

A Multilevel Sustainability Analysis of Zinc Recovery from Wastes

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Abstract

Demand for zinc and its production are increasing at the rates of 4.7% and 2.7% per year, respectively, since 2012. At the current rate of usage, its demand will reach 2.7 times of today's demand by 2050. Zinc production has been predominantly relying on primary mining, which is resource intensive. 1 kg of zinc production by primary mining from copper-lead-zinc-silver-gold ore containing 62% zinc uses 23 MJ of fossil resources and causes global warming potential (100 years) by 0.8 kg CO₂ equivalent. This is equivalent to 10.64 million tonne CO₂ emissions per year or 0.03% of global CO₂ emissions. To cut down CO₂ emissions by 80% by 2050 from its current level (i.e. to lower the emission below 2.13 million tonne CO₂ equivalent), a maximum of only 7% contribution could be allowed from primary mining to fulfil its increased demand by 2050 and the balance of the demand must be met by secondary recovery of zinc from wastes – a challenging prospect. This is the first dedicated paper on sustainability and feasibility evaluations of zinc recovery from waste streams. Sustainability and feasibility of a resource recovery from wastes in a circular economy are governed by avoided environmental impacts and cost-effective transformation of an environmental contaminant into a valuable resource, e.g. as a coproduct by making use of an existing infrastructure as much as possible. This study gives a comprehensive overview of secondary sources and processes of recovering zinc, its stock analysis by country, regional and global divisions by a Sankey diagram, policies to regulate zinc emissions and avoided

environmental impacts by zinc recovery. The economic value generations by zinc are further demonstrated 1) from steelmaking dust and (2) from municipal solid waste (MSW). The first case study estimates the amount and value of zinc that can be generated from dust emitted from various steelmaking technologies and thus additional revenue for a steelmaking facility with electric arc furnace, at the plant, national (UK), regional (EU) and global levels (11, 12, 169 and 1670 million tonne/y), (19-143), (20-157), (287-2203) and (2834-21740) million €/y, respectively. The second case study entails zinc recovery integrated mechanical biological treatment (MBT) of MSW consisting of anaerobic digestion, refuse derived fuel (RDF) incineration and combined heat and power (CHP) generation. The value analysis shows that 1552 € of economic margin can be generated from the recovery of 1 tonne of zinc in the integrated MBT plant enhancing the economic margin of the plant by 4%.

Keywords: zinc recovery from waste; municipal solid waste; heavy metal recovery from waste; mechanical biological treatment (MBT) plant; circular economy; techno-economic assessment; life cycle assessment

1. Introduction

Recovery of zinc from secondary sources – waste is important in the present context of circular economy. The production and consumption of zinc at global level have been increasing and primary resources of zinc from ore is depleting rapidly. Hence, effective extraction of zinc from secondary sources would bring several advantages such as saving in virgin resources and in fossil resources used to supply energy in primary mining processes, increased resource efficiency, reduced landfilling and loss of zinc or any metal recovered to the landfill, waste remediation, mitigation of environmental and health effects and enhancement of economic performance of an existing infrastructure. Zinc is considered as a base metal, similar to copper, iron, nickel and lead. Zinc is malleable at the temperatures of 100-150°C [1]. This is an important property of zinc that makes its easy transformation into different shapes. Zinc is originated from natural resources primarily from sphalerite (ZnS), which also contains traces of cadmium, iron, indium, gallium and germanium. The copper-lead-zinc-silver-gold ore upon smelting gives 36.8, 1.4, 61.7, 0.095 and 0.002 percentages, respectively [2]. Other primary sources of zinc include zinc oxide, zinc carbonate and zinc sulphate [3]. Zinc is also present in various geological sources: lithosphere (52 mg/kg); soil (60 mg/kg); stream water (20µg/L); sea water (1-4.9 µg/L) and biota (46 mg/kg) [4].

1 Zinc is an essential element needed in human body, particularly in building cells and
2 enzymes and helping in wound healing. Deficiency of zinc in human body leads to several
3 adverse effects, including anorexia nervosa (loss of appetite and eating disorder), taste
4 abnormality (losing sense of taste), growth retardation, lethargy (tiredness and lack of energy),
5 delayed healing of wounds and so on [5]. Other symptoms such as diarrhoea, night blindness
6 and delayed sexual maturation may occur in the case of severe zinc deficiency. It has been
7 estimated that there are approximately 17.3% of the world population suffering from zinc
8 deficiency [6]. Therefore, adequate consumption of zinc in daily diet is fairly important to
9 prevent diseases and illnesses, typically 5.5-9.5 mg/day of zinc intake is recommended for
10 men and 4.0-7.0 mg/day is recommended for women [7]. Zinc can be found in major food
11 sources such as meat (4.65-64.9 mg/kg) and fish (3.12-19.5 mg/kg) [8]. Although zinc is
12 important to human health, it should not be neglected that zinc is a carcinogen and excess
13 zinc consumption (100-500 mg/day) can lead to toxicity in human body [9]. The advisable
14 limit of zinc intake from drinking water is less than 0.2 mg/day [1].

15 Zinc is an important nutrient to plants. The typical concentration of zinc in agricultural soil is
16 10-300 mg/kg[10]. Deficiency of zinc in plant can cause chlorosis (discolouration of leaf) and
17 root apex necrosis (dieback) and further lead to reduction in crop yield [10]. Toxicity of zinc
18 in soil can occur as a consequence of using contaminated water by mining and smelting
19 industries. The symptom is obvious when the concentration of zinc is more than 300 mg/kg in
20 leaf, which can result in significant reduction in crop yield [10].

21 Zinc has prominent corrosion resistant properties, thus making it an important element in
22 steel coating (galvanising) to prevent rusting. It can also combine with other metals to form
23 alloy. Zinc, with combination of aluminium can be used to produce alloy which is used in die
24 casting. Die casting is the process of forcing molten metal into the mold cavity by applying a
25 high pressure. Brass (copper and zinc) and bronze (copper, zinc and tin) have a wide range of
26 applications including coin-making, decoration such as sculptures, musical instruments,
27 machinery parts, plumbing and electrical applications. Zinc has the main usages in
28 galvanisation, alloys, brass and bronze, semi-manufactures, chemicals and miscellaneous
29 totalling to 13.5 million tonne in year 2014 [11]. Significant amount of zinc is used in
30 galvanising, contributes to 50% towards the total usage. 17% of zinc is used for alloying such
31 as die casting and a similar proportion is used to produce brass and bronze. Other applications
32 of zinc include roofing, gutters and downpipes for housing and construction purposes (6%),
33 chemicals such as zinc oxide and zinc sulphate (6%) and miscellaneous (4%).

The world consumption of zinc has increased by 7% over the last five years (2010-2014), despite a fall in 2012[12]. The production of zinc has also increased and followed the trend of consumption. It can be seen that when primary mining of zinc falls short of its total production and the balance needs to be supplied by secondary recovery from wastes, its market price increases. This can be observed in years 2010-2011 and 2012-2014 [13]. An increase by 4% in zinc production from mine between 2011 and 2012 has resulted in 11% drop in the price of zinc from 2193.9 US\$/tonne in 2011 to 1950.4 US\$/tonne in 2012.

It has been estimated that, globally, 13.9 million tonnes of zinc has been extracted from mine in 2014 [14]. China (39%), Australia (11%) and Peru (10%) are the top three largest producers of zinc, predominantly by primary mining. Europe has produced approximately 1 million tonne of zinc in 2014, which is 8% of the total output of zinc worldwide. The Republic of Ireland (27%), Sweden (21%) and Turkey (20%) are the largest producers of zinc within the Europe [14]. An input-output model consisting of production, consumption, import and export of zinc of major regions is illustrated in Figure 1 in the form of a Sankey diagram. The data can be obtained from [14]. The width of the arrows represents the mass flowrate of zinc in thousand tonnes (kt). This diagram pinpoints three major countries/regions involving the zinc business: China (largest producer and consumer of zinc with low degree of international trading of zinc, i.e. high level of local satisfaction of resources with low dependence on import and export); Europe (equal reliance on local zinc production as well as import and export); and Australia (second largest mine producer of zinc, no zinc is imported to the country and the country exports majority of the zinc slab produced due to low consumption within the country itself). The recycle flowrates have been estimated from imbalance between production + import and consumption + export. Although the data does not directly indicate whether zinc slabs are produced from primary or secondary sources, there is sufficient evidence showing that the global consumption of zinc is heavily relying on primary sources of zinc, i.e. mining. The first piece of evidence is the close proximity between the total global mine production of zinc and global zinc slab production, i.e. 13.9 and 13.5 million tonnes, respectively. Higher mine production compared to zinc slab production shows extraneous primary extraction of resources. This occurs in year 2012-2014**Error! Reference source not found.** The second piece of evidence is the low recycle of zinc (Figure 1). This shows that zinc consumption primarily relying on its production is still prominent in most countries in the world, in particular, Australia and China. As a consequence of these activities, excessive amount of zinc is produced each year and if the

resource management is not properly controlled (i.e. supply > demand), it could induce a drop in the market price of zinc as has been the case in year 2012. The environmental impact due to zinc is significant and discussed in section 4.1. The utilisation of secondary sources of zinc should be considered as this will lessen the impact on the environment in spite of increases in energy requirement in recycling due to dilution effect due to mixing with scrap (example in the case of aluminium [15]).

