Optimisation of Electric Arc Furnace Dust Recycling and Zinc Recovery by Scrap De-zincing

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ABSTRACT

There are two remarkable trends prevailing in the EU steel industry, i.e. the shifting focus towards secondary sources of raw materials, and increasing availability of post consumer scrap. As a significant portion of this scrap is coated, the demand and price of all-black scrap is rising and consequently the need for finding ways to treat the coated scrap prior to steelmaking is driving the research on scrap de-zincing. In addition to the raw materials, the EU steel industry faces the challenge of treating the process dust as the rise in EAF steel production has lead to pronounced imbalance in the dust generation and the capacity of recycling.

Currently about 43% of the steel in the EU15 countries is produced via EAF route generating over 1 million ton process dust annually. Total installed capacity of commercial dust recyclers is about 70% of this amount. It needs to be pointed out that this capacity is not uniformly distributed across the EU as the countries have different level of implementing the environmental regulations. In order to find this distribution, statistics about steel production, dust generation and destinations of the dust were collected by a questionnaire survey. Subsequently, the transportation model of linear programming was used to find the optimum condition of dust recycling. The results indicate that under the condition of minimum transportation costs, recycling related transportation of dust across the north EU and south EU is not feasible. This implies that the total recycling capacity of 70% needs to be split accordingly. Spain and Italy in the south EU according to this division have a recycling capacity of 56% while it is 85% in the north EU.

Owing to the volatile economy of the dust recycling industry, it would not be reasonable to expect that large investments would be made in the near future to handle the rising amount of dust. Some other technical means can however be adopted in order to improve the situation; such as thermal scrap de-zincing. As this process is performed before scrap melting, much higher zinc content can be expected in the dust due to absence of ferrous content which is usually 40%. Other substantial benefits of scrap de-zincing would be shared by the steel industry and dust recyclers. There would be less dust to be recycled, existing

recycling capacity would suffice and due to higher zinc content in the dust, better economical efficiency of recycling process can be expected.

To this effect, an apparatus based on the principal of thermogravimetry was developed and de-zincing experiments were conducted using electro-galvanized scrap samples of different shapes. The mass of the scrap samples used in presented work was about 1 kg so as to understand not only the kinetics of zinc evaporation but the transport of the vapour and hydrodynamics of the packed bed. The parameters studied for this purpose are the flow rate of the carrier gas, scrap heating rate, packed bed voidage, permeability, and specific surface area. Furthermore, pressure drop measurements through packed bed of different samples and Particle Image Velocimetry (PIV) were performed to validate the experimental results.

The results confirm that it is possible to evaporate zinc in an inert atmosphere as demonstrated by other researchers also. For this purpose, the carrier gas for zinc vapours can be nitrogen or even process gases from steelmaking e.g. CO, CO₂ or a mixture of these. A certain flow rate of the carrier gas is needed for effective transport of zinc vapours and under the experimental conditions, flow rates equal to or higher than 20 l/min of nitrogen gave satisfactory results. The isotropy or anisotropy of the scrap samples and the compactness of the packed bed are determining factors for the zinc evaporation and the transport of vapours with the carrier gas. In the case of highly anisotropic scrap type like parallelepipedal or shredded sheet metal, the overlapping of the particles reduces the evaporative surface. In addition, un-even distribution of voidage and permeability leads to flow channelling effect where most of the carrier gas flows along the walls of the container. Therefore, for effective de-zincing of such scrap, it is important to have less compactness and minimization of flow channelling.

Considering the current innovations in the EAF design, there is a potential of combining the scrap pre-heating and the de-zincing processes using shaft type systems that utilize off-gases of steelmaking and auxiliary burners. Some examples of the new furnace designs that incorporate high temperature scrap pre-heating systems are the Fuchs shaft furnace and the Davy-Clecim twin shell furnace. These systems are able to heat the scrap up to 800 - 1000°C, which is a temperature range found to be optimal for scrap de-zincing in the present study.

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ZUSAMMENFASSUNG

Es gibt zwei bemerkenswerte Trends, die in der EU-Stahlindustrie vorherrschen: zum einen die Tendenz zu sekundären Rohstoffquellen, zum anderen steht immer mehr gebrauchtes Alteisen zur Verfügung.

Da ein großer Teil dieses Alteisens beschichtet ist, steigen Nachfrage und Preis für unbeschichtetes Alteisen stetig an. Folglich fördert die Notwendigkeit neuer Behandlungsmöglichkeiten des beschichteten Alteisens vor der eigentlichen Stahlerzeugung auch die entsprechenden Studien über das Entzinken von Alteisen. Zusätzlich zu der Rohstoffproblematik steht die EU-Stahlindustrie vor der Herausforderung, den mitproduzierten Stahlstaub zu recyceln, da der Aufschwung in der EAF-Stahlproduktion zu einem immensen Ungleichgewicht zwischen der Stahlstauberzeugung und den Recyclingkapazitäten geführt hat.

Heute werden etwa 43 % des Stahls in den EU-15 Ländern mit Hilfe von Lichtbogenöfen produziert, die pro Jahr über 1 Million Tonnen Stahlstaub erzeugen. Die Gesamtkapazität kommerzieller Stahlstaubrecycler liegt bei etwa 70% dieser Menge. Diese Kapazität verteilt sich jedoch nicht einheitlich über die EU, da die Länder auf unterschiedlichem Stand sind, was die Umsetzung umweltrechtlicher Bestimmungen betrifft. Um mehr über diese Verteilung herauszufinden, wurden mittels eines Fragebogens im Rahmen einer Umfrage Statistiken über Stahlproduktion, Stahlstauberzeugung und den Bestimmungsort des Stahlstaubes zusammengetragen. Anschließend wurde zur Auswertung der Daten ein Transportmodell benutzt, welches auf linearer Programmierung basiert, um die optimalen Bedingungen für das Recyceln von Stahlstaub zu bestimmen. Die Ergebnisse dieser Modellrechnung zeigen, dass - bei dem wahrscheinlichsten Szenario einer auf ein Minimum reduzierten Beförderung von Stahlstaub - der Transport zwischen Nord- und Südeuropa keine effiziente Option darstellt. Dies bedeutet, dass sich im Idealfall die gesamte Recyclingkapazität von derzeit 70% über dieses Grenzgebiet verteilen muss. Der Süden der EU hat jedoch laut dieser Aufteilung mit den Anlagen in Spanien und Italien eine Recyclingkapazität von lediglich 56%, während Nordeuropa mit 85% einen deutlich höhreren Anteil aufweist.

Aufgrund der unbeständigen Entwicklungen innerhalb der Recyclingindustrie wäre es nicht sinnvolll zu erwarten, dass in naher Zukunft mehr Investitionen getätigt werden, um diese steigende Menge an Stahlstaub zu bewältigen.

Gleichwohl können diverse andere Techniken zur Verbesserung der Situation angewandt werden, wie z. B. das thermische Entzinken von Alteisen. Da dieser Prozess stattfindet, bevor das Alteisen geschmolzen wird, kann von einem sehr viel höheren Zinkgehalt im Stahlstaub ausgegangen werden, da der Eisengehalt von normalerweise 40% nicht mehr vorhanden ist. Die Stahlindustrie und die Stahlstaubrecycler könnten auch von weiteren bedeutenden Vorteilen des Entzinkens von Alteisen profitieren. Es würde weniger Stahlstaub produziert, der recycelt werden müsste, die vorhandene Recyclingkapazität würde ausreichen und aufgrund eines erhöhten Zinkgehalts im Stahlstaub wäre eine erhöhte wirtschaftliche Effizienz des Recyclingprozesses zu erwarten.

Zu diesem Zweck wurde ein Gerät entwickelt, das auf dem Prinzip der Thermogravimetrie basiert, mittels welchem Entzinkungsexperimente an verschieden geformten galvanisch verzinkten Alteisenproben durchgeführt wurden. Die Masse der in der vorliegenden Arbeit benutzten Alteisenprobe betrug etwa 1 kg, um nicht nur Untersuchungen in Bezug auf die Kinetik der Zinkverdampfung durchführen zu können, sondern auch bezüglich der Weiterleitung des Dampfes und der Hydrodynamik des Füllkörpers.

Die für diesen Zweck untersuchten Parameter sind die Fließgeschwindigkeit des Trägergases, die Aufheizgeschwindigkeit des Alteisens, der Leerräume im Füllkörper, die Permeabilität und der spezifische Oberflächenbereich. Des Weiteren wurden bei verschiedenen Proben Messungen des Druckabfalls durch den Füllkörper sowie PIV-Messungen vorgenommen, die der Verifizierung der Ergebnisse dienen sollen.

Die Ergebnisse zeigen, dass es möglich ist, Zink in einer inerten Atmosphäre verdampfen zu lassen, was Untersuchungen anderer Forscher ebenfalls belegen. Zu diesem Zweck dienen als Trägergas für die Zinkdämpfe Stickstoff oder sogar Gase, die bei der Stahlproduktion entstehen, wie zum Beispiel CO, CO₂ oder eine Mischung aus beiden. Jedoch ist eine gewisse Fließgeschwindigkeit des Trägergases für einen effizienten Transport der Zinkdämpfe notwendig. Unter experimentellen Bedingungen ergab eine Fließgeschwindigkeit des Stickstoffs von 20 l/min oder mehr zufriedenstellende Ergebnisse. Die Isotropie oder Anisotropie

der Alteisenproben und die Kompaktheit des Füllkörpers sind entscheidende Faktoren für die Zinkverdampfung und den Transport der Dämpfe durch das Trägergas.

Falle anisotropischen Im einer hoch Alteisenart, Beispiel wie zum geschreddertem parallelepipedalem oder Blech. reduziert sich die Verdampfungsoberfläche aufgrund der Überlappung der Partikel. Zusätzlich führen eine unregelmäßige Verteilung der Leerräume und der Permeabilität zu einer Kanalisierung des Durchflusses, bei dem ein Großteil des Trägergases an den Wänden des Behälters aufsteigt. Für eine effektive Entzinkung des Alteisens sind daher eine geringe Kompaktheit und eine minimale Kanalisierung von großer Bedeutung.

Die aktuellen Innovationen im EAF-Design bergen durchaus das Potenzial, Vorwärmungs- und Entzinkungsprozesse durch das Einsetzen von Schaftsystemtypen zu kombinieren, welche Abgase der Stahlerzeugung sowie Zusatzbrenner nutzen. Zwei Bespiele für ein neues Design bei Öfen, in die Systeme zur Alteisenvorwärmung bei hoher Temperatur integriert sind, sind der Fuchs Schachtlichbogenofen und der Davy-Clecim Doppel - Lichtbogenofen. Diese Systeme erhitzen das Alteisen bis auf 800-1000°C, ein Temperaturbereich, der laut dieser Studie für die Entzinkung von Alteisen als optimal gilt.

NOMENCLATURE

Symbols	Meaning	Unit
а	Total shipment of dust from a steel plant	ton (s)
A	Area	m ²
Ar	Aspect ratio: depth/width	dimensionless
a _v	Geometrical specific surface area	m⁻¹
a _{vd}	Dynamic specific surface area	m⁻¹
b	Total amount of dust received at the recycler	ton (s)
С	Concentration	$\frac{\text{kg}}{\text{m}^3}$
с	Empirical constant	dimensionless
Ср	Specific heat	J kg⋅K
d	Distance	km
d	Diameter	m
D	Diffusion coefficient	$\frac{m^2}{s}$
D _{AB}	Binary diffusion coefficient	$\frac{m^2}{s}$
Ė	Rate of Heat Generation	Watt
h	Heat transfer coefficient	$\frac{W}{m^2\cdot K}$
h _m	Mass transfer coefficient	m s
\bar{h}_{m}	Average mass transfer coefficient	m s
J	Flux (mass)	$\frac{kg}{m^2\cdot s}$
k	Thermal conductivity	$\frac{W}{m\cdot K}$
К	Permeability	m ²
L	Length	m
Le	Lewis number	dimensionless

In	Natural logarithm	
m	Mass	kg
• m	Mass flow rate	kg s
Μ	Coefficient of kinetic energy losses	dimensionless
M_{w}	Molecular weight	 moles
Ν	Coefficient of viscous losses	dimensionless
Nu	Nusselt number	dimensionless
р	Pressure	Ра
Pr	Prandtl number	dimensionless
Q	Rate of heat transfer	Watt
q"	Heat flux	$\frac{W}{m^2}$
R	Molar (universal) gas constant	J m∙K
R _I	Remoteness index	km
⊕ R	Radius of the packed bed	m
ŕ	Radial distance from the centre in a packed bed	m
Re	Reynolds' number	dimensionless
Sc	Schmidt number	dimensionless
Sh	Sherwood number	dimensionless
T'	Recorded surface temperature of scrap sample	°C
Т	Corrected surface temperature of scrap sample	°C
Тg	Temperature of the carrier gas	°C
t	Time	S
V	Volume	m³
U	Seepage velocity / Superficial velocity	m s
	Velocity at a radial distance r from the centre of the	m
Ur	packed bed	S
х	Amount of dust sent from a particular steel plant to a particular recycler	ton (s)
Z	Objective function in linear programming	

Greek symbols

α	Thermal diffusivity	$\frac{m^2}{s}$
γ	Shape factor	dimensionless
δ(t)	Boundary layer thickness; variable with time	m
δ(x)	Boundary layer thickness along the length	m
3	Voidage/porosity	dimensionless
Ø	Diameter	mm
ξ	Tortuosity	dimensionless
μ	Dynamic viscosity	<u>kg</u> m⋅s
ν	Kinematic viscosity	$\frac{m^2}{s}$
ρ	Density	$\frac{\text{kg}}{\text{m}^3}$
Φ	sphericity	dimensionless
ψ	Forchheimer parameter (in Forchheimer equation)	m⁻¹

Indices

b	packed bed
conv	convection
eq	equivalent
f	fluid
g	gas
i	inlet
lm	log-mean
0	outlet
0	reference value
р	particle
rad	radiation
S	surface
∞	free-stream property

Abbreviations

Basic oxygen furnace
Best Available Techniques Reference Document
Direct reduced iron
Electric arc furnace
European Environmental Agency
End-of-life vehicles
Inductively coupled mass-spectrometry
Imperial Smelting Process
European Union
Life Cycle Assessment
Proportional, integral, differential controller
Particle Image Velocimetry
Polyvinyl chloride
Thermocouple

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1. INTRODUCTION

1.1 Steelmaking in the EU

Crude steel production takes place by two major routes in the EU, namely by Basic Oxygen Furnace (BOF) that relies on primary sources; iron and coke, and by Electric Arc Furnace (EAF) that relies mostly on secondary sources like ferrous scrap. Although the EAF process was mostly adopted for production of speciality and alloy steels in the past, it is increasingly being used for the production of plain carbons steels. This change is very prominent in the EU (Fig. 1.1) and the share of crude steel production by the EAF has gradually increased from 33% to about 40% in the last 15 years and is predicted to rise up to 50% by 2030 (EC & IPTS, 2002).



Figure 1.1: Steel production through EAF in the EU (IISI, 2006)

In parallel to this change, the consumption of scrap by the EU steel industry has been increasing steadily in the last 10-15 years. In the EU, a total of 160.5 million tons of steel were produced in 2003, out of which 65 million tons were produced in the EAF, i.e. 40.5% of the total amount (IISI, 2005). As a general figure, 1083-1130 kg of scrap is needed for producing one ton of steel in the EAF (ETC/RWM, 2005); that means the consumption of about 72 million tons of scrap. The possible explanation how this demand could be met can be the stock of durable goods,

construction and infrastructure material that has been continuously accumulating over the last 50-60 years is reaching the end of useful service life.

