P_2O_5 42%

The feldspar probably entered the digester in crude sludge, whereas the pyrrhotite and apatite were probably precipitated in the digester. The last three represent:

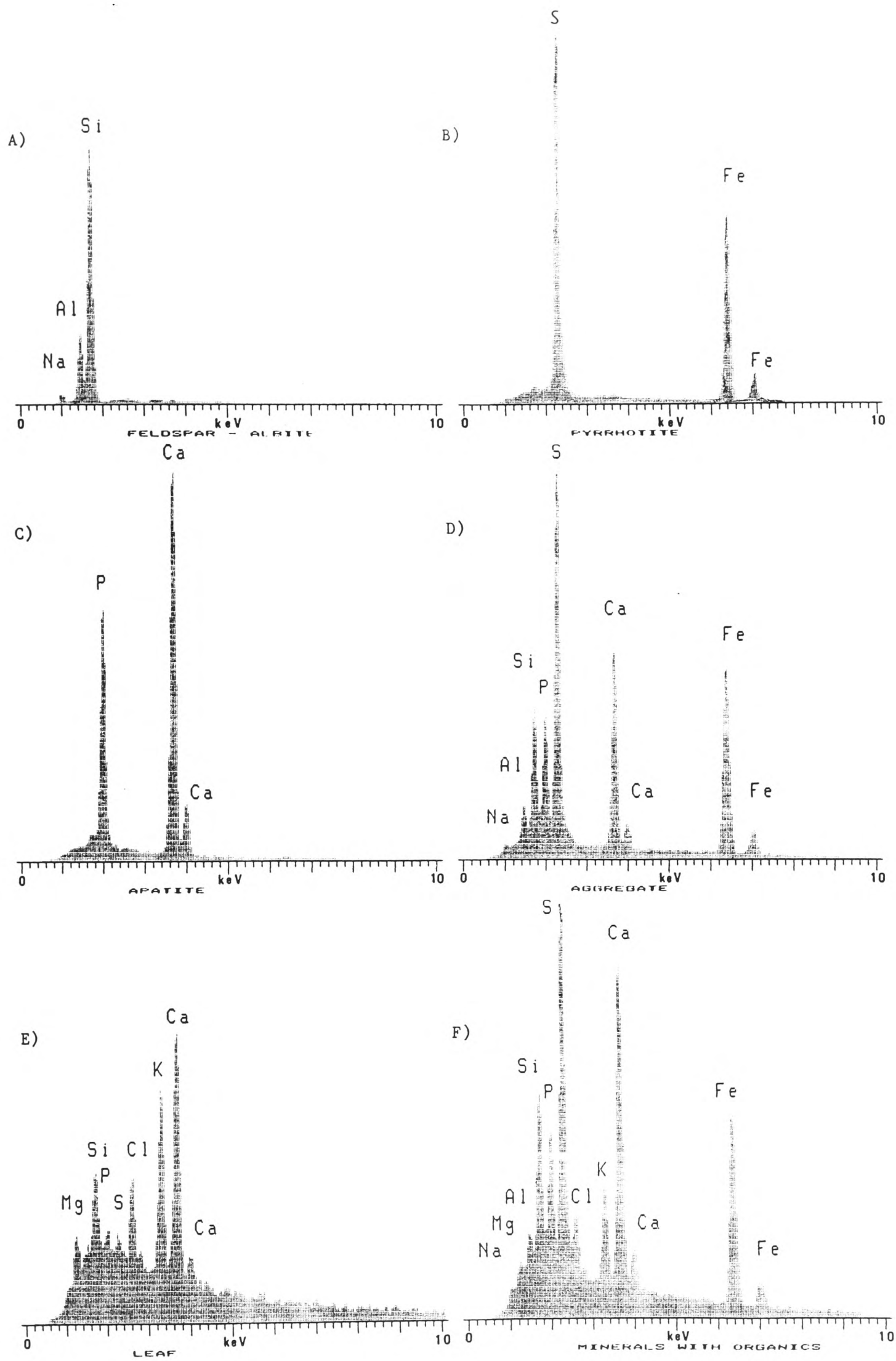
D) An aggregate of the above three minerals

E) A typical organic particle

F) A mixture of minerals and organics

Example D) was made by adding the spectra of A), B) and C) together by computer, example F) by adding D) and E) together. They are useful because they show how seemingly complex spectra might be resolved into relatively simple discrete components.

Figure 4.2 Examples of energy-dispersive spectra



Example results

Typical SEM micrographs are presented in Figures 4.3-4.5:

Figure 4.3 Calcium phosphate precipitates

A) Apatite, an irregular aggregate

B) Brushite, forming an aggregate of prismatic crystals

Figure 4.4 Fe-bearing precipitates

A) Goethite

B) Pyrrhotite encrusting quartz

Figure 4.5 Detrital fragments

A) Dolomite

B) Biogenic particle

C) Bone (apatite)

Typical micro-probe and digimap results are presented in figures 4.6-4.8:

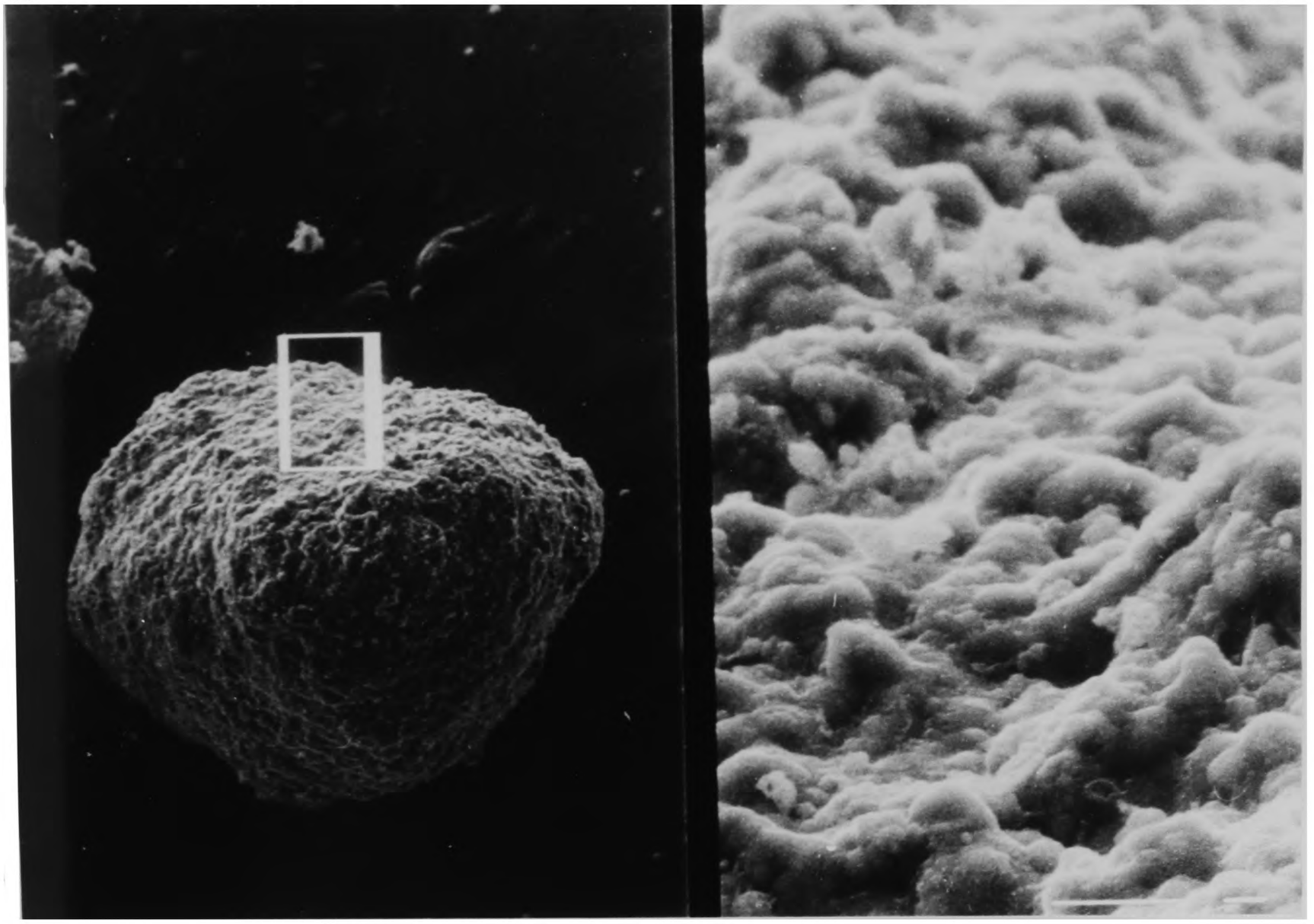
Figure 4.6 Colour scale for digimaps (NB: the colours show the relative concentration not the absolute concentration). At its side is a histogram showing how many points have a concentration corresponding to that colour - this is used to help select the best colour scale.

Figure 4.7 Example spot analysis of aggregate showing high background and many elements are present.

Figure 4.8 Fe, S, Cu, Zn, Cl, and Ti analyses of a selected area of embedded grains.

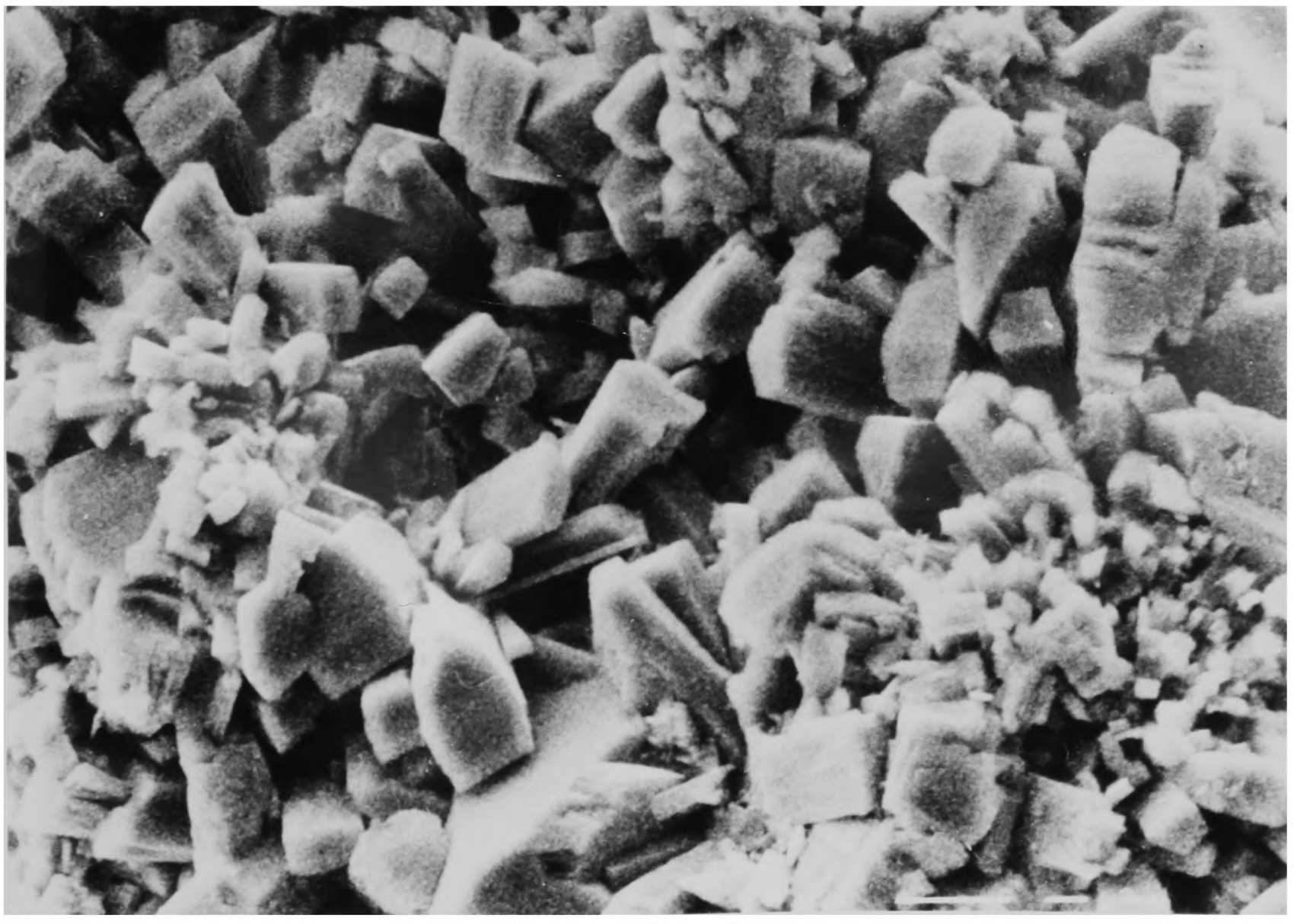
Figure 4.3

A



10 um

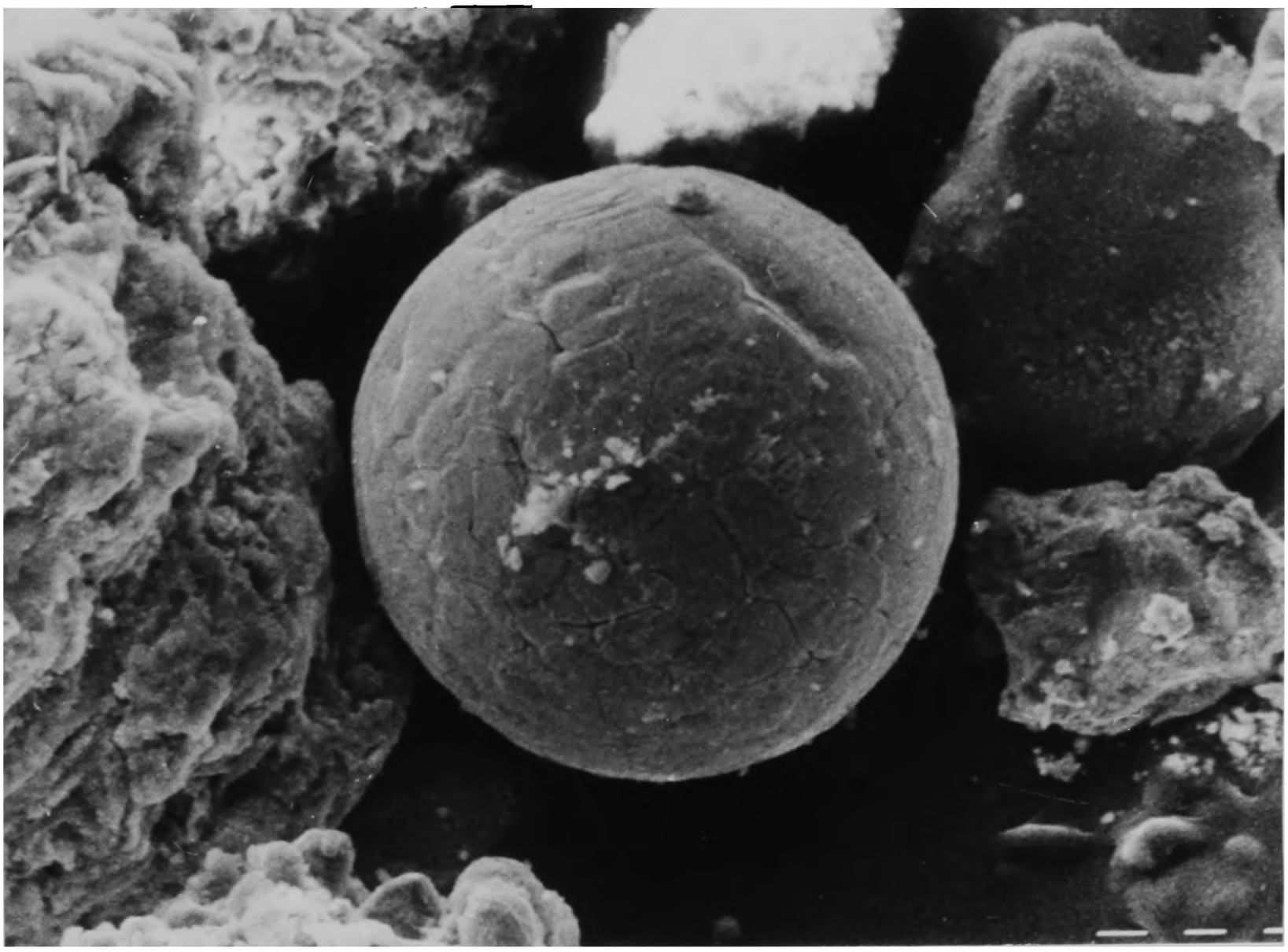
B



10 um

Figure 4.4

A



B

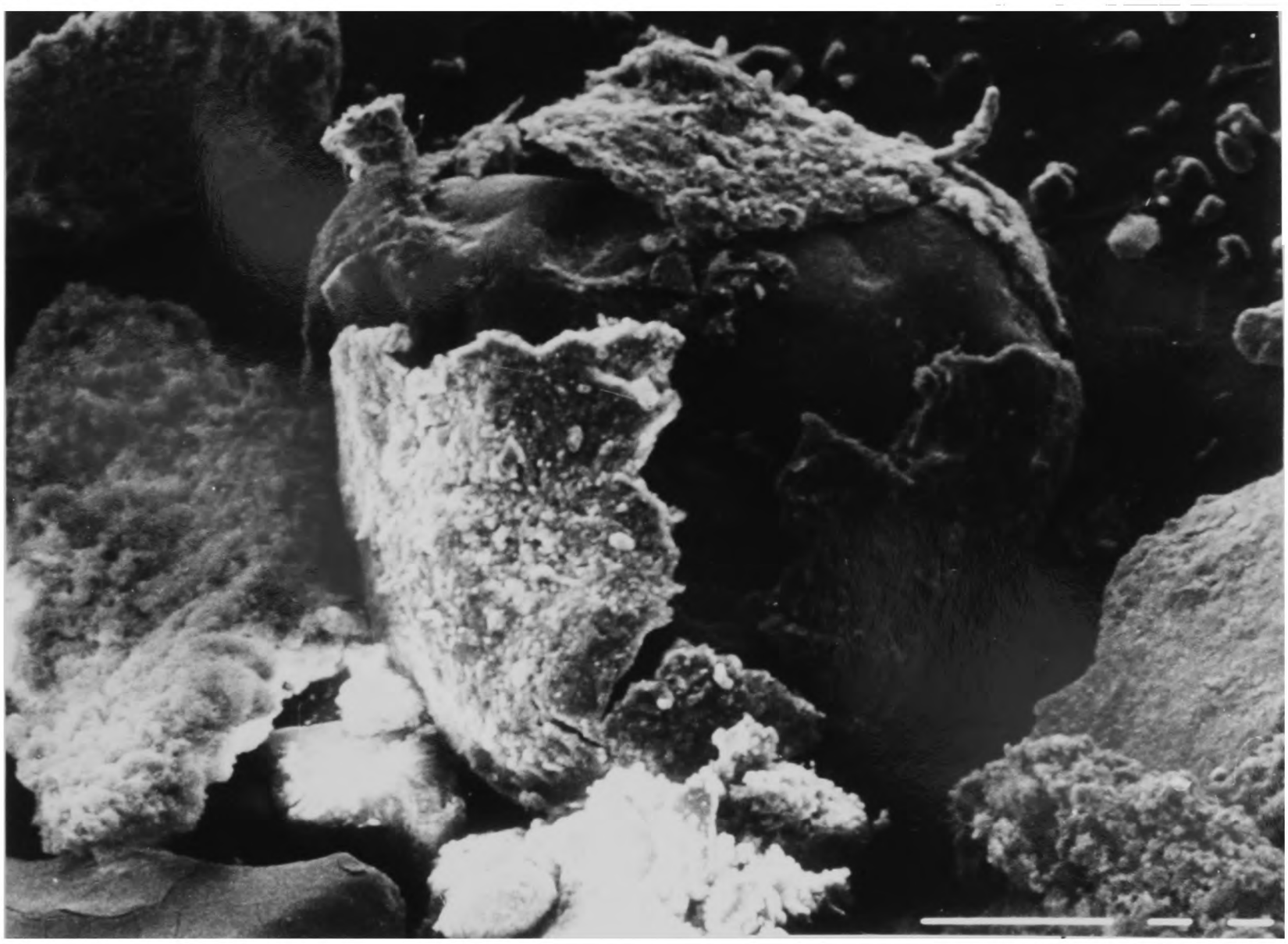
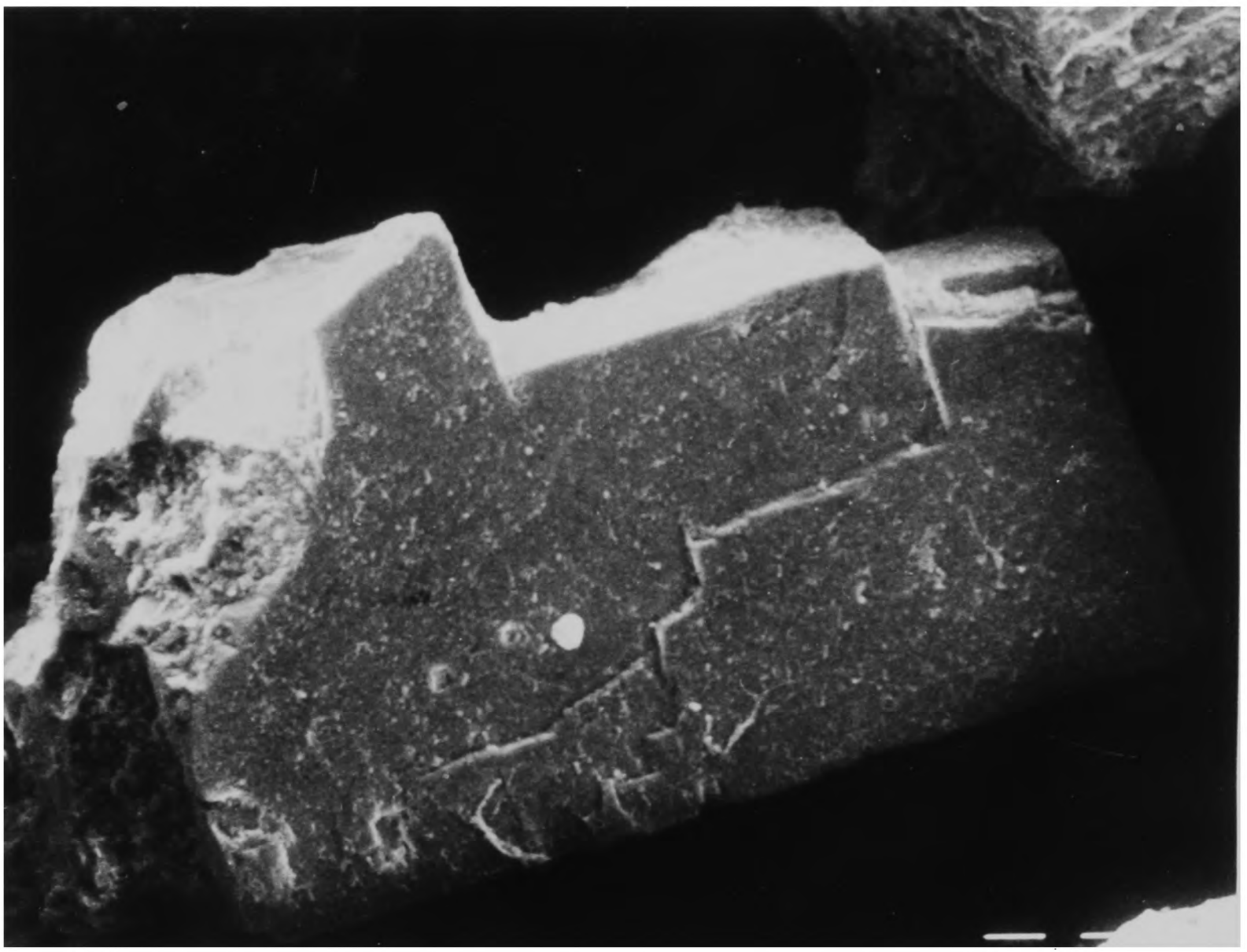


Figure 4.5

A



B

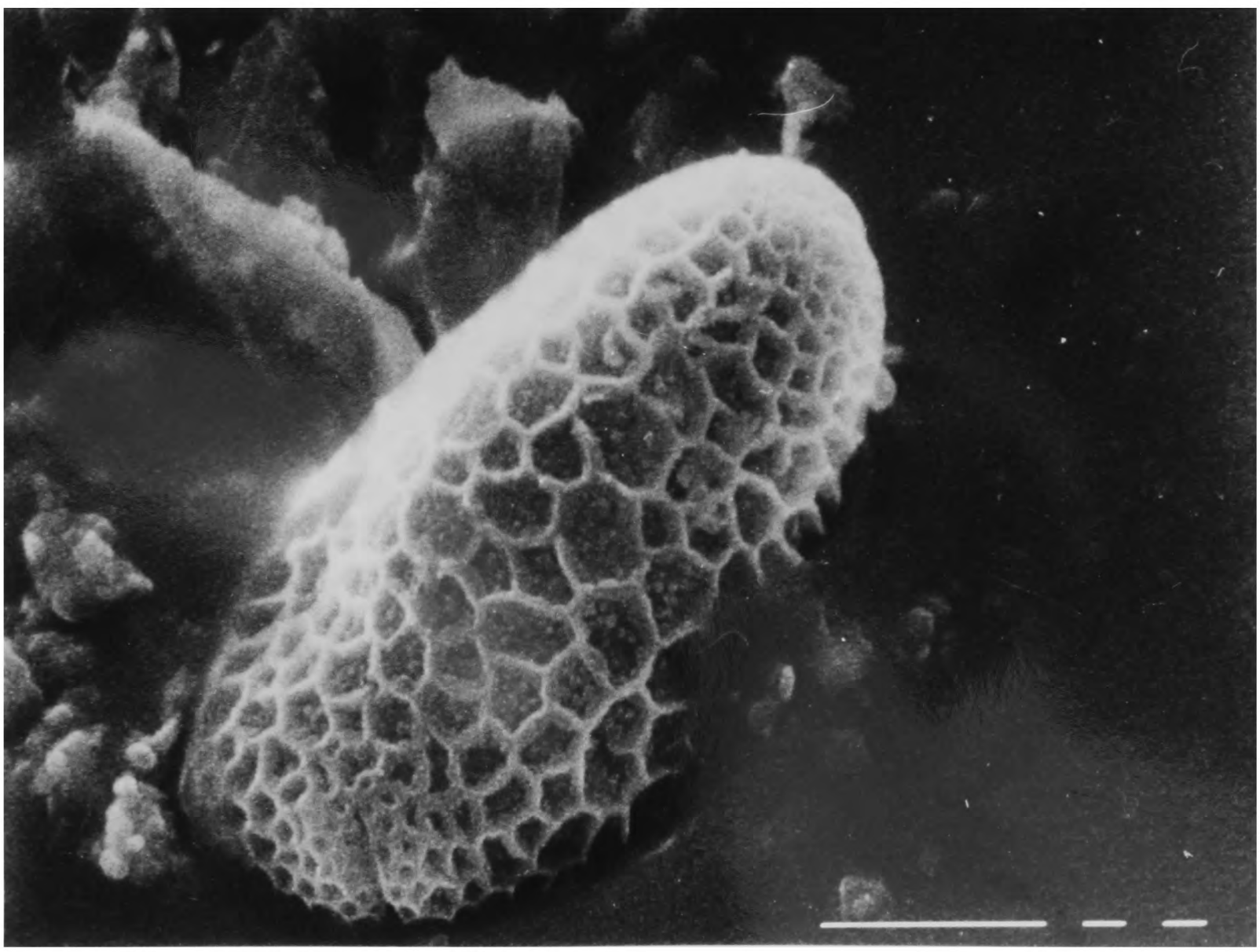


Figure 4.5 continued

C

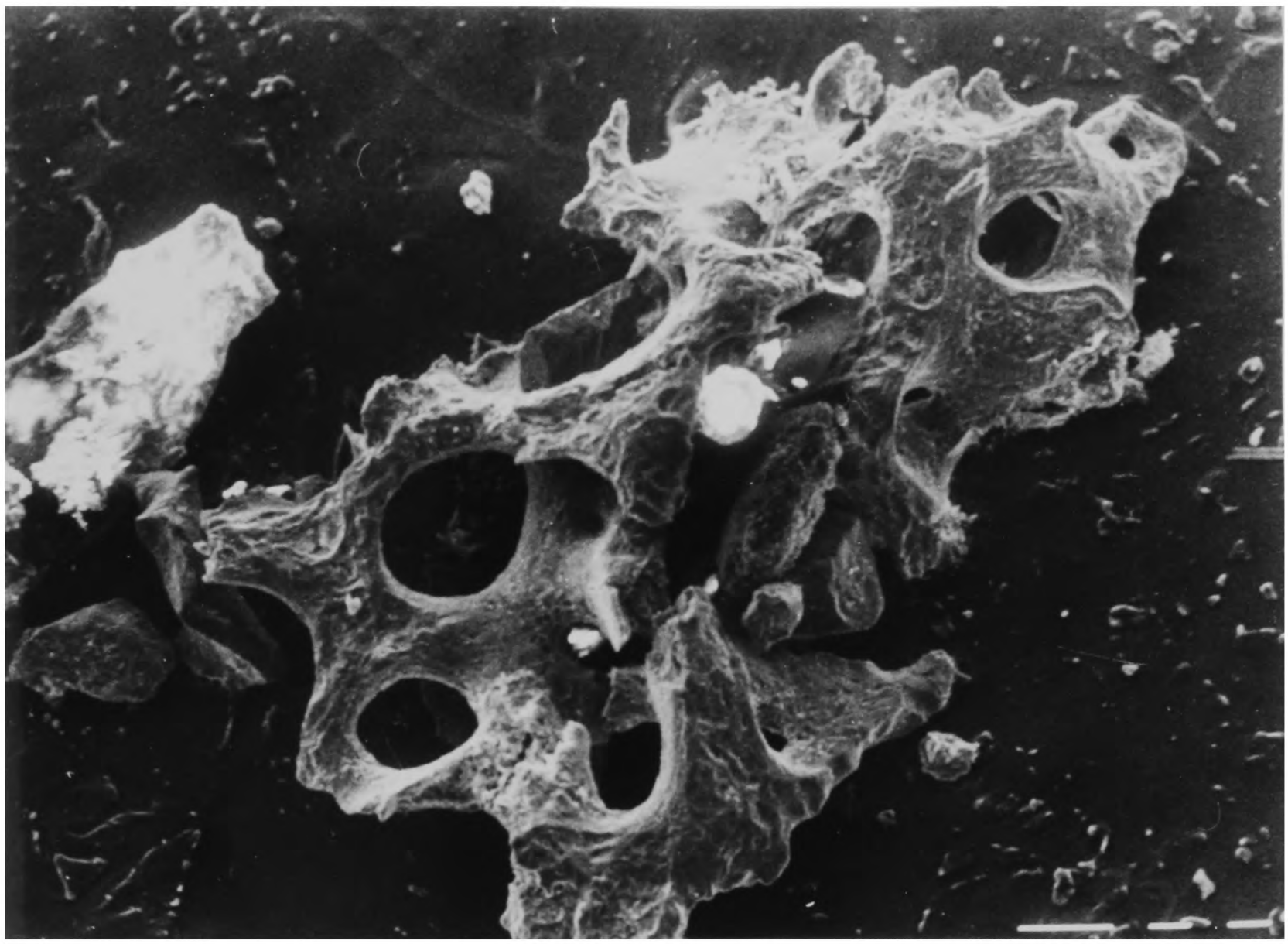
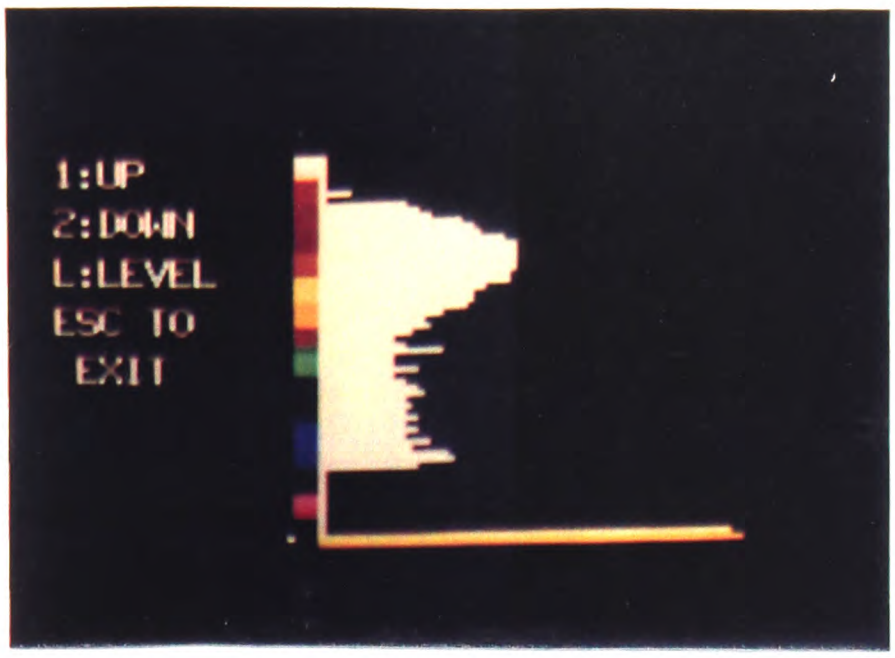


Figure 4.6 Example colour scale for digimaps



Colour scale runs:
White
Red
Yellow
Green
Blue
Pink
Black

Figure 4.7 Example spot-analysis

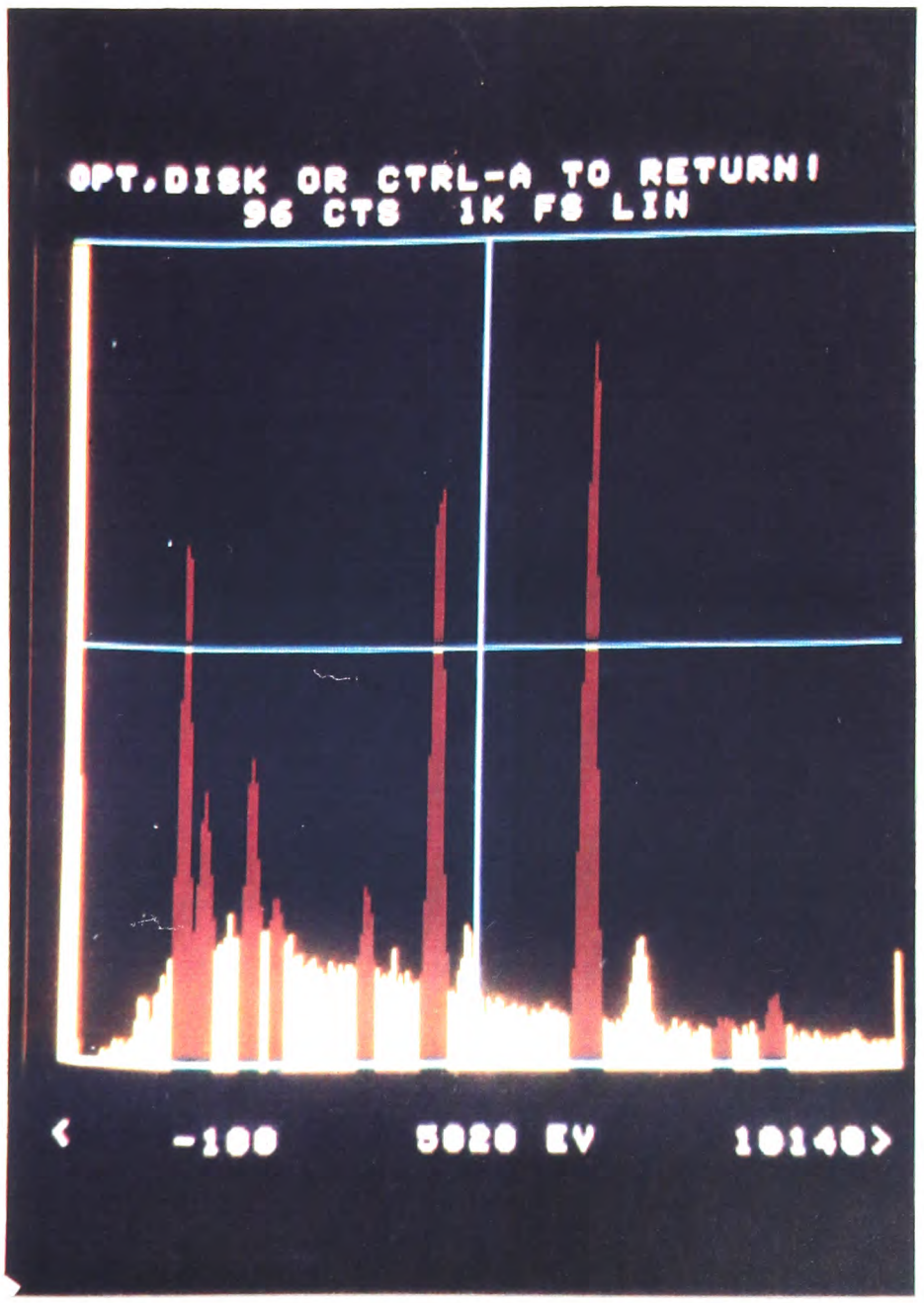
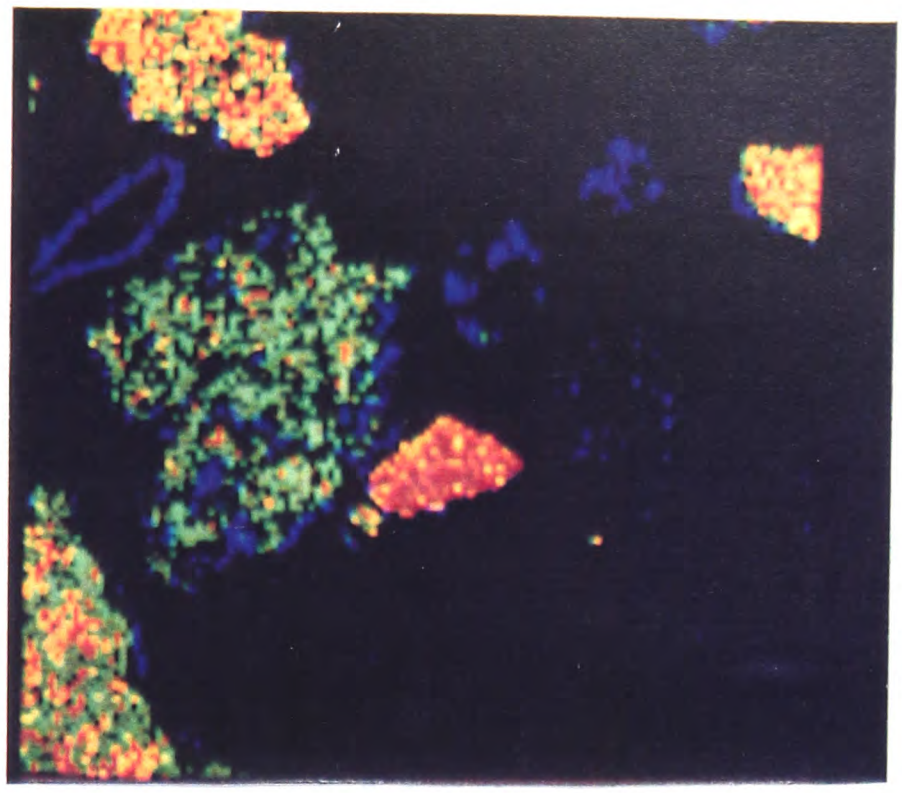
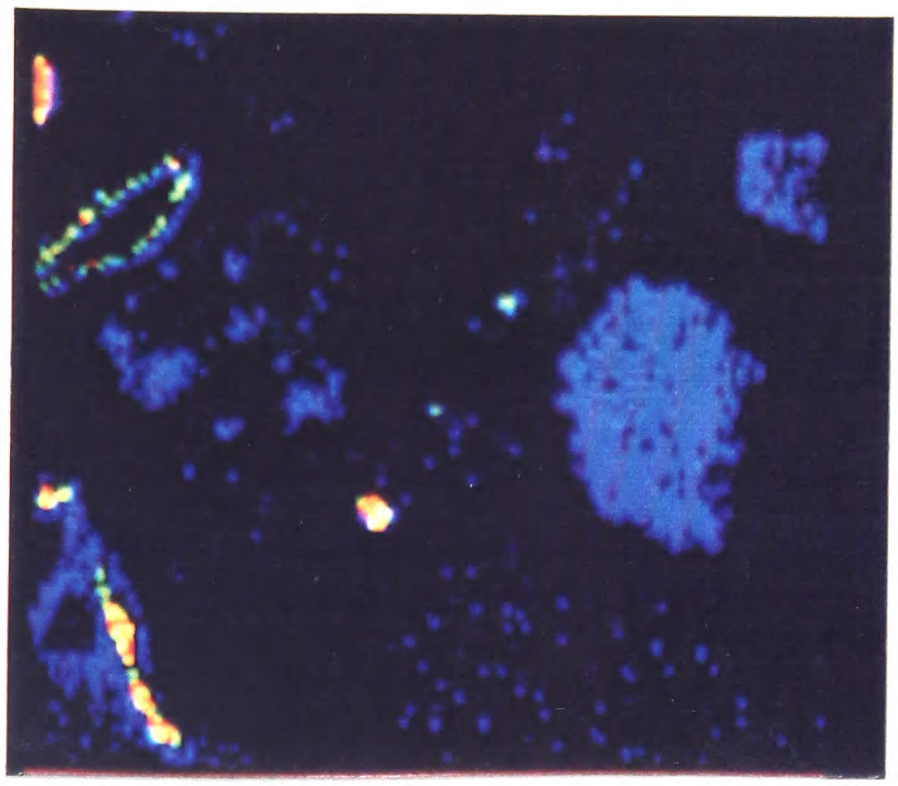


Figure 4.8 Example digimaps of a selected area of embedded grains

Fe



S



Cu

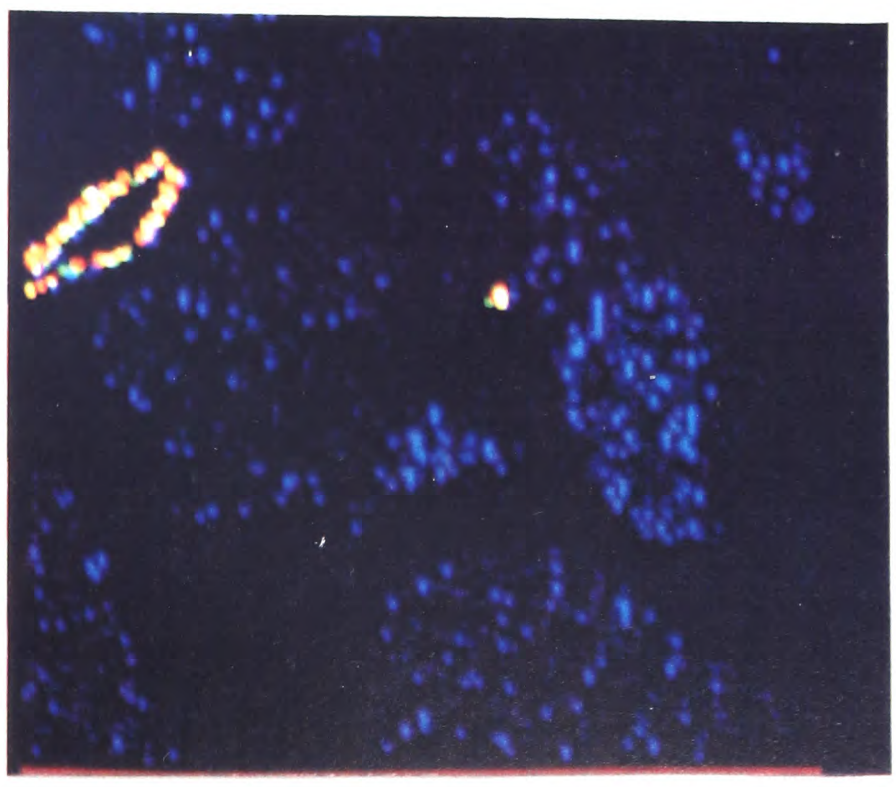
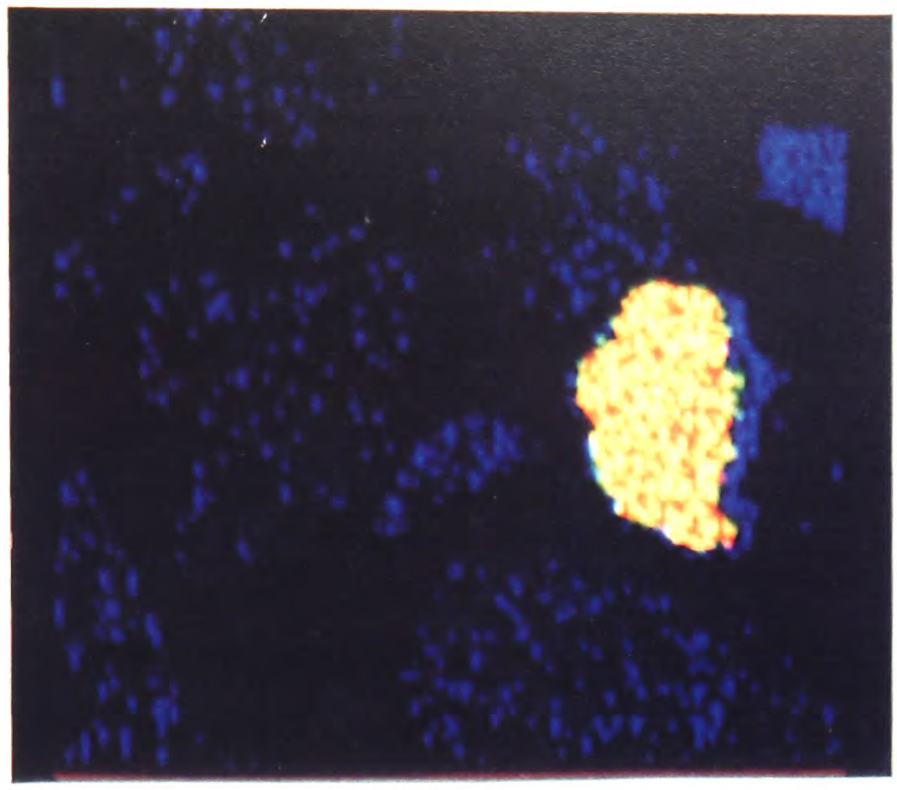
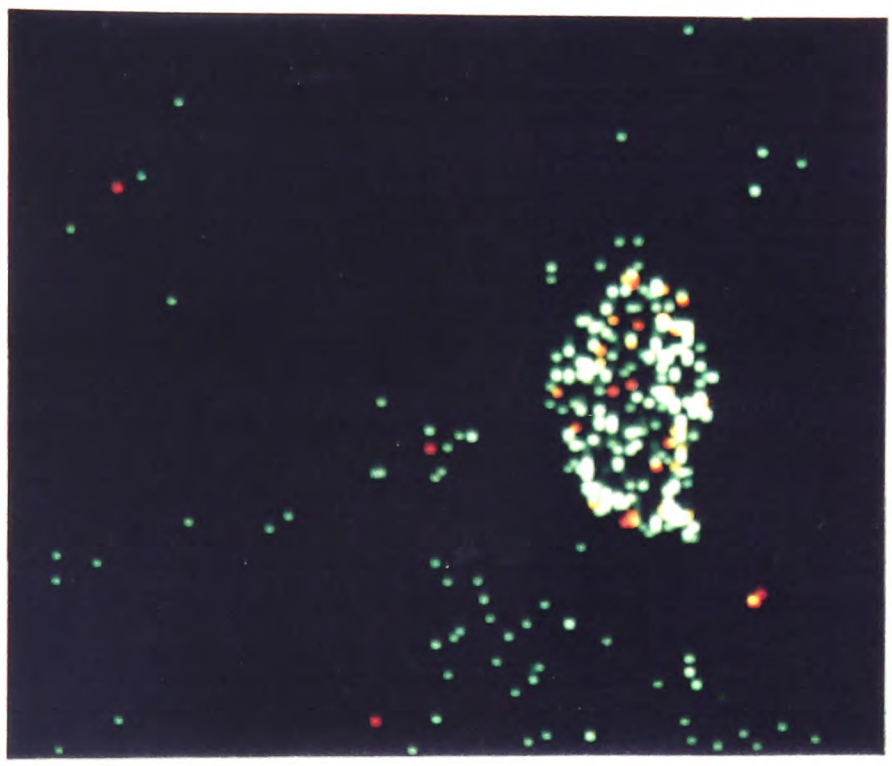


Figure 4.8 continued

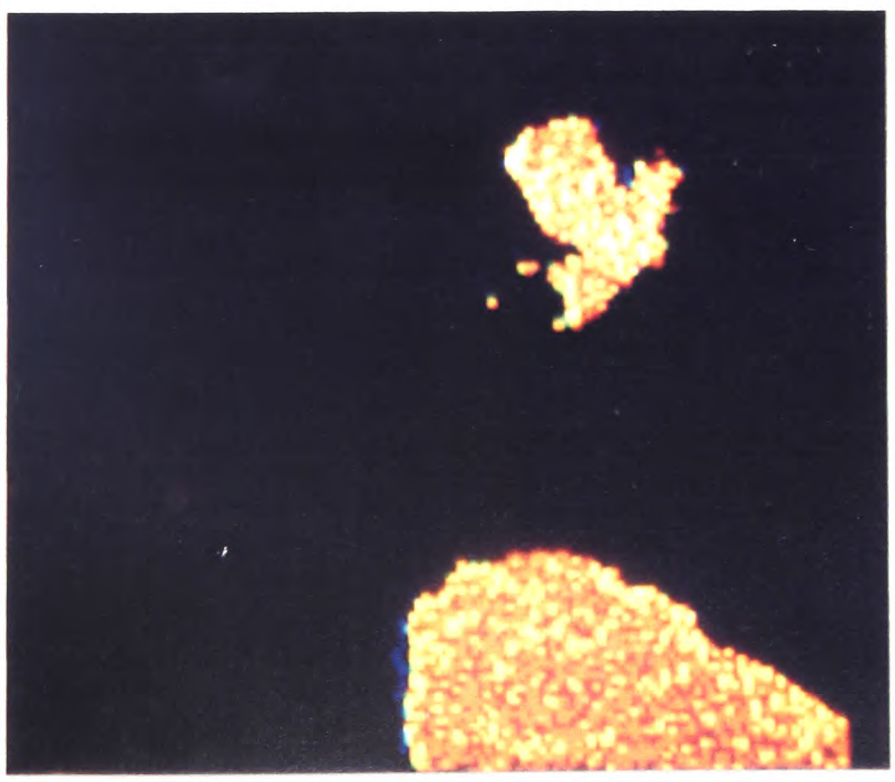
Zn



Cl



Ti



X-ray Diffraction (XRD)

X-rays are scattered (diffracted) by the electron clouds of atoms. In crystalline materials the directions in which the maxima of scattered X-rays occur are specific, because the atoms are arranged in regularly-ordered arrays. The directions (relative to the direct beam) in which X-rays are scattered depend on the crystal orientation, the distances between individual atoms in the crystal and the wavelength of the incident X-rays. The relative intensities of X-rays scattered in these directions depend largely on the elements present in the atomic array. Since a particular crystalline material is uniquely characterised by its component atoms and their spatial arrangement, X-rays scattered by a powdered crystal sample will produce a characteristic diffraction pattern which can be used to identify the crystalline substance. Extremely small crystals, or poorly crystalline or amorphous materials (with no long-range order of atoms) do not interact with X-rays to produce well-defined scattering maxima.

If X-rays diffracted from a powdered sample are allowed to fall onto a strip of photographic film in an X-ray camera they will produce a series of lines on the film whose spacings and intensities are a characteristic fingerprint of the crystalline material, provided that the grains are of sufficient size, and they are randomly orientated and there is a sufficient quantity of the material to produce detectable lines. Some crystal structures produce only a few lines but many produce several tens of lines each. Therefore a powdered sample containing a mixture of crystalline substances may produce a complex pattern with many lines. Crystalline phases can be identified by reference to the

powder diffraction file compiled by the Joint Committee on Powder Diffraction Standards (JCPDS) which records the diffraction pattern of tens of thousands of substances in the form of lists of structural spacings and intensities. Substitution of an alternative element in a particular structure alters both the positions and intensities of the lines, so if substitution is extensive the diffraction pattern may not be readily identifiable from the file.

A Guinier focusing camera was used in this study. The apparatus produces a high-quality diffraction pattern with low background intensity and excellent resolution of lines lying close together. It is therefore particularly suitable for identifying crystalline phases which are both multiple and dilute. The Guinier camera is particularly difficult to use - this machine took Dr Gordon Cressey six months to set up before it could be used. Because of this and because of the experience needed in interpreting the lines produced, all the XRD analysis and interpretation of my samples was done by Dr Barbara Cressey.

If the same material is studied by both XRD and SEM, it is often possible to correlate the chemical analyses obtained from the SEM with the crystal structures obtained by XRD. However, the XRD information has to be taken from a fairly homogeneous powdered sample, whereas the single grains analyzed by SEM may not be representative of all the material in the XRD sample. Also some 'grains' analyzed by SEM are mixtures of more than one phase. Some phases identified by SEM are amorphous and some only occur on one or two grains in the sample and so are not detectable by XRD. Both methods only use a few milligrams of sample and so great care must be taken to ensure homogeneity before assuming that the samples are

representative of very much larger quantities of material. This iis a greater problem with material that has not been density-fractioned.

Thirty-two samples of different fractions from different sludges were prepared for SEM and XRD analysis. Because of the substantial quantity of results produced, (over 1000 SEM printouts and many films of XRD analyses), appendix 5 presents an index to the 32 samples so that they can be referred to by anyone at a later date. The bound summary of the SEM printouts recorded for each sample and a summary of the XRD results for each sample are held in the Department of Plant Sciences library.

The next chapter presents specific findings culled from the mass of raw data, rather than the raw data themseleves.

ANALYSIS OF THE 'PARTICULATE' FRACTION: II

This chapter presents the results of mineralogical analyses of the 'Particulate' and 'Biofloc' fractions defined in chapter 3, using the SEM and XRD techniques described in chapter 4. Additional techniques used to clarify certain points are described in Appendix 1. The studies from which these conclusions are drawn are indexed in appendix 5. The SEM results and the XRD results listed in appendix 5 are described in a document held in the Department of Plant Sciences library which was not included because of its bulk.

1. ORGANICS

The fraction that separates below 2.2 gm cm^{-3} is entirely comprised of large particulate matter. The particles are generally low in heavy metals except where they are associated with amorphous organic matter or are cemented by secondary precipitates: probably they play little part in the heavy metal chemistry of sludge. Their structures have been described in an earlier report (Rodkiewicz, 1981) and include undegraded plant fragments, hair, insect cuticle and animal remains such as bone, and man-made substances. Figure 4.5 illustrates two biogenic fragments. The organic content of the different fractions has been presented in table 3.10.

XRD analysis of primary sludge revealed the lines for Ca-Palmitate and Ca-Myristate together with other similar but unidentifiable lines. These compounds were not identified in digested sludge and probably corresponded to large (up to a few mm) soft white lumps in the samples.

In order to aid the identification of particles and their

analyses, an extensive library of natural and man-made samples was built up. The analyses of the library samples were at times surprising, but none contained appreciable quantities of Fe, S or heavy metals, except for hair which is rich in S. Many paints, papers and fibres (such as the viscose in J-cloths) contain large quantities of Ti as pigments and fillers; a particularly high level of Ti was found in a pound note! The library of spectra covered most of the organic fragments observed, although it is not always easy to account for some of the elements in the spectra. For example, many of the organics show particularly high concentrations of Cl; this was unexpected since it is unlikely that Cl would be exchangeable at the neutral pH of sludge.

The spectra from particulate organics form specific patterns which are quite different from the amorphous organic matter in which the particles may be embedded. For example the spectrum of the amorphous matrix often showed higher Si and Al peaks resulting from its clay content and a Fe peak due to precipitated sulphides or oxides. The separation and cleaning procedures to remove 'Biofloc' and 'Colloid' described in chapter 3 were shown to reduce the peaks of the elements associated with the amorphous matrix in the spectra of particulate organics.

Under the SEM, concentrations of elements such as Fe were occasionally noticed on the surface of a particle; these were not easily dislodged by the separation procedure. We infer that these are 'secondary precipitates'. They also occur on mineral types discussed in the next section.

2. MINERALS

The majority of mineral grains in sludge are detrital and come from soil run-off and industrial sources or, like calcite, precipitate naturally in hard water areas.

The typical soil minerals found were quartz, feldspars, clays, garnets, anatase, rutile and carbonates, together with some iron oxides. Garnet, anatase and rutile may come from soil, but are more likely to be industrial. Industrial sources contribute iron oxides, abrasives (corundum, carborundum, zircon, garnet, and cerium oxide), and various metal oxides used as pigments. The presence of some of the less common substances we have observed, such as particles of Sn or metal amalgam, may account for a significant fraction of the total elemental analyses of those elements (see appendix 5: sample 14.2 on material collected from the Beckton grit traps before the sewage enters the works, and samples 4, 5 and 18 for primary settled sewage). The primary minerals can often be distinguished from their secondary counterparts by their morphology under the SEM. None of the primary minerals hold heavy metals except a few Fe-rich particles and industrial compounds, and some other unusual substances as noted above. However, they may acquire superficial deposits of secondary precipitates, either as cements binding several grains together into an aggregate or as coatings around grains. These deposits may contain heavy metals. Some secondary deposits may already have started to form in the raw sewage before reaching the works.

Table 5.1. Percentage distribution of mineral types in different fractions of sludge (mg/kg dry matter)

Mineral type	Raw	Digester sludge											Biofloc
	Beckton whole	Beckton - top				Beckton - bottom			Solihull				Beckton perox
		<2.2	2.2-2.9	2.9-3.3	>3.3	2.2-2.9	2.9-3.3	>3.3	<2.2	2.2-2.9	2.9-3.3	>3.3	
Quartz	46		37			34			1	36			17
Calcite	18		12			11			9	13			5
Aluminosilicates	22		9	45	38	15	50	4	11	33	57	11	45
Phosphates	3	33	32			34	4		33	12	6		12
Iron oxides	2			11	32	1	14	25			15	33	14
Type I sulphides	8		5	18	11	1	16	55	4		3	34	
Type II sulphides	1		1	3	6		1	2			4	8	
Type III sulphides													
TIO2				1	5		4	3				5	
Others			1	7	5	1	11	10				8	1
Aggregates		36	1	2	3	3		1				1	
Organic/Biogenic		31							21				
Total	100	100	98	87	100	100	100	100	79	94	85	100	94

Table 5.2. Densities of common mineral types

Group	Sub-group	Mineral	Density
Quartz		Quartz	2.7
Felspars		Orthoclase Microcline Plagioclase	2.5 to 2.9
Ferromagnesian minerals	Olivines	Olivine	3.3
	Pyroxenes	Diopside Augite Enstatite Hypersthene	3.1 to 3.6
	Amphiboles	Hornblende	3.0
	Micas	Muscovite Biotite	2.9 2.9
Metamorphic and accessary minerals		Garnet Staurolite Sphene Zircon Rutile Fluorite Epidote	3.8 3.7 3.5 4.7 4.2 3.1 3.3
Opaques		Iron and mixed oxides	3.5
Carbonates		Calcite Dolomite Siderite Ankerite	2.7 2.9 3.9 3.0
Phosphates		Apatite	3.2
Sulphides		Pyrite Pyrrhotite Chalcopyrite Sphalerite Galena	5.0 4.6 4.2 4.1 7.5
Sulphates		Gypsum Barytes	2.3 4.5

Sludges from different works and sludges taken from different parts of the digester contain different proportions of the range of minerals found in sludge. Table 5.1 lists the percentage distribution for the main mineral groups in raw sludge, in fresh digested Beckton sludge taken from the normal outlet of the digester, in fresh digested Beckton sludge taken by auger from the bottom of the digester, in a sludge from a soft-water area (Solihull), and for minerals in the cleared 'Biofloc' fraction.

The mineral distributions in the three main sludges may be broken down into separate distributions for each of the successive density cuts. Table 5.1 shows how density separation can be used to enrich the sulphides and iron oxides that were potentially of most interest in this project. Comparison of the distribution lists with the table of mineral densities (Table 5.2) reveals that some minerals are still separating in the 'wrong' density cut, which may probably be attributed to cemented aggregates and to secondary coatings. The quartz grain coated in pyrites shown in Figure 4.4 would have been classed as a pyrites grain had the coating not been broken open!

Each of the different classes of minerals listed in Table 5.1 will be discussed separately.

Phosphates

Raw sludge contains very few phosphate grains or precipitates (Table 5.1), but phosphates make a substantial contribution to the 'Particulate' fraction in digester sludge as crystals, cements and coatings. Phosphate is released by the hydrolysis of detergents and by the breakdown of organic matter. It then precipitates with Ca in the digester in a variety of forms.

Despite the abundance of both coarse and fine Ca-phosphate grains under the SEM, they gave only weak and diffuse lines on the XRD indicating that they are mainly amorphous or only very poorly crystalline. Where XRD lines were identifiable the patterns were usually those of apatite, although brushite was also identified by XRD.

The sizes of Ca phosphate grains ranged from several hundred μm to less than 0.1 μm, too small to see under the SEM. Three classes of Ca phosphate could be easily distinguished. Biogenic or pseudomorphing structures (eg. tubes or rods) have been described under Organics. The most common of the mineral forms found was amorphous apatite ($Ca_5(PO_4)_3OH$), in the form of irregular lumps. Comparison of analyses with museum specimens showed it to be mainly apatite but with some carbonate-apatite, in which some CO_3 substituted for PO_4, was also present, other substitutions may have been present but were not detected. Crystalline brushite ($CaHPO_4 \cdot 2H_2O$) was less common. It tended to form clusters of small euhedral, stubby prismatic crystals (figure 4.3). Some aggregates appear to be mixtures of apatite and brushite, or non-stoichiometric, or other unidentified Ca phosphates. No certain evidence for Mg/NH_4 phosphates was found. NH_4 cannot be detected by the SEM and only one sample analysed was found to contain an appreciable quantity of Mg. No XRD lines for Mg/NH_4 phosphate were found either.

It is likely that brushite precipitates first as it is the less energetically stable of the two, and then later disproportionates into apatite, first in amorphous forms and later in crystalline forms. The phosphate grains themselves do not appear to hold heavy

metals. Their elemental profile under the SEM often includes small quantities of both Fe and S, but it seems unlikely that these are mixed Ca-Fe phosphates, since a plot of the Fe content against the S content of 100 grains of calcium phosphate revealed a constant relation (Figure 5.3) between the two elements, whereas a similar plot of the Fe content against background noise (as a crude measure of the organic content) revealed no such correlation (Figure 5.4). It appears that the Fe content of phosphate grains is fully accounted for by secondary deposits of FeS on their surfaces. No evidence was found for the existence of vivianite ($Fe_3(PO_4)_2$), either in sludges from a hard-water area (London), where one would expect the phosphorus to associate preferentially with the abundant calcium, or, surprisingly, in sludge from a soft-water area (Solihull).

$MnHPO_4$ would be expected to have precipitated under the low redox environment of the digester. However, no evidence was found for its existence under the SEM: none of the grains analyzed were found to contain both P and Mn as major components. $MnHPO_4$ is homologous with brushite but Mn was not observed even as a minor component of brushite grains. Lindsay (1979) states that according to its reported solubility product, it should be very stable in soils and should be able to co-exist with apatite, but that further research is needed to clarify its solubility relationships.

Carbonates

Calcite was present in all sludges studied. It often occurs as detrital grains but some grains appear to be biogenic and many are secondary. These range in size from several hundred μm to a few μm, with a similar abundance across the range of sizes. Calcite is

precipitated in the digester, but no evidence was found for the precipitation of dolomite. Comparison of raw and digested sludge shows that detrital grains are recognizable by their clean appearance and sharp crystal faces. A plot of Fe content against S for the secondary calcites, similar to that plotted for the Ca phosphates, produced figure 5.5; unfortunately there are many fewer points as there is much less calcite than phosphate in sludge. However, though highly scattered, the points fall over the same general range as the graph for Fe/S on phosphates. It seems likely that the same conclusion may hold for calcite, ie that Fe or heavy metals associated with the calcite are in secondary deposits of Fe sulphide on the surface of the grain and not incorporated in the calcite itself. However, it is known that the calcite structure can accommodate 5-10% substitution of Fe for Ca. In addition, intergrowths of siderite ($FeCO_3$) and gypsum ($CaSO_4$) may be contributing to the scatter on the Fe/S graph for calcite.

In sample 11.3 the precipitation of calcite in sludge was forced by the addition of sodium carbonate. This precipitated sufficient calcite for it to be possible to distinguish primary calcite from secondary calcite in the X-ray diffraction pattern. From the shift in the crystal lattice spacing in the secondary calcites it appeared that around 2% cationic substitution had occurred. Geological experience suggests that this is the most that would be expected at normal temperatures. However, this degree of uptake was not observed in untreated sludges, although 2% substitution is well within the limits of detectability of the Guinier camera.