Zinc has been identified as one of the fifty-four materials that is important to the EU's economy [16]. Huge demand of zinc has given rise to rapid depletion of primary sources. Therefore, the recovery of zinc from secondary sources such as wastes is of paramount importance to sustain the activities related to zinc. There are many literatures that have provided comprehensive reviews on recovery of heavy metals, including zinc. However, no study brings together various aspects of sustainability, economic gain and avoided environmental and health impacts in a quantitative manner, and policy incentives (or otherwise) to benchmark the current market situation with zinc and thereby evaluating the future prospect of zinc recovery from waste resources. This study therefore fills the gap and helps decision makers in comparing techno-economic performances between a new technology and state-of-the-art technologies, thus enabling early selection (or rejection) of the new technologies and finding modifications around process designs, inventories and policy incentives for successful uptake of sustainable technologies (e.g. with efficiency of recovery close to theoretical efficiency). This is the first paper reviewing the recovery technologies along with cost parameters of zinc, and carrying out techno-economic analysis of zinc recovery from secondary sources – waste and thus to estimate the economic margins of zinc recovery from waste resources. The study results can be used as a benchmark of techno-economic performance of a new technology, such as electrochemical recovery of zinc from wastewaters [17-20]. Though the work focuses on zinc recovery, the methodology or strategy can be adapted to benchmark any new technology for recovery of any material resource from waste.

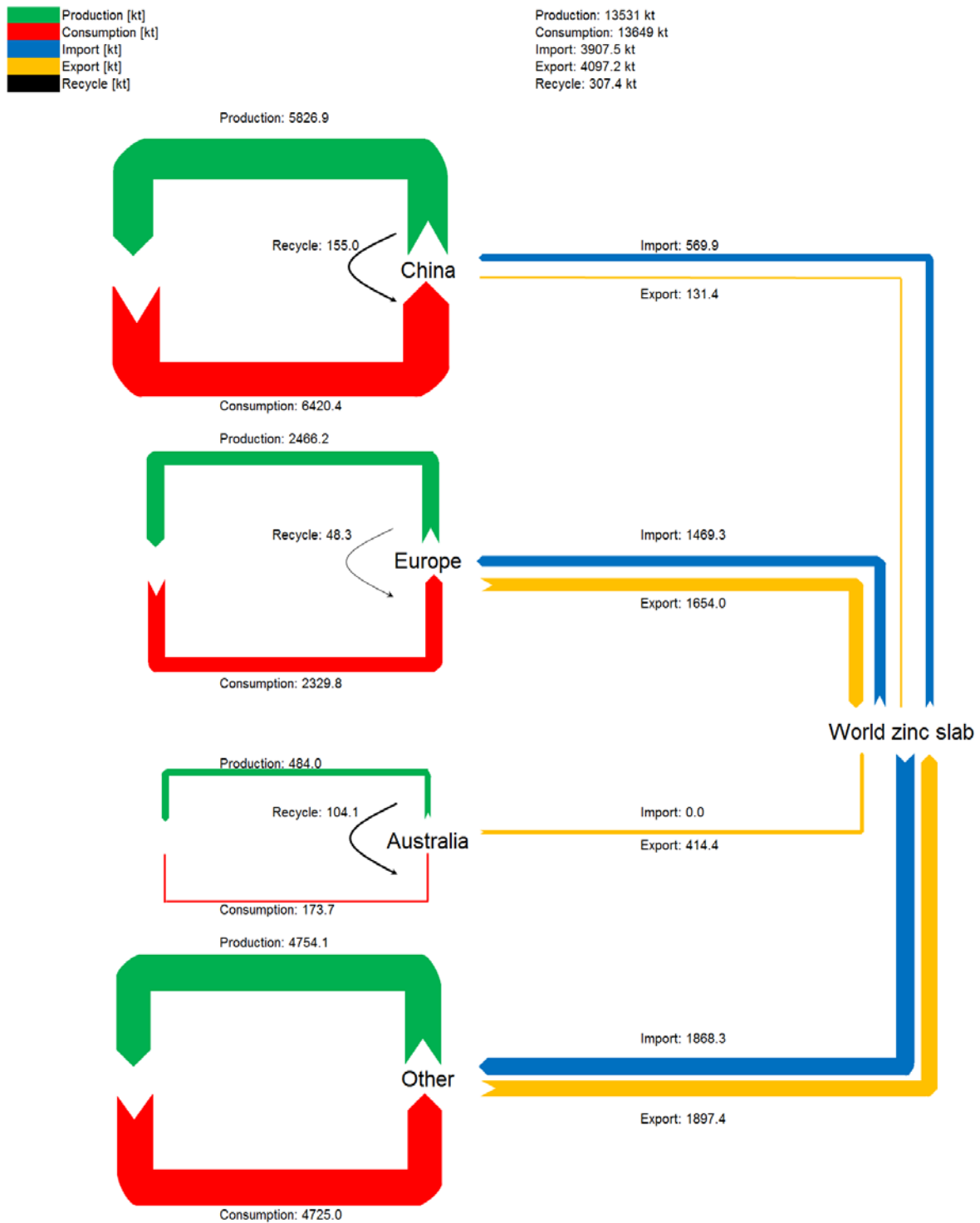


Figure 1: Sankey diagram showing flows of zinc slab production and consumption of major regions in year 2014.

The paper has been structured as follows. A comprehensive review of zinc sources has been given in Section 2. The recovery methods of zinc from waste including existing and emerging technologies have been reviewed in section 3. Figure 2 presents the recovery technologies

from various zinc sources. Section 4 gives potential environmental impacts of zinc release to the environment and thus avoided impacts by its extraction and a list of important environmental regulations and policies to support prevention, reuse and recycling of wastes. Section 5 discusses two case studies for recovering zinc: 1) in steelmaking plant and 2) from municipal solid waste (MSW) in cutting-edge mechanical-biological treatment (MBT). The former case study involved personal communications with a steelmaking industry, as they are keen to implement zinc recovery technologies in their plants. The latter has been chosen because of this involves complexity in management and value chain structure and interplay between stakeholders. The techno-economic analysis performed for the latter can thus have wider impacts in the works dealing with waste management. The case studies as discussed can be used to benchmark new zinc recovery technologies against the state-of-the-art technologies. A summary of this review is given in section 6.

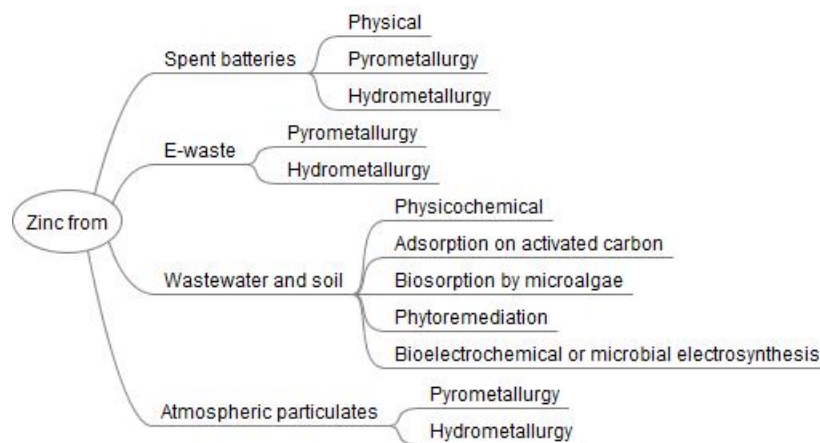


Figure 2: An overview of sources of zinc and recovery technologies.

2. Sources of Zinc from Waste

2.1 Zinc in Spent batteries

Portable batteries have become essential in supplying energy to various electronic devices such as cameras, calculators, remote controls. A considerable amount of battery wastes is generated due to the short lifespan. In particular, primary cells such as alkaline and zinc-carbon batteries are non-rechargeable and disposed of after one-off discharge. Hence, this can create serious environmental problems during disposal process as there are hazardous components such as mercury and other heavy metals contained in batteries. It has been

estimated that there are nearly 211,000 tonnes of portable batteries entered the European Union market in 2013. However, only 38% of the collection rate was achieved, i.e. 80,000 tonnes of waste portable batteries were collected. Zinc is used as anode in batteries. For a typical 1.5V single-use portable battery, the composition of zinc in alkaline manganese battery is 16%; zinc-carbon battery is 23%; silver oxide battery is 9%, alkaline manganese dioxide battery is 11% and zinc-air battery is 35%, respectively. [21].