Despite playing a major role in the economy, steelmaking has certain environmental impacts whether produced by primary or secondary means. In the case of primary steel making, emissions of carbon dioxide (CO₂) are of basic environmental concern. The technology of primary steelmaking is quite ripe in the EU, and there is a very small margin of CO_2 reduction since the process improvements are already approaching thermodynamic limits of efficiency. On the other hand, the technology of EAF is still evolving. Significant room for improvement in the environmental aspects of EAF technology exists, e.g. at different stages of steelmaking like scrap preparation, emissions control during melting and handling of collected emissions. The charge of EAF mostly consists of ferrous scrap and in some cases direct reduced iron (DRI) is used in addition. For the optimal operation of EAF, scrap purity and quality is very important. Although undesirable, the scrap contains many organic impurities like oils, paints, plastics and PVC adhered to the ferrous material. In addition to these organic impurities, a considerable portion of the scrap is galvanized and heavy metals like zinc and lead also end up in the furnace. During steelmaking, zinc -having a low boiling point- evaporates and is collected in the exhaust filters together with other metallic as well as organic and inorganic vapours after condensation. The material thus collected is called EAF dust. As the regulations on pollution of air, soil and water are in force in the EU, it is becoming increasingly difficult and expensive to landfill this dust and therefore it needs to be either neutralized or recycled. A typical melting operation of EAF generates about 10-15 kg dust/ton steel and depending on the type of scrap used and the process parameters it contains 15-25 % of zinc. This significant amount of zinc can be attributed to the galvanized portion of the scrap. As the availability of all-black, non-coated scrap is decreasing, it is worthwhile to explore the reasons of the increasing amount of galvanized scrap. The use of zinc for the corrosion protection of steel became widespread by the end of the 19th century and the number of applications of galvanized steel is growing as the new applications of steel are discovered. The list of these applications is very broad: home appliances, refrigerators, washing machines, building materials like roofing and cladding, fences, street lamps, bridges, cars,

etc. It can be seen in Fig. 1.2 that the use of galvanized steel is remarkably rising and can be taken as an indicator of increasing amounts of zinc in the EAF dust.



Figure 1.2: Deliveries of coated steel in the EU (EUROFER, 2004)

1.2 Problem Statement

The EU steel industry in particular and the metal industry in general find themselves in a tight situation due to growing price competition from developing countries on one side, and the environmental regulations on the other. It is becoming increasingly difficult to remain profitable by fulfilling the environmental regulations, and at the same time competing with economies that exploit cheap labour and have scant regard for the environment.

A certain level of scrap purity is needed for a proper operation of EAF and control over emissions. The growing amount of galvanized scrap is making the un-coated scrap a highly sought after and expensive commodity for steelmakers. In addition to concerns over raw materials, handling of by-products like dust is another matter of concern for the EAF steelmakers as handling/treatment costs need to be paid to dust recyclers.

Competition between primary and secondary sources of metal supply is common and the dust recycling industry is no exception. Factors like high sensitivity towards energy prices and unstable demand for secondary zinc make its economy volatile. This uncertainty has lead to a general lack of investment in dust recycling. Additionally, EU member countries have differing levels and paces of implementing the environmental regulations. The shifting focus towards EAF steelmaking is contributing towards increasing imbalance between dust generation and the capacity of existing recyclers. In the case of an additional 10% increase in the EAF steelmaking, there will be even much more dust to be taken care of in the next three decades. In this situation there is a strong need to explore the state of recycling in qualitative and quantitative ways so that the needs of the future are addressed by the stakeholders collectively. It is also important to find alternative technical means to recover zinc from steel recycling chain in an economical and environmentally friendly way.

2. LITERATURE SURVEY

2.1 EAF Steelmaking and Dust Generation

A study conducted by the European Commission (EC, 1996) lists an inventory of polluting emissions from the iron and steel industry. The compiled information is related to steel production, plant capacities, by-products, their recycling and use. The data about steelmaking dust is related to 1992-1994 and according to the findings, only 28% of the dust was recycled at the time, and the rest was either stored or landfilled.

Hoffmann (1997) has reported a rather improved situation of the EAF dust recycling in the Waelz plants; the leading technique of dust recycling to date. According to him, 45 % of the dust was recycled by the said process at that time and the rest was either stored or landfilled.

The techniques identified in the EC study (1996), e.g. for the collection, storage and recycling of the EAF dust, played an important role in the compilation of the Best Available Techniques Reference Document (IPPC BREF, 2001). The data described in this report is based on the previous two references (EC, 1996) and (Hoffmann, 1997), which means that the latest figures are ten years old. A study sponsored by the European Commission (EC & Okopol, 2004) lists the capacity of five Waelz plants which is 75% of the EU waste amount. Although the current rate of dust recycling is not stated, it mentions that owing to the fact that more and more galvanized steel is recovered, the availability of zinc through EAF dust will increase.

As the EAF steel production in the EU has considerably increased in the last ten years, the available information on dust recycling is not extensive due to the scarcity of literature.

2.2 Galvanized Scrap for Steelmaking

A study commissioned by the European Environmental Agency (EEA), (ETC/RWM, 2005) formed a material flow analysis of production, use and recycling/disposal of iron and steel in the EU. The study suggests that technological potentials might be investigated so that these emissions from the EAF steel industry could be avoided, either through end-of-pipe technologies or a better separation and treatment of the scrap to remove the impurities themselves. The authors point out the increasing amount of end-of-life goods in the EU and, based on a simple stock model, predict that this amount will increase in the coming decades. They further stress the need to increase the knowledge about the amount of steel stocked in the technosphere, including the amount added and released each year in order to form an important base for the strategic investment decisions of EU's iron and steel industry.

Although various studies have been conducted about the ferrous scrap and its origins, there is no concrete information available about the proportion of galvanized scrap in the EU. In order to make a reasonable estimate, the residence time, collection and recycling rate of individual products is needed. As the life span of galvanized products is diverse; ranging from a few years to 60-70 years, it becomes difficult to obtain reliable data about the production figures going back many decades in the past. For products having a relatively shorter life span, e.g. cars (10-15 years), production figures and recycling rates are easier to obtain or estimate.

Sander et al. (EC & Okopol, 2004) report on the environmental assessment of eleven waste streams including ferrous scrap and steelmaking dusts. According to their findings, only a general European-wide picture of ferrous scrap sources is available. The exemplary figures of an average scrap yard in their study show that the vehicles constitute the third largest portion (21%) after building and mechanical engineering scrap. The estimate of Pflaum (1992) about galvanized portion of three different grades of prompt scrap in the United States can be considered exemplary for the industrialised world. According to his estimate, this portion increased 10% from 1980 to 1991. According to Koros (2003), this portion increased further 10% until 2000. Van Rij et al. (1997) estimated the scrap supply

and demand in Europe and according to their calculation about 4 million tons/year of galvanized scrap corresponds to the year 2000. Scheller & Stelter (2004) report this figure to be 6 million tons.

The automotive industry is by far the largest consumer of zinc coated steel. The prevailing trends in this industry have a direct influence on the total amount of the prompt and post-consumer scrap. A remarkable trend in this sector is that the electro zinc coated sheets are being substituted by hot dipped galvanized sheets (EUROFER, 2002) and that the deliveries of hot dipped coated steel have more than doubled in the last ten years. The 'body-in-white' concept started becoming popular around 1994 and at present about 85% of the car body consists of galvanized sheet. Owing to this fact, the contribution of End of Live Vehicles (ELV) to the available galvanized ferrous scrap can not be underestimated. The author wrote an article about the amount of galvanized scrap from the production of new cars and the ELV's during the course of the thesis (Janjua, 2006). Based on an average car of 1200 Kg class, it is estimated that a total of about 4.8 million tons of galvanized scrap came from ELV's and the production of new cars in the EU in 2000.

2.3 De-zincing Techniques

The scrap de-zincing techniques can be broadly classified into two categories, i.e. techniques based on hydrometallurgy and techniques based on pyrometallurgy. The available literature on both of these techniques will be presented in the following.

2.3.1 Hydrometallurgical Techniques

Hudson & Brandiff (U.S. Patent No. 3905882, 1975) disclose a process for the recovery of metallic zinc from galvanized steel scrap in a two stage process by counter-flow acid leaching and the solution in a separate electrolytic cell. Galvanized scrap is placed in the first tank containing concentrated sulphuric acid. After this step, the scrap is partially de-zinced and fresh scrap is placed into a second tank. The weak acid from the first tank is then circulated to the second tank and concentrated acid from the electrolytic cell is re-circulated to the first tank. Although acids quickly deplete the zinc coatings, a major drawback of this process is that the acids dissolve the iron from the scrap, leaching tanks and associated piping, requiring expensive purification schemes to produce a high purity metallic zinc by-product.

Hissel (CA Pat. No. 1193996, 1985) describes a process incorporating two electrolytic cells. The first cell contains mercury and an alkaline solution. Scrap is carried into the leaching solution on a conveyor chain acting as anode and the mercury acts the cathode for deposition of zinc. The amalgam thus formed is recirculated through another cell and zinc is separated onto another cathode. The disadvantage of this process is the low utilization of the current passing through the leaching tank. Dissolution of coating from the scrap requires "line-of-sight" alignment between the anode (coated steel) and the cathode for high electrical efficiency. Additionally, dissolution may not be effective when processing scrap is compressed into bales.

De-zincing of galvanized scrap in a caustic soda solution is considered to be more economical than either of the two preceding alternatives. An advantage of this approach is that the iron layer is stable in a caustic solution and as a result zinc/iron separation after the treatment is not a major problem. A number of patents based on this approach have been granted. One of such processes for the dissolution of zinc from galvanized steel in caustic electrolyte is called "Armco process" shown by Leeker et al. (US Pat. No. 5106467, 1992) and Niedringhaus et al. (1992). For enhancement of the zinc dissolution rate, sodium nitrate acting as oxidizing agent is added to the hot caustic leaching solution. The described de-zincing plant consists of a number of tanks connected in series, with steel scrap sequentially being moved through each of these tanks and the leaching solution being circulated in counter-flow. Leaching solution depleted of its oxidant is transferred to an electrolytic cell where zinc is collected as metallic zinc powder onto a cathode. The process suffers from disadvantages of increase in costs due to the fact that the use of nitrates as a constant chemistry in the electrolyte needs to be maintained. Additionally, the formation of cyanides has been reported from reaction with oils present on galvanized scrap.

LeRoy & Janjua (US Pat No. 5302260, 1994) and LeRoy & Houlachi (US Pat. No. 5302261, 1994) disclose some other de-zincing methods. The process steps described consist of the immersion of the galvanized steel in a caustic electrolyte and electrically connecting it to a cathodic material which is of low hydrogen over voltage and is stable in the electrolyte. According to LeRoy et al., such cathodes include high-surface-area nickel-based and cobalt-based materials such as Raney Nickel type and Raney Cobalt type, nickel molybdates, nickel sulfides, nickelcobalt thiospinels and mixed sulphides, nickel aluminum alloys and electroplated active cobalt compositions. If the scrap to be processed is clean, unpainted or shredded, no external source of voltage is applied to the cathode material. If the scrap consists of bundles, they suggest applying an external source of voltage to the cathode to of increase the rate zinc stripping (U.S. Patent No. 5302261, 1994). The anodic de-zincing of bundles, however, requires large processing times, capital and electrical power costs, making this process relatively expensive. The use of cathodic materials having a low hydrogen overvoltage also increases the cost of this method.

Wittebrood (US Pat. No. 5704823, 1998) demonstrates a method for removing metallic and organic coatings from the ferrous scrap. The process consists of charging the scrap, an aqueous alkaline solution, e.g. Sodium Hydroxide and

abrasive stones, in a drum shaped vessel. The abrasive stones serve to remove the plastic and metallic coatings as the drum is set in tumbling motion. Metal powder, selected from the group consisting of Pt, Pd, Ir, Co, Ni and Fe, is also added to the drum which increases the evolution of hydrogen and thereby accelerates the removal of metallic coating. The technique suffers the drawbacks that it is not able to remove all the coatings (metallic and organic) completely. Furthermore, the inventors do not mention the treatment of alkaline solution for recovery of dissolved metallic coating or if the solution is utilized in some other way.

Wijenberg et al. conducted experiments on the dissolution of zinc from scrap in alkaline solutions. The findings are reported in the article (Wijenberg et al. 1997), and Int. patent No. WO002689 (Mooij et al., 1996). They report that the dissolution rate of zinc in alkaline solutions is controlled by the generation of hydrogen at the cathode surface. Like Wittebrood (US Pat. No. 5704823, 1998), Wijenberg et al. also suggest galvanic coupling of Zn to a metal having a larger exchange current density like Pt, Pd, Ir, Co, Ni and Fe (or steel). They point out that $Zn(OH)_4^2$ formed during the dissolution deposits at the cathode even at a low concentration, thereby inhibiting the evolution of hydrogen and decreasing the dissolution rate. According to them, the dissolution rate of Zn can be increased by maintaining a higher temperature and a higher pH value of the alkaline solution. In order to reduce the transport of $Zn(OH)_4^2$ from the anodic to the cathodic compartment, they suggest the introduction of a membrane in a divided cell. When no membrane is present between the compartments, the same purpose can be achieved by introducing an electrical resistance in the circuit that increases the cell current.

Alonzo et al. (2002) performed experiments on zinc dissolution by corrosion in an alkaline suspension and addition of various iron oxides or iron hydroxides. Enhancement of zinc dissolution in the presence of ferrous powder as reported by them is similar to the one observed by Wittebrood (US Pat. No. 5704823, 1998). The iron compounds covered the zinc surface acting as cathodic areas, thereby increasing the H_2 evolution and corrosion of zinc. They report an enhanced dissolution rate of zinc from the scrap sample that was stirred magnetically. Morgan et al. (US Pat. No. 5779878, 1998), Morgan (US Pat. No. 5855765, 1999)

and Morgan (US Pat. No. 6258248, 2001) disclose different variations of a process

in which galvanized steel is immersed in a hot electrolytic solution of sodium or potassium hydroxide and the zinc is galvanically corroded. They present similar techniques as reported by Wittebrood (U.S. Pat. No. 5704823, 1998), (Mooij et al. (1996) and Alonzo et al. (2002) for enhancement of the zinc dissolution rate, e.g. by (i) mechanically abrading or deforming the galvanized steel, (ii) mixing the galvanized steel with a material having a standard electrode potential which is intermediate of the standard electrode potentials of zinc and cadmium in the electrochemical series, (iii) moving the galvanized steel relative to the electrolyte and (iv) carrying the steel scrap through the electrolyte on a conveyer that is electrically insulated from the ground. They describe another new technique for enhancing the dissolution of zinc by initially heating the scrap to around 470-600°C to form an alloy of iron and zinc. As explained by them, contact between two dissimilar metals is increased due to the formation of the alloy layer at the scrap surface, leading to an increase in the corrosion rate of the scrap when it is immersed in the electrolyte.

Wijenberg and Droog (1999) report the results of experiments performed on dezincing of galvanealed steel. Their findings confirm the observations of Morgan et al. (US Pat. No. 5779878, 1998) that in the case of zinc alloyed (e.g. galvanealed) coating, the electrolyte can penetrate deeply into the coating layer due to the presence of cracks and craters and an increase in the dissolution rate of zinc. However, after the de-zincing, there is still a considerable amount of zinc trapped in an unknown iron-zinc phase. They suggest similar techniques to remove this phase like Morgan et al. (US. Pat. No. 5779878, 1998), e.g. mechanical abbration, deformation and de-zincing in a rotating drum.

2.3.2 Pyrometallurgical Techniques

Fujio & Kazuhiro (1992) refer to the de-zincing of car body scraps from stamping plants. Their experimental procedure consisted of baking the shredded scrap in a heat treatment furnace to convert most of the zinc into a brittle Fe₃Zn₁₀ phase that comes off by shot-blasting. They report a zinc removal rate of 85% after baking at 750°C and subsequent shot blasting for 5 minutes. A plant based on this process

was installed at Toyokin Co. in 1987 which was capable of processing 5000 tons/month of scrap at the expense of 30\$/ton. Franzen & Pluschkell (1999) performed similar experiments by annealing the zinc coated samples between 560° C – 620° C for a holding time of 300-1000 s. The delta phase Fe-Zn alloy layer created this way was removed by mechanical bending.