Analysis of scale deposited on the wall of a digester from a

sludge rich in heavy metals provides further evidence against the inclusion of heavy metals in calcite (landfill digester, sample 30). A cross-section of the concretions showed several layers differently coloured to the eye, alternating grey and rust coloured, but the SEM and XRD revealed them to consist almost entirely of calcite and monohydrocalcite, with a very low heavy metal content. A digimap taken across the layers showed no discernible differences in constitution across the deposit. The Fe present appeared to be Fe oxide co-precipitated calcite, although it is not possible to exclude the presence of siderite ($FeCO_3$).

A few examples of secondary ankerite (a mixed Fe-Ca carbonate) and siderite were found under the SEM; siderite may be recognized by its low Fe content relative to the oxides or hydroxides. Mosey had postulated the latter to explain the observed limits to the concentration of dissolved Fe in the digester (chapter 2). If siderite were to occur in detectable quantities, it would be found in the densest cut (table 5.2). The presence of siderite in this density cut was confirmed by XRD. Analysis for carbonates (by CO_2 release with acid: see appendix 1.L) showed that they could account for 0.4% of the total weight of that fraction, which itself only accounts for 1% of the total mineral matter. The carbonate analysis places an upper limit on the quantity of siderite present, although some occluded secondary calcite might have contributed to this figure there was not enough to be detectable by XRD. While siderite cannot account for a significant proportion of the mineral grains, its presence suggests that its solubility product may exert some control, even if only locally, in the digester.

Carbonates of cadmium, or the first-row transition metals

(except iron), have not been observed under the SEM, neither have any lines from their XRD spectra been observed.

Aluminosilicates

Aluminosilicates of various kinds were present in all the samples analyzed. Many of the larger grains were identifiable as feldspars. These are detrital, and may have entered the sewers from soil run-off, but are also used as mild abrasives in household substances such as toothpaste and dishwasher powder. It is not possible to distinguish between feldspars, micas and clays by their analyses under the SEM, because their compositional ranges overlap the accuracy of the analysis system used, although it is sometimes possible to distinguish them on morphological grounds. Natural feldspars were often seen under the micro-probe to be altered to clays to a greater or lesser extent, often on the sub-micron scale, so analyses usually indicated a mixture, with variable ratios of Al and Si, and of K, Ca and Na. Other detrital aluminosilicates included garnets (in the denser cuts), and Ca aluminosilicates from cements.

Two detrital silicates were identified in sludge: talc and zircon ($ZrSiO_4$). Talc was observed in several samples, and formed platy or elongate grains (10-50 μm); these were usually clean but some had small quantities of finer clays on their surfaces. Only one grain of zircon was noted under the SEM but its spectrum was not observed under the XRD. It is most likely to have originated as an industrial abrasive, although it might have come from soil run-off.

Quartz (SiO_2) was present in all sludges examined. The majority of grains appeared to be detrital but some appeared to be of biogenic origin and some appeared to be secondary (and probably

amorphous) silica. There was a continuous range in the size of the particles from a few mm down to a few μm, but the abundance of quartz decreased noticeably from the coarser to the finer fractions. Cation substitution in the quartz structure will be negligible.

Detrital clays were present in large quantities from fillers and soil run-off, but cannot easily be distinguished under the SEM. They are present as a contaminant in the 'Particulate' fraction, and are discussed in the section covering minerals in the finer fractions (p 138 ff).

Feldspars can include only limited proportions of other cations, but the sheet silicates may contain significant proportions, either in the octahedral sites within sheets or in inter-layer sites. Cations held in inter-layer sites would be easily exchangeable.

Chlorides

The only chlorides recorded in the XRD spectra are halite (NaCl) and sylvite (KCl), both from sludges that not been elutriated in water before drying. It may reasonably be concluded that they are not normally present in digester sludge.

Oxides and hydroxides

Small quantities of iron oxides and hydroxides were found in most samples, although higher proportions were found in the samples concentrated magnetically. Sizes ranged from a few μm to several hundred μm, but spot analyses on grains of other minerals also produced very high Fe contents, suggesting that grains too small to resolve (less than 0.1 μm) were present as secondary minerals or coatings on other minerals. Following the introduction of the ZAF:PB software, it was possible to determine the proportion of Fe

in the grains and, if the impurity content was low, to identify tentatively the form of the compound. The commonest was goethite (FeOOH). The next commonest were haematite and maghemite (both are Fe_2O_3), both of which have been identified by XRD. The XRD spectra of magnetite (Fe_3O_4) and wustite (FeO) were identified but neither has been identified with any certainty under the SEM. Siderite ($FeCO_3$) cannot be distinguished from the Fe oxides and hydroxides under the SEM except by its Fe analysis (see table 5.3).

Iron metal has also been identified by XRD, but surface oxidation probably precludes its identification under the SEM.

Table 5.3 Fe content of common minerals

Fe oxide/carbonate	% Fe	Fe sulphide	% Fe
Ferrous oxide	78	Troilite	64
Magnetite	72	Pyrrhotite	61
Haematite	70	Pyrite	47
Goethite	63	Chalcopyrite	35
Ferric hydroxide	52		
Siderite	48		

Analyses of Fe oxides often included small but significant amounts of S. This may indicate that some sulphides had oxidised during preparation of the sample, or that secondary sulphides have formed on detrital iron particles. Smaller amounts of Ni, Cu and Zn, occasionally Ti, Mn or Cr and very rarely V are commonly associated with Fe in coatings but less commonly in grains.

Other oxides identified include detrital corundum (Al_2O_3), rutile and anatase (TiO_2), and cerium oxide (Ce_2O_3). These are unlikely to have taken up significant quantities of cations by substitution and therefore to play any role in the heavy metal chemistry of the digester.

Sulphides

Much of the detrital material in raw sludge could clearly be seen to have started to acquire a sulphide coat in the anaerobic conditions of the digester. Two examples can be seen in the photographs in the previous chapter, figure 4.4B shows secondary pyrrhotite encrusting a grain of quartz. In figure 4.8, a ring of Cu and S can be seen in the top-left corner. The centre of this ring did not contain any elements dectable by the micro-probe and was presumably organic.

Few secondary crusts were ever found in embedded cross-sections but the thickness of the coat on other grains could be examined by changing the accelerating voltage of the primary electron beam in the SEM. At 10 keV, the penetration was approximately 0.25 μm, at 15 keV approximately 1 μm and at 30 keV approximately 6 μm. Since the machine is only calibrated for quantitative analysis at 15 keV, the ZAF:PB software cannot be used to compare the results from different voltages. To get round this problem spectra from grains in raw sewage were compared at different accelerating voltages with geological specimens of pyrites, obtained from the University museum. The comparison showed that at 6 μm penetration the Fe/S ratio of many grains in sewage is too high for any known iron sulphide, but at 1 μm penetration they gave analyses close to that of pyrite or pyrrhotite. This would suggest that the sulphide

coating on the grains in raw sewage is less than 6 µm deep. The SEM cannot distinguish a sulphide coat deeper than 6 µm from solid sulphide, while coatings of this thickness cannot easily be resolved on digimaps.

The sulphide grains from digested sludge that were recorded under the SEM, and identified by their XRD spectra, fall naturally into three groups. In order to simplify discussion these have been termed:

Type I Fe sulphides, containing Zn, Cu, Ni and Mn

Type II Pb sulphides, containing Ba, Ag, Sn and Fe

Type III Cr sulphide

Type I: Fe (Cu, Zn, Ni) sulphides

The analyses of type I sulphide grains from the digester that appeared to contain no impurities were often close to those of pyrrhotite, with analyzable elements totalling close to 100% (ZAF:PB). XRD indicated that pyrrhotite (Fe_7S_8 - FeS) is the commonest sulphide, with a smaller proportion of pyrite (FeS_2) and even less marcasite (FeS_2). However, over all the grains taken from the digester the Fe/S ratio varied over a wide range. This may suggest that there had been some oxidation of the grains during separation, storage and sample preparation. In nature, the Fe content of iron sulphides does vary considerably but always as an Fe deficiency. Pyrrhotite can be constituted $Fe_{1-x}S$ where X can be anything up to 0.125 (Deer et al, 1966).

Some cemented grains contained organic impurities (revealed by a high base-line noise level and elemental analyses totalling less

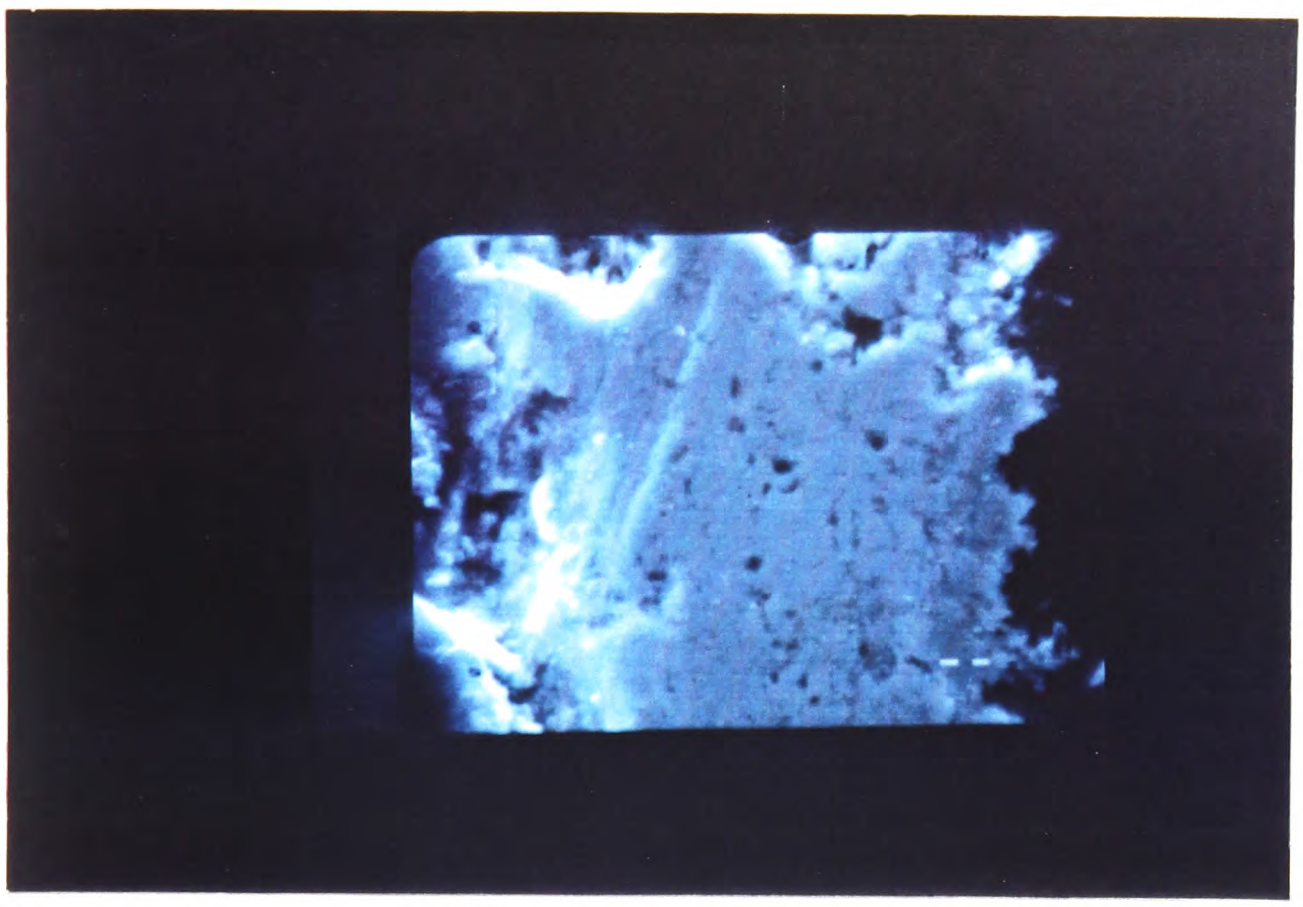
than 100%) which could have been holding other detectable elements, but even those grains which didn't contain cemented organic impurities often contained appreciable quantities of the first-row transition metals, usually Cu and/or Zn, less commonly Ni and only rarely Ti, Cr, Mn and V.

A plot of the sulphur content of such grains against the proportion of the cations accounted for by the heavy metals (Cu+Zn+Ni) is presented in figure 5.6. This was compiled from the recorded analyses of all grains containing Fe, Cu, Zn, Ni and S (but excluding those with high background noise and/or those whose ZAF:PB analyses added up to less than 90%). It showed that the sulphides occurred with all proportions of heavy metals to sulphide between FeS and Cu/Zn/NiS. Yet, as the grains are oxidised and their sulphur content reduced, the heavy metals are lost, to leave iron oxides with a relatively much smaller heavy metal content than the thhat of sulphides.

When the Fe, Zn and Cu contents of all type I sulphides recorded are plotted in a ternary diagram (figure 5.7), they extend over a range of compositions along the Fe-Cu join (low Zn), and along the Fe-Zn join, but none along the Cu-Zn join and none in the centre of the Fe-Zn-Cu diagram.

As ascertained by XRD, the discrete crystalline phases present in these mixtures or solid-solutions include sphalerite (ZnS), bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$) and digenite (Cu_9S_5), although others may have been present in proportions too small to identify.

Figure 5.1 SEM micrograph of embedded sulphide grain

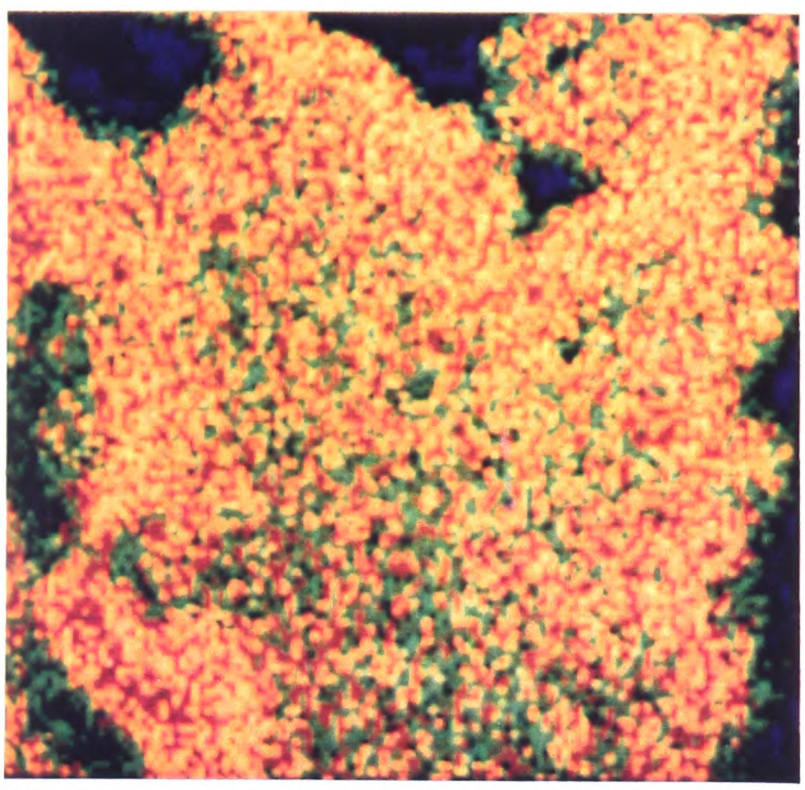


The digimaps of this grain showing the distribution of Cu, Zn and Fe are shown on the next page.

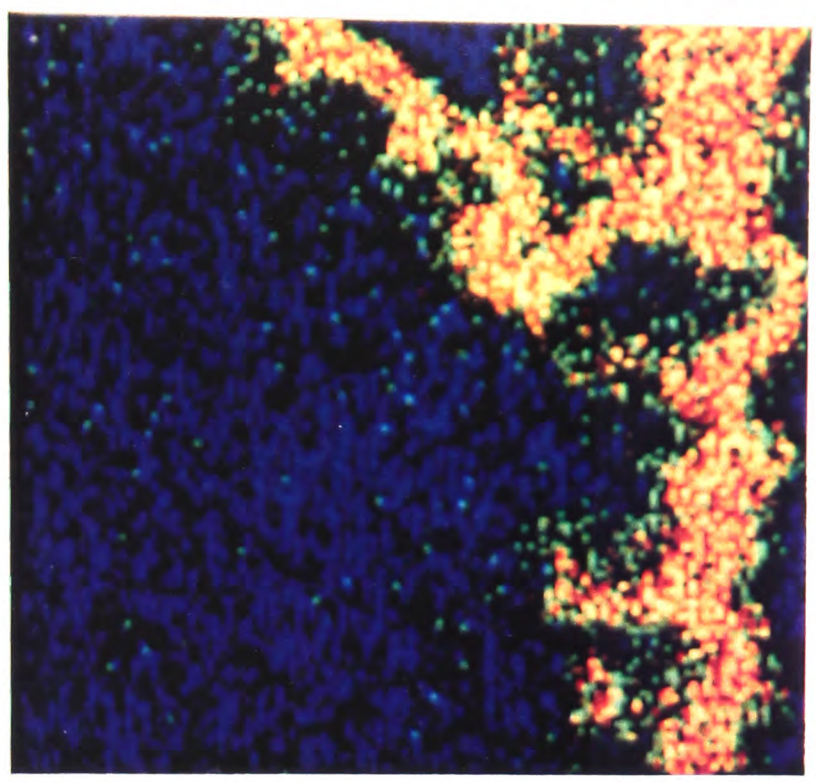
The grain came from study 33.4.

Figure 5.2 Digimaps of grain in figure 5.1

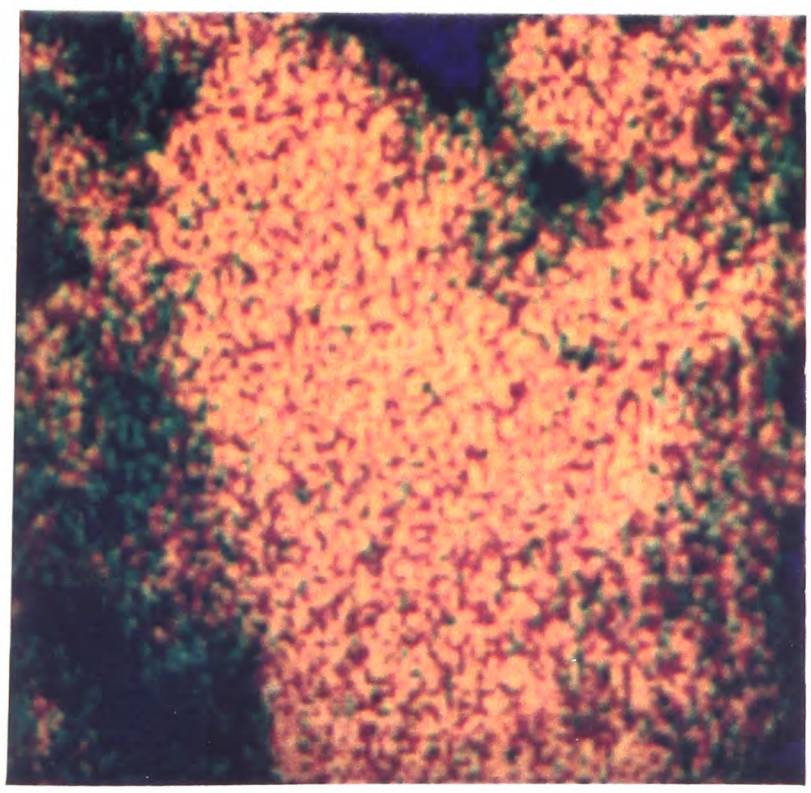
S



Fe



Cu



Zn

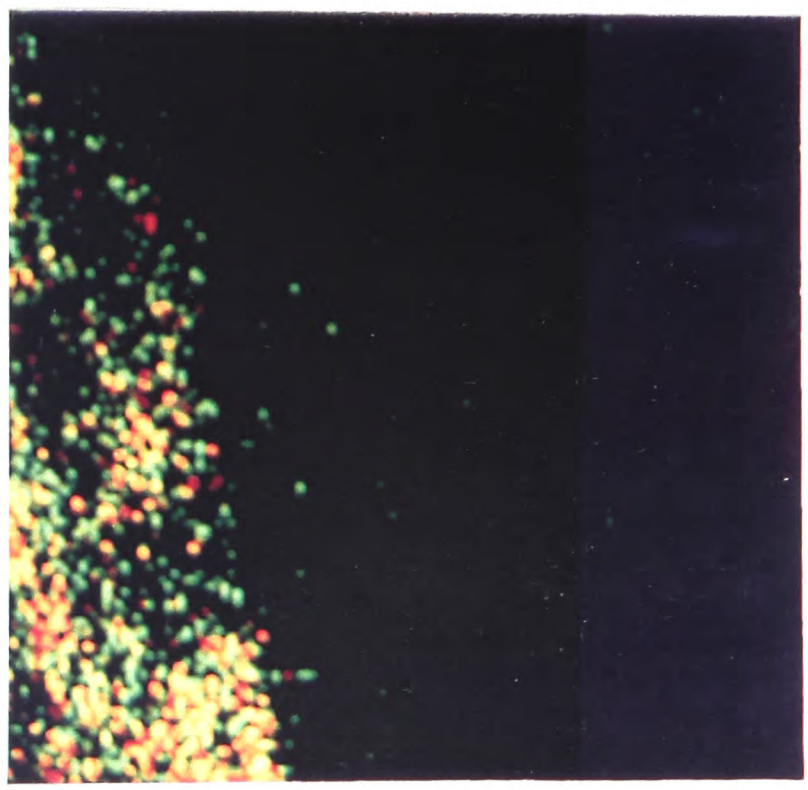


Figure 5.3 Graph of Fe against S content for Ca phosphate grains

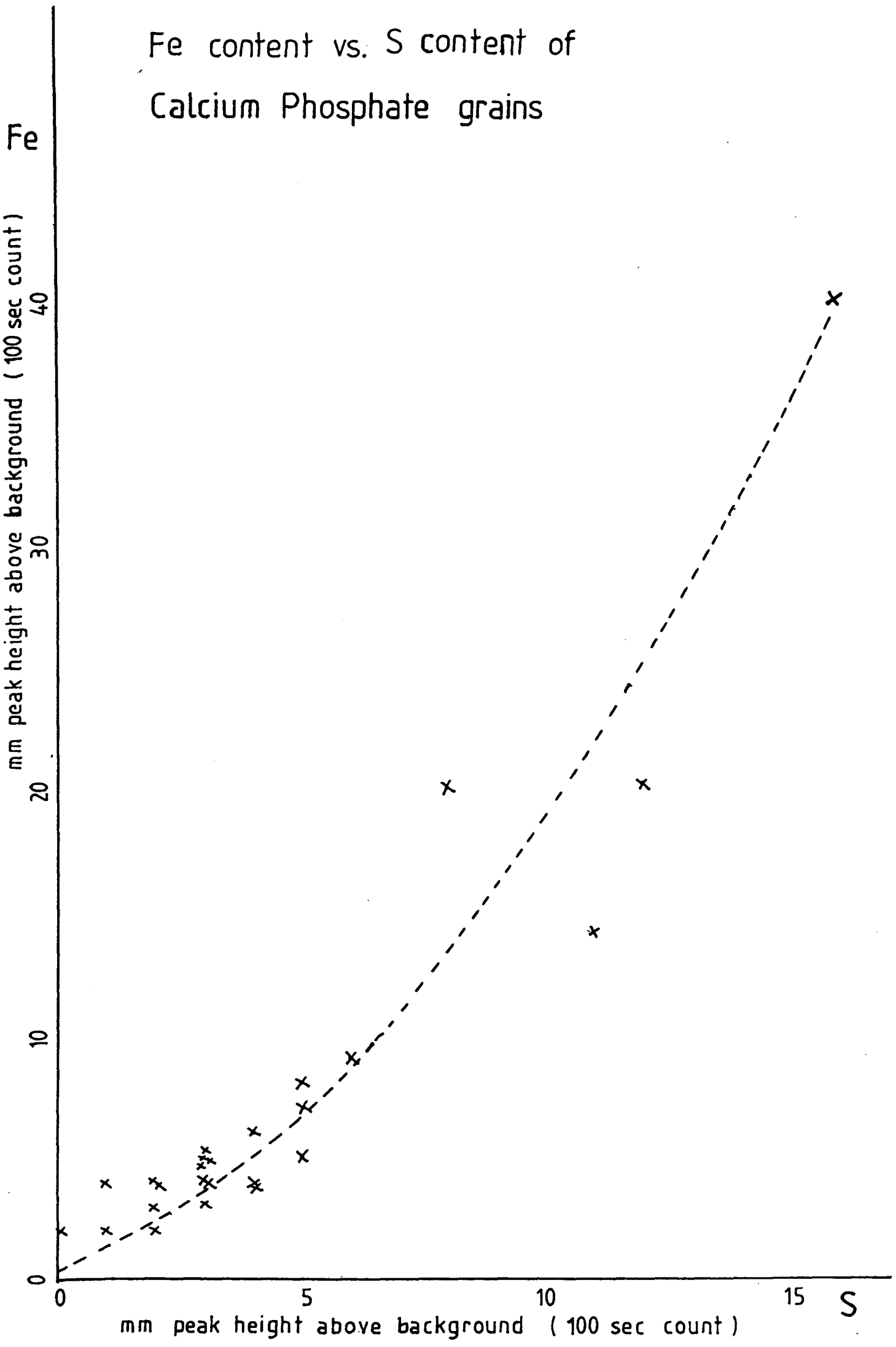


Figure 5.4 Fe content against 'background noise' for Ca phosphate grains

The 'background noise' was measured as the number of counts in 100 seconds on a channel away from that of any element.

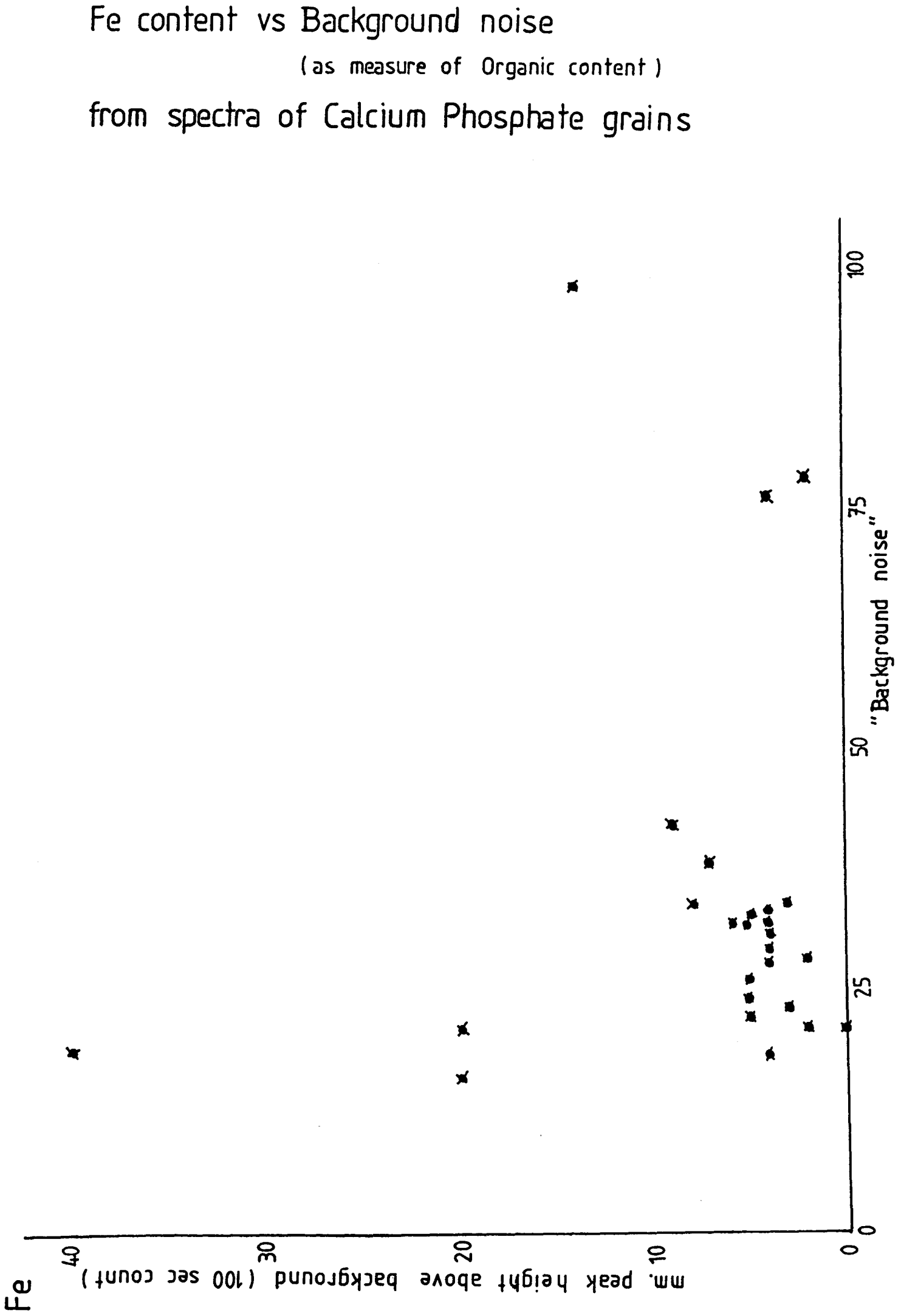


Figure 5.5 Fe content against S content for calcite grains

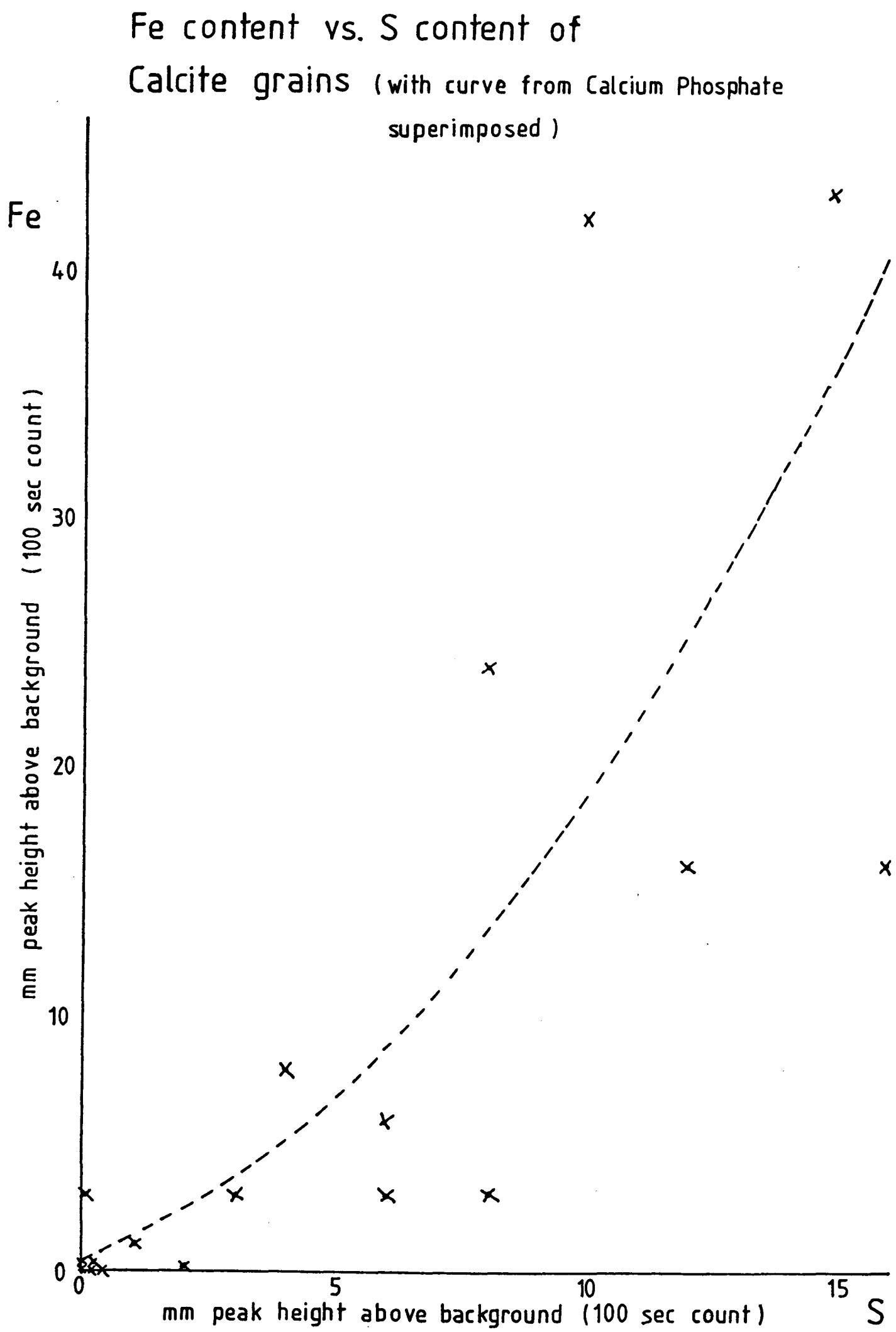


Figure 5.6 Graph of heavy metal content against S for HM and Fe grains

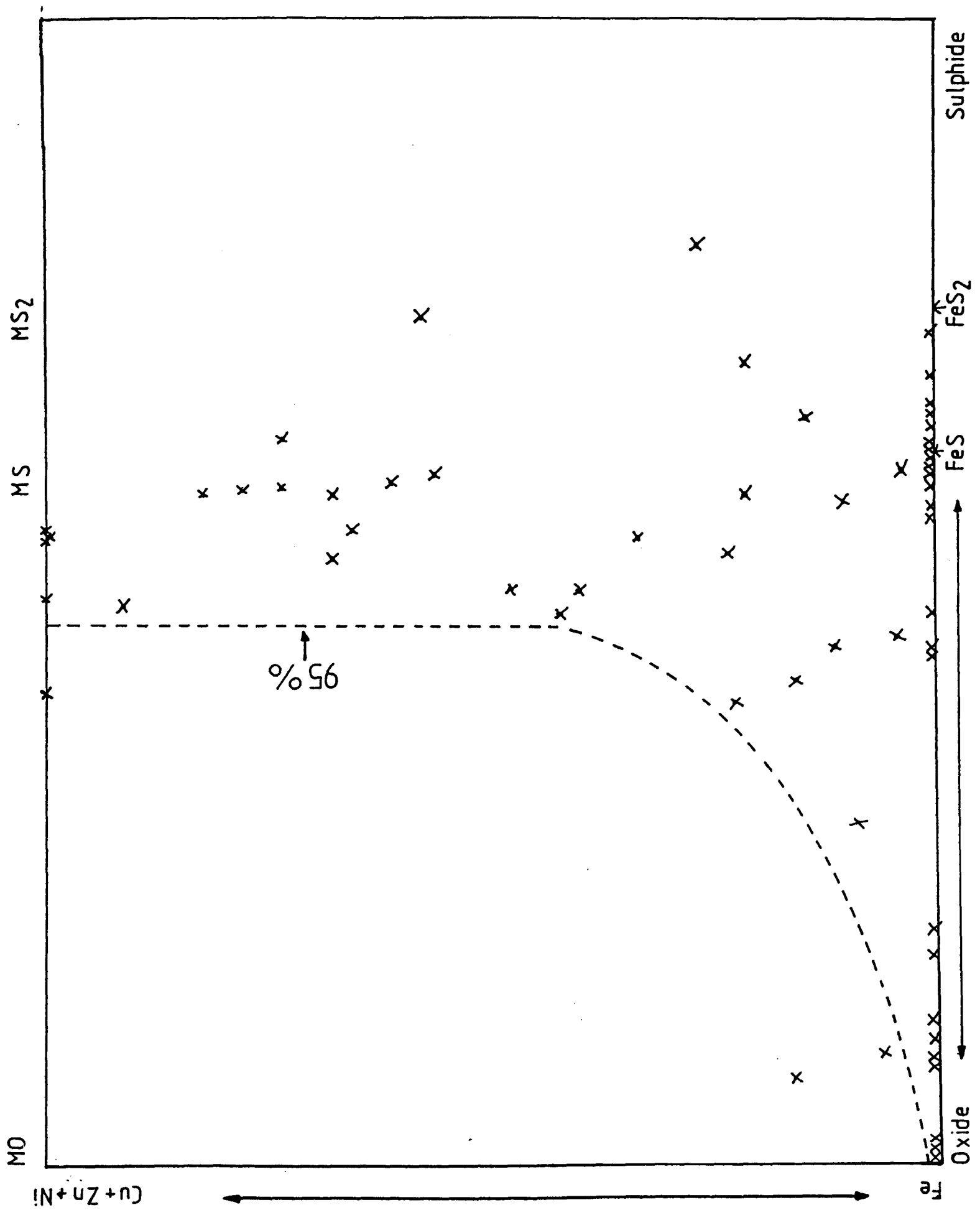
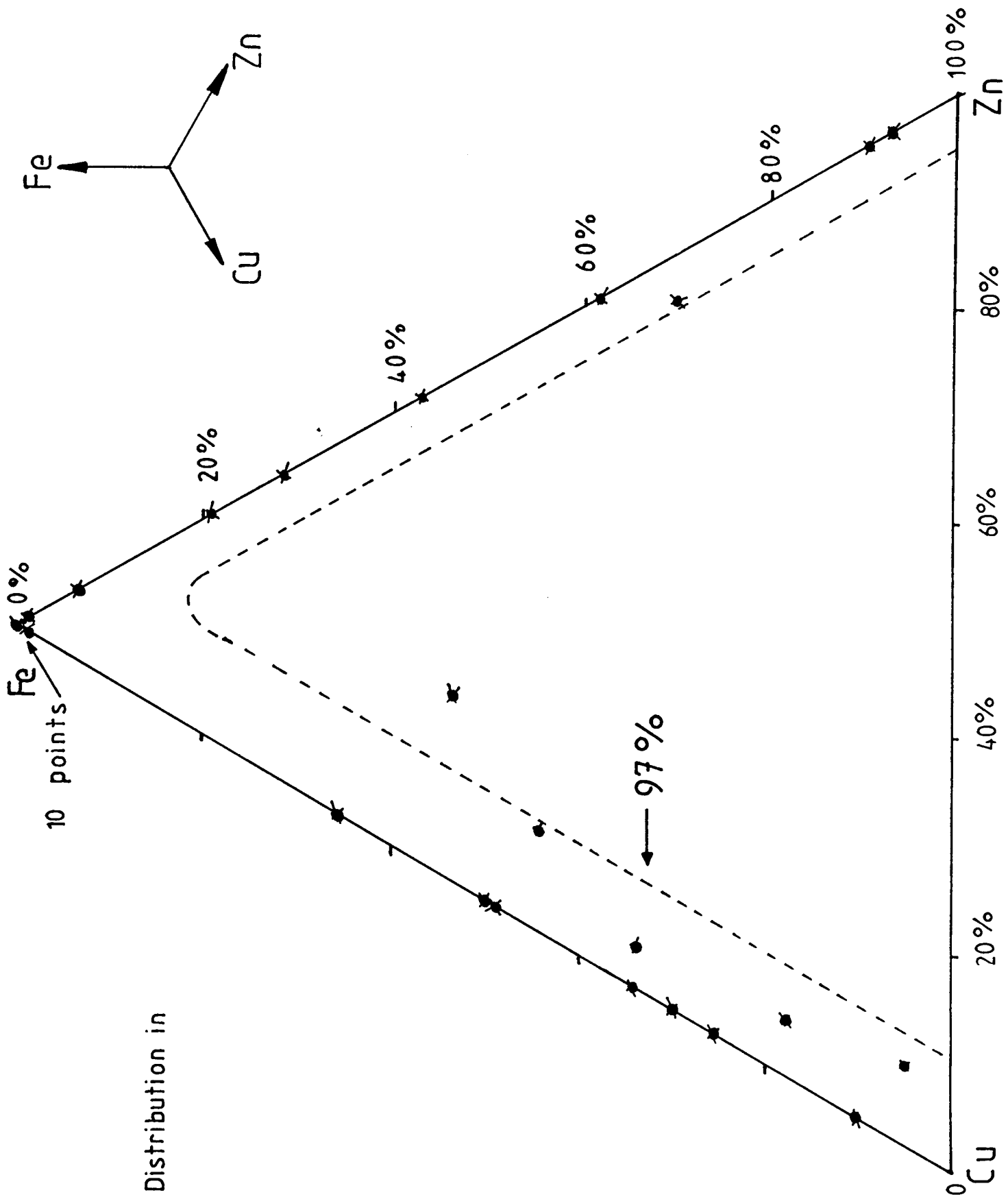


Figure 5.7 **Heavy metal distribution in sulphide grains**



Digimapping of cross-sections through these grains showed them to be heterogeneous, but also confirmed the conclusions drawn from figure 5.7. A particularly clear example of this is provided by figures 5.1 and 5.2. Figure 5.1 presents the SEM photograph of a cross-section through a grain, and figure 5.2 presents the S, Fe, Cu and Zn digimaps of the same cross-section. These digimaps show a range of compositions between Fe and Cu and between Fe and Zn, but they clearly show exclusion between Zn and Cu in the lower left-hand corner.

These results compare well with published measurements on anaerobic harbour sediments which showed discrete particles only of zinc sulphides and copper sulphides, with no increased concentration on the edge of the particles that might have indicated absorption (Lee and Kittrick, 1984).

The problem in describing these sulphides is to decide whether they occur as mixtures of discrete compounds, as true solid-solutions or as substituted solids. The question of solid-solutions can be partially answered from the mineralogical literature (particularly that concerned with the geochemistry of hydrothermal ore deposits). Much of it is concerned with high temperatures and pressures which may favour the formation of solid-solutions. Nevertheless, the Fe/Cu/S system is recognized as one of the most complicated known, and at least 18 discrete solid phases have been documented (Mills, 1974).

Pyrite (FeS_2), vaesite (NiS_2) and cattierite (CoS_2) are iso-structural and can form a complete range of solid-solutions, although these are distinguishable by the change in the crystal cell size. Hauerite (MnS_2) is also iso-structural, but only forms a very

limited range of solid-solutions with the pyrite series. It is believed that where Cu, Pb, Zn and As have been reported as impurities in pyrite they are present as inclusions of other minerals (Deer et al, 1966).

Pyrrhotite (Fe_7S_8 - FeS) can take up small quantities of Ni, Co, Mn and Cu, but cannot take up appreciable quantities of Zn.

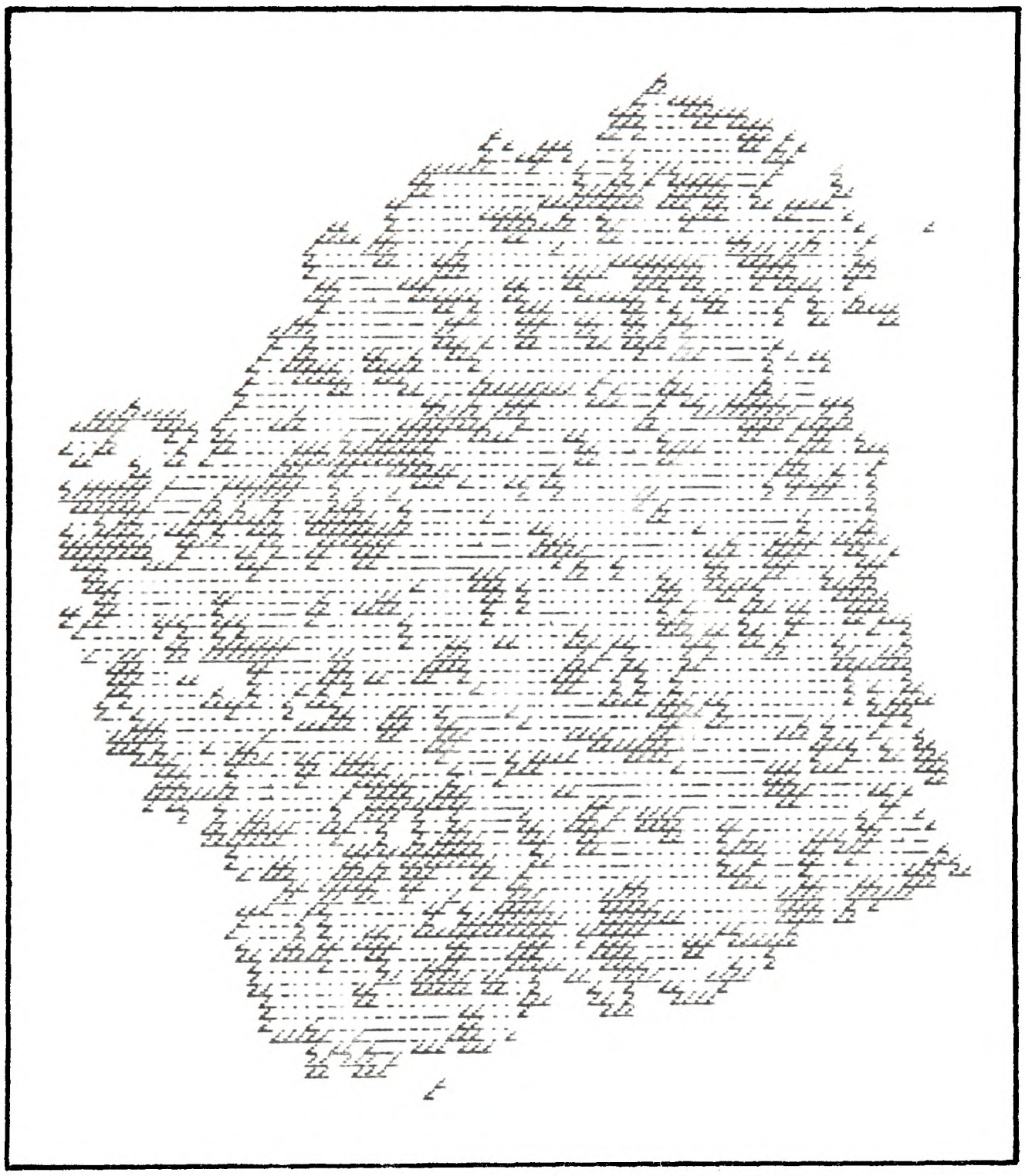
The Cu sulphides vary in their Cu/S ratio from chalcocite (Cu_2S) to digenite ($Cu_{1.8}S$). Mills (1974) states that digenite, whose presence in sludge was confirmed by XRD, is the sulphur-rich boundary of chalcocite and states that they have similar thermodynamic properties. In natural systems Cu sulphides usually contain significant amounts of iron, and they form solid-solutions very readily. Thus, digenite (Cu_9S_5) forms a solid-solution series that extends beyond bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$) and cubanite ($CuFe_2S_3$), with respect to its Fe content. Morimoto and Koto (1970) state that bornite can take up to 1% Fe as an impurity at room temperature. In contrast, covellite (CuS) has a fixed, nearly impurity-free composition at low temperature.

Natural sphalerite can take up to 40 mole % of Fe by substitution, and up to 5 mole % Cd and Mn, together with smaller quantities of Co. Where Ag, Sn and Cu have been recorded in sphalerite, it is believed they are present as inclusions of other minerals. While sphalerite dissolves to less than 0.1 mole % in either pyrite or pyrrhotite, and does not form a solid-solution with the iso-structural high-temperature form of chalcopyrite, it does form a complete solid-solution with the iso-structural CdS (Deer et al, 1966).

In view of all this, the next question that needed answering was 'to what extent can inclusions of other minerals be recognized by the analytical procedures used?'. To help answer this, some synthetic sulphides were precipitated from a variety of solutions containing heavy-metal cations in different proportions. The details and results of the experiment are given in appendix 1. Under the experimental conditions it was the disulphides (MS_2) that precipitated whereas a mixture of monosulphides (MS) and disulphides (MS_2) precipitate in the digester (Figure 5.6). But the experiment gave some useful indications. When a low proportion of impurities was present only one crystal phase was formed and the impurities were either taken up (by pyrite) or excluded (by galena). Galena (PbS) continued to exclude Fe even when the Fe concentration in the solution was one fifth of the Pb concentration.

When precipitates were formed from mixtures with more even concentrations of heavy metals, several phases precipitated simultaneously. Although vaesite and pyrite are iso-structural and are able to form a true solid-solution, they must have precipitated separately since their XRD spectra were sharp and distinct, but no variation in the Ni and the Fe content of the grains could be distinguished under the SEM. This would suggest that the resolution of the Link Systems machine is insufficient to identify a mineral phase uniquely. It is likely, then, that the sulphides exist in the digester as discrete phases of the order of a few hundred angstroms, but they remain discrete and are not true solid-solutions.

Figure 5.8 Digimap of the distribution of Ba in a Ba/Pb sulphide



Type II: Pb (Ba, Ag, Sn) sulphides

The type II sulphides are more surprising. A range of compositions between PbS and BaS was found, with a 1:1 ratio being common. The Pb:Ba ratio over the surface of one grain was mapped by Digimap (Figure 5.8) and revealed a patchy distribution of these elements. However, the analyses of Pb and S are complicated by the fact that their lines overlap on the SEM and the ZAF:PB software is not able to distinguish them fully - this leads to some uncertainty in their analyses. Despite this, the association of Ba with Pb has not been noted in geological specimens before, although Ba has been reported as a minor impurity in galena.

Ba has a suitable ionic size to substitute for Pb, and the XRD results favour the interpretation that the Ba is substituting for Pb in the galena structure. This conclusion is strengthened by the fact that the published solubility product for BaS makes it far too soluble to form in the digester (Log K = 2.3). However, the intermediate compositions we have observed may result from intergrowths of the two sulphides rather than cationic substitution. The ZAF:PB analyses did show that the Ba was present as the sulphide and not the sulphate. Ba also forms the sulphides Ba_2S and BaS_3 (Mills, 1974), though these have not been found in geological samples. Fe, Ag and Sn also occur frequently in the type II sulphides, although they rarely form more than a small fraction of the total cations. Pure and, judging by its appearance, crystalline SnS (herzenbergite) was also observed under the SEM. Herzenbergite has been found in geological samples as an intergrowth with galena. It has also been found in conjunction with pyrite, sphalerite and chalcopyrite (Moh, 1969).

Table 5.4. Heavy metal sulphides shown to occur in the digester

Type	Name	Structure	Impurities
I	Pyrite	FeS_2	Zn, Cu, Mn, V, Cr
	Marcasite	FeS_2	-
	Pyrrhotite	$Fe_{1-x}S$	Zn, Cu, Mn, V, Cr
	Bornite	Cu_5FeS_4	Ag
	Digenite	Cu_9S_5	-
	Chalcopyrite	CuFeS	Zn
	Sphalerite	ZnS	Fe
II	Galena	PbS	Ba, Ag, Sn
	-	SnS	-
III	-	Cr_7S_8	Zn, Fe

Table 5.5. Minerals identified by X-ray diffraction

Silicates	
Quartz	SiO_2
Feldspar (plagioclase)	$Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$
K-feldspar	$(K,Na)(AlSi_3O_8)$
Clays: kandites	$Al_4(Si_4O_{10})(OH)_8$
illites	$K_{1-1.5}Al_4(Si_{6.5-7}Al_{1-1.5}O_{20})(OH)_4$
smectites	$(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4((Si,Al)_8O_{20})(OH)_4$
Talc	$Mg_6Si_8O_{20}$
Mica (muscovite)	$K_2Al_4(Si_6Al_2O_{20})(OH,F)_4$
Diopside	$CaMgSi_2O_6$
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)$
Phosphates	
Apatite	$Ca_5(PO_4,CO_3)_3(OH,F,Cl)$
Brushite	$CaHPO_4 \cdot 2H_2O$
Carbonates	
Calcite/Aragonite	$CaCO_3$
Monohydrocalcite	$CaCO_3 \cdot H_2O$
Siderite	$FeCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$Ca(Mg,Fe,Mn)(CO_3)_2$
Oxides	
Corundum	Al_2O_3
Gibbsite	$Al(OH)_3$
Rutile/Anatase	TiO_2
Hematite/Maghemite	Fe_2O_3

Table 5.5 (continued)

Oxides (continued)	
Magnetite	Fe_3O_4
Goethite	FeO·OH
Wustite	FeO
Sulphides	
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Bornite	Cu_5FeS_4
Chalcopyrite	$CuFeS_2$
Digenite	$Cu_{1.8}S$
Sphalerite	ZnS
Galena	PbS
Others	
Halite*	NaCl
Sylvite*	KCl
Antlerite*	$CuSO_4(OH)_4$
Mascagnite*	$(NH_4)_2SO_4$
Anglesite**	$PbSO_4$
Anhydrite**	$CaSO_4$
Carborundum	SiC
Tungsten carbide	WoC

* By-product of early drying procedures

** Produced artificially by reagents

Table 5.6. Minerals present in the 'Biofloc' fraction, by XRD

Mineral	Characteristic peak (A)
Talc	9.4, 4.69, 3.12
Kaolinite	7.19, 3.59
Gibbsite	4.86
Quartz	4.26, 3.35
K-feldspar	3.25
Plagioclase feldspar	3.19
Calcite	3.03
Dolomite	2.89
Halite	2.81
Chlorite	14.4, 7.19, 4.74, 3.54
Mica	10.0, 5.00

Although Fe has been noted as a minor constituent of galena in mineralogical specimens, it is likely that in both these and the digester sulphides it is present as inclusions of other minerals.

Type III: Cr sulphide

On several occasions grains were observed which analyzed only as chromium and sulphur. These grains sometimes contained small levels of Fe and Zn. This is unexpected, since Cr forms the most soluble of all the first-row transition metal sulphides, and would not be expected to precipitate while any iron was free. However, it is possible that micro-environments rich in Cr could have occurred through uneven mixing in the digester. Alternatively they may represent particles of Cr metal or particles of pigment which have acquired a sulphide coat >6 μm deep. Unfortunately none of these rare grains was found in any of the digimap cross-sections. Several Cr sulphides have been documented by Jellinek (1957), and their thermodynamic data are given by Mills (1974).

Cr sulphides are not known as geological ores, although small deposits of Cr_7S_8 have been found. In nature, Cr is more usually found as chromite ($FeCr_2O_4$).

Minerals in the finer fractions

The results so far presented have been from minerals in the 'Particulate' fraction, but both the 'Biofloc' and 'Colloid' also hold fine mineral particles. Since the minerals in untreated samples of these fractions are too fine-grained and too diluted by organic matter to identify by SEM or XRD, it was necessary to resort to the use of clearing agents. There is a risk that such reagents

may create artefacts or destroy a mineral type, so for this reason the effects of several different reagents were compared in parallel studies.

Complexing agents were used to clear the 'Biofloc' fraction (appendix 5, samples 11 and 12) as described in Appendix 1; these complex the divalent cations that cross-link organic polymers, and replace them with monovalent cations. However they failed to remove a sufficiently high proportion of the organics for the mineral grains to be resolvable under the SEM, while the XRD revealed only the dominant quartz, calcite and feldspars from the native sludge, with artefacts characteristic of each reagent, ie Ca phosphate in the pyrophosphate-treated sample, and weddellite/whewellite ($CaC_2O_4 \cdot 2H_2O$ / $CaC_2O_4 \cdot H_2O$) in the sample that had been treated with oxalate.

In sample 28 peroxide was used to clear the organics. This gave clean grains under the SEM, and table 5.6 lists the minerals found. They follow the same pattern as the minerals in the 'Particulate' fraction but in different proportions. A sample of 100 grains is not enough to give much statistical confidence in the results, but does give a rough guide. On this basis, there is a much lower proportion of quartz in the 'Biofloc' than in the 'Particulate' fraction, which is to be expected since quartz is more resistant to mechanical comminution to smaller particles, and a higher proportion of the material in the 'Biofloc' that analysed as SiO_2 appears from its morphology to be secondary silica.

An XRD analysis of the 'Biofloc' fraction was carried out with a Phillips 2 kW diffractometer and Debye-Scherrer camera by Dr M Wilson of the Macaulay Institute (Aberdeen). This gives much better

resolution of highly orientated minerals such as clays. The trial also compared the effects of three clearing agents: hypobromite, chlorine dioxide and hydrogen peroxide (appendix 1.I).

The best XRD patterns were obtained from the specimens treated with chlorine dioxide or with hydrogen peroxide, and revealed chlorite, mica and dolomite which were not detected in the sample treated with hypobromite. The hypobromite treatment revealed calcite and halite which were not apparent from the other treatments. In each case, the strongest lines came from kaolinite (kandite), which is not surprising as this is used as filler in paper and in many other materials. Fainter lines were present for talc, mica and chlorite, but there was no detectable montmorillonite. None of the samples showed lines for iron oxides or sulphides; these must therefore be amorphous at this particle size.

The 'Colloid' fraction has been briefly examined by SEM and diffractometer: the SEM showed a high aluminosilicate content, but most of the particles were smaller than 1 μm and so below the resolution limits of the SEM. The diffractometer failed to confirm the existence of any crystalline phases in an untreated sample.

Conclusion

The chapter has shown that SEM and XRD are complementary techniques, and that their combined use can produce a comprehensive description of the mineral phases in digested sludge.

The list of minerals positively identified by XRD is easily the most exhaustive yet published. In particular, it provides details of the precise heavy metal sulphides precipitating in the digester that can be used as a basis for the model. It is important to know

which particular sulphide minerals precipitate, rather than to know generally that heavy metals are precipitated as sulphides, because each mineral phase has its own thermodynamic stability and will, therefore, support a particular activity of its constituent ions in solution.

The use of SEM in conjunction with XRD enables associations of ions to be described. The SEM analyses have enabled the sulphides to be categorised in three broad families depending on their associated cations. These families might indicate solid-solutions which in turn could substantially alter the solubility of the minerals concerned.

Having described the forms of combination of heavy metals in the 'Particulate' fraction, the next stage is to describe complexation by the three organic fractions. The mass balance at the end of chapter 3 showed the 'Biofloc' holding the majority of the heavy metals. It is therefore important to ascertain whether these are held as organic complexes or as enmeshed finer precipitates of the minerals already described in this chapter.

ORGANIC COMPLEXATION: I

The mass balance presented at the end of chapter 3 showed the 'Biofloc' fraction holding the largest proportion of the heavy metals. In chapter 5 it was shown that some at least of these heavy metals can be attributed to fine mineral grains present in this fraction.

The literature reports that several families of bacteria nucleate the precipitation of a variety of minerals on their cell walls. These minerals would be too intimately associated with the 'Biofloc' for them to be easily separated from it, and clearing agents to remove the organic matter are likely to destroy some mineral phases and produce other phases as artefacts. In order to ascertain what proportion of heavy metals separating with the 'Biofloc' is being held in mineral forms, we need to measure the proportion of the heavy metals that can be held by complexation. An allowance can then be made for this in calculations of the mass balance.

The fraction of the heavy metals held by organic complexation is likely to form an important pool in its own right. A good working description of the complexing ability of the organics in sludge will be needed if we are to gain a complete understanding of the forms of combination of the heavy metals in sludge, and their relation to each other. Complexation, by reducing the activity of the cation in solution, may prevent it from otherwise precipitating, or it may stabilise one redox state relative to another (Petit and Brookes, 1977).

Some of the metals may be held by complexation on sites where

binding is sufficiently strong for the proton to be unable to compete even when present in 10^6 fold higher concentration, or on sites where binding is not by proton exchange (Green and Manahan, 1977). In chapter 3, it was shown that substantial quantities of heavy metals remained after washing in 0.1 M HCl. However, these sites are unlikely to be available for reversible complexation in sludge. Other work suggests that a proportion of the copper complexed by humic acids is held so tightly that it is not 'available' to crop plants (Cheshire et al, 1977). The metals bound in such sites ought then to be regarded as lost to the system until the organic matter is destroyed. If suitable measurements were taken, a model could then allow for them in a different way from that employed for metals held by reversible binding. Unfortunately, time was not available to pursue this.

In order to describe complexation we will need to ascertain the stability constants of the potential complexes. The stability constants for the complexation of the divalent first-row transition metals by simple ligands have been shown to increase monotonically from Mn to Cu, for all ligands bonded through O or N donor atoms, and then to decrease to Zn (Irving and Williams, 1948). For complexation by humic substances the order can generally be extended:

$$Hg>Cu>Pb>Ni=Zn>Co>Fe>Mn=Cd>Ca>Mg$$

This order has been termed the Irving-Williams order and does not hold for ions with valencies other than 2, or for ligands with donor atoms other than N or O (eg S). Since it was shown in chapter 2 that ligands with O as the donor atom are the only significant forms of ligands binding Cu and Zn, this order will form an important

basis for investigating complexation of the heavy metals by the biomass and by soluble organics.

However, there are problems in describing complexation by polyvalent macromolecular ligands: they are of unknown molecular weight, and they may contain several classes of binding sites, which may exhibit positive or negative co-operativity on binding. Since the work of Irving and Williams, 2 ways have been proposed to characterise complexation by them.

One approach to these problems has been to treat the ligand as the central group in complex formation. Graphs of quantity bound against concentration (intensity) of reactants are then plotted (Q/I plots), and these graphs can be fitted to one of the variety of equations that attempt to model the change in binding affinity with degree of complexation (termed isotherms). Various graphical rearrangements can then be used to recover a stability constant for each class of binding site. The isotherm equations allow the properties of the polyvalent ligand to be summarised in a few relatively simple numbers.

However, there were 3 constraints in our model of anaerobic sludge:

1) The interaction between the cations and the organic matter had to be described mathematically in a form suitable for inclusion in existing computer models.
2) Because the different cations are likely to compete for the available sites, the interaction of as many cations as possible had to be measured.
3) The model had to be generally applicable. Since sludge is a heterogeneous mixture of highly variable proportions, it would

be pointless to produce a highly detailed description of one particular sludge. Therefore the binding had to be characterised by the minimum number of constants, and it had to be relatively easy to determine these for a new sludge sample.

If this approach had been taken, detailed descriptions of the binding characteristics of each constituent type of organic matter for each cation would have had to be measured, together with their relative proportions. Anyone then wishing to use the model would have had to measure the relative proportions in his sludge of the different organic components specified in the model. Not only would this have discouraged use of the model, but it could have introduced a potential source of error where it predicted results more specifically than the accuracy of the measurements should have allowed.

It was therefore decided to take the simpler approach, and to treat the metal cation as the central group in complex formation rather than the ligand, and to treat the ligand as if it were monovalent (Fitch and Stevenson, 1983).

On the basis of the above constraints it had already been decided to divide sludge into only 4 major fractions, 3 of which were predominantly organic. On similar grounds, it was decided to take a pragmatic approach, and to measure the binding characteristics of these 3 fractions over a small range of well-defined conditions rather than attempt an exhaustive description of the organic material.

A model based on these constraints will be valid only under the stated range of conditions. This model may not be applicable to a

new kind of sludge, but since the fractionation procedure (chapter 3) and the measurement of the equilibrium constants (chapters 6 and 7) is relatively easy it will be easy for any potential users to measure the constants for their sludge.

Before the equilibrium constants can be defined, 4 problems must be dealt with:

1) A suitable method for measuring complexation
2) A choice of convention for describing complexation
3) How to define the ligand concentration
4) How to describe ligand protonation

Methods available for measuring complexation

The methods in use for measuring stability constants fall naturally into 2 groups. In the first group, one of the equilibrium concentrations (free cation (M), complexed cation (Mb), free ligand (L) or complexed ligand (Lb)) can be measured in situ. In the second group, the phases can be separated before measurement. Fitch and Stevenson (1983) listed the most common methods under these 2 headings (table 6.1).

If an in situ method is chosen it must be shown that the act of measurement will not interfere in any way with the final equilibrium position. Nor may the act of separating the phases alter the equilibrium position (eg by changing pH, or ionic strength) and so give an inaccurate stability constant.

Table 6.1 Methods to measure metal-organic complexation

Method	Measured	Reference
1) With phase separation		
Ion-exchange/AA	M or Mb	Crosser and Allen, 1977
		Schnitzer and Hansen, 1970
Equilibrium dialysis/AA	M	Zunino and Martin, 1977
Gel filtration/UV	Mb	Mantoura and Riley, 1975
Centrifugation/AA	M	Green and Manahan, 1977
Solvent extraction	M	Nash and Choppin, 1980
2) Without phase separation, '*in situ*'		
H^+ potentiometry	Lb	Stevenson, 1976, 1977
Polarography (DPP)	M	Hanck and Dillard, 1977
Spectrofluorimetry	L or Lb	Ryan and Weber, 1982
Spectrophotometry	L	Blaser *et al*, 1980
Ion-selective electrode		Sposito and Holtzclaw, 1979
		Sposito *et al*, 1979
Anode-stripping voltametry	M	Brezonik *et al*, 1976
		Ernst *et al*, 1975

(Fitch and Stevenson, 1983)

Choice of convention

There are 3 possible conventions for describing complexation, each with a convention for its standard state, that may be adopted to express cation complexation by the organic fractions.

The most appropriate convention for use in many existing

computer models of chemical speciation is to treat the ligand as if it were monovalent, and to define the ligand concentration in terms of the molarity of ionisable sites, ie the grams per litre of ligand multiplied by the CEC in equivalents per gram.