2.2 Zinc in E-waste

The generation of tremendous amount of waste electrical and electronic equipment (WEEE) or E-waste is inevitable in modern days due to growing economy and industries, rapid advancement of technology, faster product switching rate and hence shorter product life cycle attributed to consumer needs. E-waste contains considerable amount of precious metals such as gold and silver, and other base metals such as copper, nickel and zinc. Recovering the metals from E-waste is important from various perspectives: waste management (some metals are hazardous), increasing resource utilisation (some metals are valuable) and virgin resource savings. For example, using recycled materials from aluminium, copper and zinc can achieve 95%, 85% and 60% energy savings, respectively compared to using virgin materials [22]. Metals can be found in the printed circuit board of the electronic equipment such as mobile phones, television and computers. Metals account for approximately 40 wt% of the printed circuit board, together with 30 wt% ceramic and 30 wt% plastics [23]. Zinc, however, only takes up 0.16-2.2 wt% of the total amount of metals [23]. The amount is negligible compared to other metals such as copper, and the value is much lower than the precious metals such as gold and silver. Therefore, it is sensible not to focus on zinc recovery from printed circuit board unless it is economically appealing.

2.3 Zinc in wastewater

Heavy metals such as zinc from industrial and urban systems are often washed away into wastewater causing environmental pollution. These metals are high in market values and it is beneficial to recover these metals and reuse them to achieve highest resource utilisation. The concentrations of zinc (in mg/L) in various types of wastewater are: municipal treatment plant (0.26-0.75); road wash water (0.105-1.56); tannery (0.684); mining (0.023); battery factory (0.6-17.0); copper smelting (455.6); acid mine drainage (120); electroplating industry (584); metal finishing industry (3.50-9.56); hazardous waste landfill leachate (1.15); industrially-contaminated groundwater (0.51), respectively [17, 24-35].

2.3.1 Mining wastewater

Agricultural soil pollution is often associated with the discharge of wastewater that comes from the mining industry. This wastewater contains significant amount of heavy metals such as zinc, copper and cadmium. Irrigation of the soil using the nearby contaminated water changes the chemical properties of the soil, inhibits microbial activities and affects the ecology of microbial communities in soil [36]. Long-term intake of food that comes from contaminated land will lead to serious health issues. Hu et al. [36] performed analysis on the pollution level of heavy metals on the paddy fields and the rice produced. The study has shown copper, zinc and cadmium contents in rice grains to be 1.0-17.8 mg/kg, 15.8-36.6 mg/kg and 0.0-2.8 mg/kg, respectively. Copper and cadmium levels have exceeded the maximum allowable limit in China of 10 mg/kg and 0.2 mg/kg, respectively. Although zinc content is within the limit of 50 mg/kg, the rice is considered toxic and inedible due to contamination by other metals.

2.3.2 Metal finishing / Electroplating wastewater

The effluents from metal finishing and electroplating industries pose significant threats due to the high metal ions concentration. Therefore, the wastewater discharged has to be managed and strictly regulated to avoid hazardous materials from being released to the environment. Zinc toxicity is one of the major concerns. Table 1 shows the zinc concentration in metal plating industries from various locations [37-41].

Table 1: Zinc concentration in wastewater from electroplating industry.

Plant and Location	Concentration of zinc in wastewater (mg/L)	Reference
Galvanising and nichrome plating plant, Jaihindpuram at Madurai, India	739.0	Pandian <i>et al.</i> , 2014 [37]
Zinc metal plating, Tehran, Iran	285.5	Hojati and Landi, 2015 [38]
Electroplating plant, India	45.0	Kanawade and Gaikwad, 2011 [39]
Alkali-zinc electroplating, Contagem, Minas Gerais, Brazil	43.2	Pereira <i>et al.</i> , 2009 [40]
Electroplating, Turkey	689.0	Kul and Oskay, 2015 [41]

2.4 Zinc in construction and demolition wastes

It has been reported that majority of zinc waste in the Netherlands comes from building and demolition wastes, taking up 82% of the total amount of waste (65,600 t/y) [42]. Gao et al. [43] have analysed the concentration of heavy metals in construction and demolition wastes collected from various industries and sectors, including chemical such as electroplating factory (911 ± 969 mg/kg), metallurgical such as zinc smelting plant and steel plant (3340 ± 5710 mg/kg), light industries (128 ± 53 mg/kg), residential (704 ± 289 mg/kg) and recycled aggregates (906 ± 538 mg/kg) in China. According to the study [43], high concentration of zinc can be found in these five sources of construction and demolition wastes. It carries the highest concentration among all the heavy metals such as copper, lead, chromium, cadmium and nickel in metallurgical industries, light industries, residential sector and recycled aggregates. Recovery of zinc and copper from secondary resources such as the infrastructural materials and alloys such as brass is usually via a series of pyrometallurgical reduction processes[44], microwave irradiation assisted carbothermic methods [45] and electrometallurgical processes [46], etc., discussed in the subsequent sections.

2.5 Zinc from steelmaking dust

Basic oxygen furnace [47-49], electric arc furnace [50-53] and argon oxygen decarburisation [54] are the major technologies used in steelmaking process. Dust is the major by-products generated from these processes. It has been estimated that 5-7 million tonnes of steelmaking dust are generated worldwide annually [49], of which 0.5-0.9 million tonnes of dust come from the steelmaking plants in Europe [55]. Dust is produced during the melting of steel scrap through volatilisation of heavy metals and silica particles [50]. These by-products are harmful if emitted to the atmosphere. Furthermore, accumulation of zinc in the furnace is disadvantageous for process performance and steel quality [49]. The dust generated from steelmaking process consisting of considerable amount of heavy metals, in particularly zinc. It is desirable to recover zinc from dust to enhance the overall economics of the steelmaking process while mitigating environmental impacts from the emission of these particles. Table 2 presents the rate at which dust is produced and the composition of zinc in the dust. A general observation from the results is that electric arc furnace produces dust with the highest zinc content (20.3-29.1 wt%) compared to basic oxygen furnace (2.57 wt%) and argon oxygen decarburisation (4.7-9.9 wt%) [47, 50, 51, 54].

Table 2: Rate of dust production from various steelmaking processes and the composition of zinc in the dust.

Steelmaking process	Rate of dust production (kg dust /tonne of steel produced)	Composition of zinc in dust (wt%)	References
Basic oxygen furnace	7-15	2.6 ⁱ	Trung <i>et al.</i> , 2011 [45]
Electric arc furnace	10-20	29.1	Shawabkeh, 2010 [48]
	15-20	20.3	Oustadakis <i>et al.</i> , 2010 [49]
Argon oxygen decarburisation	15-30	4.7-9.9	Virolainen <i>et al.</i> , 2013 [52]

ⁱ Average value of zinc content in basic oxygen furnace dust from various researchers.

2.6 Zinc from municipal waste

The amount of municipal waste generated in the EU-28 is estimated to be 213.4 million tonnes per year in 2012, while in the UK there are 27.5 million tonnes per year of municipal waste generated [56]. UK and EU have similar mass of waste generated per capita, which are 477 and 488 kg per capita (2012), respectively [57]. The EU and UK have achieved recycling rates of 41.2% and 42.8% [58], respectively in 2012, which are fairly close to the EU target of 50% by 2020. Germany has the highest recycling rate for municipal waste, i.e. 65.2% in 2012 [58]. There are 8% of metal content in municipal waste [59]. Zinc composition in MSW has been reported in several studies: 109.3–1077.9 mg kg⁻¹ [60], 400-1400 ppm [61] and 167-503 mg/kg [62].

3. State-of-the-art Zinc Recovery Process

3.1 Recovery of zinc from spent batteries

Zinc and other valuable metals can be recovered from spent batteries through physical processes, followed by either pyrometallurgical or hydrometallurgical methods. Sayilgan *et al.* [63] provided a comprehensive review of the technologies for recovering metals, in particularly zinc and manganese from spent batteries.

Physical process involves a series of sorting, dismantling / shredding, milling, sieving, magnetic, electrostatic and eddy current separation. This process is essential to accelerate the rate of metal dissolution [63]. Pyrometallurgical process is the most widely applied technology in recovering metal from spent batteries [63, 64]. Pyrometallurgy is a thermal treatment process, which involves volatilisation and condensation of metal. Pyrometallurgy is capable of recovering zinc to produce high grade products through simpler operating procedures and battery dismantling is not needed. However, the process takes place at high temperature (e.g. above 800°C) and higher energy consumption is expected, thus resulting in more expensive operation compared to hydrometallurgy [64]. While there could be some concerns over water pollution issues in the case of hydrometallurgy, pyrometallurgy has some other environmental issues due to emissions of dust and gases [63, 64]. Hydrometallurgical process is also becoming important in the metal recovery industry [63, 64]. The process involves leaching (dissolution) of metals using acidic or basic solutions followed by concentration or purification using precipitation, cementation, solvent extraction and ion-exchange. Lastly the recovery of metals can be done by precipitation or electrochemical methods.