Okada & Fujio (US Pat. No. 5350438, 1994) reveal a method and apparatus for removing plated metal -for example zinc and aluminium- from shredded scrap having non-metallic contaminations like paint, oil, plastics, etc. from car shredders. The scrap is purified in essentially two steps: at first by evaporating the organic material between 200°C-500°C under reduced pressure, and subsequently by evaporating the metallic coating at a temperature range of about 500°C-950°C under reduced pressure. In the final step, the steel sheet scraps are cooled by gas (air or non-oxidizing gas) and later used for smelting materials. The technique suffers from difficulties in thorough heating of the scrap and the inventors suggest an embodiment in which the treatment chamber includes a means of rotating the drum containing scrap. In another embodiment the scraps are heated with a gas at a pressure close to the atmospheric pressure for effective heating.

Saotome et al. (1996) comment on similar experiments using VARS technology for the removal of zinc from automotive process scraps. In their experiments, the evaporation was carried out between 700-1200°C under vacuum and the reported purity of the zinc is 99.86%.

Ozturk & Fruehan (1996) conducted experiments on zinc vaporization from galvanized scrap in nitrogen, air, CO and CO₂ atmospheres. The tests performed at constant temperatures indicate that the rate of zinc vaporization is very fast in nitrogen and carbon monoxide atmospheres at temperatures higher than 950°C. Simultaneous oxidation and vaporization of zinc occurred in carbon dioxide and air whereby gas phase mass transport controlled the evaporation. Although these results provide important information about the suitable atmosphere for zinc evaporation; the information about the transport kinetics of the zinc vapour and scrap heating is not available as the size of their sample is too small to reflect conditions of a possible scale-up.

Tee & Fray (1999) performed lab-scale tests for zinc removal from electrogalvanized and iron-zinc galvanized scrap using air and chlorine mixtures. Using an air and chlorine mixture (10:1), they report that zinc chlorinates to form

zinc chloride and iron oxidizes to form a protective oxide layer at 800°C. Although they present an economical analysis for the implementation of their process, the details of their experimental procedure and technical implementation are missing.

Franzen & Pluschkell (2001) describe zinc evaporation experiments from scrap in Ar, N₂ and He environments using a thermogravimetric apparatus. According to their findings, zinc can be evaporated effectively by holding the galvanized samples at 600°C for 5 minutes. Further results on zinc evaporation are reported using a laboratory scale vaporizer that consists of a quartz tube charged with a galvanized scrap sample. The scrap is heated by an induction coil that moves upwards with controlled speed and an inert gas enters the tube at the bottom and leaves at the top. They report on the zinc evaporation rate in terms of the speed of the induction coil and the information about scrap heating rate; its temperature and the gas flow rate are not reported.

Experiments on pyrometallurgical de-zincing of electrogalvanized and hot-dip galvanized scrap in nitrogen atmosphere are conducted by Antrekowitsch J. & Antrekowitsch H. (2001). The investigated parameters were the temperature of the scrap and the treatment time. A complete removal of zinc from hot dip galvanized steel was not possible but high yields of >90% were attained by treatment temperatures of 950°C.

Viklund-White (2000) used Life Cycle Assessment (LCA) for the environmental assessment of the recycling of galvanized scrap. The study compares various process routes for zinc recovery, including the de-zincing of scrap and dust recycling processes like EZINEX, Waelz kiln and DC furnace. According to her findings, the de-zincing process has the highest environmental impact as it consumes a large amount of electricity. This conclusion is based on only one de-zincing process that uses leaching by caustic soda and electrolysis for zinc recovery. In the absence of comparison with the other de-zincing options like acid leaching or pyrometallurgical processes, this is a rather subjective conclusion.

2.4 EAF Dust Treatment

There are various possible processes to recycle EAF dust, i.e. the hydrometallurgical, pyrometallurgical and hybrid processes. The product obtained from these processes consists of either high grade zinc or zinc oxide, which is further refined to obtain high grade zinc. Some of these recycling processes demand a certain amount of zinc to be present in the dust, and therefore the dust is charged back to the EAF a number of times until the desired level of zinc is reached. In addition to recycling, an alternative is also proposed in literature which is neutralization to obtain an inert product that can be used as building material. Zunkel (2001) presents an extensive list of processes and options of EAF dust treatment and recovery of ferrous and non-ferrous content.

2.4.1 Pyrometallurgical EAF Dust Recycling Processes

Most of the commercially available dust recycling processes are based on pyrometallurgy. A common feature of these processes is the carbo-thermic reduction of dust to obtain zinc that is bonded with iron. A list of these processes is presented below.

- Waelz process (USA, Germany, Italy, France, Spain, Japan, Taiwan, Mexico)
- ISP (Imperial Smelting Process) (UK, Germany)
- Flame reactor (USA)
- MF furnace (Japan)
- Electrothermic furnace (Japan), (US Pat. 4323391)
- Vacuum heating reduction (Japan)
- Rotary kiln (Jap. Pat. 63117911A)
- FASTMET
- Rotary hearth furnace
- Modified ZINCEX process

Some of the processes operate on a large scale and therefore the dust is collected from various steelworks and transported to the recycling sites. Others operate in dedicated plants installed at the steelworks. Pyrometallurgical recycling of EAF dust is an active area of research. A brief overview of the ongoing research in this area is presented here.

Best and Pickles (2001) performed a thermodynamic study of the selective reduction of EAF dust in a carbon monoxide atmosphere. They report that the reduction of iron is required to achieve high recoveries of zinc in a completely selective manner. Lee.Y and Lee J (1997) studied the behaviours of zinc, lead and chlorine during the recycling of EAF dust in an oxidation and reduction atmosphere between 800-1300°C. According to their findings, the removal of chlorine was favourable under the oxidation atmosphere, whereas the reduction atmosphere was favourable for the evaporation of zinc. Best and Pickles (1994) studied the recovery of zinc from EAF dust in a carbon monoxide atmosphere in a plasma furnace. Donald and Pickles (1996) inform about thermodynamic studies on the reaction of EAF dust with solid electrolytic iron powder as a reducing agent. Furukawa et al. (2004) describe trials on direct separation of iron and zinc from EAF exhaust gases. The process consists of two stages where iron and slag are collected in a coke bed filter and zinc and lead immediately afterwards by rapid cooling in a condenser. Kumar reports on a research project of Cambridge University (Kumar 2001) aimed at using zinc oxide contained in the EAF dust as a reagent for desulphurising steel melt. Savov and Janke (2001) report on their research on removal of tin and zinc from liquid metal as well as from ferrous scrap prior to melting. Bishop et al. (CA Pat. No. 1308262, 1992) disclose a method for the recovery of heavy metals by pyrometallurgical treatment of EAF dust and sludges using carbonaceous reductant and converting the remaining iron into directly reduced iron pellets. Bilter & Baranski (US Pat. No. 5942023, 1999) describe a technique in which the EAF dust is reduced by a carbonaceous reductant in a sealed atmosphere plasma arc furnace. The vaporized heavy metals are brought into contact with an alkali metal gettering agent to inhibit the formation of heavy metal chlorides in the off-gas.

The enrichment of steelmaking dust by charging it back to the EAF is practiced at many steelworks. The described benefits of this process are the reduction in the amount of dust to be recycled and the higher value due to the high zinc content. Jensen & Wolf (1997) refer to the injection of dust in the EAF at Det Danske Stalvalsevaerk A/S. Drissen et al. (2005) describe a similar practice at Edelstahlwerke Suedwestfalen.

2.4.2 Hydrometallurgical Processes

Hydrometallurgical processes are not as successful as the pyrometallurgical processes in terms of large scale commercial application. As the EAF dust contains significant amounts of franklinite ZnFe₂O₄, it is difficult to leach zinc from stable bond using alkaline and dilute acidic solutions. According to the author's knowledge, at present there is only one hydrometallurgical process running in the development stages in the EU. The process called EZINEX was developed by Engitec SpA and several pilot stage feasibility studies are being conducted at steelworks in Luxembourg, France and Germany; and one plant is commissioned in Italy. Orhan (2005) lists difficulties encountered by various researchers in leaching zinc using HCl, H₂SO₄ and HNO₃. A common procedure for dust recycling in alkaline solutions is the washing with water to remove halide salts, the leaching of zinc in an aqueous state, the precipitation of other metals and the subsequent electrowinning. Orhan (2005) and Youcai & Stanforth (2000) report experiments with caustic leaching, Antrekowitsch J. & Antrekowitsch H. (2001) performed experiments with caustic as well as acid leaching, Ruiz et al. (2007) suggest zinc recovery using ammonium carbonate, Dutra et al. (2005) conducted experiments on alkaline dissolution of zinc using conventional agitation and pressure leaching as well as microwave and ultra-sonic assisted agitation. Xia and Pickle (2000) also describe their findings with caustic leaching of EAF dust assisted by microwave agitation. Havlík et al. (2006) present their findings on zinc recovery using sulphuric acid leaching and an extensive list of references related to hydrometallurgical treatment of EAF dust.

2.4.3 EAF Dust Neutralization/Vitrification

Several alternatives to dust recycling like neutralization and disposal in landfills as well as vitrification are proposed in literature. The process of vitrification consists of binding the leachable heavy metals like lead and zinc in a silica glass structure at a high temperature. The product thus obtained can then be used in ceramics or as building material. In a glassy material, crystallinity needs to be avoided as it increases the leachability of hazardous materials. As iron oxides promote this phenomenon, there is an upper limit of ferrous content in the EAF dust. Beyond a certain level of ferrous content, the vitrification process becomes un-economical as an significant amount of silica needs to be added thereby requiring a higher energy input.

lonescu et al. (1997) report on their experiments on EAF dust samples to determine the effect of Fe₂O₃ and ZnO on vitrification. According to their findings, EAF dust containing up to 35% of Fe_2O_3 can be economically vitrified. Pereira C. F. et al (2001) describe the dust solidification/stabilization (S/S) using coal fly ash as fundamental raw material and main binder. Pelino et al. (2002) studied vitrification of EAF dust from carbon steel and stainless steel production. According to their findings, the Si/O ratio needs to be higher than 0.33 for the formation of a stable glass structure. Moreover, they report that zinc evaporation from the dust results in even better glass structure. Cheng (2003) reports on experiments related to glass-ceramics formation by the combination of stainless steel dust and incinerator fly ash with the ratio of 1:9. The major phases of the resulting products were Augite, Akermanite and Donathite that can be used as building or refractory materials. Mikhael et al. (1998) refer to experiments on vitrifying EAF dust with clay. Polsilapa and Wangyao (2007) conducted their experiments on vitrification by mixing the EAF dust with fly ash and bagasse ash. Aota (US Pat. No. 5672146, 1997) discloses a process for making clinker by the addition of silica and alumina to EAF dust that can be used in ceramics or road construction. Frame (CA Pat. No. 2093615, 1993) and Lee (KR Pat. No. 100234883B, 1999) propose to include EAF dust in conventional material for making bricks. Lynn & Jablonski (US Pat. No. 4840671, 1989) and Lynn & Jablonski (US Pat. No. 4911757, 1990) disclose a technique for the pozzolanic reaction of materials containing anhydrous alumino-silicates, lime, water and chemicals that physically entrap the heavy metals present in EAF dust into a calcium-alumino-silicate matrix. Smith (US Pat. No. 5245122, 1993) describes methods in which the dust is incorporated into a cementitious system including lime kiln dust, fly ash, ferrous sulphate, and hydrated lime, to which water is added to make cement. Richards (CA Pat. No. 2080842, 1991) gives a description of a specialised glass-making furnace in which materials such as EAF dust can be included for making borosilicate glass.

3. RESEARCH FOCUS AND OBJECTIVES

In a broader sense, the theme of the presented research is optimization of the recovery options of zinc from ferrous scrap and the process dust of the EAF steelmaking. Zinc coatings ensure corrosion protection and their expected life is usually longer than the service life of the steel products. Despite this benefit, several difficulties are encountered in steelmaking by using galvanized scrap. Although most of the zinc evaporates from the scrap at elevated temperatures, still a significant portion gets dissolved in the melt. This dissolved portion has an adverse effect on the refractory lining of the furnace. Furthermore, the release of 'white fumes' i.e. zinc oxide during tapping and casting can raise safety concerns. The effect of zinc as an alloying element on the mechanical properties of steel is not well known; however steelmakers try to keep the zinc level to a minimum by use of intensive ladle metallurgy.

The evaporated portion of zinc ends up in steelmaking dust that contains other metallic, organic and inorganic compounds. Due to environmental and economical considerations, this dust is recycled and metallic zinc is extracted in two stages: first at the dust recycler in the form of zinc oxide, and then at the zinc smelter where pure zinc is obtained. Usually, the amount of zinc present in the dust is not high enough to be economically recycled. In order to overcome this difficulty and reduce the amount of dust and related handling costs, steelmakers recycle this dust internally by injecting it back to the EAF until its zinc content reaches a certain acceptable level for dust recyclers. This step, though seemingly beneficial for the environment, intensifies the metallurgical difficulties mentioned earlier.

Over the last decade, the capacity of recycling has not followed the rise in steelmaking dust. The Waelz process is still the only option for EAF dust treatment at commercial level. There were two ISP plants operating in Europe; one in Germany and the other one in Italy, but due to operational and economical difficulties, currently both are out of operation. Although there are some pilot recycling plants operating at some steelworks, the potential of their wide-spread success can not be anticipated. The dust neutralization and vitrification are preferable practices compared to landfilling. Nevertheless, there are two inherent
disadvantages related: first, the long term stability of their product is unclear; second, precious amount of metals goes out of circulation.

In this situation where environmental regulations are becoming ever tougher and the competition from the growing economies is mounting, the only viable solution is constant innovation in technology and modifications in the recovery chain of zinc. There is a strong need for comprehensive and joint efforts from the EU steel and zinc industry. The research on technical means of improvement will be less meaningful without the consideration of the outlook of the steel industry and the existing infrastructure of dust recycling. The available data about dust generation and treatment in the EU is relatively old. Additionally, it is not representative of the current situation since the EAF steelmaking was going through a rapid transformation and structural changes when the data was collected, as pointed out by the reports (EC, 1996) and (IPPC BREF, 2001). The portion of EAF steelmaking has increased from 30% to 40% since these reports were published. There are concerns over insufficient capacity of dust recycling in the EU, but the information related to gaps in this capacity is missing. The first objective of the research is therefore to obtain and present information about dust generation, recycling capacity and the break-up of this capacity across the EU. This objective is complementary to the technical research as it provides an important information base for discussion at the regulatory level and the decision-making over investment in de-zincing.

A possible step in improving this situation can be scrap pre-treatment or dezincing. It holds manifold benefits: clean scrap, reduction of metallurgical problems in steelmaking, a product rich in zinc, reduction in the total amount of dust to be recycled and the utilization of the existing dust recycling capacity.

