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DEVELOPMENT AND ASSESSMENT OF A HYDROMETALLURGICAL PROCESS TO TREAT CHROMIUM-CONTAINING DUSTS

by

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SYNOPSIS

Dusts containing leachable toxic chromium arise in the production of ferrochromium and stainless steel. After capture in emission control devices, attention must be given to the treatment, recycling or safe disposal of these hazardous wastes.

Several pyrometallurgical processes to recover valuable metals and to produce a non-leachable slag have been proposed or are operational for the treatment of such dusts from stainless steel production. These processes are known to be energy-intensive and it has been suggested that they transfer adverse environmental impacts from steel production to energy generation.

A hydrometallurgical approach is explored in this thesis. Two dust samples, representative of the ferrochromium and stainless steel industries, were studied experimentally and it was found that:

* residues with significantly reduced leachable chromium content can be produced by slurrying with nitric acid. Further research related to the atmospheric oxidation of chromium is recommended to validate that these residues can be disposed safely.

* elements undesirable in feed materials to steel production furnaces can be at least partially removed from the dusts by nitric acid leaching, allowing the residues to be recycled.

* sulphuric acid is not suitable to prepare the dusts for either disposal or recycle, as lead sulphate accumulates in the leach residue.

From analyses of the leachates it was predicted that a metal hydroxide sludge containing mostly zinc can be produced as a byproduct, with treatment of the remaining saline solution being a factor of receiving water quality guidelines. The experimental findings were used to conceptually design a process for the treatment and recycle of a stainless steel furnace dust. The objective of the design was to compare the environmental performance of such a process with that of a pyrometallurgical alternative. Waste Minimisation principles were used in the design.

The comparison was carried out with the help of Environmental Life Cycle Assessment (LCA), which allowed the impacts associated with "upstream" processes, such as electricity generation, to be incorporated.

The results of the comparison show that the hydrometallurgical process has generally lower environmental impacts than thermal treatment, but only if the nitric acid reagent can be replaced with an acidic waste stream also arising in steel production. Zero environmental liability can be assigned to the production of the acid in this case.

The practice of disposing untreated dusts could not be assessed comparatively, as Life Cycle Assessment methodology is still poorly developed in this field. It is recommended that research be directed at this topic.

An analysis was then made of the value of the formalised environmental management tools of Waste Minimisation and Environmental Life Cycle Assessment to developing the treatment process. A number of conclusions were drawn with respect to their roles in process engineering and design:

* Life Cycle Assessment can be used as an evaluative tool in process design. Moreover, it can be applied in the early stages of design and used to guide environmental improvements.

* A principle of Waste Minimisation, viz. to re-use waste, was validated by Life Cycle Assessment in the context of the case study.

* Life Cycle Assessment and Waste Minimisation can possibly be used in combination in process design, with an "Impact Minimisation" taking the place of LCA Improvement Assessment, for which as yet no procedures have been developed. It is recommended that this possibility be explored further.

Finally, if the hydrometallurgical treatment of chromium-containing dusts is to be pursued, it is recommended that:

* the marketability of the zinc-containing byproduct be investigated;

* an economic feasibility study of the process be undertaken; and

* the implications of recycling leach residues to steel production furnaces be determined by pyrometallurgical simulation.

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In carrying out the LCA reported in the thesis, use was made of the PEMS LCA computer model. Without it, this study could not have been completed.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GLOSSARY

Abbreviations:

AOD	Argon Oxygen Decarburising (Vessel)
BAT	Best Available Technology
CJV	Columbus Joint Venture
EAF	Electric Arc Furnace
EPA	(United States) Environmental Protection Agency
LCA	(Environmental) Life Cycle Assessment
SEM	Scanning Electron Microscope
TEW	Thyssen Edelstahl Werke
tpa	ton (1000 kg) per annum
XRF	X-ray Fluorescence

Technical terms:

carbothermic	with a carbonaceous material at high temperature, used in conjunction with reduction
hexavalent	in the +6 valence state (atom with six electrons removed)
pickle	activity giving the desired surface finish to steel; can consist of electrolytic and acidic treatment
reduction	the change from a higher valence state to a lower one; in this thesis in particular the change from a metal oxide to a metal or, for chromium, the change from the hexavalent to the trivalent form
smelting	the concurrent melting and reduction of an ore

1. INTRODUCTION: OBJECTIVES, HYPOTHESES AND STRUCTURE OF THE THESIS

1.1 BACKGROUND

1.1.1 A Hazardous Waste in Metallurgy

Flue gases from furnaces in the metallurgical industry often contain significant amounts of fine particulates. Baghouses, wet scrubbers or electrostatic precipitators are employed to lower particulate emissions to the atmosphere to acceptable limits. The dusts or slurries collected in such equipment generally contain heavy metals and constitute a hazardous waste, which, in most industrialised countries, requires treatment before disposal.