Hydrometallurgy using biological method (bioleaching) is an important technology that provides lower environmental impact solution compared to the traditional hydrometallurgy. Bioleaching process is conducted at milder operating conditions and lower cost compared to hydrometallurgical process to recover zinc from spent batteries [65]. The method uses autotrophic bacteria such as *Alicyclobacillus sp.* (sulphur-oxidising bacteria) and *Sulfobacillus sp.* (iron-oxidising bacteria), are less harmful compared to the acids used in hydrometallurgical process such as H₂SO₄ or HCl with the addition of reducing agents such as H₂O₂, SO₂, ascorbic acid, citric acid and oxalic acid. [65-68]. The autotrophic bioleaching process is also applicable for recovering metals from lead-zinc smelting slag. A case study has shown a highest extraction efficiency of 90% for zinc [67]. A more expensive option using heterotrophic bioleaching method, which employs yeast extract and glucose as energy and carbon sources, is also available. This could be a more favourable route to recover certain metals such as lead and arsenic under the circumstances where autotropic bioleaching is not competent in handling it [67].

Metal dissolution is an important phenomenon which influences the extraction performance of zinc from spent batteries. Adding metallic ion catalyst can potentially enhance the rate of

electron transfer and thus improving the extraction performance [69]. Niu et al. [69] demonstrated that the extraction efficiency of zinc from spent batteries can be enhanced from 47.7% to 62.5% through the addition of 0.8 g/L of Cu^{2+} catalyst.

Xiang et al. [70] investigated the feasibility of vacuum separation followed by inert gas condensation to recover zinc from spent zinc manganese batteries to produce zinc nanoparticles such as nano hexagonal prisms (diameter 100-300 nm), fibriform and sheet shapes. This method exploits the difference in vapour pressure of metals and can achieve high separation efficiency of 99.68% and purity above 99 wt%.

3.2 Recovery of zinc from E-waste

The recovery of zinc from E-waste can be carried out through pyrometallurgical and hydrometallurgical processes, similar to spent batteries, discussed in section 3.1.

3.3 Recovery of zinc from wastewater and soil

The removal of heavy metals from wastewater can be done through conventional physicochemical methods such as chemical precipitation, lime coagulation, ion-exchange, reverse osmosis, solvent extraction and electrochemical methods [71, 72]. Table 3 shows some examples of zinc removal using various types of conventional treatment methods [41, 73-78]. However, conventional approaches are normally inefficient in removing heavy metals present at low concentration (10-100 mg/L) and the operations are costly and energy intensive [79-81]. Microbial electrosynthesis process serves the purpose of recovery of heavy metals including iron, copper and zinc, present at low concentration in wastewaters [82].

Table 3: Zinc removal from wastewater using conventional physicochemical methods.

Treatment method	Operating Condition	Removal efficiency	Reference
Chemical precipitation	Precipitant: $\text{Ca}(\text{OH})_2$ Optimum dose of precipitant: 10 g/L Optimum pH: 11.0	99.8%	Charerntanyarak, 1999 [71]
Coagulation-flocculation	Coagulant: Na_2S Dose of coagulant: 100 mg/L Optimum pH: 11.0	99.9%	Charerntanyarak, 1999 [71]
Floatation	Precipitant: $\text{Fe}(\text{OH})_3$ Optimum dose of precipitant: 20 mg/L Optimum pH: 5.5	98.6%	Rubio and Tessele, 1997 [72]
Ultrafiltration	Pressure: 2 bar Optimum pH: 8.5-9.5 Membrane: YM10	95.0% (rejection rate)	Juang and Shiao, 2000 [73]
Reverse osmosis	Pressure: 4.5 bar Optimum pH: 3-5 Membrane: Sulfonated polysulfone	99.0% (rejection rate)	Ujang and Anderson, 1996 [74]
Ion exchange	Dose: 10 g/L Adsorption efficiency: 3.47 mg/g Ion exchanger: Clinoptilolite	90.0%	Álvarez-Ayuso <i>et al.</i> , 2003 [75]
Solvent extraction	Reagent: 10 vol% Aliquat 336 2-stage	99.9%	Kul and Oskay, 2015 [41]
Electrocoagulation	Optimum pH: 4-9 Current density: 20 mA/cm^2	98.0%	Dermentzis <i>et al.</i> , 2011 [76]

Adsorption using activated carbon is a promising method in removing zinc and other metals from wastewater. The subject of research interest lies predominantly in reducing the cost of carbon materials. Low-cost alternatives using agricultural wastes to prepare activated carbon as the adsorbent is also available such as using orange peel [83], apple pulp [84], bagasse [85] and *Ceiba pentandra* hulls [86]. Kazemipour *et al.* [87] investigated the feasibility of removing zinc and other metals from industrial wastewater using adsorption process by employing carbon developed from nutshells of walnut, hazelnut, pistachio, almond and apricot. This study aims to reduce the cost of raw materials in producing the carbon and has found that the removal efficiency of zinc can be 58.8%-71.0%, and a removal efficiency of

50% in one pass is generally achievable for all metals under consideration (i.e. lead, cadmium and copper). Adsorption of zinc and other heavy metals in wastewater using carbon nanotubes is also one of the areas of interest within the field due to the high adsorption capacities of the materials [88-90].

Heavy metals including zinc can also be removed from wastewater through biosorption process using microalgae [79, 80, 91-94]. Microalgae have versatile roles in CO₂ sequestration, biofuel production and wastewater treatment, which are crucial in mitigating various environmental impacts [95]. A few recent examples of the employment of microalgae in removing zinc from wastewater are presented in Table 4 [80, 91-94]. Biomass is also efficient in removing zinc and other metals from wastewater. Adsorption of zinc from alkaline zinc electroplating wastewater is found to be approximately 95% using either wood sawdust or sugarcane bagasse, modified using succinic anhydride to introduce carboxylic acid functional group into the materials [40]. Pandian et al. [37] have demonstrated a case study of using microorganism *Pseudomonas aeruginosa* to remove zinc and other metals from electroplating effluent. It has been found that the removal of zinc can be up to 71% after 20 days. Chen et al. [96] have employed *Pseudomonas putida* and zinc can be removed up to 83.8%.

Table 4: Zinc removal from wastewater by various microalgae.

Algal	Removal efficiency*	Researcher/Reference
<i>Cladophora fracta</i>	85.0%	Ji <i>et al.</i> , 2012 [90]
<i>Spirogyra neglecta</i> , <i>Pithophora oedogonia</i> , <i>Hydrodictyon reticulatum</i> , <i>Cladophora calliceima</i> , <i>Aulosira fertilissima</i>	83.0% 58.0% 34.0% 63.0% 64.0%	Singh <i>et al.</i> , 2007 [91]
<i>Acutodesmus obliquus</i> <i>Desmodesmus subspicatus</i> <i>Desmodesmus armatus</i>	30.0% 40.0% 18.0%	Güçlü and Ertan, 2012 [89]
<i>Scenedesmus obliquus</i> <i>Desmodesmus pleiomorphus</i>	30.2% 31.4%	Monteiro <i>et al.</i> , 2011 [88]
<i>Chlorella vulgaris</i> <i>Spirulina maxima</i>	96.3% 94.9%	Chan <i>et al.</i> , 2014 [78]

* Only the highest removal efficiency in the corresponding studies is reported.

Utilising industrial waste as low-cost adsorbent is also a major research direction in the field. Ahmaruzzaman [97] have investigated the technical feasibilities of using various types of industrial wastes such as fly ash, blast furnace slag and sludge, black liquor lignin, red mud and waste slurry. Salam et al. [98] have examined the use of peanut husk charcoal, fly ash, natural zeolite as low-cost adsorbent to remove copper and zinc from mining finishing wastewater. Clay minerals can also be employed as an adsorbent, as studied by Hojati and Landi [38]. Their study has shown that more than 95% of total zinc concentration can be removed from zinc metal plating wastewater using sepiolite under the optimum conditions, i.e. suspension pH = 9, contact time = 720 min, dose = 16 g/L, size = less than 2 μ m [38]. Cork powder can remove up to 91% of zinc from electroplating wastewater, as demonstrated in a case study by Kanawade and Gaikwad [39].

Phytoremediation is another method of removing heavy metals from soil and water by using aquatic plants [99]. This technology is becoming more and more important in handling mining wastewater (e.g. tin [100], gold mines [101], lead-zinc [102]) as well as municipal wastewater [103]. Phytoremediation includes phytoextraction, phytofiltration, phytostabilisation, phytovolatilisation, phytodegradation and phytodesalination [104]. A comprehensive review of these technologies can be found in [104, 105]. Phytoremediation uses aquatic plants that floats on water (metal is accumulated in its roots) and also that submerges in water (metal is accumulated in the whole plant). Abu Bakar et al. [101] have investigated the potential of accumulating arsenic, aluminium and zinc using three different submerged aquatic plants, i.e. *Cabomba piauhyensis*, *Egeria densa*, and *Hydrilla verticillata*. It has been found that zinc can have highest accumulation in *Hydrilla verticillata* (93.7%), while *Egeria densa* and *Cabomba piauhyensis* can accumulate arsenic (95.2%) and aluminium (83.8%). Thus, these methods are effective in reducing the metals in mining wastewater. Phytoremediation employs hyper-accumulating plants to recover the metals from the soil. In the context of zinc, those that are capable of accumulating more than 10,000 mg/kg of zinc in their shoots when grown on metal rich soils are considered as hyper-accumulating plants [106].