The literature survey reveals several limitations of the hydrometallurgical processes of scrap de-zincing. For instance, the by-products of these processes need an additional recycling step. Furthermore, most of these processes can handle only the process scrap of automotive manufacturing which has a much higher purity compared to the scrap from end-of-life products. The difficulty of de-zincing the scrap which is painted or has an oily surface is obvious for these processes. In addition, these processes can not be seamlessly integrated with the

steelmaking as the treated scrap needs to be dried, shredded, baled and transported before being charged in the furnace. On the other hand, pyrometallurgical processes have the advantage that the charging of treated scrap can also improve the thermodynamical efficiency of steelmaking. Although some research on scrap de-zincing by pyrometallurgical techniques has been done in the past, it did not gain sufficient attention and advancement due to concerns about higher energy costs. Scrap pre-heating by off-gases of steelmaking are considered as a means of energy recovery and among the 'Best Available Technologies' (IPPC BREF, 2001). This technique is already practiced at many steel works in the EU, and part of the heat required for zinc evaporation can be attained this way. According to a survey (Birat, 2000), installation of scrap preheating facilities is expected to increase by a factor of 3 from 10 to 30% of the newly-built furnaces. This remarkable trend is not only important for energy saving, but for the purity of scrap as well. The scrap pre-heating is carried out employing low temperature processes (~300°C) using the off-gases, and high temperature process (800°C-1000°C) that utilise the auxiliary burners together with heat from the off-gases (Birat, 2000). The high temperature processes have not only the advantage of clean emissions marked by minimum dioxin levels but a potential of scrap de-zincing that takes place at temperatures > 500°C. Two such high temperature processes are Shinseiko Forum Technology and Consteel (IISI EAF, 2000).

In order to investigate the potential of utilising shell type scrap pre-heating facilities for de-zincing, the kinetics of zinc evaporation and transport through the scrap need to be understood. The literature survey indicates that although some attempts have been made in this direction, important information from the industrial point of view is missing. As the scrap from the shredders is available in different grades having different compactness/densities, this will have additional influence on heat transfer and transport of zinc vapour. One important research objective is to find the influence of such parameters and quantify their effect so that scrap de-zincing can be applied on an industrial level.

On 1st May 2004, the EU expanded by annexation of ten additional countries from Eastern Europe. These countries developed a different economical structure due to the presence of the iron curtain. For reasons of simplicity; the first objective is

focused on the EU 15 region comprising Western Europe. Throughout the report, 'EU' refers to the EU 15 region.

In the light of the research theme, the present study deals with two main objectives:

- Identification of gaps in dust recycling capacity and suggestions for increasing dust recycling in the EU for zinc recovery
- Contribution towards available knowledge of thermal scrap de-zincing; a process that can recover most of the zinc prior to steelmaking thereby lowering the total amount of dust to be recycled.

4. IMPROVEMENTS IN THE DUST RECYCLING CHAIN

For the economical operation of the recycling process, steelmaking dust should contain at least 18-35 % of zinc. Owing to this fact, dusts generated from carbon or low alloy steel production through EAF are attractive raw material for commercial dust recyclers. Although some steelmakers operate their own mini recycling facilities, the literature survey indicated that most of the dust is still treated by the Waelz process in the EU. As the above mentioned steel sector and recycling technique represent most of the situation, the present analysis includes only these two.

4.1 Methodology

Information about the EAF installations was initially collected from various sources like the European Confederation of Iron and Steel Industries (EUROFER), the International Iron and Steel Institute (IISI) and the national iron and steel federations of the individual EU countries. Subsequently, the installations engaged only in carbon or low alloy steel production were identified and information was collected about their techniques, EAF size, steel production and dust generation. The data thus collected was not substantial as there are differing practices of reporting the environmental data and production figures. Therefore a questionnaire was formulated and sent to these steelmakers asking for information about steel production, dust generation, its composition as well as the destination of dust and the mode of transportation. The information about Waelz plants, their capacity and production figures was collected through their published information material and reports of the European Commission (EC).

The questionnaire sent in November 2004 resulted in reply from only ten companies. Subsequent reminders in January, May and July 2005 contributed towards a total of 39 replies (Table 4.1).

Country/Region	Replies	Coverage of EAF steel production (%)
U.K.	4	84
Spain	6	29
France	2	21
Italy	5	24
Scandinavia	4	39
BENELUX	4	65
Greece	1	62
Germany	13	76
Total	39	50

Table 4.1: Overview of questionnaire replies

Most of the data about steel production and dust is related to 2003 and 2004, and in a few cases average annual figures are quoted. The total steel production of the companies participating in the survey is about 50% of the total EAF output in the EU, therefore the data can be considered representative of this sector.

Information about the location of steel production sites, the dust generation rate, destination and mode of transportation was used to form a transportation model of linear programming. The purpose of this model was to identify gaps in recycling by estimating/tracking the most probable flow of steelmaking dust. Landfilling, although contrary to environmental regulations in most of the countries, exists as an alternative to recycling and therefore it is important to check the validity of the model. Although only a few companies revealed the destination of dust, alternative information about its mode of transportation and respective distance was used to infer this information.

In addition to recycling, another inference is drawn about the practice of dust minimization by internal recycling from the composition of dust and the ratio of dust to steel production. Finally, the information about alternative uses of the dust will be presented.

4.2 EAF Steel Production and Dust Recycling in the EU

There are about 81 sites producing carbon and low alloy steel via EAF in the EU. The major share comes from Italy, Spain, Germany and France (Table 4.2). A total of 65 million tons of steel was produced by this particular sector in 2003 and over 1 million tons of dust corresponds with this figure.

Country	Number of sites	Steel production (k.tons) *	Dust generation (k.tons) **
Italy	16	16,898	270
Germany	16	13,432	215
Spain	16	12,528	200
France	14	7,770	124
BENELUX	7	5,619	90
U. Kingdom	5	2,638	42
Sweden + Finland	4	3179	51
Greece	2	1,701	27
Portugal	n/a	730	12
Austria***	1	555	9
Total	81	65,050	1,041

Table 4.2: Steel production by EAF in the EU (2003)

* IISI 2005

** estimate based on information gathered through questionnaire

*** estimate based on average EU figures

On the recycling side, there are seven major sites in the EU (Table 4.3).

Table 4.3: EAF dust red	yclers and their capacities
-------------------------	-----------------------------

No.	Name	Location	Capacity of recycling (tons)
1	Harz-Metall**	Germany	60,000
2	B.U.S Zinkrecycling*	Germany	220,000
3	B.U.S. Metall*	Germany	100,000
4	Recytech*	France	80,000
5	Portovesme***	Italy	75,000
6	Pontenossa*	Italy	100,000
7	ASER*	Spain	105,000
		Total	740,000
* ⊏(2 & Okonol 2004	** Metaleuron 2004	*** EC 1007

EC & Okopol, 2004 * Metaleurop 2004 ゙ EC 1997 It can be concluded from the information presented in Table 4.2 and Table 4.3, that there is an overall gap of 30% in the dust generation and the recycling capacity in the EU. This conclusion can be considered reasonable as these sites are never running at 100% of their capacity and the in-house recycling facilities at some steel plants can not cover the gap of 30%. According to USGS (2005), the facility in Portovesme closed down its operation due to high electricity costs and it is not clear if or when it will restart. In this case, the gap becomes 36%. Nevertheless, some important questions need to be answered in order to understand the scenario of recycling:

- 1. Is this gap uniformly distributed over the EU or there are some regions where it is wider than in others? and,
- 2. Are the recycling sites located in optimal proximities of steel plants and do they have sufficient capacity?

The transportation model of linear programming was used to find the answer to these questions.

4.3 Transportation Model

In order to find the location of the gap in recycling, it is important to discover how the existing capacity of dust recycling is assigned to steelmakers in the EU. The transportation model is based on the obvious condition of minimum transportation cost of dust recycling. The cost of transportation depends on many factors like shipment size and the possibility of loading cargo back in order to decrease empty ways. As the present model is only intended for estimating the probable flow of dust, the cost of transportation can be assumed to be a linear function of the distance between steel plants and recycling sites. The information collected through the questionnaire indicted that about 89% of the dust is transported by road. Taking this fact into consideration, road distances were calculated from each of the 63 plants (for which steel production was known and dust generation was either known from the questionnaire replies or estimated) to each of the recycling sites. Two instances of the model are developed; one with seven recycling sites and the other with six sites (with the absence of Portovesme).

4.3.1 Formulation of the Model

Suppose there are (n) numbers of steelworks and (m) numbers of dust recyclers. Shipments a_1 ,, a_n of dust are transported from each of the (n) steelworks and are received in amounts b_1 ,, b_m at each of the (m) recyclers (Fig. 4.1).

Let X_{ij} = shipment of dust be sent from a steel plant (i) to recycler (j). In an optimal condition, the capacity of recyclers should be fulfilled at minimum transportation costs. Therefore the objective function is to determine the shipment X_{ij} of dust to be transported between each origin-destination pair, i=1,...., n; j=1,....,m to satisfy the transportation requirements and minimize the total cost.



Figure 4.1: Matrix showing the shipment of dust between steel plants and dust recyclers

Let d_{ij} = distance between the i-th origin (steelwork) and the j-th destination (recycler). (Fig. 4.2)





The objective function can then be written as:

$$Z = \sum_{i=1}^{n} \sum_{j=1}^{m} d_{ij} \cdot X_{ij} \text{ (minimum)} \qquad \begin{array}{l} i = 1, \dots 63 \text{ (steel plant)} \\ j = 1, \dots .7 \text{ (recycler)} \end{array}$$
(4.1)

where,

- ---

d_{i j} = distance in kms

 X_{ij} = shipment of dust in tons

The solution has to satisfy the constraints of supply and demand, i.e. each supply point has a limited production capacity and each demand point has a limited recycling capacity.

or;

$$\sum_{j=1}^{m} X_{ij} \le a_i \text{ (constraints on supply)}$$
(4.2)
$$\sum_{i=1}^{n} X_{ij} \ge b_j \text{ (constraints on demand)}$$
(4.3)

Additionally, the transported quantity can not be negative:

$$X_{ij} \ge 0, \tag{4.4}$$

As the supply is greater than the demand, i.e. $\sum_{i=1}^{n} a_i > \sum_{j=1}^{m} b_j$, it is an un-balanced problem and the dust that can not be transported will appear as slack in the supply constraint. The solution to the problem consists in finding the entries in the matrix (Fig. 4.1) to satisfy the objective function Z (Eq. 4.1). The number of variables

and the number of constraints:

involved in the calculation is therefore:

$$i + j + 1 = 71$$
(supply) (demand) (non-negativity) (4.6)

The model was solved using a simplex algorithm from commercial software Premium Solver [™] integrated with MS Excel [™].

4.4 Results of the Transportation Model

4.4.1 Distribution of Dust Recycling Capacity across the EU

The transportation model resulted in a total transportation volume of 282 million tons-kms whereby the total capacity of the recyclers is utilised. As the cumulative capacity of the 7 dust recycling facilities is lower than the total dust generation of the 63 steel plants, the rest appears as slack in the model; stored at the steel plants. The optimal assignment of dust from each country (based on data from 63 steel plants) to each of the seven recycling facilities and the transportation volume are presented in Table 4.4 and Table 4.5, respectively.

	To recycling facilities						
		Nor	th EU		South EU		
Shipments (tons)	Harz	B.U.S.	B.U.S.	Recytech	Portovesme	Pontenossa	ASER
from:	Metall	Metall	Zink.	-			
U.K.	-	-	-	49,050	-	-	-
France	-	-	30,726	23,816	14,584	-	7,372
Sweden	-	-	15,653	-	-	-	-
Luxembourg	-	41,800	-	-	-	-	-
Austria	-	-	6,205	-	-	-	-
Belgium	-	13,156	-	7,134	-	-	-
Germany	100,000	41,744	157,916	-	-	-	-
Netherlands	-	3,300	-	-	-	-	-
Spain	-	-	-	-	60,416	-	97,628
Italy	-	-	9,500	-	-	100,000	-
Total	100,000*	100,000	220,000	80,000	75,000	100,000	105,000

 Table 4.4: Optimal allocation of dust to the recycling facilities

* Estimate based on (EC & Okopol, 2004) and (Recylex 2007)

Table 4.5: Volume of dust transportation to the recycling facilities

	To recycling facilities						
		Nor	th EU		South EU		
Transportation	Harz	B.U.S.	B.U.S.	Recytech	Portovesme	Pontenossa	ASER
volume (k.ton x km)	Metall	Metall	Zink.	-			
U.K.	-	-	-	20,755	-	-	-
France	-	-	18,175	3,331	9,833	-	1,216
Sweden	-	-	18,605	-	-	-	-
Luxembourg	-	12,665	-	-	-	-	-
Austria	-	-	3,996	-	-	-	-
Belgium	-	2,717	-	820	-	-	-
Germany	24,200	6,609	59,573	-	-	-	-
Netherlands	-	667	-	-	-	-	-
Spain	-	-	-	-	60,986	-	5,396
Italy	-	-	8,579	-	-	24,872	-
Total	24,200	22,658	108,928	24,906	70,819	24,872	6,613

It is interesting that according to the model results, under the condition of minimum transportation, there are negligible shipments of dust between the north and south EU. This implies that there are two distinct zones in the assignment of recycling capacity. Based on this result, the logistic boundary between the north and south EU, and the gaps in recycling capacities are presented in Fig 4.3 and Fig 4.4, respectively.



Figure 4.3: Logistic boundary of dust transportation in the EU



a. North EU



Figure 4.4: Gaps in the recycling capacities in the EU

In the case of six recycling sites, i.e. Portovesme being indefinitely out of operation, the recycling gap in the south EU becomes even smaller (40%).

4.4.2 Remoteness Index of Recycling Sites

Transportation costs can be considered as a strong function of the distance between sources of supply and demand. The model gives important information about how remote the dust supply sources are from the recycling facilities. The remoteness index R_I (Table 4.6), based on the total shipment of dust (Table 4.4) and the transportation volume (Table 4.5) for each recycling site is calculated as:

$$R_{I} = \frac{\text{Total transportation volume of dust}}{\text{Total Shipment of Dust}} \text{ (kms)}$$
(4.7)

Table 4.6: Remoteness Index for dust recycling facilities (kms)

	No		South EU			
Harz Metall	B.U.S. Metall	B.U.S. Zink.	Recytech	Portovesme	Pontenossa	ASER
242	227	495	311	944	249	63

4.5 Additional Information from the Questionnaire

4.5.1 Non-recycling Use of Dust

For reasons of confidentiality, the steelmakers were given the choice not to disclose the destination of dust and therefore this question was transformed into 'distance to which the dust is transported for treatment' in the questionnaire. Response to this question is presented in Fig. 4.5.



Figure 4.5: Destinations and use of EAF dust

It can be observed from Fig. 4.5 that for 59% of the dust only the distance of transportation is known. Therefore, in order to investigate if it is sent for recycling, road distances from the respective steelmakers to the seven dust recyclers were used for comparison with the distance disclosed in the questionnaire. It was found out that 13 out of 23 steel plants are not anywhere close to the dust recyclers. This means that 159,000 tons which is 31% of the production from 39 steel plants, is neither recycled nor is its use known.

4.5.2 Correlation between the Dust Generation Rate and the Zinc Content

The average dust generation rate (kg dust/tons of steel) and mass content in % of zinc in the dust is presented in Fig. 4.6. An average of ~16 kgs/tons of steel is a consistent figure with a standard deviation (S.D) of 4.21. On the other side, the percentage of zinc varies considerably with a standard deviation of 8.16. Additionally, it can be inferred from the low dust generation rate in comparison to high percentage zinc, that internal recycling of dust for enrichment is practiced at around 14 steelworks. It is to be mentioned that the dust generation rate is an average quantity and the % of zinc can vary from one heat to the other. In any case, the mentioned practice can be taken as a reasonable indication of internal recycling.



Figure 4.6: Rate of dust generation and zinc content of 40 EAF steelworks in the EU

4.6 Discussion

The results of the transportation model indicate that under the condition of economical transportation, the overall dust recycling capacity of 70% needs to be split among the north EU and the south EU. According to this split, the recycling capacity in the north EU is not a serious issue and the void in recycling is mostly influenced by economical factors and the competition from alternatives to recycling, like mine backfilling and the use in cement, etc. The steel industry in this region is widely scattered and the unusually large remoteness index for Recytech and B.U.S. Zinkrecycling indicates excessive transportation, as the latter facility has the highest capacity of all (30%).

Italy and Spain, respectively, represent the 1st and 3rd major EAF steel producing countries in the EU. In contrast to the north EU, the recycling capacity of only 56% of the total dust generated in the south EU indicates a huge void in need of filling. In case the Portovesme facility is closed down permanently, this gap becomes even smaller, i.e. 40%.