For the ferroalloy and iron and steel industries these dusts were listed in the mid 1980's by the US EPA as hazardous wastes from specific sources, designated K091 and K061 respectively (Federal Regulations, 1992). The main reason for the hazard rating is the mobility of the heavy metals lead, cadmium and chromium (Dreisinger *et al*, 1990). Disposal of the untreated dusts or slurries has now been prohibited or severely curtailed in several countries.

As a result of this increasing legislative pressure, a large amount of research and development has taken and continues to take place, with electric arc furnace (EAF) dusts from steel production commanding the most attention. Today, an impressive array of technologies is offered to steel producers to deal with the problem. One observer has even gone so far as to declare the problem of EAF dust "technically solved" (Kola, 1993). In this respect, the large number of steel producers in the industrialised countries (USA, Europe and Japan) provided a substantive market for technology developers and service providers targeting steel production furnace dusts.

1.1.2 "Adding Value" Leads to New Challenges

These steel producers all operate under similar conditions: their raw materials, except steel scrap, are largely imported and the environmental standards to which they have to comply do not differ much (Kola, 1993). In contrast, producers in developing countries wishing to add value to their exported products are faced with different situations. The proximity to raw materials, allowing vertically integrated production, and generally lower environmental standards increase competitive margins. On the other hand, producers with a market focus targeting exports should be sensitive to the possibility of environmentally motivated trade

embargoes. Lowering production costs at the expense of environmental degradation might be labelled an unfair trade practice. For this reason, steel producers such as the Columbus Joint Venture in South Africa (which has been identified as a developing economy with significant growth potential within its minerals processing industry) are implementing pollution control measures that "will be in line with that of the best stainless steel producers in the world" (Johansson, 1994).

The vertical integration of steel production with raw material extraction and processing does, however, imply that such "developed economy" pollution control measures will increasingly also be applied to activities such as mining, mineral processing and primary metallurgy. This offers new challenges to develop technologies for the treatment of wastes and, more importantly, new opportunities to minimise the production of wastes by applying integrated pollution control measures across the entire production domain.

On an integrated stainless steel production site (where chromite ore is the feedstock and ferrochromium an intermediate product), a challenge of this sort arises out of the need to treat furnace flue dusts from the ferrochromium smelters, as well as those from the stainless-steelmaking process. Both dusts are characterised by a leachable chromium content.

1.1.3 Approaches to the Hazardous Waste Problem

One of the approaches to the treatment of metal-containing dusts follows a simple but persuasive argument: If the heavy metals contained in the dust dissolve - unwantedly - into water, why not use water and modified conditions which accelerate the dissolution to produce a residue free of such heavy metals? (Dreisinger, 1990).

In particular, if the emission control system is a wet scrubber, or if previously disposed dusts have to be recovered (by slurrying, which is the only practical method), it stands to reason to explore hydrometallurgical techniques to achieve an environmentally acceptable outcome. Hydrometallurgy has been described in *Chemical Engineering* as a means of "winning metals with water" (Canterford, 1985).

Taking a more formal approach, different waste management strategies, such as recycling, resource recovery, treatment and planned disposal, including stabilisation and solidification (S/S) can be - and have been - applied to hazardous metallurgical flue dusts. The choice of strategy, and hence technology, is subject to factors such as location, legislation, installed technology, expansion plans and corporate strategy. Most proposed solutions for dusts from steel works consist of a combination of the above strategies, with resource recovery featuring prominently. The potential of recovering valuable and scarce metals from this type of dust

impacts favourably on cost considerations. The preferred technology (in some cases certified by government agencies such as the US EPA as the Best Available Technology, BAT) is usually a pyrometallurgical one, e.g. treatment in a plasma-arc furnace or a rotary kiln. Such processes are capital- and energy-intensive and profit from economies of scale.