Table 5 shows some examples of hyper-accumulating plants that are relevant to remediation of zinc [102, 107-111].

Table 5: List of hyper-accumulating plants for remediation of zinc.

Species	Part of plant involved	Medium	Accumulation of zinc (mg/kg)	Researcher/Reference
<i>Arabis paniculata</i> Franch	Roots	Water	12400	Tang <i>et al.</i> , 2009 [106]
<i>Eleocharis acicularis</i>	Shoots	Water	11200	Sakakibara <i>et al.</i> , 2011 [105]
<i>Sedum alfredii</i>	Leaves	Soil	13799	Jin <i>et al.</i> , 2009 [107]
<i>Euphorbia cheiradenia</i>	Shoots	Soil	1873	Chehregani and Malayeri, 2007 [108]
<i>Thlaspi caerulescens</i>	Shoots	Soil	500-52000	Zhao <i>et al.</i> , 2003 [104]
<i>Sonchus asper</i>	Roots	Soil	7894	Yanqun <i>et al.</i> , 2005 [99]

Bioremediation of wastewater using bioelectrochemical system is another emerging area of research and technology [17, 82, 112, 113]. In bioelectrochemical systems, microorganism is used to convert the chemical energy stored in organic matter in wastewater into electric current (microbial fuel cell) and chemicals (microbial electrolysis cell). The microorganism at anode breaks down the organic matter in wastewater into electrons and protons. Electrons flow to the cathode through external wire and protons flow through the electrolyte and membrane (optional) to the cathode. The application of bioelectrochemical system for wastewater treatment offers significant advantages in minimizing environmental pollution while recovering energy and valuable resources such as metals [114-116]. Fradler et al. [20] have studied an integrated acetate-fed microbial fuel cells and liquid-liquid extraction using supported liquid membrane to recover zinc and at the same time increasing power production. This approach has achieved 93% removal efficiency of zinc and an enhanced power production by 2.4 folds compared to using microbial fuel cell alone. Another study conducted by Abourached et al. [19] shows a removal efficiency of zinc by 97% alongside high power generation of 3.6 W/m² using an air-cathode microbial fuel cell. Modin et al. [18] have performed experiments of recovering zinc from a mixed solution containing lead, cadmium, copper and zinc using carbon felt as anode material and titanium wire as cathode material. It has been found that the removal efficiency of zinc is only 44.2% while a high energy consumption of 283.9 kWh/kg of zinc has been incurred. This is mainly due to hydrogen generation and low cathodic coulombic efficiency.

3.4 Recovery of zinc from air pollution particles

Pyrometallurgical and hydrometallurgical methods are the primary recovery technologies used in recovering zinc from steelmaking dust. Hydrometallurgical methods using acidic leaching such as sulphuric acid are the most common one reported in most literatures [47, 49-51, 54]. Hydrometallurgical method is more favourable mainly due to its flexibilities and the process is less costly. The discussions of pyrometallurgical and hydrometallurgical methods have been given in section 3.1. Table 6 presents the optimum operating conditions of recovery of zinc and the corresponding efficiency.

Table 6: Recovery of zinc from dust and sludge from steelmaking process.

Steelmaking process	Recovery of zinc (%)	Optimum operating condition	Reference
Basic oxygen furnace	70	1 M H ₂ SO ₄ 80°C 15 min	Trung <i>et al.</i> , 2011 [45]
Electric arc furnace	72	0.1 M H ₂ SO ₄ 900 rpm mixing speed 50°C 10-20 min	Shawabkeh, 2010. [48]
	80	3 N H ₂ SO ₄ 60°C	Oustadakis <i>et al.</i> , 2010 [49]
Argon oxygen decarburisation	67	0.5 M H ₂ SO ₄ 170 rpm mixing speed 30°C	Virolainen <i>et al.</i> , 2013 [52]

4. Environmental Aspects of Zinc

4.1 Environmental impact characterisation

The emission of zinc causes certain impacts on the environment. By using life cycle impact assessment (LCIA) methods, it is possible to quantify the primary, mid- and end-point environmental impacts of zinc extraction [95]. The environmental impact potentials in terms of abiotic element, metal and primary fossil resource depletions by zinc extraction are estimated by the CML [117], ReCiPe [118] and Impact 2002+ [119], methods respectively. The environmental impact potentials in terms of human toxicity and freshwater and marine aquatic ecotoxicity by zinc release to the environment are estimated by the CML method [117]. Their values per kg of zinc extraction (in case of resource depletion potentials) or per

kg of zinc emission (in case of toxicity potentials) in respective units are shown in Figure 3. The quantities shown as environmental impacts and economic costs shown in Figure 3 can therefore be saved if zinc is retained in a closed loop cycle or in a cradle to cradle system towards a circular economy, involving acquisition, logistics, use and reuse of zinc in closed loop cycle. From Figure 3, it can be inferred that recovering 1 kg of zinc from secondary resources such as wastes, can save up to 1.89 MJ primary fossil resource, indicated by mineral extraction impact category (Impact 2002+). Similarly, if zinc extraction from zinc containing ores (by 4 weight %) can be avoided, upto 0.075 MJ/kg of primary fossil resource can be saved (Impact 2002+). In terms of avoided output impacts, the human toxicity potential is explained: this can be decreased by 63.74 and 104.44 kg 1,4-Dichlorobenzene (DCB) equivalent by 1 kg of avoided zinc emission (or recovered zinc as resource from waste materials) from agricultural soil and air, respectively.



Figure 3: Environmental impact characterisation values of 1 kg zinc using various LCIA methods.

Primary mining of zinc is energy intensive. For example, copper-lead-zinc-silver-gold ore smelting in a combined refinery uses 40.92 MJ of primary fossil energy, 60 m³ of water depletion per kg combined metal processing to produce 36.8, 1.4, 61.7, 0.095 and 0.002

percentages, respectively. 35% of the total energy and 37% of the total water consumptions are due to zinc mining based on an allocation by economic value. The global warming impact potential from the cradle to gate system is 1.53 kg CO₂ equivalent per kg of combined metal processing, out of which 32.5% is due to zinc mining. The life cycle inventory (LCI) databases have been assimilated from the Ecoinvent 3.0 [2] and the life cycle assessment (LCA) has been undertaken using GaBi 6.0.

4.2 Regulations and Policies

Zinc is contained in various sources of wastes, including batteries, WEEE, household and industrial wastes and wastewaters, which are regulated by legislatures to mitigate environmental and health impacts. These wastes should be controlled by following the waste hierarchy: prevention, reuse, recycle, recovery and disposal to meet the regulations. Table 7 presents important directives and legislations related to zinc emission in the EU and UK [120-125].

Table 7: Environmental regulation related to zinc.

Industry / Area	Region	Legislation	Objective	Reference
Battery	EU	Batteries Directives 2006/66/EC	<ul style="list-style-type: none"> Minimise the negative impact of batteries and accumulators and the corresponding waste on the environment. Achieve minimum collection rates for portable batteries of 25% by 2012 and 45% by 2016. 	European Parliament, Council of the European Union, 2006 [117]
	UK	The Waste Batteries and Accumulators Regulations 2009	<ul style="list-style-type: none"> Implement 2006/66/EC <i>Directive</i> Minimise the negative impact of waste batteries and accumulators on the environment Collection targets consistent to EU directive. Introducing “producer responsibility” obligation 	Her Majesty’s Stationery Office, 2009 [118]

			<ul style="list-style-type: none"> • Restriction on cadmium and mercury in batteries 	
E-waste / WEEE	EU	EU Waste Electrical and Electronic Equipment Directive 2012/19/EU	<ul style="list-style-type: none"> • Prevent electrical and electronic waste by requiring EU countries to ensure the equipment is recovered, reused or recycled. • Collection target of 4 kg per head of population per year • Collection rate in 2016 onwards will be on a variable basis (calculated based on the average weight of products placed on the market in a given country in the 3 preceding years): 45% between 2016-2019; 65% in 2019 and thereafter 	European Parliament, Council of the European Union, 2012 [119]
	UK	The Waste Electrical and Electronic Equipment Regulations 2013	<ul style="list-style-type: none"> • Implement 2012/19/EU Directive • Prevent, reuse, recycling of WEEE to reduce disposal to landfill. 	Her Majesty's Stationery Office, 2013 [120]
Water / Wastewater	EU	Water Framework Directive	<ul style="list-style-type: none"> • Prevent and reduce pollution, promote sustainable water usage, protect the environment, improve the state of aquatic eco-systems and reduce the effects of floods and droughts. • Established protection of inland surface waters, groundwater, transitional waters and coastal waters 	European Parliament, Council of the European Union, 2000 [121]

Waste	EU	Waste Framework Directive 2008/98/EC	<ul style="list-style-type: none"> • Protect the environment and human health through the prevention of the harmful effects of waste generation and waste management. • Waste hierarchy: Prevention, reuse, recycle, recovery and disposal. • Reuse and recycle 70% of construction and demolition waste by 2020. • Achieve recycling rate of 50% for household waste by 2020. 	European Parliament, Council of the European Union, 2008 [122]
Metal in sludge	EU	Directive 86/278/EEC	<ul style="list-style-type: none"> • Annual limit for the concentration of zinc in sludge when applied to land is 2500-4000 mg/kg dry matter as 90th percentiles or 30000 g/ha/year. 	European Parliament, Council of the European Union, 2008 [126]

1 Effluent discharge standards in wastewater vary across different countries and it is essential
2 to conform to local standards. The maximum allowable limits of zinc present in wastewater
3 effluent in some countries such as Hong Kong and Thailand are 5 mg/L while in the US, the
4 limit is stricter which is 4.2 mg/L for 1 day and 2.6 mg/L for 4 consecutive days (for metal
5 finishing industry) [127-129].