Problems related to an uneven distribution of dust recycling capacity are evident from the discussion so far. Formerly, there were eight recyclers serving the needs of dust recycling. Due to rising energy prices, this number has dropped down to six at present. It would not be reasonable to expect that more sites would be erected in the future to handle the rising amount of dust. At present, internal recycling of dust by injecting it back to the EAF is done as a means of dust minimization and raising the zinc content at many steelworks. This step is done repeatedly until the zinc content reaches about 30%. This benefit comes at the cost of lower thermodynamic efficiency of the steelmaking process and intensive ladle metallurgy in order to separate the higher amount of zinc from the melt. The same objective can be achieved by thermal scrap de-zincing leading to the elimination of metallurgical problems. As this process is performed before scrap melting, much higher zinc content in the dust can be expected due to the absence of ferrous content which is usually 40%. Other substantial benefits of scrap de-zincing would be shared by the steel industry and dust recyclers. There would be less dust to be recycled, existing recycling capacity would suffice and due to higher zinc content in the dust, a better economical efficiency of the recycling process can be

expected. In order to develop a process that can achieve this goal, it is important to further the existing knowledge of the underlying science and the parameters that can be controlled in an industrial application. The details of de-zincing experiments conducted to this end will be presented in the next chapters.

5. SCRAP DE-ZINCING EXPERIMENTS

The existing installations of scrap de-zincing usually treat only the process scrap which is not pained and is mostly free of oil. It is clear from the literature survey that the current state of research on thermal de-zincing is not comprehensive. The research done by Ozturk & Fruehan (1996) and Franzen & Pluschkell (2001) provides basic information on the evaporation kinetics of zinc from small scrap samples. While this information is vital as a starting point, the kinetics and transportation of zinc vapour from scrap with respect to industrial situations where scrap is of mixed grades and in different densities still needs to be studied. To this effect, an apparatus capable of thermal de-zincing and accurate measurement of the zinc evaporation rate was developed. Scrap samples of different shapes were prepared by electro-galvanising and experiments were performed in order to investigate various process parameters important for industrial application. Subsequently, several confirmatory tests were performed to validate the experimental results. The details of these steps are presented in the following sections.

5.1 De-zincing Apparatus

The apparatus is based on the principal of thermogravimetry (TG). The scrap sample is placed in a crucible that rests on a platform (Fig. 5.1). For the measurement of mass, this platform is placed on a microbalance (Mettler Toledo XP6002S). As the experiments were to be performed in a controlled atmosphere, the crucible and the balance are enclosed in an air-tight box. The quartz cylinder is put in place after loading the sample and is sealed with vacuum grease at the bottom. The carrier gas is introduced through the hole at the bottom of the crucible and its flow is controlled with a regulator, Bronkhorst FLOW-BUS F-201AC-RBA-33-P.



Figure 5.1: De-zincing apparatus

An induction coil surrounds the part of the quartz cylinder in which the crucible is placed. After passing through the sample, the carrier gas is let out through a U-shaped pipe that terminates in a water filter. In order to maintain the gas flow, a level of 1 mm Hg below atmospheric pressure is maintained in the system with the help of an exhaust pump in the filter. The top end of the quartz cylinder houses an enclosure filled with water and therefore the vibrations coming from the exhaust system are damped and an airtight coupling is ensured. The apparatus incorporates two thermocouples; thermocouple TC1 measures the temperature of the carrier gas at the exit of the crucible. A computer program written in LabView is used to acquire the reading of temperature, pressure and mass. This program is interfaced with the induction generator through a PID controller (Fig. 5.2) and controls the heating rate of the sample in a feedback loop by taking input of the temperature from the thermocouple TC1 housed in the crucible (Fig. 5.1).



Figure 5.2: Control loop of the experimental setup

During the trial runs of the apparatus, it turned out that the electromagnetic force of the induction coil renders it impossible to record the mass accurately; the reason being that the coil acts as a solenoid and the scrap placed in the crucible acts as the core of an electromagnet (Fig. 5.3).



Figure 5.3: Magnetic forces acting on the crucible

In order to overcome this difficulty, the heating cycles were designed in such a way that the induction power is turned off for 10 seconds and during this time the mass is measured, and for the next 20 seconds induction is turned on, and so forth.

5.1.1 Temperature Correction

A typical heating cycle, where the sample in the crucible is subjected to a constant heating rate of 100°C/min, can be seen in Fig. 5.4. In this figure the temperature of the scrap sample (T'_s) and the gas temperature at the crucible exit (Tg_o) are plotted against time.



Figure 5.4: A typical scrap sample heating cycle

The sample is heated from room temperature up to 900°C and then the temperature is held constant until the end of the experiment.



Figure 5.5: Conservation of energy on the elementary sample in the crucible

Applying the conservation of energy at the elementary sample in the crucible (Fig. 5.5) at time t:

$$\dot{\mathsf{E}} - (\mathsf{q''}_{conv} + \mathsf{q''}_{rad}) \cdot \mathsf{A}_{s} = \mathsf{m} \cdot \mathsf{Cp} \cdot \frac{\mathsf{dT'}_{s}}{\mathsf{dt}}$$
(5.1)

In Eq. 5.1, \dot{E} is the heat generation rate in the scrap sample through induction, q_{conv}^{*} is the flux of heat carried by the carrier gas through convection and q_{rad}^{*} is the heat flux transferred to the surroundings through radiation. A_s, m and Cp are the surface area, mass and specific heat of the sample, respectively. As the PID controller is programmed to hold the temperature in the crucible constant after the sample has attained 900°C, according to Eq. 5.1, T's and T_{go} should be constant at this state. However, as can be seen in Fig. 5.4, this is not the case as T_{go} achieves a steady state in time t_o after T's registers ~ 900°C.

In order to understand the reason why there is a time gap in the steady state of the two thermocouples, let us consider their physical positions. The thermocouple TC1 installed in the crucible (Fig. 5.6) is protected against the aggressive atmosphere of zinc vapours by inserting it in a thin ceramic tube. As the thermocouple TC2 is bare, its response time should be shorter than the response time of the thermocouple TC1 and not vice versa, the reason being that the heat transfer to TC1 faces resistance from the ceramic tube and there is a finite time delay before the thermal equilibrium between the thermocouple and the sample can be established. This implies that during the heating up stage, TC1 registers a biased temperature which is lower than the actual temperature of the scrap. Furthermore, when it shows T's ~ 900°C just at the beginning of the constant temperature stage, the actual temperature is higher than 900°C and during time t_0 eventually comes down to 900°C.



Figure 5.6: Position of the thermocouples TC1 and TC2 relative to the crucible

In control and automation it is not uncommon to encounter situations where the response of a thermocouple needs to be corrected. This can be achieved if the time constant of the system can be estimated. In a system incorporating two thermocouples, the response time of a slower thermocouple can be estimated from the temperature history of the system (Lawton & Klingenberg, 1996). In Fig. 5.4, the gas temperature Tg_o is rising in an approximately linear fashion during the heating-up stage. Therefore, it is reasonable to expect that T's is also rising linearly as both TC and TC2 are in thermal exchange with the scrap sample. An implication of this similarity is that the response of TC1 can be rectified using the model of a first order system subjected to a step change. The corrected response of TC1 can therefore be written in a linear way as:

$$T_{s} = T'_{s} + t_{o} \cdot \frac{dT'_{s}}{dt}$$
(5.2)

Here T_s is the corrected temperature of the sample and $\frac{dT'_s}{dt}$ is the rate of change of T_s as registered by TC1. The corrected response from the Eq. 5.2 can be expected to be noisy and therefore needs to be smoothed. A commercial software GraphPad Prism was used for this purpose and by applying LOESS technique of curve smoothing, the rectified response of TC1 is presented in Fig. 5.7



Figure 5.7: Corrected response of thermocouple TC1

5.2 Experimental Plan

The experimental plan was designed to study the zinc evaporation from scrap samples by including the necessary parameters omitted in the previous studies. For a possible scale-up it is important that the size of the scrap sample is representative enough in the experiments, so that not only the evaporation but the transport kinetics of zinc vapour through the packed bed can be studied as well. Another consideration in this regard was to simulate a possible industrial application, e.g. different heating rates of the scrap. Owing to these considerations, the following parameters were included in the experimental plan:

- Flow rate of the carrier gas
- Transient effects related to different scrap heating rates
- Effect of scrap density / packing
- Effect of scrap geometry

Particular care was taken in the experimental design that during the study of one parameter the rest of the parameters were kept constant. Therefore, it was important to first determine the minimum gas flow rate required in order to aid evaporation by keeping the zinc concentration in the system at a minimum.

After the selection of the suitable flow rate, different scrap heating rates were investigated to see the influence on evaporation. The scrap for steelmaking comes in different grades and densities. This is an important factor influencing the transport of zinc vapour. Its influence has not been checked in the previous studies as outlined in the literature survey. Therefore, it was decided to include this parameter in the experimental plan and additionally the scrap geometry, i.e. the shape of scrap, was included in the experimental plan.

5.3 Materials used in the Experiments

5.3.1 Scrap Samples

The scrap samples were selected in line with the experimental plan and spring washers were chosen for the lower density. For higher density the same washers were cut into 4 pieces with the hand-operated mechanical shearer, hence after called 'quarter washers'. Additionally, nuts and rivets were selected to diversify the scrap geometries and packing characteristics (Table 5.1).

Scrap sample type		Average Zn (% of sample mass)
Spring washers DIN 127-B, M14	C S	0.62
Quarter washers DIN 127-B, M14	3	0.62
Nuts M10	Contraction of the second seco	0.58
Rivets DIN 661, 5x16 mm		0.35

Table 5.1: Scrap samples used in the experiments

These samples were electro-galvanized and their zinc content was determined by chemical dissolution and subsequent ICP Mass Spectrometry (ICP-MS) technique. The zinc content for each sample type discovered by this analysis is presented in Fig. 5.8.



a. Spring washers, quarter washers





Figure 5.8: Zinc content (% by mass) of the scrap samples

5.3.1.1 Packing Characteristics

The crucible filled with scrap sample can be thought of as a packed bed which is usually characterised by two parameters, i.e. particle size and voidage. In addition to these parameters, the specific surface area of the sample is needed in order to calculate the heat and mass transfer coefficients. These parameters are calculated from the definitions in the following sections.

5.3.1.2 Particle Size

Particle size is an important parameter in describing fluid flow and correlating heat and mass transfer coefficients through a packed bed. The dimensionless numbers used in these correlations are based on the characteristic length that depends on the model chosen to describe the hydrodynamics of the bed. In the case of the capillary model, the fluid is thought to flow through numerous capillaries formed by the empty spaces between the particles and the hydraulic diameter is used as the characteristic length. On the other hand, in the particle model, the fluid is thought of flowing around the particles and the characteristic length is taken as the diameter of the particles. For spherical particles, it is usually taken as the diameter of the spheres. In the case of non-spherical particles, a modified characteristic length is used which is the diameter of a sphere whose volume is equal to that of the non-spherical particle (Ziółkowska & Ziółkowski, 2007). Therefore, according to this definition:

Equivalent diameter,
$$d_{eq} = \sqrt[1/3]{\frac{6 \cdot V_p}{\pi}}$$
 (5.3)

where V_p = volume of the particle

The use of this simplified approach can lead to inconsistent results as the packings having the same equivalent particle diameter but different shapes can have different permeabilities (Teng & Zhao, 2000). Therefore, the validity of application of equivalent diameter becomes questionable as the particles depart from the spherical shape. In order to overcome this difficulty, Levenspiel (1986) suggests a correction with sphericity, i.e.:

$$\mathbf{d}^{*}_{eq} = \boldsymbol{\phi} \cdot \mathbf{d}_{eq} \tag{5.4}$$

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where ϕ = sphericity, defined as the ratio of the surface area of the sphere to the non-spherical particle of equal volume, i.e.

$$\phi = \left(\frac{\text{surface of sphere}}{\text{surface of particle}}\right)_{\text{same volume}} \le 1$$
(5.5)

5.3.1.3 Packed Bed Voidage

Bed voidage is defined as the ratio of the empty space to the total volume of the bed. According to this definition, if a bed is composed of (n) number of particles each having a volume (V_p) filling a container of volume (V_b), then the voidage (ϵ) is given as:

$$\varepsilon = \frac{V_{\rm b} - n \cdot V_{\rm p}}{V_{\rm b}} \tag{5.6}$$

If the shape of particles strongly deviates from that of a sphere, significant differences in bed voidage can be observed in different beds packed with the same particles. The reason is that the spheres by virtue of their symmetry in three dimensions are hardly able to influence the structure of the bed. On the other hand, non-spherical particles can orientate themselves at different angles relative to the axis of the bed leading to different values of permeability. These differences can be observed in packed beds of different particle shapes, which nevertheless have the same voidage (Nemec & Levec, 2005).

5.3.1.4 Geometric Specific Surface Area

The rates of heat transfer and mass transfer in a packed bed are strongly influenced by the surface area of the particles exposed to the fluid flow. A quantitative measure for comparison between beds of different particles is the geometric specific surface area. It represents the interfacial area per unit volume of the pores exposed to the fluid flow (Miller & Clesceri, 2002) given as:

$$a_{v} = \frac{A_{p}}{(1-\varepsilon)}$$
(5.7)

where A_p is the surface area per unit volume of an elementary particle. The packing characteristics of the samples used in the de-zincing experiments calculated from these definitions are presented in Table 5.2.

Table 5.2. Facking charact	Table 5.2. Facking characteristics of scrap samples					
Packing	d _{eq} (mm)	Φ	d* _{eq} (mm)	3	a _v (m⁻¹)	
Spring washers	10.54	0.58	6.11	0.74	4700.10	
Nuts	13.98	0.58	8.11	0.65	2043.84	
Rivets	8.95	0.62	5.55	0.52	2002.80	
Quarter washers	6.64	0.67	4.45	0.52	3849.47	

Table 5.2: Packing characteristics of scrap samples

5.3.2 Carrier Gas

The experiments were conducted using high purity nitrogen gas with the following specifications:

N ₂	=	99.999 %
H ₂ O	≤	3 ppm
O ₂	≤	3 ppm
H ₂	≤	2 ppm
C_nH_m	≤	1 ppm

5.4 Chemical Analysis of Scrap Samples after the Experiments

The samples were analysed for the amount of remaining zinc after the experiments by ICP-MS.

5.5 Pressure Drop and Permeability Measurement

The structure of the packed bed is very influential in determining the hydrodynamics of fluid flow and ultimately heat and mass transport. To this end, an apparatus was developed to measure the pressure drop and permeability of the scrap samples in the form of a packed bed (Fig. 5.9). The column is filled with the scrap sample and compressed air at regulated flow rate is introduced at the bottom. The pressure drop through the packed column is measured at different positions with taps attached to an electronic differential pressure sensor.



Figure 5.9: Apparatus for measuring pressure drop

5.6 PIV Measurements of Flow Distribution through Scrap Samples

The variation in geometry and packing density of samples leads to different flow patterns of the carrier gas and the number of 'dead-pockets' eventually determines the flow distribution across the packed bed cross section. Particle Image Velocimetry (PIV) measurements were performed in order to see the flow distribution and the velocity profile of gas through the crucible packed with different samples. The testing arrangement is presented in Fig. 5.10.



Figure 5.10: Experimental determination of fluid velocity through scrap samples using PIV technique

5.7 Theoretical Background and Calculation Procedure

The analysis of zinc evaporation through a packed bed of scrap sample needs a consideration of various parameters influencing the process of mass transfer. Before embarking on this task, important mechanisms of mass transport will be discussed in order to form a conceptual base for further discussion.