The relatively small amounts of dust (5 000 to 10 000 tpa) originating even from larger steelworks (500,000 tpa) have led to the establishment of centralised treatment plants offering a service to steel producers. The absence of such facilities in developing countries favour approaches such as the hydrometallurgical one. Pyrometallurgical solutions tailored to this situation are, however, also being developed (Schoukens *et al*, 1993).

1.1.4 Is Treatment the Best Option?

Over the last two decades, a large amount of research and development has been directed not only at remediation and pollution abatement (as e.g., in the case of steel works flue dust), but also at the general appropriateness of different environmental strategies, such as treatment.

It has been found that, in the past, so-called "treatment" of wastes has often resulted in the transfer of pollution from one medium to another. Some water treatment ponds, for example, transfer volatile pollutants to the atmosphere, while gas cleaning scrubbers produce polluted water at the expense of cleaned flue gases. Since the mid-1980's the concept of Waste Minimisation has been developed to address this problem (Patterson, 1989).

Underlying this approach is the recognition that wastes not only create environmental problems, but also represent losses of valuable raw materials and energy (Crittenden and Kolackowski, 1992:5). Fundamental to Waste Minimisation is the premise that prevention is better than cure.

Procedures for carrying out Waste Minimisation assessments have been developed by the US EPA (described in the Waste Minimisation Opportunity Assessment Manual) and adapted elsewhere, e.g. by The Institution of Chemical Engineers (Crittenden and Kolackowski, 1992). A Waste Minimisation programme consists of the following stages: (1) Project planning and team selection, (2) information gathering, (3) identification of opportunities, (4) ranking of options, (5) feasibility analysis (technical and economic), and (6) implementation, commencing with recommendations and ending with audits of the completed work. The Waste Minimisation procedure is strongly process- or company-specific, as exemplified by its approach to information gathering, which revolves around a site visit (Resch, 1988).

Central to the methodology of Waste Minimisation is the hierarchy of waste management practices (see, e.g. Wentz *et al*, 1988):

1. Elimination
2. Source reduction
3. Recycling
4. Reuse and recovery
5. Treatment
6. Disposal

Figure 1.1: Waste management practices in descending order of preference.

From Figure 1.1 it can be seen that, within the Waste Minimisation hierarchy, treatment ranks fairly low, being preferred only to secure disposal. This preference is expressed by several authors, e.g. Crittenden and Kolaczkowski (1992), Wentz (1989) and Kosson (1988).

Another important finding of environmental strategy research is that technology has to be assessed holistically before it can be declared to be "clean" or to have a lower environmental load than another process. The reason for this is that activities such as treatment sometimes only transfer environmental impacts to "upstream" suppliers or to "downstream" use or disposal (Clift and Longley, 1994). For example, the energy-intensive treatment methods for steel plant dusts mentioned above can be seen to contribute to environmental problems related to electricity generation. What is needed, in order to provide an objective measure of the environmental performance of a technology, is an assessment methodology which can be extended to include all its environmental "upstream" and "downstream" consequences. Hence, a method known as Environmental Life Cycle Assessment or LCA has been developed for this type of "cradle-to-grave" appraisal.

Figure 1.2 shows how Environmental Life Cycle Assessment differs from Waste Minimisation with respect to the type of system being targeted. Another important difference between the two procedures is that LCA is primarily a quantitative assessment method which can also identify improvement opportunities, while Waste Minimisation specifically aims to improve processes.