If the metal cation is treated as the central group, then a series of species of the type ML_n can be defined. For the divalent heavy metals, 2 species could exist:

$$M^{++} + L^{-} \iff ML^{+}$$

$$ML^{+} + L^{-} \iff ML_2$$

The stability constants for these reactions would be:

$$k_1 = [ML^{+}] / [M^{++}][L^{-}]$$

$$k_2 = [ML_2] / [ML^{+}][L^{-}]$$

However, with a substance as heterogeneous as the 'Biofloc' fraction, these are unlikely to correspond to any structural chemical reality. Instead, the model simply needs to define the total proportion of the cation bound. So we can simply treat all complexed cations as:

$$M^{++} + 2L^{-} = ML_2$$

for which:

$$K_s = k_1 k_2 = [ML_2] / [M^{++}][L^{-}]^2$$

But under experimental conditions, exchange with the proton is likely to predominate:

$$M^{++} + 2HL = ML_2 + 2H^{+}$$

where:

$$K_e = [ML_2][H^{+}]^2 / [M^{++}][HL]^2$$

The standard state of the ligand for this convention would be protonated sites at a concentration equivalent to one 1 molal, and their deviation from ideality would be in terms of Henry's law (ie

activity would be proportional to concentration).

In order to calculate the stability constant from the measured cation-proton exchange constant, the complementary proton-association constant K_a for the reaction:

$$H^+ + L^- \langle=\rangle HL$$

for which:

$$K_a = [HL] / [H^+][L^-]$$

is also required.

Alternatively, the reaction may be defined in terms of ion-exchange. The exchanger may be defined as a separate phase, and the activity of the proton and of copper on the exchanger may be expressed in terms of mole fractions or equivalent fractions.

In terms of mole fractions (Vanselow convention) the constant is defined:

$$K_V = N_M . a_H^2 / N_H^2 \cdot a_M$$

where N_M and N_H are the mole fractions of copper and the proton on the exchanger respectively. It may also be defined in terms of equivalent fractions (Gapon convention), when the constant is defined:

$$K_G = E_M \cdot a_H / E_H \cdot a_M^{1/2}$$

where E_M and E_H are the equivalent fractions of copper and proton on the exchanger. For these 2 the standard state of the ligand is defined as the homoionic form, and deviations from ideality in terms of Raoult's law.

Equivalent fractions may be converted into mole fractions by:

$$X_i = (E_i / Z_i) / \sum_{j=1}^{J} (E_j / Z_j)$$

where Z_i is the charge on any ion, E_i is its equivalent fraction and X_i its mole fraction.

Equilibrium constants

Stability constants may be specified either as thermodynamic or as conditional constants. Thermodynamic constants are calculated using activities, usually by taking measurements at several ionic strengths and extrapolating back to infinite dilution. Conditional constants are defined when one or more of the activities are replaced by concentrations and their values depend by definition on the composition of the solution (Fleck, 1966).

If measured concentrations are to be converted to activities, a convention must be adopted on how to calculate the theoretical single-ion activity coefficients. Each of the different equations published offers a trade-off between the ionic range it covers, and simplicity. The Davis equation has been used in the calculation of all the experimental results in this thesis; it offers a good approximation up to 0.1 M and continues with errors of only a few percent up to 0.5 M (Davis, 1963). It is:

$$\log y_i = -AZ_i^2 \, (I^{1/2} / (1+I^{1/2}) - 0.3I)$$

where y_i is the activity coefficient for ion i, I is the true ionic strength, Z_i is the charge on ion i, and A is the Debye-Huckel Limiting Law constant, which is temperature-dependent:

0.4953 $litre^{1/2}mol^{-1/2}$ at 5°C

0.5116 " at 25°C

0.5212 " at 35°C (in the digester)

The true ionic strength may be approximated by the stoichiometric ionic strength (calculated using total concentrations of all the ions in solution) and then refined iteratively allowing for ion-pair formation. The activity constants of neutral complexes may be calculated from the Setchenow-Harned-Owen equation:

$$\log y_i = k_m I$$

where k_m is the salting coefficient (Harned and Owen, 1958). An average value of K_m = 0.1 mol kg^{-1} has been used in all calculations of experimental results in this thesis.

The complications introduced by side reactions and ion-pair formation mean that the dominant anion in the system must be carefully chosen. Sposito and Holtzclaw (1979) argued that ClO_4^- offered the fewest problems in the study of fulvic acid-Cu complexes, since it forms weaker complexes than most anions. Complexation must be defined relative to some measurable free state and some workers have defined ClO_4^- as forming no complexes with the heavy metal cations. In fact, Raman spectroscopy clearly shows that ClO_4^- does form weak complexes with the heavy metal cations but these have been ignored (P Fletcher, pers comm).

Where the effects of side reactions and ion-pair formation have not been calculated, and allowed for in calculating a stability constant, the constant must be reported as an <u>apparent</u> constant (Fleck, 1966). The use of apparent constants in well-defined contexts or in complex but well-known media such as sea-water can be useful, but sludge is unlikely to offer a sufficiently constant ionic background for them to be useful in this model. A heavy bout of rain may swell the daily flow at the Beckton works from the average 200 million litres per day up to the works' full capacity of 800 million litres per day (ie 4-fold dilution).

<u>Ligand concentration</u>

We must be able to define the concentration of ligand present. The organic material in sludge is highly heterogeneous, containing

material recently added to the digester, older well-humified material and bacterial debris. Consequently, we shall not be able to define the concentration of our organic ligands in molar units, although some classes of complex natural ligands (eg humic substances) have been sufficiently well defined that it is possible to calculate molar concentrations (Bresnahan et al, 1978; Sposito et al, 1979).

A variety of conventions have been adopted to answer this problem. Mantoura and Riley (1975) used the average molecular weight for humic acids to calculate a molar concentration. Alternatively, the concentration of reactive sites can be used instead of the concentration of ligand. If so, the relation between the mass of ligand present and the site density must then be specified. The maximum binding ability can be calculated by extrapolation from the Langmuir isotherm (Zunino and Martin, 1977). Saturation binding may be measured directly by continued addition of cation until no more is bound. Fletcher and Beckett (Pt 1, 1987) measured free cation concentrations at saturation using an ion-selective electrode (ISE) and calculated the amount absorbed by difference. Crosser and Allen (1977) measured free cation concentrations at saturation by AA and compared these with the uptake by a known quantity of ion-exchanger.

Alternatively, the maximum binding ability has been estimated by base titration of the functional groups (Stevenson, 1976; Takamatsu and Yoshida, 1978). This is related to the number of sites able to complex cations because the proton is able to accept electrons from the electron-donor atoms that could also co-ordinate the cations. Consequently, proton exchange often forms a dominant feature of metal complexation in the environmental pH range. However, this does assume that all ionisable groups can contribute to complex formation.

Other methods available for estimating the molarity of reactive sites include potentiometric titration, spectrophotometric titration, spectrofluorimetry, and equilibrium dialysis (Fitch and Stevenson, 1983).

Ligand protonation

In order to calculate the stability constants for the various cations, the complementary proton-association constant K_a is also required (see above). Baham and Sposito (1986) determined the average proton-association constants for functional groups titrated between pH 3 and 11 for a sludge water-soluble-extract (WSE) much finer than that defined for our 'Soluble' fraction. The fitted constants corresponded to pK_as of 4.1, 6.6 and 9.4.

However, the effective K_a for each of the 3 predominantly organic fractions defined in chapter 3 could not be determined for 2 reasons. The incomplete characterisation of the fractions leads to uncertainty in the anion uptake and the behaviour of the ions originally present in the solution. Secondly, the titration curves of the 'Biofloc' and the 'Soluble' fractions (Fletcher and Beckett, 1987), unlike those found for fulvic acids (Sposito et al, 1979) and WSE (Baham and Sposito, 1986), could only be the consequence of a smooth continuum of sites and not clusters of similar and discrete sites which could be easily modelled. Therefore complexation must be described in terms of a constant that implicitly defines competitive exchange with the proton. Such a constant may be defined simply in terms of the concentrations of protonated ligand and complexed ligand.

Computer models such as GEOCHEM and MINEQL require K_s and K_a; we were able to measure K_e but not K_s or K_a. The exchange constant K_e can be split up into K_s and K_a by simply assigning an arbitrarily high value to K_a that would operationally define all the uncomplexed ligand sites to be protonated in the pH range of interest; a suitable value for pK_a is 10. This is simply a mathematical device that ensures that the computer model reassembles the measured value of K_e when calculating complexation. So:

$$pK_s = pK_e + ZpK_a$$

where Z is the charge on the complexing cation. For the divalent heavy metals:

$$pK_s = pK_e + 20$$

Then the initial concentration of protonated sites can be defined as the total concentration of ionisable sites (CEC), which can be measured by one of the methods discussed above. The CEC should be measured as accurately as possible, but if there is a small error in its measurement it should not matter as long as the same value is used for calculating the equilibrium constant, and for entering the concentration of ligand as a component when running the computer model. If a large proportion of the sites is occupied, too small a value for the CEC would distort the calculated equilibrium constant.

Complexation by the 'Soluble' fraction

The 3 fractions that contain mainly organic residues which were defined in chapter 3 fall into 2 distinct groups. Both the 'Biofloc' and the 'Colloid' were operationally defined on their separation by centrifugation and their complexation can therefore be measured by phase separation methods, while the 'Soluble' fraction which is the

supernatant from centrifugation obviously cannot.

In order to complete the model in the time available, I was able to benefit from the collaboration of Dr Philip Fletcher who measured the heavy metal binding characteristics of the 'Soluble' fraction. The method he used and the results he obtained for the 'Soluble' fraction have been published (Fletcher and Beckett, Pts 1 and 2, 1987). The remainder of this chapter reviews his results. Chapter 7 then presents the results of my own analyses of heavy metal binding by the 'Biofloc' and 'Colloid' fractions.

The 'Soluble' fraction is that which remains in solution after centrifugation of anaerobic sludge at 12,000 rpm for 30 minutes. The inorganic analysis of this fraction has already been presented in chapter 3. Its organic content averages 1.15 gm/litre, as determined by loss of weight on combustion at 600°C. (Note that the weight loss and the organic content might not be coincident if there were decomposition of any organic salts).

Before this fraction could be used for binding studies it had to be freed of existing bound cations. The cleaning procedure described in chapter 3 reduced the content of all heavy metals to below one tenth of their previous level, and reduced the organic content to between 0.3 and 0.6 gm $litre^{-1}$. There was no discernible difference in the pH titration curves of cleaned and uncleaned samples of the 'Soluble' fraction, suggesting that the cleaning procedure had not altered the nature of the organic material. The 'Soluble' fraction was diluted to give a standard concentration of 0.25 grams per litre of organic matter and sodium perchlorate was added to give a constant ionic background.

Copper complexation

Copper binding was measured by adding copper perchlorate to aliquots of the 'Soluble' fraction, to give stoichiometric activity ratios (aH^2/aCu) in the range 2 to 10^{-8}. After equilibration overnight, the activity of the free copper remaining was measured by a copper ion-selective electrode. The measured activity of the copper in solution was converted to concentration by the Davis equation; allowance was made for hydrolysis to $CuOH^+$ and $Cu(OH)_2^0$; and the quantity of copper bound was defined by the difference:

$$Q = Cu_t - [Cu^{2+}] - [CuOH^+] - [Cu(OH)_2^0]$$

The stoichiometric ionic strength was used in the Davis equation on the assumption that ion-pair formation in the perchlorate background would be negligible.

It proved possible to saturate the copper-binding sites at pH 6.5 before supersaturation with respect to the copper hydroxide solubility product predominated. At pH 6.5 the maximum uptake of copper was 8.86×10^{-3} meq gm^{-1}. Copper binding was shown to be pH-sensitive and dominated by proton-exchange. It was also shown to be freely reversible. The addition of small aliquots of strong acid to copper-saturated material led to the concomitant release of copper: by pH 2 all the bound copper had been released. The reverse points fell on the same uptake curve as the forward-measured points. The quantity of copper bound was not a straight function of the stoichiometric activity ratio.

The copper exchange-constant was calculated in terms of all 3 conventions. Only the mole fraction convention gave a constant value between pH 5.5 and 8. Below pH 5.5 the constants were pH-dependent for all 3 conventions.

Complexation of the other divalent cations

Ion-selective electrodes are available for both cadmium and lead, so these were used to measure Pb and Cd stability constants directly, using the same method as above. These showed that the maximum uptake for Cd was 70% of the maximum uptake of Cu. The maximum uptake of lead could not be measured directly because of lead hydroxide precipitation, but reasonable extrapolation suggested that the limit was the same as for Cu.

The stability constants for Ca, Mg, Co, Mn, Zn and Ni were measured by exchange between these elements and the 'Soluble' fraction saturated with copper, based on the assumption that there are no sites for divalent cations to bind except on sites already binding Cu. This assumption was shown to be reasonable by comparing the stability constants obtained by direct measurement of Cd binding, as well as by this indirect method. The maximum level of uptake was the same for all cations at around 72% of the maximum for Cu or Pb. The calculated K_v for each cation was constant over the pH range measured (5.7-7.0).

Because of this pattern of uptake, the description of binding could be simplified into a 2-site model. One site, accounting for 28% of the total sites, could bind only H, Pb and Cu; the second site could bind all the cations. The maximum uptake at these 2 sites was 2.4×10^{-3} mol gm^{-1} and 6.38×10^{-3} mol gm^{-1} respectively.

The stability constant for Fe(II) was not measured due to problems in preventing oxidation during equilibration and repeated measurements. However, on the basis of the Williams-Irving order, the co-ordination chemistry of Fe(II), and comparison with other systems where Fe(II) binding has been measured it can usefully be

approximated by the constant measured for cobalt. A stability constant for Fe(III) was measured, but $Fe(OH)_3$ precipitation introduced significant uncertainty into its value.

Table 6.2 Conditional equilibrium constants

For the exchange reaction, (I=0.1):

$$M^{2+}_{(soln)} + 2H^{+}_{(bound)} \Leftrightarrow M^{2+}_{(bound)} + 2H^{+}_{(soln)}$$

Ion	Site 1		Site 2		
Pb(II)	269	+/- 50	42	+/- 8	$K_v \times 10^{10}$
Cu(II)	82.5	14	17	4	
Cd(II)	22.3	4.5	-		
Zn(II)	12.9	2.5	-		
Ni(II)	8.6	2	-		
Co(II)	5.6	1	-		
Mn(II)	4.5	1	-		
Ca(II)	2.8	0.6	-		
Mg(II)	1.4	0.3	-		

(Fletcher and Beckett, Pt 2, 1987)

This simplification into a 2-site model was tested by comparing computer predictions against measured pCu on the ion-selective electrode with a variety of competing ions present. When the copper activity was greater than 10^{-7} M, the predictions were generally within 10-15% of the measured value.

This model suggested a further simplification. The dominant divalant cation in the digester solution is calcium. At a calcium concentration of 0.1 M, the measured exchange constants would predict

that >90% of the 'site 1' sites would be binding calcium.

A final series of experiments confirmed that in the presence of 0.1 M Ca, only Cd was bound in significant quantities on 'site 1' sites, and that Zn, Ni, Co and Mn would not be bound on the 'Soluble' organic matter to any significant extent. It was also confirmed that neither Ca nor Cd interfered with Cu and Pb binding to 'site 2' sites. Although the activity of Ca in the digester is significantly lower than 0.1 M (table 9.2), the 'Soluble' fraction is unlikely to hold a significant proportion of the heavy metals.

Conclusion

A working model of heavy metal chemistry in sludge must include a working model of heavy metal complexation by the various organic fractions. Given the heterogeneous nature of these organic materials, it was unlikely to be possible and would probably not be useful to present detailed descriptions of heavy metal binding for every class of organic groups in the organic matter. Fortunately, the requirements of a computer model merely dictate the need for a working mathematical description of binding under the conditions about which the model is going to be asked to make predictions.

Such a working description of one of the 3 predominantly organic fractions defined in chapter 3, the 'Soluble' fraction, was produced by Dr Philip Fletcher using the ion-selective electrode method. This showed that the binding could be described by a 2-site model, and could best be characterised in terms of an ion-exchange constant with the proton. 'Site 1' sites accounting for 72% of the total exchange capacity bind all divalent ions, but 'site 2' sites accounting for 28% of the total exchange capacity bind only H, Cu and Pb.

ORGANIC COMPLEXATION: II

The 'Biofloc' and 'Colloid' fractions

In chapter 6 it was concluded that a rigorous description of the cation-binding properties of the different organic fractions of sludge was unlikely to be either feasible or necessary for the model; rather, that it would be sufficient to develop a mathematical description, valid over the relevant range of conditions, of the overall cation-binding properties of the 3 functionally defined fractions of organic matter.

On this basis, Dr P Fletcher had analysed the cation-binding properties of the 'Soluble' fraction which I had defined; the results he obtained are presented at the end of chapter 6. This chapter describes the methods used to measure complexation by the 'Biofloc' and the 'Colloid' fractions, and presents the results obtained.

Cleaning the fractions

The 'Biofloc' fraction was defined in chapter 3 as the material thrown down by centrifugation at 3,500 rpm for 30 minutes after the 'Particulate' fraction had first been removed by elutriation. The 'Colloid' fraction was defined as the material thrown down by centrifugation at 12,000 rpm for 30 minutes, after the sludge had first been centrifuged at 3,500 rpm for 30 minutes and the pellet removed. As collected, both fractions contain substantial quantities of heavy metals in inorganic forms. Before use in binding experiments, they need to be cleaned from bound cations and heavy metal precipitates. The cleaning procedure detailed in chapter 3

still leaves a significant fraction of the divalent cations behind: 42% of the Fe, 60% of the Cu, 5% of the Zn, 5% of the Ca but less than 1% of the Ni remained on the 'Biofloc' after cleaning (calculated from table 3.8).

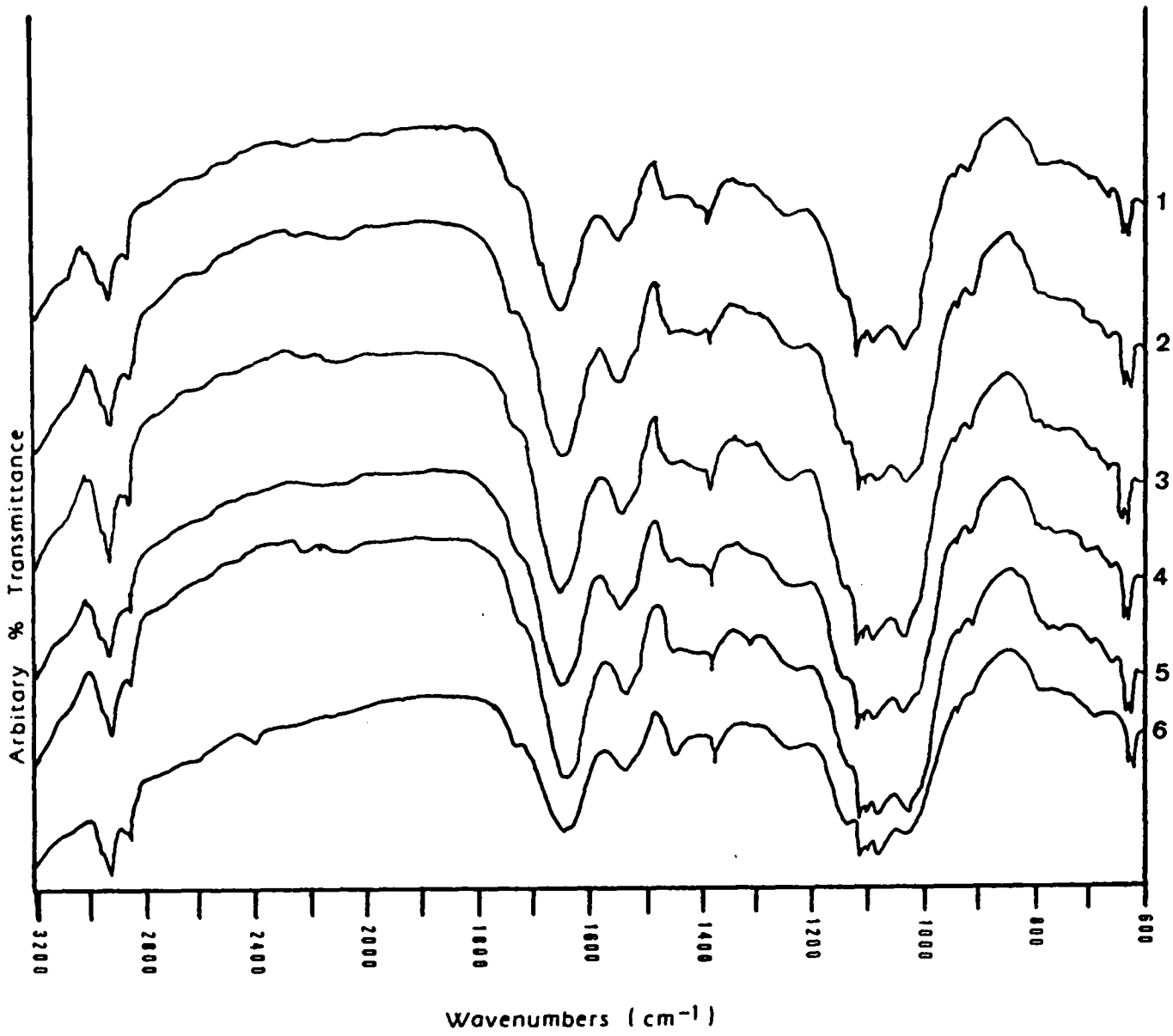
Gosset et al (1986) had shown that all complexed heavy metals except some of the Ni were released from complexation by peat at pH 1.5. Published work on extractants (Lake et al, 1984) indicates that if the contaminating metals are not 'available' to 0.1 M HCl, then they are most likely to be present in the form of inorganic precipitates. It was assumed that minute quantities of these precipitates were unlikely to interfere with the measurement of cation binding.

Infrared analysis of 'Biofloc' and 'Colloid'

Infrared (IR) analysis had been used by Boyd et al (1979) to show that amide linkages were involved in cation complexation. Schaumberg et al (1980) used IR to follow the changes to sludges organic matter on incubation with soil. They showed a general loss of carbohydrate and protein band with an increase in more oxidised carboxylates; these changes were essentially complete within 10 weeks. The interpretation of IR spectra of mixtures of substances as complex as sludge does require a degree of circumspection.

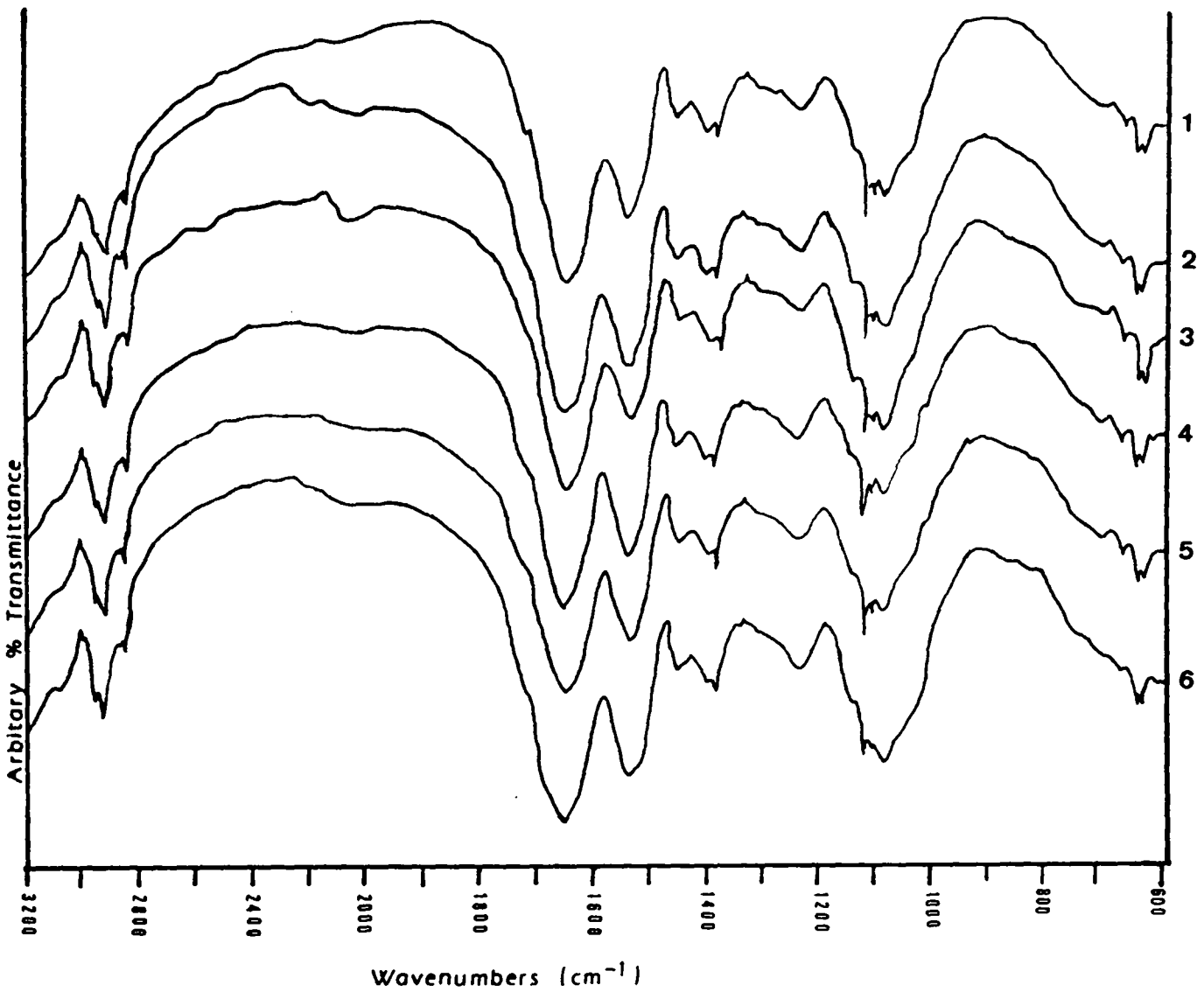
The IR spectra of the 'Biofloc' and of the 'Colloid' fractions were measured in a joint study with Dr J Cegarra. Before taking the IR spectra of these two fractions, the fractions were both cleaned in the same way as before measurements of equilibrium binding, and then adjusted to pH 7.4. The results are presented in figure 7.1.

Figure 7.1 Infrared spectra of the 'Biofloc' fraction



Line	Description
1	Biofloc pH 7.4
2	Biofloc/Mn pH 7.3
3	Biofloc/Zn pH 7.4
4	Biofloc pH 5.6
5	Biofloc/Mn pH 5.8
6	Biofloc/Zn pH 5.7

Figure 7.1 cont'd Infrared spectra of the 'Colloid' fraction



Line	Description
1	Colloid pH 7.4
2	Colloid/Mn pH 7.3
3	Colloid/Zn pH 7.3
4	Colloid pH 5.9
5	Colloid/Mn pH 5.9
6	Colloid/Zn pH 5.9

The spectra of both fractions are broadly similar, which indicates that they have broadly similar chemical compositions. There are, however, some differences.

1) Aliphatic groups The wide band at 2,900 cm^{-1} shows a similar intensity in both fractions, and indicates, as expected, large amounts of aliphatic carbon groups: -CH, $-CH_2$, and $-CH_3$.
2) Acidic groups The band near 1,720 cm^{-1} indicating -COOH groups is more intense in the 'Biofloc' than in the 'Colloid'. (The weak band at 910 cm^{-1} also indicates -COOH groups, and is only visible in the spectra for the 'Biofloc' fraction).
3) Proteins The band close to 1,540 cm^{-1} (and part of the peak-height around 1,650 cm^{-1}) indicates peptide links (-NH-CO-); it is more intense in the 'Colloid' fraction than in the 'Biofloc'. This was confirmed by chemical analysis for organic nitrogen (table 7.1).

Table 7.1 Organic nitrogen content of organic fractions

Fraction	Org N	Estimated protein
'Biofloc'	3.82%	23.9%
'Colloid'	8.87%	55.5%

4. Polysaccharides The peak near 1,050 cm^{-1}, attributed to polysaccharides and seen in the spectra from the 'Biofloc' fraction, is not present in the spectra for the 'Colloid' fraction.

5. Clays The peak at 1,080 cm^{-1} attributed to Si-O-Si linkages is more intense in the 'Colloid' than in the 'Biofloc' fractions as would be expected from the mineralogical analyses in chapter 5. (The wide band centred on 1,100 cm^{-1} attributed to both Si-O-Si linkages and to C-O stretching in polysaccharides was narrower in the spectra of the 'Colloid' fraction than of the 'Biofloc').

6. Alcoholic and phenolic The band at 1,240 cm^{-1} attributed to alcoholic and phenolic groups was relatively more intense in the 'Colloid' fraction than in the 'Biofloc'.

So both the organic fractions broadly share the same chemical composition, but 'Biofloc' is richer in polysaccharides and acidic groups, while the 'Colloid' is richer in proteins, clays and alcoholic groups.

In an exploratory experiment, it was shown that complexing the fractions with Zn or Mn at pH 5.9 and pH 7.3 caused no appreciable change in their IR spectra.

Measurement of complexation

The first attempts at measuring complexation by the 'Biofloc' followed the method developed for the 'Soluble' fraction. These attempts failed for two reasons.

The hydroxide solubility products of Cu and Pb severely restrict the concentrations of these metals that can be used in the relevant pH range (pH 5.0-8.0). The cation concentrations in equilibrium with their solid amorphous hydroxide phases at pH 7.0 are presented in table 7.2.

In some instances metastable solutions of these metals have been prepared and used at concentrations higher than their solubility products would allow; Fletcher and Beckett (Pts 1 and 2, 1987) were able to use Cu at concentrations substantially above its expected limit in studies on the 'Soluble' fraction. However, the addition of even the smallest quantity of 'Biofloc' to supersaturated solutions caused the immediate precipitation of the hydroxide phase, and the Cu concentration as measured by the ion-selective electrode fell to around the level expected from the hydroxide solubility product. The initiation of precipitation may have been due to nucleation by mineral forms already within the 'Biofloc', or by the regular array of surface hydroxyls on the sugar monomers of bacterial cell walls.

Table 7.2 Hydroxide solubility products

Cation	Solid	Ksp	Max $[M^{++}]$ at pH 7
Copper	$Cu(OH)_2$	8.68	4.8×10^{-6}
Lead	$Pb(OH)_2$	8.16	1.4×10^{-6}
Zinc	$Zn(OH)_2$	12.48	3.0×10^{-2}
Nickel	$Ni(OH)_2$	10.80	6.3×10^{-4}
Cadmium	$Cd(OH)_2$	13.65	4.4×10^{-1}

NB: the maximum cation concentration in solution decreases by 2 orders of magnitude with every unit increase in pH.

The second problem was more serious. Ion-selective electrodes can be very sensitive to interference. The Cu ISE is more reliable and susceptible to fewer interferences than most, although both

sunlight and chloride interfere with it. The 'Soluble' fraction appeared not to have caused any problems with the ISE, but the 'Biofloc' fraction caused a noticeable instability in the readings obtained. This instability in the presence of the 'Biofloc' fraction could vary the apparent Cu concentration by as much as 10-fold. It appeared to be caused by 'Biofloc' binding to the surface of the membrane because cleaning the surface of the ISE with abrasive powder gave temporary relief; unfortunately, ISEs do not tolerate repeated cleaning for long. Repeated attempts to avoid this instability were unsuccessful, and it was concluded that the Cu ISE could not be used for measuring complexation by the 'Biofloc'.

Since both the 'Biofloc' and the 'Colloid' had been defined by phase separation it seemed appropriate to adopt one of the methods for determining complexation based on phase separation (table 6.1). Centrifugation to separate the phases and Atomic Absorption spectroscopy to measure the cation concentration remaining in solution after complexation by the solid phase had been used by Green and Manahan (1977) to measure cupric ion binding to coal humic acids over the pH range 1-3. They added aliquots of copper sulphate solutions to known aliquots of the sodium salt of the humic acid, adjusted the pH with additions of HCl or NaOH, and left the suspension to equilibrate overnight. The mixture was centrifuged, and the supernatant analysed for Cu by AA. Coal humic acids are insoluble below pH 4, and quantitative recovery of the humic acids was confirmed by weighing the freeze-dried pellet.

In the pH range used by Green and Manahan, ion-pairing as $CuOH^+$ will have been negligible. However, Cu forms strong ion-pairs with sulphate ions (Log K = 2.36), and at the concentrations used $CuSO_4^o$

would have accounted for between 0.5% and 5% of the total copper. Though very careful with their other measurements, the authors appear to have made no allowance for this systematic error. Sulphate ion-pairs also account for a highly significant proportion of copper in the soil solution (Lindsay, 1979), making copper sulphate an inappropriate reagent for use in experiments on Cu-binding.

A similar method was also used by Gosset et al (1986) to measure complexation of Cu, Ni, Zn and Cd by peat moss in the pH range 1.5-6.5.

So the method used here for both the 'Biofloc' and the 'Colloid' was based on the method of Green and Manahan, but further refined as follows:

1) Between 10 and 100 mg of freeze-dried material were added to a tared 100 ml polypropylene centrifuge tube. If less than 10 mg of material was used, it appeared not to pellet firmly and recovery by centrifugation might have been incomplete.

2) The experimental solutions were based on the perchlorate anion: a standard solution of the perchlorate salt of the metal cation was made up in 0.1 M $NaClO_4$. Perchlorate salts are deliquescent, so the actual concentration of the standard solution was determined by AA against SPECTROSOL standards diluted in 0.1 M $NaClO_4$.

3) Aliquots of the standard solution were made up to 50 ml with 0.1 M $NaClO_4$ and added to the tubes. The tubes were adjusted to the required pH with 1 M NaOH, and placed on an orbital shaker.

4) The pH in the tubes was re-adjusted with 1 M NaOH every 30 minutes over 6 hours to compensate for protons released by ion-exchange.

5) The tubes were then left to equilibrate for 48 hours on the shaker in a constant 25°C room, and the final pH (+/- 0.02 pH unit) and weight (+/- 0.05 mg) were then recorded.

6) The tubes were first centrifuged for 5 minutes in a swing-out rotor at 3,500 rpm to remove any ligand from the sides of the tubes, and then centrifuged for 30 minutes at 16,000 rpm to separate the phases.

7) The equilibrium solution was carefully decanted and stored in polypropylene bottles, and the tubes weighed to record the residual weight (+/- 0.05 mg). The initial weight of the ligand was subtracted from the recorded residual weight to give the residual volume of solution, which was typically less than 0.5 ml for the 'Biofloc' and less than 0.25 ml for the 'Colloid', which formed a much firmer pellet.

8) The pellets were re-suspended in 50 ml 0.1 M HCl, and shaken overnight. This recovered the cations bound by exchange with the proton but, unlike acid-digestion, it would not displace intra-cellular cations.

9) The tubes were re-centrifuged as in (7), and an aliquot of the supernatant removed and stored in polypropylene bottles.

10) The cation concentration in the equilibrium solution was measured by AA against SPECTROSOL standards diluted with 0.1 M $NaClO_4$. The bound metal recovered in the acid wash was measured by AA against SPECTROSOL standards diluted with 0.1 M HCl. An allowance was made for the residual volume of the equilibrium solution that remained with the pellet and for hydroxide ion-pairs.

The advantage of recording both the bound and free metal is that the calculations can be based on whichever one gives the larger proportionate change. If only 1% of the metal was bound, that is likely to be measured more accurately than the difference between the original solution and the remaining 99%, and vice versa. It also provides a check to ensure that there is quantitative recovery of the bound cation in the acid wash. It is unlikely that any sites would take up cations not removable by 0.1 M HCl because the ligand had been similarly acid-washed before the experiment.

The disadvantage of this method with the 'Biofloc' and 'Colloid' fractions is that, though these fractions are by definition insoluble, they may disintegrate on handling and release some soluble organic matter too fine to be centrifuged out. The effect of this would be to raise the proportion of the metal retained in the equilibrium solution (7) causing a systematic error that would increase with the proportion of the metal bound. If it had been possible to use the copper ISE with this material, breakdown of the ligand material would not have caused an error in the measurement because the measured activity of the cation would not have included any cation bound by soluble organic matter. The copper ISE would also have extended the possible range of measurements to lower

concentrations than are possible with AA.

The measurements for different fractions and cations are listed in table 7.3.

The reversibility of complexation was tested by measuring Mg complexation with 18 forward points and 6 reverse points at different pHs. The tubes to be used for the reverse points were equilibrated at pH 8.0 for 24 hours on a shaker before $HClO_4$ was added to bring them into the pH range 5.0-7.5. The reverse points lay exactly on the graph of the forward points (shown in figure 7.2).

Table 7.3 Binding experiments performed

Cation	'Biofloc'	'Colloid'	'Soluble'*
Mg	Y	-	Y
Ca	Y	-	Y
Mn(II)	Y	Y	Y
Fe(II)	-	-	-
Co(II)	Y	Y	Y
Ni(II)	Y	-	Y
Cu(II)	Y	Y	Y
Zn(II)	Y	Y	Y
Cd	Y	-	Y
Pb	-	-	Y

* Fletcher and Beckett (1987)

The 'Biofloc' and 'Colloid' fractions presented the same problems as with the 'Soluble' fraction:

1) a constant describing complexation must be defined in a form that allows it to be included in one of the available computer models;
2) the concentration of the ligand must be defined;
3) the protonation of the ligand must be described (see chapter 6).

The titration curve for the 'Biofloc' was measured using material which had been adjusted to pH 5.0, then dialysed for 48 hours against deionised water to remove as much exchangeable material as possible. Successive 25 ul aliquots of 0.433 M NaOH were then added to 50 mg of 'Biofloc' suspended in 20 ml water (double-distilled and then deionised) in a Radiometer automatic titrimeter, which ensured thorough equilibration.

The results showed an almost featureless curve except for a small hump around pH 6.0-6.5. The concentration of protons bound over a specified pH range may be calculated directly by comparing the titration curves with a blank titration obtained in the absence of the organic fraction (Stumm and Morgan, 1971). If it were assumed that the material possessed no anion-exchange capacity, then 3.96 millimoles of protons were bound per gram of ligand over the pH range 3 to 11.

This result can be compared to the 7.23 mmol H^+ gm^{-1} obtained for a sludge water-soluble-extract by Baham and Sposito (1986), and to between 0.36 and 2.6 mmol H^+ gm^{-1} obtained by Gosset et al (1986) for various peats. However, it is significantly less than the 0.1 moles H^+ gm^{-1} observed by Dr P Fletcher for the 'Soluble' fraction. It can also be compared to the value of 0.65 meq gm^{-1} maximum specific uptake of metals by bacterial extracellular polymers, and to

the 6.85 meq gm^{-1} for activated sludge polymers obtained by Rudd et al (1984).

Fitch and Stevenson (1983) noted that when they attempted to measure the total number of ionisable groups in the presence of metal cations, the titration curve was displaced horizontally. It was suggested that this may have been due to release of otherwise non-titratable protons from the organic matter or to the release of protons from hydration water bound by the cations (Stevenson, 1976, 1977). These factors may have contributed to the anomalous value for the 'Soluble' fraction which, by definition, could not be cleaned by dialysis before measurement.

The protonation capacity of the 'Colloid' fraction was not measured, and it was assumed to be the same as that of the 'Biofloc' for the purpose of calculating equilibrium constants in order to simplify the model.

Because the acid titration curve of the 'Biofloc' suggested a smooth continuum of sites and no discrete clustering that could be mathematically modelled easily, it was necessary to define the proton-dissociation constant for these fractions in solution. As with the 'Soluble' fraction (see chapter 6), it was decided to define an arbitrarily high constant that would operationally define all the uncomplexed sites to be protonated. The value chosen for Log K_a for all 3 organic fractions was 10.

Since we are defining complexation implicitly as the exchange of a cation for one or more protons, a simple measurement of the concentration of proton-exchange sites should suffice to define the ligand concentration, rather than attempting to measure saturation binding as was done in the case of the 'Soluble' fraction.

Ideally, the constant defined should be independent of pH. This had dictated the adoption of the Vanselow convention (ie mole fractions) for the 'Soluble' fraction. However, when equilibrium constants were calculated for the 'Biofloc' fraction, none of the 3 conventions described in chapter 6 gave a value that was independent of pH. So, the equilibrium constants for the 'Biofloc' were defined in terms of complexation with a monovalent ligand rather than in terms of ion-exchange because many of the widely available computer models do not handle ion-exchange (for example, MINEQL).

It must be noted that because the constants for the 'Soluble' and the 'Biofloc' fractions have been calculated using different conventions their values cannot be compared directly.

Calculation

The method outlined above required the following measurements: the weight of ligand, the initial cation concentration, the initial ionic strength, the volume of the equilibrium solution, the cation concentration in the equilibrium solution, the residual volume left after decanting the equilibrium solution, the volume of the acid wash and the cation concentration in the acid wash.

$[M^{++}]$

The activity of the free metal was calculated from the concentration of the cation in the equilibrium solution by using GEOCHEM and allowing for complexation by OH^-, and by CO_3^{2-} in equilibrium with air (CO_2 at 3.0×10^{-7} kilobars). It was assumed that perchlorate did not complex the cation.

[H^+]

The activity of the hydrogen ion was known from the pH.

[ML_2]

The concentration of bound ligand can be calculated from the quantity of cation in the acid wash after allowing for the cation carried over from the equilibrium solution in the residual volume (j).

[HL]

The concentration of the uncomplexed ligand is taken to be the remainder after subtracting the concentration of bound ligand multiplied by the charge of the cation from the total concentration of sites. (The arbitrary constant chosen for K_a means that all the unbound ligand can be treated as if it were in the protonated form).

Results

Overall, the equilibrium binding of 13 combinations of the 2 organic fractions and cations was measured (table 7.4). When Log K for any of the 13 combinations was plotted against pH, it produced a straight line. A least-squares procedure was used to determine the coefficients for expressing Log K as a function of pH. These lines had correlation coefficients in the range 0.964 to 0.999, indicating very little scatter. These equations may be used to calculate Log K for any pH in the pH 5.0-8.0 range covered by these experiments. It would be unwise to use them outside this range.

The fraction labelled 'Bacterial culture' in table 7.4 was obtained from a bench digester maintained by Dr F Mosey at WRC which utilised synthetic nutrients rather than settled sewage. The sample was processed exactly as for 'Biofloc', but was largely free of the

particulate inorganic material associated with the corresponding fraction separated from sludge.

The material from the bench digester was used for the first of the heavy metal complexation experiments while the method was still under development. The complexation by this fraction was measured against a background ionic strength of 0.05 M $NaClO_4$ instead of the 0.1 M $NaClO_4$ used for later experiments. The graphs for Ni binding to 'Biofloc' and to the bacterial extract produced the same slopes but showed that the bacterial extract bound nickel slightly more strongly. One possible explanation of this may be that the bacterial extract had a higher surface area because it would not have had any larger detrital material in it. If so, it would have offered more sites which would create the appearance of stronger binding when the equilibrium constants were calculated using the same CEC.

When Log K was plotted against pH, the lines for the 'Biofloc' and 'Colloid' fractions were found to lie almost on top of each other. In the light of the overall similarity of the IR spectra of the 2 fractions discussed earlier in this chapter, it was decided to combine the 2 fractions in the model and label them 'Biofloc' to produce a single equation for Log K for each cation. This decision removed the 'Colloid' fraction from the model altogether.

The combined lines gave slightly lower correlation coefficients than the separate lines, but all the correlation coefficients were still better than 0.962. Table 7.4 summarises the results. Figure 7.2 presents the results to which these lines were fitted.

Calculation of constants for other cations

In order to complete the model, constants were needed for other major cations which had not been measured either for lack of time, eg Pb, or because of difficulties with the stability of the cation in solution: Fe(II), Fe(III) and Cu(I). Some of these elements are important; for example, the omission of Cu(I) binding by the organic fractions may seriously distort the picture presented by the model of Cu(I) chemistry in the digester.

Nieboer and McBryde (1973) have presented a formula which links the standard free energy of complexation per mole of ligand charge, Log $K/Z_m Z_H$, to an empirical parameter Q. This parameter is related to the charge, radius and polarisability of the cation, and may be calculated from Allred's electronegativity values (Allred, 1961). The authors suggest that Q represents the geometric mean of covalent and ionic bonding indices, and that it generally holds true for complexation through oxygen and nitrogen donors.

Figure 7.3 presents a graph of Q against Log $K/Z_m Z_H$ at pH 7.0 for the 'Biofloc'. The line fitted to this graph using a least-squares procedure was:

$$\text{Log } K/Z_m Z_H \text{ at pH } 7.0 = -8.2557 + 1.0812\ Q$$

The same procedure was applied to site 1 of the 'Soluble' fraction, except that the value for the Fe(III) constant was omitted because $Fe(OH)_3$ precipitation introduced significant uncertainty into its measurement. The line fitted was:

$$\text{Log } K/Z_m Z_H = -5.9264 + 0.4164\ Q$$

The omission of the Fe(III) point gave a slightly different line from that offered in Fletcher and Beckett (1987):

$$\text{Log } K/Z_M Z_H = -5.8972 + 0.4105\ Q$$

For the 'Biofloc' r^2 = 0.754, and for the site 1 of 'Soluble' fraction r^2 = 0.886 when the Fe(III) constant is omitted. While these correlation coefficients are not as good as those for the lines fitted to the graphs of Log K against pH, they still give reasonable confidence in the use of the equation.

Table 7.4 Conditional equilibrium constants*

Cation	Fraction	Log K	r^2	No points
Ni	Bact cult	1.82 - 1.64pH	0.997	12
Cu	Bf & Coll	2.23 - 1.43pH	0.963	21
Zn	Bf & Coll	1.04 - 1.43pH	0.983	30
Ni	Bf	2.23 - 1.65pH	0.999	17
Mn	Bf & Coll	0.99 - 1.47pH	0.967	35
Co	Bf & Coll	1.60 - 1.60pH	0.976	34
Cd	Bf	2.34 - 1.58pH	0.997	18
Ca	Bf	2.77 - 1.84pH	0.999	18
Mg	Bf	1.87 - 1.68pH	0.997	24

(*) I = 0.1 M

Bf - 'Biofloc' fraction

Coll - 'Colloid' fraction

Bact cult - 'Biofloc' fraction from bench digester

Figure 7.2 Complexation constants for the 'Biofloc' and 'Colloid'

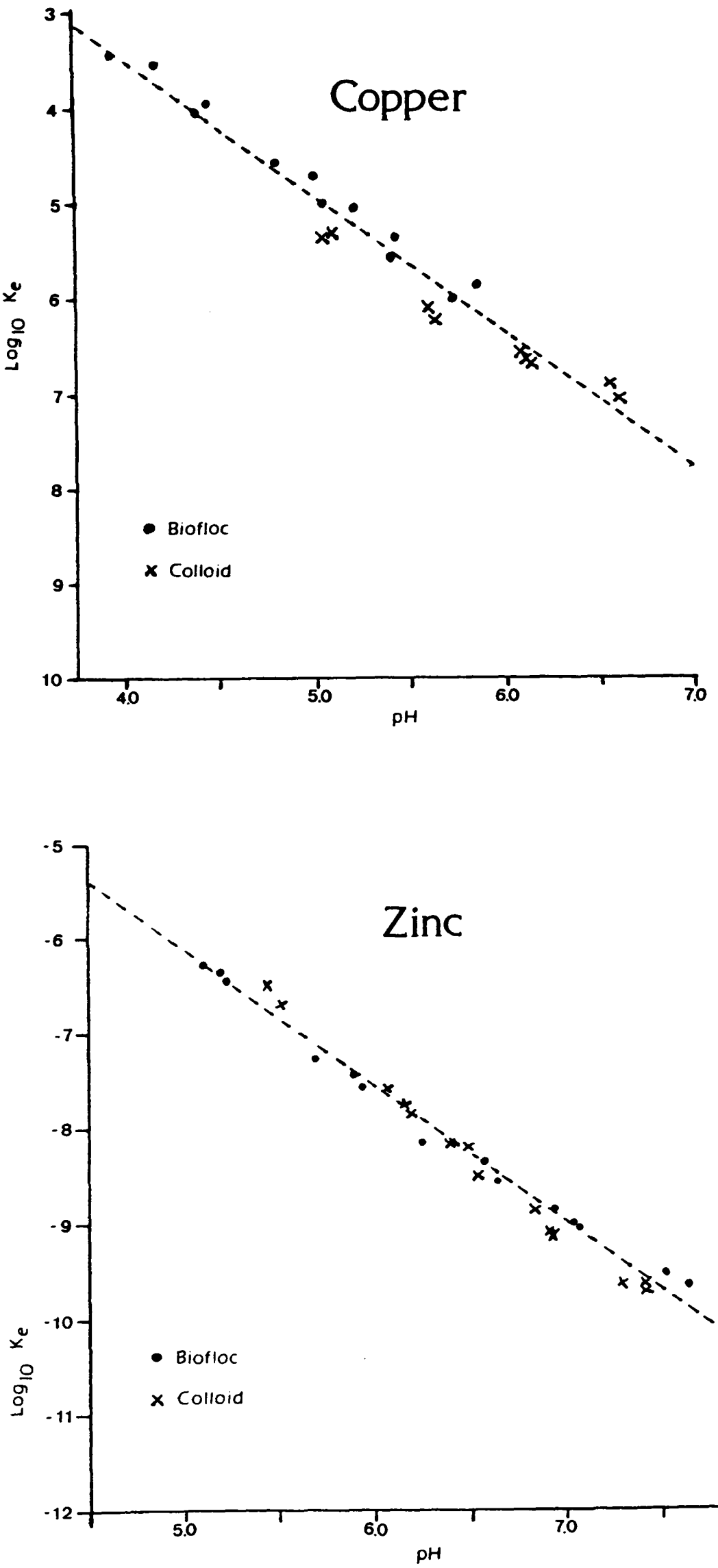


Figure 7.2 cont'd Complexation constants for the 'Biofloc' and 'Colloid'

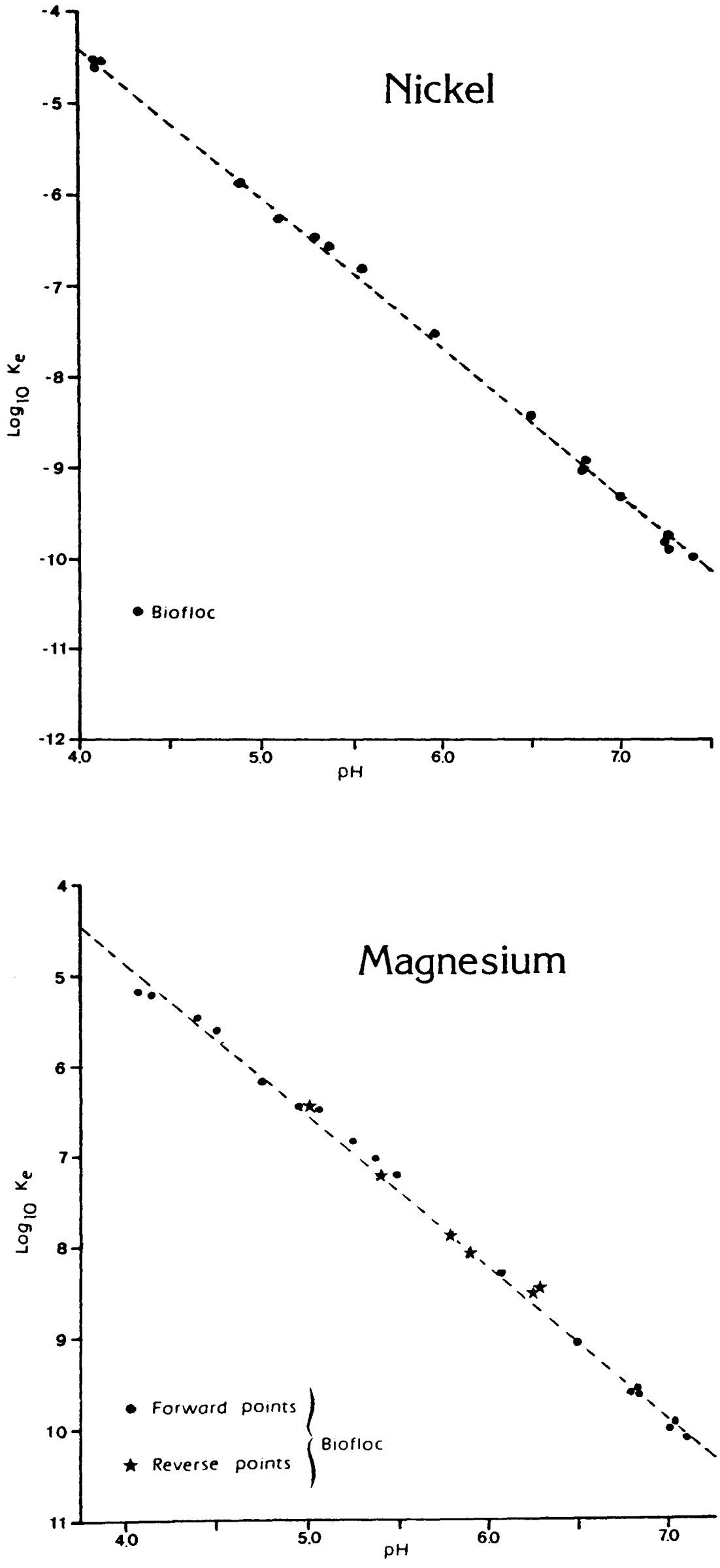


Figure 7.3 Standard energy of complexation against the stability parameter 'Q'

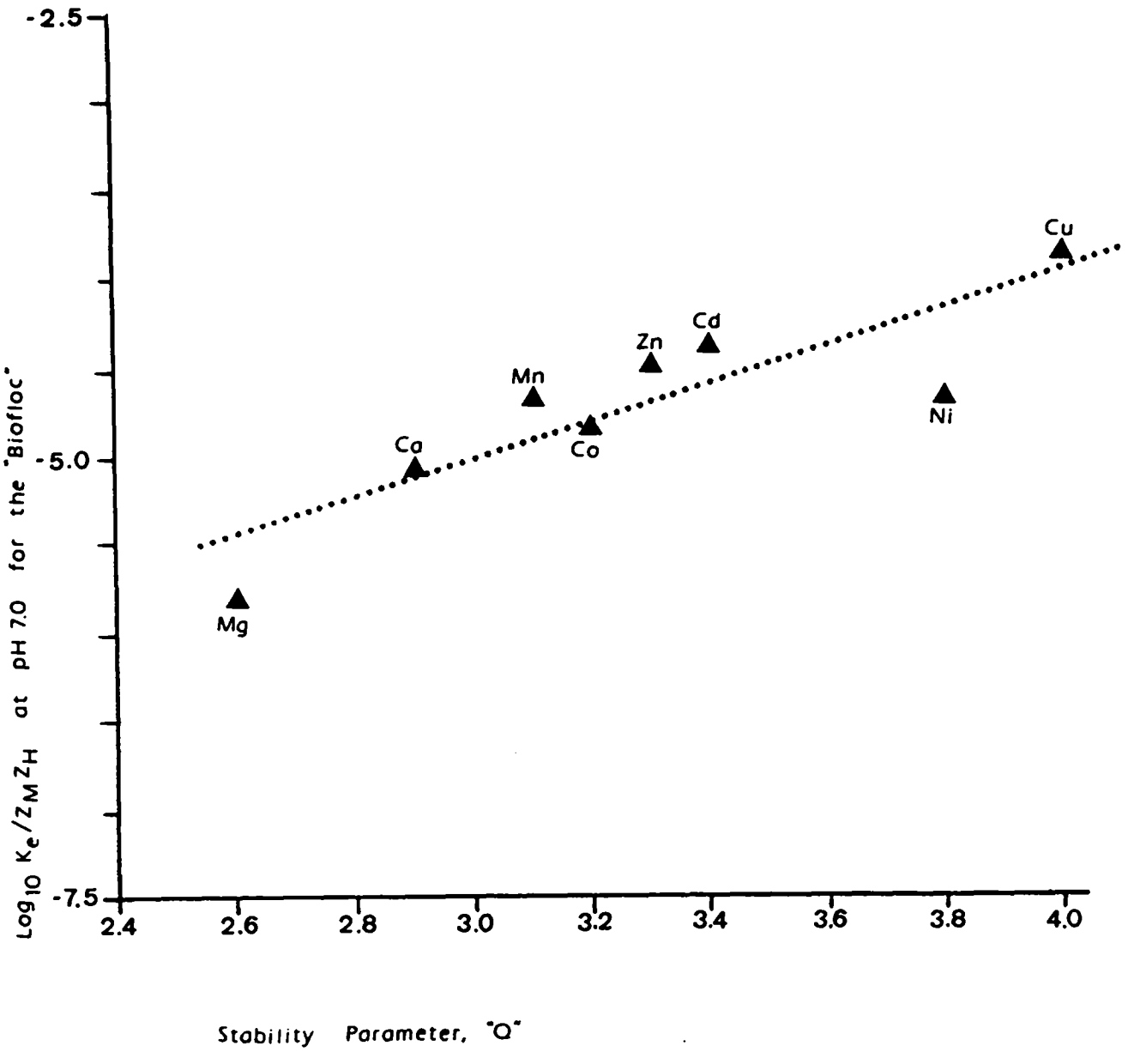


Table 7.5 Stability index, 'Q', for different cations and calculated values of Log K

Cation	Z	Q	SOM(1)	Biofloc pH 7.0
Mg	2	2.6	-	-
Ca	2	2.9	-	-
Cr	2	3.3	-9.10	-9.38
Mn	2	3.1	-	-
Fe	2	3.2	-9.19	-9.59
Fe	3	4.2	-12.53	-11.14
Co	2	3.2	-	-
Ni	2	3.8	-	-
Cu	1	3.6	-4.43	-4.36
Cu	2	4.0	-	-
Zn	2	3.3	-	-
Ag	1	3.7	-4.39	-4.26
Cd	2	3.4	-	-
Sn	2	3.9	-8.60	-8.08
Ba	2	2.3	-9.94	-11.54
Hg	2	4.0	-8.52	-7.86
Pb	2	5.4	-	-4.84

Z is the oxidation state of the cation

Q is Nieboer and McBryde's stability index

Measured values shown '-'

NB: Constants for the 'Biofloc' and the 'Soluble' fractions cannot be compared because they are based on different conventions.

Stability constants for various cations were then calculated from the list of values of Q (table 7.5). Because the stability constants for the 'Biofloc' vary with pH and the slope of the line of Log K against pH was not known for the calculated constants, Log K was calculated at pH 7.0 and a median value of 1.58 for the slope of Log K against pH was used. For the reasons discussed above, a calculated value for the Fe(III)-'Soluble' fraction was preferred to the measured constant.

Inevitably, the calculated constants must be treated with some caution. Nevertheless, they do give a reasonable description of the chemistry of the cations and their inclusion in the model is likely to lead to fewer errors than their omission.

It was assumed that where calculated constants had to be used, cations could only be bound on site 1 on the 'Soluble' fraction.

Limits of confidence

The measurements from which Log K is calculated are:

1) Mass of the ligand and residual volume. These were measured on an electronic self-calibrating balance with an uncertainty of +/- 0.05 mg, which would result in an uncertainty of +/- 0.1% in the ligand weight and +/- 0.01% in the residual volume.

2) Cation concentration in the initial solution, the equilibrium solution and the acid wash. The use of AA is discussed in appendix 1; it would result in an uncertainty of +/- 1% under ideal conditions (eg the initial solution, where the ionic background is known exactly and can be reproduced in the standards) and of up to +/- 5% where the effects of any residual organic matter and background ionic composition cannot be matched in the prepared standards.

3) pH was measured after calibration against pH 4.0, 5.6 and 7.4 standards (Radiometer and Sigma). Uncertainty due to the pH meter in simple salt solutions would be in the order of +/- 0.02 pH unit. The actual uncertainty would be greater because of potential interference from suspended organic matter, and an error of +/- 0.05 pH units is likely. This is the dominant uncertainty in the calculation of Log K, and it is unlikely that the uncertainty in this reading could be significantly reduced. It leaves a total uncertainty in the calculated Log K of +/- 0.1.

Conclusion

Existing computer models like GEOCHEM expect equilibrium constants to be independent of pH. If constants are pH-dependent then either the program has to be modified, or the database has to be edited each time the model is run at a different pH. So, if a convention can be chosen that does give a constant that is independent of pH then it is better to use that convention. Fortuitously, the mole-fraction convention gave a constant that was independent of pH for the 'Soluble' fraction.

None of the 3 conventions described in chapter 6 gave a constant that was independent of pH for either the 'Biofloc' or 'Colloid' fractions. This is in keeping with other reported results (Fitch and Stevenson, 1983). Takamatsu and Yoshida (1978) noted comparable pH-dependence for metal-humic acid complexes. The constants given by them are calculated on the assumption that all functional groups are fully protonated below the apparent point of neutralisation (pH 7.4), and take the form:

$$k_1 k_2 = [ML_2] / [M^{++}][L^-]^2$$

Since they assume [L^-] equals [HL], their constants can be converted to be comparable with the constants given in table 7.4 by:

$$\text{Log } K_e = \text{Log } k_1 k_2 - 2pH$$

On this basis:

Cu: $\text{Log } K_e = 5.4 - 1.35pH$

Pb: $\text{Log } K_e = 6.85 - 1.7pH$

Cd: $\text{Log } K_e = 3.1 - 1.37pH$

These equations have slopes directly comparable to those presented in table 7.4 for the 'Biofloc', but the larger constant in the equations represents stronger overall binding by the humic acids. The authors suggest 3 reasons for this pH-dependency:

1) charge densities of the functional groups bound to metal cations will increase with increased dissociation of groups adjacent to the complex;
2) at higher pH, cations will be bound selectively to functional groups forming the strongest complexes, while at lower pH such groups are likely to be occupied with protons competitively;
3) steric stabilisation would be derived by producing chelate rings.

Log K for the 'Biofloc' was calculated for pH 6.0 and 7.0 from the equations presented in table 7.3. At pH 7.0, they are in the order:

$$H >> Cu > Cd > Zn > Mn > Ni = Co > Mg > Ca$$

and at pH 6.0 in the order:

$$H >> Cu > Cd > Zn > Ni > Mn > Co > Mg > Ca$$

These differ from the Irving-Williams order in several respects (see chapter 6). Cadmium is forming much stronger complexes than the

Irving-Williams order would predict - where it should be equivalent to Mn; Mn and Co are transposed compared to the Irving-Williams order, as are Mg and Ca. Nickel is forming weaker complexes than the Irving-Williams order predicts.

By comparison, the sequence found for the 'Soluble' organic matter:

H >> Pb > Cu > Cd > Zn > Ni > Co > Mn > Ca > Mg

follows the sequence predicted by the Irving-Williams order more closely, except that again, Cd was found to complex much more strongly than predicted.

These sequences can also be compared to the order of the stability parameter Q (Nieboer and McBryde, 1973):

H >> Pb > Cu > Ni > Cd > Zn > Co > Mn > Ca > Mg

The results for the 'Biofloc' again show Ni forming much weaker complexes than predicted, but the results obtained for Cd conform more closely to this order than to the Irving-Williams order.

The results for Ni are surprising when compared to the results obtained by Rudd et al (1984) for extracellular polymers extracted from Klebsiella aerogenes, which showed Ni forming stronger complexes than Cu:

Ni > Cu > Cd > Co > Mn > Tl

However, their results for activated sludge did conform more closely to the Irving-Willliams order:

Cu > Ni > Cd > Co > Tl > Mn

Rudd et al (1984) reported that Ni preferentially associated with the soluble rather than flocculated polymers. This finding might indicate that the 'Biofloc' was losing some soluble material during the complexation experiments and so introducing a systematic error

into the results reported. Gosset et al (1986) also reported Ni forming stronger complexes than Cu for moss peat.

Complexation by the 'Biofloc' and 'Colloid' were only measured for Beckton sludge and only over a relatively narrow range of cation and complexant concentrations. Ideally, complexation should have been measured over a wider part of the isotherm. Sludge is a thick viscous liquid, and the effects of very high complexant concentration will need to be checked to ensure that the constants are valid at the concentration of organic matter found in the digester. Finally, the constants for organic matter from a few other rural and urban sludges will need to be measured to ensure that a model using them is generally valid.

COMPUTER MODELLING: I

From chapter 2, we have values for the total analyses of different sludges obtained by different authors, and chapter 3 presented the analyses of digested Beckton sludge. Chapter 5 presented the results of the mineralogical analysis of the 'Particulate' fraction, and chapter 7 presented the measured complexation constants for the organic fractions.

We are now in a position to ask: "How are the heavy metals in anaerobic sludge distributed between different chemical (as opposed to physical) fractions?" and "How will this speciation be affected by, for example, oxidation, or by the degradation of its organic content?".

The thermodynamic stability of each potential chemical species is defined by its stability constant. Clearly, with several hundred possible species the overall speciation can only be solved by computer techniques.

There are 2 essential parts to solving the speciation: an "aqueous chemical model", and the computer program which executes calculations based on the model. Nordstrom et al (1979) define a model as "a theoretical construction which allows us to predict the thermodynamic properties of electrolyte solutions".