5.7.1 Mechanisms of Mass Transfer

Mass transfer is the transport of a pure substance or the components of a mixture within a phase or across the phase boundary. Transport within a phase is simply called "mass transport" and when it occurs across the phase boundary, it is termed as "overall mass transfer". There are two basic mechanisms of this transfer, i.e. diffusion and convection.

5.7.1.1 Mass Transfer by Diffusion

Mass transport by diffusion takes place due to a difference in concentration, temperature and pressure. However, at the macroscopic level the mass transfer is usually induced by concentration difference only, i.e. movement of species from regions of abundance to the regions of scarcity. According to Fick's law, in the transfer of substances in a binary mixture of A and B, the diffusional flux of component A along a coordinate axis, e.g. the y-axis is proportional to the concentration gradient $(\frac{dC_A}{dy})$, i.e. :

$$J_{A} = -D_{AB} \cdot \frac{dC_{A}}{dy}$$
(5.8)

Eq. 5.8 is a general form of Fick's law of diffusion when the mixture composition C = $C_A + C_B$ is constant. Here J_A is the diffusional flux of component A, the proportionality factor D_{AB} is the binary diffusion coefficient. For gas mixtures it can

be considered to be independent of the concentration at pressures around 1 atm. (Bennett & Myers, 1974). If an ideal gas behaviour is assumed, by kinetic theory it can be found that (Incropera & Witt 1996):

$$D_{AB} \sim p^{-1} \cdot T^{\frac{3}{2}}$$
 (5.9)

where p is the pressure and T is the absolute temperature of the mixture. A considerable number of relations based on this theory are available in literature (Fuller et al., 1966), (Wilke & Lee, 1955), (Chapman & Cowling, 1977), (Hirschfelder et al., 1964). Although these relations are derived from monoatomic and non-polar gases, they can be useful for the case of polyatomic non-polar gases as well with an accuracy of about 5% (Bird et al., 2002).

For the present study, experimentally determined binary diffusion coefficients of zinc and nitrogen reported by Gardner et al. (1991) are used. Gardner et al. used the relation by Chapman & Cowling (1977) and fitted experimental results to derive the temperature dependence of these diffusion coefficients at 1 atm. pressure in the temperature range of 690-1140 °K. The relation is of the form:

$$\mathsf{D}_{\mathsf{Zn}-\mathsf{N2}} = \mathsf{D}_{\mathsf{O}} \cdot (\frac{\mathsf{T}}{\mathsf{T}_{\mathsf{O}}})^{\mathsf{c}}$$
(5.10)

where $D_o = (1.879\pm0.090) \times 10^{-5} \frac{m^2}{s}$ is the diffusion coefficient at the reference temperature T_o (273.15 K), T is the absolute temperature of the mixture, and c = 1.673±0.038 is the constant fitted by linear regression.

5.7.1.2 Mass Transfer by Convection

Unlike molecular diffusion, convective mass transport occurs due to the bulk movement of fluids. As in the case of heat transfer by convection, the mass transfer in convection occurs in a similar way by the bulk motion of the fluid and can be described by the following equation:

$$\mathbf{\dot{m}}_{i} = \frac{\mathrm{dm}_{i}}{\mathrm{dt}} = \mathbf{h}_{m} \cdot \mathbf{A} \cdot \Delta \mathbf{C}_{i}$$
(5.11)

Here m_i is the mass transfer rate of a single component i in a mixture, h_m is the mass transfer coefficient, A is the reaction area and ΔC_i is the driving force for the mass transfer due to the concentration difference across the phase boundary given as:

$$\Delta \mathbf{C}_{i} = \mathbf{C}_{is} - \mathbf{C}_{i\infty} \tag{5.12}$$

 $C_{i\infty}$ is the concentration of the component i outside the boundary layer and can be assumed to be zero in the case of a moderate rate of mass transfer. C_{is} is the saturated concentration of the component i at the evaporating surface. In case of mass transfer by evaporation, it can be found as:

$$C_{i_{s}} = \frac{p \cdot M_{w}}{R \cdot T}$$
(5.13)

Here, M_w is the molecular weight of the evaporating component, p is its saturated vapour pressure at the system temperature T, and R is the universal gas constant. In calculating the zinc evaporation rate, the vapour pressure is taken from Li et al. (1995a) who used the data bank Therdas (1980):

$$\log(p_{Zn}) = -\frac{6660}{T} - 1.271 \cdot \log(T) + 9.567$$
(5.14)

The calculation of mass transfer coefficient requires reasonable information about the concentration gradient at the phase boundary. For simple geometries like sphere, plate and cylinder, etc. in laminar flow, exact solutions of Navier-Stokes differential equations are available. In situations involving turbulent flow, mass transfer problems can not be dealt with analytically (Bennett & Myers, 1974). However, using the analogies between thermal, momentum and concentration boundary layers, the analysis can be simplified. One such analogy is the *Heat and mass transport analogy*, based on the similarity of the energy and mass conservation equations. According to the definition of this analogy, for a particular geometry the heat and mass transfer relationships should be interchangeable. For

example, if heat transfer data is available, the relationships (Nu, Pr) can be interchanged by (Sh, Sc) to obtain information about the mass transfer. The analogy can be used directly to relate the heat and mass transfer coefficients. The requirement for the applicability of this analogy is that the dimensionless boundary conditions in the thermal and momentum boundary layers are similar (Fig. 5.11). Additionally, no form drag should be present and the magnitude of heat and mass transfer should not be as large as to affect the velocity boundary layer.



Figure 5.11: Development of momentum, thermal and concentration boundary layers over a flat plate

If these conditions are met, the derivation of an analogous relationship between the heat and mass transfer coefficients is fairly simple. This process involves the use of dimensionless numbers whose role in the simultaneous transport is presented in Table 5.3.

For a particular geometry and flow condition, the Nusselt number is a function of the Reynolds number and the Prandtl number, i.e.:

$$Nu = c \cdot Re^{n} \cdot Pr^{m}$$
(5.15)
Group	Functional form	Physical Significance
Reynolds number	$Re = \frac{V \cdot L}{v}$	Ratio of inertial forces to viscous forces
Prandtl number	$\Pr = \frac{v}{\alpha}$	Ratio of momentum and energy transport in the velocity boundary layer to thermal boundary layer
Schmidt number	$Sc = \frac{v}{D_{AB}}$	Ratio of momentum and mass transport in the velocity boundary layer to concentration boundary layer
Nusselt number	$Nu = \frac{h \cdot L}{k_f}$	Ratio between heat transfer by convection and conduction
Sherwood number	$Sh = \frac{h_m \cdot L}{D_{AB}}$	Ratio between mass transfer by convection and diffusion
Lewis number	$Le = \frac{Sc}{Pr} = \frac{\alpha}{D_{AB}}$	Ratio of thermal diffusivity to mass diffusivity in simultaneous heat and mass transfer by convection.

Table 5.3: Dimensionless numbers used in the analysis of heat and mass transfer

Similarly, the Sherwood number is a function of the Reynolds number and the Schmidt number, i.e:

$Sh = c \cdot Re^n \cdot Sc^m$ ((5.16)
	•	

where c is a constant depending on flow and geometry.

Dividing Eq 5.15 by Eq. 5.16

Nu _	_(Pr) ^r	n (5 17)
Sh _	$\left(\frac{1}{Sc}\right)$	(5.17)

From the definition of dimensionless numbers given in Table 5.3, substituting the values:

$$\frac{\mathbf{h} \cdot \mathbf{L}}{\mathbf{k}_{f}} \mathbf{x} \frac{\mathbf{D}_{AB}}{\mathbf{h}_{m} \cdot \mathbf{L}} = \left(\frac{\mathbf{v}}{\alpha} \mathbf{x} \frac{\mathbf{D}_{AB}}{\mathbf{v}}\right)^{m}$$
(5.18)

or

$$h_{m} = \frac{h}{Cp \cdot \rho} Le^{m-1}$$
(5.19)

For an ideal gas mixture, the exponent m is usually taken $\approx \frac{1}{3}$ (Baehr & Stephan 1998), (Incropera & Witt 1996).

5.7.2 Heat and Mass Transport through a Packed Bed

The analysis of mass transport through a packed bed is complicated due to several factors, such as packing characteristics of the bed, porosity distribution, non-uniform velocity distribution due to the flow channelling effect, the extent of stagnation zones, etc. Therefore, it becomes necessary to resort to empirical correlations or to conduct experiments on heat transfer. The heat transfer coefficient thus obtained can be used to calculate the mass transfer coefficient, subject to the fulfilment of the aforementioned conditions. Nevertheless, discrepancies in the experimentally observed and calculated mass transfer rate can be expected due to the above mentioned factors.

5.7.2.1 Heat and Mass Transfer Coefficients

Consider a bed of particles at temperature T_s packed in a cylindrical vessel in Fig. 5.12. In a steady state condition, the fluid having specific heat capacity Cp enters the vessel at temperature (Tg_i) and leaves at a higher temperature (Tg_o).

The heat transferred Q, to the fluid flowing at a mass flow rate of m is:

$$\mathbf{Q} = \mathbf{m} \cdot \mathbf{C} \mathbf{p} \cdot (\mathbf{T} \mathbf{g}_{o} - \mathbf{T} \mathbf{g}_{i})$$
(5.20)

If it is assumed that the walls of the vessel are isothermal and the heat generated by the bed is carried by the fluid only, then on the bed side, the heat transferred is given by:

$$Q = h \cdot A_{pt} \cdot \Delta T_{lm}$$

$$Tg_{o} > Tg_{i} \qquad Tg_{o}$$

$$Tg_{o} \sim Tg_{i} \qquad Tg_{o} \qquad Tg_{o}$$

$$Tg_{o} \sim Tg_{o} \qquad Tg_{o} \qquad Tg_{o}$$

Figure 5.12: Heat transfer to the fluid flowing through a packed bed

where A_{pt} is the surface area of the particles, h is the heat transfer coefficient and ΔT_{im} is the log-mean temperature difference between the bed and the fluid as it travels through the entire length of the bed given by:

$$\Delta T_{Im} = \frac{Tg_o - Tg_i}{In\left(\frac{T_s - Tg_i}{T_s - Tg_o}\right)}$$
(5.22)

from Eq. 5.20 and 5.21

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$$\mathbf{m} \cdot \mathbf{C} \mathbf{p} \cdot (\mathbf{T} \mathbf{g}_{o} - \mathbf{T} \mathbf{g}_{i}) = \mathbf{h} \cdot \mathbf{A}_{pt} \cdot \Delta \mathbf{T}_{lm}$$
(5.23)

or,

$$h = \frac{\mathbf{\dot{m}} \cdot \mathbf{Cp}}{\mathbf{A}_{pt}} \cdot \ln\left(\frac{\mathbf{T}_{s} - \mathbf{Tg}_{i}}{\mathbf{T}_{s} - \mathbf{Tg}_{o}}\right)$$
(5.24)

In using Eq. 5.24, the fluid properties should be evaluated at the fluid inlet temperature Tg_i . The mass transfer coefficient h_m can be calculated from Eq. 5.19 and 5.24.

5.8 Calculation of Experimental and Theoretical Zinc Evaporation Rates

The mass loss of galvanized samples was recorded by the balance. The data thus recorded was smoothed by the LOESS technique of regression analysis using commercial software GraphPad PRISM. Using the same software, the smoothed data was differentiated with respect to time in order to obtain the evaporation rate curves.

Theoretical evaporation rate curves were calculated using Equations 5.10 - 5.14, 5.19, and 5.24.

5.9 Results and Discussion

5.9.1 Effect of the Carrier Gas Flow Rate

These experiments were performed to observe the zinc evaporation at different flow rates / velocities of the carrier gas under the test conditions presented in Table 5.4.

Cable 5.4: Experimental conditions in variation of the gas flow rate					
Scrap sample	Heating cycle	Gas flow rate		Mass of sample	
		(l/r	nin)	(g)	
Spring washers	Surface temperature T_s raised from room	a.	10	903-903.7	
	temp. to 900°C using a heating rate of	b.	20		
	100°C / min; thereafter holding at 900°C for	C.	30		
	10 minutes	d.	40		

The observed mass loss of the samples at different flow rates of nitrogen is plotted against time in Fig. 5.13.



Time (s)

Figure 5.13: Loss in mass of spring washers recorded at different flow rates of the carrier gas

For these experiments the heat transfer and the theoretical mass transfer coefficients of zinc according to Eq. 5.24 and Eq. 5.19 at steady-state conditions of $T_s = 900^{\circ}$ C are presented in Table 5.5.

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Gas flow rate (I/min)	A _{pt} (m²)	Tg _i (°C)	Tg₀ (°C)	h (<u>₩</u>) m² · °k	h _m (m/s)	
10	0.0958	21.8	331.3	0.888	0.0017	
20	0.0958	24.0	402.7	2.329	0.0045	
30	0.0958	31.4	482.6	4.416	0.0087	
40	0.0958	28.6	568.5	7.908	0.0179	

Table 5.5: Heat and mass transfer coefficients for different flow rates of nitrogen at steadystate surface temperature of scrap ($T_s = 900^{\circ}C$)

The theoretical zinc evaporation curves were calculated using h_m and are presented in Fig. 5.14 to Fig. 5.17 together with the observed evaporation rate for different gas flow rates.



Figure 5.14: Rate of zinc evaporation from spring washers heated at 100°C/min. in nitrogen at a flow rate of 10 l/min



Figure 5.15: Rate of zinc evaporation from spring washers heated at 100°C/min. in nitrogen at a flow rate of 20 l/min



Figure 5.16: Rate of zinc evaporation from spring washers heated at 100°C/min. in nitrogen at a flow rate of 30 l/min



Figure 5.17: Rate of zinc evaporation from spring washers heated at 100°C/min. in nitrogen at a flow rate of 40 l/min

In these experiments an initial burst of fog was observed in the crucible as the induction power was turned on. Together with that, at some points in the crucible where the pieces of scrap sample were intensively coupled to the induction, glowing hot-spots could also be noted. In addition to these observations, a sharp peak in the evaporation rate at the start of the experiments can be seen in Fig. 5.14 to Fig. 5.17. Owing to this fact, it can be assumed that the zinc coating from these hot-spots evaporates quickly, and the bare surface of the samples reacts with the trapped oxygen in the system, due to which an increase in mass was recorded after the first 60-70 seconds. The sharp peak in T_s is due to the time constant of TC1 and as these figures show, after a certain time, this peak is damped as the real time approaches the characteristic time of TC1.

The melting point of zinc is ~ 420°C. During the experiments it was observed that the zinc layer is separated from the samples at 500-600°C and recedes into the recesses in the packed bed. A similar effect was observed by Savov and Janke (2001) during the de-tinning and de-zincing experiments. Due to this phenomenon, the heat and mass transfer rates do not follow the same trend beyond 500-600°C as the available area for both transport mechanisms is different. In the absence of the coating melt-down, the evaporation rate should follow the theoretical

evaporation curve at an ascending rate as the sample temperature increases. On the contrary, the observed trend is that it follows a Gaussian-type curve. An important observation can be made from Fig. 5.13 that with the exception of 10 l/min, the evaporated fraction of zinc is almost the same at flow rates of 20, 30 and 40 l/min. The chemical analysis of samples (Fig. 5.18) conducted after the experiments to check the zinc fraction left over is in accordance with these results.