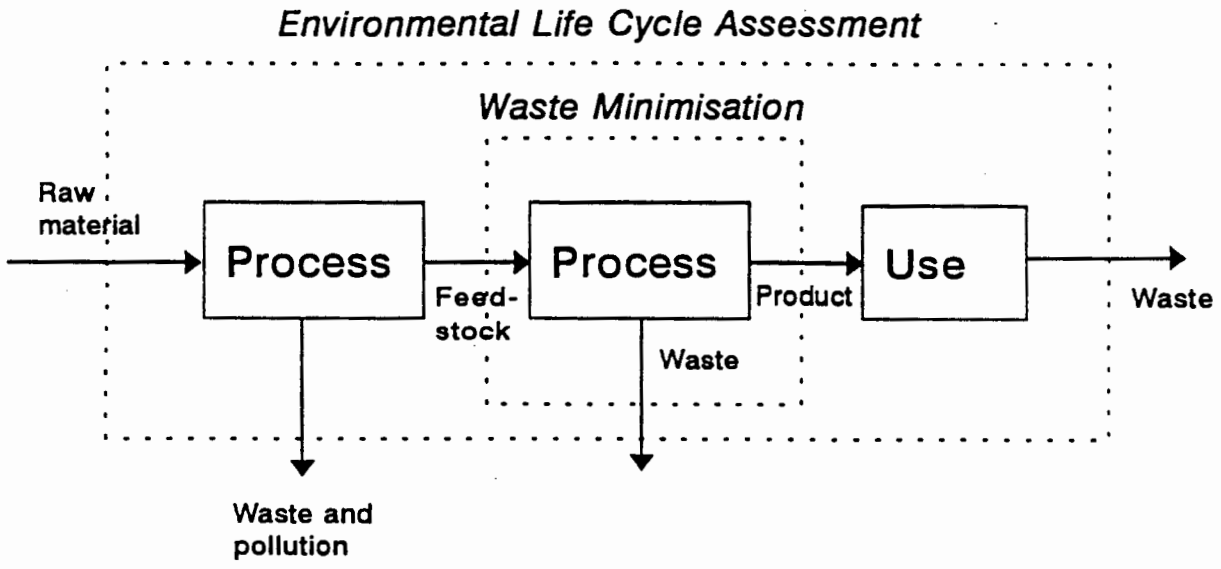


Figure 1.2: The Focus of Waste Minimisation and Environmental Life Cycle Assessment

From the above discussion on treatment as an appropriate environmental strategy and in the context of the chromium-containing dusts introduced in section 1.1.2, the following questions arise:

* (1) whether and how Waste Minimisation, or similar formalised approaches to environmental protection, can be applied to improve process engineering and design as applied to metallurgical flue dusts; and

* (2) whether a "solution" consisting of treatment actually represents an improvement over existing practices, in particular if measured objectively.

1.2 PROBLEM STATEMENT

1.2.1 Objectives

Against the background presented in the previous section, three objectives were set for this thesis:

1. It is the first aim to examine whether a hydrometallurgical treatment technology can be developed for chromium-containing flue dusts.

2. The second aim is to determine whether such a technology would in fact be preferable to an energy-intensive alternative in terms of adverse environmental impacts.

3. A third aim is to explore the contribution of formalised environmental management systems such as Waste Minimisation to the development of a treatment process for chromium-containing flue dusts.

1.2.2 Statement of the Hypotheses

Corresponding with the three objectives, three hypotheses are proposed for investigation:

(a) The first objective requires a demonstration that a chromium-containing dust can be made non-hazardous by a water-based treatment process. Acid leaching was selected, because most metals are much more soluble in acidic solutions than in water. This leads to the statement of the first hypothesis:

> **Hypothesis 1:** By treating with acid, chromium-containing dusts collected from the flue gases of furnaces in the ferrochromium and stainless steel industries can be either upgraded to be suitable for return to process or made environmentally benign and acceptable for disposal. All effluents and wastes originating in the treatment will also be non-hazardous.

(b) The word "preferable" in the second objective has several domains. In a financial context it would mean "cheaper" or "more cost effective". To an operator of the treatment plant it could mean "safer" or "easier to operate". In the context of environmental protection, which informs the need for treatment, it should mean "less detrimental interaction with the human and natural environment".

In this thesis, the second objective is investigated from this last point of view only. Furthermore, it is postulated that the examination should be as complete as possible, taking into account all environmental interactions that arise as a result of the treatment process. A method that can be used for this objective was identified in the sections 1.1.4 as Environmental Life Cycle Assessment (LCA).

To enable a meaningful comparison of hydrometallurgical with thermal treatment, a process or set of processes available for treating chromium-containing dusts by the latter method needs to be identified. For simplicity, only a single process was chosen: the plasma-arc technology employed to treat a large fraction (30 000 tpa) of the stainless steel EAF dusts originating in Europe.

The second hypothesis is thus stated:

> **Hypothesis 2:** The hydrometallurgical process to be developed will be preferable to the plasma-arc process normally applied to the treatment of chromium-containing dusts on the basis of superior environmental performance. This preference will be evident from the environmental profiles of the two processes as determined by an Environmental Life Cycle Assessment (LCA).

(c) In the introductory discussion, Waste Minimisation was identified as an environmental management strategy especially applicable to hazardous wastes. As such, it should provide a structure against which an improvement analysis (involving the assessment of design options for hazardous chromium-containing dusts) can be conducted.