There are now over a dozen well known computer programs available either free from their authors or commercially. The programs and their underlying assumptions and restrictions have been extensively reviewed in a joint paper by 19 of their authors (Nordstrom et al, 1979). This paper also compared the results of using 14 different models on the same problem, which involved the

speciation of sea-water. The authors attempted to explain some of the more divergent results predicted by their respective programs. This paper forms a good starting-point for a discussion of the problems involved in computer modelling.

Models

There are 2 possible ways to model the thermodynamic properties of solutes: an ion-association model or a specific interaction model, (Pitzer, 1957). The fundamental difference between these 2 groups of models is that the Specific Interaction model describes the properties of each solute in terms of macroscopic measurable quantities using total molalities of components, whereas the Ion-association model describes the properties of each solute in terms of the molalities of its separate constituent species. Since, by definition, the properties of an individual ionic species cannot be measured in isolation, additional extra-thermodynamic conventions are required.

In this project, the actual speciation of the heavy metals was wanted because both the biological uptake of these pollutants and their toxicity (both in the sewage works and on disposal to land) have been shown to be highly dependent on their speciation. This was demonstrated by earlier workers who added sulphate to the digester to protect the bacteria responsible for anaerobic digestion from heavy metals, and by agronomists who added lime to reduce the toxicity of applied heavy metals to crops.

Therefore we must adopt an ion-association model, as have nearly all other workers in this field. Within this group of models, there are 2 numerically distinct approaches to solving speciation at

equilibrium. Equilibrium can be defined either directly by the minimisation of Gibbs free energy of the system, or indirectly in terms of equilibrium constants derived from the Gibbs free energy for the species involved in each equilibrium. These 2 approaches are thermodynamically related at equilibrium through the equation:

$$\Delta G^{\circ} + RT\ln K = 0$$

Systems formulated in terms of equilibrium constants require fewer variables than those formulated in terms of Gibbs free energies, and simpler mathematical techniques can be used to solve the system. Consequently, the majority of the generalised programs written use the equilibrium constant approach.

The mathematics for the equilibrium constant approach were first worked out by Brinkley (1946, 1947). This led to the development of the first major program, HALTAFELL, by Sillen (Ingri et al, 1967), and several other programs: EQ3, WATEQ and SOLMNEQ, which Nordstrom et al (1979) define as the 'first-generation'.

A second and independent family of programs derive from the program REDEQL written by Morel and Morgan (1972). This group of programs offered more comprehensive models that included the effects of adsorption of solute species on a solid phase, and allowed solid phases to be imposed so that the equilibrium solution in contact with them could be calculated. These 'second-generation' programs include MINEQL and GEOCHEM.

Sposito (1984) listed the key points in the use of the equilibrium constant approach to solve speciation; his list can be clarified as:

1) At fixed temperature and pressure the master variables are the total molalities of components.

2) The system is divided (arbitrarily) between:

   i) a set of mutually independent components, which may be either elements or species

   ii) other molecular species which can be related to this set of components (2(i)) through stability constants.

3) The component species form other molecular species according to their activities, which are the products of their concentration and their composition-dependent single-ion activity coefficients, and according to the composition-independent equilibrium constants that describe the formation of the new species.

4) Single-ion activities may be calculated according to an extra-thermodynamic convention conforming to the Debye-Huckel limit.

5) The single-ion activities are used to modify the equilibrium constants so that they may be expressed in the form of concentration rather than activity.

6) A mole balance is defined for each component so that its total molality is equivalent to the weighted sum of all the molecular species of which it forms part. The mole balance equations are then converted to a set of coupled non-linear equations by substituting for the molality of each species an expression that includes its stability constant and the molalities of the species which have been defined to be components of the system.

7) Starting with 'guessed' final activities for the components of the system, the mole-balance equations are solved

self-consistently so that when the calculated final activities of the components are used to calculate the concentrations of all the species, their sums will equal the total concentrations.

We may illustrate this by writing out the equations in general and for the specific case of solid $CaCl_2$ in equilibrium with its aqueous solution. The components of this system can be defined to be Ca^{++} and Cl^- ions, and thus the possible species are solid $CaCl_2$, the $CaCl^+$ ion, free Ca^{++} and free Cl^-.

Complex formation

For the formation of $CaCl^+$:

$$Ca^{++} + Cl^- = CaCl^+$$

$$K_a = [CaCl^+] / [Ca^{++}][Cl^-]$$

Expressed generally, in a system of J primary components that can form I complexes, the reaction to form the i-th complex is given by:

$$C_i = \sum_{j=1}^{J} a_{(i,j)} C_j$$

where C_i is the concentration of complex i, C_j is the concentration of component j, and $a_{(i,j)}$ is the stoichiometry of component j in complex i. The association constant K_a for the formation of the i-th complex is then given by:

$$K_a = C_i \; / \; \prod_{j=1}^{J} C_j^{a(i,j)}$$

Solids

For the dissolution of solid $CaCl_2$:

$$CaCl_2(s) = Ca^{++} + 2Cl^-$$

$$K_{sp} = [Ca^{++}][Cl^-]^2$$

Expressed generally, the solubility product of the n-th solid S_n in a system of J primary components of concentration C_j is expressed:

$$K_{sp} = \prod_{j=1}^{J} C_j^{a(i,j)}$$

Mass balance

The solution and solid phases can then be combined to give an overall mass balance for the system. The total concentrations of Ca and Cl are given by:

$$TCa = [Ca^{++}] + [CaCl^+] + [CaCl_{2(s)}]$$

$$TCl = [Cl^-] + [CaCl^+] + 2[CaCl_{2(s)}]$$

Again, this can be expressed generally. The mass-balance equation for the k-th primary component in our system of J components, I complexes and N solids is given by the summation of all the species which contain the component and is:

$$TC_k = C_k + \sum_{i=1}^{I} a_{(i,k)} C_i + \sum_{n=1}^{N} a_{(n,k)} S_n$$

where: TC_k is the total concentration of component k

C_k is the concentration of the free ion k

C_i is the concentration of the complexed species i

S_n is the concentration of the solid n

$a_{(i,k)}$ is the stoichiometry number of component k in species i

This mass-balance equation can be simplified by expressing the concentrations of the complexes in terms of concentrations of primary components. Since the concentration of the complex is given by the product of its stability constant and the concentrations of its components:

$$[CaCl^+] = Ka[Ca^{++}][Cl^-]$$

Then:

$$TCa = [Ca^{++}] + Ka[Ca^{++}][Cl^-] + [CaCl_{2(s)}]$$

$$TCl = [Cl^-] + Ka[Ca^{++}][Cl^-] + 2[CaCl_{2(s)}]$$

So, the complex C_i in the general mass balance can be replaced:

$$C_i = a_{(i,k)} K_i \prod_{j=1}^{J} C_j^{a(i,j)}$$

The mass-balance equation then becomes:

$$TC_k = C_k + \sum_{i=1}^{I} a_{(i,k)} K_i \prod_{j=1}^{J} C_j^{a(i,j)} + \sum_{n=1}^{N} a_{(n,k)} S_n$$

Solving the system

We now have 3 and 2 equations, unless we exclude the solids in which case there are 2 equations and 2 unknowns and we can solve the system directly. In models like MINEQL, the equation for the solubility product has generally been used to remove the third unknown (Morel and Morgan, 1972).

Since $[Ca^{++}] = K_{sp}/[Cl^-]^2$

$$TCa = Ks/[Cl^-]^2 + K_{sp}/[Cl^-]^2 . K_a[Cl^-] + [CaCl_{2(s)}]$$

$$TCl = [Cl^-] + K_{sp}/[Cl^-]^2 \cdot K_a[Cl^-] + 2[CaCl_{2(s)}]$$

Which simplify to:

$$TCa = K_{sp}/[Cl^-]^2 + K_a \cdot K_{sp}/[Cl^-] + [CaCl_{2(s)}]$$

$$TCl = [Cl^-] + K_a \cdot K_{sp}/[Cl^-] + 2[CaCl_{2(s)}]$$

The term for the solid can then be removed by using the guessed concentrations of components to calculate the amount that should precipitate and subtracting this amount precipitated from the total concentrations of the components involved. The system is then solved to produce a refined estimate of the amount precipitated and the calculations repeated until they converge.

For the computer program mainly used in this project (SCRAM -

see final section of this chapter) it was decided that it would be simpler to add the solubility product equations to those for the complexes and to solve for all the unknowns directly:

$$0 = TCa - [Ca^{++}] - K_a[Ca^{++}][Cl^-] - [CaCl_{2(s)}]$$

$$0 = TCl - [Cl^-] - K_a[Ca^{++}][Cl^-] - 2[CaCl_{2(s)}]$$

$$0 = Ks - [Ca^{++}][Cl^-]$$

This set of coupled non-linear equations can then be solved by the iterative Newton-Raphson technique which finds a number x for the function f such that f(x)=0. The slope (differential) of the equation is used to calculate an improved guess x_{n+1} from the guess at the nth stage x_n:

$$x_{n+1} = x_n - f(x_n)/(df/dx|_{x_n})$$

or, written in matrix terms:

$$\Delta X = (X_n - X_{n+1}) = Z^{-1} \cdot F(n)$$

where ΔX is a vector of the current guessed concentrations of components, F(n) is a vector of the current error in the mass balance and Z is a square matrix, the Jacobian. In our example:

$$\begin{bmatrix} [Ca^{++}] - [Ca^{++}] \\ [Cl^-] - [Cl^-] \\ [CaCl_2] - [CaCl_2] \end{bmatrix} = \begin{bmatrix} df(0)_1/d[Ca^{++}] & df(0)_1/d[Cl^-] & df(0)_1/d[CaCl_2] \\ df(0)_2/d[Ca^{++}] & \cdots & \cdots \\ df(0)_3/d[Ca^{++}] & \cdots & \cdots \end{bmatrix}^{-1} \bullet \begin{bmatrix} f(0)_1 \\ f(0)_2 \\ f(0)_3 \end{bmatrix}$$

where $f(0)_i$ is the current error in the mass balance for component i.

The system is solved when every element of the vector F(0) reaches zero, or in practice when it either reaches a defined error level (ie 1 part in 10^6) or the change in the concentration vector between iterations becomes insignificant.

The partial differentials are simple, for equation 1:

$$f(0)_1 = TCa - [Ca^{++}] - Ka[Ca^{++}][Cl^-] - [CaCl_{2(s)}]$$

$$df(0)_1/d[Ca^{++}] = 0 - 1 - Ka[Cl^-] - 0$$

The generalised expression for each element of the Jacobian $Z_{(j,k)}$, in which $f(0)_i$ is differentiated with respect to C_k for the rows referring to complexes, is:

$$Z_{(j,k)} = (df(0)_i/dC_k) = 1 + \sum_{i=1}^{I} a_{(i,k)}{}^2 K_i \prod_{j=1}^{J} C_j{}^q$$

Where $q = a_{(i,j)}$, except for j=k when $q = a_{(i,j)} - 1$

The vector of improvement in the guessed component concentrations at the nth stage can be calculated either:

i) by multiplying the inverse (Gauss-Jordan) of the Jacobian matrix by the vector of F(0) at the nth stage, $Z^{-1} \cdot F(0) = \Delta X$. This method is used in MICROQL.

ii) by Gaussian elimination and back substitution to solve ΔX, $Z \cdot \Delta X = F(0)$. This method is used in GEOCHEM, MINEQL and SCRAM. However, because the jacobian is a sparse matrix, the pivot element will often be zero. Therefore a full pivot system should be used to transpose the columns and rows beyond the element being

eliminated in order to choose the coefficient of the largest magnitude; the matrix is then unpivoted at the end.

The FORTRAN source for Gauss-Jordan inversion and for Gaussian elimination and full pivoting is given in Monro (1982).

Selecting the 'correct' mineral assembly

The last major problem in writing a computer program is how the program should select the correct set of solid mineral phases. Unfortunately, there is no unambiguous way of calculating this because of the problem of interrelated solids (ie solid phases sharing a cation or anion in common).

This problem has been discussed by Morel and Morgan (1972). The approach usually adopted is to calculate the equilibium state of the aqueous phase, then to calculate the ratio of the ion-activity product to the solubility product for each possible solid (IAP/K_{sp}). Then, if an existing solid is undersaturated, it should be dissolved, or the solid with the highest saturation factor should be precipitated. The new equilibrium state of the system is then calculated. Only one solid is dissolved or precipitated at a time until no selected solids dissolve and no possible minerals exceed their solubility products.

The problem with equilibrium models is that the thermodynamically most stable solid must be precipitated whereas in real life a thermodynamically less stable but kinetically favoured solid may precipitate. The program used in this project has the facility to print the list of possible minerals together with their saturation factors, and allow the user to select a restricted set of minerals for the program then to consider.

Programs available

Of the existing well known programs, the following were available to me for use:

1) GEOCHEM, made available by G Sposito

2) MINEQL, purchased from J C Westall

3) WATEQ,

4) EQ3NR, made available by T J Wolery

5) MICROQL, entered from source published by J C Westall

and a new model:

6) SCRAM, made available by P Fletcher

All these models, except MICROQL, are written in FORTRAN 77 and were either available to run on a VAX, or were adapted from IBM FORTRAN to run on the VAX (GEOCHEM). Because the normal floating point range of FORTRAN on the VAX is $10^{+/-39}$, the 'g_floating' compiler was used which gives a numeric range of $10^{+/-600}$. MICROQL, as the name suggests, had been written to run on desk-top micro-computers using BASIC.

I have also written a simple program of my own, in FORTRAN 77, purely in order to clarify my own thinking about other peoples more extensive programs that I was using. This enabled me to write out the mathematical process outlined in the first half of this chapter, so that anyone could construct his own program in order to make use of my constants.

The next section presents a comparison of the key differences between the 6 available models and assesses their usefulness in speciating heavy metals in anaerobic sewage sludge.

1) GEOCHEM

Written by G Sposito and C Mattigod at Riverside, California, GEOCHEM is one of the second-generation programs of the REDEQL school. It has subsequently been developed by several generations of post-graduate students at Riverside, and consequently it would be relatively inefficient and hard to follow if modifications were required.

Judging by the proportion of papers published on the speciation of heavy metals in natural waters, GEOCHEM has probably found the most widespread use of any program yet.

Language:	FORTRAN 77
Numerical:	Newton-Raphson
Gases:	N_2 , O_2 , CO_2 only
Redox pairs:	24 max
Mixed minerals:	20 max
Activity:	Davies equation
Temperature:	Fixed, database at 25°C
Pressure:	No
Activity of H_2O:	No
Adsorption:	James-Healey model
Ion-exchange:	Yes
Database expandable:	Yes

Advantages:

1) GEOCHEM is supplied with the largest database of any model yet: data for 36 cations, 69 anions, 2000 complexes and 185 minerals are included

2) It is very easy to extend the GEOCHEM database. Six complexes and 3 minerals are allowed for each cation/ligand pair, and it allows up to 24 mixed solids to be specified, eg $CuFeS_2$ or $MgNH_4PO_4$ which have been shown to precipitate under certain conditions in the digester. Mixed solids are handled separately from other solids to ensure that the Phase rule is not broken

3) Because GEOCHEM appears to be the most widely used program, its use would enable the results to be more easily compared by other workers

Disadvantages:

1) Only limited attempts have been made to ensure the thermodynamic consistency of the database, although the database does include space for notes on the origin of each constant or the initials of the person entering it

2) GEOCHEM operates at a fixed temperature, so to calculate speciation at 35°C for the digester, or 5°C for the soil, requires that all the constants in the database be recalculated and the new constants edited in

3) Equilibrium constants can only be held to +/- 0.1 log units, which implies an uncertainty of 15% in the results; many published equilibrium constants are not reliable even to this accuracy but many are; the cumulative effects of this rounding may be considerable compared with other models

4) It would be extremely difficult for anyone outside Riverside to adapt GEOCHEM to make it possible for the partial pressure of H_2S to be specified

5) GEOCHEM has little numerical protection on its Gaussian

elimination; this results in a significant number of crashes from floating point overflow when trying to solve complex sulphide precipitation under digester conditions

6) The current state of the GEOCHEM source code makes it difficult for an outsider to adapt the code for his own use

2) MINEQL

MINEQL was written by J C Westall, J L Zachery and F M Morel at Massachusetts Institute of Technology. It was developed directly from REDEQL (which ran on desk-top computers with only 64K memory), to allow more complex problems to be solved. The source code for MINEQL is only half the length of GEOCHEM and is well structured and documented; it can therefore be adapted relatively easily for particular purposes.

Language:	FORTRAN 77
Numerical:	Newton-Raphson
Gases:	Any for which constants are available
Redox pairs:	18 included
Mixed minerals:	Not allowed
Activity:	Davies equation
Temperature:	Fixed, database at 25°C
Pressure:	Not considered
Activity of H_2O:	Not considered
Adsorption:	Not considered
Ion-exchange:	Not considered
Database expandable:	Yes, dimension statements may need changing

Advantages:

1) MINEQL is particularly versatile in allowing the partial pressure of any gas to be specified, and allowing the activity of any component or species to be fixed. This allows back calculations to be performed. For example, since the activity of Cu in the digester for the onset of toxicity is known, the total safe Cu concentration may be calculated for a given sludge if all else remains constant.

2) MINEQL is the best behaved mathematically of all the programs used. It is the least prone to crashing from floating point overflow when solving complex sulphide precipitation. It also fails to converge less frequently than the other programs used.

3) Because MINEQL is the most efficient of all the FORTRAN models, I was able to run it on my own personal computer. A small problem involving only solution species and no precipitation which took 5 seconds of CPU time on the VAX, took 90 seconds to solve on a PC.

Disadvantages:

1) Mixed solids cannot be considered. This may not be a significant problem since, for example, $CuFeS_2$ can be considered as separate precipitates of CuS and FeS. But it is less than ideal and may lead to systematic errors in the calculations.

2) Ion-exchange is not considered, making Fletcher's constants for the 'Soluble' fraction harder to use.

3) MINEQL does not correct the ionic strength for complex formation after the initial calculation of ionic strength, although the program may be modified to force it to do so.

3) As with GEOCHEM, MINEQL is limited to 25°C, unless all the constants are edited by hand.

3) EQ3NR/EQ6

The EQ3/EQ6 pair of programs were written by Wolery at the Lawrence Livermore Laboratory (Wolery, 1979). EQ3 solves the state of an aqueous solution at equilibrium based on total concentrations and a thermodynamic database, but does not consider solid phases. EQ6 is a kinetic model that allows reaction paths to be followed as solids dissolve or precipitate. The 2 packages may be used together to allow solid phases at equilibrium to be calculated. The results of each stage are passed backwards and forwards between the 2 programs until the system is calculated to be in equilibrium. EQ6 can be asked to precipitate all the solid phases required by the solubility products in one go rather than a bit at a time. This 2-stage approach offers many possibilities but makes the program very cumbersome to use for simply speciating a system in equilibrium with solid phases.

EQ3NR is a new version of the EQ3 program which has been made slightly simpler to use, and the calculation stage has been speeded up.

EQ3NR offers the most comprehensive functionality of any of the widely available programs. In particular, it would allow the reaction path to be modelled when sulphate is added to protect a digester threatened by heavy metal toxicity.

Language:	FORTRAN 77
Numerical:	Newton-Raphson
Gases:	Yes, if constants available
Redox pairs:	Yes, if constants available
Mixed minerals:	Yes, if constants available
Activity:	B-dot (EQ3) or Pitzer (EQ3NR)
Temperature:	0-300°C

Pressure: Liquid/vapour equilibrium

Activity of H_2O: Yes (Helgeson's equation)

Adsorption: Not considered

Ion-exchange: Not considered

Database expandable: Yes

Advantages:

1) It uses a more comprehensive equation for activity than the other widely available programs (Pitzer),

2) It allows temperature to be considered by incorporating a database with constants at 0-25-60-100-150-200-250-300°C and curve-fitting,

3) It calculates the activity of water

4) It allows the partial pressure of any gases in equilibrium to be specified and allows any mixed solids to be specified

5) It allows ideal solid-solutions to be specified from data for the end-member states.

6) It also allows the presence of any solid to be imposed and the solution in equilibrium to be calculated, or the final activity of any reactant to be specified and the total concentration required to support that activity to be calculated.

7) The authors of EQ3NR seem to be aware of the problems caused by inconsistent data and have taken great care in the compilation and documentation of the database supplied with EQ3NR.

8) It can be used with EQ6 for kinetic studies

Disadvantages:

1) The database has a complicated structure and requires much more effort to amend it or to add new species than MINEQL, GEOCHEM or SCRAM.

2) It does not handle ion-exchange, therefore Fletcher's data for the 'Soluble' fraction could not be used directly.

3) In order to speed up the calculation, it uses a mass-balance equation which contains equilibrium constants and an expression for activity coefficients. The other models all use mass-action constants directly, which are modified for the calculated ionic strength at each iteration. This means that the Jacobian matrix contains the differential of the activity coefficient expression. For this reason, the equation used to calculate activity coefficients cannot be changed without a major re-write of the program, whereas with all the other programs, the equation can be changed simply by changing a subroutine. The B-dot equation used by EQ3 and WATEQF to calculate activity coefficients is bad at high ionic strengths.

4) The manual supplied with EQ3NR states that special mathematical techniques have been employed to make the calculation resistant to non-convergence; however, in use, EQ3NR appears to be both slow and prone to crashing from floating point overflow.

5) The biggest disadvantage is that EQ6 must be used as well if solids are to be considered, making the program very cumbersome to use.

4) WATEQF

WATEQ was written by Truesdell and Jones (1974) of the US Geological Survey. It was originally written in PL/1 and then re-written in FORTRAN as WATEQF.

The main problem with WATEQF is that it is supplied with a very limited database (192 constants) and it is very tedious to add or edit equilibrium constants since these must be compiled into the program each time. Since WATEQF is one of the older family of programs its use

was not pursued.

Language:	FORTRAN 77
Numerical:	Continued fraction
Gases:	Not considered
Redox pairs:	Yes, if constants available
Activity:	B-dot or Davies equation
Temperature:	0-100°C
Pressure:	Not considered
Activity of H_2O:	Not considered
Adsorption:	Not considered
Ion-exchange:	Not considered
Database expandable:	Constants compiled into program

5) MICROQL

MICROQL is a simple program written in BASIC, it is only 85 lines long but it doesn't contain a database. The constants required must be entered in DATA statements in the program each time the program is run.

Language:	BASIC
Numerical:	Newton-Raphson
Gases:	Not considered
Redox pairs:	Not considered
Activity:	Not considered, conditional constants used
Temperature:	Not considered
Pressure:	Not considered
Activity of H_2O:	Not considered

Adsorption: Not considered

Ion-exchange: Not considered

Database: No database, constants entered each time

The absence of a database means that the user is responsible for selecting and entering the constants accurately every time the program is run. This means that it was not useful for solving complex problems involving natural waters.

However, because of its simplicity, I changed it so that it allowed for activity coefficients and used it to calculate the quantities of a metal cation in solution that would have been complexed by hydroxide and carbonate (open to the air) in order to calculate the binding constants in the 'Biofloc' experiments.

6) SCRAM

SCRAM is a new program that has been developed by P Fletcher for use within the oil industry. It is unlikely to become generally available for academic use. However, it does have several advantages for modelling sludge chemistry.

Language: FORTRAN 77

Numerical: Newton-Raphson

Gases: Any, if constants available

Redox pairs: Any, if constants available

Activity: Extended Helgeson

Temperature: 0-300°C

Pressure: Liquid/vapour equilibrium

Activity of H_2O: Yes

Adsorption: Not considered

Ion-exchange: Yes

Database: Can be expanded, no limit on any type of interaction

Advantages:

1) SCRAM was written with the benefit of hindsight after its author had used the above-mentioned models and worked with Sposito on GEOCHEM

2) The database is easily modified without limits on any type of interaction. The temperature dependence of the constant is held as a simple fifth-order polynomial in terms of temperature (°C).

3) SCRAM considers all the types of speciation required by the model

4) SCRAM is the only program to use Helgeson's full equation for the calculation of activity constants

5) SCRAM allows the model to be run with precipitation disallowed and it then prints a list of all minerals whose solubility product had been exceeded and by how much. This list may be used to select a restricted list of minerals for the program to consider. This means that, for example, brushite rather than apatite could be selected as the Ca/PO_4 solid. It also makes the program far less prone to crash from floating point overflow because irrelevant solids can be excluded from consideration.

Disadvantages:

1) SCRAM does not allow any back calculations, so solids may not be imposed, nor may the activity of any solute be fixed.

2) The database supplied with SCRAM was designed for detailed calculation of silicate chemistry and contained few constants relevant to this model

3) SCRAM does not perform transformation of bases on its database set. This means that, for example, if you presented MINEQL with the Fe^{++} and Fe^{+++} redox constant and the $FeOH^{++}$ stability constant, MINEQL could work out the activity of $FeOH^{++}$ from the Fe^{++} activity, the pH and the pe. Because SCRAM cannot do this, you have to provide SCRAM with a database containing all the constants involving redox ions in duplicate, ie expressed in terms of each ion in turn.

For example, for the precipitation of chalcopyrite, SCRAM needs no less than 8 separate constants in its database to cope with any combination of Fe^{++} or Fe^{+++}, Cu^{+} or Cu^{++}, and S^{--} or SO_4^{--}, in the data-set fed into the model (table 8.1). This is very tedious, but it is not a limitation.

Table 8.1 Equilibrium constants for chalcopyrite

Reaction	Log K
$Fe^{++} + Cu^{++} + 2S^{--} = CuFeS_2$	61.78
$Fe^{+++} + Cu^{++} + 2S^{--} + e^- = CuFeS_2$	74.78
$Fe^{++} + Cu^{++} + 2SO_4^{--} + 8H_2O + 16e^- = CuFeS_2 + 16OH^-$	-121.80
$Fe^{+++} + Cu^{++} + 2SO_4^{--} + 8H_2O + 17e^- = CuFeS_2 + 16OH^-$	-108.80
$Fe^{++} + Cu^{+} + 2S^{--} = CuFeS_2 + e^-$	59.16
$Fe^{+++} + Cu^{+} + 2S^{--} = CuFeS_2$	72.16
$Fe^{++} + Cu^{+} + 2SO4^{--} + 8H2O + 15e^- = CuFeS_2 + 16OH^-$	-124.42
$Fe^{+++} + Cu^{+} + 2SO_4^{--} + 8H2O + 16e^- = CuFeS_2 + 16OH^-$	-111.42

This does, however, make SCRAM more resistant to crashing from floating point overflow because only mathematical problems with the

analysis data-set can crash the program; the calculated results never cause mathematical problems. SCRAM does fail to converge occasionally when asked to calculate the precipitation of solid phases when the anion concentration is dependent on the partial pressure of a gas (CO_2/CO_3^{--} and H_2S/S^{--}).

Using the 'Soluble' constants with GEOCHEM

It is not possible to use the ion-exchange constants for the 'Soluble' fraction directly in GEOCHEM, but since this program has found the most widespread use, I have included a method for incorporating them.

GEOCHEM calculates the concentration of species in mol dm^{-3} whereas the 'Soluble' equilibrium constants are defined in mole fraction units. These can be written (see chapter 6):

$$K_v = N_m \cdot a_B^2 \; / \; N_B^2 \cdot a_M$$

where the mole fractions N_M and N_B have been defined:

$$N_M = n_M \; / \; (n_B + \Sigma\, n_M)$$

$$N_B = n_B \; / \; (n_H + \Sigma\, n_M)$$

where n is the amount of each ion bound in mol gm^{-1}. The n's can be replaced by molarities by dividing the top and bottom of the equations by the concentration of the exchanger in solution (g dm^{-3}) and for simplicity we have defined all divalent cation complexes to be ML_2. So our mole fraction constant becomes:

$$K_v = \frac{([ML_2] / ([HL] + [ML_2])) \cdot a_H^2}{([HL] / ([HL] + [ML_2]))^2 \cdot a_M}$$

which simplifies to:

$$K_v = \frac{[ML_2] \cdot a_H^2}{[HL]^2 \cdot a_M} ([HL] \cdot [ML_2])$$

The constants required by GEOCHEM are in the form:

$$K_e = [ML_2] \cdot a_H^2 / [HL]^2 \cdot a_M$$

So: $K_e = K_v / ([HL] + [ML_2])$

The speciation presented in the next chapter shows that, in the digester, both sites are largely protonated. So, for each site [HL] and $[ML_2]$ can be approximated by:

$[ML_2] = 0$

$[HL] = CEC \cdot Q$

where Q is the g dm^{-3} of the 'Soluble' fraction specified in the data set fed into GEOCHEM. So:

$$\text{Log } K_e = \text{Log } K_v - \text{Log}(CEC \cdot Q)$$

In an oxidised environment (see chapter 10), both sites will be largely occupied with metal cations rather than protons. So:

$[HL] = 0$

$[ML_2] = CEC \cdot Q/2$

and therefore:

$$\text{Log } K_e = \text{Log } K_v - \text{Log}(CEC \cdot Q/2)$$

This does represent a fudge, but the resulting errors are well within the limits of confidence of the entire model.

Conclusion

The model is actually the thermodynamic database, but a computer program is also required to solve the mathematical problem.

The only 3 generally available programs that provide the required functionality for modelling heavy metal chemistry in anaerobic sewage sludge are GEOCHEM, MINEQL and EQ3NR. Each of these programs has disadvantages. SCRAM was written in order to avoid the weaknesses of existing programs and it is ideal for this work. However, it is not generally available. SCRAM is similar to EQ3NR in functionality but not in design.

Because I was fortunate in that SCRAM was available to me, it was used for producing all the speciation results presented in the remainder of this thesis. SCRAM was not used for some of the unpublished work where I wanted to solve back to the required total concentration of an element to support a specified final activity;

calculations of this type were performed using MINEQL because it was relatively resistant to crashing and its database was easily modified.

If SCRAM had not been available, MINEQL would probably have been the one chosen because of its ease of use. Although some modifications of the program would have been required, these would have been relatively easy because of the excellent design of the program's structure.

The possibilities offered by the use of the EQ3/EQ6 pair of programs to aid digester management ought to be pursued.

COMPUTER MODELLING: II

The model of anaerobic sludge

Having chosen the computer program that will be used to solve the model under a given set of conditions, the last stage is to assemble the model itself in terms of the equilibrium constants used in the program's database and the data-set used to drive the model for particular situations.

This chapter describes the database, the strategy for the model's use, and the speciation of an 'average' sludge taken from the tables at the end of chapter 2. The next chapter goes on to describe the speciation of the 'average' sludge as various key variables are changed.

The database

To obtain meaningful results from the model, the database must contain constants for all the major solution species, and these constants must be checked as far as possible for thermodynamic consistency and reliability.

The working definition that was adopted for a solution species that ought not to be neglected by the model was that it could account for at least 1 part in 10^{10} of the total concentration of that species under most of the conditions for which the model might be used.

For example, the inclusion of the $Fe(OH)_4^-$ ion in the database does not help the model because precipitation stops it ever being present in significant concentration; its inclusion only slows the program down.

Initially, all potential complexes were included, then those

whose concentration never exceeded 10^{-30} moles $litre^{-1}$ were gradually eliminated.

This problem was not encountered with solids because SCRAM can be run with solid precipitation disallowed; if so, it produces a list of all the potential solids in the database together with their saturation factors: IAP/K_{sp} (the ratio of the predicted ion-activity product of a solid species to its solubility product). This made it possible to hand-select the set of solids that the program was to consider when the model was run with solid precipitation allowed. This simplified the mathematics and considerably speeded up the program. The cpu time needed was typically reduced by a factor of 4.

For example, there was no point in the program considering the possible precipitation of Cu, Fe, Zn, Pb and Ni phosphates in the digester, since under most circumstances it is only Ca, Mn and $MgNH_4$ phosphates that are ever likely to be precipitated. The hand-selection of the solid set for a particular run also allows us, for example, to allow kinetically favoured but thermodynamically less stable solids to be considered (eg brushite rather than apatite as the Ca-phosphate, or iron hydroxides rather than oxides).

Equilibrium constants used

The full database used has been included for reference purposes as appendix 2 together with the exact reactions referred to. (SCRAM always expresses equations in terms of OH^- rather than H^+).

The model which SCRAM had originally been designed to solve was that of aluminosilicate chemistry under high temperatures and pressures for the oil industry. All the constants in its database had been taken from Helgeson's data (Helgeson, 1969) in the form of

fifth-order poly-nomials:

$$\text{Log } K = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

where T is in degrees Celsius. Helgeson's data had the advantage that they had been carefully checked to be internally self-consistent, and were consistent with the equation used by SCRAM to calculate activity coefficients.

As originally supplied, the SCRAM database contained no constants dealing with heavy metals, sulphides or phosphates. Consequently, considerable work was required to build the database needed for the sludge model.

The first stage in building the database was to simplify it by removing all the aluminosilicate chemistry. Aluminosilicates were considered unlikely to affect the heavy metal chemistry significantly. Constants for a few cations and anions not included in the sludge model were also removed (lithium, caesium, gold, strontium, tin, chromium, bromide, iodide, borate and antimonyl) to make the database easier to handle.

Having stripped the database of all the constants not required by the sludge model, extra constants were added. First, five new primary components were added to SCRAM: phosphate, cobalt, Biofloc, SOM(1) and SOM(2). Any additional constants relevant to the sludge model in Helgeson's data were taken and included, and where he didn't provide solubility products or stability constants, but did provide the free energies of formation of the primary components and of their complexes or solids, the constants were calculated from these.

Where constants were not available from Helgeson, five sources were used: W L Lindsay (1979), Stumm and Morgan (1981), MINEQL's database, EQ3NR's database and GEOCHEM's database. The constants from

these sources often agreed, but occasionally they diverged by several orders of magnitude. Where they diverged, preference was usually given to values supplied by Lindsay.

Published constants could not be found for some of the more obscure sulphides that had been shown to occur in the digester: digenite ($Cu_{1.8}S$), herzenbergite (SnS), BaS and Cr_7S_8. Equilibrium constants for all of these, except digenite, were calculated from the standard enthalpies and entropies collated by Mills (1974). He states that digenite is only the sulphur rich boundary of chalcocite, and suggests that its thermodynamic data are comparable to chalcocite. On this basis, digenite was treated as chalcocite in the model.

In addition to constants for as many as possible of the required inorganic complexes and solids, constants for the two SOM exchange sites (see table 6.2) and the 'Biofloc' complexes were added (see table 7.4 & 7.5), both for the cations whose constants had been measured, and for those whose constants had been calculated using the equation presented at the end of chapter seven.

Finally, the constants for complexes and solids that included primary components that could exist in more than one oxidation state in the model (Fe, Cu and S/SO_4) had to be calculated and entered for every possible combination of the oxidation states of their primary components (see chapter 8, p 217).

The final database included data for 33 primary components, 2 gases, 313 complexes, 42 exchange reactions and 129 solids.

Weaknesses in the database

1. There remains some risk of inconsistency in the constants not taken from Helgeson's data and, regrettably, there was insufficient time for checking the assumptions and conventions used by the authors of the papers they were taken from.
2. The constants not taken from Helgeson's data were not in a temperature-dependent form. Most of the sources used give constants for 25°C only. If more time had been available, constants could have been calculated in a temperature dependant form where standard enthalpies and entropies of the primary components and products have been published.
3. Missing solution species. Table 9.1 lists the full component set considered by the model. Comparison of the component set with the all-element analysis presented in table 2.13 shows that virtually all the major constituents have been considered. However, significant errors might arise if there proved to be important complexes whose constants were not available or for some of the less studied cations. In particular, the complexation by the organic fractions was measured for only a few of the most important elements and had to be calculated for the other cations.
4. Missing solids. Solubility products or free energies of formation were available for all of the solids shown to exist in digested sludge and whose primary components were included in the model except ankerite, and there was uncertainty over the constant for $MnHPO_4$ (see below).
5. The removal of aluminosilicate chemistry might cause indirect effects on the speciation of other components.

Table 9.1 Component set for SCRAM

No	Component	No	Component	No	Component
1	proton	17	copper(II)	33*	chromium(III)
2	hydroxide	18*	mercury(II)	34*	chromium(II)
3*	lithium	19	iron(II)	35	cadmium
4	sodium	20	manganese(II)	36*	manganese(III)
5	potassium	21	iron(III)	37	nickel
6*	caesium	22*	aluminium	38	-
7	ammonia	23*	gold(III)	39*	$mercury(I)_2$
8	silver	24*	silicic acid	40*	borate
9	copper(I)	25	fluoride	41*	antimonyl
10*	gold	26	chloride	42	ammonium
11	magnesium	27*	bromide	43	montmorillonite
12	calcium	28*	iodide	44	montmorillonite edge
13*	strontium	29	nitrate	45	SOM(1)
14	barium	30	sulphate	46	SOM(2)
15	lead	31	sulphide	47	phosphate
16	zinc	32	carbonate	48	cobalt

* primary components in SCRAM not used in this model

Strategy

Having defined a model of sludge, and a program that can solve the model, one could spend hours having great fun running the program with different total analyses and under different conditions.

However, it is important to test the model against the analyses of 'real' sludge to test its validity and make any refinements that are necessary. Having validated the model, it can then be used to make exploratory studies on the effects of various parameters, and for this an overall strategy was needed:

1. The speciation of an 'average' anaerobic sludge
2. The effect on this speciation of changes in the total concentration of the most important elements: Fe, Zn, Cu, Ni, Cd, S, and organic matter
3. The effects of changes in the master variables pH and pe
4. The effect on the speciation of the oxidation of sulphide that follows the removal of sludge from the digester
5. The effect on speciation of further oxidation that results in the loss of organic matter
6. A preliminary look at sludge/soil interactions
7. A preliminary look at sludge/sea-water interactions

The rest of this chapter presents the results of the speciation of the 'average' sludge and compares the results with the experimental observations.

The next chapter presents some of the initial findings from using the model for the earlier stages of the strategy outlined above (stages 1-3, 6 and 7). These seemed to be sufficient to confirm the

general validity of the model, and there has not been time to do more. It is hoped to follow the other stages later, when time allows.

The definition of the 'average' sludge used

Given that digested sludge is naturally such a heterogeneous substance, it is necessary to define an 'average' sludge that can be used as the starting point to explore the speciation of its components. From the analyses presented at the end of chapter 2, an 'average' sludge was defined - its components and their concentrations are presented in table 9.2.

The 'average' sludge is based primarily on table 2.15 and the other components were taken from tables 2.12 and 2.13. The concentrations of 'Biofloc' and 'Soluble' present were based on my analyses for their concentrations in gm litre^{-1} (chapter 3) and their measured CEC (monovalent sites per gram). The 'Biofloc' was specified at 20 gm litre^{-1} and the 'Soluble' material at 1 gm litre^{-1}.

The composition of the digester gas was taken to be 30% CO_2 and 70% CH_4 (IWPC Manual of British Practice, 1979). Rather than impose a partial pressure of H_2S on the digester, a total concentration based on table 2.15 of inorganic sulphur (sulphide and sulphate) in solution was added as a component. Obviously, the partial pressure of H_2S and soluble sulphide are closely related.

Of the components listed, S, N and P raise the most problems because a fraction of these components is held in an organic pool and therefore not available to take part in the equilibrium chemistry of the solution. The speciation of sludge under the anaerobic conditions of the digester is heavily dependent on the total concentration of inorganic sulphur.

Table 9.2. Components of the 'average' sludge

Type	Element	Dry sludge	Wet sludge	
		mg kg^{-1}	moles $litre^{-1}$	pM
Cations	Na	7,300	7.93e-3	-2.10
	Mg	4,800	5.00e-3	-2.30
	K	3,000	1.92e-3	-2.72
	Ca	49,000	3.06e-2	-1.51
	Mn	280	1.27e-4	-3.89
	Fe	12,000	5.36e-4	-2.27
	Co	20	8.47e-6	-5.07
	Ni	85	3.60e-5	-4.44
	Cu	1,000	3.94e-4	-3.40
	Zn	1,890	7.27e-4	-3.14
	Ag	110	2.55e-5	-4.59
	Cd	16	3.57e-6	-5.45
	Ba	500	9.13e-5	-4.04
	Hg	6	7.46e-7	-6.13
	Pb	540	6.52e-5	-4.19
	NH_4/NO_3	5,000	6.94e-3	-2.16
Anions	F	120	1.58e-4	-3.80
	Cl	3,600	2.54e-3	-2.60
	S/SO_4	5,000	1.30e-3	-2.88
	PO_4	14,000	3.68e-3	-2.43
	Biofloc		8.00e-2	-1.10
Exchangers	SOM(1)		6.30e-3	-2.20
	SOM(2)		2.70e-3	-2.60
	Mont		1.00e-3	-3.00
Gases	CO_2		3.00e-4 kilobars	

The figures used for S, N, and P are based on analyses presented for 'inorganic' components rather than on the total analyses of these elements. The total inorganic sulphur concentration specified as a component in the 'average' sludge was equivalent to 65% of the total load of Cu, Zn, Ni, Cd, Pb, Mn, Hg and Fe in the sludge.

The concentration of montmorillonite (1e-3M exchange sites), added as a sample clay, was judged to be a reasonable figure.

The pH was fixed at 7.4. The pe was fixed at -4.5, which is equivalent to -266.1 mV (Eh).

The concentrations of the components in solution were calculated on the basis of 2.5% dry solids in the sludge.

Some figures in table 9.2 could be replaced by the average figures from the Beckton works in table 9.3 (taken from table 2.14).

Table 9.3 Components for 'Beckton' sludge

Type	Element	Dry sludge	Wet sludge*	
		mg kg^{-1}	moles $litre^{-1}$	pM
Cations	Ni	92	3.90e-5	-4.41
	Cu	780	3.07e-4	-3.51
	Zn	3,400	1.31e-3	-2.88
	Cd	25	5.58e-6	-5.25
	Pb	930	1.12e-4	-3.95

* calculated on 2.5% dry solids

Of the elements listed in the all-element analyses (table 2.13) which were present in greater quantity than 25 mg kg^{-1}, only Cr, Sn,

B, V, As, Ti, Al, Si, Sr, Ce and Rb have been omitted. Of these V has recently been placed on the EEC's list of elements causing concern. However, its chemistry is complex and needs to be elucidated further before it can be included in a model such as this.

Finally, time was not available to calculate the temperature dependence of the constants not obtained from Helgeson's data (this can be done if the enthalpies and entropies of all the products and reactants are available). For this reason it was decided to run the model at 25°C for which published constants were available rather the 35°C of the digester at this stage.

The speciation of the 'average' sludge

Using SCRAM, the full speciation of the 'average' digester sludge was calculated in 5 minutes of cpu time on a VAX 785 fitted with a floating point accelerator; it considered 28 components, 170 complexes, 32 ion-exchange reactions but only 20 of the 72 possible minerals.

The full results of the speciation are presented in appendix 4, divided into five sections:

1. The final concentrations of the components in solution
2. The concentrations of all solution species
3. The concentrations of ion-exchanged species
4. The concentrations of the precipitated solids
5. A percentage breakdown of each element according to its forms of combination

The results are summarised in this section.

Mineral phases

Seventy-two possible minerals were found. When the model was first run with solid precipitation disallowed, 38 of these were undersaturated, 1 was at possible equilibrium, 3 were slightly oversaturated, 16 were moderately oversaturated and 14 were grossly oversaturated.

Table 9.4 Mineral phases that the model predicted as precipitates

Mineral name	Formula
Chalcopyrite	$CuFeS_2$
Chalcocite	Cu_2S
Greenockite	CdS
Acanthite	Ag_2S
Cinnabar	HgS
Galena	PbS
Sphalerite	ZnS
Apatite	$Ca_5(PO_4)_3OH$
Calcite	$CaCO_3$
Fluorapatite	$Ca_5(PO_4)_3F$
$MnHPO_4$	$MnHPO_4$
a-Magnetite	Fe_3O_4
Witherite	$BaCO_3$

The model was then run with solid precipitation allowed but only the 14 grossly oversaturated minerals considered. This immediately revealed a problem. If the digester gas contained 30% CO_2, azurite

was the copper mineral phase that was thermodynamically most stable rather than any of the copper sulphides. Azurite is the basic copper carbonate ($Cu_3(CO_3)_2(OH)_2$), but XRD had failed to identify it in the mineral phase. It is reasonable to assume that kinetic considerations stopped azurite forming in the digester, so it was removed from the list of considered minerals. This was the only adjustment that was made while speciating the 'average' sludge.

Having identified which of the grossly oversaturated mineral phases precipitated, then the moderately oversaturated minerals that did not contain elements removed from solution by the grossly oversaturated minerals were also included.

The final set of 13 minerals which the model predicted as precipitates are listed in table 9.4. The mineral phase is dominated by sulphide (Cu, Fe, Cd, Ag, Hg, Pb and Zn) and carbonate (Ba and Ca) precipitation. A total of 0.15 moles CO_2 $litre^{-1}$ was dissolved and all the Ba and 79% of the Ca precipitated as carbonates.

This table may be compared with the list of minerals positively identified by XRD (see table 5.5). Of the 13 predicted minerals, 6 were not observed.

Of these 6, some would probably have been present in too small a quantity to be observed by XRD (acanthite, greenockite, cinnabar).

Witherite was not observed, but a mixed Ba/Pb sulphide was. The published solubility product for BaS ($\log K = 2.3$) indicates that it is very soluble and shouldn't precipitate in the digester, so there is a clear anomaly here. This may indicate either a new relatively insoluble mineral or a solid-solution with galena.

Chalcocite (Cu_2S) was not observed but the sulphur rich digenite ($Cu_{1.8}S$) was; however, since their thermodynamic data are similar (see

above), the model treats them as the same species.

The main anomaly in the predicted list of solids is $MnHPO_4$. This solid is homologous with brushite, but its XRD pattern is sufficiently distinct for it to have been easily distinguished from brushite. Following these results, the XRD data were carefully re-checked for the lines characteristic of $MnHPO_4$ but they were not found. Either it does not precipitate in the digester, or if it does precipitate then it is too amorphous to identify by XRD. No association of Mn and P was observed in the SEM microprobe analyses either.

If it does not precipitate, this could be for one of several reasons: the published constant could be wrong, there could be kinetic reasons, or the manganese may never be released from detrital forms in sufficient quantity. Lindsay (1979) had reported that $MnHPO_4$ can co-exist with apatite and that at low pe+pH it may be more stable than apatite but urged that the solubility relationships of the manganese phosphates be re-examined.

The model predicts that both calcite and apatite should precipitate in the digester and that calcite should account for 79% of the Ca in the solid phase. The distribution of the mineral grains observed under the SEM for Beckton sludge is presented in table 5.1. These figures show that while they both do precipitate, a higher proportion of phosphate grains than calcite grains was counted. (It must be noted that the proportion of the grains counted does not indicate their relative mass).

Table 9.5. Summary of speciation results*

Component	Percent	Name
Barium	99.99	Witherite
Cadmium	99.95	Greenockite
Calcium	79.00	Calcite
	8.91	Apatite
	2.57	Fluorapatite
	4.91	On SOM
	3.98	On Biofloc
Cobalt	60.94	On Biofloc
	38.24	On SOM
Copper	50.09	Chalcopyrite
	49.91	Chalcocite
Iron	46.64	a-Magnetite
	36.82	Chalcopyrite
	11.31	On Biofloc
	4.34	On SOM
Lead	99.98	Galena
Manganese	99.86	$MnHPO_4$
Mercury	99.98	Cinnabar
Nickel	50.07	On Biofloc
	38.10	On SOM
	10.25	$NiCO_3$
Silver	99.98	Acanthite
Zinc	99.79	Sphalerite
Sulphide	55.80	Sphalerite
	30.36	Chalcopyrite
	7.56	Chalcocite
	5.01	Galena
Biofloc	87.51	Uncomplexed
	8.97	Ca
	3.04	Mg
SOM(1)	47.70	Ca
	33.90	Mg
	17.06	Uncomplexed
SOM(2)	99.69	Uncomplexed

* Species accounting for more than 1% of the primary component

See Table 9.4 for the formula of minerals

The speciation predicts that 38.7% (44 mg litre^{-1}) of the phosphate will remain in solution, mainly as HPO_4^{--}. This compares well with the ICP analysis of Beckton sludge (table 3.3), which showed 69 mg litre^{-1} in solution, but does seem to indicate that the 'average' sludge has a lower inorganic P content than Beckton sludge. It is also likely that the activity of CO_2 in the digester solution might not be as high as its partial pressure would suggest. These two factors might account for the relatively lower level of apatite precipitation predicted for the 'average' sludge than was observed in Beckton sludge.

Of the thirty-five or so solids identified by XRD, there were many which the model did not predict as precipitates. Twelve of these were aluminosilicates and their chemistry had not been included in the model because it was thought unlikely to affect the speciation of the heavy metals.

The precipitation of siderite ($FeCO_3$) had been predicted by Mosey (see chapter 2), and its presence was confirmed by XRD, but no conditions could be found under which the model predicted that it, rather than magnetite, would be precipitated in the digester.

The rest are accounted for by the fact that a thermodynamic model can only consider the most stable solid for a combination of elements, for example, if apatite is considered, then brushite cannot be precipitated.

The overall effect of sulphide precipitation on the heavy metals was that Cu, Zn, Cd, Hg and Pb were entirely removed from solution into mineral sulphide forms, but with the level of sulphide defined in the 'average' sludge, Ni sulphide would not form.

The model predicted that the Fe in the mineral phase would have

been removed as a mixture of 56% a-magnetite and 44% chalcopyrite precipitates (table 9.5). This ratio can be compared with the relative proportions observed in the density cuts greater than 2.9 gm cm^{-3} of the 'Particulate' fraction (table 5.1), where of the grains where Fe was the dominant cation, 60% were Fe oxide and 40% Fe sulphide.

The organics

The question left unanswered at the end of chapter 3 was whether the heavy metals associated with the 'Biofloc' fraction in the mass balance were held as complexes or as fine enmeshed precipitates.

The speciation results show that in the 'average' sludge precipitation would remove virtually all the transition row cations into the solid phase except for Ni. But of the Ni, 50% would be removed to the solid phase by complexation to the 'Biofloc', while the remaining 50% would remain in solution complexed by the 'Soluble' fraction and by carbonate. It did not predict that any Ni minerals would form.

While there were no lines for NiS under the XRD, and no sulphide grains were observed where Ni was the dominant cation, SEM microprobe analyses of type-I sulphides frequently recorded a significant level of Ni as a constituent. So there appears to be a discrepancy here between the model and Beckton sludge.

However, the quantity of sulphide defined in the 'average' sludge was based on the analyses for inorganic sulphur presented in chapter 2. The final pS in the speciated sludge was 15.9, while typical urban sludges have a measured pS of around 12. It may be that insufficient of the total sulphur had been allocated to the inorganic fraction in

the data-set. The next chapter presents the effects of changing the total sulphide to a give a final pS in the range 9 to 30. They show that in order to achieve a final pS of 12.4, the 'average' sludge needed a total concentration of 1.7e-3M sulphide (see figure 10.2). Increasing the total sulphide to this figure removed 99.9% of the Ni as the sulphide.

With a final pS of 15.9, the organic ('Soluble' plus 'Biofloc') fraction was left holding 15% of the Fe, 90% of the Ni, 98% of the Co and substantial quantities of Ca and Mg, but the majority of the complexation sites were still unbound (88% of the Biofloc, 17% of SOM site 1 and nearly 100% of SOM site 2).

When the total sulphide was increased to give a realistic final pS of 12.4, the organic fractions were left holding negligible quantities of transition row cations apart from Fe, all the rest of which were precipitated as sulphides. If so, the heavy metals that separated with the 'Biofloc' fraction in the mass balance (see table 3.12) are likely to have been entirely in the form of fine enmeshed precipitates.

The digester solution

The digester solution contains the 'Soluble' organic fraction, inorganic complexes and free ions. Its importance lies in the fact that heavy metal toxicity to the digestion process will be largely determined by the activities of their cations in solution. Also, Fe is an essential nutrient for the bacteria responsible for anaerobic fermentation.

The figures for the final activities of various ions are likely to be the most misleading results of the model, since the equilibrium

constants used in the model for the mineral phases will fix the activity of the cations as though they were in equilibrium with pure crystalline forms. In the digester, the minerals are unlikely to be either pure or perfectly crystalline, and consequently are likely to support higher activities of their cations in solution. Since the digester receives fresh raw sewage on a daily basis it is unlikely to attain equilibrium anyway.

Table 9.6 presents the activities calculated for the heavy metals, and for Fe and Cd in the digester solution both with the initial quantity of sulphide as defined in the 'average' sludge and with the more realistic level that produced a pS of 12.4. For comparison, it presents the measured levels of the cations in the solution which will have included complexed forms (from table 3.3).

At a pS of 15.9, 4.3% (1.28 mg litre^{-1}) of the Fe remained in solution complexed by the 'Soluble' fraction, and at the more realistic pS of 12.4, 3.6% (1.08 mg litre^{-1}) of the Fe still remained complexed. Chelated Fe is likely to be more readily released back to the solution as a nutrient than it would be from precipitated mineral forms. These figures compare well with the ICP analysis which showed 0.31 mg litre^{-1} Fe in the solution separated from Beckton sludge (table 3.3 - centrifuged for 60 minutes).

Higher levels of the heavy metals remain in the solution from Beckton sludge than the model predicts. In particular, a much higher level of Cu remains. This may represent Cu bound tightly on the specific sites represented by SOM(2) or stabilized in colloidal forms, from which it may not readily be released.

Table 9.6 Predicted activities of various cations in solution (pM)

	Sulphide activity		ICP
Cation	pS 15.9	pS 12.4	analysis*
Fe	6.76	6.83	5.26
Ni	7.26	10.49	6.37
Zn	8.92	12.41	6.70
Cu	16.10	23.02	5.08
Cd	11.89	15.40	nd

* these figures will include complexed cations

Conclusion

With the exception of $MnHPO_4$, the model predicts the precipitation of a range of minerals broadly in line with observations. The observed dominance of sulphide precipitation would lead, at equilibrium, to virtually none of the transition row cations remaining in solution or being held, complexed, by the 'Biofloc'. If so, this indicates that the majority of the heavy metals which separated with the 'Biofloc' in the mass balance were held as fine enmeshed sulphide precipitates. The observed low levels of heavy metals in the analysis of the 'Soluble' fraction probably indicate that the digester was not at equilibrium.

COMPUTER MODELLING: III

Using the model

At the end of the previous chapter, the model which had been built up over the previous chapters was used to elucidate the speciation in an 'average' digester sludge. This chapter presents some further tentative results (sections 1 and 2) from using the model to predict the effects of various changes to the sludge following the first two stages of the strategy outlined in chapter 9 (p 227). There was no time to pursue in detail the later stages of the strategy outlined. Strictly, the model as it stands is only designed to provide a picture of sludge in the digester. There remain some unsolved problems in using the model on sludge in oxidised environments - notably the role of the oxides and hydroxides of reoxidised Fe in holding heavy metals by adsorption and occlusion (Jenne, 1968; Tiller et al, 1984; Bruemmer et al, 1988), and in the transformation of the organic matter in the sludge (eg its oxidation and population by different kinds of microflora). However, brief exploratory studies were made of the later stages in the strategy (sections 3 to 5).

The chapter is divided into five sections. These examples were chosen partly to check the model, and partly to demonstrate the character of the results it can produce:

1. The effect of changing the digester pH
2. The effect of sulphide concentration in the digester
3. Oxidation of the anaerobic sludge (preliminary)
4. Sludge in soil (preliminary)
5. Sludge disposal at sea (preliminary)

1. Effect of digester pH

This study examined the effect of varying one of the master variables: pH. The model was run at 0.2 pH intervals pH 6.0 to 8.0, first with the precipitation of solids disallowed to help select the correct set of solids, then with an appropriate set of possible solids allowed. The concentrations of the components were kept the same, and pe was left fixed at -4.5.

With precipitation allowed, SCRAM failed to converge at pH values 6.8 and 7.2 because of an as yet unresolved problem with CO_2 chemistry in the program. In order to complete these studies the level of CO_2 dissolving was fixed at 0.15 M, although more CO_2 would be expected to dissolve with increasing pH.

The graph in figure 10.1 shows the effect of pH on the activities of some of the most important ions in the digester: Cu, Zn, Ni, Fe, S, and Ca. Over the pH range 6.0 to 8.0, the speciation of Fe, Ca, and P undergoes major changes, but pH has little effect on the speciation of the heavy metals. As the pH increases, more CO_2 dissolves leading to an increasing proportion of the Ca being precipitated as calcite, and a decreasing proportion precipitated as apatite. On the other hand, if the pH falls below 7.0 the organic fractions are better able to compete for the Ca until at pH 6.0, 60% of the Ca is complexed organically (see figure 10.2). This results because the complexation constants for the 'Biofloc' are pH-dependent and indicate stronger binding at lower pH.

Figure 10.1 Activity of major ions against pH

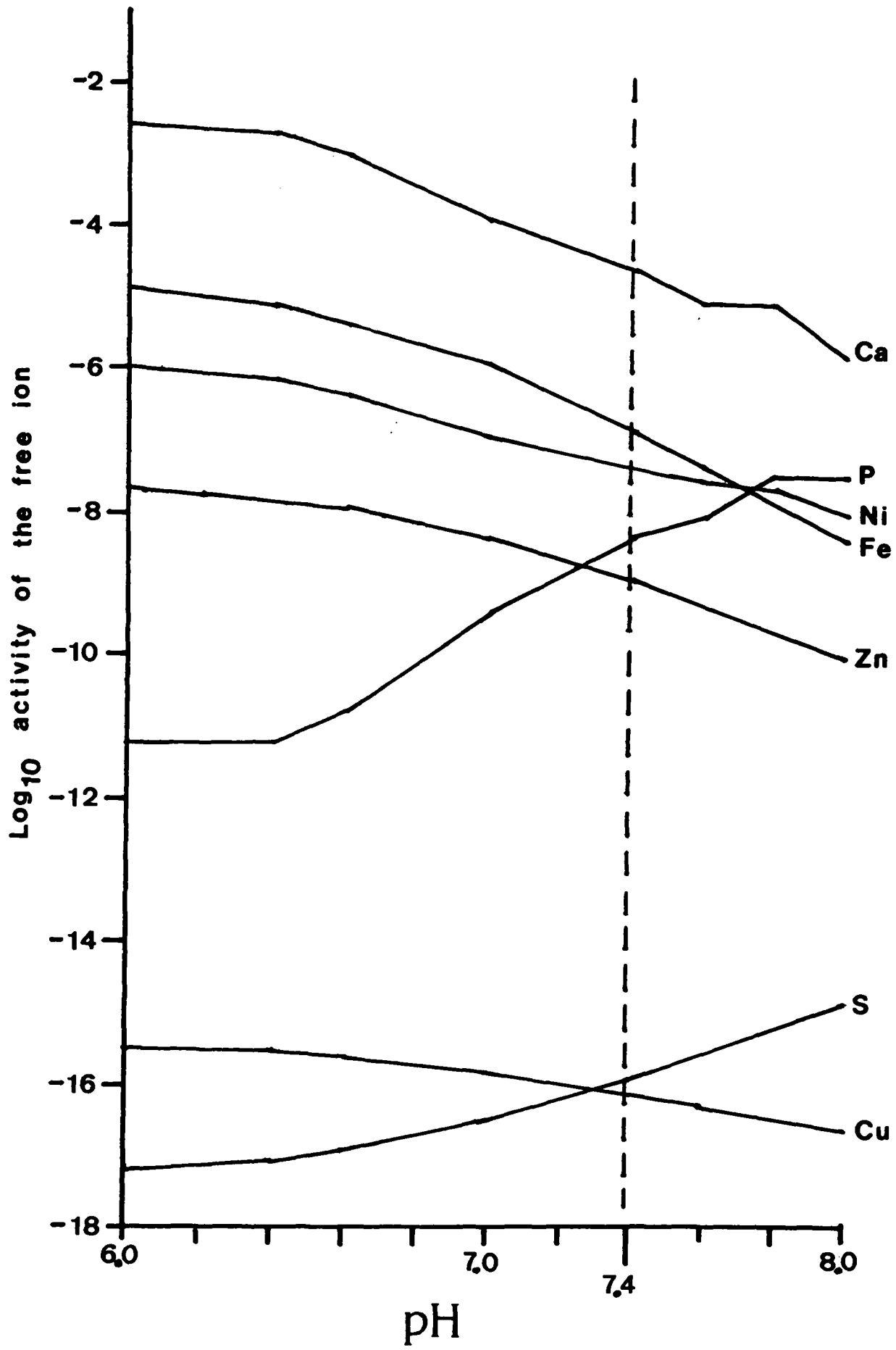


Figure 10.2 Effects of pH on Calcium speciation

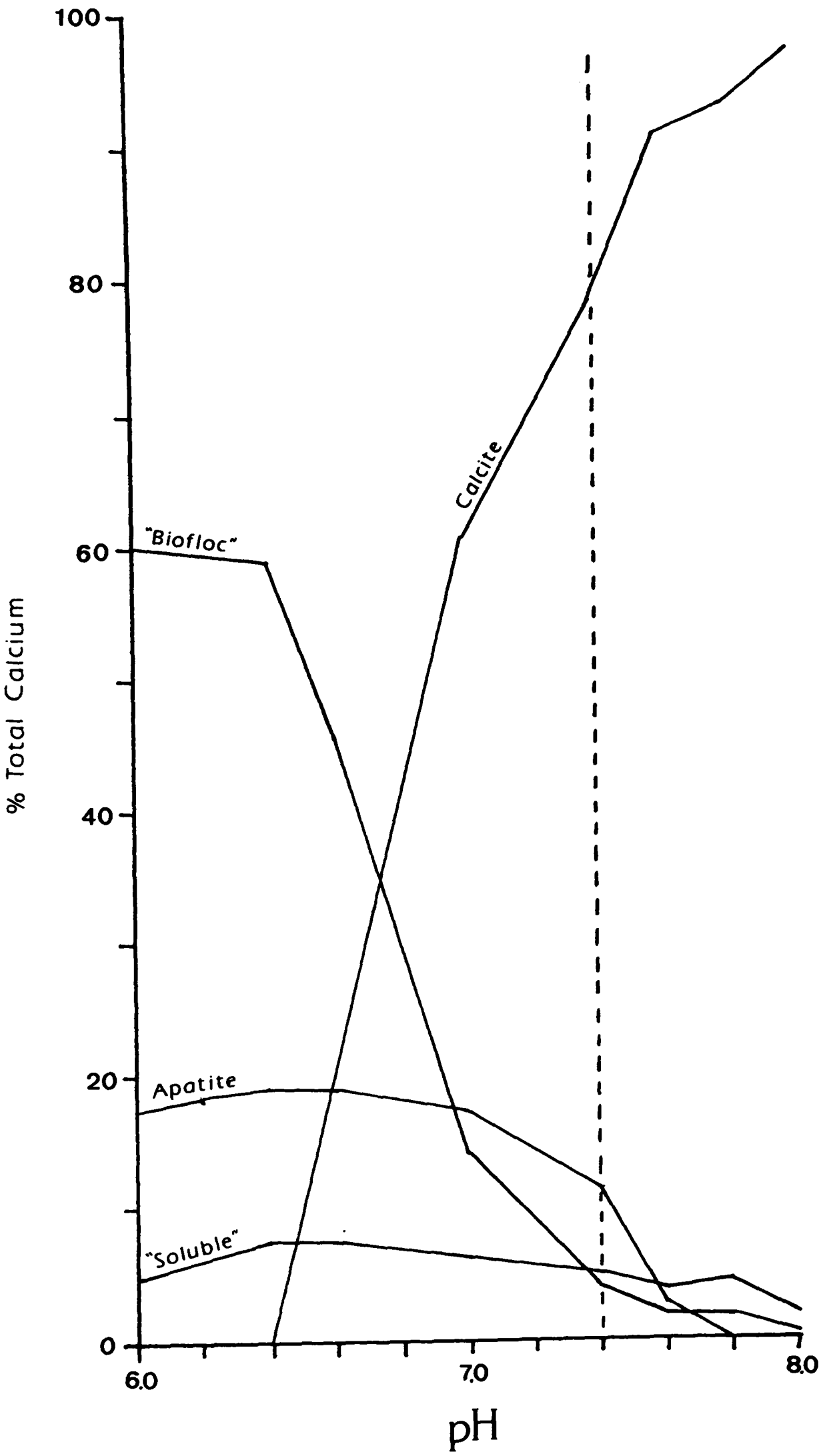


Figure 10.3 Effects of pH on Iron speciation

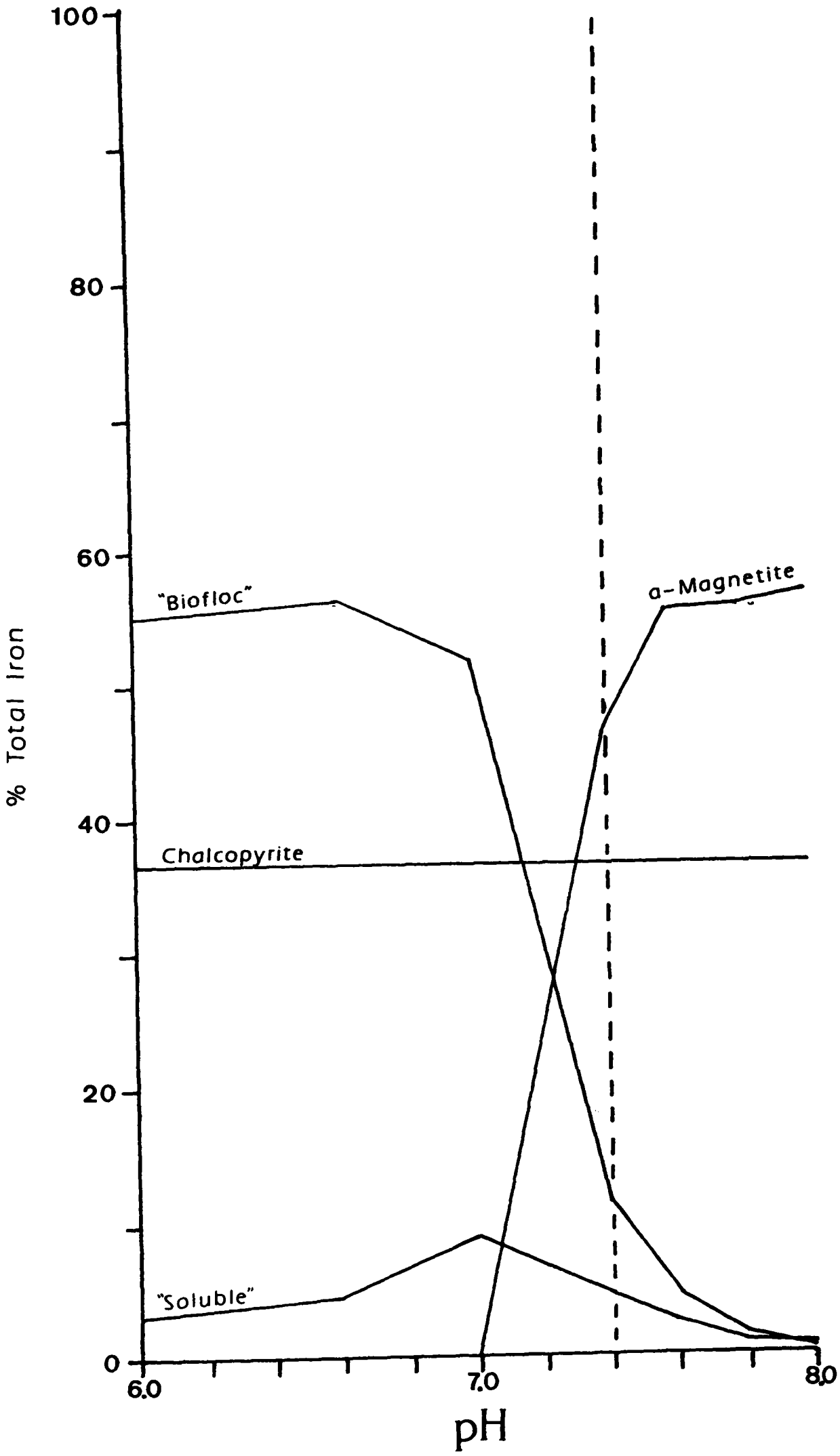


Figure 10.2 shows that a small increase in the digester pH from the median value of pH 7.4 could significantly affect the proportion of the phosphate removed to the solid phase. At pH 7.4, the model predicted that 38.7% of the total phosphate would remain in solution, while at pH 7.6, 83% would remain. When operating problems are encountered, the digester pH often falls to pH 7.0 or below. At pH 7.0, only 10.6% of the phosphate will remain in solution.