Figure 5.18: Amount of zinc left-over on spring washers after experiments on variation of carrier gas flow

The theoretical mass transfer coefficients for gas flow rates of 20, 30 and 40 l/min (Table 5.5) are different from each other, therefore in the ideal case the amount of zinc evaporated in a given time should be higher with the higher gas flow rate. In a situation where the evaporating component is receding away from the carrier fluid, the rate of evaporation is controlled by the increasing thickness of the concentration boundary layer. Park et al. (1989) describe a model for a similar situation where the mass transfer takes place between a stagnant region and the main contacting flow. According to their findings, the material trapped in the cavity is mixed by the rotation of an eddy and the driving force for the mass transfer from the cavity to the main flow is not the diffusivity of the matter, but the rotational speed of the eddy. They quantified the rate of mass transfer in this situation as:

$$Sh = 2.29 \times 10^{-5} \cdot Re^{2.18} \cdot Sc^{1.03} \cdot Ar^{0.186}$$
(5.25)

Here, Ar is the aspect ratio of the cavity, i.e. the cavity depth divided by the cavity width, and was varied in their experiments from 1 to 4. The variation of the

Reynolds number in their experiments was 25 to 100 and that of the Schmidt number from 100 to 10000. As these results are related to the mass transfer in a single phase and between liquids, it is not easy to infer some similarity with our conditions where two phases, liquid (zinc) and gas (zinc vapour and nitrogen), are present. Additionally, the Schmidt number in our experimental conditions is of the order of 1.

Ho & Udell (1991) and Ho & Udell (1992) developed a conceptual model for the removal of contaminants held in homogeneous and heterogeneous porous media. According to their model, during convective venting of contaminants trapped in a low permeability zone with a high permeability zone above, a concentration boundary layer develops at the interface of the two layers (Fig. 5.19). The thickness of the boundary layer in the high permeability zone is $\delta(x)$. The distance between the interface and the liquid $\delta(t)$ increases in time t, as the evaporation proceeds and the liquid recedes further into the low permeability zone. This is a period of quasi-steady-state evaporation ultimately leading to a gradual decay in the evaporation as the diffusion length increases.



Figure 5.19: Schematic of a concentration boundary layer and a stagnant diffusion layer development during the vaporization of liquid trapped in a low permeability zone.

Looking at the Figures 5.14 - 5.17, three distinct periods in the evaporation rate can be observed. During the first period, the rate of evaporation increases with a rise in temperature of the scrap. After it attains a maximum value, it starts decreasing although the temperature is still rising. It can also be observed that

with the increase in the gas flow rate, the maximum evaporation rate is higher and is attained in shorter time (Table 5.6).

Table 5.6: Maximum zinc evaporation rate at different flow rates of the carrier gas						
Gas flow rate	dm (max)	t				
(I/min)	(g/s)	(s)				
10	0.019	394.8				
20	0.020	310.3				
30	0.023	265.3				
40	0.023	245.0				

Due to the similarity with the model of Ho & Uddel (1991, 1992), the evaporation during this period can be considered to be controlled by the convective mass transport. After this, the second period marked by rapid decrease in evaporation rate starts, which is still partially controlled by convective transport. In the third period, when most of the zinc exposed to the main gas flow has evaporated, the diffusion length in the boundary layer and the zinc trapped in the recesses is perhaps the limiting factor (Fig. 5.20).





The conjecture of increasing diffusion length in the packed bed consisting spring washers / rings is further supported by the findings of Carman (1937) and Sonntag (1960) cited in Nemec & Levec (2005). Sonntag (1960) derived the correction of Ergun constants for a possible dead space within a ring shaped particle. His results suggested that only about 20% of the interior of the ring was available for the gas flow. That means, the zinc trapped in the recesses experiences very limited flow of the carrier gas and from these regions, the evaporation is mostly limited by the diffusion length. The unusually high amount of left-over zinc in the case of 10 l/min can be attributed to the insignificant flow of the carrier gas whose reach to the zinc trapped in the recesses is limited by the narrow annulus passages presented by the spring washers.

5.9.2 Transient Effects Related to Different Scrap Heating Rates

Another set of experiments was conducted to simulate the transient conditions of the de-zincing operation using different heating rates of scrap samples. The conditions in these experiments are presented in Table 5.7. From experiments on the flow rate variation it was clear that even 20 l/min of nitrogen flow gave satisfactory results. Therefore, these experiments were conducted at 20 l/min of nitrogen and the observed evaporation rates are presented in Fig. 5.21 and Fig. 5.22. The heating rate of 100°C/min is already covered in the previous set of experiments (Fig. 5.15).

Scrap sample	Heating cycle	Gas flow rate	Mass of sample	
		(l/min)	(g)	
Spring	Surface temperature T_{s} raised from room temp.	20	903-903.7	
washers	to 900°C using heating rates of:			
	a. 50°C/min			
	b. 70°C/min			
	c. 100°C/min			
	thereafter holding at 900°C for 10 minutes			

Table 5.7: Experimental conditions in variation of scrap heating rate



Figure 5.21: Rate of zinc evaporation from spring washers heated at 50°C/min. in nitrogen at a flow rate of 20 I/min



Figure 5.22: Rate of zinc evaporation from spring washers heated at 70°C/min. in nitrogen at a flow rate of 20 l/min

As these experiments were conducted at different heating rates of the samples, the amount of zinc evaporated in a given time is different. In order to compare the results in a meaningful way, the average evaporation rate (g/s) until the samples attained the temperature $T_s = 900^{\circ}$ C is plotted in Fig. 5.23.



Figure 5.23: Average zinc evaporation from spring washers heated at different rates

From Fig. 5.23 it is difficult to detect any significant transient effects due to differing heating rates of the scrap samples. With the exception of heating rate, all the other conditions in these experiments were identical. In the absence of transient heating effects, the variation of heat transfer coefficients and mass transfer coefficients should not be significant. Additionally, the amount of zinc evaporated until a given temperature is reached should be directly proportional to the time of evaporation; which seems to be the case in Fig. 5.23. This inference is further supported by the results of Nield & Bejan (1992) who studied transient forced convection near a suddenly heated plate in a porous medium. They report on two cases of heat transfer: The wall with suddenly imposed uniform temperature and the wall with suddenly imposed uniform heat flux. According to their findings, the flow remains steady as the embedded plate is suddenly heated or cooled to a different temperature. The chemical analysis of the samples after the experiments (Fig. 5.24) provides further evidence that the transient effects are indeed very small.



Figure 5.24: Amount of zinc left-over on spring washers heated at different rates

5.9.3 Effect of Particle Shape and Bed Voidage

Further experiments were conducted to study the effect of scrap geometry and packing characteristics on zinc evaporation using rivets, nuts and quarter washers. The experimental conditions are described in Table 5.8.

Scrap sample	Gas flow rate	Mass of sample	Heating cycle
	(l/min)	(g)	
Rivets	20	652.2-653.0	Surface temperature Ts raised from room
Nuts	20	931.9-932.7	temp. to 900°C at 100°C/min and holding
Quarter washers	20	903.0-903.7	thereafter for ~10 minutes

 Table 5.8: Experimental conditions in variation of scrap geometry and packing

As these samples contained different amounts of zinc coating, the evaporation curves are calculated in percentage of the original mass of zinc contained (Fig. 5.25) in order to compare the results with those of the spring washers.



Figure 5.25: Mass loss recorded during the de-zincing of rivets, nuts, spring washers and quarter washers heated at 100°C/min. in nitrogen at a flow rate of 20 l/min

The bed voidage and the amount of left-over zinc on these samples are given in Table 5.9.

Sample	Bed voidage	Portion of zinc left after de-zincing
		(% of sample mass)
Rivets	0.48	0.001
Nuts	0.52	0.007
Spring washers	0.72	0.007
Quarter washers	0.52	0.041

 Table 5.9: Voidage of bed consisting in different samples and % of zinc left-over

It can be seen from Fig. 5.25 and Table 5.9, that despite different bed voidages and shapes of nuts, rivets and spring washers; the zinc evaporation curves are similar. Therefore, it is difficult to draw any conclusions about the influence of these parameters on the evaporation kinetics.

In contrast to the previous three sample geometries, the experiment conducted with quarter washers gave rather interesting results. As mentioned earlier in section 5.3.1, this sample was prepared by mechanical shearing of the spring washers and thus contained the same mass of zinc coating as the parent sample.

Furthermore, the experimental conditions during the de-zincing of this sample were also the same as in the case of spring washers. Despite these facts, the difference in the evaporation rate curves for the two samples from Fig. 5.26 and Fig. 5.15 can be easily detected.



Figure 5.26: Rate of zinc evaporation from quarter washers heated at 100°C/min. in nitrogen at a flow rate of 20 I/min

In the case of quarter washers, the maximum rate of evaporation as well as the amount of zinc evaporated in a given time is considerably lower than that of the spring washers. Additionally, it takes longer to complete the evaporation, as can be seen in the width of the evaporation curve. For a better comparison of the results, various parameters for the two samples are presented in Table 5.10.

Table 5.10: Comparison of zinc evaporation f	rom spring washers and quarter washers

		Scrap sample		
		Spring washers	Quarter washers	
Max. zinc evaporation rate; dm/dt _{max} (g/s)		0.020	0.017	
Observed at:				
T _s (°C)		820.33	829.64	
time	(s)	310.33	281.09	
Mass reduction of the sample (g)		6.03	5.53	
time span of compariso	1754.40	1754.01		
Amount of left over zinc (% of sample mass)		0.007	0.041	

As is clear from the results of other scrap geometries, it is difficult to correlate the evaporation kinetics to the bed voidage which varied from 0.48 to 0.72. For the quarter washers this value was 0.52, and the smaller amount of zinc which evaporated, compared to the other sample geometries, further suggests that some other factor is responsible for this fact. In order to explore the causes of this phenomenon, it was decided to see if the orientation of the scrap particles is responsible for this. As a first step, the samples were cast in epoxy in a container of a similar shape as the crucible used in the experiments. After solidification, the cast was taken out of the mould and cut in vertical section. The patterns of orientation of the different particles are presented in Fig 5.27.



a. Spring washers*



b. Nuts



c. Rivets



d. Quarter washers*

Figure 5.27: Vertical section of scrap samples cast in epoxy *(Mass of samples a. and d. in de-zincing experiments was the same. However volume occupied by sample d. in crucible during these experiments was smaller than shown here) In Fig. 5.27, numerous instances of particles overlapping can be detected in the case of quarter washers. The rivets have an approximately cylindrical shape and can not overlap each other as much. The spring washers, as the name says, are like single turn of a spring having a square cross section. Owing to this particular shape, the instances of overlapping can hardly be detected in Fig. 5.27 (a). The nuts are hexagonal in shape and can be approximated as cylindrical with a diameter length ratio of ~ 2 . Due to this particular shape, the probability of overlapping for the nuts is small.

The effect of overlapping is to reduce the dynamic surface area or the wetted area, which is the actual surface area of the particles the fluid comes in contact with. Except in the case of spheres, this area is always smaller than the geometrical surface area (Chhabra et al., 2001). Comiti & Renaud (1989) recognized that this effect is especially pronounced in the packed bed consisting plate like or parallelepipedal shaped particles having a square cross section. These particles have a low thickness-to-side ratio. The packing characteristics of such particles are anisotropy, stratification and overlapping. The rate of evaporation is directly proportional to the surface area. This means that in the case of quarter washers (having square cross section) at least one reason for less zinc evaporated can be a smaller surface area exposed to the carrier gas. The structure of a packed bed has a strong influence on the flow distribution and ultimately the heat and mass transfer processes; and the porosity is simply not enough to define these processes (Nemec & Levec, 2005). The structural parameters such as permeability, tortuosity and a dynamic specific surface area suggested by Comiti & Renaud (1989), have been successfully used by other researchers for modelling the fluid flow through anisotropic media, namely Brasquet & Le Cloirec (2000), Moreira & Coury (2004) and Lee & Bennington (2005).

Due to the success of using these parameters in flow modelling through diverse media types, it was decided to investigate their applicability in understanding the zinc evaporation kinetics through scrap samples used in our experiments. For this purpose, the experimental setup mentioned in section 5.5 was used in order to record the pressure drop through different samples. The pressure drop of the packed bed measured per unit length at various superficial velocities of air at room temperature is presented in Fig. 5.28.



Figure 5.28: Pressure drop through column packed with various scrap samples at different superficial velocities of air

Darcy's law has traditionally been used for modelling fluid flow through packed bed and porous media at low fluid velocities. Forchheimer (1901) included the quadratic term in order to account for the non-linearity of a pressure drop at higher fluid velocities and termed it kinetic energy losses. According to his expression, the pressure drop through porous medium is given as:

$$-\frac{dp}{dx} = \frac{\mu}{K} \cdot U + \psi \cdot \rho \cdot U^2$$
(5.26)

where $\frac{dp}{dx}$ is the pressure drop per unit length of the bed, U is the seepage velocity defined as the velocity of the fluid through the empty column, μ and ρ are fluid viscosity and density, respectively, K is the permeability of the porous medium, and ψ is termed as Forchheimer parameter having a dimension that is inverse of length. Over the years this equation has been modified and there are several versions available in literature. Nevertheless, in all of them the first term on

the right hand side of Eq. 5.26 represents viscous losses and the second term describes kinetic losses. The pressure drop model proposed by Comiti & Renaud (1989) has a similar form:

$$-\frac{dp}{dx} = N \cdot V + M \cdot V^2$$
(5.27)

Here, N and M are the coefficients of the viscous and kinetic losses, respectively. The structural parameters, such as dynamic specific surface area a_{vd} and tortuosity ζ as defined by Comiti & Renaud (1989), are related to these coefficients as:

$$a_{vd} = \left[\frac{N^{3}}{M^{2}} \cdot \frac{(0.0968 \cdot \rho)^{2}}{(2 \cdot \gamma \cdot \mu)^{3}} \cdot \frac{\epsilon^{3}}{(1 - \epsilon)^{4}}\right]^{\frac{1}{4}}$$
(5.28)

$$\xi = \left[\frac{\mathsf{M}^2}{\mathsf{N}} \cdot \frac{2 \cdot \gamma \cdot \mu \cdot \varepsilon^3}{(0.0968 \cdot \rho)^2}\right]^{\frac{1}{4}}$$
(5.29)

Here ε is the voidage / porosity and γ is the pore shape factor. As these equations are related to the capillary model of the packed bed, the pores are assumed to be cylindrical in shape and γ is usually taken as 1.

Using Eq. 5.27, the values of parameters N and M were calculated by the least square technique from Fig. 5.28. In a further step, the structure parameters for the scrap samples calculated using Eq. 5.28 and Eq. 5.29 are presented in Table 5.11.

Table 5.11: Structure parameters of packed bed consisting scrap samples

Scrap sample	N	М	K	R^2	3	a _{vd}	av	ξ
			(m²)			(m⁻¹)	(m⁻¹)	
Spring washers	47.66	406.44	3.84x10 ⁻⁷	0.99	0.75	2076.31	4808.53	1.43
Nuts	97.81	808.69	1.87x10 ⁻⁷	0.99	0.51	962.57	1472.31	1.26
Rivets	216.70	1466.50	8.44x10 ⁻⁸	0.99	0.47	1130.68	1804.00	1.31
Quarter washers	461.57	4630.10	4.01x10 ⁻⁸	1.00	0.58	1630.82	3243.41	2.28

It would be interesting to compare the wetted / dynamic specific surface area a_{vd} and the geometrical specific surface area a_v for the scrap samples in a graphical form (Fig. 5. 29).



Figure 5.29: Comparison of geometrical and wetted specific surface area of scrap samples

An important observation can be made from Fig. 5.29: in the case of the spring washers, the wetted specific surface area is about 43% of the geometrical surface area. This fact is similar to the observations of Carman (1937) and Sonntag (1960), according to which the total wetted surface area of ring-like particles is reduced due to the annulus passages. As the fluid passes through these passages, the internal wetted surface area is only 20% of the geometrical surface area of the spring washers did not have any significant effect on zinc evaporation in comparison to the nuts and rivets (Fig. 5.25).

In the case of the quarter washers the higher kinetic energy loss term M (Table 5.11) can be explained by the orientation of the particles with respect to the flow direction. According to the observations of Comiti & Renaud (1989), in tightly packed beds of plate-like particles the main orientation of the particles is perpendicular to the fluid flow and a jet-type flow occurs when the fluid meets the main face of the plates. Together with the less wetted surface area, another

phenomenon seems to be responsible for less zinc evaporation from this sample. The higher value of tortuosity and the least permeability compared to the other samples indicates that the flow distribution of the carrier gas through the quarter washers is non-uniform.