6 5. Case Studies

7 Recovering resources from waste is exigent in light of rapid depletion of primary resources. It
8 is generally agreed that resource recovery from waste can bring some benefits to the overall
9 economics in the industry and also mitigating environmental impacts. Therefore, case studies
10 have been carried out to examine the economic potential of recovering resources from waste.
11 In this study, two representative sources of wastes have been investigated, i.e. steelmaking
12 dust (section 5.1) and municipal solid waste (section 5.2). The techno-economic analysis

methodology for zinc recovery, presented here, can be replicated for other sectors as well as for other metals.

5.1 Steelmaking dust

Recovering zinc from steelmaking dust has the potential of generating additional revenue for the steel plant. Variations can be seen in the amount of zinc in dust generation from different steelmaking technologies, shown in Table 2. Values of zinc in the dust from different technologies have been estimated, presented in Table 8. The price of zinc is 1656.5 \$/t (equivalent to 1490.9 €/t) (30th September 2015) [130].

Table 8: Estimation of value of zinc in dust from various steelmaking processes.

Steelmaking process	Concentration of zinc ⁱ (kg/kg dust)		Price of zinc (€/kg zinc)	Value of zinc in dust or sludge (€/kg dust)	
	min	max		min	max
Basic oxygen furnace	0.01	0.04	1.49	0.01	0.07
Electric arc furnace	0.20	0.29		0.30	0.43
Argon oxygen decarburisation	0.05	0.10		0.07	0.15

ⁱ Obtained from Table 2.

A holistic analysis has been carried out to examine the annual production of dust from steelmaking industry at a plant level as well as at a regional level, shown in Table 9. Crude steel production capacities have been collected in the UK and Europe [131]. At regional levels, UK, Europe, China (highest production in the world) and worldwide production of crude steel have been investigated [132].

Table 9: Estimation of dust production based on plant and regional production capacities.

Scope	Location	Crude steel production capacity (million tonne/y)	Rate of dust production (kg dust or sludge/tonne of steel produced) ⁱ		Dust production (thousand tonne/y)	
			min	max	min	max
Plant	Tata Steel, UK (inc. Port Talbot, Rotherham, Scunthorpe)	11	6	30	62	330
	Tata Steel, Europe	20			112	600
Regional	United Kingdom	12			68	362
	Europe (European Union - 28)	169			948	5077
	China	823			4607	24681
	World	1670			9354	50111

ⁱ Obtained from Table 2.

Table 10 presents the values of zinc in the dust in two scenarios: (a) low dust production and (b) high dust production. This analysis combines plant and regional scopes with different steelmaking technologies with the aim of achieving an understanding of the potential of recovering zinc from dust in steelmaking industries. The analysis has assumed 100% recovery of zinc from dust and has considered minimum and maximum value of zinc based on different concentration of zinc in dust, shown in Table 8.

Table 10: Estimation of value of zinc in the dust at (a) low dust production (b) high dust production from plant and regional levels with different steelmaking processes.

(a) Low dust production scenario

Scope	Location	Value of dust (million €/y)					
		Basic oxygen furnace		Electric arc furnace		Argon oxygen decarburisation	
		min	max	min	max	min	max
Plant	Tata Steel, UK (inc. Port Talbot, Rotherham, Scunthorpe)	0.5	4	19	27	4	9
	Tata Steel, Europe	0.9	7	34	49	8	17
Regional	United Kingdom	0.5	4	20	29	5	10
	Europe (European Union - 28)	7	62	287	411	66	140
	China	35	300	1396	1999	323	682
	World	71	609	2834	4058	655	1385

(b) High dust production scenario

Scope	Location	Value of dust (million €/y)					
		Basic oxygen furnace		Electric arc furnace		Argon oxygen decarburisation	
		min	max	min	max	min	max
Plant	Tata Steel, UK (inc. Port Talbot, Rotherham, Scunthorpe)	3	21	100	143	23	49
	Tata Steel, Europe	5	39	182	260	42	89
Regional	United Kingdom	3	24	110	157	25	54
	Europe (European Union - 28)	39	331	1538	2203	356	752
	China	188	1608	7477	10708	1729	3654
	World	381	3265	15181	21740	3511	7419

Some observations from the case study is summarised as follows:

- The lowest value of zinc in dust (0.01 €/kg) can be found in the case of basic oxygen furnace while the highest value of zinc can be found in the dust produced from electric arc furnace (0.43 €/kg). See Table 8.
- China has the highest production capacity of crude steel, i.e. approximately 50% of the world production and thus also leads to the highest dust production. This implies that severe environmental pollution is expected in China and appropriate treatment for dust is highly recommended. See Table 9.
- On the positive side, there is a great amount of zinc contained in the dust and tremendous revenue can be generated if zinc is recovered, i.e. 35 - 1999 million €/y in low dust production scenario and 188 - 10708 million €/y in high dust production scenario for the case in China. See Table 10.
- Recovering zinc from dust through worldwide steelmaking industry can potentially generate 71 - 4058 million €/y in low dust production scenario and 381 - 21740 million €/y in high dust production scenario, respectively. See Table 10.
- The analysis gives an understanding of the potential amount and values of dust that could be generated if a particular technology is used. It also provides the capacities, indication of environmental impact due to emission of dust and the revenue from recovering of zinc at both plant and regional levels. See Table 8-Table 10.
- The methodology presented can be applied to recover zinc from piping, sheet metal, bolts and other zinc-coated steel objects and brass. The cost of recovering zinc via a smelting process can be estimated at £100/t [133]. However, the cost of metal recovery is a variable as the method of recovery is case specific, which depends on the types of metal mixture. The interest of the present analysis is to provide the estimates of the lowest and highest amounts and values of zinc that can be recovered from steelmaking dust, for the steelmaking industry to help them in making a decision about implementation of zinc recovery technologies.

5.2 Municipal solid waste

This study investigated the economic feasibility of MSW treatment plant through a MBT system and the potential of simultaneous recovery of valuable resources, including metals such as iron, aluminium, copper and zinc, RDF and energy. MBT is an integrated facility where MSW is first separated into different fractions such as metals and RDF. The