The speciation of Fe also changes dramatically over this pH range (figure 10.3). At pH 6.0, 60% of the Fe is held complexed by the 'Biofloc', by pH 8.0, 60% is held in magnetite precipitates and virtually none is held in organic complexes. The precipitation of chalcopyrite is not affected by pH and accounts for a steady 37% of the Fe between pH 6.0 and 8.0. While the model predicts that the speciation of Fe will change substantially over the fall in pH experienced by a 'sick' digester, this should not affect the proportion of the Fe removed with the solids.

However, as was discussed in the previous chapter, Fe is an essential nutrient for the bacteria responsible for anaerobic digestion. It is likely that Fe held complexed by the 'Biofloc' would be released back into solution more readily than it would be from mineral precipitates. Figure 10.3 suggests that if the health of a digester were threatened because excess sulphide was lowering the Fe activity, then lowering the pH of the digester might help alleviate the problem. This would also help reduce the sulphide activity by reducing H_2S solubility.

The overall speciation of Cu and Zn is relatively unaffected by pH between pH 6.0 and 8.0. As the pH is increased, more of the

sulphur becomes available as sulphide leading to a lower pS in solution. So pS decreases by 2.31, and there is a concomitant rise of 1.13 in pCu (Cu is in the +1 oxidation state) and 2.31 in pZn. With the level of total inorganic sulphur defined in the 'average' sludge, pNi increases by 2.02, and most of the Ni shifts from complexation by the 'Biofloc' to the 'Soluble' fraction. At a more realistic pS of 12.4, the Ni would remain as a sulphide precipitate, and pNi would fall by 2.31, the same as for Zn.

This confirms that it is important to stop the pH falling in a 'sick' digester suffering from heavy metal toxicity, since a fall in pH would lead to a decreasing proportion of the H_2S produced by anaerobic fermentation being retained in the solution to aid the removal of the toxic cations to the mineral phase.

2. Effect of sulphide on the speciation of the 'average' sludge

The second study involved changing the concentration of total inorganic sulphur, a key primary component, over a wide range of values. The model was run with 10 different concentrations of total inorganic sulphur from 2.0e-3 M down to 1.0e-4 M, which gave increasing final pS values of 9 down to 30. All other primary components were kept the same as in the 'average' sludge. The pe was left fixed at -4.5.

In digesters, the pS of the solution is usually in the range 10 to 15 and a pS of 12 is typical in urban sludges; heavy metal toxicity usually ensues when the pS has fallen to 17 (see chapter 2). However, high digester pS is more likely to be caused by excess levels of heavy metals and of Fe than by a low total concentration of sulphide, so this study might not mimic a digester with a high

pS.

The results are presented in figures 10.4 and 10.5. Figure 10.4 shows the effects of changing the total inorganic sulphur concentration in the 'average' sludge on the final activity of the heavy metal cations and on the activity of the sulphide ion in solution. Figure 10.5 presents the same results as a graph of the activity of the heavy metal cations against pS. Figure 10.5 presents a much clearer picture of what is happening, and indicates the controlling phase for each cation over the pS range.

Figure 10.5 confirms that at pS 12 (a typical urban sludge), the activity of all the heavy metals in the sludge would be controlled by their respective sulphide precipitates.

It also shows that although Fe is precipitated as a mixture of chalcopyrite and magnetite over most of the range of pS values typical of sludge (pS 12.5 to 16), its activity is controlled by precipitation of magnetite, and is independent of pS. This suggests that above pS 12.5, sulphide will have no effect on the availability of Fe as a nutrient in the digester.

It should be noted that in the typical pS range, the model predicts that Cu will be precipitated as a mixture of chalcocite and chalcopyrite, but the activity of Fe is not controlled by the precipitation of chalcopyrite at any pS: control passes directly from magnetite to pyrrhotite at pS 12.5. Chalcopyrite, digenite, and pyrrhotite were all observed in Beckton sludge (the model treats chalcocite and digenite as the same mineral: see chapter 5, pp 135-136).

Figure 10.4 Effects of total sulphur on speciation

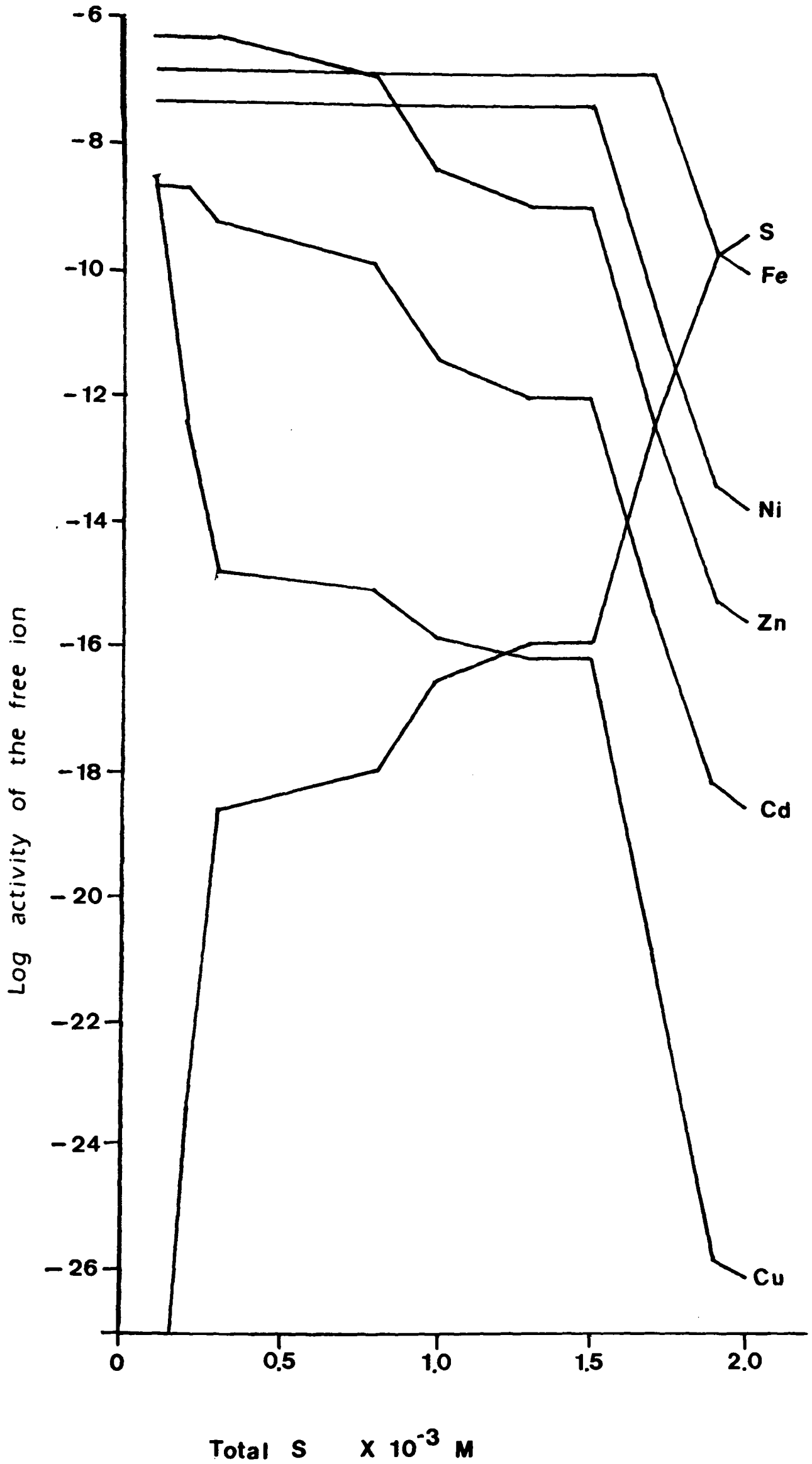
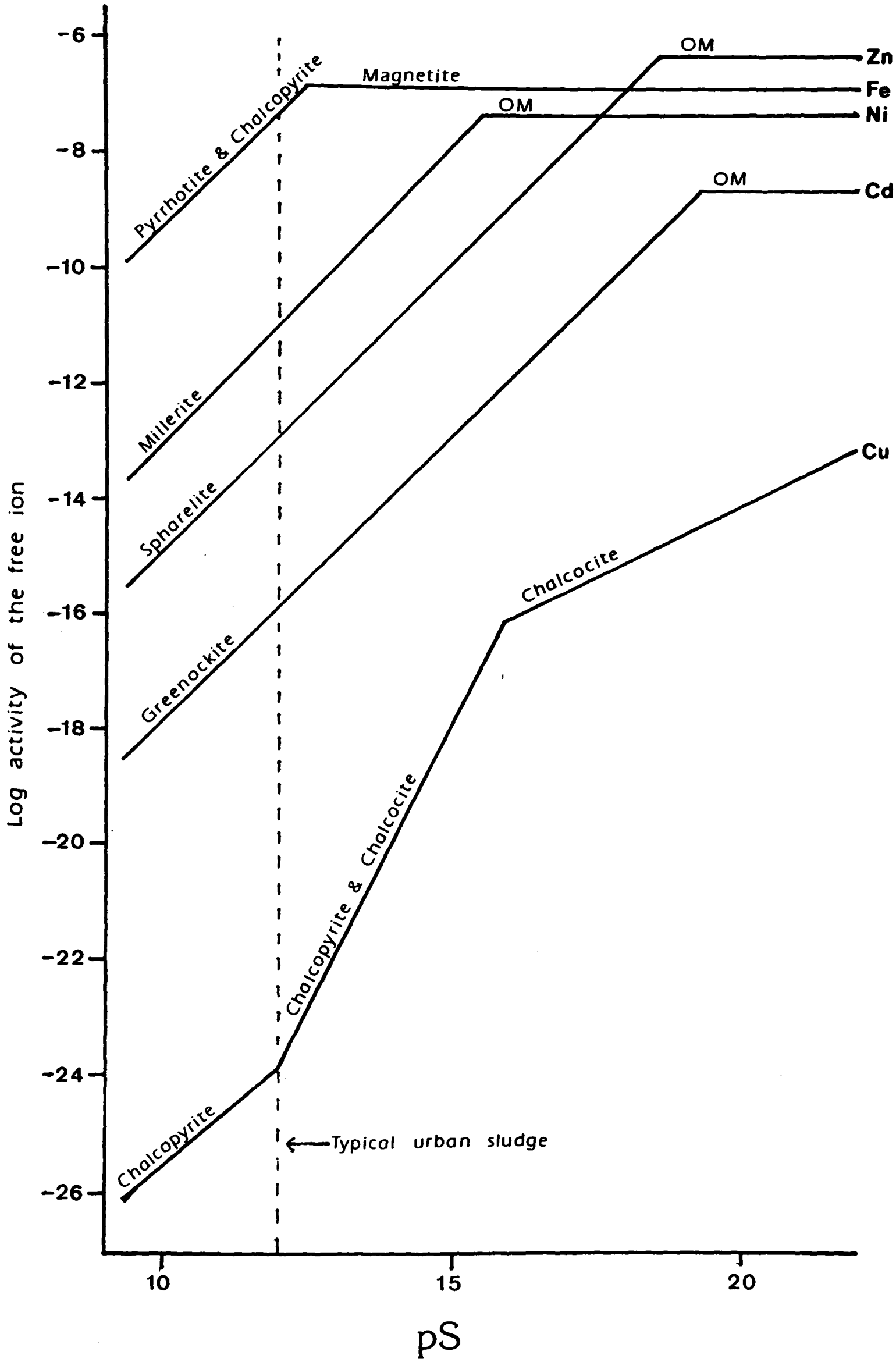


Figure 10.5 Effects of pS on speciation



An equilibrium model can only consider the most thermodynamically stable mineral for any set of primary components, and did not predict the precipitation of bornite and pyrite though these were also observed. This would also seem to be a further demonstration of heterogeneity in the digester.

For none of the transition row cations, except Cu, does the concentration of sulphide affect which of the possible sulphide mineral phases for the cation is precipitated. With Cu, however, it predicts that at pS <12, only chalcopyrite precipitates, at pS >12 and <16 both chalcopyrite and chalcocite precipitate, and at pS >16 only chalcocite precipitates.

As the pS falls, control of the solution activity of the transition row cations passes from a sulphide mineral phase to the organic matter ('Biofloc' plus 'Soluble'), for Ni at pS 15.5, Zn at pS 18.6, Cd at pS 19.3 and Cu(I) at pS >20.

A pS >20 would be unlikely to occur in any environment with sufficiently low pe for Cu to be in the Cu(I) oxidation state, so it is unlikely that Cu(I) activity would ever be controlled by the organic matter.

Figure 10.5 shows that at the pS associated with the onset of heavy metal toxicity to the digestion process (pS 17), it is only the activity of Ni that is not controlled by its mineral sulphide phase. The activity of Zn will still be 2 log units below the value that it would be fixed by organic complexation, and the activity of Cu will still be very low. This, together with the fact that Ni is complexed much less strongly by the organic matter than the other heavy metals, indicates that total concentration of Ni is particularly important in assessing a 'sick' digester.

3. Oxidation

In the first of the three brief exploratory studies of the later stages of the strategy (p 227), the effects of oxidising an anaerobic sludge were examined. Work is currently under way to predict the overall speciation across the entire pe range (-4.5 to 13.6) as sludge is slowly oxidised. This work is slow because of the care needed to select the correct set of minerals to be considered in each case and to skirt around data-sets on which SCRAM fails to converge. All the programs described in chapter 8 either fail to converge or crash occasionally when asked to produce a set of runs such as these - SCRAM is more resilient than most.

Full oxidation of the sludge was simulated by running the model with all the primary components that could exist in more than one oxidation state in their most oxidised state: Fe as Fe(III), Cu as Cu(II), and S as SO_4. This state represents the end-member of a range of runs. In this preliminary study, the pe was left undefined; this has the unfortunate side-effect of preventing SCRAM from considering redox minerals such as Fe_3O_4. This is because either Fe(II) or Fe(III) can be specified as a component in SCRAM, but not both. SCRAM's database contains constants for all Fe(II) species in terms of Fe(III) and an electron and vice versa. The pe of water in equilibrium with atmospheric oxygen (pO_2 = 2.1e-4 kilobars) at pH 7 and 25°C is 13.6 (Stumm and Morgan, 1981).

The model currently only considers Mn in the Mn(II) oxidation state; Mn oxidation has not yet been considered because of the extra complications it will introduce.

The pH was left at 7.4, although in practice the pH of sludge falls as it oxidises.

Table 10.1. Summary of speciation of oxidised sludge*

Component	Percent	Name
Barium	99.6	Barite
Cadmium	99.4	Biofloc
Calcium	59.0	Biofloc
	9.4	SOM(1)
	17.0	Apatite
	2.6	Fluorapatite
Cobalt	89.0	Biofloc
	7.2	SOM(1)
Copper	99.1	Biofloc
	0.9	SOM(2)
Iron	100.0	Haematite
Lead	0.4	SOM(1)
	18.0	SOM(2)
	81.5	$PbSO_4$ (soln)
Manganese	29.3	Biofloc
	69.6	$MnHPO_4$ (s)
Nickel	2.0	Ni^{++} (soln)
	88.5	Biofloc
	0.3	Exchanged on clay
	8.7	SOM(1)
Zinc	0.7	Zn^{++} (soln)
	97.2	Biofloc
	2.0	SOM(1)
Biofloc	40.9	Uncomplexed
	1.0	Cu
	1.8	Zn
	45.1	Ca
	10.9	Mg
SOM(1)	2.6	Uncomplexed
	91.4	Ca
	5.3	Mg
SOM(2)	98.9	Uncomplexed
	0.3	Cu
	0.9	Pb

* Species accounting for more than 0.1% of the primary component

When the model was run without solid precipitation allowed, and without pe being defined, the program found 54 possible minerals. Of these, the model suggested that 12 were, to varying degrees, oversaturated.

When the model was run with solid precipitation allowed, it predicted only 5 precipitates: apatite, fluorapatite, $MnHPO_4$, barite ($BaSO_4$), and haematite (Fe_2O_3).

Table 10.1 presents a summary of the speciation results showing all the species that accounted for more than 0.1% of a primary component.

Two important conclusions can be drawn from the predicted speciation. The first is that when sulphide precipitates are oxidised, only Fe, of the transition row cations, will remain immobilized in the mineral phase (as haematite). All the rest will be released into solution where they will be mostly complexed by organic material ('Biofloc' plus 'Soluble').

The model predicts that when anaerobic sludge is oxidised, Fe will be released from Fe(II) sulphides to reprecipitate as fresh Fe(III) oxides and hydroxides. Bruemmer et al (1988) state that heavy metals are coprecipitated with Fe and also adsorbed onto the surface but then become occluded both by the precipitation of fresh Fe and also by diffusion into the grain. This is shown by the hysteresis of adsorption and desorption of heavy metals on Fe oxides and might lead to the long-term loss of heavy metals in sludged soils to extractable fractions. Tiller et al (1984) showed that adsorption of heavy metals by clays and goethite might control heavy metals in the soil solution when their concentrations were too low for any of their mineral phases to precipitate.

Cd is known to be adsorbed on calcite at low Cd concentrations, but to form a solid-solution at higher concentrations (Papadopolous and Rowell, 1988). This means that while Cd is controlled by greenockite in the digester, in oxidised environments, where there is insufficient Cd for $CdCO_3$ to precipitate, Cd might still be removed to the mineral phase with calcite.

The question this leaves is "what proportion of the heavy metals released on oxidation of the sludge will be removed to the mineral phase?". The heavy metal content of Fe oxide and sulphide grains analysed under the SEM microprobe was presented in figure 5.7. It showed that the Fe grains that contained negligible quantities of sulphide could also contain a few percent of heavy metals. A computer model of sludge leaving the digester for more oxidised environments will have to consider both reversible adsorption on Fe oxides and diffused/occluded heavy metals which should be treated as a precipitate. The model in its current state does not allow for this and should therefore be used with caution when speciating sludge in oxidised environments.

The second conclusion is that the organic material in sludge has more than sufficient complexation capacity to take up all the transition row cations, and Pb, Hg and Cd in an average sludge.

Although the SOM(1) sites form stronger complexes with the heavy metals than the 'Biofloc' does, the model predicts that most of the heavy metals will be complexed by the 'Biofloc' because of its greater concentration. This would suggest that, even after the sulphide precipitates have been oxidised, the heavy metals might still be removed efficiently by sedimentation of the 'Biofloc' fraction.

4. Sludged soil

The next exploratory study involves a system in isolation from the solid phase with which it is in equilibrium.

In table 1.2 it was shown that TWA disposes of 47% of its sludge by spreading it on farmland. As discussed (pp 9 - 11), the eventual aim of this project was to produce a working model of sludge in soil that would be of use to those responsible for sludge disposal. The first stage has been to produce a model of sludge in the digester. Nevertheless, the model has been used to take a preliminary look at sludged soil.

Detailed analyses of a soil solution extracted from sludged plots have been presented by Campbell and Beckett (1988). The soil was a typical argillic brown earth of the Sutton series. Different plots had received additions of digested sludge from TWA's Sandford works of 0, 150 (treatment S1) and 330 (treatment S2) tonnes dry matter ha^{-1} in 1978 (S1 and S2 are equal to 2 and 4.5 times the ADAS recommended 30 year limit) 7 years before the soil solution was extracted for measurement. In the meantime, it had been cropped with perennial Ryegrass.

The soil solution was extracted from soil sampled from a depth of 0-20 cm (Campbell, 1985). Where the addition of sludge had a significant effect on the solution concentration of an element, the figures to be used were taken from the plot which had received the heaviest application of sludge (treatment S2). Where the addition of sludge had not affected the concentration of an element significantly, the concentrations used were the mean of the two treatments, (S1 and S2). The pH of the top-soil was 6.5. The carbonate concentration was calculated by opening the system to the

atmosphere with a partial pressure of CO_2 of 3.17e-7 kilobars (SCRAM uses kilobars as the units for the partial pressure of gases since it is designed to model systems at high pressures as well as at high temperatures).

Unfortunately, there was no direct information on the redox state of the soil. However, it contained considerable quantities of Fe(III) oxides and no gleying so the system was treated as fully oxidised and pe was left undefined. The temperature was fixed as 5°C (although some constants in the data base are for 25°C, this is only a preliminary study).

Table 10.2 Data set for sludge/soil interaction

Treatment S2		Treatment S1 & S2	
Element	Concentration moles litre-1	Element	Concentration moles litre^{-1}
Mg	8.55e-5	Na	3.35e-4
Ca	1.24e-3	K	4.09e-4
Fe	5.17e-5	Mn	1.58e-6
Cu	1.30e-6	Ni	2.30e-7
Zn	2.00e-6	Cl	8.29e-4
Ba	2.20e-7		
SO_4	4.65e-4		
PO_4	9.60e-5		
NO_3	2.80e-3		
Biofloc	4.69e-4		

(taken from Campbell and Beckett, 1988)

The soluble organic matter was calculated from the DOC (measured as 4.1e-3 moles litre^{-1}) to be 0.084 gm litre^{-1}, and was taken to be equivalent to the 'Biofloc' fraction for the purposes of calculating the speciation since this has a lower complexation capacity than the 'Soluble' fraction and might be more representative of soil organics.

Since, by definition, there were no solids present in the system, solid precipitation was not considered and the program was asked to produce a list of all the mineral phases whose ion-activity products (IAP) exceeded their solubility products. The results of speciating this data-set are presented in full in appendix 4.

Table 10.3 Speciation of heavy metals in soil solution

Cation	Percent	Species
Cu	50	Biofloc
	45	$Cu^{++}_{(soln)}$
	2	$CuSO_{4(soln)}$
Zn	96	$Zn^{++}_{(soln)}$
	3	$ZnSO_{4(soln)}$
Ni	97	$Ni^{++}_{(soln)}$
	3	$NiSO_{4(soln)}$

Table 10.3 summarises the speciation results for the heavy metals. The model predicts that at the low concentrations of heavy metals found in the soil solution they will mostly be in the form of free cations (pCu=6.4, pZn=5.9 and pNi=6.8), and that only Cu will

be complexed by the organic matter to any significant degree. The calculated Fe activity is very surprising (pFe=9.9), which is far higher than can be explained by equilibrium with any Fe solid phase. Precipitation of magnetite would lower pFe to 17.3, and equilibrium with the 'soil-Fe' defined by Lindsay (1979) would lower pFe to 16.8 at pH 6.5. My 'Solution' fraction (see table 3.3) also has a very high level of Fe. Cameron and Liss (1984) have shown directly that humic substances are capable of stabilizing 'dissolved' Fe at concentrations several orders of magnitude above that expected, but that simple anions were not capable of doing so. This might indicate that the solutions, which were separated by displacement and centifugation, still contain significant quantities of colloidal Fe. It is likely that the 'Solution' fraction, as defined in chapter 3, will also contain fine colloidal Fe.

The ultimate question that a future model of sludge will have to answer is "what is the eventual fate of the heavy metals in the soil?". There were only five minerals whose IAPs exceeded their solubility products; three of these were Fe minerals: haematite (Fe_2O_3), $Fe(OH)_3$ and $FePO_4$. (Magnetite (Fe_3O_4) was not considered because no redox potential was defined, but it would probably have been stable). $MnHPO_4$ was also moderately oversaturated, and barite ($BaSO_4$) was slightly oversaturated. The IAPs of a further seven minerals were within an order of magnitude of their solubility products: apatite, octa-Ca phosphate, brushite, tenorite (CuO), malachite ($CuCO_3(OH)_2$), witherite ($BaCO_3$), and gypsum ($CaSO_4$).

It is interesting to note that when this data-set was run at 25°C (as it would be, for example, on GEOCHEM), barite was predicted to be undersaturated.

Lindsay (1979) suggests that soil Cu may be controlled by cupric ferrite ($CuFe_2O_4$), and soil Zn by franklinite ($ZnFe_2O_4$). These two soil minerals were not included in the model of the digester.

$$Cu^{++} + 2Fe^{+++} + 4H_2O = CuFe_2O_4 + 8H^+ \qquad \text{Log K} = -10.13$$

$$Zn^{++} + 2Fe^{+++} + 4H_2O = ZnFe_2O_4 + 8H^+ \qquad \text{Log K} = -9.85$$

Comparison of the predicted activities of Cu, Fe and Zn and the solubility products of cupric ferrite and franklinite shows that they are both grossly oversaturated. If the activity of Fe was fixed by precipitation of magnetite, then at pH 6.5, precipitation of cupric ferrite would fix pCu at 7.2, and precipitation of franklinite would fix pZn at 7.5. (These figures are highly pH-dependent: an increase of 0.1 pH unit would increase pCu and pZn by 0.8).

It is known from digimaps of embedded samples that heavy metals associate with Fe concretions in these soils (P Beckett, pers comm). Substantial additional experimental work is obviously needed before the model can be applied to soils. In particular, adsorption of the heavy metals on soil minerals, particularly Fe oxides, Fe hydroxides, carbonates and clays, would have to be described in a form suitable for inclusion in a computer program (see previous study).

Table 10.4 Composition of sea water and trial data set

Cation	Sea water		Average sludge	Data set
	mg litre^{-1}	moles litre^{-1}	moles litre^{-1}	moles litre^{-1}
Na	10,770	4.68e-1	7.93e-3	4.63e-1
Mg	1,290	5.38e-2	5.00e-3	5.33e-2
K	399	1.02e-2	1.92e-3	1.01e-2
Ca	412	1.03e-2	3.06e-2	1.05e-2
Cl	19,354	5.45e-1	2.54e-3	5.40e-1
SO_4	2,712	2.83e-2	1.30e-3	2.80e-2
F	1.3	6.80e-5	1.58e-4	6.89e-5
P	0.062	2.00e-6	3.68e-3	3.88e-5
Mn	8.4 pM	3.98e-9	1.27e-4	1.27e-6
Fe	7.5	3.17e-8	5.36e-4	5.39e-6
Co	9.1	7.94e-10	8.47e-6	8.54e-8
Ni	7.6	2.51e-8	3.60e-5	3.85e-7
Cu	8.1	7.94e-9	3.94e-4	3.95e-6
Zn	4.9	1.26e-5	7.27e-4	1.97e-5
Ag	9.4	2.98e-10	2.55e-5	2.55e-7
Cd	9.0	1.00e-9	3.57e-6	3.67e-8
Ba	6.8	1.58e-7	9.13e-5	1.07e-6
Hg	9.8	1.58e-10	7.46e-7	7.62e-9
Pb	9.7	2.00e-10	6.52e-5	6.52e-7
Biofloc (including SOM)			9.00e-2	9.00e-4

5. Sludge disposal in sea-water

Thames Water disposes of 37% dry weight of its sludge by dumping it in the North Sea (Table 1.2). The last exploratory study uses the model to present a preliminary look at the speciation of sludge in sea-water.

A data-set for the model was calculated on the basis that the 'average' sludge was diluted 1/100 in sea-water. The concentrations of the major elements already present in sea-water were taken from Stumm & Morgan (1981), and based on a salinity of 35 gm kg^{-1} of dissolved inorganic material.

- The carbonate concentration was calculated by opening the system to the atmosphere with a partial pressure of CO_2 of 3.17e-7 kilobars. The pH was fixed at 8.2 which is normal for sea-water. The temperature was fixed at 5°C.

The pe was left undefined and it was assumed that all Fe would be Fe(III), that all Cu would be Cu(II) and that all inorganic S would be SO_4.

This might not be realistic as concentrated sludge deposition might reduce the sea-bed to euxenic conditions by consuming all the O_2 or oxidised forms.

The characterisation of the organic matter was simplified by taking all the organic matter in sludge to be 'Biofloc' and assuming that there had been no further organic matter in sea-water. Later, this must be taken account of.

This data-set was run twice, first with solid precipitation disallowed, then with it allowed. With the relatively low dilution here and the relatively high pH of sea-water, 14 minerals were predicted to be oversaturated, and 14 more were within an order of

magnitude of their solubility products - these are listed in table 10.5. The predicted mineral phase is dominated by phosphates, oxides and hydroxides.

When this data-set was run with solid precipitation allowed, the model predicted that only Cu of the heavy metals would be precipitated, with 80% being removed as tenorite (CuO). Virtually all of the Fe would also remain in the mineral phase as haematite.

Table 10.5 Oversaturated and near-saturated mineral phases

Oversaturated	Near saturated
Apatite	Smithsonite
Fluorapatite	Mg phosphate
$MnHPO_4$	Brushite
Fe (III) hydroxide	Octa-Ca phosphate
Calcite	Cu phosphate
Aragonite	Cu hydroxide
Dolomite	Zn hydroxide
Magnesite	Brucite
Barite	Anhydrite
Witherite	Gypsum
Haematite	Fluorite
Tenorite	Sellaite
Fe(III) phosphate	Rhodachrosite
Malachite	Azurite

If solids are not considered, the predicted speciation of the solution bears some resemblance to the results for the previous study. Of the heavy metals, only Cu is organically complexed to a significant extent (45%), while negligible quantities of Ni and Zn are complexed organically; 52% of the Ni and 83% of the Zn but only 8% of the Cu remain in solution as free cations. This gives predicted values of pCu 7.2, pZn 5.5 and pNi 7.4. If tenorite precipitation were to happen, this would increase pCu to 8.7. At the high pH of sea-water, 43% of the Cu is predicted to complexed by carbonate. However, the $CuCO_3^o$ complex is less stable at higher temperatures, and when the model was run at 25°C, only 7.5% was preedicted to be complexed by carbonate and 90% was complexed organically.

The chemistry of minor elements in the sea has been reviewed by Bruland (1983), who states that Ni is believed to exist primarily as the free cation, Cu as organic, carbonate and hydroxide complexes, and Zn as the free cation and as hydroxide and carbonate complexes.

Mantoura et al (1978) isolated humic materials from fresh-water and from sea-water, measured their complexation constants and used the program HALTAFALL (Ingri et al, 1967) to build a model of heavy metal speciation in natural waters. Their model predicted that while 90% of the Cu in fresh-water may be complexed organically, only 10% would be in sea-water because of competition from Ca and Mg. They came to the same conclusion as I did, that apart from Cu, none of the transition row cations will be complexed organically to any significant extent in sea-water.

Cadmium, which has been causing concern to marine environmentalists, is predicted to be mobilized entirely in the form

of inorganic complexes. The model predicts that 10% of the Cd will exist as the free cation, 90% as various chloro complexes, and 0.04% will be complexed organically.

Bruland (1983) states that in the sea Cd is believed to exist primarily as chloro complexes. But Abdullah et al (1972) showed that while there is 4.2 µg litre^{-1} in the Avon estuary, there is less than 0.2 µg litre^{-1} in the Irish sea, and suggested that Cd is rapidly removed to the sediment. Moore and Ramamoorthy (1984) state that in fresh-water 90% of the Cd exists as the free cation and 3% is complexed organically, but in estuarine-water only 1% is complexed organically.

The predicted results might be taken suggest that the majority of the heavy metals in sludge dumped in the sea will, at this level of dilution, eventually be mobilized in solution where they may be toxic to marine life. However, it is unlikely that much of the dumped sludge would ever come to equilibrium with sea-water before being buried under sediments.

As with the previous two studies, the model in its currrent form does not consider the role of adsorption on hydrous Fe and Mn oxides; this has been shown to have a significant effect on heavy metals in sea-water (Jenne, 1968).

Conclusion

The speciation of the 'average' sludge in chapter 9 showed that the model in its current state forms a useful description of heavy metal chemistry in the digester. The first two studies in this chapter presented the results of using the model to predict the effect of changing the concentration of a major component and of a

master variable.

Time has not been available to check these predictions experimentally. Ideally, the model's predictions should be tested against real sludges and the results used to fine-tune the model.

I designed the fractionation scheme outlined in chapter 3 to be simple enough to use quickly with any sludge. While it may be possible to find working digesters with a reasonable range of concentrations of key components, using sludges from a variety of digesters would introduce extra variables and it would be difficult to work on the chemistry of 'sick' or poisoned digesters in this way. Validation should probably be carried out using bench digesters under controlled conditions, despite the problems in obtaining sufficient 'Particulate' fraction for SEM and XRD analyses.

Such validation could be used to adjust the solubility products used for some of the solids to allow for the fact that solids precipitating in the digester are unlikely to be either pure or perfectly crystalline. It is preferable that the model should reflect reality rather than pure test-tube chemistry.

FINAL CONCLUSION

The ultimate aim of the research, of which this project was the first step, was to develop a working chemical model of heavy metal pollutants in sludged soil. This first step was to identify the forms of combination of the heavy metals in the digester. Once their forms of combination are known, the subsequent changes in them can be followed as the sludge leaves the digester, becomes oxidised, and interacts with the soil environment. These later steps have been explored in a preliminary way.

The project fell naturally into three stages:

a) devising a suitable way of fractionating sludge;

b) describing these fractions in a form suitable for inclusion in a model;

c) using the model to ascertain the overall speciation of the heavy metals in digester sludge under various circumstances.

Fractionation of sludge

A literature review had shown that sludge is highly heterogeneous and of variable composition. Since it is unlikely that different components will react with heavy metals in the same way or release them in the same form when sludge reacts with soil, progress depended upon producing defined uniform fractions to work with.

A detailed fractionation of sludge into discrete chemical components was unlikely to be either feasible or desirable. Rather, a model would require a functional fractionation of sludge that was sufficiently simple and pragmatic to be easily repeatable for any sludge with which people wished to use the model.

The review had shown that the heavy metals were likely to be held in three pools:

a) as precipitated and detrital mineral phases;

b) as complexes with the flocculated biomass;

c) as organic and inorganic complexes in solution.

It was therefore important to separate the pools, to quantify the heavy metals held, and to ascertain the stabilities of their combined forms.

A simple three-fold separation was based upon the physical properties of the pools in water:

a) 'Particulate' fraction made up of precipitates and detrital minerals separated from sludge by elutriation, and later divided by density separation.

b) 'Biofloc' fraction holding the bulk of organic matter and clays. After removal of the 'Particulate' fraction it is separated from the 'Solution' by centrifugation. As separated, the 'Biofloc' may hold finer enmeshed minerals from which it can be freed by acid-washing.

c) 'Solution' fraction which is the clear supernatant left after removal of the 'Particulate' and 'Biofloc' fractions.

It was shown that any further physical or chemical treatments were more likely to create artefacts than to purify the separates.

A mass balance between the fractions showed that in a typical urban sludge the 'Particulate' fraction held only 5-16% of the heavy metals, but contained them in the highest concentration. The high concentrations in the fractions of highest density supported the view that they were present as sulphides or oxides. The 'Biofloc' was shown to hold 82-94% of the heavy metals, but the mass balance

could not indicate whether they were held there as finer mineral phases or as organic complexes.

Mineral phases present in the digester

The 'Particulate' fraction was examined by XRD and SEM. Both techniques had been used separately before, but they are more effective if used in a complementary way. XRD positively identifies mineral phases which are relatively crystalline and present in significant quantity, while the analytical SEM can show associations of elements which are not crystalline or are present in smaller quantities.

The development of a 'float/sink' density separation procedure allowed significant quantities of the rarer sulphide grains to be concentrated, and their XRD spectra observed free from masking by more common detrital soil minerals. The use of solvent washing was shown to obviate the need for surfactants in the density separation procedure, reduce the background noise on microprobe analyses, and improve identification of discrete mineral phases with the ZAF:PB software.

Thirty-four minerals were identified by XRD in the 'Particulate' fraction; many of these were detrital soil minerals, clay fillers or industrial abrasives. Eleven minerals were also identified in samples of the 'Biofloc' which had been treated with clearing agents.

The SEM was used to identify mineral phases that had precipitated in the digester as secondary coatings on detrital grains or as cements binding aggregates. They included calcite, calcium phosphates, and various sulphides. Other precipitates were identified by comparing the XRD data for raw sludge with those of

digester sludge. Siderite ($FeCO_3$), which had been predicted by Mosey, was identified in this way.

The heavy metal sulphides were often amorphous and were divided into three types on the basis of the cation associations observed under the SEM:

1) Fe, Cu, Zn, Ni, Mn

2) Pb, Ba, Sn, Ag, Fe

3) Cr only

However, several of them were sufficiently crystalline to confirm the presence of eight known Zn, Cu, CuFe and Fe sulphides by XRD. Ni sulphide was not observed, but Ni was observed as a minor component of other sulphide grains.

Organic complexation

The fractionation scheme had defined two fractions which could hold heavy metals by organic complexation.

Complexation by the 'Soluble' fraction was measured by a colleague using ion-selective electrodes (Fletcher and Beckett, Pts 1 & 2, 1987). Complexation by this fraction could be described in terms of a two-site model. Site 1 accounted for 72% of the total exchange capacity and bound all the divalent cations tested. Site 2 accounted for 28% of the total exchange capacity and bound only Cu and Pb. Of the three commonly used conventions, only the mole fraction convention gave a complexation constant that was independent of pH between pH 5.5 and 8.0. Below pH 5.5 all three gave pH-dependent constants.

The 'Biofloc' was found to interfere with the Cu ion-selective electrode sufficiently to make it unusable, so complexation constants had to be measured by a phase separation technique.

Initially, a third fraction which held heavy metals as complexes had been defined (the 'Colloid'), but the constants for the 'Biofloc' and the 'Colloid' were sufficiently close for the fractions to be aggregated. Complexation was measured for eight cations and all three of the commonly used conventions were found to give pH-dependent constants. The 'Biofloc' bound the heavy metals less tightly than the 'Solution', and had half its cation exchange capacity per gram.

Plots of the measured standard free energies of complexation against the stability parameter 'Q' gave reasonably straight lines ('Solution' r^2 = 0.886; 'Biofloc' r^2 = 0.754). Constants for cations whose complexation could not be measured directly were calculated from these.

The model

A model consists of a set of components and a database of the thermodynamic constants that describe their interactions. The model built contained 33 primary components and 2 gases (CO_2 and H_2S), together with 313 possible complexes, 42 possible exchange reactions and 129 possible precipitates. The model offers 'SOM(1)', 'SOM(2)' and 'Biofloc' as organic complexants and contains solubility products for all the relevant solids that had been observed in sludge except for ankerite, and the solubility product of chalcocite had to be used for digenite. The thermodynamic consistency of the database was improved by using data from Helgeson wherever possible and using Helgeson's equation for calculating activity coefficients.

Validation of the model

To check the validity of the model, an 'average' sludge, whose component concentrations were based on published analyses, was

defined and speciated using the model.

The model predicted that thirteen of the seventy-two possible mineral phases would precipitate. Broadly, these thirteen were those observed.

It predicted that Ca would precipitate as a mixture of apatite and calcite as observed. Fe was predicted to precipitate as a mixture of oxides and sulphides, as observed. Of the heavy metals, Cu and Zn were both predicted to precipitate as sulphides. Ni was predicted to be largely bound on the 'Biofloc'. However, the final pS was 15.9; if the total inorganic sulphur had been increased to give a realistic final pS, the model predicted that the Ni would have been removed entirely as a mineral sulphide phase.

Only Ca, Mg and Fe were predicted to be bound by the organic fractions to any significant extent. This suggests that the 84-95% of the heavy metals that separate with the 'Biofloc' are held almost entirely as fine enmeshed sulphide precipitates and that organic complexation does not play a significant role in the chemistry of the heavy metals in the digester, if normal quantities of sulphide are present.

Using the model

As further checks, five preliminary explorations were made in which the model was asked to predict the effects of changing various parameters:

1) The predicted speciation of the heavy metals was relatively unaffected by pH between pH 6 and 8; the model confirmed the importance of maintaining the pH of the digester when it is threatened by heavy metal toxicity. Conversely, it predicted that lowering the pH would help digesters threatened by excess

sulphide and lack of Fe as a nutrient.

2) Changing the total inorganic sulphur concentration confirmed that, over the pS range typical of urban sludges, the heavy metals would all be controlled by their mineral sulphide phases. However, below pS 12.5 the Fe activity, and therefore its availability as a nutrient, might be controlled by an oxide rather than by the sulphide. The model predicted that at the pS associated with the onset of heavy metal toxicity to the digester, only Ni would not be controlled by its mineral sulphide phase.

3-5) The model was used to speciate sludge in three oxidised environments. The predicted results showed that on oxidation of the mineral sulphides, only Fe would remain in the mineral phase, reprecipitated as the oxide. The bulk of the heavy metals would probably be held as organic complexes. These results emphasized that the model must eventually be expanded to consider the effects of heavy metal adsorption on Fe oxides and on or in other soil minerals.

The final conclusion

This project has produced a pragmatic working model of sludge in the digester which appears to predict the effects actually observed. The thermodynamic database describing the components and their interactions is in such a form that it could be used by anyone with one of the commonly available programs. SCRAM is unlikely to be widely available, so MINEQL probably offers the best facilities for running this model. If MINEQL were to be used, three minor changes would be required:

1) to force it to recalculate activity coefficients after precipitating each mineral phase;
2) to make it calculate the pH-dependent complexation constants for the 'Biofloc' from the pH;
3) to recalculate the SOM constants as complexation rather than as ion-exchange constants (these would also be pH-dependent);

Finally, there is an urgent need for a relatively simple model to take account of the adsorption of heavy metals on precipitating iron oxides and their loss by occlusion and by diffusion. A similar model may also be required for carbonates. Such a model could be included in MINEQL as a subroutine called by the code that handles mineral precipitation.

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SUMMARY OF METHODS

This appendix provides full details of the methods referred to in the text. It is not intended to be read as a chapter in its own right, but to be used for reference when individual details of a particular method are needed. The use of the analytical scanning electron microscope (SEM), and X-ray diffraction (XRD) are covered separately in chapter 4.

All reagents used were BDH ANALAR grade, except: sulphuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, boric acid, sodium chloride and hydrogen peroxide which were BDH ARISTAR grade. Sodium chlorite, sodium perchlorate and copper perchlorate were

supplied by Aldrich. Calcium, cadmium, chromium, manganese, nickel and zinc perchlorates and ultrapure lanthanum nitrate were supplied by Alfa. Aerosol-OT, cellulose and 18-crown-6 ether were supplied by Sigma.

All water used was double-distilled in glass stills, unless otherwise stated.

All samples were stored in polypropylene bottles before analysis.

Grade 'A' glassware was used for making standards for calibration lines; otherwise all glassware was grade 'B'.

All glassware and polypropylene bottles were washed overnight in decon and then in 10% ANALAR HCl before finally being rinsed in deionised water.

A) Elutriation

For elutriation to work, the sludge must be diluted sufficiently for the colloidal structure to break open. To separate the 'Particulate' fraction, 50 ml of sludge were diluted to a volume of 3 litres with deionised water, stirred with a glass rod and allowed to settle for one minute per 10 cm depth. The supernatant was decanted carefully by suction pump. The sediment was then resuspended and the procedure repeated twice more. This was the only fraction collected by sedimentation. Since not all the material would have an equal distance to fall, the purity of the fraction was related to the number of washings and the residual volume after decanting.

B) Centrifugation

The material defined as 'Biofloc' was pelleted by centrifugation after the 'Particulate' fraction had first been removed by elutriation. This meant that a large volume had to be processed to gain sufficient material to work with: 50 ml sludge diluted to 3 litres will typically contain 1 gm 'Biofloc' dry weight. For convenience, the cut-off point between the 'Biofloc' and the 'Colloid' was defined as the material pelleted by centrifugation at 3,500 rpm in a 250 ml polypropylene bottle for 30 minutes (in an MSE Centaur bench centrifuge). The dilution to 3 litres resulted in much of the contaminating 'Colloid' being washed out from the 'Biofloc'.

Both the 'Solution' and the 'Colloid' had to be collected from whole sludge. The 'Particulate' and 'Biofloc' fractions were both removed by centrifuging at 3,500 rpm as above. The supernatant was collected by decanting and re-centrifuged at 12,000 rpm in 100 ml polypropylene tubes for 30 minutes (in an MSE High Speed 18). This final supernatant was decanted and defined as 'Solution' and the pellet was defined as 'Colloid'. These procedures were not repeated and to avoid artefacts the fractions were not washed.

C) Drying

The 'Particulate' matter was dried by successive washing in industrial methylated spirits (IMS), acetone and ether and oven-dried from ether at 90°C for one hour. At the IMS stage the fraction was agitated on a whirlimixer for 60 seconds to break open any loose aggregates and ensure thorough drying.

D) Density separation

'Particulate' matter dried according to (C) was separated into fractions of different density by successive 'float/sink' operations. 0.5 gm of material and 10 ml of high density liquid were mixed in a 60 ml polypropylene screw-top tube by whirlimixer and allowed to stand for at least 30 minutes (Greenland and Ford, 1964), then centrifuged at 3,500 rpm for 30 minutes. The tubes were then frozen in dry ice and acetone and the 2 fractions recovered by sawing the tube in half and allowing them to melt into separate beakers. This gave a far cleaner recovery than either floating the top fraction off or removing the bottom fraction by pipette. The high density liquids used were:

trichlorotrifluoroethane	1.5 gm cm^{-3}
perchlorethylene	1.6 "
dibromoethane	2.2 "
tetrabromoethane	2.9 "
diiodomethane	3.3 "

These may be mixed to give any density required. Clerici's solution provides a still higher density (Vassar, 1925). This is a saturated solution of thallium formate and thallium malonate in water, and gives densities up to 4.5 gm cm^{-3}. The organic liquids should not be centrifuged at speeds higher than 3,500 rpm because of the danger of explosion (MSE pers comm). The advantage of drying in organic solvents is that surfactants were not necessary in the centrifugation stage, as would have been the case for 'Particulate' matter oven-dried from water. (NB: some suppliers add metallic

copper to their diiodomethane.)

E) Acid-digestion

Procedures for dissolution of samples for elemental analyses have been comprehensively reviewed by Lim and Jackson (1982). Both tri-acid and HF methods were used:

i) Tri-acid mixture was normally used for total elemental analysis. A 0.2 gm sample was added to 10 ml of 7:2:1 concentrated ARISTAR nitric:sulphuric:perchloric acids then heated in stages at 110°C, 150°C, 200°C, 250°C and 300°C to prevent the tube boiling over. The digest was held at the final temperature for 4 hours, or longer if any black colouration from undecomposed organic matter remained. The residue was taken up in 50 ml double-distilled water. $NaClO_2$ extracts (see below) tended to detonate violently with the tri-acid mixture, so a 1:1 mixture of hydrochloric and nitric acids was used for these.

ii) Hydrofluoric acid was used for samples which left an undissolved residue with the tri-acid mixture. To a 100 mg sample in a tared 250 ml polypropylene bottle were added 2 ml each concentrated ARISTAR nitric and hydrochloric acids and 10 ml 48% ARISTAR hydrofluoric acid. The bottle was shaken for 48 hours at room temperature; if any residue still remained it was heated to 75°C for 1 hour and then cooled. 100 ml saturated ARISTAR boric acid was then added and the bottle shaken for 1 hour to dissolve metal fluorides as soluble borofluorides and to quench any gaseous SiF_4, which would be corrosive. Finally the bottle was diluted to 200 gm tared weight.

Blank digests were performed for both methods, but no detectable levels of relevant cations could be measured.

F) Heavy metal analysis

1) Atomic absorption spectroscopy (AA)

For the mass balance and during the development of the fractionation procedure most samples were only analysed for Fe, Cu, Zn, Ni and Cd. These were done on a Varian AA-6 atomic absorption spectrometer, as were the Ca, Pb, Co, Mn and Cr analyses for the equilibrium binding experiments.

The problems of using AA to analyse samples containing heavy metals in complex matrices have been discussed by several authors (Mubarak et al, 1980; Sterritt and Lester, 1980; Webster, 1980). While AA does not suffer from interferences to the same extent as flame emission spectroscopy, care must be taken to prevent problems occuring.

Since the wave lengths at which the elements absorb are well defined there is little possibility of 2 elements absorbing at the same wavelength, so AA is free from spectral interference. However, anionic interference can be a problem. Oxygenated anions like phosphate, sulphate and nitrate depress the analysis of the alkaline metals in an air/acetylene flame, by forming relatively stable compounds, and thereby depressing the formation of free cations. This can be overcome by changing to the hotter nitrous oxide/acetylene flame (an option which was not available to us), or by the use of a high concentration of a releasing agent like lanthanum. These work by preferentially forming stable compounds with the interfering anion. Lastly, the light scattering by particles in the flame can interfere. This can be corrected for automatically, for wavelengths between 193.7 nm (As) and 357.9 nm (Cr), by the use of a hydrogen continuum lamp. The beam from this

lamp is combined by a partially silvered mirror to coincide exactly with the path from the lamp for the element in question. The analytical signals from the 2 lamps are electronically separated, and the information used to correct the final absorbence measurement.

Readings were analysed against standards made from BDH spectrosol reagents diluted in a suitable background matrix:

1) acid-digests - 1% ARISTAR sulphuric acid
2) equilibrium solutions - 0.1 M $NaClO_4$
3) acid washes - 0.1 M ARISTAR hydrochloric acid
4) calcium analyses - 10,000 ppm lanthanum (the BDH $LaCl_3$ solution adds 0.25 ppm Ca to the sample)

The accuracy of AA readings was affected by a number of factors:

1) accuracy of standards
2) precision of measurement
3) accuracy of interpolation between points on the calibration line
4) linearity of the calibration line
5) satisfactory matching of standards and sample matrices

In order to improve the accuracy of readings, I devised a method of using a BBC micro-computer to read the analogue output from the AA via a 10 bit A/D converter. First a minimum of 5 standards, read in duplicate from 3 second integrations of the absorption signal, were taken and a least squares procedure was used to calculate first and second order lines. The machine was then

tuned until the discrepancy of the first order constant of the two lines was less than 1% (ie until the calibration line was straight). The constant from the first order line was then used to calculate the concentration of unknowns. Each of the unknowns was measured in triplicate using 10 second integrations of the absorption signal. The A/D converter used had an inherent accuracy of 1 in 1024, ie 0.1%. The inherent precision of the machine was around 0.5% rsd, and the overall accuracy of the measurements was better than 5%.

2) Inductively-coupled plasma spectroscopy (ICP)

When analyses of elements that were not available on the AA were needed, these were measured by inductively-coupled plasma spectroscopy (ICP), courtesy of Duncan Campbell, BGS Hydrogeology Research Group, Wallingford. The ICP was developed to overcome the problems of matrix interference caused by compounds stable in the flame of the AA; ICP is a form of flame emission spectroscopy (Greenfield et al, 1964; Greenfield, 1980). It had the advantage of allowing several elements to be analysed at once, and of giving straight calibration lines over concentrations varying by several orders of magnitude. The aqueous sample was first nebulised in argon, with any droplets larger than 10 um being removed by an impactor bead. The high temperature needed (6,000 to 10,000°K) was created first by an electrical discharge and then maintained by a high frequency current causing ohmic heating. The light emitted was diffracted, and the intensities at certain chosen wavelengths measured. These are compared by a mini-computer with readings from standards, and the results printed. The precision was of the order of 1% rsd, while the overall accuracy should have been better than 5%.

G) Dialysis

Fractions to be dialysed were held in 9 mm Visking tubing in a 3 litre beaker of double-distilled water which was stirred magnetically, and the water was changed every 12 hours for 5 days.

H) Ultrasonic dispersion

Material in a 60 ml polypropylene tube was treated with USD (20 kilocycles, 1 cm probe on a Mullard Ultrasonicator) for 60 seconds and then either centrifuged or left to settle before being decanted. The pellet was resuspended and the treatment repeated 3 times. The decanted supernatants were added together and freeze-dried before analysis.

I) Clearing agents

These reagents fall into two categories: those to dissolve organic matter by complexation or other reactions, and those to destroy organic matter.

i) Dissolution of organics

These reagents have been developed for use in soil studies. In this case the 'Biofloc' fraction was shaken in a 40-fold excess of one of the reagents listed below in a 250 ml conical flask for 48 hours, then re-centrifuged at 3,500 rpm for 30 minutes and the supernatant decanted. The pellets produced were used for SEM and XRD studies 11 and 12 (see appendix 5). The reagents used were:

Pyrophosphate	0.1 M, pH 8
EDTA	0.05 M, pH 7
Sodium carbonate	0.1 M
Sodium hydroxide	0.1 M
Sodium oxalate	0.2 M

ii) Destruction of organics

a) The mildest oxidising agent used was hypobromite. Bromine was slowly dissolved in an equimolar quantity of 0.1 M NaOH in an ice bucket; when kept at 4°C it remained usable for 48 hours. To a suspension of 1 gm dry weight of the material to be cleared in a water bath at 75°C, 5 ml aliquots of the reagent were added, until no further effect was observed.

b) The next in strength was chlorine dioxide. To a suspension of 1 gm dry weight of the material to be cleared, in a water bath at 75°C in a fume cupboard, 0.2 gm $NaClO_2$ and 0.5 ml 10% acetic acid were added at 1 hour intervals for 4 hours.

c) The strongest of the oxidising agents used was peroxide. To a suspension of 1 gm dry weight of the material to be cleared in a water bath at 75°C, 5 ml aliquots of 100 vol ARISTAR hydrogen peroxide were added until no further effect was observed.

d) For study 14 where the sample was not diluted in water at any point (to avoid dissolving any labile heavy metal deposits) we found the sample could be cleared while suspended in acetone, by the addition of potassium permanganate held in one of the crown ethers (18-crown-6) also suspended in acetone, at room temperature. Unfortunately, this method could leave colloidal manganese IV oxide on the surface of some of the grains, although this did not appear to have happened to the samples from study 14.

J) Carbon content

I wanted to know the residual organic content of the mineral fractions; COD analysis by dichromate oxidation would yield erroneous results because of assumptions about the oxidation state of sulphides and Fe(II) and Cu(I), (and about the carbon present).

There are a number of methods for determining the carbon conntent of samples. All involve either dry or wet combustion to CO_2. The evolved CO_2 can then be measured by gravimetric, titrimetric, spectrophotometric or gas-chromatographic techniques. The first of these two techniques suffer from interferences and the last two techniques were not easily available. A simple new method based on dry-combustion and Draeger gas analysis tubes was devised. These tubes are used for industrial 'health and safety' work, and have a sensitivity range of 0.05-6.0 mg C.

Samples were cleared of carbonates by reacting with a small quantity of 1 M HCl, then dried at 105°C before weighing. Aliquots were analyzed by heating to cherry heat in pure oxygen in a 25 ml peardrop flask, then flushing the resulting CO_2 out with more oxygen through a gas analysis tube for a standard period of time at a standard pressure. This gave a direct readout of the CO_2 formed by the length of bluish-violet colouration down the side of the tube with an accuracy of around 10%. The tubes work by reacting the CO_2 with hydrazine to form carbonic acid monohydrazide, with crystal violet as a redox indicator:

$$CO_2 + N_2H_4 = H_2N\text{-}NH\text{-}CO\text{-}OH$$

A sample of around 10-20 mg was used with the 0.01% CO_2 tubes, attached to a 25 ml peardrop flask. The system was calibrated against BDH cellulose. The length of time used for flushing and the pressure are critical as the edge of the purple colouration slowly migrates.

This system was tried with wet-combustion using dichromate but it caused a side reaction in the indicator tube.

K) Ashing

The volatile content was analysed by first drying the material at 105°C until constant weight was acheived, weighing, then heating the material in a furnace to 550°C until constant weight was again achieved. A sample size of 300 mg was used in 10 ml porcelain crucibles.

Ashing will give erroneous results with mineral fractions because many mineral forms will change weight: clays will loose water still held at 105°C and sulphides will oxidise to oxides..

L) Carbonate analysis

The carbonate content of the >3.3 gm cm^{-3} sample was analysed by adding 2 ml of 25% HCl to a 25 mg sample in a closed 50 ml peardrop flask, and flushing the liberated CO_2 out with CP grade nitrogen through a 0.1% Draeger gas analysis tube. The CO_2 content was read directly off the scale on the side of the tube, with an accuracy of 5-10% (see (J) - Carbon content). The system was calibrated against $CaCO_3$ and found to give a recovery rate of 90%.

The CP grade nitrogen was checked for CO_2 content by flushing through a tube for 1 hour; no colouration was detectable.

COMPARISON OF SLUDGE DISPOSAL GUIDELINES

The guidelines drawn up to allay farmers' fears about possible ill-effects of the sludge they were taking have been described in chapter 1 (pp 6-8). This appendix provides a brief comparison of the precise recommendations showing how they changed between successive guidelines. The possible ill-effects of sludge fall into 2 broad categories of short and long term.

Short-term problems

The short-term problems include water pollution, public nuisance, disease, toxicity to grazing animals from ingestion of sludge on herbage, and phytotoxicity from mobile elements. Immobile elements also create a short-term problem, but as this continues in the long-term they will be discussed under that heading.

1) Water pollution

ADAS-10 - no mention

1977 - "No sludge should be applied to land close to ditches or rivers or where there is a danger of polluting sources of water supply. Untreated sludge should not be applied where it is likely to give offence to the public. Particular attention should be paid to wind direction when rain-gun spraying. Sludge should not be applied to deeply frozen ground as this increases the risk of pollution by liquid run-off" (6.1.48).

1981 - expands the discussion of water contamination which now accounts for a whole section of the guidelines: warnings are given about where an aquifer is close to the surface of highly fissured rock, and about leaving margins around fields, about heavy poorly drained soils, steeply sloping ground, saturated ground, sun-baked ground and about deeply frozen ground. The 1981 report points out that the main contaminant of water is nitrate, which is less of a problem in spring or summer.

2) Public nuisance

ADAS-10 - no mention.

1977 - restricts itself to the generalised comment quoted above.

1981 - talks about problems from tankers: damaging soil structure (3.24), noise and traffic, and physical contamination of roads (6.56). Odour is a common cause of complaints and especially a problem with cesspit waste ie untreated sewage (6.57); the effects of wind direction and ploughing are discussed.

3) Disease

ADAS-10 - no mention

1976 - gives some guidelines but says: "the risk of transmission of diseases to animals and man through the use of treated sludges cannot be entirely excluded, this risk is very low and certainly even lower than that from the use of farm slurry'.

1981 - concludes "the possibility of disease being transmitted by sewage sludge is very small" (4.5).

4) Grazing livestock

ADAS-10 - "as a general precaution livestock should not be allowed to graze fields to which sewage has recently been applied until after rain has washed the herbage clean" in the only comment.

1977 - "sludge being spread evenly ... no adverse effects on crops or livestock grazing the land. Data on the composition of grass and other crops grown on sludge-treated land are reassuring" (3.2.29).

The report refers to 2 studies on sewage farms, which suggested that increases in the metal content of food and fodder crops were likely to be small, and found only a small increase in the metal content of meat and milk (3.2.30, 3.2.37).

The recommendations suggested "animals should not be grazed until 21 days after the application of treated sludge to land.

In the case of cattle that produce milk which is not to be pasteurized, the period of delay should be 5 weeks" (6.1.40).

1981 - reiterates the view that few problems have been found to be due to grazing on sludge-treated land, while pointing out the difficulty of detection (5.19) and expands the safeguards to include a 6 month no-grazing limit for sludges that have not received a specified minimum treatment and so may contain viable tapeworm eggs (6.11).

5) Mobile elements

All 3 guidelines are unanimous in putting boron on this list but not fluorine or molybdenum. Boron is assigned an annual limit, rather than a long-term limit, which is higher for the first year than for subsequent years to allow for some retention. The only changes between reports are that a higher limit was introduced for grassland in 1976 and rescinded in 1981 owing to new evidence.

ADAS-10 - points out that cereals and potatoes are particularly sensitive to boron (para 6).

1977 and 1981 - point out that boron is principally a phytotoxin rather than a danger to man or grazing livestock.

Long-term problems

Probably the only long term problem for sludge application is the build up of immobile metals in the soil and on this there has been a shift in emphasis in successive guidelines from concern over phytotoxicity to concern over toxic metals in the human food chain, on which the 1981 report states "Cadmium gives most cause for concern".

The main problem in drawing up the guidelines was uncertainty on what happens to the metals in sludge when the sludge was mixed with soil, and particularly uncertainties about the extent to which metals in the sludge will be available to plants and whether any transformation of the metals occurs with time.

Availability and changes in availability

Initially it was assumed that any non-available metals would continue to remain non-available, and that 'availability' was adequately measured by extractants.

ADAS-10 - uses the terms 'available' and 'extractable' interchangeably without comment, and goes on to say: "where the contamination has been in the soil for a long time, say more than three years, any part of the metal that is not detected by the test for available metal probably is not and will not become available to plants" (para 4).

These guidelines also specify that the toxicity of recently contaminated soils should be assessed on their total content of

heavy metals, but that "generally ... using tests for 'available' metals would be better".

1977 - "The availabilities of trace elements in soils and their uptake by crops depend on a number of complex interacting factors relating to the elements themselves, the soil and the crop involved" (3.2.19).

"The solubility of metallic compounds in soils is low, and the proportion extracted with the chemicals normally used for estimating 'available' levels is usually below 15% of the total, and in many cases below 1%" (3.2.22).

The report goes on to discuss the effects of soil pH, CEC and organic matter content (3.2.23-25).

On the relationship between 'available' and 'extractable' it says: "the amounts available to plants are usually only small proportions of the total content. Extraction with a suitable reagent, which perfectly simulated plant behaviour in so far as the uptake of all elements was concerned, would give a true reflection of the availability of soil and sludge constituents. Since such an ideal extractant does not exist, arbitrary assessments have to be made by extracting under standard conditions ... and the concentration subsequently determined on the extract has sometimes been related by field experimentation to plant uptake of the element or crop yield response" (3.2.82).

1977 goes on to say: "It seems likely that the metals in sewage sludge to a large extent become combined with or bound to organic matter in soils, and when this decomposes the metals become available to to crops. The 'total' metals may therefore be considered as an indicator of the likely ultimate effect of sludge on crops and should be used in calculating sludge application rates" (6.1.8).

This contradicts Williams (1975) of ADAS who explained ADAS-10: "in terms of the acetic-acid-soluble zinc content of the soil, the safe level was set at 125 mg/kg and this is approximately equivalent to 250 mg/kg of total zinc in the soil which is the concentration in soil above which plant growth would be adversely affected ... this assumes that 50% of the total zinc is soluble in acetic acid. If the proportion which is soluble in acetic acid is greater than 50%, the safe addition would be lower".