However, because the Waste Minimisation procedure is strongly process- or company-specific, it can be expected to exhibit limitations in the context of environmental performance optimised over a system extended to include upstream and downstream activities. It is proposed that LCA, which was developed for the analysis of such extended systems, can help to identify targets for the Waste Minimisation procedure.

Finally, Life Cycle Assessment is not only an assessment tool, but can also serve to identify improvements. However, in contrast to its assessment function, no formal procedure has, as yet, been developed for the improvement component of LCA. In the context of the current work it is hypothesised that Waste Minimisation can fulfil this function of LCA.

These proposals are formally stated in the third hypothesis:

> **Hypothesis 3:** Considerations of Waste Minimisation will lead to improvements in the process to be developed. Life Cycle Assessment will identify targets for the Waste Minimisation procedure in this respect. In turn, Waste Minimisation will function as the improvement component of Life Cycle Assessment.

1.3 THE APPROACH TO DATA COLLECTION

The approach taken to substantiate the three hypotheses commenced with a survey of the published literature in the areas of flue dust treatment, as well as in the areas of LCA and Waste Minimisation.

It was hoped that the literature would indicate whether experimental work would be required to assist in the development of the hydrometallurgical process. In this event, experiments would be conducted on dust samples obtained from ferrochromium and stainless steel production furnaces. Further, the two dust samples would be studied to establish whether they are similar to the materials on which the plasma-arc process is operating. Similarity was deemed essential for a meaningful comparison of the two processes.

While this work was in progress, LCA methodology was studied and a computer model, designed to assist in the execution of LCA, was evaluated. This identified the type of data required to assess the two processes.

From here, work continued in parallel: the LCA model was constructed as soon as the first data became available from literature and experiment, while the "early" LCA results were used to make design choices resulting in lower environmental impacts, as the aim was to develop an improved process. The design choices, in turn, required experimental verification. The results presented in this thesis were thus derived iteratively.

The principles of Waste Minimisation were used to shape the experimental and process design work.

This process of data collection is depicted graphically in part (a) of figure 1.3.