Tortuosity is defined as the ratio of the length of the actual path taken by the fluid to the length of the packed bed (Miller & Clesceri, 2002), i.e.:

$$\xi = \frac{L_p}{L} \tag{5.30}$$

where, L_p is the actual length of the path taken by the fluid to negotiate past the irregular pores that are sometimes twisting and sometimes closed; L is the actual length of the packed bed. Due to the layered structure of packed beds containing anisotropic particles, the path taken by the fluid through an equal length of the bed is longer than through the bed containing isotropic particles (Comiti & Renaud, 1989). Therefore, the highest tortuosity value of 2.28 for the bed containing quarter washers means that the assumption of a zero free stream concentration of zinc in the carrier gas may not be valid. Furthermore, it implies that a gradient of zinc concentration in the free gas stream exists across the height of the crucible leading to uneven evaporation.

Together with the higher value of tortuosity, the packed bed containing quarter washers has the least permeability due to compactness. The fluids have a natural tendency of taking the path of least resistance and in tightly packed beds there is a region closer to the wall where the porosity has a maximum value as the particles can not arrange themselves in a symmetrical fashion (White & Tien, 1987). Due to this reason, most of the fluid flows through this region and a sharp peak in the velocity is observed. This phenomenon is called flow channelling (Nield & Bejan, 1992) and is responsible for an uneven flow distribution in a packed bed. In the case of highly anisotropic media like parallelepipedal plates, Seguin et al. (1998) observed that the symmetrical structure of the media is broken close to the wall where many plates are oriented in a parallel direction to the wall. Owing to the observations of these researchers, it was therefore decided to verify the existence of variation in the radial porosity and permeability of scrap samples by Particle

Image Velocimetry (PIV). These experiments were conducted under the same conditions for different scrap sample outlined in Table 5.12.

Table 5.12: Experimental conditions in the PIV experiments				
Seeding material	Carrier medium	Flow rate; Q	Seepage velocity; U	
		(l/min)	(m/s)	
Oil	Air	40	0.14	
(particles size ~ 5 µm)				

....

For the ease of comparison between different scrap samples, the velocity of the carrier gas U_r recorded at different radial positions at the top of the crucible (Fig. 5.30) was normalised according to the following:



Figure 5.30: Measurement of fluid velocity U_r at different radial positions

The normalised velocity profiles calculated according to Eq. 5.31 for different scrap samples are plotted in Fig. 5.31 to Fig. 5.34. In these figures the abscissa is the normalized radial position taken as:

Normalised radial position =
$$\frac{\text{Radial position of U}_{r}}{\text{Radius of the crucible}} = \frac{\vec{r}}{\frac{\oplus}{R}}$$
 (5.32)



Figure 5.31: Normalised velocity profile at the top of the crucible filled with spring washers

Fig 5.31 supports earlier observation made through pressure drop experiments that in the case of spring washers the wetted area is indeed less than the geometrical surface area (Fig. 5.29). Several sharp peaks in the velocity mean that the air flow through this sample is divided into several channels formed due to the particular ring type shape of the spring washers. The narrow width of these peaks is due to the less wetted internal surface area, as observed by Carman (1937) and Sonntag (1960).



Figure 5.32: Normalised velocity profile at the top of the crucible filled with nuts

The case of nuts (Fig. 5.32) is slightly different as the peaks in the velocity profile are broader than that of the spring washers. The ratio of the wetted surface area to the geometrical surface area for this sample is 65%; while that of the spring washers is 43%. Therefore despite having less geometrical surface area, the zinc evaporation curve of the nuts is similar to the spring washers.



Figure 5.33: Normalised velocity profile at the top of the crucible filled with rivets

Two sharp peaks in the velocity profile near the crucible walls can be seen in the case of rivets (Fig. 5.33), while in the intermediate radial position the velocity profile is not as sharp. This observation can be taken as a hint of flow channelling.



Figure 5.34: Normalised velocity profile at the top of the crucible filled with quarter washers

Looking at Fig. 5.34, it can be observed that this effect is more pronounced in the case of quarter washers. Apart from the sharp peaks in the velocity profile near the crucible walls, the intermediate region is more or less flat and there seems to be negligible air flow through this region. As this sample had the same geometrical surface area and a slightly less wetted surface area compared to the spring washers, another reason for its reduced zinc evaporation can be the adverse flow channelling effect. Sederman et al. (1998) used the magnetic resonance imaging (MRI) technique to observe the velocity and volume distribution of the flow of water through a packed bed of ballotini. They made similar observations of the flow channelling effect and report that in a typical image slice along the height of the bed, a small fraction of the pores (8%) carry a significant portion of the volume flow rate (40%). According to their findings, such pores are situated towards the walls of the packed bed where the structure of the packing is significantly modified. Furthermore, these pores are characterised by a high interfacial surface area to the adjoining pores, leading to higher permeability and a high local Reynolds number. Owing to these observations, it can be concluded that the reduced zinc evaporation from quarter washers compared to the other samples is due to uneven flow distribution of the carrier gas through the crucible together with the least evaporative surface area as a result of strong mutual overlapping of the particles.

5.9.4 Zinc Evaporation in the Industrial Steelmaking Processes

The zinc from galvanized coatings of ferrous scrap can be evaporated in the low temperature de-zincing processes. Although metallic zinc can be removed this way, the zinc present in the intermetallic compounds like zinc-ferrites of hot-dip or galvanealed coatings needs temperatures close to the melting point of steel for separation. Some techniques have been proposed for separation of such coatings by baking and subsequent shot-blasting e.g. by Fujio & Kazuhiro (1992), Franzen & Pluschkell (1999); they are limited to only a particular type of scrap e.g. sheet metal from ELV's. In consideration of this fact it is important to discuss the kinetics of zinc evaporation after the melt-down of scrap, and the influence of oxidizing and reducing environment in the steelmaking processes.

Zinc shows very low solubility in liquid iron at the steelmaking temperatures (~1600°C) and most of it evaporates out of the melt. However, up to 0.15-0.2 % of the original input of zinc still remains in the melt depending on the amount of coated material (Hegewaldt 1999). Li et al. (1995a) have investigated the behaviour of zinc in steel melts and found that there is a correlation between zinc partial pressure in the furnace atmosphere and the solubility of zinc (in % of total melt volume) in the steel bath at 1600°C:

$$[\%Zn] = \begin{cases} 0.406 \cdot p_{Zn} & \text{(for iron-zinc melts)} \\ 0.346 \cdot p_{Zn} & \text{(for iron-zinc melts saturated with carbon)} \end{cases}$$
(5.33)

This implies that dissolved carbon reduces the solubility of zinc and therefore, a higher tendency of separation exists in the case of carbon saturated melts. As the amount of dissolved carbon in the melt is different in the EAF and BOF, another important implication is that the rate of zinc removal is also different in the two processes. Pluschkell & Janke (1992) describe the BOF process to be more efficient in comparison to EAF in this aspect. The reason for this difference is the high process gas production rate in the BOF, leading to low residual zinc content of liquid steel and slag.

One consequence of the high gas production rate can be the dilution of zinc vapour and hence lower partial pressure of zinc in the furnace. For typical BOF

processes the estimated zinc partial pressure in the furnace atmosphere and the off gases is not higher than 5×10^{-3} bar. In consideration of this fact, the zinc content in the steel bath should not exceed 20 ppm. The results of the steel samples taken after blowing validate this estimate; showing usually about 10 ppm Zn (Kühn & Drissen, 1996).

In comparison to BOF, an electric arc furnace is a rather slow reactor with a lower gas production rate. As a result, the partial pressure of zinc in the furnace is relatively higher; estimated to be about $2x10^{-2}$ bar. Therefore the steel bath can contain Zn content as high as 80-100 ppm before tapping (Kühn & Drissen, 1996). Some measures can be taken in order to improve the quality of melt, e.g. by increasing the amount of direct reduced iron (DRI); where CO boiling process or decarburization enhances the zinc evaporation up to the end of melting (Birat 1996). During tapping, a relatively high step down in zinc and lead is usually observed; perhaps as a result of strong turbulence and drop in steel temperature (Stercken, 1996). After tapping, reduction of zinc can be achieved by other means; e.g. by stirring, gas bubbling or treatment in the ladle furnace (Kühn & Drissen, 1996).

The effect of furnace atmosphere on the chemical and physical reactions taking place during steelmaking has been a topic of many research studies. Turkdogan et al. (1963), in a pioneers work describe the evaporation of different metals in the flowing stream of oxygen and argon. According to their findings, the rate of vaporization of metals is directly proportional to the oxygen partial pressure. According to Li et al. (1995b), the evaporation of iron and zinc from the steel melts can be considered as a counter-flux transport process in the flowing stream of oxygen. At some short distance from the melt surface, iron and zinc vapours react with oxygen, forming an oxide mixture of FeO and ZnO. The formation of oxides reduces the vapour pressure of metals being evaporated at the melt surface. As a consequence of the released pressure, solubility of the evaporating metals in the melt is reduced according to Eq. 5.33. For a given temperature and a mass transfer coefficient, the total rate of evaporation increases linearly with increasing partial pressure of oxygen as the thickness of the boundary layer between the melt surface and the free stream decreases. There are however upper and lower limits to the effective evaporation of zinc this way. The minimum rate of total evaporation

is reached at a partial pressure of oxygen below which the metal oxides do not form. At the higher end, the oxygen partial pressure can be increased until the thickness of the boundary layer reduces to the scale of the mean free path of atoms. At this point the form of Fick's law governing the transport mechanism fails as the maximum evaporation can not exceed the evaporation into vacuum (Turkdogan et al., 1963). In this case, the melt is oxidized by the excess oxygen on its surface and the rate of evaporation is slowed down due to the extremely low vapour pressure of zinc at high oxygen partial pressure. The experiments performed by Li et al. (1995b) support the above mentioned evaporation kinetics of zinc from steel melt. They performed experiments on the evaporation of iron and zinc from an alloy of Fe-0.2%Zn weighing 1.5 g at 1600°C in a gas mixture of argon and oxygen. The amount of total dust and the fractions of iron and zinc at different partial pressure of oxygen in the gas mixture are reported in Fig. 5.35.



Figure 5.35: Total amount of dust, zinc and iron fraction in the dust at different partial pressures of oxygen (Li et al. (1995b)

It can be seen from Fig. 5.35 that the total amount of dust increases with the increase in the partial pressure of oxygen. After attaining a maximum value, it starts decreasing and falls to almost zero when the oxygen partial pressure approaches 1 bar. Evaporation of iron and zinc takes place at different pace owing to their different vapour pressures at a given temperature. Li et al. (1995a) conclude that the value of partial pressure of oxygen for effective zinc evaporation

depends on the amount of zinc present in the iron bath. In the reported case of iron melt consisting 0.2% Zn, this value is about 0.2 bar at 1600°C bath temperature.

From the above discussion, it can be reasonably concluded that slightly oxidizing atmosphere in the furnace can help in zinc evaporation. Care should however be taken as excessive oxygen flow rate can lead to significant amount of iron going into the process dust.

6. SUMMARY AND CONCLUSIONS

Various trends prevailing in steelmaking and handling of the process dust in the EU were analysed in this study. Although the increasing availability of post consumer scrap is an opportunity for the EAF steelmaking, there are certain operational consequences of using the galvanized scrap. Likewise the use of noncoated scrap as an alternative is not very feasible as it raises the price of the endproduct. In addition to the scarcity of clean raw material, the steel industry has equal concerns over by-products of steelmaking. The rise in EAF steel production has lead to an increase in the process dust while the existing capacity of recycling is shrinking. The results of the transportation model suggest that there is an uneven distribution of this capacity which is 85% of the total dust generation in the north EU and about 56% in the south EU. In case the Portovesme plant in Sardinia remains closed indefinitely, the capacity in the south EU will sink further to 40%. Considering the volatile nature of the secondary zinc market and the technical difficulties of zinc extraction from the dust, the likelihood of large investment in dust recycling in the near future is unforeseeable. As the share of EAF steelmaking is likely to rise in the EU to 50% in the coming decades, it makes a strong case for research in de-zincing. It has the potential to be not only a means of providing high quality scrap, but a product rich in zinc as well, which is attractive for the secondary zinc smelters.

Considering the current innovations in the EAF design, there is a potential of combining the scrap pre-heating and de-zincing processes using shaft type systems based on a mixture of auxiliary burners and off-gases of steelmaking. The Fuchs shaft furnace and Davy-Clecim twin shell electric arc furnace designs employ a similar technique for scrap-preheating. Contiarc process developed by SMS-Demag is another example of such a process where scrap is pre-heated in a shell situated at the top of the EAF. These techniques are able to pre-heat the scrap up to 800 - 1000°C. Results obtained through the present research show that this temperature range is optimal for de-zincing in an inert atmosphere such as nitrogen or process gases from steelmaking, e.g. CO, CO₂ as suggested by

other researchers. These findings can be used in operational modifications of the scrap pre-heating systems in order to incorporate the scrap de-zincing step.

A significant point regarding the current research is that the scrap sample was reasonable to reflect the influence of structural parameters such as packed bed voidage, permeability and the specific surface area on the zinc evaporation kinetics. The results obtained from the experiments on spring washers show that the carrier gas flow rate has some effect on the zinc evaporation rate. As the zinc melts down between 500-600°C and the evaporative area changes, it was not possible to calculate the evaporation rate per unit surface area. During the earlier period of the experiments, a higher rate of zinc evaporation was observed with an increase in the flow rate of the carrier gas. When most of the zinc exposed to the main gas flow is evaporated, the evaporation rate starts declining as the zinc trapped in the recesses in the scrap sample is less exposed to the main portion of the flow. The flow rate of 10 l/min of the carrier gas was found to be insignificant for the convective mass transfer of zinc and the flow rates equal to or higher than 20 I/min gave satisfactory results as most of the zinc evaporated. The higher evaporation rates observed at a higher flow of the carrier gas at the start of the dezincing process are balanced out during the end phase as the effect of the convective transport becomes weak.

For identical samples the time of de-zincing was directly proportional to the scrap heating rate at a given flow rate of the carrier gas. It can be inferred that scrap heating rate has no direct influence on the zinc evaporation.

The shape of the scrap samples, anisotropy and the structure parameters of packing were found to have a definite effect on the evaporation kinetics. This fact was especially prominent in the case of sample consisting quarter washers that are highly anisotropic marked by a parallelepipedal shape. This scrap sample was found to have less wetted surface area caused by strong mutual overlapping of the particles; and ultimately, the total amount of evaporated zinc was small due to reduction of the evaporating surfaces. In addition, an uneven distribution of voidage and permeability of the packed bed contained in this sample leads to the flow channelling effect where most of the carrier gas flows along the walls of the container. This is an important finding for the de-zincing of the sheet metal, e.g. from the shredders, as the plate-like objects have a natural tendency of

overlapping. In order to achieve meaningful de-zincing of such scrap, it should not be in a compacted form in contrast to the common practice to compact the shredded scrap for saving the space and handling. Furthermore, the means to reduce the flow channelling should be adopted by modification of the walls of the de-zincing apparatus or shaft.

There is a potential of separating zinc from the steel life cycle at relatively lower overall cost by implementation of scrap de-zincing. A part of the costs in such a process can be offset by recovering heat from the exhaust gases of steelmaking. This is equivalent to 10-30 % of the energy input to an EAF (Manning & Fruehan 2001). The average iron content of the EAF dust is usually about 40%. As the de-zincing process precedes the scrap melting, in the absence of iron the zinc content in the product can be expected to be over 60% and can potentially be used by zinc smelters. The fraction of zinc not recoverable this way can be obtained by recycling of steelmaking dust. With the de-zincing facilities in place, the total amount of steelmaking dust can be reduced to an extent that the existing recycling capacity in the EU can suffice.

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