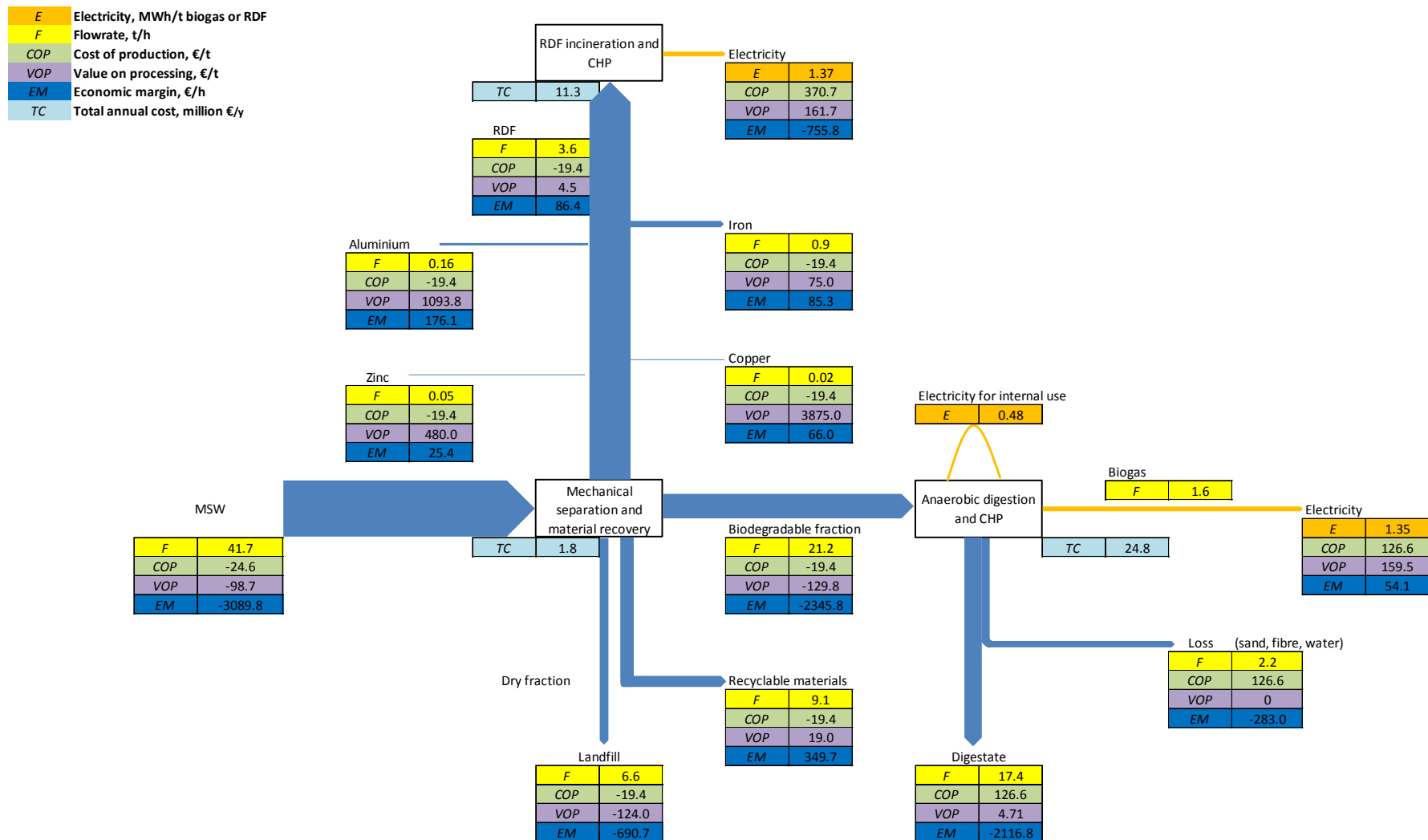
biodegradable fraction subsequently undergoes biological treatment, in this case, anaerobic digestion has been considered. Biogas rich in methane produced from anaerobic digestion can be used in CHP generation. Digestate from anaerobic digestion can be sold as fertiliser product. RDF can be marketed as sole product which can be used as fuel to produce energy required in cement kiln. In this study, RDF is used in incineration process to generate energy. Residues from the system are then sent to landfilling. The treatment of MSW through the MBT system is able to lessen the burden on landfilling and thus mitigating the environmental impacts.

5.2.1 Mass and energy balances

Mass and energy balances have been performed based on the estimation provided in the literatures [134-136], presented in Figure 4.

Figure 4 also provides results generated from value analysis which will be discussed in section 5.2.2. The following basis has been adopted.

- MSW input: 1000 t/d (equivalent to 41.7 t/h and 333.3 kt/y)
- Operating hours per year: 8000 hours
- Fraction of mixed RDF and metal stream: 78.4% by weight of MSW [135]
- Fraction of RDF: 70.2% by weight of MSW [135]
- Fraction of residues to landfill: 1.9% by weight of MSW [135]
- Energy generation from anaerobic digestion and CHP [135]:
 - Total heat generation: 2.40 MWh per tonne of biogas
 - Total electricity generation: 1.83 MWh per tonne of biogas
- Distribution of heat and electricity between internal use and selling [134]:
 - Heat: 28% (internal use) and 72% (sold), based on total heat generation
 - Electricity: 26% (internal use) and 74% (sold), based on total electricity generation
- Energy generation from RDF incineration and CHP [136]:
 - Total heat generation: 4.15 MWh per tonne of RDF
 - Total electricity generation: 1.37 MWh per tonne of RDF



1

2 **Figure 4:** Mass and energy balances of integrated MBT, anaerobic digestion, RDF incineration and CHP system.

5.2.2 Value analysis

Value analysis [95, 137-139] has been adopted in this study to evaluate the economic margins of individual streams and processing pathways in the MBT system. The objective is to identify which products are economically profitable to produce, how much value of materials is lost from the system and what is the economic margin of individual resources recovered from waste streams. Such analysis enables effective tracking and mapping of cost and value and thereby economic margin of each stream. Aggregation of economic margins of all mass flows gives the overall economic margin of the system. Thus, maximising positive economic margins (profit) and minimising negative economic margins (loss) of streams can ensure overall highest economic margin of the system. Economic margin of a stream i , EM_i is calculated by multiplying the flowrate of the stream, F_i with the difference between its value on processing (VOP) and its cost of production (COP), shown in equation 1. The unit of F could be t/h and that of COP and VOP is €/t and EM is €/h.

$$EM_i = F_i \times (VOP_i - COP_i) \quad (1)$$

As defined by Martinez-Hernandez et al. (2014), the VOP of a stream is the prices of products that will ultimately be produced from it, subtracted by the costs of auxiliary raw materials, utilities and annualised capital cost of equipment that will contribute to its further processes into these final products [140, 141].

The COP of a stream is the summation of all associated cost components, i.e. the costs of feedstocks, auxiliary raw materials, utilities and annualised capital cost that have contributed to the production of the stream [140]. This means that only those fractional costs involved with the stream's production are included in its COP .

Further, the concise equations 2-3 for representation of VOP and COP of a stream are given in [95].

VOP of a feed f to a process unit k is calculated from the known values of the product streams p and the total costs of the process unit k , shown in equation 2.

$$VOP_f = [\sum_{p=1}^q VOP_p P_p - \bar{O}_k] / \sum_{f=1}^g F_f \quad (2)$$

where q is the number of products (excluding emissions / wastes), g is the number of feedstock considered as main material streams (excluding auxiliary raw materials). P_p and F_f correspond to the mass flow rates of product and feedstock, respectively.

COP of a product p from a process unit k is calculated from the known prices or costs of the feed streams f and the total costs of the process unit k , shown in equation 3.

$$COP_p = [\sum_{f=1}^q COP_f P_f + \bar{O}_k] / \sum_{f=1}^g F_f \quad (3)$$

Capital cost consists of direct and indirect capital costs. The direct capital cost comprises the costs of equipment, installation, instrumentation and control, piping, electrical systems, building, yard improvements and service facilities. Cost of equipment can be estimated using cost and size correlation, shown in equation 4. The cost estimation parameters such as base cost, base scale and scale factor [142-145] for mechanical separation and material recovery, anaerobic digestion, incineration, flue gas treatment plant and heat export facilities are given in Supplementary Materials (Table S.1). The unit operations involved in the mechanical separation and material recovery section are shredder, screen, magnetic separator, eddy current separator, manually sorting cabin, ballistic separator and post-shredder.

$$\frac{COST_{size2}}{COST_{size1}} = \left(\frac{SIZE_2}{SIZE_1} \right)^R \quad (4)$$

where

$SIZE_1$ is the capacity of the base system, t/h or t/y,

$SIZE_2$ is the capacity of the system after scaling up/down, t/h or t/y,

$COST_{size1}$ is the cost of the base system, €

$COST_{size2}$ is the cost of the system after scaling up/down, €

R is the scaling factor.

The estimated purchased cost of equipment is considered as free-on-board (f.o.b.) cost, i.e. without delivery cost. The delivered cost of equipment has been estimated by incorporating 10% of the f.o.b. cost [95]. Other direct costs, indirect costs and working capital can be estimated using Lang factor, given in Supplementary Materials (Table S.2). Total capital cost is the summation of direct costs, indirect costs and working capital. An annual capital charge of 13% has been determined using discounted cash flow method with the assumptions of

discount rate of 10%, plant life of 15 years and start-up period of 2 years (capital expenditures of 25% and 75% on the 1st and 2nd year) [95]. Operating cost consists of fixed and variable costs. The parameters for estimating fixed operating costs such as maintenance, laboratory, supervision and plant overheads are given in Supplementary Materials (Table S.3). There is no variable utility or operating cost, because heat and electricity needed by the plant are satisfied by on-site generation, which also gives excess electricity for export.

Figure 4 shows the results generated from value analysis. The following basis has been applied.

- Cost of feedstock: The purchasing cost of MSW is assumed to be zero. However, fees exchanged between a MSW treatment plant owner and its local authority should be considered. An average waste collection fees of 84.5 €/t has been assumed [146], which has to be paid by the treatment plant owner to the local authority. The MBT treatment plant owner on the other hand receives a gate fee from the local authority. This rate is assumed to be 109.12 €/t for treating MSW [147]. Therefore, the *COP* of MSW is estimated to be $(0 + 84.5 - 109.1) = -24.6$ €/t.
- Value of residues to landfill: The median rate of gate fee for landfilling (including Landfill Tax) in 2014/2015 at 124 €/t [147] has been specified.
- Value of digestate: The market price of digestate has been taken to be 4.71 €/t [148].
- Value of electricity: The market price of electricity has been taken to be 0.118 €/kWh [149]. The electricity generation from the anaerobic digestion and CHP section in per energy unit has been transformed into per mass unit ($0.118 \text{ €/kWh} \times 1.35 \text{ MWh/t of biogas} \times 1000 \text{ kWh/MWh}$) = 159.5 €/t biogas going into the CHP system (1.6 t/h). For electricity generation from the RDF incineration and CHP section, thus the value obtained is $(0.118 \text{ €/kWh} \times 1.37 \text{ MWh/t of RDF} \times 1000 \text{ kWh/MWh}) = 161.7$ €/t RDF going into the CHP system (3.6 t/h).
- Value of metals: The metal containing stream has 80% iron, 14% aluminium, 4.5% zinc and 1.5% copper, respectively [150, 151], based on which their recovered flowrates were decided. The prices of iron, aluminium, zinc and copper are 75, 1093.8, 480, 3875.0 €/t [152, 153].
- The analysis does not include the cost of metal purification as the methods of metal separation are case specific which depends on the types of metal mixtures. The interest of the present analysis is to provide the estimates of the amount and value of zinc, aluminium and copper that can be recovered from municipal wastes, based on

100% recovery at current market price. The fluctuation of zinc prices over time is also not part of the scope of the current study.