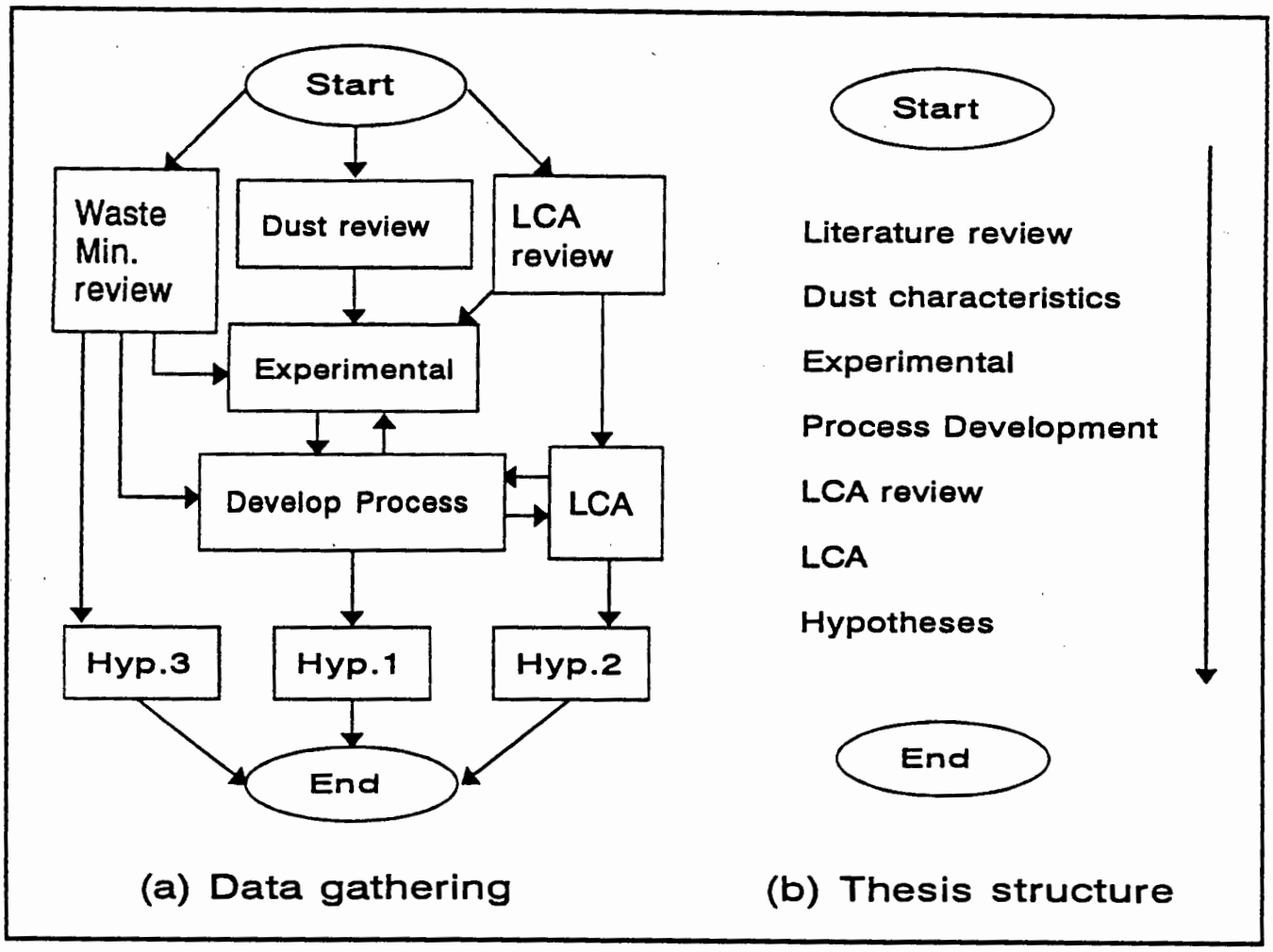


Figure 1.3: Elements of the thesis

1.4 THE STRUCTURE OF THE THESIS

In contrast to the approach taken in the gathering of data, the presentation of the methods and data in the thesis follows a linear layout as shown in part (b) of figure 1.3.

This discrepancy between data gathering and the development of the arguments in the thesis is likely to cause difficulties as some of the choices made in the earlier chapters were based on considerations which are only stated in the later chapters. In particular, by introducing the LCA method only in chapter 6, the discussion on the experimental and process development sections proceeds without prior introduction of one of its inputs.

However, care has been taken to ensure that even to readers without a knowledge of LCA these chapters are self-contained and fully understandable. A question that such readers are likely to ask is why certain data sets are being constructed in these parts. The following should be of help:

In deciding on environmental performance as the parameter by which to compare the treatment processes, it was postulated that the evaluation should be as complete as possible, taking into account the environmental interactions associated with the entire life cycle of all inputs and outputs of both processes. Such an approach, also referred to as a "cradle to grave" assessment, requires that the amounts of all materials and energy entering and leaving each process be known, that their origin or destination be known and that the material and energies flowing through these, in turn, be known. This is perpetuated until all inputs have been traced to extraction and all outputs to final disposal. Fortunately, databases (although still limited) can be accessed to simplify this procedure of data collection.

For a process to be assessed in this way, it is therefore necessary to have a complete list of all the material inputs and outputs, as well as the energy requirements and any energy exports, if applicable.

The chapters of the thesis are arranged as follows:

* The nature, characteristics, toxicity and treatment technologies for metallurgical flue dusts are reviewed in chapter 2. The application of Waste Minimisation to steel production is also reviewed here.

* The characteristics of the two dusts selected for the experimental work are described in chapter 3.

* Experiments to gather data for hydrometallurgical processing are presented and discussed in chapter 4.

* In chapter 5 the experimental results are used to formulate a process for dust treatment to the level of conceptual design, with critical flows identified and quantified.

* Chapter 6 contains a review of LCA methodology. This is introduced late in the thesis to be read in conjunction with the application of the method in chapter 7.

* The comparative Life Cycle Assessment for the proposed process and the pyrometallurgical alternative is presented in chapter 7.

* The validity of the hypotheses is then appraised in chapter 8, followed by concluding remarks and recommendations. The contributions of Waste Minimisation and LCA to finding a better solution to the treatment of chromium-containing dusts are also analysed in this chapter.

1.5 CONSTRAINTS AND SCOPE

A number of constraints arose as a result of the extensive scope identified for the thesis. These pertain firstly to data quality (and the resulting possibility of error) and secondly to the applicability of the findings (which were often generalised) to particular industrial situations.

1.5.1 Acceptable Error in the Thesis

Errors are likely to be present in the data collected and presented in this thesis for a number of reasons:

(a) Measurement in the experiments introduces random error to the experimental results. Where possible, experiments and readings have been repeated to obtain a measure of their variability.