1981 - the uncertainty of this relationship is further emphasised: "There is at present no certain way of predicting the metal uptake by crops from the 'total' metal analysis of soil. Attempts have been made to relate crop uptake and the 'extractable' metal analyses of soil, but these have met with varied success because the amounts of metals assimilated by crops depend on the plant, soil, metal and its form and the extractable determinations depend on the reagent used".

Additivity of effects

The other major underlying assumption is on the behaviour of toxic metals in combination. Sludge will normally contain several toxic elements. ADAS-10 states that "little is known about how Zinc, Copper and Nickel behave in combination ... there is some evidence that although the metals may affect different functions in the plant their toxic effects are additive and for the present it will be assumed that this is so".

Hence the concept of the zinc equivalent, in which the concentrations of zinc, copper and nickel are multiplied by their relative toxicities (1, 2 and 8 respectively) and added together. This concept has not changed in successive guidelines.

1977 states that "Insufficient is known of the interaction between metals in sludge applied to land but for the present it should be assumed that they are additive" (3.2.18).

1981 states "When several metals are added at the same time, as is usual with sewage sludge applications, interactions between them may occur. It may be assumed for convenience that phytotoxic effects are additive" (4.39). "There is still insufficient evidence to recommend a change ... remains a convenient and reasonable guide" (6.32).

However, 1977 did note the US proposal to change the relative toxicity of nickel from 8 to 4, which would have been closer to the results of the Lee Valley and Luddington trials. 1981 noted that the zinc equivalent concept had been dropped in the US and in

Europe, and that relative toxicities vary with soil and crop.

Recommendations

On the basis of these assumptions the following recommendations were made:

ADAS-10 "Where there is no previous contamination of the soil ... it is permissible to add to the soil zinc equivalent amounting to 250 ppm of the top soil". This refers to 'total' metal.

Where previous contamination exists, it is to be allowed for as follows:

1) if added at least 3 years before, by subtraction of available metal already in the soil from the 250 ppm allowance;

2) if added within 3 years, by subtraction of the total added.

So any contamination not detected as available after 3 years "probably is not and will not become available to plants".

1977 gives the same limit of 250 ppm total elements that can be added and the same provision for subtraction of the initial available level.

However, the 1981 report gives the same figure of 250 maximum total addition quoted as 250 kg ha^{-1}. In a second table it states that this is equivalent to increasing the extractable levels in soil by 250 ppm and that the actual net guideline is that extractable in soil must not exceed 250 ppm (6.25).

So over 3 guidelines the emphasis has changed from total in soil to extractable in soil. But 1981 still implies, but does not directly state that all the metal in sludge may be available to plants after mixing with soil.

Other considerations

1977 introduced limits for metals other than zinc, copper, nickel and boron.

1981 the only changes on these are the removal of the 'total' limit for lead, the introduction of limiting the Cd in sludges used to 20 ppm, and the introduction of a 'total' limit on fluorine (placing it in the list of immobile elements).

Factors affecting metal extractability/availability are mentioned, but only in general qualitative terms.

pH

ADAS-10 - "It must be emphasized that the degree of toxicity of metals to crops depends very greatly on the pH value of the soil ... if the soil is allowed to become acid after the level of toxic metals ... builds up, damage to crops is possible".

1977 - "Soil pH can be important as most trace elements have a lower availability to crops at high pH values", except Se and Mo.

1981 recommends maintaining pH at 6.5 for arable land, 6.0 for grassland and asking advice if pH is lower (4.36). It also warns about problems of high Mo sludge on grassland with a high pH.

CEC

1977 - "A number of soil factors can affect the behaviour of trace elements in relation to crops, especially the contents of clay and organic matter which can influence the capacity of soil to adsorb cations ... the cation exchange capacity may affect the release of metals to crops" (3.2.23).

THE THERMODYNAMIC DATABASE

This appendix contains a listing of the thermodynamic database used to define the model. SCRAM expresses the equilibrium constants in a temperature-dependent form, but few programs can make use of this innformation. In order to make the model more easily usable with other programs, the constants have been calculated and printed for 25°C, which is the standard temperature used for the databases supplied with GEOCHEM and MINEQL. The listing contains 3 sets of constants:

1) Gas solubilities
2) Solution complexes (including ion-exchange reactions)
3) Mineral phases

In contrast to most programs, SCRAM uses constants expressed in terms of OH^- rather than in terms of H^+, so care must be taken to check the number of moles of water produced or consumed before converting the constants for use with other programs.

NB:

1) The 'Soluble' fraction is denoted as SOM(1) and SOM(2), and the 'Biofloc' as BIO.
2) Please note the comment on constants for redox reactions made in chapter 8 (p 216).

GAS	REACTION EQUATION	log K
CO2(g)	CO2(g) + H2O = H2CO3	-1.46
H2S(g)	H2S(g) = H2S	-7.47
HCl(g)	HCl(g) = HCl	0.18

COMPLEX	REACTION EQUATION	log K
H+	H2O - OH- = H+	-14.00
HS-	SO4-- + 5H2O + 8e- = HS- + 9OH-	-103.80
H2S	SO4-- + 6H2O + 8e- = H2S + 10OH-	-92.87
HSO4-	S-- + 7OH- = HSO4- + 3H2O + 8e-	83.72
Fe(II)PO4-	Fe+++ + e- + PO4--- = FePO4-	20.90
Fe(II)HPO4	Fe+++ + e- + PO4--- + H2O = FeHPO4 + OH-	15.80
Fe(II)CO3	Fe+++ + e- + CO3-- = FeCO3	18.30
Fe(II)HCO3+	Fe+++ + e- + CO3-- + H2O = FeCO3+ + OH-	9.77
Fe(II)BIO2	Fe+++ + e- + 2BIO- = FeBIO2	23.68
Fe(II)F+	Fe+++ + e- + F- = FeF+	13.83
Fe(II)SO4	Fe+++ + e- + SO4-- = FeSO4	15.20
Fe(III)NO3++	Fe++ + NO3- = FeNO3++ + e-	-12.00
Fe(III)CO3+	Fe++ + CO3-- = FeCO3+ + e-	-0.10
Fe(III)H2PO4++	Fe++ + PO4--- + 2H2O = FeH2PO4++ + 2OH- + e-	-16.02
Fe(III)HPO4+	Fe++ + PO4--- + H2O = FeHPO4+ + OH- + e-	-3.74
HPO4--	PO4--- + H2O = HPO4-- + OH-	-1.65
H2PO4-	PO4--- + 2H2O = H2PO4- + 2OH-	-8.45
Fe(III)HPO4+	Fe+++ + PO4--- + H2O = FeHPO4+ + OH-	9.26
Fe(III)H2PO4++	Fe+++ + PO4--- + 2H2O = FeH2PO4++ + 2OH-	-3.02
Fe(III)(SO4)2-	Fe+++ + 2SO4-- = Fe(SO4)2-	5.38
SO4--	S-- + 8OH- = 8e- + SO4-- + 4H2O	91.79
S--	SO4-- + 4H2O + 8e- = S-- + 8OH-	-91.79
Cu(II)	Cu++ + e- = Cu+	2.62
Cu(I)	Cu+ = Cu++ + e-	-2.62
Mn(III)	Mn++ = Mn+++ + e-	-25.55
Mn(IV)	Mn++ = Mn++++ + 2e-	-51.06
Cu(II)PO4-	Cu+ + PO4--- = CuPO4- + e-	7.18
Cu(II)HPO4-	Cu+ + PO4--- + H2O = CuHPO4 + e- + OH-	-0.02
Cu(II)CO3	Cu+ + CO3-- = CuCO3 + e-	4.18
Cu(II)HCO3+	Cu+ + CO3-- + H2O = CuHCO3 + OH- + e-	-6.45
Cu(II)OH+	Cu+ + OH- = CuOH + e-	3.38
Cu(II)OH2	Cu+ + 2OH- = CuOH2 + e-	7.68
Cu(II)NO3+	Cu+ + NO3- = CuNO3+ + e-	-2.22
Cu(II)Cl+	Cu+ + Cl- = CuCl+ + e-	-2.81
Cu(II)Cl2	Cu+ + 2Cl- = CuCl2 + e-	-3.32
Cu(II)Cl3-	Cu+ + 3Cl- = CuCl3- + e-	-4.92
Cu(II)Cl4--	Cu+ + 4Cl- = CuCl4-- + e-	-7.21
Cu(II)SO4	Cu+ + SO4-- = CuSO4 + e-	-0.10
Cu(II)F+	Cu+ + F- = CuF+ + e-	-1.97
Cu(II)(NH3)++	Cu+ + NH3 = CuNH3++ + e-	-1.60
Cu(II)(NH3)++	Cu+ + 2NH3 = Cu(NH3)2++ + e-	5.17
Cu(II)(NH3)3++	Cu+ + 3NH3 = Cu(NH3)2++ + e-	8.13
Cu(II)(NH3)4++	Cu+ + 4NH3 = CuNH3++ + e-	10.32
Cu(II)(NH3)++	Cu+ + NH4 + OH = CuNH3++ + H2O + e-	6.36
Cu(II)(NH3)2++	Cu+ + 2NH4 + 2OH = Cu(NH3)2++ + 2H2O + e-	14.68
Cu(II)(NH3)3++	Cu+ + 3NH4 + 3OH = Cu(NH3)3++ + 3H2O + e-	22.40
Cu(II)(NH3)4++	Cu+ + 4NH4 + 4OH = Cu(NH3)4++ + 4H2O + e-	29.34
Cu(I)Cl2-	Cu++ + 2Cl + e- = CuCl2-	7.58
Cu(I)Cl2-	Cu++ + 3Cl + e- = CuCl3-	7.77
Cu(I)(NH3)+	Cu++ + NH3 + e- = Cu(NH3)+	8.56
Cu(I)(NH3)2+	Cu++ + 2NH3 + e- = Cu(NH3)2+	13.48
Cu(I)(NH3)+	Cu++ + NH4 + e- + OH = Cu(NH3)+ + H2O	13.35

Cu(I)(NH3)+	Cu++ + 2NH4 + e- + 2OH = Cu(NH3)+ + 2H2O	22.99
CaPO4-	Ca++ + PO4--- = CaPO4+	6.50
MgPO4-	Mg++ + PO4--- = MgPO4-	6.50
KPO4--	K+ + PO4--- = KPO4--	1.90
Fe(III)PO4	Fe+++ + PO4--- = FePO4	12.20
Fe(II)PO4-	Fe++ + PO4--- = FePO4-	7.90
MnPO4-	Mn++ + PO4--- = MnPO4-	7.20
Cu(II)PO4-	Cu++ + PO4--- = CuPO4-	9.80
ZnPO4-	Zn++ + PO4--- = ZnPO4-	8.00
NiPO4-	Ni++ + PO4--- = NiPO4-	8.40
CdPO4-	Cd++ + PO4--- = CdPO4-	6.50
PbPO4-	Pb++ + PO4--- = PbPO4-	6.50
CaHPO4	Ca++ + H2O + PO4--- = CaHPO4 + OH-	0.60
MgHPO4	Mg++ + H2O + PO4--- = MgHPO4 + OH-	1.10
KHPO4-	K+ + H2O + PO4--- = KHPO4- + OH-	-0.80
Fe(III)HPO4+	Fe+++ + H2O + PO4--- = FeHPO4+ + OH-	6.70
Fe(II)HPO4	Fe++ + H2O + PO4--- = FeHPO4 + OH-	2.20
MnHPO4	Mn++ + H2O + PO4--- = MnHPO4 + OH-	2.20
Cu(II)HPO4	Cu++ + H2O + PO4--- = CuHPO4 + OH-	2.60
CdHPO4	Cd++ + H2O + PO4--- = CdHPO4 + OH-	1.67
ZnHPO4	Zn++ + H2O + PO4--- = ZnHPO4 + OH-	1.70
NiHPO4	Ni++ + H2O + PO4--- = NiHPO4 + OH-	1.30
PbHPO4	Pb++ + H2O + PO4--- = PbHPO4 + OH-	1.50
KHCO3	K+ + H2O + CO3-- = KHCO3 + OH-	-6.03
Fe(III)HCO3++	Fe+++ + H2O + CO3-- = FeHCO3++ + OH-	-1.23
Fe(II)HCO3+	Fe++ + H2O + CO3-- = FeHCO3+ + OH-	-3.23
MnHCO3+	Mn++ + H2O + CO3-- = MnHCO3+ + OH-	-1.90
Cu(II)HCO3+	Cu++ + H2O + CO3-- = CuHCO3+ + OH-	-3.83
CdHCO3+	Cd++ + H2O + CO3-- = CdHCO3+ + OH-	-3.83
ZnHCO3+	Zn++ + H2O + CO3-- = ZnHCO3+ + OH-	-3.13
NiHCO3+	Ni++ + H2O + CO3-- = NiHCO3+ + OH-	-2.83
PbHCO3+	Pb++ + H2O + CO3-- = PbHCO3+ + OH-	-2.23
Cu(OH)2	Cu++ + 2OH- = Cu(OH)2	10.30
CuNO3+	Cu++ + NO3- = CuNO3+	0.40
CuCO3	Cu++ + CO3-- = CuCO3	6.80
ZnNO3+	Zn++ + NO3- = ZnNO3+	0.40
ZnCO3	Zn++ + CO3-- = ZnCO3	4.80
Ni(OH)2	Ni++ + 2OH- = Ni(OH)2	9.00
CaCl+	Ca++ + Cl- = CaCl+	-1.00
MgCl+	Mg++ + Cl- = MgCl+	-1.00
NiCl+	Ni++ + Cl- = NiCl	0.40
CoCl+	Co++ + Cl- = CoCl	0.40
CaF+	Ca++ + F- = CaF	0.60
NiF+	Ni++ + F- = NiF+	1.10
NiCO3	Ni++ + CO3-- = NiCO3	5.80
Pb(OH)3	Pb++ + 3OH- = Pb(OH)3	13.90
Pb(OH)4	Pb++ + 4OH- = Pb(OH)4	16.30
PbF+	Pb++ + F- = PbF+	1.30
CaNO3+	Ca++ + NO3- = CaNO3+	0.68
PbNO3+	Pb++ + NO3- = PbNO3+	1.20
PbCO3	Pb++ + CO3-- = PbCO3	7.00
CdCl3	Cd++ + 3Cl- = CdCl3	2.40
CdCl4	Cd++ + 4Cl- = CdCl4	2.60
CdSO4	Cd++ + SO4-- = CdSO4	2.50
CdCO3	Cd++ + CO3-- = CdCO3	4.10
MnCO3	Mn++ + CO3-- = MnCO3	4.50
FeCO3	Fe++ + CO3-- = FeCO3	5.30
FeNO3++	Fe+++ + NO3- = FeNO3++	1.00
FeCO3+	Fe+++ + CO3-- = FeCO3+	12.90
KCO3-	K+ + CO3-- = KCO3-	0.90

HBIO	H2O + BIO- = HBIO + OH-	-4.00
MnBIO2	Mn++ + 2BIO- = MnBIO2	10.83
CuBIO2	Cu++ + 2BIO- = CuBIO2	14.25
CuBIO2	Cu+ + 2BIO- = CuBIO2 + e-	11.63
ZnBIO2	Zn++ + 2BIO- = ZnBIO2	11.11
NiBIO2	Ni++ + 2BIO- = NiBIO2	10.68
FeBIO2	Fe++ + 2BIO- = FeBIO2	10.68
CdBIO2	Cd++ + 2BIO- = CdBIO2	11.28
CaBIO2	Ca++ +2BIO- = CaBIO2	9.89
MgBIO2	Mg++ + 2BIO- = MgBIO2	10.11
BaBIO2	Ba++ + 2BIO- = BaBIO2	8.46
CoBIO2	Co++ + 2BIO- = FeBIO2	10.40
FeBIO3	Fe+++ + 3BIO- = FeBIO3	18.86
AgBIO	Ag+ + BIO- = AgBIO	5.75
CuBIO	Cu+ + BIO- = CuBIO	6.07
CdCl+	Cd++ + Cl- = CdCl+	-1.50
CdF+	Cd++ + F- = CdF+	1.15
CdCl2	Cd++ + 2Cl- = CdCl+	-2.60
CdCl+	Cd++ + Cl- = CdCl+	-1.50
CdNO3+	Cd++ + NO3- = CdNO3+	0.11
Cd(OH)+	Cd++ + OH- = Cd(OH)+	4.08
Cd(OH)2	Cd++ + OH- = Cd(OH)2	7.70
Cd(OH)3	Cd++ + OH- = Cd(OH)3-	8.99
KCl	K+ + Cl- = KCl	-0.57
KSO4-	K+ + SO4- = KSO4-	0.84
BaOH	Ba++ + OH- = BaOH+	2.22
NaCl	Na+ + Cl- = NaCl	-1.40
NaCO3-	CO3-- + Na+ = NaCO3-	1.27
NaSO4-	Na+ + SO4-- = NaSO4-	0.53
Sr(OH)+	Sr++ + OH- = Sr(OH)+	0.82
Ca(OH)+	Ca++ + OH- = Ca(OH)+	1.23
CaCO3	Ca++ + CO3-- = CaCO3	3.20
CaHCO3+	Ca++ + CO3-- + H2O = CaHCO3+ + OH-	-5.47
CaSO4	Ca++ + SO4-- = CaSO4	2.31
Mg(OH)+	Mg++ + OH- = Mg(OH)+	2.59
MgCO3	Mg++ + CO3-- = MgCO3	3.40
MgHCO3+	Mg++ + CO3-- + H2O = MgHCO3+ + OH-	-2.79
MgSO4	Mg++ + SO4-- = MgSO4	2.25
MgF+	Mg++ + F- = MgF+	1.22
Fe(II)(OH)+	Fe++ + OH- = Fe(OH)+ +	5.71
Fe(II)(OH)2	Fe++ + 2OH- = Fe(OH)2	9.17
Fe(II)Cl+	Fe++ + Cl- = FeCl+	-0.62
Fe(II)Cl2	Fe++ + 2Cl- = FeCl2	-1.83
Fe(II)Cl3-	Fe++ + 3Cl- = FeCl3-	-4.40
Fe(II)F+	Fe++ + F- = FeF+	0.83
CrCl++	Cr+++ + Cl- = CrCl++	1.42
CrCl2+	Cr+++ + 2Cl- = CrCl2+	1.46
Fe(II)SO4	Fe++ + SO4-- = FeSO4	-2.20
Fe(III)(OH)++	Fe+++ + OH- = Fe(OH)++	11.77
Fe(III)(OH)2+	Fe+++ + 2OH- = Fe(OH)2+	20.83
Fe(III)(OH)3	Fe+++ + 3OH- = Fe(OH)3	10.02
Fe(III)(OH)4-	Fe+++ + 4OH- = Fe(OH)4-	34.10
Fe(III)Cl++	Fe+++ + Cl- = FeCl++	1.48
Fe(III)Cl2+	Fe+++ + 2Cl- = FeCl2+	2.17
Fe(III)Cl3	Fe+++ + 3Cl- = FeCl3	1.16
Fe(III)Cl4-	Fe+++ + 4Cl- = FeCl4-	-0.75
Fe(III)SO4+	Fe+++ + SO4-- = FeSO4+	-4.14
Fe(III)F++	Fe+++ + F- = FeF++	5.07
Fe(III)F2+	Fe+++ + 2F- = FeF2+	9.02
Fe(III)F3	Fe+++ + 3F- = FeF3	11.85

Fe(III)F4-	Fe+++ + 4F- = FeF4-	14.98
MnOH+	Mn++ + OH- = MnOH+	3.40
MnOH2	Mn++ + 2OH- = MnOH2	5.80
MnOH3-	Mn++ + 3OH- = MnOH3-	7.20
MnSO4	Mn++ + SO4-- = MnSO4	2.29
MnCl+	Mn++ + Cl- = MnCl+	0.04
MnF+	Mn++ + F- = MnF+	0.62
AgCl	Ag+ + Cl- = AgCl	3.31
AgCl2-	Ag+ + 2Cl- = AgCl2-	5.24
AgCl3--	Ag+ + 3Cl- = AgCl3--	5.25
AgCl4---	Ag+ + 4Cl- = AgCl4---	5.51
AgSO4-	Ag+ + SO4-- = AgSO4-	1.29
Ni(OH)+	Ni++ + OH- = NiOH+	3.36
AgNH3+	Ag+ + NH3 = AgNH3+	3.31
Ag(NH3)2+	Ag+ + 2NH3 = Ag(NH3)2+	7.21
CuCl2-	Cu+ + 2Cl- = CuCl2-	4.96
CuCl3--	Cu+ + 3Cl- = CuCl3--	5.15
Cu(NH3)+	Cu+ + NH3 = Cu(NH3)+	5.94
Cu(NH3)2+	Cu+ + 2NH3 = Cu(NH3)2+	10.86
HSO4-	SO4-- + H2O = HSO4- + OH-	-12.01
HS-	S-- + H2O = HS- + OH-	-1.08
H2S	S-- +2H2O = H2S + 2OH-	-8.08
HCO3-	CO3-- + H2O = HCO3- + OH-	-3.67
H2CO3	CO3-- + 2H2O = H2CO3 + 2OH-	-11.30
HCl	Cl- + H2O = HCl + OH-	-20.10
HF	F- + H2O = HF + OH-	-10.84
HF2	2F- + H2O = HF2 + OH-	-10.25
PbOH+	Pb++ + OH- = PbOH+	7.83
Pb(OH)2	Pb++ + 2OH- = Pb(OH)2	10.83
PbCl+	Pb++ + Cl- = PbCl+	1.59
PbCl2	Pb++ + 2Cl- = PbCl2	1.78
PbCl3-	Pb++ + 3Cl- = PbCl3-	1.67
PbCl4--	Pb++ + 4Cl- = PbCl4--	1.38
PbSO4	Pb++ + SO4-- = PbSO4	7.77
Zn(OH)+	Zn++ + OH- = ZnOH+	4.52
Zn(OH)3-	Zn++ + 3OH- = Zn(OH)3-	13.22
ZnCl+	Zn++ + Cl- = ZnCl+	-0.96
ZnCl2	Zn++ + 2Cl- = ZnCl2	0.20
ZnCl3-	Zn++ + 3Cl- = ZnCl3-	-1.44
ZnCl4--	Zn++ + 4Cl- = ZnCl4--	-1.46
ZnSO4	Zn++ + SO4-- = ZnSO4	2.38
Zn(NH3)++	Zn++ + NH3 = Zn(NH3)++	2.23
Zn(NH3)2++	Zn++ + 2NH3 = Zn(NH3)2++	4.53
Zn(NH3)3++	Zn++ + 3NH3 = Zn(NH3)3++	6.89
Zn(NH3)++	Zn++ + 4NH3 = Zn(NH3)4++	9.43
ZnF+	Zn++ + F- = ZnF+	0.65
NiSO4	Ni++ + SO4-- = NiSO4	2.32
Cu(OH)+	Cu++ + OH- = Cu(OH)+	6.00
CuCl+	Cu++ + Cl- = CuCl+	-0.19
CuCl2	Cu++ + 2Cl- = CuCl2	-0.70
CuCl3-	Cu++ + 3Cl- = CuCl3-	-2.30
CuCl4--	Cu++ + 4Cl- = CuCl4--	-4.59
CuSO4	Cu++ + SO4-- = CuSO4	2.52
Cu(NH3)++	Cu++ + NH3 = Cu(NH3)++	4.22
Cu(NH3)2++	Cu++ + 2NH3 = Cu(NH3)2++	7.79
Cu(NH3)3++	Cu++ + 3NH3 = Cu(NH3)3++	10.76
Cu(NH3)4++	Cu++ + 4NH3 = Cu(NH3)4++	12.94
CuF+	Cu++ + F- = CuF+	0.65
Hg2SO4	Hg2++ + SO4-- = Hg2SO4	1.30
HgCl+	Hg++ + Cl- = HgCl+	6.26

HgCl2	Hg++ + 2Cl- = HgCl2	13.24
HgCl3-	Hg++ + 3Cl- = HgCl3-	15.34
HgCl4--	Hg++ + 4Cl- = HgCl4--	14.91
HgSO4	Hg++ + SO4-- = HgSO4	1.40
Hg(NH3)++	Hg++ + NH3 = Hg(NH3)++	8.80
Hg(NH3)2++	Hg++ + 2NH3 = Hg(NH3)2++	17.61
Hg(NH3)3+++	Hg++ + 3NH3 = Hg(NH3)3++	18.54
Hg(NH3)4++	Hg++ + 4NH3+ = Hg(NH3)4++	19.21
HgF+	Hg++ + F- = HgF+	1.13
NH4+	NH3 + H2O = NH4+ + OH-	-4.86
NH4SO4-	NH3 + H2O + SO4-- = NH4SO4- + OH-	-12.89
BaHCO3+	Ba++ + CO3-- + H2O = BaHCO3+ + OH-	-12.53
BaSO4	Ba++ + SO4-- = BaSO4	2.31
SrCO3	Sr++ + CO3-- = SrCO3	2.84
SrHCO3+	Sr++ + CO3-- + H2O = SrHCO3+ + OH-	-12.74
SrSO4	Sr++ + SO4-- = SrSO4	2.19
CrF++	Cr+++ + F- = CrF++	5.20
CrF2+	Cr+++ + 2F- = CrF2+	8.54
CrF3	Cr+++ + 3F- = CrF3	10.02
Ni(NH3)++	Ni++ + NH3 = NiNH3++	3.05
Ni(NH3)2++	Ni++ + 2NH3 = Ni(NH3)2++	5.11
Ni(NH3)3++	Ni++ + 3NH3 = Ni(NH3)3++	6.88
Ni(NH3)4++	Ni++ + 4NH3 = Ni(NH3)4++	8.11
NH3	NH4+ + OH- = NH3 + H2O	4.75
NHSO4-	NH4+ + SO4-- = NH4SO4-	-8.14
Fe(II)	Fe+++ + e- = Fe++	12.97
Fe(III)	Fe++ = Fe+++ + e-	-12.97
Fe(II)(OH)+	Fe+++ + OH- + e- = Fe(OH)+	18.68
Fe(II)(OH)2	Fe+++ + 2OH- + e- = Fe(OH)2	22.14
Fe(II)Cl+	Fe+++ + Cl- + e- = FeCl+	12.33
Fe(II)Cl2	Fe+++ + 2Cl- + e- = FeCl2	11.14
Fe(II)Cl3-	Fe+++ + 3Cl- + e- = FeCl3-	8.57
Fe(II)SO4	Fe+++ + SO4-- + e- = FeSO4	10.77
Fe(III)(OH)++	Fe++ + OH- = Fe(OH)++ + e-	-1.20
Fe(III)(OH)2+	Fe++ + 2OH- = Fe(OH)2+ + e-	7.86
Fe(III)(OH)3	Fe++ + 3OH- = Fe(OH)3 + e-	-2.95
Fe(III)(OH)4-	Fe++ + 4OH- = Fe(OH)4- + e-	21.13
Fe(III)Cl++	Fe++ + Cl- = FeCl++ + e-	-11.49
Fe(III)Cl2+	Fe++ + 2Cl- = FeCl2+ + e-	-10.80
Fe(III)Cl3	Fe++ + 3Cl- = FeCl3 + e-	-11.82
Fe(III)Cl4-	Fe++ + 4Cl- = FeCl4- + e-	-13.72
Fe(III)SO4+	Fe++ + SO4-- = FeSO4+ + e-	-17.11
Fe(III)(SO4)2-	Fe++ + 2SO4-- = Fe(SO4)2- + e-	-22.27
Fe(III)F++	Fe++ + F- = FeF++ + e-	-7.91
Fe(III)F2+	Fe++ + 2F- = FeF2+ + e-	-3.96
Fe(III)F3	Fe++ +3F- = FeF++ + e-	-1.12
Fe(III)F4-	Fe++ + 4F- = FeF++ + e-	2.00
Fe(III)F5-	Fe++ + 5F- = FeF++ + e-	2.36
AgNH3+	Ag+ + NH4+ + OH- = AgNH3+ + H2O	8.06
CuNH3+	Cu+ + NH4+ + OH- = CuNH3+ + H2O	10.69
ZnNH3++	Zn++ + NH4+ + OH- = ZnNH3++ + H2O	6.98
CuNH3++	Cu++ + NH4+ + OH- = CuNH3++ + H2O	8.98
HgNH3++	Hg++ + NH4+ + OH- = HgNH3++ + H2O	13.56
NiNH3++	Ni++ + NH4+ + OH- = NiNH3++ + H2O	7.80
Ag(NH3)2+	Ag+ + 2NH4+ + 2OH- = Ag(NH3)2+ + 2H2O	16.72
Cu(NH3)2+	Cu+ + 2NH4+ + 2OH- = Cu(NH3)2+ + 2H2O	20.37
Zn(NH3)2++	Zn++ + 2NH4+ + 2OH- = Zn(NH3)2++ + 2H2O	14.04
Cu(NH3)2++	Cu++ + 2NH4+ + 2OH- = Cu(NH3)2++ + 2H2O	17.30
Hg(NH3)2++	Hg++ + 2NH4+ + 2OH- = Hg(NH3)2++ + 2H2O	27.11
Ni(NH3)2++	Ni++ + 2NH4+ + 2OH- = Ni(NH3)2++ + 2H2O	14.62

Zn(NH3)3++	Zn++ + 3NH4+ + 3OH- = Zn(NH3)3++ + 3H2O	21.15
Cu(NH3)3++	Cu++ + 3NH4+ + 3OH- = Cu(NH3)3++ + 3H2O	25.02
Hg(NH3)3++	Hg++ + 3NH4+ + 3OH- = Hg(NH3)3++ + 3H2O	32.80
Ni(NH3)3++	Ni++ + 3NH4+ + 3OH- = Ni(NH3)3++ + 3H2O	21.14
Zn(NH3)4++	Zn++ + 4NH4+ + 4OH- = Zn(NH3)4++ + 4H2O	28.45
Cu(NH3)4++	Cu++ + 4NH4+ + 4OH- = Cu(NH3)4++ + H2O	31.96
Hg(NH3)4++	Hg++ + 4NH4+ + 4OH- = Hg(NH3)4++ + H2O	38.23
Ni(NH3)4++	Ni++ + 4NH4+ + 4OH- = Ni(NH3)4++ + 4H2O	27.13
Ni(NH3)5++	Ni++ + 5NH4+ + 5OH- = Ni(NH3)5++ + 5H2O	32.68
NaF	Na+ + F- = NaF	-0.20
KF	K+ + F- = KF	-0.65
Na(Mont Edge)	Na+ + Mont Edge- = Na(Mont Edge)	10.00
H(Mont Edge)	H2O + Mont Edge- = H(Mont Edge) + OH-	0.00
K(Mont Edge)	K+ + Mont Edge- = K(Mont Edge)	10.20
Ca(Mont Edge)2	Ca+ + 2Mont Edge- = Ca(Mont Edge)2	24.20
Mg(Mont Edge)2	Mg+ + 2Mont Edge- = Mg(Mont Edge)2	24.20
Cu(Mont Edge)2	Cu+ + 2Mont Edge- = Cu(Mont Edge)2	24.18
Ni(Mont Edge)2	Ni++ + 2Mont Edge- = Cu(Mont Edge)2	23.60
Zn(Mont Edge)2	Zn++ + 2Mont Edge- = Zn(Mont Edge)2	24.18
Ba(Mont Edge)2	Ba++ + 2Mont Edge- = Ba(MontEdge)2	24.20
Sr(Mont Edge)2	Sr++ + 2Mont Edge- = Sr(Mont Edge)2	24.20
Na(Mont)	Na+ + Mont- = NaMont	10.00
H-Mont	H2O + Mont- = HMont + OH-	-3.50
K(Mont)	K+ + Mont- = KMont	10.20
Ca(Mont)2	Ca+ + 2Mont- = Ca(Mont)2	20.18
Mg(Mont)2	Mg+ + 2Mont- = Mg(Mont)2	20.18
MgCl(Mont)	Mg+ + Cl- + Mont- = MgClMont	12.19
Sr(Mont)2	Sr+ + 2Mont- = SrMont2	20.18
SrCl(Mont)	Sr+ + Cl- + Mont- = SrClMont	12.30
Ba(Mont)2	Ba+ + 2Mont- = BaMont2	20.18
BaCl(Mont)	Ba+ + Cl- + Mont- = BaClMont	12.35
Cu(Mont)2	Cu+ + 2Mont- = CuXMont2	20.18
CuCl(Mont)	Cu+ + Cl- + Mont- = CuClMont	12.40
Ni(Mont)2	Ni+ + 2Mont- = NiMont2	20.25
NiCl(Mont)	Ni+ + Cl- + Mont- = NiClMont	11.00
Zn(Mont)2	Zn+ + 2Mont- = Zn(Mont)2	20.18
ZnCl(Mont)	Zn+ + Cl- + Mont- = ZnClMont	13.00
Cd(Mont)2	Cd++ + 2Mont- = CdMont2	20.18
CdCl(Mont)	Cd+ + Cl- + Mont- = CdClMont	13.00
Pb(Mont)2	Pb++ + 2Mont- = Pb(Mont)2	20.18
PbCl(Mont)	Pb+ + Cl- + Mont- = PbClMont	13.00
H-SOM(1)	H2O + SOM(1)- = HSOM(1) + OH-	-4.00
Ca(SOM(1))2	Ca++ + 2SOM(1)- = Ca(SOM(1))2	10.45
Mg(SOM(1))2	Mg++ + 2SOM(1)- = Mg(SOM(1))2	10.11
Ba(SOM(1))2	Ba++ + 2SOM(1)- = Ba(SOM(1))2	10.09
Cu(SOM(1))2	Cu++ + 2SOM(1)- = Cu(SOM(1))2	11.92
Cu(SOM(1))	Cu++ + e- + SOM(1)- = CuSOM(1)	8.47
Pb(SOM(1))2	Pb++ + 2SOM(1)- = Pb(SOM(1))2	12.43
Zn(SOM(1))2	Zn++ + 2SOM(1)- = Zn(SOM(1))2	10.94
Ni(SOM(1))2	Ni++ + 2SOM(1)- = Ni(SOM(1))2	11.10
Co(SOM(1))2	Co++ + 2SOM(1)- = Ni(SOM(1))2	10.76
Mn(SOM(1))2	Mn++ + 2SOM(1)- = Mn(SOM(1))2	10.65
Fe(SOM(1))3	Fe+++ + 3SOM(1)- = Ca(SOM(1))3	17.84
Fe(SOM(1))2	Fe++ + 2SOM(1)- = Fe(SOM(1))2	10.84
Cu-SOM(1)	Cu+ + SOM(1)- = CuSOM(1)	5.57
Ag-SOM(1)	Ag+ + SOM(1)- = AgSOM(1)	5.62
Cu-SOM(1)	Cu+ + SOM(1)- = CuSOM(1)	5.85
H-SOM(2)	H2O + SOM(2)- = HSOM(2) + OH-	-4.00
Cu(SOM(2))2	Cu++ + 2SOM(2)- = Cu(SOM(2))2	11.23
Cu(SOM(2))2	Cu+ + 2SOM(2)- = Cu(SOM(2))2 + e-	8.51

Pb(SOM(2))2	Pb++ + 2SOM(2)- = Pb(SOM(2))2	11.62
Fe(II)(SOM(1))2	Fe+++ + e- + 2SOM(1)- = Fe(SOM(1))2	23.84
Fe(III)(SOM(1))	Fe++ + 3SOM(1)- = Fe(SOM(1))3 + e-	4.84

MINERAL	REACTION EQUATION	log K
CUPRITE	2Cu++ + 2e- + 2OH- = Cu2O(s) + H2O	32.72
CHALCOCITE	2Cu++ + 2e- + S-- = Cu2S(s)	50.72
Fe(III)3(PO4)2	3Fe+++ + 2PO4 + 3e- = Fe3(PO4)2(s)	72.30
Fe(III)(PO4)	Fe++ + PO4 = Fe(PO4)(s) + e-	12.80
Fe(II)O	Fe+++ + e- + 2OH = FeO(s) + H2O	57.31
Fe(III)(OH)3	Fe++ + 3OH = Fe(OH)3(s) + e-	25.02
Fe(II)(OH)2	Fe+++ + 2OH + e- = Fe(OH)2(s)	28.05
GOETITE	Fe++ + 3OH = FeOOH(s) + H2O + e-	-6.94
HEMATITE	2Fe++ + 6OH - = Fe2O3(s) + 3H2O + 2e-	53.69
SIDERITE	Fe+++ + CO3-- + e- = FeCO3(s)	25.73
MILLERITE	Ni++ + SO4-- + 4H2O + 8e- = NiS(s) + 8OH-	-68.89
GREENOCKITE	Cd++ + SO4-- + 4H2O + 8e- = CdS(s) + 8OH-	-64.72
COVELITE	Cu++ + SO4-- + 4H2O + 8e- = CuS(s) + 8OH-	-55.69
PYRRHOTITE	Fe++ + SO4-- + 4H2O + 8e- = FeS(s) + 8OH-	-73.05
TROILITE	Fe++ + SO4-- + 4H2O + 8e- = FeS(s) + 8OH-	-75.58
GALENA	Pb++ + SO4-- + 4H2O + 8e- = PbS(s) + 8OH-	-64.28
SPHALERITE	Zn++ + SO4-- + 4H2O + 8e- = ZnS(s) + 8OH-	-67.09
WURTZITE	Zn++ + SO4-- + 4H2O + 8e- = ZnS(s) + 8OH-	-69.29
CINNABAR	Hg++ + SO4-- + 4H2O + 8e- = HgS(s) + 8OH-	-39.76
Meta-CINNABAR	Hg++ + SO4-- + 4H2O + 8e- = HgS(s) + 8OH-	-40.13
ALBANITE	Mn++ + SO4-- + 4H2O + 8e- = MnS(s) + 8OH-	-78.95
CHALCOPYRITE	Fe+++ + Cu++ + 2S-- + e- = CuFeS2(s)	74.75
CHALCOPYRITE	Fe+++ + Cu+ + 2S-- = CuFeS2(s)	72.16
CHALCOPYRITE	Fe++ + Cu++ + 2SO4-- + 8H2O + 16e- = solid + 16OH-	-121.80
CHALCOPYRITE	Fe+++ + Cu++ + 2SO4-- + 8H2O + 17e- = solid + 16OH-	-108.80
CHALCOPYRITE	Fe+++ + Cu+ + 2SO4-- + 8H2O + 16e- = solid + 16OH-	-111.41
ACANTHITE	2Ag+ + 2SO4-- + 4H2O + 8e- = AgS(s) + 8OH-	-42.77
CHALCOCITE	2Cu+ + SO4-- + 4H2O + 8e- = Cu2S(s) + 8OH-	-43.25
Cu3(PO4)2	3Cu++ + 2PO4 = Cu3(PO4)2(s) + 3e-	29.84
CHALCOPYRITE	Cu+ + 2S-- + Fe++ = CuFeS2(s) + e-	59.17
CHALCOPYRITE	Cu+ + 2SO4-- + Fe++ + 8H2O + 15e- = CuFeS2(s) + 16OH-	-124.42
MALACHITE	2Cu+ + CO3-- + 2OH- = solid + 2e-	27.13
AZURITE	3Cu+ + 2CO3-- + 2OH- = Cu3(CO3)2(OH)2(s) + 3e-	31.65
Cu(II)OH2	Cu+ + 2OH- = Cu(OH)2(s) + e-	16.18
BORNITE	5Cu++ + 4S- + Fe++ + 4e = Cu5FeS4(s)	107.15
BORNITE	5Cu++ + 4S- + Fe+++ + 5e = Cu5FeS4(s)	120.16
BORNITE	5Cu++ + 4SO4- + Fe++ + 16H2O + 36e = solid + 32OH-	-259.13
BORNITE	5Cu++ + 4SO4- + Fe+++ + 16H2O + 37e = solid + 32OH-	-246.13
HAUERITE	Mn++ + 2S-- = MnS2(s) + 2e-	30.38
HAUERITE	Mn++ + 2SO4-- + 8H2O + 14e- = MnS2(s) + 16OH-	-153.20
S(Rhombic)	SO4-- + 4H2O + 6e- = S(s) + 8OH-	-76.22
S(Rhombic)	S-- = S(s) + 2e-	15.57
PYROSULITE	Mn++ + 4OH- = MnO2(s) + 2H2O + 2e-	14.11
HAUSMANNITE	3Mn++ + 8OH- = Mn3O4(s) + 4H2O + 2e-	48.97
MANGANITE	Mn++ + 3OH- = MnOOH(s) + H2O + e-	16.73
Cu3(PO4)2	3Cu++ + 2PO4--- = Cu3(PO4)2(s)	37.70
Zn3(PO4)2	3Zn++ + 2PO4--- = Zn3(PO4)2(s)	36.70
Ni3(PO4)2	3Ni++ + 2PO4--- = Ni3(PO4)2(s)	30.20
Cd3(PO4)2	3Cd++ + 2PO4--- = Cd3(PO4)2(s)	32.54
Pb3(PO4)2	3Pb++ + 2PO4--- = Pb3(PO4)2(s)	43.00
Mn3(PO4)2	3Mn++ + 2PO4--- = Mn3(PO4)2(s)	23.83
Fe(II)3(PO4)2	3Fe++ + 2PO4--- = Fe3(PO4)2(s)	33.30
Fe(III)PO4	Fe+++ + PO4--- = Fe(III)PO4(s)	25.80
Mg3(PO4)2	3Mg++ + 2PO4--- = Mg3(PO4)2(s)	23.90
MgNH4PO4	Mg++ + NH4 + PO4--- = MgNH4PO4(s)	12.60

APATITE	5Ca++ + 3PO4--- + OH- = Ca5(PO4)3OH(s)	54.35
FLUORAPATITE	5Ca++ + 3PO4--- + F- = Ca5(PO4)3F(s)	54.02
OCTA Ca-PHOSPH	4Ca++ + 3PO4--- + H2O = Ca4H(PO4)3(s) + OH-	34.20
BRUSHITE	Ca++ + PO4--- + 3H2O = CaHPO4(s).2H2O + OH-	4.91
PbHPO4	Pb++ + PO4--- + H2O = PbHPO4(s) + OH-	-1.40
MnHPO4	Mn++ + PO4--- + H2O = MnHPO4(s) + OH-	11.27
Zn HYDROXIDE	Zn++ + 2OH- = Zn(OH)2(s)	15.55
LEAD HYDROXIDE	Pb++ + 2OH- = Pb(OH)2(s)	20.70
LEAD FLUORIDE	Pb++ + 2F- = PbF2(s)	7.60
LEAD SULPHATE	Pb++ + SO4-- = PbSO4(s)	7.70
FLUORITE	Ca++ + 2F- = CaF2(s)	10.70
SELLAITE	Mg++ + 2F- = MgF2(s)	8.00
PYROCHROITE	Mn++ + 2OH- = Mn(OH)2	12.81
MANGANOSITE	Mn++ + 2OH- = MnO + H2O	10.07
MILLERITE	Ni++ + S-- = NiS	22.90
COBALT SULPHIDE	Co++ + S-- = CoS	23.25
NICKEL CARB	Ni++ + CO3-- = NiCO3	8.20
OTAVITE	Cd++ + CO3-- = CdCO3	11.30
GREENOCKITE	Cd++ + S-- = CdS	27.80
CADMIUM HYDROX	Cd++ + 2OH- = Cd(OH)2(s)	14.40
FERROUS OXIDE	Fe++ + 2OH- = FeO(s) + H2O	16.69
Fe(III) HYDROXI	Fe+++ + 3OH- = Fe(OH)3(s)	38.02
a-MAGNETITE	3Fe++ + 8OH- = Fe3O4(s) + 2e- + 4H2O	82.12
a-MAGNETITE	3Fe+++ + 8OH- + e- = Fe3O4(s) + 4H2O	121.17
LIME	Ca++ + 2OH- = CaO(s) + H2O	-4.40
PERICLASE	Mg++ + 2OH- = MgO(s) + H2O	6.64
BRUCITE	Mg++ + 2OH- = Mg(OH)2(s)	11.73
PORTLANDITE	Ca++ + 2OH- = Ca(OH)2(s)	5.37
CALCITE	Ca++ + CO3-- = CaCO3(s)	8.53
ARAGONITE	Ca++ + CO3-- = CaCO3(s)	8.37
DOLOMITE	Ca+++ + Mg++ + 2CO3-- = CaMg(CO3)2(s)	18.07
MAGNESITE	Mg++ + CO3-- = MgCO3(s)	7.91
CHALCOPYRITE	Fe++ + Cu++ + 2S-- = CuFeS2(s)	61.78
TENORITE	Cu++ + 2OH- = CuO(s) + H2O	20.34
TENORITE	Cu+ + 2OH- = CuO(s) + H2O + e-	17.72
CUPRITE	2Cu+ + 2OH- = Cu2O(s) + H2O	30.10
SYLVITE	K+ + Cl- = KCl(s)	-0.86
HALITE	Na+ + Cl- = NaCl(s)	-1.58
BARITE	Ba++ + SO4-- = BaSO4(s)	10.16
BARITE	Ba++ + S-- + 8OH- = BaSO4(s) + 4H2O + 8e-	101.96
ANHYDRITE	Ca++ + SO4-- = CaSO4(s)	4.40
GYPSUM	Ca++ + SO4-- + 2H2O = CaSO4.2H2O(s)	4.62
ANGLESITE	Pb++ + SO4-- = PbSO4(s)	7.86
WITHERITE	Ba++ + CO3-- = BaCO3(s)	13.35
SIDERITE	Fe++ + CO3-- = FeCO3(s)	12.73
RHODACHROSITE	Mn++ + CO3-- = MnCO3(s)	10.54
CERUSSITE	Pb++ + CO3-- = PbCO3(s)	13.47
STRONTIANITE	Sr++ + CO3-- = SrCO3(s)	11.44
SMITHSONITE	Zn++ + CO3-- = ZnCO3(s)	9.89
MALACHITE	2Cu++ + CO3-- + 2OH- = Cu2(CO3)(OH)2(s)	32.37
AZURITE	3Cu++ + 2OH- + 2CO3-- = Cu3(CO3)2(OH)2(s)	39.48
ACANTHITE	S-- + 2Ag+ = Ag2S(s)	35.70
CHALCOCITE	S-- + 2Cu+ = Cu2S(s)	48.10
COVELLITE	S-- + Cu++ = CuS(s)	36.04
PYRRHOTITE	S-- + Fe++ = FeS(s)	19.24
PYRITE	2S-- + Fe++ = FeS2(s) + 2e-	45.48
PYRITE	Fe++ + 2SO4-- + 8H2O + 14e- = FeS2(s) + 16OH-	-138.10
PYRITE	Fe+++ + 2S-- = FeS2(s) + e-	58.50
PYRITE	Fe+++ + 2SO4-- + 8H2O + 15E- = FeS2(s) + 16OH-	-125.08
GALENA	S-- + Pb++ = PbS(s)	28.03

SPHARELITE	S-- + Zn++ = ZnS(s)	24.82
WURTZITE	S-- + Zn++ = ZnS(s)	22.54
CINNIBAR	S-- + Hg++ = HgS(s)	52.17
METACINNIBAR	S-- + Hg++ = HgS(s)	51.82
ALBANITE	Mn++ + S-- = MnS(s)	13.99
NI HYDROXIDE	Ni + 2OH- = Ni(OH)2(s)	15.26
BUNSENITE	Ni + 2OH = NiO(s) + H2O	15.55
TROILITE	Fe++ + S-- = FeS	18.86
FE(II) HYDROXID	Fe++ + 2OH- = Fe(OH)2(s)	15.05
CU(II) HYDROXID	Cu++ + 2OH- = Cu(OH)2(s)	18.80
GOETHITE	Fe+++ + 3OH- = FeO(OH)(s) + H2O	6.06
HEMATITE	2Fe+++ + 6OH- = Fe2O3(s) + 3H2O	79.69
BARIUM SULPHIDE	Ba++ + S-- = BaS(s)	2.70
CUPRIC FERRITE	Cu++ + 2Fe+++ + 8OH- = CuFe2O4 + 4H2O	45.87

SPECIATION RESULTS FROM SCRAM

This appendix presents the output from four of the runs using SCRAM.

	Data-set	See	pH	pe	temp	page
1.	The 'average' sludge	Ch 9	7.4	-4.5	25	A4 - 1
2.	Oxidised sludge	Ch 10.3	7.4	nd	25	A4 - 19
3.	Sludge/soil	Ch 10.4	6.5	nd	5	A4 - 36
4.	Sludge/sea-water	Ch 10.5	8.2	nd	5	A4 - 45

nd - not defined

The output from SCRAM is divided into five sections:

1. Primary components - giving the total concentration, the activity coefficient and the final activity.
2. Aqueous complexed species - giving the final concentration and activity, the adjusted equilibrium constant and the activity coefficient.
3. Ion-exchanged species - giving the final concentration, the adjusted equilibrium constant, the mole fraction and the equivalent fraction.
4. List of solid phases. In (1) and (2) this is the list of solid phases which were predicted to precipitate and the quantity precipitating; in (3) and (4) this is the list of all possible solids together with the IAP/K_{sp} ratio showing whether they are under- or over-saturated.
5. Percentage breakdown of each species at equilibrium.

Sewage
Temperature 25.00 C
Pressure 0.0010000 kbar

Concentrations of Primary Aqueous Components - mol/kg

		Total	Final	Activity	gamma i	v bar
1	proton	0.0000E+00	0.4972E-07	0.3981E-07	0.80072	7.4000
2	hydroxide	0.0000E+00	0.3038E-06	0.2470E-06	0.81325	6.6072
3	barium	0.9130E-04	0.9576E-09	0.4062E-09	0.42423	9.3912
4	cadmium	0.3570E-05	0.2961E-11	0.1265E-11	0.42722	11.8979
5	calcium	0.3060E-01	0.6338E-04	0.2707E-04	0.42704	4.5676
6	cobalt	0.8470E-05	0.6624E-07	0.2845E-07	0.42952	7.5459
7	copper(I)	0.3940E-03	0.9826E-16	0.7937E-16	0.80781	16.1003
8	iron(II)	0.5360E-03	0.4005E-06	0.1720E-06	0.42952	6.7644
9	lead	0.6520E-04	0.1766E-11	0.7509E-12	0.42527	12.1244
10	magnesium	0.5000E-02	0.9645E-04	0.4151E-04	0.43042	4.3818
11	manganese(II)	0.1270E-03	0.6300E-09	0.2702E-09	0.42888	9.5683
12	nickel	0.3600E-04	0.1271E-06	0.5456E-07	0.42913	7.2631
13	potassium	0.1920E-02	0.1807E-02	0.1454E-02	0.80479	2.8374
14	sodium	0.7930E-02	0.7635E-02	0.6167E-02	0.80771	2.2100
15	zinc	0.7270E-03	0.2818E-08	0.1210E-08	0.42952	8.9171
16	chloride	0.2540E-02	0.2538E-02	0.2050E-02	0.80753	2.6883
17	fluoride	0.1580E-03	0.6469E-06	0.5269E-06	0.81459	6.2782
18	ammonium	0.1000E-02	0.9889E-03	0.7955E-03	0.80450	3.0993
19	phosphate	0.3680E-02	0.3659E-07	0.4993E-08	0.13647	8.3017
20	sulphide	0.1300E-02	0.2956E-15	0.1253E-15	0.42374	15.9021
21	mont	0.1000E-02	0.5596E-11	0.4529E-11	0.80929	11.3440
22	silver	0.2550E-04	0.1570E-09	0.1264E-09	0.80528	9.8981
23	biofloc	0.8000E-01	0.2039E-03	0.1787E-03	0.87603	3.7480
24	som(1)	0.6300E-02	0.3337E-05	0.2700E-05	0.80929	5.5686
25	som(2)	0.2700E-02	0.8355E-05	0.6762E-05	0.80929	5.1699
26	carbonate	0.1500E+00	0.2561E-03	0.1090E-03	0.42557	3.9627

Concentrations of Aqueous Complexed Species - mol/kg

		Final	log Keq	Activity	gamma c	-log a
1	HSO4-	0.4821E-14	47.7150	0.3838E-14	0.79610	14.4159
2	Fe(III)CO3+	0.5915E-15	-4.6000	0.4709E-15	0.79610	15.3271
3	Fe(III)H2PO4++	0.9900E-22	-20.5200	0.4110E-22	0.41515	22.3862
4	Fe(III)HPO4+	0.2471E-16	-8.2400	0.1967E-16	0.79610	16.7061
5	HPO4--	0.1072E-02	-1.6500	0.4449E-03	0.41515	3.3517
6	H2PO4-	0.3526E-03	-8.4500	0.2807E-03	0.79610	3.5518
7	SO4-- (redox)	0.2760E-12	55.7900	0.1146E-12	0.41515	12.9409
8	Cu(I) (redox)	0.1450E-22	-7.1200	0.6021E-23	0.41515	23.2203
9	Mn(III) (redox)	0.1736E-38	-30.0500	0.2408E-39	0.13874	39.6183
10	Mn(IIII) (redox	0.8420E-68	-60.0600	0.2353E-69	0.02795	69.6283
11	Cu(II)PO4-	0.2383E-21	2.6800	0.1897E-21	0.79610	21.7220
12	Cu(II)HPO4-	0.4690E-22	-4.5200	0.4764E-22	1.01582	22.3220
13	Cu(II)CO3	0.4076E-20	-0.3200	0.4140E-20	1.01582	20.3830
14	Cu(II)HCO3+	0.4853E-24	-10.9500	0.3863E-24	0.79610	24.4130
15	Cu(II)OH+	0.1868E-23	-1.1200	0.1487E-23	0.79610	23.8276
16	Cu(II)OH2	0.7217E-26	3.1800	0.7332E-26	1.01582	26.1348
17	Cu(II)Cl+	0.1005E-25	-7.3080	0.8005E-26	0.79610	26.0967
18	Cu(II)Cl2	0.4945E-29	-7.8220	0.5024E-29	1.01582	29.2990
19	Cu(II)Cl3-	0.3226E-33	-9.4250	0.2569E-33	0.79610	33.5903
20	Cu(II)Cl4--	0.6609E-38	-11.7080	0.2744E-38	0.41515	38.5616
21	Cu(II)F+	0.1776E-28	-6.4710	0.1414E-28	0.79610	28.8496
22	Cu(II)(NH3)2++	0.1156E-24	10.1800	0.4798E-25	0.41515	25.3189

23	Cu(II)(NH3)3++	0.1204E-26	17.8970	0.4998E-27	0.41515	27.3012
24	Cu(II)(NH3)4++	0.2100E-29	24.8380	0.8719E-30	0.41515	30.0595
25	CaPO4-	0.5368E-06	6.5000	0.4273E-06	0.79610	6.3692
26	MgPO4-	0.8233E-06	6.5000	0.6554E-06	0.79610	6.1835
27	KPO4--	0.1389E-08	1.9000	0.5767E-09	0.41515	9.2390
28	Fe(II)PO4-	0.8570E-07	7.9000	0.6822E-07	0.79610	7.1661
29	MnPO4-	0.2686E-10	7.2000	0.2138E-10	0.79610	10.6700
30	ZnPO4-	0.7591E-09	8.0000	0.6043E-09	0.79610	9.2187
31	NiPO4-	0.8595E-07	8.4000	0.6842E-07	0.79610	7.1648
32	CdPO4-	0.2509E-13	6.5000	0.1997E-13	0.79610	13.6995
33	PbPO4-	0.1489E-13	6.5000	0.1186E-13	0.79610	13.9261
34	CaHPO4	0.2108E-05	0.6000	0.2142E-05	1.01582	5.6693
35	MgHPO4	0.1022E-04	1.1000	0.1039E-04	1.01582	4.9835
36	KHPO4-	0.5754E-05	-0.8000	0.4581E-05	0.79610	5.3391
37	Fe(II)HPO4	0.5334E-06	2.2000	0.5418E-06	1.01582	6.2661
38	MnHPO4	0.8379E-09	2.2000	0.8511E-09	1.01582	9.0700
39	CdHPO4	0.1158E-11	1.6700	0.1176E-11	1.01582	11.9296
40	ZnHPO4	0.1187E-08	1.7000	0.1206E-08	1.01582	8.9188
41	NiHPO4	0.2130E-07	1.3000	0.2163E-07	1.01582	7.6648
42	PbHPO4	0.4646E-12	1.5000	0.4719E-12	1.01582	12.3261
43	KHCO3	0.5796E-06	-6.0300	0.5887E-06	1.01582	6.2301
44	Fe(II)HCO3+	0.5520E-07	-3.2300	0.4394E-07	0.79610	7.3571
45	MnHCO3+	0.1854E-08	-1.9000	0.1476E-08	0.79610	8.8310
46	CdHCO3+	0.1020E-12	-3.8300	0.8117E-13	0.79610	13.0906
47	ZnHCO3+	0.4889E-09	-3.1300	0.3892E-09	0.79610	9.4098
48	NiHCO3+	0.4397E-07	-2.8300	0.3501E-07	0.79610	7.4558
49	PbHCO3+	0.2409E-11	-2.2300	0.1918E-11	0.79610	11.7171
50	ZnCO3	0.8193E-08	4.8000	0.8322E-08	1.01582	8.0797
51	Ni(OH)2	0.3278E-11	9.0000	0.3330E-11	1.01582	11.4776
52	CaCl+	0.6969E-08	-1.0000	0.5548E-08	0.79610	8.2559
53	MgCl+	0.1069E-07	-1.0000	0.8509E-08	0.79610	8.0701
54	NiCl+	0.3528E-09	0.4000	0.2809E-09	0.79610	9.5515
55	NiCl2	0.5538E-21	-8.6100	0.5626E-21	1.01582	21.2498
56	CoCl+	0.1840E-09	0.4000	0.1465E-09	0.79610	9.8342
57	CaF+	0.7133E-10	0.6000	0.5678E-10	0.79610	10.2458
58	NiF+	0.4546E-12	1.1000	0.3619E-12	0.79610	12.4414
59	NiCO3	0.3693E-05	5.8000	0.3751E-05	1.01582	5.4258
60	Pb(OH)3	0.1130E-17	13.9000	0.8993E-18	0.79610	18.0461
61	Pb(OH)4	0.1344E-21	16.3000	0.5580E-22	0.41515	22.2534
62	PbF+	0.9917E-17	1.3000	0.7895E-17	0.79610	17.1026
63	PbCO3	0.8056E-09	7.0000	0.8183E-09	1.01582	9.0871
64	CdCl3	0.3437E-17	2.4000	0.2736E-17	0.79610	17.5629
65	CdCl4	0.2141E-19	2.6000	0.8888E-20	0.41515	20.0512
66	CdSO4	0.4094E-17	2.5000	0.1081E-18	0.02641	18.9662
67	CdCO3	0.1709E-11	4.1000	0.1736E-11	1.01582	11.7605
68	MnCO3	0.9167E-09	4.5000	0.9312E-09	1.01582	9.0310
69	FeCO3	0.3682E-05	5.3000	0.3740E-05	1.01582	5.4271
70	KCO3-	0.1581E-05	0.9000	0.1259E-05	0.79610	5.9000
71	HL	0.7001E-01	-4.0000	0.7112E-01	1.01582	1.1480
72	MnL2	0.1488E-06	10.8300	0.1512E-06	1.01582	6.8205
73	CuL2	0.7872E-17	7.1300	0.7996E-17	1.01582	17.0971
74	ZnL2	0.1318E-05	11.1100	0.1339E-05	1.01582	5.8732
75	NiL2	0.1802E-04	10.6800	0.1831E-04	1.01582	4.7373
76	FeL2	0.6061E-04	10.6800	0.6157E-04	1.01582	4.2106
77	CdL2	0.1775E-08	11.2800	0.1803E-08	1.01582	8.7440
78	CaL2	0.1217E-02	9.8900	0.1236E-02	1.01582	2.9079
79	MgL2	0.3590E-02	10.1100	0.3646E-02	1.01582	2.4381
80	BaL2	0.8617E-09	8.4600	0.8753E-09	1.01582	9.0578
81	CoL2	0.5164E-05	10.4000	0.5246E-05	1.01582	5.2802
82	AgL	0.2891E-08	5.7450	0.2937E-08	1.01582	8.5322

CuL		0.3836E-14	6.0700	0.3896E-14	1.01582	14.4093
CdCl+		0.1030E-15	-1.5000	0.8200E-16	0.79610	16.0862
CdF+		0.1183E-16	1.1500	0.9417E-17	0.79610	17.0261
CdCl2		0.1314E-19	-2.6000	0.1335E-19	1.01582	19.8745
CdCl+		0.1030E-15	-1.5000	0.8200E-16	0.79610	16.0862
Cd(OH)+		0.4720E-14	4.0800	0.3757E-14	0.79610	14.4251
Cd(OH)2		0.3809E-17	7.7000	0.3870E-17	1.01582	17.4123
Cd(OH)3		0.2341E-22	8.9900	0.1864E-22	0.79610	22.7296
Cd(OH)4		0.5821E-29	8.7100	0.2417E-29	0.41515	29.6168
KCl		0.7838E-06	-0.5733	0.7962E-06	1.01582	6.0990
BaOH		0.2076E-13	2.2166	0.1653E-13	0.79610	13.7818
NaCl		0.4933E-06	-1.4018	0.5011E-06	1.01582	6.3001
NaCO3-		0.1561E-04	1.2670	0.1243E-04	0.79610	4.9057
Ca(OH)+		0.1442E-09	1.2347	0.1148E-09	0.79610	9.9401
CaCO3		0.4589E-05	3.1988	0.4662E-05	1.01582	5.3314
CaHCO3+		0.4966E-07	-5.4728	0.3953E-07	0.79610	7.4031
Mg(OH)+		0.4988E-08	2.5879	0.3971E-08	0.79610	8.4011
MgCO3		0.1123E-04	3.4015	0.1140E-04	1.01582	4.9430
MgHCO3+		0.3686E-04	-2.7880	0.2934E-04	0.79610	4.5325
MgF+		0.4539E-09	1.2179	0.3613E-09	0.79610	9.4421
Fe(OH)+	(II)	0.2710E-07	5.7055	0.2157E-07	0.79610	7.6661
Fe(OH)2	(II)	0.1529E-10	9.1700	0.1553E-10	1.01582	10.8089
FeCl+	(II)	0.1059E-09	-0.6213	0.8432E-10	0.79610	10.0740
FeCl2	(II)	0.1052E-13	-1.8300	0.1069E-13	1.01582	13.9711
FeCl3-	(II)	0.7407E-19	-4.4000	0.5897E-19	0.79610	19.2294
FeF+	(II)	0.7698E-12	0.8300	0.6128E-12	0.79610	12.2126
MnOH+		0.2106E-12	3.4000	0.1677E-12	0.79610	12.7755
MnOH2		0.1024E-16	5.8000	0.1040E-16	1.01582	16.9828
MnOH3-		0.8110E-22	7.2000	0.6457E-22	0.79610	22.1900
MnOH4--		0.1215E-27	7.7000	0.5044E-28	0.41515	28.2972
MnCl+		0.7628E-12	0.0400	0.6073E-12	0.79610	12.2166
MnF+		0.7456E-15	0.6200	0.5936E-15	0.79610	15.2265
AgCl		0.5180E-09	3.3076	0.5262E-09	1.01582	9.2788
AgCl2-		0.1170E-09	5.2441	0.9318E-10	0.79610	10.0307
AgCl3--		0.4687E-12	5.2522	0.1946E-12	0.41515	12.7109
AgCl4---		0.5177E-14	5.5077	0.7182E-15	0.13874	15.1437
Ni(OH)+		0.3878E-10	3.3600	0.3088E-10	0.79610	10.5104
CuCl2-		0.3785E-16	4.9560	0.3013E-16	0.79610	16.5210
CuCl3--		0.2339E-18	5.1525	0.9710E-19	0.41515	19.0128
HS-		0.5264E-10	-1.0755	0.4191E-10	0.79610	10.3777
H2S		0.1644E-10	-8.0752	0.1670E-10	1.01582	10.7774
HCO3-		0.1168E+00	-3.6688	0.9299E-01	0.79610	1.0316
H2CO3		0.8591E-02	-11.2964	0.8727E-02	1.01582	2.0592
HCl		0.6361E-16	-20.1013	0.6462E-16	1.01582	16.1897
HF		0.2997E-10	-10.8383	0.3044E-10	1.01582	10.5165
HF2		0.7839E-16	-10.2483	0.6241E-16	0.79610	16.2048
PbOH+		0.1576E-10	7.8302	0.1255E-10	0.79610	10.9015
Pb(OH)2		0.3085E-14	10.8349	0.3134E-14	1.01582	14.5039
PbCl+		0.7598E-13	1.5944	0.6049E-13	0.79610	13.2183
PbCl2		0.1877E-15	1.7814	0.1907E-15	1.01582	15.7197
PbCl3-		0.3757E-18	1.6652	0.2991E-18	0.79610	18.5242
PbCl4--		0.7599E-21	1.3767	0.3155E-21	0.41515	21.5010
Zn(OH)+		0.1245E-10	4.5203	0.9908E-11	0.79610	11.0040
Zn(OH)3-		0.3802E-15	13.2197	0.3026E-15	0.79610	15.5191
Zn(OH)4--		0.6851E-35	-0.2000	0.2844E-35	0.41515	35.5460
ZnCl+		0.3425E-12	-0.9590	0.2726E-12	0.79610	12.5644
ZnCl2		0.7890E-14	0.1976	0.8014E-14	1.01582	14.0961
ZnCl3-		0.4748E-18	-1.4404	0.3780E-18	0.79610	18.4225
ZnCl4--		0.1782E-20	-1.4606	0.7396E-21	0.41515	21.1310
ZnF+		0.3553E-14	0.6468	0.2828E-14	0.79610	14.5485