5.2.3 Results and discussions

The results of value analysis discussed in the earlier section (equations 1-3) are shown in Figure 4.

The MBT system produces electricity from RDF incineration and anaerobic digestion followed by their respective CHP sections and digested matter (in a business as usual case) and additionally, zinc, copper and aluminium in the resource recovery case. In Figure 4, the cost of feedstock is -24.6 €/t and it enters the process at 41.7 t/h . The first operation it undergoes is mechanical separation and material recovery, which incurs total operating and annualised capital costs of 1.8 million €/y . Then, the COP of the outlet streams from the mechanical separation and material recovery unit going to the RDF incineration and CHP section; anaerobic digestion and CHP section; and landfill is the result of the sum of total cost of feedstock ($-24.6 \times 41.7 \times 8000 \text{ €/y}$) (assuming there are 8000 operating hours in a year) and the total operating and annualised capital costs of the mechanical separation and material recovery unit (1.8 million €/y) and divided by the mass flowrate of the feedstock ($41.7 \times 8000 \text{ t/y}$): $(-24.6 \times 41.7 \times 8000 + 1800000) / (41.7 \times 8000) = -19.4 \text{ €/t}$. The product mass flowrates (t/h) from this unit are RDF (3.6), iron (0.9), aluminium (0.16), copper (0.02), zinc (0.05), biodegradable fraction (21.2), recyclable materials (9.1) and the flow going to landfill (6.6), respectively. All these products have a COP of -19.4 €/t . Thus, a market price of a product greater than this cost means positive economic margin from the product. Thus, the market prices of 75, 1093.8, 480 and 3875 €/t of iron, aluminium, zinc and copper give economic margins of $0.9 \times (75.0 - (-19.4)) = 85.3$, $0.16 \times (1093.8 - (-19.4)) = 176.1$, $0.05 \times (480 - (-19.4)) = 25.4$ and $0.02 \times (3875.0 - (-19.4)) = 66.0 \text{ €/t}$, respectively. The economic margin of recyclable materials is $9.1 \times (19.0 - (-19.4)) = 349.7$. The stream going to landfill thus incurs an economic loss: $6.6 \times (-124 - (-19.4)) = -690.7 \text{ €/t}$. For the exhaust gas or the electricity from the RDF incineration and CHP section and the outlet streams from the anaerobic digestion and CHP section, the exhaust gas (or the electricity), digestate matter and loss streams, their COP is obtained after adding the respective units' total operating and annualised costs $((11.3 \times 1000000) / (3.6 \times 8000) = 392.4 \text{ €/t}$ and $(24.8 \times 1000000) / (8.2 \times 8000) = 378 \text{ €/t}$) to the COP (-19.4 €/t) of their feed streams (RDF and biodegradable fraction) as follows: 370.7 and 126.6 €/t, respectively. As can be noted, the anaerobic digestion and CHP section contributes to 65% of the total operating and annualised capital cost of the plant.

For the end products, the economic margins calculated using equation 1 are as follows.

Business as usual case (without metal recovery):

- 1) Electricity generation from the RDF incineration and CHP section: $3.6 \times (161.7 - 370.7) = -755.8 \text{ €/h}$
- 2) Electricity generation from the anaerobic digestion and CHP section: $1.6 \times (159.5 - 126.6) = 54.1 \text{ €/h}$
- 3) Digestate matter from anaerobic digestion: $17.4 \times (4.7 - 126.6) = -2116.8 \text{ €/h}$
- 4) Recyclable materials from mechanical separation: $9.1 \times (19.0 - (-19.4)) = 349.7 \text{ €/h}$
- 5) Loss from anaerobic digestion: $2.2 \times (0 - 126.6) = -283.0 \text{ €/h}$
- 6) Landfill from mechanical separation: $6.6 \times (-124 - (-19.4)) = -690.7 \text{ €/h}$
- 7) Total: $-755.8 + 54.1 + (-2116.8) + 349.7 + (-283.0) + (-690.7) = -3442.5 \text{ €/h}$

Metal recovery added to business as usual case:

- 1) Iron: $0.9 \times (75 - (-19.4)) = 85.3 \text{ €/h}$
- 2) Aluminium: $0.16 \times (1093.8 - (-19.4)) = 176.1 \text{ €/h}$
- 3) Copper: $0.02 \times (3875 - (-19.4)) = 66 \text{ €/h}$
- 4) Zinc: $0.05 \times (480 - (-19.4)) = 25.4 \text{ €/h}$
- 5) Total: $85.3 + 176.1 + 66 + 25.4 = 352.8 \text{ €/h}$

It is clear that if metals are recovered, these will create major economic incentives for the MBT plants. In the business as usual case, recyclable materials are very important to ensure the profitability of the MBT plant. The gate fee received from the local authority by the plant owner is also critical that makes the business as usual case as a viable case.

It is also possible to calculate *VOP* of the intermediate stream, biodegradable fraction and then for the MSW feedstock using equation 2, explained as follows. From the biodegradable fraction the main products generated are electricity, digestate matter and a loss stream, from the anaerobic digestion and CHP section, which entails total operating and annualised capital costs of 24.8 million €/y. Then, the *VOP* of the inlet biodegradable fraction (€/h) to the anaerobic digestion and CHP section is the total of the *VOP* times the mass flowrate of individual products minus the total operating and annualised capital costs of the anaerobic digestion and CHP section and divided by its mass flowrate:

$$\frac{(1.6 \times 159.5 + 2.2 \times 0 + 17.4 \times 4.7) \times 8000 - 24800000}{21.2 \times 8000} = -129.8 \text{ €/h}$$

Similarly, *VOP* of inlet MSW to the MBT is calculated as follows:

$$\frac{[(0.9 \times 75) + (0.05 \times 480) + (0.02 \times 3875) + (0.16 \times 1093.8) + (3.6 \times 4.5) + (21.2 \times (-129.8)) + (6.6 \times (-124))]{41.7 \times 8000}}{= -98.7 \text{ €/h}}$$

As the focus of this study is on zinc recovery, it has been estimated that 0.0012 tonne of zinc/tonne of MSW can be recovered, which provides additional profit of 25.4 €/h or 0.2 million €/y, shown in Figure 4.

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Further increases in economic margin can be achieved if residues to landfill as well as loss from anaerobic digestion unit are eliminated and unit operating and capital costs are reduced in particular of the anaerobic digestion and CHP section.

6. Conclusions

Rapid depletion of primary resources, increasing emission and waste releases into the environment, and recent advocate in circular economy formed strong driving forces for evaluation of sustainability of recovery of metals from secondary resources such as wastes. Zinc at a current usage rate of 13.5 million tonne per year in products (e.g. galvanisation, alloys, brass and bronze, semi-manufactures, chemicals and miscellaneous) plays an important role in achieving circular economy via secondary recovery from waste. It is shown that in order to achieve the greenhouse gas emission cuts from the sector, the primary mining has to be slashed down and resource recovery from secondary sources – wastes has to be implemented. Thus, a benchmarking exercise is needed for each metal that has prospect in renewable and circular economy – zinc is one such element. This paper reviews various secondary sources of zinc, spent batteries, wastes from electric and electronic equipment, industrial wastewaters, construction and demolition wastes, steelmaking dust and municipal solid wastes. Various technological data have been assimilated including physico-chemical, hydrometallurgical and pyrometallurgical processes, remediation using aquatic plant and biological treatment method. The avoided environmental impacts by not releasing zinc as a contaminant to the environment, but instead recovering as resources, have been presented using important LCIA methods. The current regulations on wastes and wastewaters have also been discussed. Two case studies have been presented to further investigate the economic performance of recovering zinc from steelmaking dust and municipal solid wastes. The

economic potential of recovering zinc from steelmaking dust is compelling as worldwide steelmaking industry can potentially generate 71 - 4058 million €/y in low dust production scenario and 381 - 21740 million €/y in high dust production scenario. The value analysis approach has been undertaken in examining the economic performance of an integrated MBT system, comprising mechanical separation, material recovery, anaerobic digestion, RDF incineration and CHP systems. The study has also demonstrated that 0.0012 tonne of zinc per tonne of MSW can be recovered, which increases the MBT plant economic margin by 0.2 million €/y.

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