(b) Non-representative data sets might have been chosen in some instances. For example, the plasma-arc process chosen for the comparison of environmental performance might be significantly different from other high-temperature processes achieving similar results. Similarly, the literature cited represents only a subset of the total knowledge on the topic.

As far as possible, reasons are given why certain data sets have been used in preference to others.

(c) Assumptions had to be made to compensate for incomplete data sets. These have been justified by careful consideration of all available facts.

Under these conditions, it was decided that the assessment would only be labelled a "first-order assessment", with all numbers accurate to within 10-15%. The data and results had to be interpreted in this context. The sensitivity of the results to uncertainty and error is assessed in chapter 7.

1.5.2 The Relevance of the Thesis to Particular Situations

The work reported in this thesis was carried out in the Department of Chemical Engineering at the University of Cape Town during 1993 and 1994. Related consulting work was undertaken for the Columbus Joint Venture (CJV), an integrated ferrochromium and stainless steel production facility, at the same time. The experiments presented in this thesis were conducted on samples from this company. Nevertheless, since the samples were physically and chemically similar to materials discussed by other researchers (see e.g. Law *et al*, 1983 and Cox *et al*, 1985), the results did not need to be restricted to the particular industrial situation. On the contrary, the Life Cycle Assessment made use of average European data. Therefore, the findings of the work do not necessarily apply to the activities of the Columbus Joint Venture either.

Rather, the value of the thesis should be seen in the method employed and in an exposé of environmental strategy illustrated by a case study in ferrous metallurgy. Of particular importance is the application of the tool of Environmental Life Cycle Assessment to process design and selection.

Finally, for the reasons of data reliability discussed above, the findings on an environmentally preferred technology for treating chromium-containing dusts should be seen as guidelines to be verified in each particular situation.

2. THE NATURE, TOXICITY AND TREATMENT OF FERROMETALLURGICAL FLUE DUSTS: AN OVERVIEW

2.1 INTRODUCTION

The first objective of the work reported in this thesis is the development of a hydrometallurgical process to treat chromium-containing flue dusts. Such dusts originate mainly in the metallurgical industry, particularly in the production of ferrochromium and stainless steel. Another potential source are municipal solid waste (MSW) incinerators, which produce bottom and fly ashes containing heavy metals such as lead, cadmium and chromium (Legiec *et al*, 1989).

It is the first purpose of this chapter to present a review of chromium-containing flue dusts: their origin, toxicity, physical properties and chemical composition are discussed. The focus of the review is on dusts from carbon and stainless steel electric arc furnaces. The listing of such materials as hazardous wastes by the US EPA, resulting in a landfill ban which was scheduled to take effect from August 1988 (McAloon, 1987), stimulated a large amount of research and development on their nature and treatment.

Despite extensive literature surveys, which included keyword searches of computer databases, studies of cited references and forward tracing by the Science Citation Index, little published research could be found on dusts from ferrochromium and other ferroalloy sources, even though this type of waste was also declared hazardous in the United States. This is probably due to the fact that ferrochromium is not produced in significant amounts in the USA (Kirk-Othmer, 1993-v6:241) or other industrialised countries and that, because of a perceived conflict with economic growth, a lower priority is attached to environmental issues in developing economies such as those of Russia and South Africa, which are the main producers of ferrochromium.

The second objective of the thesis is the comparison of the environmental performance of the hydrometallurgical process with that of an industry-accepted pyrometallurgical treatment process.
Corresponding to this objective, the second purpose of this chapter is to review technologies which have been proposed or implemented to treat chromium-containing dusts. These treatment technologies are discussed and linked to other waste management strategies such as recycle, recovery and disposal in the context of Waste Minimisation. In the discussion, one commercial plasma-arc process is chosen to represent high-temperature treatment in the comparison of environmental performance. This process is described in more detail.

2.2 THE ORIGIN OF CHROMIUM-CONTAINING METALLURGICAL FLUE DUSTS

2.2.1 Background

Smelters and other metallurgical furnaces produce molten metal for casting from metallic oxides. The chemical reduction is generally accomplished by the contacting of the solid phase oxides with a gaseous reductant, typically carbon monoxide, which is formed by the partial oxidation of coal or coke at the prevailing high temperatures. The gaseous reaction products, carbon monoxide and dioxide, arise in large volumes and constitute the major part of the flue gases leaving the furnace. These gases generally contain a significant amount of particulates and need to be cleaned before they can be emitted to the atmosphere.