143	BaHCO3+		0.6504E-19	-12.5319	0.5178E-19	0.79610	19.2858
144	NH3		0.1115E-04	4.7533	0.1132E-04	1.01582	4.9460
145	Fe(III)-redox		0.4167E-23	-17.4736	0.5781E-24	0.13874	24.2380
146	Fe(OH)++	(III)	0.2048E-18	-5.6988	0.8503E-19	0.41515	19.0704
147	Fe(OH)2+	(III)	0.3003E-16	3.3575	0.2391E-16	0.79610	16.6214
148	Fe(OH)3	(III)	0.8996E-34	-7.4530	0.9138E-34	1.01582	34.0391
149	Fe(OH)4-	(III)	0.3428E-16	16.6294	0.2729E-16	0.79610	16.5640
150	FeCl++	(III)	0.8673E-25	-15.9909	0.3600E-25	0.41515	25.4436
151	FeCl2+	(III)	0.4513E-27	-15.3035	0.3593E-27	0.79610	27.4446
152	FeCl3	(III)	0.7012E-31	-16.3180	0.7123E-31	1.01582	31.1474
153	FeCl4-	(III)	0.2279E-35	-18.2236	0.1814E-35	0.79610	35.7413
154	FeF++	(III)	0.8592E-25	-12.4051	0.3567E-25	0.41515	25.4477
155	FeF2+	(III)	0.2093E-27	-8.4574	0.1666E-27	0.79610	27.7783
156	FeF3	(III)	0.5959E-31	-5.6189	0.6053E-31	1.01582	31.2180
157	FeF4-	(III)	0.5308E-34	-2.4968	0.4225E-34	0.79610	34.3741
158	FeF5-	(III)	0.1227E-39	-2.1375	0.5092E-40	0.41515	40.2931
159	AgNH3+		0.3683E-11	8.0646	0.2932E-11	0.79610	11.5328
160	CuNH3+		0.9868E-15	10.6948	0.7856E-15	0.79610	15.1048
161	ZnNH3++		0.5622E-11	6.9845	0.2334E-11	0.41515	11.6319
162	NiNH3++		0.1673E-08	7.8040	0.6944E-09	0.41515	9.1584
163	Ag(NH3)2+		0.3292E-12	16.7151	0.2620E-12	0.79610	12.5816
164	Cu(NH3)2+		0.9363E-15	20.3713	0.7454E-15	0.79610	15.1276
165	Zn(NH3)2++		0.1273E-13	14.0388	0.5286E-14	0.41515	14.2769
166	Ni(NH3)2++		0.2172E-11	14.6169	0.9019E-12	0.41515	12.0448
167	Zn(NH3)3++		0.3297E-16	21.1514	0.1369E-16	0.41515	16.8636
168	Ni(NH3)3++		0.1462E-14	21.1443	0.6071E-15	0.41515	15.2168
169	Zn(NH3)4++		0.1298E-18	28.4459	0.5390E-19	0.41515	19.2684
170	Ni(NH3)4++		0.2815E-18	27.1280	0.1169E-18	0.41515	18.9323
171	Ni(NH3)5++		0.2005E-22	32.6800	0.8325E-23	0.41515	23.0796
172	NaF		0.2018E-08	-0.2000	0.2050E-08	1.01582	8.6882
173	KF		0.1689E-09	-0.6500	0.1715E-09	1.01582	9.7656

Concentrations of Ion Exchanged Species - mol/kg

		Final	Log Keq	Mole Fract	Equiv Fract
1	Na(Mont)	0.2793E-03	10.0000	0.4035E+00	0.2793E+00
2	H-Mont	0.5701E-08	-3.5000	0.8237E-05	0.5701E-05
3	K(Mont)	0.1044E-03	10.2000	0.1508E+00	0.1044E+00
4	Ca(Mont)2	0.1214E-03	20.1800	0.1754E+00	0.2428E+00
5	Mg(Mont)2	0.1862E-03	20.1800	0.2690E+00	0.3724E+00
6	MgCl(Mont)	0.5968E-06	12.1900	0.8623E-03	0.5968E-03
7	Ba(Mont)2	0.1822E-08	20.1800	0.2632E-05	0.3644E-05
8	BaCl(Mont)	0.8441E-11	12.3500	0.1220E-07	0.8441E-08
9	Ni(Mont)2	0.2875E-06	20.2500	0.4154E-03	0.5750E-03
10	NiCl(Mont)	0.5064E-10	11.0000	0.7317E-07	0.5064E-07
11	Zn(Mont)2	0.5428E-08	20.1800	0.7843E-05	0.1086E-04
12	ZnCl(Mont)	0.1123E-09	13.0000	0.1623E-06	0.1123E-06
13	Cd(Mont)2	0.5674E-11	20.1800	0.8198E-08	0.1135E-07
14	CdCl(Mont)	0.1174E-12	13.0000	0.1697E-09	0.1174E-09
15	Pb(Mont)2	0.3368E-11	20.1800	0.4866E-08	0.6736E-08
16	PbCl(Mont)	0.6970E-13	13.0000	0.1007E-09	0.6970E-10
17	H-Som(1)	0.1075E-02	-4.0000	0.2917E+00	0.1707E+00
18	Ca(Som(1))2	0.1502E-02	10.4480	0.4076E+00	0.4772E+00
19	Mg(Som(1))2	0.1068E-02	10.1140	0.2897E+00	0.3392E+00
20	Ba(Som(1))2	0.9888E-08	10.0900	0.2683E-05	0.3141E-05
21	Pb(Som(1))2	0.3999E-08	12.4300	0.1085E-05	0.1270E-05
22	Zn(Som(1))2	0.2062E-06	10.9350	0.5594E-04	0.6549E-04
23	Ni(Som(1))2	0.1372E-04	11.1040	0.3721E-02	0.4356E-02
24	Co(Som(1))2	0.3239E-05	10.7600	0.8788E-03	0.1029E-02

25	Mn(Som(1))2	0.2394E-07	10.6510	0.6494E-05	0.7603E-05
26	Fe(Som(1))2	0.2328E-04	10.8350	0.6315E-02	0.7394E-02
27	Cu-Som(1)	0.1521E-15	5.8510	0.4126E-13	0.2415E-13
28	Ag-Som(1)	0.1423E-09	5.6200	0.3862E-07	0.2261E-07
29	Cu-Som(1)	0.1521E-15	5.8510	0.4126E-13	0.2415E-13
33	Fe(III)(som(1))	0.5456E-18	0.3400	0.1480E-15	0.2599E-15
30	H-Som(2)	0.2692E-02	-4.0000	0.1000E+01	0.1000E+01
31	Cu(Som(2))2	0.1386E-19	4.0120	0.5149E-17	0.1030E-16
32	Pb(Som(2))2	0.5354E-08	11.6230	0.1989E-05	0.3978E-05

Concentrations of Solids - mol/kg

		Final	log Keq	ICP	SP
1	CHALCOPYRITE	0.1974E-03	54.6690	0.3440E-53	0.3440E-53
2	APATITE	0.5455E-03	54.3500	0.1522E-49	0.1522E-49
3	FLUORAPATITE	0.1574E-03	54.0210	0.3241E-49	0.3241E-49
4	MnHPO4	0.1268E-03	11.2700	0.7588E-10	0.7588E-10
5	GREENOCKITE	0.3568E-05	27.8000	0.8755E-27	0.8755E-27
6	a-MAGNETITE	0.8332E-04	73.1220	0.4657E-71	0.4657E-71
7	CALCITE	0.2417E-01	8.5302	0.1623E-07	0.1623E-07
8	WITHERITE	0.9129E-04	13.3539	0.2452E-12	0.2452E-12
9	ACANTHITE	0.1275E-04	35.6983	0.7289E-35	0.7289E-35
10	CHALCOCITE	0.9832E-04	48.1028	0.2854E-47	0.2854E-47
11	GALENA	0.6519E-04	28.0265	0.5220E-27	0.5220E-27
12	SPHARELITE	0.7255E-03	24.8192	0.8331E-24	0.8331E-24

Fixed pH

pH 7.400

Ionic strength 0.68181E-01 mol/kg

pE -4.500 Electrode Potential (Eh) -266.1 mV

The activity of water 0.99978222

****

Predictions of Density

Density of the Aqueous Phase:	1.01741844294297	-	g/cc
Density of the Solid Phase:	1.77506160142167	-	g/cc
Total Fluid Density:	1.02295246407328	-	g/cc

****

Primary Distribution of Species

barium

Uncomplexed Aqueous Species = 0.00105 %

Aqueous Complexes and Ion Exchangers

BaL2	0.00094 %
BaOH	0.00000 %
BaHCO3+	0.00000 %
Ba(Mont)2	0.00200 %
BaCl(Mont)	0.00001 %
Ba(Som(1))2	0.01083 %

Minerals

WITHERITE	99.98517 %

cadmium

Uncomplexed Aqueous Species = 0.00008 %

Aqueous Complexes and Ion Exchangers

CdPO4-	0.00000 %
CdHPO4	0.00003 %
CdHCO3+	0.00000 %
CdCl3	0.00000 %
CdCl4	0.00000 %
CdSO4	0.00000 %
CdCO3	0.00005 %
CdL2	0.04972 %
CdCl+	0.00000 %
CdF+	0.00000 %
CdCl2	0.00000 %
CdCl+	0.00000 %
Cd(OH)+	0.00000 %
Cd(OH)2	0.00000 %
Cd(OH)3	0.00000 %
Cd(OH)4	0.00000 %
Cd(Mont)2	0.00016 %
CdCl(Mont)	0.00000 %

Minerals

GREENOCKITE	99.94995 %

calcium

Uncomplexed Aqueous Species = 0.20714 %

Aqueous Complexes and Ion Exchangers

CaPO4-	0.00175 %
CaHPO4	0.00689 %
CaCl+	0.00002 %
CaF+	0.00000 %
CaL2	3.97687 %
Ca(OH)+	0.00000 %
CaCO3	0.01500 %
CaHCO3+	0.00016 %

Ca(Mont)2	0.39672 %
Ca(Som(1))2	4.90994 %

Minerals

APATITE	8.91384 %
FLUORAPATITE	2.57108 %
CALCITE	79.00057 %

cobalt

Uncomplexed Aqueous Species = 0.78202 %

Aqueous Complexes and Ion Exchangers

CoCl+	0.00217 %
CoL2	60.97230 %
Co(Som(1))2	38.24351 %

Minerals

No Minerals Present

copper(I)

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

Cu(I) (redox)	0.00000 %
Cu(II)PO4-	0.00000 %
Cu(II)HPO4-	0.00000 %
Cu(II)CO3	0.00000 %
Cu(II)HCO3+	0.00000 %
Cu(II)OH+	0.00000 %
Cu(II)OH2	0.00000 %
Cu(II)Cl+	0.00000 %
Cu(II)Cl2	0.00000 %
Cu(II)Cl3-	0.00000 %
Cu(II)Cl4--	0.00000 %
Cu(II)F+	0.00000 %
Cu(II)(NH3)2++	0.00000 %
Cu(II)(NH3)3++	0.00000 %
Cu(II)(NH3)4++	0.00000 %
CuL2	0.00000 %
CuL	0.00000 %
CuCl2-	0.00000 %
CuCl3--	0.00000 %
CuNH3+	0.00000 %
Cu(NH3)2+	0.00000 %
Cu-Som(1)	0.00000 %
Cu-Som(1)	0.00000 %
Cu(Som(2))2	0.00000 %

Minerals

CHALCOPYRITE	50.09090 %
CHALCOCITE	49.90910 %

iron(II)

Uncomplexed Aqueous Species = 0.07472 %

Aqueous Complexes and Ion Exchangers

Fe(III)CO3+		0.00000 %
Fe(III)H2PO4++		0.00000 %
Fe(III)HPO4+		0.00000 %
Fe(II)PO4-		0.01599 %
Fe(II)HPO4		0.09952 %
Fe(II)HCO3+		0.01030 %
FeCO3		0.68697 %
FeL2		11.30840 %
Fe(OH)+	(II)	0.00506 %
Fe(OH)2	(II)	0.00000 %
FeCl+	(II)	0.00002 %
FeCl2	(II)	0.00000 %
FeCl3-	(II)	0.00000 %
FeF+	(II)	0.00000 %
Fe(III)-redox		0.00000 %
Fe(OH)++	(III)	0.00000 %
Fe(OH)2+	(III)	0.00000 %
Fe(OH)3	(III)	0.00000 %
Fe(OH)4-	(III)	0.00000 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %
FeF5-	(III)	0.00000 %
Fe(Som(1))2		4.34285 %
Fe(III)(som(1))		0.00000 %

Minerals

CHALCOPYRITE	36.82055 %
a-MAGNETITE	46.63563 %

lead

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

PbPO4-	0.00000 %
PbHPO4	0.00000 %

PbHCO3+	0.00000 %
Pb(OH)3	0.00000 %
Pb(OH)4	0.00000 %
PbF+	0.00000 %
PbCO3	0.00124 %
PbOH+	0.00002 %
Pb(OH)2	0.00000 %
PbCl+	0.00000 %
PbCl2	0.00000 %
PbCl3-	0.00000 %
PbCl4--	0.00000 %
Pb(Mont)2	0.00001 %
PbCl(Mont)	0.00000 %
Pb(Som(1))2	0.00613 %
Pb(Som(2))2	0.00821 %

Minerals

GALENA	99.98438 %

magnesium

Uncomplexed Aqueous Species = 1.92895 %

Aqueous Complexes and Ion Exchangers

MgPO4-	0.01647 %
MgHPO4	0.20450 %
MgCl+	0.00021 %
MgL2	71.79394 %
Mg(OH)+	0.00010 %
MgCO3	0.22452 %
MgHCO3+	0.73712 %
MgF+	0.00001 %
Mg(Mont)2	3.72375 %
MgCl(Mont)	0.01194 %
Mg(Som(1))2	21.35850 %

Minerals

No Minerals Present

manganese(II)

Uncomplexed Aqueous Species = 0.00050 %

Aqueous Complexes and Ion Exchangers

Mn(III) (redox)	0.00000 %
Mn(IIII) (redox	0.00000 %
MnPO4-	0.00002 %
MnHPO4	0.00066 %
MnHCO3+	0.00146 %
CdSO4	0.00000 %
MnCO3	0.00072 %
MnL2	0.11720 %
MnOH+	0.00000 %

MnOH2	0.00000 %
MnOH3-	0.00000 %
MnOH4--	0.00000 %
MnCl+	0.00000 %
MnF+	0.00000 %
Mn(Som(1))2	0.01885 %

Minerals

MnHPO4	99.86060 %

nickel

Uncomplexed Aqueous Species = 0.35316 %

Aqueous Complexes and Ion Exchangers

NiPO4-	0.23874 %
NiHPO4	0.05916 %
NiHCO3+	0.12215 %
Ni(OH)2	0.00001 %
NiCl+	0.00098 %
NiCl2	0.00000 %
NiF+	0.00000 %
NiCO3	10.25836 %
NiL2	50.06502 %
Ni(OH)+	0.00011 %
NiNH3++	0.00465 %
Ni(NH3)2++	0.00001 %
Ni(NH3)3++	0.00000 %
Ni(NH3)4++	0.00000 %
Ni(NH3)5++	0.00000 %
Ni(Mont)2	0.79859 %
NiCl(Mont)	0.00014 %
Ni(Som(1))2	38.09893 %

Minerals

No Minerals Present

potassium

Uncomplexed Aqueous Species = 94.11070 %

Aqueous Complexes and Ion Exchangers

KPO4--	0.00007 %
KHPO4-	0.29967 %
KHCO3	0.03019 %
KCO3-	0.08236 %
KCl	0.04082 %
KF	0.00001 %
K(Mont)	5.43619 %

Minerals

No Minerals Present

sodium

Uncomplexed Aqueous Species = 96.27530 %

Aqueous Complexes and Ion Exchangers

NaCl	0.00622 %
NaCO3-	0.19683 %
NaF	0.00003 %
Na(Mont)	3.52162 %

Minerals

No Minerals Present

zinc

Uncomplexed Aqueous Species = 0.00039 %

Aqueous Complexes and Ion Exchangers

ZnPO4-	0.00010 %
ZnHPO4	0.00016 %
ZnHCO3+	0.00007 %
ZnCO3	0.00113 %
ZnL2	0.18132 %
Zn(OH)+	0.00000 %
Zn(OH)3-	0.00000 %
Zn(OH)4--	0.00000 %
ZnCl+	0.00000 %
ZnCl2	0.00000 %
ZnCl3-	0.00000 %
ZnCl4--	0.00000 %
ZnF+	0.00000 %
ZnNH3++	0.00000 %
Zn(NH3)2++	0.00000 %
Zn(NH3)3++	0.00000 %
Zn(NH3)4++	0.00000 %
Zn(Mont)2	0.00075 %
ZnCl(Mont)	0.00002 %
Zn(Som(1))2	0.02836 %

Minerals

SPHARELITE	99.78770 %

chloride

Uncomplexed Aqueous Species = 99.92547 %

Aqueous Complexes and Ion Exchangers

Cu(II)Cl+	0.00000 %
Cu(II)Cl2	0.00000 %
Cu(II)Cl3-	0.00000 %

Cu(II)Cl4--		0.00000 %
CaCl+		0.00027 %
MgCl+		0.00042 %
NiCl+		0.00001 %
NiCl2		0.00000 %
CoCl+		0.00001 %
CdCl3		0.00000 %
CdCl4		0.00000 %
CdCl+		0.00000 %
CdCl2		0.00000 %
CdCl+		0.00000 %
KCl		0.03086 %
NaCl		0.01942 %
FeCl+	(II)	0.00000 %
FeCl2	(II)	0.00000 %
FeCl3-	(II)	0.00000 %
MnCl+		0.00000 %
AgCl		0.00002 %
AgCl2-		0.00001 %
AgCl3--		0.00000 %
AgCl4---		0.00000 %
CuCl2-		0.00000 %
CuCl3--		0.00000 %
HCl		0.00000 %
PbCl+		0.00000 %
PbCl2		0.00000 %
PbCl3-		0.00000 %
PbCl4--		0.00000 %
ZnCl+		0.00000 %
ZnCl2		0.00000 %
ZnCl3-		0.00000 %
ZnCl4--		0.00000 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
MgCl(Mont)		0.02350 %
BaCl(Mont)		0.00000 %
NiCl(Mont)		0.00000 %
ZnCl(Mont)		0.00000 %
CdCl(Mont)		0.00000 %
PbCl(Mont)		0.00000 %

Minerals

No Minerals Present

fluoride

Uncomplexed Aqueous Species = 0.40942 %

Aqueous Complexes and Ion Exchangers

Cu(II)F+	0.00000 %
CaF+	0.00005 %
NiF+	0.00000 %
PbF+	0.00000 %
CdF+	0.00000 %
MgF+	0.00029 %

FeF+	(II)	0.00000 %
MnF+		0.00000 %
HF		0.00002 %
HF2		0.00000 %
ZnF+		0.00000 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %
FeF5-	(III)	0.00000 %
NaF		0.00128 %
KF		0.00011 %

Minerals

FLUORAPATITE	99.58884 %

ammonium

Uncomplexed Aqueous Species = 98.88503 %

Aqueous Complexes and Ion Exchangers

Cu(II)(NH3)2++	0.00000 %
Cu(II)(NH3)3++	0.00000 %
Cu(II)(NH3)4++	0.00000 %
NH3	1.11480 %
AgNH3+	0.00000 %
CuNH3+	0.00000 %
ZnNH3++	0.00000 %
NiNH3++	0.00017 %
Ag(NH3)2+	0.00000 %
Cu(NH3)2+	0.00000 %
Zn(NH3)2++	0.00000 %
Ni(NH3)2++	0.00000 %
Zn(NH3)3++	0.00000 %
Ni(NH3)3++	0.00000 %
Zn(NH3)4++	0.00000 %
Ni(NH3)4++	0.00000 %
Ni(NH3)5++	0.00000 %

Minerals

No Minerals Present

phosphate

Uncomplexed Aqueous Species = 0.00099 %

Aqueous Complexes and Ion Exchangers

Fe(III)H2PO4++	0.00000 %
Fe(III)HPO4+	0.00000 %
HPO4--	29.12316 %
H2PO4-	9.58149 %
Cu(II)PO4-	0.00000 %
Cu(II)HPO4-	0.00000 %

CaPO4-	0.01459 %
MgPO4-	0.02237 %
KPO4--	0.00004 %
Fe(II)PO4-	0.00233 %
MnPO4-	0.00000 %
ZnPO4-	0.00002 %
NiPO4-	0.00234 %
CdPO4-	0.00000 %
PbPO4-	0.00000 %
CaHPO4	0.05729 %
MgHPO4	0.27785 %
KHPO4-	0.15635 %
Fe(II)HPO4	0.01449 %
MnHPO4	0.00002 %
CdHPO4	0.00000 %
ZnHPO4	0.00003 %
NiHPO4	0.00058 %
PbHPO4	0.00000 %

Minerals

APATITE	44.47230 %
FLUORAPATITE	12.82748 %
MnHPO4	3.44628 %

sulphide

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

HSO4-	0.00000 %
SO4-- (redox)	0.00000 %
HS-	0.00000 %
H2S	0.00000 %

Minerals

CHALCOPYRITE	30.36279 %
GREENOCKITE	0.27448 %
ACANTHITE	0.98062 %
CHALCOCITE	7.56315 %
GALENA	5.01460 %
SPHARELITE	55.80435 %

mont

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

Na(Mont)	27.92643 %
H-Mont	0.00057 %
K(Mont)	10.43748 %
Ca(Mont)2	24.27938 %
Mg(Mont)2	37.23749 %
MgCl(Mont)	0.05968 %
Ba(Mont)2	0.00036 %
BaCl(Mont)	0.00000 %
Ni(Mont)2	0.05750 %
NiCl(Mont)	0.00001 %
Zn(Mont)2	0.00109 %
ZnCl(Mont)	0.00001 %
Cd(Mont)2	0.00000 %
CdCl(Mont)	0.00000 %
Pb(Mont)2	0.00000 %
PbCl(Mont)	0.00000 %

Minerals

No Minerals Present

silver

Uncomplexed Aqueous Species = 0.00062 %

Aqueous Complexes and Ion Exchangers

AgL	0.01134 %
AgCl	0.00203 %
AgCl2-	0.00046 %
AgCl3--	0.00000 %
AgCl4---	0.00000 %
AgNH3+	0.00001 %
Ag(NH3)2+	0.00000 %
Ag-Som(1)	0.00056 %

Minerals

ACANTHITE	99.98498 %

biofloc

Uncomplexed Aqueous Species = 0.25493 %

Aqueous Complexes and Ion Exchangers

HL	87.51534 %
MnL2	0.00037 %
CuL2	0.00000 %
ZnL2	0.00330 %
NiL2	0.04506 %
FeL2	0.15153 %
CdL2	0.00000 %
CaL2	3.04231 %
MgL2	8.97424 %

BaL2	0.00000 %
CoL2	0.01291 %
AgL	0.00000 %
CuL	0.00000 %

Minerals

No Minerals Present

som(1)

Uncomplexed Aqueous Species = 0.05297 %

Aqueous Complexes and Ion Exchangers

H-Som(1)	17.06309 %
Ca(Som(1))2	47.69659 %
Mg(Som(1))2	33.90238 %
Ba(Som(1))2	0.00031 %
Pb(Som(1))2	0.00013 %
Zn(Som(1))2	0.00655 %
Ni(Som(1))2	0.43542 %
Co(Som(1))2	0.10283 %
Mn(Som(1))2	0.00076 %
Fe(Som(1))2	0.73897 %
Cu-Som(1)	0.00000 %
Ag-Som(1)	0.00000 %
Cu-Som(1)	0.00000 %
Fe(III)(som(1))	0.00000 %

Minerals

No Minerals Present

som(2)

Uncomplexed Aqueous Species = 0.30945 %

Aqueous Complexes and Ion Exchangers

H-Som(2)	99.69015 %
Cu(Som(2))2	0.00000 %
Pb(Som(2))2	0.00040 %

Minerals

No Minerals Present

carbonate

Uncomplexed Aqueous Species = 0.17071 %

Aqueous Complexes and Ion Exchangers

Fe(III)CO3+	0.00000 %
Cu(II)CO3	0.00000 %
Cu(II)HCO3+	0.00000 %

KHCO3	0.00039 %
Fe(II)HCO3+	0.00004 %
MnHCO3+	0.00000 %
CdHCO3+	0.00000 %
ZnHCO3+	0.00000 %
NiHCO3+	0.00003 %
PbHCO3+	0.00000 %
ZnCO3	0.00001 %
NiCO3	0.00246 %
PbCO3	0.00000 %
CdCO3	0.00000 %
MnCO3	0.00000 %
FeCO3	0.00245 %
KCO3-	0.00105 %
NaCO3-	0.01041 %
CaCO3	0.00306 %
CaHCO3+	0.00003 %
MgCO3	0.00748 %
MgHCO3+	0.02457 %
HCO3-	77.87317 %
H2CO3	5.72716 %
BaHCO3+	0.00000 %

Minerals

CALCITE	16.11612 %
WITHERITE	0.06086 %

Iterations 9 53 16 17 18 28 19 19 32 3 6 22 18
Primary charge balance is -0.320679420000000 mol per kg
Final mass balance is 1.665334536937735E-016 mol per kg
Solution Charge Balance is -0.111808863510821 mol per kg

Oxidised Sewage pH 7.4
Temperature 25.00 C
Pressure 0.0010000 kbar

Concentrations of Primary Aqueous Components - mol/kg

		Total	Final	Activity	gamma i	-log a
1	proton	0.0000E+00	0.4522E-07	0.3981E-07	0.88037	7.4000
2	hydroxide	0.0000E+00	0.2846E-06	0.2504E-06	0.87990	6.6013
3	barium	0.9130E-04	0.2106E-06	0.1276E-06	0.60593	6.8940
4	cadmium	0.3570E-05	0.1933E-07	0.1173E-07	0.60698	7.9305
5	calcium	0.3060E-01	0.3071E-02	0.1864E-02	0.60692	2.7296
6	cobalt	0.8470E-05	0.3172E-06	0.1928E-06	0.60778	6.7149
7	copper(II)	0.3940E-03	0.1981E-08	0.1204E-08	0.60786	8.9194
8	iron(III)	0.5360E-03	0.2782E-19	0.9045E-20	0.32508	20.0436
9	lead	0.6520E-04	0.2766E-08	0.1677E-08	0.60630	8.7754
10	magnesium	0.5000E-02	0.3858E-03	0.2346E-03	0.60809	3.6297
11	manganese(II)	0.1270E-03	0.5168E-06	0.3140E-06	0.60756	6.5031
12	nickel	0.3600E-04	0.7364E-06	0.4475E-06	0.60765	6.3492
13	potassium	0.1920E-02	0.1889E-02	0.1664E-02	0.88122	2.7788
14	sodium	0.7930E-02	0.7854E-02	0.6927E-02	0.88201	2.1595
15	zinc	0.7270E-03	0.4954E-05	0.3011E-05	0.60778	5.5213
16	chloride	0.2540E-02	0.2528E-02	0.2220E-02	0.87837	2.6536
17	fluoride	0.1580E-03	0.6068E-06	0.5342E-06	0.88025	6.2723
18	ammonium	0.6940E-02	0.6852E-02	0.6038E-02	0.88115	2.2191
19	phosphate	0.3680E-02	0.1370E-10	0.4297E-11	0.31356	11.3669
20	sulphate	0.1300E-02	0.9065E-03	0.5425E-03	0.59841	3.2656
21	mercury(II)	0.7500E-06	0.2442E-15	0.1481E-15	0.60658	15.8294
22	mont	0.1000E-02	0.1005E-11	0.8832E-12	0.87884	12.0539
23	silver	0.2550E-04	0.1625E-05	0.1432E-05	0.88136	5.8441
24	biofloc	0.8000E-01	0.9202E-04	0.8246E-04	0.89611	4.0838
25	som(1)	0.6300E-02	0.4801E-06	0.4219E-06	0.87884	6.3747
26	som(2)	0.2700E-02	0.7609E-05	0.6687E-05	0.87884	5.1747
27	carbonate	0.1600E-03	0.2306E-06	0.1382E-06	0.59940	6.8594

Concentrations of Aqueous Complexed Species - mol/kg

		Final	log Keq	Activity	gamma c	-log a
1	HPO4--	0.6332E-06	-1.6500	0.3829E-06	0.60471	6.4169
2	H2PO4-	0.2746E-06	-8.4500	0.2416E-06	0.87986	6.6170
3	Fe(III)HPO4+	0.3199E-15	9.2600	0.2815E-15	0.87986	15.5505
4	Fe(III)H2PO4++	0.9725E-21	-3.0200	0.5881E-21	0.60471	21.2306
5	Fe(III)(SO4)2-	0.7257E-21	5.3800	0.6385E-21	0.87986	21.1948
6	CaPO4-	0.2878E-07	6.5000	0.2532E-07	0.87986	7.5965
7	MgPO4-	0.3623E-08	6.5000	0.3188E-08	0.87986	8.4965
8	KPO4--	0.9394E-12	1.9000	0.5680E-12	0.60471	12.2456
9	Fe(III)PO4	0.6133E-19	12.2000	0.6159E-19	1.00425	19.2105
10	MnPO4-	0.2430E-10	7.2000	0.2138E-10	0.87986	10.6700
11	Cu(II)PO4-	0.3710E-10	9.8000	0.3264E-10	0.87986	10.4863
12	ZnPO4-	0.1470E-08	8.0000	0.1294E-08	0.87986	8.8882
13	NiPO4-	0.5489E-09	8.4000	0.4830E-09	0.87986	9.3161
14	CdPO4-	0.1812E-12	6.5000	0.1594E-12	0.87986	12.7974
15	PbPO4-	0.2590E-13	6.5000	0.2279E-13	0.87986	13.6423
16	CaHPO4	0.1264E-06	0.6000	0.1269E-06	1.00425	6.8965
17	MgHPO4	0.5030E-07	1.1000	0.5052E-07	1.00425	7.2966
18	KHPO4-	0.5128E-08	-0.8000	0.4512E-08	0.87986	8.3457
19	Fe(III)HPO4+	0.8812E-18	6.7000	0.7753E-18	0.87986	18.1105
20	MnHPO4	0.8475E-09	2.2000	0.8511E-09	1.00425	9.0700
21	Cu(II)HPO4	0.8163E-11	2.6000	0.8198E-11	1.00425	11.0863

22	CdHPO4	0.9348E-11	1.6700	0.9388E-11	1.00425	11.0274
23	ZnHPO4	0.2570E-08	1.7000	0.2581E-08	1.00425	8.5882
24	NiHPO4	0.1521E-09	1.3000	0.1527E-09	1.00425	9.8161
25	PbHPO4	0.9034E-12	1.5000	0.9072E-12	1.00425	12.0423
26	KHCO3	0.8511E-09	-6.0300	0.8547E-09	1.00425	9.0682
27	Fe(III)HCO3++	0.4846E-21	-1.2300	0.2931E-21	0.60471	21.5330
28	MnHCO3+	0.2472E-08	-1.9000	0.2175E-08	0.87986	8.6625
29	Cu(II)HCO3+	0.1114E-12	-3.8300	0.9799E-13	0.87986	13.0088
30	CdHCO3+	0.1085E-11	-3.8300	0.9551E-12	0.87986	12.0200
31	ZnHCO3+	0.1396E-08	-3.1300	0.1228E-08	0.87986	8.9108
32	NiHCO3+	0.4139E-09	-2.8300	0.3642E-09	0.87986	9.4387
33	PbHCO3+	0.6177E-11	-2.2300	0.5435E-11	0.87986	11.2648
34	Cu(OH)2	0.1500E-11	10.3000	0.1507E-11	1.00425	11.8220
35	CuCO3	0.1046E-08	6.8000	0.1050E-08	1.00425	8.9788
36	ZnCO3	0.2615E-07	4.8000	0.2626E-07	1.00425	7.5807
37	Ni(OH)2	0.2795E-10	9.0000	0.2806E-10	1.00425	10.5518
38	CaCl+	0.4703E-06	-1.0000	0.4138E-06	0.87986	6.3832
39	MgCl+	0.5920E-07	-1.0000	0.5209E-07	0.87986	7.2832
40	NiCl+	0.2837E-08	0.4000	0.2496E-08	0.87986	8.6028
41	CoCl+	0.1222E-08	0.4000	0.1075E-08	0.87986	8.9685
42	CaF+	0.4505E-08	0.6000	0.3963E-08	0.87986	8.4019
43	NiF+	0.3420E-11	1.1000	0.3009E-11	0.87986	11.5215
44	NiCO3	0.3886E-07	5.8000	0.3903E-07	1.00425	7.4086
45	Pb(OH)3	0.2378E-14	13.9000	0.2093E-14	0.87986	14.6793
46	Pb(OH)4	0.2177E-18	16.3000	0.1316E-18	0.60471	18.8806
47	PbF+	0.2032E-13	1.3000	0.1788E-13	0.87986	13.7477
48	PbCO3	0.2309E-08	7.0000	0.2319E-08	1.00425	8.6348
49	CdCl3	0.3667E-13	2.4000	0.3227E-13	0.87986	13.4913
50	CdCl4	0.1878E-15	2.6000	0.1135E-15	0.60471	15.9448
51	CdSO4	0.8995E-11	2.5000	0.1165E-11	0.12953	11.9336
52	CdCO3	0.2033E-10	4.1000	0.2042E-10	1.00425	10.6899
53	MnCO3	0.1367E-08	4.5000	0.1373E-08	1.00425	8.8625
54	FeCO3+	0.1129E-13	12.9000	0.9931E-14	0.87986	14.0030
55	KCO3-	0.2077E-08	0.9000	0.1827E-08	0.87986	8.7381
56	HL	0.3268E-01	-4.0000	0.3282E-01	1.00425	1.4838
57	MnL2	0.3727E-04	10.8300	0.3743E-04	1.00425	4.4268
58	CuL2	0.3905E-03	14.2500	0.3922E-03	1.00425	3.4065
59	ZnL2	0.7065E-03	11.1100	0.7095E-03	1.00425	3.1490
60	NiL2	0.3185E-04	10.6800	0.3199E-04	1.00425	4.4950
61	CdL2	0.3548E-05	11.2800	0.3563E-05	1.00425	5.4482
62	CaL2	0.1806E-01	9.8900	0.1813E-01	1.00425	1.7416
63	MgL2	0.4371E-02	10.1100	0.4390E-02	1.00425	2.3575
64	BaL2	0.5834E-07	8.4600	0.5858E-07	1.00425	7.2322
65	CoL2	0.7541E-05	10.4000	0.7573E-05	1.00425	5.1207
66	FeL3	0.8599E-14	18.8600	0.8635E-14	1.00425	14.0637
67	AgL	0.1528E-04	5.7450	0.1535E-04	1.00425	4.8139
68	CdCl+	0.9364E-12	-1.5000	0.8239E-12	0.87986	12.0841
69	CdF+	0.1006E-12	1.1500	0.8854E-13	0.87986	13.0528
70	CdCl2	0.1447E-15	-2.6000	0.1453E-15	1.00425	15.8377
71	CdCl+	0.9364E-12	-1.5000	0.8239E-12	0.87986	12.0841
72	Cd(OH)+	0.4015E-10	4.0800	0.3533E-10	0.87986	10.4518
73	Cd(OH)2	0.3673E-13	7.7000	0.3688E-13	1.00425	13.4332
74	Cd(OH)3	0.2047E-18	8.9900	0.1801E-18	0.87986	18.7445
75	KCl	0.9830E-06	-0.5733	0.9871E-06	1.00425	6.0056
76	KSO4-	0.7034E-05	0.8360	0.6189E-05	0.87986	5.2084
77	BaOH	0.5982E-11	2.2166	0.5263E-11	0.87986	11.2787
78	NaCl	0.6072E-06	-1.4018	0.6098E-06	1.00425	6.2148
79	NaCO3-	0.2012E-07	1.2670	0.1771E-07	0.87986	7.7519
80	NaSO4-	0.1447E-04	0.5300	0.1273E-04	0.87986	4.8951
81	Ca(OH)+	0.9107E-08	1.2347	0.8013E-08	0.87986	8.0962

82	CaCO3		0.4054E-06	3.1988	0.4072E-06	1.00425	6.3902
83	CaHCO3+		0.3924E-08	-5.4728	0.3453E-08	0.87986	8.4618
84	CaSO4		0.2046E-03	2.3080	0.2055E-03	1.00425	3.6872
85	Mg(OH)+		0.2586E-07	2.5879	0.2275E-07	0.87986	7.6430
86	MgCO3		0.8140E-07	3.4015	0.8175E-07	1.00425	7.0875
87	MgHCO3+		0.2390E-06	-2.7880	0.2103E-06	0.87986	6.6771
88	MgSO4		0.2277E-04	2.2545	0.2287E-04	1.00425	4.6408
89	MgF+		0.2353E-08	1.2179	0.2070E-08	0.87986	8.6840
90	Fe(OH)++	(III)	0.2230E-14	11.7748	0.1349E-14	0.60471	14.8701
91	Fe(OH)2+	(III)	0.4369E-12	20.8311	0.3844E-12	0.87986	12.4152
92	Fe(OH)3	(III)	0.1483E-29	10.0206	0.1489E-29	1.00425	29.8270
93	Fe(OH)4-	(III)	0.5125E-12	34.1030	0.4509E-12	0.87986	12.3459
94	FeCl++	(III)	0.1009E-20	1.4827	0.6103E-21	0.60471	21.2145
95	FeCl2+	(III)	0.7498E-23	2.1701	0.6597E-23	0.87986	23.1807
96	FeCl3	(III)	0.1411E-26	1.1556	0.1417E-26	1.00425	26.8487
97	FeCl4-	(III)	0.4443E-31	-0.7500	0.3909E-31	0.87986	31.4079
98	FeSO4+	(III)	0.4047E-27	-4.1392	0.3561E-27	0.87986	27.4485
99	FeF++	(III)	0.9356E-21	5.0685	0.5658E-21	0.60471	21.2474
100	FeF2+	(III)	0.3045E-23	9.0162	0.2679E-23	0.87986	23.5720
101	FeF3	(III)	0.9824E-27	11.8547	0.9866E-27	1.00425	27.0058
102	FeF4-	(III)	0.7935E-30	14.9768	0.6982E-30	0.87986	30.1560
103	MnOH+		0.2245E-09	3.4000	0.1975E-09	0.87986	9.7044
104	MnOH2		0.1237E-13	5.8000	0.1242E-13	1.00425	13.9057
105	MnOH3-		0.8883E-19	7.2000	0.7816E-19	0.87986	19.1070
106	MnSO4		0.3272E-07	2.2854	0.3286E-07	1.00425	7.4833
107	MnCl+		0.8688E-09	0.0400	0.7644E-09	0.87986	9.1167
108	MnF+		0.7947E-12	0.6200	0.6992E-12	0.87986	12.1554
109	AgCl		0.6429E-05	3.3076	0.6456E-05	1.00425	5.1900
110	AgCl2-		0.1408E-05	5.2441	0.1238E-05	0.87986	5.9071
111	AgCl3--		0.4633E-08	5.2522	0.2802E-08	0.60471	8.5526
112	AgCl4---		0.3471E-10	5.5077	0.1120E-10	0.32271	10.9507
113	AgSO4-		0.1738E-07	1.2941	0.1529E-07	0.87986	7.8155
114	Ni(OH)+		0.2918E-09	3.3600	0.2567E-09	0.87986	9.5905
115	HSO4-		0.2423E-08	-12.0056	0.2132E-08	0.87986	8.6712
116	HCO3-		0.1341E-03	-3.6688	0.1180E-03	0.87986	3.9283
117	H2CO3		0.1102E-04	-11.2964	0.1107E-04	1.00425	4.9559
118	HCl		0.6970E-16	-20.1013	0.7000E-16	1.00425	16.1549
119	HF		0.3073E-10	-10.8383	0.3086E-10	1.00425	10.5106
120	HF2		0.7289E-16	-10.2483	0.6413E-16	0.87986	16.1929
121	PbOH+		0.3229E-07	7.8302	0.2841E-07	0.87986	7.5465
122	Pb(OH)2		0.7163E-11	10.8349	0.7193E-11	1.00425	11.1431
123	PbCl+		0.1664E-09	1.5944	0.1464E-09	0.87986	9.8345
124	PbCl2		0.4978E-12	1.7814	0.4999E-12	1.00425	12.3011
125	PbCl3-		0.9654E-15	1.6652	0.8494E-15	0.87986	15.0709
126	PbCl4--		0.1605E-17	1.3767	0.9705E-18	0.60471	18.0130
127	PbSO4		0.5315E-04	7.7684	0.5338E-04	1.00425	4.2726
128	Zn(OH)+		0.2839E-07	4.5203	0.2498E-07	0.87986	7.6024
129	Zn(OH)3-		0.8913E-12	13.2197	0.7842E-12	0.87986	12.1056
130	ZnCl+		0.8349E-09	-0.9590	0.7346E-09	0.87986	9.1339
131	ZnCl2		0.2330E-10	0.1976	0.2340E-10	1.00425	10.6309
132	ZnCl3-		0.1359E-14	-1.4404	0.1195E-14	0.87986	14.9225
133	ZnCl4--		0.4190E-17	-1.4606	0.2534E-17	0.60471	17.5962
134	ZnSO4		0.3883E-06	2.3780	0.3900E-06	1.00425	6.4090
135	ZnF+		0.8106E-11	0.6468	0.7132E-11	0.87986	11.1468
136	NiSO4		0.5004E-07	2.3160	0.5025E-07	1.00425	7.2989
137	Cu(OH)+		0.3427E-09	6.0000	0.3015E-09	0.87986	9.5207
138	CuCl+		0.1971E-11	-0.1879	0.1734E-11	0.87986	11.7609
139	CuCl2		0.1174E-14	-0.7018	0.1179E-14	1.00425	14.9283
140	CuCl3-		0.7422E-19	-2.3050	0.6530E-19	0.87986	19.1851
141	CuCl4--		0.1250E-23	-4.5879	0.7558E-24	0.60471	24.1216

142	CuSO4	0.2144E-09	2.5180	0.2153E-09	1.00425	9.6670
143	CuF+	0.3260E-14	0.6493	0.2868E-14	0.87986	14.5424
144	HgCl+	0.6754E-12	6.2569	0.5942E-12	0.87986	12.2260
145	HgCl2	0.1268E-07	13.2415	0.1273E-07	1.00425	7.8950
146	HgCl3-	0.4061E-08	15.3432	0.3573E-08	0.87986	8.4469
147	HgCl4--	0.4884E-11	14.9140	0.2953E-11	0.60471	11.5297
148	HgSO4	0.2010E-17	1.4000	0.2018E-17	1.00425	17.6950
149	HgF+	0.1202E-20	1.1259	0.1057E-20	0.87986	20.9758
150	BaHCO3+	0.2345E-19	-12.5319	0.2064E-19	0.87986	19.6854
151	BaSO4	0.1404E-07	2.3090	0.1410E-07	1.00425	7.8507
152	NH3	0.8558E-04	4.7533	0.8595E-04	1.00425	4.0658
153	NHSO4-	0.2718E-13	-8.1366	0.2391E-13	0.87986	13.6214
154	AgNH3+	0.2864E-06	8.0646	0.2520E-06	0.87986	6.5986
155	ZnNH3++	0.7286E-07	6.9845	0.4406E-07	0.60471	7.3559
156	CuNH3++	0.2852E-08	8.9752	0.1725E-08	0.60471	8.7633
157	HgNH3++	0.1340E-10	13.5570	0.8100E-11	0.60471	11.0915
158	NiNH3++	0.7148E-07	7.8040	0.4322E-07	0.60471	7.3643
159	Ag(NH3)2+	0.1943E-06	16.7151	0.1709E-06	0.87986	6.7672
160	Zn(NH3)2++	0.1252E-08	14.0388	0.7573E-09	0.60471	9.1207
161	Cu(NH3)2++	0.9144E-09	17.3002	0.5529E-09	0.60471	9.2573
162	Hg(NH3)2++	0.7327E-06	27.1140	0.4431E-06	0.60471	6.3535
163	Ni(NH3)2++	0.7046E-09	14.6169	0.4261E-09	0.60471	9.3705
164	Zn(NH3)3++	0.2462E-10	21.1514	0.1489E-10	0.60471	10.8272
165	Cu(NH3)3++	0.7201E-10	25.0156	0.4354E-10	0.60471	10.3611
166	Hg(NH3)3++	0.5385E-09	32.7994	0.3257E-09	0.60471	9.4872
167	Ni(NH3)3++	0.3600E-11	21.1443	0.2177E-11	0.60471	11.6622
168	Zn(NH3)4++	0.7357E-12	28.4459	0.4449E-12	0.60471	12.3518
169	Cu(NH3)4++	0.9557E-12	31.9576	0.5779E-12	0.60471	12.2381
170	Hg(NH3)4++	0.2193E-12	38.2282	0.1326E-12	0.60471	12.8775
171	Ni(NH3)4++	0.5259E-14	27.1280	0.3180E-14	0.60471	14.4975
172	Ni(NH3)5++	0.2843E-17	32.6800	0.1719E-17	0.60471	17.7646
173	NaF	0.2325E-08	-0.2000	0.2335E-08	1.00425	8.6318
174	KF	0.1982E-09	-0.6500	0.1990E-09	1.00425	9.7011

Concentrations of Ion Exchanged Species - mol/kg

		Final	Log Keq	Mole Fract	Equiv Fract
1	Na(Mont)	0.6118E-04	10.0000	0.1127E+00	0.6118E-01
2	H-Mont	0.1112E-08	-3.5000	0.2049E-05	0.1112E-05
3	K(Mont)	0.2330E-04	10.2000	0.4293E-01	0.2330E-01
4	Ca(Mont)2	0.4055E-03	20.1800	0.7473E+00	0.8111E+00
5	Mg(Mont)2	0.5105E-04	20.1800	0.9407E-01	0.1021E+00
6	MgCl(Mont)	0.7126E-06	12.1900	0.1313E-02	0.7126E-03
7	Ba(Mont)2	0.2777E-07	20.1800	0.5118E-04	0.5554E-04
8	BaCl(Mont)	0.5603E-09	12.3500	0.1033E-05	0.5603E-06
9	Cu(Mont)2	0.2620E-09	20.1800	0.4828E-06	0.5239E-06
10	CuCl(Mont)	0.5931E-11	12.4000	0.1093E-07	0.5931E-08
11	Ni(Mont)2	0.1144E-06	20.2500	0.2108E-03	0.2288E-03
12	NiCl(Mont)	0.8776E-10	11.0000	0.1617E-06	0.8776E-07
13	Zn(Mont)2	0.6551E-06	20.1800	0.1207E-02	0.1310E-02
14	ZnCl(Mont)	0.5904E-07	13.0000	0.1088E-03	0.5904E-04
15	Cd(Mont)2	0.2553E-08	20.1800	0.4705E-05	0.5107E-05
16	CdCl(Mont)	0.2301E-09	13.0000	0.4241E-06	0.2301E-06
17	Pb(Mont)2	0.3650E-09	20.1800	0.6726E-06	0.7299E-06
18	PbCl(Mont)	0.3289E-10	13.0000	0.6062E-07	0.3289E-07
19	H-Som(1)	0.1680E-03	-4.0000	0.5194E-01	0.2666E-01
20	Ca(Som(1))2	0.2879E-02	10.4480	0.8901E+00	0.9139E+00
21	Mg(Som(1))2	0.1679E-03	10.1140	0.5193E-01	0.5331E-01
22	Ba(Som(1))2	0.8645E-07	10.0900	0.2673E-04	0.2745E-04

23	Cu(Som(1))2	0.5462E-07	11.9160	0.1689E-04	0.1734E-04
24	Pb(Som(1))2	0.2485E-06	12.4300	0.7686E-04	0.7891E-04
25	Zn(Som(1))2	0.1427E-04	10.9350	0.4413E-02	0.4531E-02
26	Ni(Som(1))2	0.3130E-05	11.1040	0.9679E-03	0.9938E-03
27	Co(Som(1))2	0.6108E-06	10.7600	0.1889E-03	0.1939E-03
28	Mn(Som(1))2	0.7739E-06	10.6510	0.2393E-03	0.2457E-03
29	Fe(Som(1))3	0.4495E-16	17.8400	0.1390E-13	0.2141E-13
30	Ag-Som(1)	0.2519E-06	5.6200	0.7789E-04	0.3998E-04
31	H-Som(2)	0.2662E-02	-4.0000	0.9943E+00	0.9887E+00
32	Cu(Som(2))2	0.3423E-05	11.2310	0.1279E-02	0.2543E-02
33	Pb(Som(2))2	0.1176E-04	11.6230	0.4393E-02	0.8737E-02

Concentrations of Solids - mol/kg

		Final	log Keq	ICP	SP
1	APATITE	0.1039E-02	54.3500	0.2000E-51	0.2000E-51
2	FLUORAPATITE	0.1574E-03	54.0210	0.4264E-51	0.4264E-51
3	MnHPO4	0.8840E-04	11.2700	0.2488E-10	0.2488E-10
4	BARITE	0.9090E-04	10.1597	0.1909E-09	0.1909E-09
5	HEMATITE	0.2680E-03	79.6910	0.4115E-78	0.4115E-78

Fixed pH

pH 7.400

Ionic strength 0.18435E-01 mol/kg

The activity of water 0.99816027

0.139E-04 mol/kg CO2 released. ppCO2 0.320E-06 kbar

****

Predictions of Density

Density of the Aqueous Phase:	1.01854634543065	-	g/cc
Density of the Solid Phase:	1.66609189856798	-	g/cc
Total Fluid Density:	1.02274213461111	-	g/cc

****

Primary Distribution of Species

barium

Uncomplexed Aqueous Species = 0.23070 %

Aqueous Complexes and Ion Exchangers

BaL2	0.06389 %
BaOH	0.00001 %
BaHCO3+	0.00000 %

BaSO4	0.01538 %
Ba(Mont)2	0.03042 %
BaCl(Mont)	0.00061 %
Ba(Som(1))2	0.09468 %

Minerals

BARITE	99.56430 %

cadmium

Uncomplexed Aqueous Species = 0.54153 %

Aqueous Complexes and Ion Exchangers

CdPO4-	0.00001 %
CdHPO4	0.00026 %
CdHCO3+	0.00003 %
CdCl3	0.00000 %
CdCl4	0.00000 %
CdSO4	0.00025 %
CdCO3	0.00057 %
CdL2	99.37820 %
CdCl+	0.00003 %
CdF+	0.00000 %
CdCl2	0.00000 %
CdCl+	0.00003 %
Cd(OH)+	0.00112 %
Cd(OH)2	0.00000 %
Cd(OH)3	0.00000 %
Cd(Mont)2	0.07152 %
CdCl(Mont)	0.00645 %

Minerals

No Minerals Present

calcium

Uncomplexed Aqueous Species = 10.03537 %

Aqueous Complexes and Ion Exchangers

CaPO4-	0.00009 %
CaHPO4	0.00041 %
CaCl+	0.00154 %
CaF+	0.00001 %
CaL2	59.00430 %
Ca(OH)+	0.00003 %
CaCO3	0.00132 %
CaHCO3+	0.00001 %
CaSO4	0.66870 %
Ca(Mont)2	1.32525 %
Ca(Som(1))2	9.40702 %

Minerals

APATITE	16.98430 %
FLUORAPATITE	2.57163 %

cobalt

Uncomplexed Aqueous Species = 3.74504 %

Aqueous Complexes and Ion Exchangers

CoCl+	0.01443 %
CoL2	89.02957 %
Co(Som(1))2	7.21097 %

Minerals

No Minerals Present

copper(II)

Uncomplexed Aqueous Species = 0.00050 %

Aqueous Complexes and Ion Exchangers

Cu(II)PO4-	0.00001 %
Cu(II)HPO4	0.00000 %
Cu(II)HCO3+	0.00000 %
Cu(OH)2	0.00000 %
CuCO3	0.00027 %
CuL2	99.11534 %
Cu(OH)+	0.00009 %
CuCl+	0.00000 %
CuCl2	0.00000 %
CuCl3-	0.00000 %
CuCl4--	0.00000 %
CuSO4	0.00005 %
CuF+	0.00000 %
CuNH3++	0.00072 %
Cu(NH3)2++	0.00023 %
Cu(NH3)3++	0.00002 %
Cu(NH3)4++	0.00000 %
Cu(Mont)2	0.00007 %
CuCl(Mont)	0.00000 %
Cu(Som(1))2	0.01386 %
Cu(Som(2))2	0.86883 %

Minerals

No Minerals Present

iron(III)

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

Fe(III)HPO4+		0.00000 %
Fe(III)H2PO4++		0.00000 %
Fe(III)(SO4)2-		0.00000 %
Fe(III)PO4		0.00000 %
Fe(III)HPO4+		0.00000 %
Fe(III)HCO3++		0.00000 %
FeCO3+		0.00000 %
FeL3		0.00000 %
Fe(OH)++	(III)	0.00000 %
Fe(OH)2+	(III)	0.00000 %
Fe(OH)3	(III)	0.00000 %
Fe(OH)4-	(III)	0.00000 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
FeSO4+	(III)	0.00000 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %
Fe(Som(1))3		0.00000 %

Minerals

HEMATITE	100.00000 %

lead

Uncomplexed Aqueous Species = 0.00424 %

Aqueous Complexes and Ion Exchangers

PbPO4-	0.00000 %
PbHPO4	0.00000 %
PbHCO3+	0.00001 %
Pb(OH)3	0.00000 %
Pb(OH)4	0.00000 %
PbF+	0.00000 %
PbCO3	0.00354 %
PbOH+	0.04953 %
Pb(OH)2	0.00001 %
PbCl+	0.00026 %
PbCl2	0.00000 %
PbCl3-	0.00000 %
PbCl4--	0.00000 %
PbSO4	81.52216 %
Pb(Mont)2	0.00056 %
PbCl(Mont)	0.00005 %
Pb(Som(1))2	0.38120 %
Pb(Som(2))2	18.03844 %

Minerals

No Minerals Present

magnesium

Uncomplexed Aqueous Species = 7.71605 %

Aqueous Complexes and Ion Exchangers

MgPO4-	0.00007 %
MgHPO4	0.00101 %
MgCl+	0.00118 %
MgL2	87.42553 %
Mg(OH)+	0.00052 %
MgCO3	0.00163 %
MgHCO3+	0.00478 %
MgSO4	0.45541 %
MgF+	0.00005 %
Mg(Mont)2	1.02094 %
MgCl(Mont)	0.01425 %
Mg(Som(1))2	3.35858 %

Minerals

No Minerals Present

manganese(II)

Uncomplexed Aqueous Species = 0.40693 %

Aqueous Complexes and Ion Exchangers

MnPO4-	0.00002 %
MnHPO4	0.00067 %
MnHCO3+	0.00195 %
CdSO4	0.00001 %
MnCO3	0.00108 %
MnL2	29.34452 %
MnOH+	0.00018 %
MnOH2	0.00000 %
MnOH3-	0.00000 %
MnSO4	0.02576 %
MnCl+	0.00068 %
MnF+	0.00000 %
Mn(Som(1))2	0.60940 %

Minerals

MnHPO4	69.60881 %

nickel

Uncomplexed Aqueous Species = 2.04563 %

Aqueous Complexes and Ion Exchangers

NiPO4-	0.00152 %
NiHPO4	0.00042 %
NiHCO3+	0.00115 %
Ni(OH)2	0.00008 %
NiCl+	0.00788 %

NiF+	0.00001 %
NiCO3	0.10796 %
NiL2	88.48205 %
Ni(OH)+	0.00081 %
NiSO4	0.13899 %
NiNH3++	0.19855 %
Ni(NH3)2++	0.00196 %
Ni(NH3)3++	0.00001 %
Ni(NH3)4++	0.00000 %
Ni(NH3)5++	0.00000 %
Ni(Mont)2	0.31777 %
NiCl(Mont)	0.00024 %
Ni(Som(1))2	8.69496 %

Minerals

No Minerals Present

potassium

Uncomplexed Aqueous Species = 98.36862 %

Aqueous Complexes and Ion Exchangers

KPO4--	0.00000 %
KHPO4-	0.00027 %
KHCO3	0.00004 %
KCO3-	0.00011 %
KCl	0.05120 %
KSO4-	0.36633 %
KF	0.00001 %
K(Mont)	1.21342 %

Minerals

No Minerals Present

sodium

Uncomplexed Aqueous Species = 99.03806 %

Aqueous Complexes and Ion Exchangers

NaCl	0.00766 %
NaCO3-	0.00025 %
NaSO4-	0.18249 %
NaF	0.00003 %
Na(Mont)	0.77151 %

Minerals

No Minerals Present

zinc

Uncomplexed Aqueous Species = 0.68137 %

Aqueous Complexes and Ion Exchangers

ZnPO4-	0.00020 %
ZnHPO4	0.00035 %
ZnHCO3+	0.00019 %
ZnCO3	0.00360 %
ZnL2	97.18542 %
Zn(OH)+	0.00391 %
Zn(OH)3-	0.00000 %
ZnCl+	0.00011 %
ZnCl2	0.00000 %
ZnCl3-	0.00000 %
ZnCl4--	0.00000 %
ZnSO4	0.05341 %
ZnF+	0.00000 %
ZnNH3++	0.01002 %
Zn(NH3)2++	0.00017 %
Zn(NH3)3++	0.00000 %
Zn(NH3)4++	0.00000 %
Zn(Mont)2	0.09011 %
ZnCl(Mont)	0.00812 %
Zn(Som(1))2	1.96300 %

Minerals

No Minerals Present

chloride

Uncomplexed Aqueous Species = 99.51993 %

Aqueous Complexes and Ion Exchangers

CaCl+		0.01852 %
MgCl+		0.00233 %
NiCl+		0.00011 %
CoCl+		0.00005 %
CdCl3		0.00000 %
CdCl4		0.00000 %
CdCl+		0.00000 %
CdCl2		0.00000 %
CdCl+		0.00000 %
KCl		0.03870 %
NaCl		0.02391 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
MnCl+		0.00003 %
AgCl		0.25311 %
AgCl2-		0.11083 %
AgCl3--		0.00055 %
AgCl4---		0.00001 %
HCl		0.00000 %
PbCl+		0.00001 %
PbCl2		0.00000 %
PbCl3-		0.00000 %
PbCl4--		0.00000 %
ZnCl+		0.00003 %

ZnCl2		0.00000 %
ZnCl3-		0.00000 %
ZnCl4--		0.00000 %
CuCl+		0.00000 %
CuCl2		0.00000 %
CuCl3-		0.00000 %
CuCl4--		0.00000 %
HgCl+		0.00000 %
HgCl2		0.00100 %
HgCl3-		0.00048 %
HgCl4--		0.00000 %
MgCl(Mont)		0.02805 %
BaCl(Mont)		0.00002 %
CuCl(Mont)		0.00000 %
NiCl(Mont)		0.00000 %
ZnCl(Mont)		0.00232 %
CdCl(Mont)		0.00001 %
PbCl(Mont)		0.00000 %

Minerals

No Minerals Present

fluoride

Uncomplexed Aqueous Species = 0.38408 %

Aqueous Complexes and Ion Exchangers

CaF+		0.00285 %
NiF+		0.00000 %
PbF+		0.00000 %
CdF+		0.00000 %
MgF+		0.00149 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %
MnF+		0.00000 %
HF		0.00002 %
HF2		0.00000 %
ZnF+		0.00001 %
CuF+		0.00000 %
HgF+		0.00000 %
NaF		0.00147 %
KF		0.00013 %

Minerals

FLUORAPATITE	99.60996 %

ammonium

Uncomplexed Aqueous Species = 98.73375 %

Aqueous Complexes and Ion Exchangers

NH3	1.23318 %
NHSO4-	0.00000 %
AgNH3+	0.00413 %
ZnNH3++	0.00105 %
CuNH3++	0.00004 %
HgNH3++	0.00000 %
NiNH3++	0.00103 %
Ag(NH3)2+	0.00560 %
Zn(NH3)2++	0.00004 %
Cu(NH3)2++	0.00003 %
Hg(NH3)2++	0.02112 %
Ni(NH3)2++	0.00002 %
Zn(NH3)3++	0.00000 %
Cu(NH3)3++	0.00000 %
Hg(NH3)3++	0.00002 %
Ni(NH3)3++	0.00000 %
Zn(NH3)4++	0.00000 %
Cu(NH3)4++	0.00000 %
Hg(NH3)4++	0.00000 %
Ni(NH3)4++	0.00000 %
Ni(NH3)5++	0.00000 %

Minerals

No Minerals Present

phosphate

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

HPO4--	0.01721 %
H2PO4-	0.00746 %
Fe(III)HPO4+	0.00000 %
Fe(III)H2PO4++	0.00000 %
CaPO4-	0.00078 %
MgPO4-	0.00010 %
KPO4--	0.00000 %
Fe(III)PO4	0.00000 %
MnPO4-	0.00000 %
Cu(II)PO4-	0.00000 %
ZnPO4-	0.00004 %
NiPO4-	0.00001 %
CdPO4-	0.00000 %
PbPO4-	0.00000 %
CaHPO4	0.00343 %
MgHPO4	0.00137 %
KHPO4-	0.00014 %
Fe(III)HPO4+	0.00000 %
MnHPO4	0.00002 %
Cu(II)HPO4	0.00000 %
CdHPO4	0.00000 %
ZnHPO4	0.00007 %
NiHPO4	0.00000 %
PbHPO4	0.00000 %

Minerals

APATITE	84.73690 %
FLUORAPATITE	12.83020 %
MnHPO4	2.40226 %

sulphate

Uncomplexed Aqueous Species = 69.73412 %

Aqueous Complexes and Ion Exchangers

Fe(III)(SO4)2-	0.00000 %
KSO4-	0.54104 %
NaSO4-	1.11320 %
CaSO4	15.74007 %
MgSO4	1.75158 %
FeSO4+ (III)	0.00000 %
MnSO4	0.00252 %
AgSO4-	0.00134 %
HSO4-	0.00019 %
PbSO4	4.08865 %
ZnSO4	0.02987 %
NiSO4	0.00385 %
CuSO4	0.00002 %
HgSO4	0.00000 %
BaSO4	0.00108 %
NHSO4-	0.00000 %

Minerals

BARITE	6.99248 %

mercury(II)

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

HgCl+	0.00009 %
HgCl2	1.69080 %
HgCl3-	0.54150 %
HgCl4--	0.00065 %
HgSO4	0.00000 %
HgF+	0.00000 %
HgNH3++	0.00179 %
Hg(NH3)2++	97.69334 %
Hg(NH3)3++	0.07181 %
Hg(NH3)4++	0.00003 %

Minerals

No Minerals Present

mont

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

Na(Mont)	6.11808 %
H-Mont	0.00011 %
K(Mont)	2.32976 %
Ca(Mont)2	81.10529 %
Mg(Mont)2	10.20942 %
MgCl(Mont)	0.07126 %
Ba(Mont)2	0.00555 %
BaCl(Mont)	0.00006 %
Cu(Mont)2	0.00005 %
CuCl(Mont)	0.00000 %
Ni(Mont)2	0.02288 %
NiCl(Mont)	0.00001 %
Zn(Mont)2	0.13102 %
ZnCl(Mont)	0.00590 %
Cd(Mont)2	0.00051 %
CdCl(Mont)	0.00002 %
Pb(Mont)2	0.00007 %
PbCl(Mont)	0.00000 %

Minerals

No Minerals Present

silver

Uncomplexed Aqueous Species = 6.37170 %

Aqueous Complexes and Ion Exchangers

AgL	59.93793 %
AgCl	25.21133 %
AgCl2-	5.51962 %
AgCl3--	0.01817 %
AgCl4---	0.00014 %
AgSO4-	0.06816 %
AgNH3+	1.12328 %
Ag(NH3)2+	0.76189 %
Ag-Som(1)	0.98779 %

Minerals

No Minerals Present

biofloc

Uncomplexed Aqueous Species = 0.11502 %

Aqueous Complexes and Ion Exchangers

HL	40.85609 %
MnL2	0.09317 %
CuL2	0.97629 %
ZnL2	1.76634 %

NiL2	0.07963 %
CdL2	0.00887 %
CaL2	45.13829 %
MgL2	10.92819 %
BaL2	0.00015 %
CoL2	0.01885 %
FeL3	0.00000 %
AgL	0.01911 %

Minerals

No Minerals Present

som(1)

Uncomplexed Aqueous Species = 0.00762 %

Aqueous Complexes and Ion Exchangers

H-Som(1)	2.66606 %
Ca(Som(1))2	91.38250 %
Mg(Som(1))2	5.33108 %
Ba(Som(1))2	0.00274 %
Cu(Som(1))2	0.00173 %
Pb(Som(1))2	0.00789 %
Zn(Som(1))2	0.45305 %
Ni(Som(1))2	0.09937 %
Co(Som(1))2	0.01939 %
Mn(Som(1))2	0.02457 %
Fe(Som(1))3	0.00000 %
Ag-Som(1)	0.00400 %

Minerals

No Minerals Present

som(2)

Uncomplexed Aqueous Species = 0.28183 %

Aqueous Complexes and Ion Exchangers

H-Som(2)	98.59341 %
Cu(Som(2))2	0.25357 %
Pb(Som(2))2	0.87119 %

Minerals

No Minerals Present

carbonate

Uncomplexed Aqueous Species = 0.15780 %

Aqueous Complexes and Ion Exchangers

KHCO3	0.00058 %

Fe(III)HCO3++	0.00000 %
MnHCO3+	0.00169 %
Cu(II)HCO3+	0.00000 %
CdHCO3+	0.00000 %
ZnHCO3+	0.00096 %
NiHCO3+	0.00028 %
PbHCO3+	0.00000 %
CuCO3	0.00072 %
ZnCO3	0.01789 %
NiCO3	0.02659 %
PbCO3	0.00158 %
CdCO3	0.00001 %
MnCO3	0.00094 %
FeCO3+	0.00000 %
KCO3-	0.00142 %
NaCO3-	0.01377 %
CaCO3	0.27744 %
CaHCO3+	0.00269 %
MgCO3	0.05570 %
MgHCO3+	0.16357 %
HCO3-	91.73403 %
H2CO3	7.54234 %
BaHCO3+	0.00000 %

Minerals

No Minerals Present

Iterations 9 151 5 93 10 23 151 11 2 2 1 1 1
Primary charge balance is -1.380791999999999E-002 mol per kg
Final mass balance is 2.775557561562891E-017 mol per kg
Solution Charge Balance is 1.892512619651007E-002 mol per kg

Sludge/Soil
Temperature 5.00 C
Pressure 0.0010000 kbar

Concentrations of Primary Aqueous Components - mol/kg

		Total	Final	Activity	gamma i	-log a
1	proton	0.0000E+00	0.3400E-06	0.3162E-06	0.93006	6.5000
2	hydroxide	0.0000E+00	0.6425E-08	0.5958E-08	0.92728	8.2249
3	barium	0.2200E-06	0.2090E-06	0.1540E-06	0.73677	6.8126
4	calcium	0.1240E-02	0.1180E-02	0.8696E-03	0.73713	3.0607
5	copper(II)	0.1300E-05	0.5936E-06	0.4378E-06	0.73748	6.3587
6	iron(III)	0.5170E-04	0.2775E-09	0.1398E-09	0.50379	9.8545
7	magnesium	0.8550E-04	0.8348E-04	0.6157E-04	0.73756	4.2106
8	manganese(II)	0.1560E-05	0.1490E-05	0.1099E-05	0.73737	5.9590
9	nickel	0.2300E-06	0.2221E-06	0.1637E-06	0.73740	6.7858
10	potassium	0.4090E-03	0.4083E-03	0.3782E-03	0.92626	3.4223
11	sodium	0.3350E-03	0.3348E-03	0.3102E-03	0.92651	3.5084
12	zinc	0.2000E-05	0.1911E-05	0.1409E-05	0.73745	5.8510
13	chloride	0.8290E-03	0.8289E-03	0.7682E-03	0.92680	3.1145
14	nitrate	0.2800E-02	0.2788E-02	0.2583E-02	0.92620	2.5879
15	phosphate	0.9600E-04	0.1195E-11	0.6002E-12	0.50213	12.2217
16	sulphate	0.4650E-03	0.4140E-03	0.3052E-03	0.73737	3.5154
17	biofloc	0.6700E-03	0.4277E-07	0.3988E-07	0.93243	7.3992
18	carbonate	0.1000E-01	0.2458E-08	0.1813E-08	0.73774	8.7416

Concentrations of Aqueous Complexed Species - mol/kg

		Final	log Keq	Activity	gamma c	-log a
1	HPO4--	0.3054E-05	-1.6500	0.2255E-05	0.73846	5.6468
2	H2PO4-	0.6473E-04	-8.4500	0.5998E-04	0.92657	4.2220
3	Fe(III)HPO4+	0.2766E-04	9.2600	0.2563E-04	0.92657	4.5913
4	Fe(III)H2PO4++	0.3056E-08	-3.0200	0.2257E-08	0.73846	8.6465
5	Fe(III)(SO4)2-	0.3372E-11	5.3800	0.3124E-11	0.92657	11.5052
6	CaPO4-	0.1781E-08	6.5000	0.1651E-08	0.92657	8.7824
7	MgPO4-	0.1261E-09	6.5000	0.1169E-09	0.92657	9.9323
8	KPO4--	0.2442E-13	1.9000	0.1803E-13	0.73846	13.7440
9	Fe(III)PO4	0.1328E-09	12.2000	0.1330E-09	1.00130	9.8762
10	MnPO4-	0.1128E-10	7.2000	0.1046E-10	0.92657	10.9807
11	Cu(II)PO4-	0.1789E-08	9.8000	0.1658E-08	0.92657	8.7804
12	ZnPO4-	0.9130E-10	8.0000	0.8460E-10	0.92657	10.0726
13	NiPO4-	0.2664E-10	8.4000	0.2469E-10	0.92657	10.6075
14	CaHPO4	0.3483E-06	0.6000	0.3487E-06	1.00130	6.4575
15	MgHPO4	0.7798E-07	1.1000	0.7808E-07	1.00130	7.1075
16	KHPO4-	0.6516E-08	-0.8000	0.6038E-08	0.92657	8.2191
17	Fe(III)HPO4+	0.7617E-07	6.7000	0.7058E-07	0.92657	7.1513
18	MnHPO4	0.1752E-07	2.2000	0.1755E-07	1.00130	7.7558
19	Cu(II)HPO4	0.1753E-07	2.6000	0.1756E-07	1.00130	7.7556
20	ZnHPO4	0.7106E-08	1.7000	0.7115E-08	1.00130	8.1478
21	NiHPO4	0.3287E-09	1.3000	0.3291E-09	1.00130	9.4827
22	KHCO3	0.1073E-09	-6.0300	0.1074E-09	1.00130	9.9690
23	Fe(III)HCO3++	0.3392E-11	-1.2300	0.2505E-11	0.73846	11.6012
24	MnHCO3+	0.4543E-08	-1.9000	0.4210E-08	0.92657	8.3757
25	Cu(II)HCO3+	0.2126E-10	-3.8300	0.1970E-10	0.92657	10.7055
26	ZnHCO3+	0.3431E-09	-3.1300	0.3179E-09	0.92657	9.4977
27	NiHCO3+	0.7953E-10	-2.8300	0.7369E-10	0.92657	10.1326
28	Cu(OH)2	0.3096E-12	10.3000	0.3100E-12	1.00130	12.5086
29	CuNO3+	0.3065E-08	0.4000	0.2840E-08	0.92657	8.5467
30	CuCO3	0.5001E-08	6.8000	0.5008E-08	1.00130	8.3003

31	ZnNO3+		0.9868E-08	0.4000	0.9143E-08	0.92657	8.0389
32	ZnCO3		0.1610E-09	4.8000	0.1612E-09	1.00130	9.7926
33	Ni(OH)2		0.5804E-14	9.0000	0.5812E-14	1.00130	14.2357
34	CaCl+		0.7210E-07	-1.0000	0.6680E-07	0.92657	7.1752
35	MgCl+		0.5105E-08	-1.0000	0.4730E-08	0.92657	8.3251
36	NiCl+		0.3410E-09	0.4000	0.3160E-09	0.92657	9.5004
37	NiCO3		0.1871E-09	5.8000	0.1873E-09	1.00130	9.7274
38	CaNO3+		0.1160E-04	0.6800	0.1075E-04	0.92657	4.9686
39	MnCO3		0.6293E-10	4.5000	0.6301E-10	1.00130	10.2006
40	FeNO3++		0.4889E-11	1.0000	0.3611E-11	0.73846	11.4424
41	FeCO3+		0.2173E-05	12.9000	0.2013E-05	0.92657	5.6961
42	KCO3-		0.5878E-11	0.9000	0.5447E-11	0.92657	11.2639
43	HL		0.6685E-03	-4.0000	0.6693E-03	1.00130	3.1744
44	MnL2		0.6443E-09	10.8300	0.6451E-09	1.00130	9.1903
45	CuL2		0.6456E-06	14.2500	0.6464E-06	1.00130	6.1895
46	ZnL2		0.1504E-08	11.1100	0.1506E-08	1.00130	8.8223
47	NiL2		0.8361E-10	10.6800	0.8372E-10	1.00130	10.0772
48	CaL2		0.8959E-07	9.8900	0.8971E-07	1.00130	7.0472
49	MgL2		0.8757E-08	10.1100	0.8768E-08	1.00130	8.0571
50	BaL2		0.4366E-12	8.4600	0.4371E-12	1.00130	12.3594
51	FeL3		0.3989E-12	18.8600	0.3994E-12	1.00130	12.3986
52	KCl		0.4237E-07	-0.8356	0.4243E-07	1.00130	7.3724
53	KSO4-		0.6321E-06	0.7053	0.5856E-06	0.92657	6.2324
54	BaOH		0.1490E-12	2.1777	0.1381E-12	0.92657	12.8599
55	NaCl		0.1359E-07	-1.2434	0.1360E-07	1.00130	7.8663
56	NaCO3-		0.4038E-11	0.8230	0.3742E-11	0.92657	11.4269
57	NaSO4-		0.2033E-06	0.2987	0.1883E-06	0.92657	6.7250
58	Ca(OH)+		0.8162E-10	1.1643	0.7563E-10	0.92657	10.1213
59	CaCO3		0.1697E-08	3.0324	0.1699E-08	1.00130	8.7698
60	CaHCO3+		0.1342E-09	-6.3281	0.1243E-09	0.92657	9.9055
61	CaSO4		0.4812E-04	2.2589	0.4819E-04	1.00130	4.3171
62	Mg(OH)+		0.1239E-09	2.4955	0.1148E-09	0.92657	9.9400
63	MgCO3		0.2836E-09	3.4055	0.2840E-09	1.00130	9.5467
64	MgHCO3+		0.2856E-08	-3.8500	0.2646E-08	0.92657	8.5774
65	MgSO4		0.1923E-05	2.0105	0.1925E-05	1.00130	5.7155
66	Fe(OH)++	(III)	0.8343E-06	11.8690	0.6161E-06	0.73846	6.2104
67	Fe(OH)2+	(III)	0.2090E-04	21.5913	0.1936E-04	0.92657	4.7130
68	Fe(OH)3	(III)	0.3002E-24	10.0072	0.3006E-24	1.00130	24.5220
69	Fe(OH)4-	(III)	0.5929E-07	35.4941	0.5494E-07	0.92657	7.2601
70	FeCl++	(III)	0.2013E-11	1.1411	0.1486E-11	0.73846	11.8279
71	FeCl2+	(III)	0.5474E-14	1.7887	0.5072E-14	0.92657	14.2948
72	FeCl3	(III)	0.2782E-18	0.6429	0.2785E-18	1.00130	18.5551
73	FeCl4-	(III)	0.2046E-23	-1.4096	0.1896E-23	0.92657	23.7222
74	FeSO4+	(III)	0.7619E-19	-5.7814	0.7059E-19	0.92657	19.1512
75	MnOH+		0.1775E-10	3.4000	0.1645E-10	0.92657	10.7839
76	MnOH2		0.2458E-16	5.8000	0.2461E-16	1.00130	16.6088
77	MnOH3-		0.3975E-23	7.2000	0.3683E-23	0.92657	23.4338
78	MnSO4		0.4571E-07	2.1349	0.4576E-07	1.00130	7.3395
79	MnCl+		0.9991E-09	0.0400	0.9257E-09	0.92657	9.0335
80	Ni(OH)+		0.2412E-11	3.3600	0.2235E-11	0.92657	11.6507
81	HSO4-		0.5810E-08	-12.9784	0.5384E-08	0.92657	8.2689
82	HCO3-		0.2234E-04	-4.1672	0.2070E-04	0.92657	4.6839
83	H2CO3		0.2028E-04	-12.4005	0.2030E-04	1.00130	4.6924
84	HCl		0.2591E-16	-21.6963	0.2594E-16	1.00130	16.5860
85	Zn(OH)+		0.2960E-09	4.5141	0.2743E-09	0.92657	9.5618
86	Zn(OH)3-		0.9560E-17	13.4731	0.8858E-17	0.92657	17.0527
87	ZnCl+		0.5689E-10	-1.3126	0.5271E-10	0.92657	10.2781
88	ZnCl2		0.5537E-12	-0.1762	0.5544E-12	1.00130	12.2562
89	ZnCl3-		0.8895E-17	-1.8894	0.8241E-17	0.92657	17.0840
90	ZnCl4--		0.6851E-20	-1.9868	0.5059E-20	0.73846	20.2959

91	ZnSO4	0.6935E-07	2.2079	0.6944E-07	1.00130	7.1584
92	NiSO4	0.6888E-08	2.1398	0.6897E-08	1.00130	8.1613
93	Cu(OH)+	0.3573E-08	6.1035	0.3310E-08	0.92657	8.4801
94	CuCl+	0.9712E-10	-0.5725	0.8999E-10	0.92657	10.0458
95	CuCl2	0.1779E-13	-1.1614	0.1782E-13	1.00130	13.7492
96	CuCl3-	0.2704E-18	-2.8988	0.2505E-18	0.92657	18.6012
97	CuCl4--	0.7838E-24	-5.4206	0.5788E-24	0.73846	24.2375
98	CuSO4	0.2973E-07	2.3479	0.2977E-07	1.00130	7.5262
99	BaHCO3+	0.1620E-20	-13.4943	0.1501E-20	0.92657	20.8236
100	BaSO4	0.1104E-07	2.3713	0.1105E-07	1.00130	7.9567

Solid Precipitation/Dissolution Prohibited

Fixed pH

pH 6.500

Ionic strength 0.56266E-02 mol/kg

The activity of water 0.99989388

0.996E-02 mol/kg CO2 released. ppCO2 0.320E-06 kbar

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SOLUTION SATURATION CONDITION

Number of Possible Minerals is 40

Mineral	IAP/SP	log Ks	Condition
Cu3(PO4)2	0.686E-01	37.7000	Undersaturated
Zn3(PO4)2	0.433E-01	36.7000	Undersaturated
Ni3(PO4)2	0.120E-02	30.2000	Undersaturated
Mn3(PO4)2	0.200E-03	23.8300	Undersaturated
Fe(III)PO4	0.728E+02	25.8000	Moderate Oversaturation
Mg3(PO4)2	0.232E-02	23.9000	Undersaturated
APATITE	0.224E+00	54.3500	Undersaturated
OCTA Ca-PHOSPH	0.155E+00	34.2000	Undersaturated
BRUSHITE	0.192E+00	4.9100	Undersaturated
MnHPO4	0.274E+01	11.2700	Moderate Oversaturation
Zn HYDROXIDE	0.562E-02	15.5500	Undersaturated
PYROCHROITE	0.632E-03	12.8100	Undersaturated
MANGANOSITE	0.773E-04	10.0730	Undersaturated
NICKEL CARB	0.217E-03	8.2000	Undersaturated
Fe(3) HYDROXIDE	0.127E+02	38.9471	Moderate Oversaturation
LIME	0.536E-08	-5.3012	Undersaturated
PERICLASE	0.156E-04	6.2383	Undersaturated
BRUCITE	0.124E-02	11.9452	Undersaturated
PORTLANDITE	0.171E-04	5.2075	Undersaturated
CALCITE	0.212E-01	8.4545	Undersaturated
ARAGONITE	0.175E-01	8.2872	Undersaturated
DOLOMITE	0.181E-01	17.7869	Undersaturated
MAGNESITE	0.205E-02	7.5748	Undersaturated
TENORITE	0.150E+00	20.3400	Undersaturated
SYLVITE	0.234E-03	-0.7237	Undersaturated
HALITE	0.913E-04	-1.4564	Undersaturated
BARITE	0.128E+01	10.5427	Slight Oversaturation
ANHYDRITE	0.597E-01	4.1283	Undersaturated
GYPSUM	0.106E+00	4.6306	Undersaturated

WITHERITE	0.131E+00	13.7864	Undersaturated
RHODACHROSITE	0.793E-02	10.4988	Undersaturated
SMITHSONITE	0.373E-02	9.7371	Undersaturated
MALACHITE	0.107E+00	33.0627	Undersaturated
AZURITE	0.130E-01	39.8143	Undersaturated
NI HYDROXIDE	0.255E-02	15.4570	Undersaturated
BUNSENITE	0.275E-02	15.5520	Undersaturated
CU(II) HYDROXID	0.461E-01	18.8000	Undersaturated
GOETHITE	0.762E-07	6.0580	Undersaturated
HEMATITE	0.213E+02	79.6910	Moderate Oversaturation
CUPRIC FERRITE	0.658E-04	45.8700	Undersaturated

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Predictions of Density

Density of the Aqueous Phase:	1.00339040119449	-	g/cc
Total Fluid Density:	1.00339040119449	-	g/cc

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Primary Distribution of Species

barium

Uncomplexed Aqueous Species = 94.98377 %

Aqueous Complexes and Ion Exchangers

BaL2	0.00020 %
BaOH	0.00007 %
BaHCO3+	0.00000 %
BaSO4	5.01597 %

calcium

Uncomplexed Aqueous Species = 95.14210 %

Aqueous Complexes and Ion Exchangers

CaPO4-	0.00014 %
CaHPO4	0.02809 %
CaCl+	0.00581 %
CaNO3+	0.93561 %
CaL2	0.00723 %
Ca(OH)+	0.00001 %
CaCO3	0.00014 %
CaHCO3+	0.00001 %
CaSO4	3.88086 %

copper(II)

Uncomplexed Aqueous Species = 45.66254 %

Aqueous Complexes and Ion Exchangers

Cu(II)PO4-	0.13764 %
Cu(II)HPO4	1.34865 %
Cu(II)HCO3+	0.00164 %
Cu(OH)2	0.00002 %
CuNO3+	0.23577 %
CuCO3	0.38473 %
CuL2	49.65949 %
Cu(OH)+	0.27481 %
CuCl+	0.00747 %
CuCl2	0.00000 %
CuCl3-	0.00000 %
CuCl4--	0.00000 %
CuSO4	2.28724 %

iron(III)

Uncomplexed Aqueous Species = 0.00054 %

Aqueous Complexes and Ion Exchangers

Fe(III)HPO4+		53.49284 %
Fe(III)H2PO4++		0.00591 %
Fe(III)(SO4)2-		0.00001 %
Fe(III)PO4		0.00026 %
Fe(III)HPO4+		0.14733 %
Fe(III)HCO3++		0.00001 %
FeNO3++		0.00001 %
FeCO3+		4.20287 %
FeL3		0.00000 %
Fe(OH)++	(III)	1.61366 %
Fe(OH)2+	(III)	40.42188 %
Fe(OH)3	(III)	0.00000 %
Fe(OH)4-	(III)	0.11468 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
FeSO4+	(III)	0.00000 %

magnesium

Uncomplexed Aqueous Species = 97.63970 %

Aqueous Complexes and Ion Exchangers

MgPO4-	0.00015 %
MgHPO4	0.09120 %
MgCl+	0.00597 %
MgL2	0.01024 %
Mg(OH)+	0.00014 %
MgCO3	0.00033 %
MgHCO3+	0.00334 %
MgSO4	2.24892 %

manganese(II)

Uncomplexed Aqueous Species = 95.54442 %

Aqueous Complexes and Ion Exchangers

MnPO4-	0.00072 %
MnHPO4	1.12326 %
MnHCO3+	0.29124 %
MnCO3	0.00403 %
MnL2	0.04130 %
MnOH+	0.00114 %
MnOH2	0.00000 %
MnOH3-	0.00000 %
MnSO4	2.92984 %
MnCl+	0.06404 %

nickel

Uncomplexed Aqueous Species = 96.54915 %

Aqueous Complexes and Ion Exchangers

NiPO4-	0.01158 %
NiHPO4	0.14290 %
NiHCO3+	0.03458 %
Ni(OH)2	0.00000 %
NiCl+	0.14826 %
NiCO3	0.08134 %
NiL2	0.03635 %
Ni(OH)+	0.00105 %
NiSO4	2.99478 %

potassium

Uncomplexed Aqueous Species = 99.83348 %

Aqueous Complexes and Ion Exchangers

KPO4--	0.00000 %
KHPO4-	0.00159 %
KHCO3	0.00003 %
KCO3-	0.00000 %
KCl	0.01036 %
KSO4-	0.15454 %

sodium

Uncomplexed Aqueous Species = 99.93526 %

Aqueous Complexes and Ion Exchangers

NaCl	0.00406 %
NaCO3-	0.00000 %
NaSO4-	0.06068 %

zinc

Uncomplexed Aqueous Species = 95.56117 %

Aqueous Complexes and Ion Exchangers

ZnPO4-		0.00457 %
ZnHPO4		0.35531 %
ZnHCO3+		0.01715 %
ZnNO3+		0.49339 %
ZnCO3		0.00805 %
ZnL2		0.07519 %
Zn(OH)+		0.01480 %
Zn(OH)3-		0.00000 %
ZnCl+		0.00284 %
ZnCl2		0.00003 %
ZnCl3-		0.00000 %
ZnCl4--		0.00000 %
ZnSO4		3.46750 %

chloride

Uncomplexed Aqueous Species = 99.98376 %

Aqueous Complexes and Ion Exchangers

CaCl+		0.00870 %
MgCl+		0.00062 %
NiCl+		0.00004 %
KCl		0.00511 %
NaCl		0.00164 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
MnCl+		0.00012 %
HCl		0.00000 %
ZnCl+		0.00001 %
ZnCl2		0.00000 %
ZnCl3-		0.00000 %
ZnCl4--		0.00000 %
CuCl+		0.00001 %
CuCl2		0.00000 %
CuCl3-		0.00000 %
CuCl4--		0.00000 %

nitrate

Uncomplexed Aqueous Species = 99.58520 %

Aqueous Complexes and Ion Exchangers

CuNO3+	0.00011 %
ZnNO3+	0.00035 %
CaNO3+	0.41434 %
FeNO3++	0.00000 %

phosphate

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

HPO4--	3.18096 %
H2PO4-	67.42919 %
Fe(III)HPO4+	28.80812 %
Fe(III)H2PO4++	0.00318 %
CaPO4-	0.00186 %
MgPO4-	0.00013 %
KPO4--	0.00000 %
Fe(III)PO4	0.00014 %
MnPO4-	0.00001 %
Cu(II)PO4-	0.00186 %
ZnPO4-	0.00010 %
NiPO4-	0.00003 %
CaHPO4	0.36279 %
MgHPO4	0.08123 %
KHPO4-	0.00679 %
Fe(III)HPO4+	0.07934 %
MnHPO4	0.01825 %
Cu(II)HPO4	0.01826 %
ZnHPO4	0.00740 %
NiHPO4	0.00034 %

sulphate

Uncomplexed Aqueous Species = 89.02164 %

Aqueous Complexes and Ion Exchangers

Fe(III)(SO4)2-	0.00000 %
KSO4-	0.13592 %
NaSO4-	0.04371 %
CaSO4	10.34896 %
MgSO4	0.41351 %
FeSO4+ (III)	0.00000 %
MnSO4	0.00983 %
HSO4-	0.00125 %
ZnSO4	0.01491 %
NiSO4	0.00148 %
CuSO4	0.00639 %
BaSO4	0.00237 %

biofloc

Uncomplexed Aqueous Species = 0.00638 %

Aqueous Complexes and Ion Exchangers

HL	99.77088 %
MnL2	0.00019 %
CuL2	0.19271 %
ZnL2	0.00045 %
NiL2	0.00002 %
CaL2	0.02674 %

MgL2	0.00261 %
BaL2	0.00000 %
FeL3	0.00000 %

carbonate

Uncomplexed Aqueous Species = 0.00548 %

Aqueous Complexes and Ion Exchangers

KHCO3	0.00024 %
Fe(III)HCO3++	0.00001 %
MnHCO3+	0.01014 %
Cu(II)HCO3+	0.00005 %
ZnHCO3+	0.00077 %
NiHCO3+	0.00018 %
CuCO3	0.01116 %
ZnCO3	0.00036 %
NiCO3	0.00042 %
MnCO3	0.00014 %
FeCO3+	4.84882 %
KCO3-	0.00001 %
NaCO3-	0.00001 %
CaCO3	0.00379 %
CaHCO3+	0.00030 %
MgCO3	0.00063 %
MgHCO3+	0.00637 %
HCO3-	49.86297 %
H2CO3	45.24816 %
BaHCO3+	0.00000 %

Iterations 4 4 2 1 1 1 1 1 1 1 1 1 1
Primary charge balance is -1.956279999999999E-003 mol per kg
Final mass balance is 8.673617379884035E-019 mol per kg
Solution Charge Balance is -1.196334811745991E-003 mol per kg

Sludge/Seawater
Temperature 5.00 C
Pressure 0.0010000 kbar

Concentrations of Primary Aqueous Components - mol/kg

		Total	Final	Activity	gamma i	-log a
1	proton	0.0000E+00	0.8491E-08	0.6310E-08	0.74311	8.2000
2	hydroxide	0.0000E+00	0.4103E-06	0.2933E-06	0.71491	6.5327
3	barium	0.1070E-05	0.9288E-06	0.1792E-06	0.19296	6.7466
4	cadmium	0.3670E-07	0.3571E-08	0.7354E-09	0.20594	9.1335
5	calcium	0.1050E-01	0.9235E-02	0.1894E-02	0.20513	2.7225
6	cobalt	0.8540E-07	0.6606E-07	0.1430E-07	0.21645	7.8447
7	copper(II)	0.3950E-05	0.3139E-06	0.6826E-07	0.21748	7.1659
8	iron(III)	0.5390E-05	0.4340E-13	0.1337E-14	0.03079	14.8740
9	lead	0.6520E-06	0.1181E-10	0.2331E-11	0.19741	11.6325
10	magnesium	0.5330E-01	0.4884E-01	0.1078E-01	0.22069	1.9674
11	manganese(II)	0.1270E-05	0.9638E-06	0.2058E-06	0.21348	6.6867
12	nickel	0.3850E-06	0.1985E-06	0.4261E-07	0.21463	7.3705
13	potassium	0.1010E-01	0.9633E-02	0.6213E-02	0.64505	2.2067
14	sodium	0.4630E+00	0.4541E+00	0.3029E+00	0.66703	0.5187
15	zinc	0.1970E-04	0.1632E-04	0.3531E-05	0.21645	5.4520
16	chloride	0.5400E+00	0.5335E+00	0.3573E+00	0.66970	0.4470
17	fluoride	0.6890E-04	0.5502E-04	0.3994E-04	0.72584	4.3986
18	phosphate	0.3880E-04	0.2575E-08	0.4450E-10	0.01728	10.3517
19	sulphate	0.2800E-01	0.1955E-01	0.3773E-02	0.19302	2.4233
20	mercury(II)	0.7620E-08	0.2902E-22	0.5831E-23	0.20092	23.2343
21	silver	0.2550E-06	0.1194E-11	0.7747E-12	0.64871	12.1109
22	biofloc	0.9000E-03	0.2061E-05	0.2934E-05	1.42319	5.5326
23	carbonate	0.1000E-01	0.2178E-04	0.4474E-05	0.20542	5.3493

Concentrations of Aqueous Complexed Species - mol/kg

		Final	log Keq	Activity	gamma c	-log a
1	HPO4--	0.1420E-04	-1.6500	0.3336E-05	0.23495	5.4768
2	H2PO4-	0.2663E-05	-8.4500	0.1770E-05	0.66484	5.7520
3	Fe(III)HPO4+	0.5450E-09	9.2600	0.3624E-09	0.66484	9.4409
4	Fe(III)H2PO4++	0.2710E-14	-3.0200	0.6368E-15	0.23495	15.1960
5	Fe(III)(SO4)2-	0.6865E-14	5.3800	0.4564E-14	0.66484	14.3406
6	CaPO4-	0.4010E-06	6.5000	0.2666E-06	0.66484	6.5742
7	MgPO4-	0.2281E-05	6.5000	0.1517E-05	0.66484	5.8191
8	KPO4--	0.9347E-10	1.9000	0.2196E-10	0.23495	10.6583
9	Fe(III)PO4	0.8369E-13	12.2000	0.9425E-13	1.12622	13.0257
10	MnPO4-	0.2182E-09	7.2000	0.1451E-09	0.66484	9.8383
11	Cu(II)PO4-	0.2882E-07	9.8000	0.1916E-07	0.66484	7.7175
12	ZnPO4-	0.2364E-07	8.0000	0.1571E-07	0.66484	7.8037
13	NiPO4-	0.7163E-09	8.4000	0.4762E-09	0.66484	9.3222
14	CdPO4-	0.1556E-12	6.5000	0.1035E-12	0.66484	12.9851
15	PbPO4-	0.4932E-15	6.5000	0.3279E-15	0.66484	15.4842
16	CaHPO4	0.9978E-06	0.6000	0.1124E-05	1.12622	5.9493
17	MgHPO4	0.1795E-04	1.1000	0.2022E-04	1.12622	4.6943
18	KHPO4-	0.2207E-06	-0.8000	0.1467E-06	0.66484	6.8335
19	Fe(III)HPO4+	0.1501E-11	6.7000	0.9980E-12	0.66484	12.0009
20	MnHPO4	0.4314E-08	2.2000	0.4859E-08	1.12622	8.3135
21	Cu(II)HPO4	0.3595E-08	2.6000	0.4049E-08	1.12622	8.3927
22	CdHPO4	0.4551E-11	1.6700	0.5125E-11	1.12622	11.2903
23	ZnHPO4	0.2342E-07	1.7000	0.2637E-07	1.12622	7.5789
24	NiHPO4	0.1125E-09	1.3000	0.1267E-09	1.12622	9.8974
25	PbHPO4	0.9750E-14	1.5000	0.1098E-13	1.12622	13.9594

26	KHCO3	0.7713E-07	-6.0300	0.8687E-07	1.12622	7.0611
27	Fe(III)HCO3++	0.5018E-14	-1.2300	0.1179E-14	0.23495	14.9285
28	MnHCO3+	0.5836E-07	-1.9000	0.3880E-07	0.66484	7.4111
29	Cu(II)HCO3+	0.2275E-09	-3.8300	0.1512E-09	0.66484	9.8203
30	CdHCO3+	0.2451E-11	-3.8300	0.1630E-11	0.66484	11.7879
31	ZnHCO3+	0.5899E-07	-3.1300	0.3922E-07	0.66484	7.4065
32	NiHCO3+	0.1420E-08	-2.8300	0.9440E-09	0.66484	9.0250
33	PbHCO3+	0.3092E-12	-2.2300	0.2056E-12	0.66484	12.6870
34	Cu(OH)2	0.1040E-09	10.3000	0.1172E-09	1.12622	9.9312
35	CuCO3	0.1711E-05	6.8000	0.1927E-05	1.12622	5.7152
36	ZnCO3	0.8851E-06	4.8000	0.9969E-06	1.12622	6.0014
37	Ni(OH)2	0.3255E-11	9.0000	0.3666E-11	1.12622	11.4358
38	CaCl+	0.1018E-03	-1.0000	0.6769E-04	0.66484	4.1695
39	MgCl+	0.5793E-03	-1.0000	0.3851E-03	0.66484	3.4144
40	NiCl+	0.5752E-07	0.4000	0.3824E-07	0.66484	7.4175
41	CoCl+	0.1930E-07	0.4000	0.1283E-07	0.66484	7.8916
42	CaF+	0.4531E-06	0.6000	0.3012E-06	0.66484	6.5211
43	NiF+	0.3222E-10	1.1000	0.2142E-10	0.66484	10.6691
44	NiCO3	0.1068E-06	5.8000	0.1203E-06	1.12622	6.9199
45	Pb(OH)3	0.7027E-17	13.9000	0.4672E-17	0.66484	17.3305
46	Pb(OH)4	0.1465E-20	16.3000	0.3442E-21	0.23495	21.4632
47	PbF+	0.2793E-14	1.3000	0.1857E-14	0.66484	14.7311
48	PbCO3	0.9258E-10	7.0000	0.1043E-09	1.12622	9.9819
49	CdCl3	0.1268E-07	2.4000	0.8427E-08	0.66484	8.0743
50	CdCl4	0.2031E-07	2.6000	0.4772E-08	0.23495	8.3213
51	CdSO4	0.5354E-10	2.5000	0.4785E-13	0.00089	13.3201
52	CdCO3	0.3678E-10	4.1000	0.4142E-10	1.12622	10.3828
53	MnCO3	0.2585E-07	4.5000	0.2911E-07	1.12622	7.5360
54	FeCO3+	0.7144E-07	12.9000	0.4750E-07	0.66484	7.3234
55	KCO3-	0.3321E-06	0.9000	0.2208E-06	0.66484	6.6560
56	HL	0.8723E-03	-4.0000	0.9824E-03	1.12622	3.0077
57	MnL2	0.1837E-08	10.8300	0.2069E-08	1.12622	8.6842
58	CuL2	0.1793E-05	14.2500	0.2019E-05	1.12622	5.6948
59	ZnL2	0.6712E-07	11.1100	0.7559E-07	1.12622	7.1215
60	NiL2	0.1638E-09	10.6800	0.1844E-09	1.12622	9.7342
61	CdL2	0.1366E-10	11.2800	0.1538E-10	1.12622	10.8130
62	CaL2	0.6983E-06	9.8900	0.7865E-06	1.12622	6.1043
63	MgL2	0.1026E-04	10.1100	0.1156E-04	1.12622	4.9372
64	BaL2	0.5032E-11	8.4600	0.5667E-11	1.12622	11.2466
65	CoL2	0.3312E-10	10.4000	0.3730E-10	1.12622	10.4283
66	FeL3	0.2777E-14	18.8600	0.3127E-14	1.12622	14.5048
67	AgL	0.1428E-13	5.7450	0.1608E-13	1.12622	13.7937
68	CdCl+	0.1250E-10	-1.5000	0.8310E-11	0.66484	11.0804
69	CdF+	0.6240E-12	1.1500	0.4149E-12	0.66484	12.3821
70	CdCl2	0.2094E-12	-2.6000	0.2358E-12	1.12622	12.6274
71	CdCl+	0.1250E-10	-1.5000	0.8310E-11	0.66484	11.0804
72	Cd(OH)+	0.3901E-11	4.0800	0.2593E-11	0.66484	11.5861
73	Cd(OH)2	0.2816E-14	7.7000	0.3171E-14	1.12622	14.4988
74	Cd(OH)3	0.2728E-19	8.9900	0.1814E-19	0.66484	19.7414
75	KCl	0.2879E-03	-0.8356	0.3242E-03	1.12622	3.4892
76	KSO4-	0.1789E-03	0.7053	0.1189E-03	0.66484	3.9247
77	BaOH	0.1190E-10	2.1777	0.7914E-11	0.66484	11.1016
78	NaCl	0.5486E-02	-1.2434	0.6179E-02	1.12622	2.2091
79	NaCO3-	0.1356E-04	0.8230	0.9016E-05	0.66484	5.0450
80	NaSO4-	0.3419E-02	0.2987	0.2273E-02	0.66484	2.6433
81	Ca(OH)+	0.1220E-07	1.1643	0.8111E-08	0.66484	8.0909
82	CaCO3	0.8109E-05	3.0324	0.9132E-05	1.12622	5.0394
83	CaHCO3+	0.2005E-07	-6.3281	0.1333E-07	0.66484	7.8751
84	CaSO4	0.1152E-02	2.2589	0.1298E-02	1.12622	2.8869
85	Mg(OH)+	0.1488E-05	2.4955	0.9896E-06	0.66484	6.0046

86	MgCO3		0.1089E-03	3.4055	0.1227E-03	1.12622	3.9113
87	MgHCO3+		0.3430E-04	-3.8500	0.2281E-04	0.66484	4.6419
88	MgSO4		0.3699E-02	2.0105	0.4166E-02	1.12622	2.3803
89	MgF+		0.6595E-05	1.0079	0.4384E-05	0.66484	5.3581
90	Fe(OH)++	(III)	0.1234E-08	11.8690	0.2900E-09	0.23495	9.5376
91	Fe(OH)2+	(III)	0.6750E-06	21.5913	0.4487E-06	0.66484	6.3480
92	Fe(OH)3	(III)	0.3045E-24	10.0072	0.3430E-24	1.12622	24.4648
93	Fe(OH)4-	(III)	0.4642E-05	35.4941	0.3086E-05	0.66484	5.5106
94	FeCl++	(III)	0.2813E-13	1.1411	0.6609E-14	0.23495	14.1798
95	FeCl2+	(III)	0.1578E-13	1.7887	0.1049E-13	0.66484	13.9792
96	FeCl3	(III)	0.2379E-15	0.6429	0.2680E-15	1.12622	15.5719
97	FeCl4-	(III)	0.1276E-17	-1.4096	0.8483E-18	0.66484	18.0715
98	FeSO4+	(III)	0.1255E-22	-5.7814	0.8342E-23	0.66484	23.0787
99	FeF++	(III)	0.2000E-13	4.9446	0.4699E-14	0.23495	14.3280
100	FeF2+	(III)	0.2025E-14	8.8003	0.1346E-14	0.66484	14.8710
101	FeF3	(III)	0.2299E-16	11.4830	0.2589E-16	1.12622	16.5868
102	FeF4-	(III)	0.1561E-17	14.4846	0.1038E-17	0.66484	17.9838
103	MnOH+		0.2280E-09	3.4000	0.1516E-09	0.66484	9.8193
104	MnOH2		0.9918E-14	5.8000	0.1117E-13	1.12622	13.9520
105	MnOH3-		0.1238E-18	7.2000	0.8230E-19	0.66484	19.0846
106	MnSO4		0.9404E-07	2.1349	0.1059E-06	1.12622	6.9751
107	MnCl+		0.1212E-06	0.0400	0.8061E-07	0.66484	7.0936
108	MnF+		0.5153E-10	0.6200	0.3426E-10	0.66484	10.4653
109	AgCl		0.7171E-09	3.4650	0.8077E-09	1.12622	9.0928
110	AgCl2-		0.4703E-07	5.4999	0.3127E-07	0.66484	7.5049
111	AgCl3--		0.4255E-07	5.4516	0.9997E-08	0.23495	8.0001
112	AgCl4---		0.1647E-06	5.6804	0.6049E-08	0.03673	8.2183
113	AgSO4-		0.8096E-13	1.2652	0.5383E-13	0.66484	13.2690
114	Ni(OH)+		0.4306E-10	3.3600	0.2863E-10	0.66484	10.5432
115	HSO4-		0.1997E-08	-12.9784	0.1328E-08	0.66484	8.8769
116	HCO3-		0.1533E-02	-4.1672	0.1019E-02	0.66484	2.9917
117	H2CO3		0.1771E-04	-12.4005	0.1995E-04	1.12622	4.7002
118	HCl		0.2138E-15	-21.6963	0.2408E-15	1.12622	15.6184
119	HF		0.2387E-09	-11.6968	0.2688E-09	1.12622	9.5705
120	HF2		0.7554E-13	-11.0268	0.5022E-13	0.66484	13.2991
121	PbOH+		0.1174E-09	8.0577	0.7808E-10	0.66484	10.1075
122	Pb(OH)2		0.3320E-13	11.2706	0.3739E-13	1.12622	13.4272
123	PbCl+		0.4962E-10	1.5979	0.3299E-10	0.66484	10.4816
124	PbCl2		0.1493E-10	1.7521	0.1681E-10	1.12622	10.7743
125	PbCl3-		0.6651E-11	1.6190	0.4422E-11	0.66484	11.3544
126	PbCl4--		0.2865E-11	1.2484	0.6731E-12	0.23495	12.1719
127	PbSO4		0.6517E-06	7.9215	0.7340E-06	1.12622	6.1343
128	Zn(OH)+		0.5090E-07	4.5141	0.3384E-07	0.66484	7.4706
129	Zn(OH)3-		0.3984E-11	13.4731	0.2649E-11	0.66484	11.5769
130	ZnCl+		0.9240E-07	-1.3126	0.6143E-07	0.66484	7.2116
131	ZnCl2		0.2668E-06	-0.1762	0.3005E-06	1.12622	6.5221
132	ZnCl3-		0.3126E-08	-1.8894	0.2078E-08	0.66484	8.6823
133	ZnCl4--		0.2526E-08	-1.9868	0.5934E-09	0.23495	9.2267
134	ZnSO4		0.1910E-05	2.2079	0.2151E-05	1.12622	5.6674
135	ZnF+		0.7914E-09	0.5717	0.5261E-09	0.66484	9.2789
136	NiSO4		0.1970E-07	2.1398	0.2218E-07	1.12622	7.6540
137	Cu(OH)+		0.3822E-07	6.1035	0.2541E-07	0.66484	7.5950
138	CuCl+		0.9817E-08	-0.5725	0.6526E-08	0.66484	8.1853
139	CuCl2		0.5336E-09	-1.1614	0.6010E-09	1.12622	9.2211
140	CuCl3-		0.5912E-11	-2.8988	0.3931E-11	0.66484	11.4055
141	CuCl4--		0.1798E-13	-5.4206	0.4224E-14	0.23495	14.3743
142	CuSO4		0.5095E-07	2.3479	0.5738E-07	1.12622	7.2412
143	CuF+		0.1644E-10	0.6030	0.1093E-10	0.66484	10.9614
144	HgCl+		0.1058E-16	6.5284	0.7034E-17	0.66484	17.1528
145	HgCl2		0.6098E-10	13.9650	0.6867E-10	1.12622	10.1632

146	HgCl3-	0.5762E-08	16.1585	0.3831E-08	0.66484	8.4167
147	HgCl4--	0.1797E-08	15.6475	0.4221E-09	0.23495	9.3746
148	HgSO4	0.4907E-24	1.4000	0.5526E-24	1.12622	24.2576
149	HgF+	0.4246E-26	1.0836	0.2823E-26	0.66484	26.5493
150	BaHCO3+	0.1294E-18	-13.4943	0.8603E-19	0.66484	19.0654
151	BaSO4	0.1412E-06	2.3713	0.1590E-06	1.12622	6.7986
152	NaF	0.6777E-05	-0.2000	0.7633E-05	1.12622	5.1173
153	KF	0.4933E-07	-0.6500	0.5556E-07	1.12622	7.2553

Solid Precipitation/Dissolution Prohibited

Fixed pH

pH 8.200

Ionic strength 0.51624E+00 mol/kg

The activity of water 0.98227688

0.826E-02 mol/kg CO2 released. ppCO2 0.320E-06 kbar

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SOLUTION SATURATION CONDITION

Number of Possible Minerals is 53

Mineral	IAP/SP	log Ks	Condition
Cu3(PO4)2	0.126E+00	37.7000	Undersaturated
Zn3(PO4)2	0.794E-01	36.7000	Undersaturated
Ni3(PO4)2	0.300E-02	30.2000	Undersaturated
Cd3(PO4)2	0.771E-03	32.5400	Undersaturated
Pb3(PO4)2	0.302E-02	43.0000	Undersaturated
Mn3(PO4)2	0.411E-03	23.8300	Undersaturated
Fe(III)PO4	0.194E+01	25.8000	Slight Oversaturation
Mg3(PO4)2	0.288E+00	23.9000	Undersaturated
APATITE	0.224E+01	54.3500	Moderate Oversaturation
FLUORAPATITE	0.355E+01	54.0210	Moderate Oversaturation
OCTA Ca-PHOSPH	0.704E+00	34.2000	Undersaturated
BRUSHITE	0.281E+00	4.9100	Undersaturated
PbHPO4	0.240E-05	-1.4000	Undersaturated
MnHPO4	0.179E+01	11.2700	Slight Oversaturation
Zn HYDROXIDE	0.103E+00	15.5500	Undersaturated
LEAD HYDROXIDE	0.465E-01	20.7000	Undersaturated
LEAD FLUORIDE	0.529E-04	7.6000	Undersaturated
LEAD SULPHATE	0.664E-03	7.7000	Undersaturated
FLUORITE	0.533E+00	10.7000	Undersaturated
SELLAITE	0.120E+00	8.0000	Undersaturated
PYROCHROITE	0.485E-02	12.8100	Undersaturated
MANGANOSITE	0.597E-03	10.0730	Undersaturated
NICKEL CARB	0.550E-02	8.2000	Undersaturated
OTAVITE	0.256E-01	11.3000	Undersaturated
CADMIUM HYDROX	0.251E-02	14.4000	Undersaturated
Fe(3) HYDROXIDE	0.131E+02	38.9471	Moderate Oversaturation
LIME	0.940E-07	-5.3012	Undersaturated
PERICLASE	0.118E-02	6.2383	Undersaturated
BRUCITE	0.935E-01	11.9452	Undersaturated
PORTLANDITE	0.297E-03	5.2075	Undersaturated
CALCITE	0.155E+01	8.4545	Slight Oversaturation

ARAGONITE	0.128E+01	8.2872	Slight Oversaturation
DOLOMITE	0.398E+01	17.7869	Moderate Oversaturation
MAGNESITE	0.135E+01	7.5748	Slight Oversaturation
TENORITE	0.109E+01	20.3400	Possible Equilibrium
SYLVITE	0.205E-01	-0.7237	Undersaturated
HALITE	0.615E-01	-1.4564	Undersaturated
BARITE	0.486E+01	10.5427	Moderate Oversaturation
ANHYDRITE	0.310E+00	4.1283	Undersaturated
GYPSUM	0.543E+00	4.6306	Undersaturated
ANGLESITE	0.872E-03	7.9373	Undersaturated
WITHERITE	0.700E+01	13.7864	Moderate Oversaturation
RHODACHROSITE	0.170E+00	10.4988	Undersaturated
CERUSSITE	0.270E-01	13.8454	Undersaturated
SMITHSONITE	0.294E+00	9.7371	Undersaturated
MALACHITE	0.116E+01	33.0627	Slight Oversaturation
AZURITE	0.167E+00	39.8143	Undersaturated
NI HYDROXIDE	0.219E-01	15.4570	Undersaturated
BUNSENITE	0.237E-01	15.5520	Undersaturated
CU(II) HYDROXID	0.333E+00	18.8000	Undersaturated
GOETHITE	0.792E-07	6.0580	Undersaturated
HEMATITE	0.222E+02	79.6910	Moderate Oversaturation
CUPRIC FERRITE	0.116E-03	45.8700	Undersaturated

****

Predictions of Density

Density of the Aqueous Phase:	1.03076188285467	- g/cc
Total Fluid Density:	1.03076188285467	- g/cc

****

Primary Distribution of Species

barium

Uncomplexed Aqueous Species = 86.80418 %

Aqueous Complexes and Ion Exchangers

BaL2	0.00047 %
BaOH	0.00111 %
BaHCO3+	0.00000 %
BaSO4	13.19424 %

cadmium

Uncomplexed Aqueous Species = 9.73028 %

Aqueous Complexes and Ion Exchangers

CdPO4-	0.00042 %
CdHPO4	0.01240 %
CdHCO3+	0.00668 %

CdCl3	34.53820 %
CdCl4	55.34768 %
CdSO4	0.14588 %
CdCO3	0.10021 %
CdL2	0.03722 %
CdCl+	0.03406 %
CdF+	0.00170 %
CdCl2	0.00057 %
CdCl+	0.03406 %
Cd(OH)+	0.01063 %
Cd(OH)2	0.00001 %
Cd(OH)3	0.00000 %

calcium

Uncomplexed Aqueous Species = 87.95590 %

Aqueous Complexes and Ion Exchangers

CaPO4-	0.00382 %
CaHPO4	0.00950 %
CaCl+	0.96968 %
CaF+	0.00431 %
CaL2	0.00665 %
Ca(OH)+	0.00012 %
CaCO3	0.07723 %
CaHCO3+	0.00019 %
CaSO4	10.97260 %

cobalt

Uncomplexed Aqueous Species = 77.35714 %

Aqueous Complexes and Ion Exchangers

CoCl+	22.60409 %
CoL2	0.03878 %

copper(II)

Uncomplexed Aqueous Species = 7.94568 %

Aqueous Complexes and Ion Exchangers

Cu(II)PO4-	0.72972 %
Cu(II)HPO4	0.09101 %
Cu(II)HCO3+	0.00576 %
Cu(OH)2	0.00263 %
CuCO3	43.31140 %
CuL2	45.39369 %
Cu(OH)+	0.96763 %
CuCl+	0.24852 %
CuCl2	0.01351 %
CuCl3-	0.00015 %
CuCl4--	0.00000 %
CuSO4	1.28988 %
CuF+	0.00042 %

iron(III)

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

Fe(III)HPO4+		0.01011 %
Fe(III)H2PO4++		0.00000 %
Fe(III)(SO4)2-		0.00000 %
Fe(III)PO4		0.00000 %
Fe(III)HPO4+		0.00003 %
Fe(III)HCO3++		0.00000 %
FeCO3+		1.32538 %
FeL3		0.00000 %
Fe(OH)++	(III)	0.02290 %
Fe(OH)2+	(III)	12.52232 %
Fe(OH)3	(III)	0.00000 %
Fe(OH)4-	(III)	86.11926 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
FeSO4+	(III)	0.00000 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %

lead

Uncomplexed Aqueous Species = 0.00181 %

Aqueous Complexes and Ion Exchangers

PbPO4-	0.00000 %
PbHPO4	0.00000 %
PbHCO3+	0.00005 %
Pb(OH)3	0.00000 %
Pb(OH)4	0.00000 %
PbF+	0.00000 %
PbCO3	0.01420 %
PbOH+	0.01801 %
Pb(OH)2	0.00001 %
PbCl+	0.00761 %
PbCl2	0.00229 %
PbCl3-	0.00102 %
PbCl4--	0.00044 %
PbSO4	99.95456 %

magnesium

Uncomplexed Aqueous Species = 91.63178 %

Aqueous Complexes and Ion Exchangers

MgPO4-	0.00428 %

MgHPO4	0.03368 %
MgCl+	1.08683 %
MgL2	0.01925 %
Mg(OH)+	0.00279 %
MgCO3	0.20434 %
MgHCO3+	0.06436 %
MgSO4	6.94030 %
MgF+	0.01237 %

manganese(II)

Uncomplexed Aqueous Species = 75.88989 %

Aqueous Complexes and Ion Exchangers

MnPO4-	0.01718 %
MnHPO4	0.33969 %
MnHCO3+	4.59562 %
CdSO4	0.00422 %
MnCO3	2.03515 %
MnL2	0.14466 %
MnOH+	0.01795 %
MnOH2	0.00000 %
MnOH3-	0.00000 %
MnSO4	7.40448 %
MnCl+	9.54709 %
MnF+	0.00406 %

nickel

Uncomplexed Aqueous Species = 51.56098 %

Aqueous Complexes and Ion Exchangers

NiPO4-	0.18604 %
NiHPO4	0.02921 %
NiHCO3+	0.36881 %
Ni(OH)2	0.00085 %
NiCl+	14.93936 %
NiF+	0.00837 %
NiCO3	27.73685 %
NiL2	0.04254 %
Ni(OH)+	0.01118 %
NiSO4	5.11582 %

potassium

Uncomplexed Aqueous Species = 95.37203 %

Aqueous Complexes and Ion Exchangers

KPO4--	0.00000 %
KHPO4-	0.00219 %
KHCO3	0.00076 %
KCO3-	0.00329 %
KCl	2.85010 %
KSO4-	1.77114 %

KF	0.00049 %

sodium

Uncomplexed Aqueous Species = 98.07207 %

Aqueous Complexes and Ion Exchangers

NaCl	1.18498 %
NaCO3-	0.00293 %
NaSO4-	0.73855 %
NaF	0.00146 %

zinc

Uncomplexed Aqueous Species = 82.81956 %

Aqueous Complexes and Ion Exchangers

ZnPO4-	0.11998 %
ZnHPO4	0.11886 %
ZnHCO3+	0.29943 %
ZnCO3	4.49308 %
ZnL2	0.34070 %
Zn(OH)+	0.25837 %
Zn(OH)3-	0.00002 %
ZnCl+	0.46902 %
ZnCl2	1.35455 %
ZnCl3-	0.01587 %
ZnCl4--	0.01282 %
ZnSO4	9.69373 %
ZnF+	0.00402 %

chloride

Uncomplexed Aqueous Species = 98.80420 %

Aqueous Complexes and Ion Exchangers

CaCl+		0.01885 %
MgCl+		0.10727 %
NiCl+		0.00001 %
CoCl+		0.00000 %
CdCl3		0.00001 %
CdCl4		0.00002 %
CdCl+		0.00000 %
CdCl2		0.00000 %
CdCl+		0.00000 %
KCl		0.05331 %
NaCl		1.01601 %
FeCl++	(III)	0.00000 %
FeCl2+	(III)	0.00000 %
FeCl3	(III)	0.00000 %
FeCl4-	(III)	0.00000 %
MnCl+		0.00002 %
AgCl		0.00000 %
AgCl2-		0.00002 %

AgCl3--	0.00002 %
AgCl4---	0.00012 %
HCl	0.00000 %
PbCl+	0.00000 %
PbCl2	0.00000 %
PbCl3-	0.00000 %
PbCl4--	0.00000 %
ZnCl+	0.00002 %
ZnCl2	0.00010 %
ZnCl3-	0.00000 %
ZnCl4--	0.00000 %
CuCl+	0.00000 %
CuCl2	0.00000 %
CuCl3-	0.00000 %
CuCl4--	0.00000 %
HgCl+	0.00000 %
HgCl2	0.00000 %
HgCl3-	0.00000 %
HgCl4--	0.00000 %

fluoride

Uncomplexed Aqueous Species = 79.86168 %

Aqueous Complexes and Ion Exchangers

CaF+		0.65758 %
NiF+		0.00005 %
PbF+		0.00000 %
CdF+		0.00000 %
MgF+		9.57126 %
FeF++	(III)	0.00000 %
FeF2+	(III)	0.00000 %
FeF3	(III)	0.00000 %
FeF4-	(III)	0.00000 %
MnF+		0.00007 %
HF		0.00035 %
HF2		0.00000 %
ZnF+		0.00115 %
CuF+		0.00002 %
HgF+		0.00000 %
NaF		9.83624 %
KF		0.07160 %

phosphate

Uncomplexed Aqueous Species = 0.00664 %

Aqueous Complexes and Ion Exchangers

HPO4--	36.59056 %
H2PO4-	6.86219 %
Fe(III)HPO4+	0.00140 %
Fe(III)H2PO4++	0.00000 %
CaPO4-	1.03339 %
MgPO4-	5.87941 %
KPO4--	0.00024 %
Fe(III)PO4	0.00000 %

MnPO4-	0.00056 %
Cu(II)PO4-	0.07429 %
ZnPO4-	0.06092 %
NiPO4-	0.00185 %
CdPO4-	0.00000 %
PbPO4-	0.00000 %
CaHPO4	2.57160 %
MgHPO4	46.26714 %
KHPO4-	0.56879 %
Fe(III)HPO4+	0.00000 %
MnHPO4	0.01112 %
Cu(II)HPO4	0.00927 %
CdHPO4	0.00001 %
ZnHPO4	0.06035 %
NiHPO4	0.00029 %
PbHPO4	0.00000 %

sulphate

Uncomplexed Aqueous Species = 69.81231 %

Aqueous Complexes and Ion Exchangers

Fe(III)(SO4)2-	0.00000 %
KSO4-	0.63888 %
NaSO4-	12.21248 %
CaSO4	4.11472 %
MgSO4	13.21136 %
FeSO4+ (III)	0.00000 %
MnSO4	0.00034 %
AgSO4-	0.00000 %
HSO4-	0.00001 %
PbSO4	0.00233 %
ZnSO4	0.00682 %
NiSO4	0.00007 %
CuSO4	0.00018 %
HgSO4	0.00000 %
BaSO4	0.00050 %

mercury(II)

Uncomplexed Aqueous Species = 0.00000 %

Aqueous Complexes and Ion Exchangers

HgCl+	0.00000 %
HgCl2	0.80020 %
HgCl3-	75.62262 %
HgCl4--	23.57719 %
HgSO4	0.00000 %
HgF+	0.00000 %

silver

Uncomplexed Aqueous Species = 0.00047 %

Aqueous Complexes and Ion Exchangers

AgL	0.00001 %
AgCl	0.28123 %
AgCl2-	18.44440 %
AgCl3--	16.68598 %
AgCl4---	64.58788 %
AgSO4-	0.00003 %

biofloc

Uncomplexed Aqueous Species = 0.22905 %

Aqueous Complexes and Ion Exchangers

HL	96.92162 %
MnL2	0.00041 %
CuL2	0.39846 %
ZnL2	0.01492 %
NiL2	0.00004 %
CdL2	0.00000 %
CaL2	0.15518 %
MgL2	2.28032 %
BaL2	0.00000 %
CoL2	0.00001 %
FeL3	0.00000 %
AgL	0.00000 %

carbonate

Uncomplexed Aqueous Species = 1.25097 %

Aqueous Complexes and Ion Exchangers

KHCO3	0.00443 %
Fe(III)HCO3++	0.00000 %
MnHCO3+	0.00335 %
Cu(II)HCO3+	0.00001 %
CdHCO3+	0.00000 %
ZnHCO3+	0.00339 %
NiHCO3+	0.00008 %
PbHCO3+	0.00000 %
CuCO3	0.09827 %
ZnCO3	0.05084 %
NiCO3	0.00613 %
PbCO3	0.00001 %
CdCO3	0.00000 %
MnCO3	0.00148 %
FeCO3+	0.00410 %
KCO3-	0.01908 %
NaCO3-	0.77891 %
CaCO3	0.46576 %
CaHCO3+	0.00115 %
MgCO3	6.25598 %
MgHCO3+	1.97042 %
HCO3-	88.06840 %
H2CO3	1.01723 %
BaHCO3+	0.00000 %

```
Iterations          8   3   2   1   1   1   1   1   1   1   1   1   1
Primary charge balance is   3.685438439999983E-003 mol per kg
Final mass balance is   2.220446049250313E-016 mol per kg
Solution Charge Balance is  2.695787373050301E-003 mol per kg
```

SUMMARY OF XRD AND SEM STUDIES

Sludge from several sources was analysed by SEM ad XRD (see chapter four) unseparated, or after separation into 'Particulate', 'Biofloc' and 'Colloid' fractions (see chapter three). In some cases chemical treatments (peroxide, carbonate, oxalate, pyrophosphate, EDTA) and physical treatments had been used (USD, magnetic separation, freeze-drying). The following table lists the main batches of material examined.

The work was organised into a series of "Studies". Sets of trials or analyses on a particular sample are numbered 1., 2., etc. Different treatments or separations are numbered .1, .2, etc, eg 1.2, 2.3.

Types of sludge

Taken in order through the sewage works, the types of sample taken are:

Grit trap. Large gritty fragments are removed before the sewage enters the works; may contain fine gravel, toothbrushes, cigarette ends etc.

Raw or primary sewage. This is undigested sludge taken after primary settlement, and is representative of sludge entering the digesters.

Digester sludge. This is material taken from the outlet of the digester and is regarded as typical of material in the digester. Sludge for analyses of the particulate fraction was taken by auger from the bottom four feet of the digester while the digester was

being pumped out ready for cleaning; this material is much thicker and richer in mineral content.

Digester grit. This is sandy mineral matter dug from the bottom of the digester after the digester had been fully pumped out for cleaning, and while it was being washed out using high pressure hoses. This material is partially washed and partially oxidised, though it is still black in colour.

Digested sludge. This is material taken from the outlet of the digester, or from a secondary digester tank, and may have become partially oxidised through time and storage.

The following terms are used:

Sources of sludge:

R = Reading	TWA works	
S = Sandford	"	
B = Beckton	"	
M = Mogden	"	
L = Slough	"	, courtesy of T Evans
P = Perry Oaks	"	, " "
F = Landfill digester	"	, courtesy of F Mosey

Age of sludge:

W, M, Y = weeks, months and years, may or may not still be anaerobic

F = fresh and still anaerobic

Treatments: Refer to chapter three and to appendix 1 for description of separation and cleaning methods.

No	Source	Type	Age	SEM	XRD	Fraction	Density	Stat count	Treatment
1.1	R	Digested	9 M	Y	Y	Particulate	-	-	Mild oxidation
1.2	R	Digested	9 M	Y	Y	Particulate	-	-	
1.3	R	Digested	9 M	Y	Y	Particulate	-	-	
1.4	R	Digested	9 M	Y	Y		-	-	
2.1	R	Digested	9 M	Y	Y	Particulate	-	-	
2.2	R	Digested	9 M	Y	Y	Particulate	-	-	
2.3	R	Digested	9 M	Y	Y	3 minute	-	-	
2.4	R	Digested	9 M	Y	Y	Gunge	-	-	
3.1	R	Digested	9 M	Y	Y	Particulate	-	-	Sonication
3.2	R	Digested	9 M	Y	Y	3 minute	-	-	"
3.3	R	Digested	9 M	Y	Y	Gunge	-	-	"
3.4	R	Digested	9 M	Y	Y	Gunge	-	-	"
4.1	R	Raw	8 M	Y	Y	Particulate	-	-	Sonication
4.2	R	Raw	8 M	Y	Y	Particulate	-	-	"
4.3	R	Raw	8 M	Y	Y	3 minute	-	-	"
4.4	R	Raw	8 M	Y	Y	Gunge	-	-	"
5.1	S	Raw	F	Y	Y	Particulate	-	-	Sonication
5.2	S	Raw	F	Y	Y	Particulate	-	-	"
5.3	S	Raw	F	Y	Y	3 minute	-	-	"
5.4	S	Raw	F	Y	Y	Gunge	-	-	"
6	S	Digester	F	Y	Y	Whole	-	-	Peroxide
7.1	S	Digester	1 M	Y	Y	Whole	-	-	
7.2	S	Digester	1 M	Y	Y	Whole	-	-	Peroxide
8	B	Digester	F	Y	Y	Particulate	-	-	
9	B	Digester	1 M	Y	Y	Gunge	-	-	
10.1	B	Digester	1 M	Y	Y	Particulate	-	-	Peroxide
10.2	B	Digester	1 M	Y	Y	Particulate	-	-	
10.3	B	Digester	1 M	Y	Y	Biofloc	-	-	Acetone then peroxide
10.4	B	Digester	1 M	Y	Y	Biofloc	-	-	Peroxide, conc HNO_3
11.1	B	Digester	F	Y	Y	Biofloc	-	-	
11.2	B	Digester	F	Y	Y	Biofloc	-	-	EDTA
11.3	B	Digester	F	Y	Y	Biofloc	-	-	Sodium carbonate
11.4	B	Digester	F	Y	Y	Biofloc	-	-	Pyrophosphate
12.1	B	Digester	F	Y	Y	Biofloc	-	-	
12.2	B	Digester	F	Y	Y	Biofloc	-	-	NaOH
12.3	B	Digester	F	Y	Y	Biofloc	-	-	Peroxide
12.4	B	Digester	F	Y	Y	Biofloc	-	-	Oxalate
13	B	Digested	3 M	Y	Y	Particulate	-	-	As for study 8, 3 months later
14.1	B	Digester	F	Y	Y	Gunge	-	-	
14.2	M	Grit trap	-	Y	Y	Particulate	-	-	Elutriated in EtOH
14.3	M	Digester	F	Y	Y	Particulate	-	-	"
14.4	M	Digester	F	Y	Y	Particulate	-	-	"
15	B	Digester	F	Y	Y	Particulate	1.6	-	
16	B	Digester	F	Y	Y	Particulate	1.6	-	

No	Source	Type	Age	SEM	XRD	Fraction	Density	Stat count	Treatment
17	B	Digester	F	Y	Y	Particulate	2.2	Y	Mechanically shaken
18	B	Raw	F	Y	N	Particulate	2.2	Y	Magnetic separation
19	B	Digester	F	Y	N	Gunge	-	-	Freeze-dried
20	B	Digester	F	Y	Y	Particulate	2.2	Y	
21	L	Lagoon	20 Y	Y	Y	Particulate	1.6	Y	Sieved 2 mm
22	B	Digester	1 M	Y	N	Particulate	2.2	Y	Magnetic separation
23	B	Digester	1 M	Y	N	Particulate	2.9	Y	
24	B	Digester	F	Y	Y	Particulate	3.3	Y	
25	-	Sludge/ soil	-	Y	N		-	Y	
26	B	Lagoon	-	Y	N	Particulate	2.2	Y	
27	B	Lagoon	-	Y	N	Particulate	2.9	Y	
28	B	Digester	F	Y	N	Biomass	-	Y	Peroxide
29	P	Lagoon	15 Y	Y	N	Particulate	2.9	Y	
30	F	Scale	2 Y	Y	Y	Whole	-	-	
31.1	F	Digester	F	Y		Particulate	2.2	Y	Taken from bottom of No 4 digester
31.2	F	Digester	F	Y		Particulate	2.9	Y	"
31.3	F	Digester	F	Y		Particulate	3.3	Y	"
32.1	F	Digester	F	Y	N	Particulate	2.2	Y	USD
32.2	F	Digester	F	Y	N	Particulate	2.2	Y	Peroxide
32.3	F	Digester	F	Y	N	Particulate	2.2	Y	Chlorine dioxide
32.4	F	Digester	F	Y	N	Particulate	2.2	Y	Dialysis