Electrostatic precipitators, wet scrubbers or fabric filters ("baghouses") are commonly employed for the cleaning of such flue gases. The installation of such equipment was made mandatory for steel producers in the United States by the 1970 Clean Air Act (Hagni *et al*, 1991b). Particulate removal is now generally accepted practice in most countries; the equipment specifications and allowable emissions may, however, vary.

The dusts and sludges collected in this way (also referred to as "emission control dusts and sludges") have traditionally been consigned to waste deposits with minimum regard to their long-term environmental stability. With the passage of the Resource Conservation and Recovery Act (RCRA) in 1976 in the USA, such practices began to change (Neumeier and Adam, 1988). The listing of these emission control dusts and sludges from ferroalloy and iron and steel electric furnaces as hazardous waste, and the ban on land disposal of untreated hazardous waste under the 1984 RCRA amendments (McAloon, 1987) have made the option of disposal unavailable to steel producers in the USA and, increasingly, unacceptable in other developed countries. The reason for the legal changes stems from growing public concern over the leaching of toxic substances (heavy metals such as Cr, Pb and Cd in the case of these dusts) into surface and subsurface aquifers.

2.2.2 Metallurgical Processes in which Chromium-containing Dusts Arise

Cox *et al* (1985) list a number of sources of chromium pollution, which include kilns, smelting furnaces, boilers, the burning of coal, oil and wood, the incineration of municipal refuse and sewage sludge, cement production, asbestos mining and the routine wear of chromium-containing items such as brake linings. Although the focus of this thesis is on metallurgical flue dusts, the findings developed here should be of relevance to any emission control dust or sludge from the above or similar processes.

To provide a background for the development of a treatment process for chromium-containing dusts from metallurgical sources, a brief overview is given in the following paragraphs of the processes in which such dusts arise.

Chromium is a major and irreplaceable constituent of stainless steel. Other uses are in furnace refractories and in chemical applications such as leather tanning and electroplating. In the natural environment, chromium occurs primarily as the mineral chromite. The chemical form of this mineral is $FeO.Cr_2O_3$, but it can contain Mg^{2+} instead of Fe^{2+} and Al^{3+} and Fe^{3+} instead of Cr^{3+}.

The conversion of the chromium and iron in this mineral into stainless steel is usually achieved in a two stage process. The mined ore is first reduced with a carbonaceous reductant in a submerged arc furnace to produce ferrochromium, an iron-chromium carbide. Ferrochromium is typically produced in the countries in which chromite is mined and is then exported to stainless steel producers. These producers then melt the ferrochromium in an electric arc furnace with other iron sources to yield the desired amount of chromium in the steel. Drives in exporting countries to add value to exported commodities are changing this situation, resulting in the production of stainless steel from chromite on a single site. In South Africa, this trend is exemplified by the Columbus project described by Johansson (1994).

While the ferrochromium production process is relatively simple after furnace tapping - it consists of breaking and packing of the product - the stainless steel process only commences with the EAF. In two subsequent metallurgical operations, typically the AOD and a ladle, the composition of the product is adjusted. A slab is then cast, continuously in most modern plants, and passed on to the mills where its thickness is reduced. This is followed by surface treatment - annealing and pickling - before final forming of the desired product in the cold mill (Kirk-Othmer, 1993:v6).

Furnace emission control dust is just one of a range of waste materials arising at a typical steel plant. Together with spent pickling acid (pickling sludge) it is, however, regarded as the most hazardous. Table 2.1, compiled from information presented by Hanewald *et al* (1991), Neumeier and Adam (1988) and Phillip and Maas (1984) lists other wastes typically arising in steel works. The need to treat or recycle these wastes should be kept in mind when considering a strategy for furnace dust treatment.

Table 2.1: Waste materials from a typical steel plant

Waste material	Source
Slags	Furnaces, ladle, casting
Spent refractory	Furnaces, ladle
Mill scale	Hot mill
Grinding swarf	Final shaping
Pickling sludge	Pickling lines
Electrolyte solution	Descaling after annealing
Rinse waters	Descaling, pickling

2.2.3 Dust Amounts Generated in Metallurgical Furnaces

The magnitude of the concerns over furnace dust disposal is illustrated by the fact that an estimated 500,000 ton of electric furnace dust are generated annually by steel production in the United States alone (McAloon, 1987; Hagni *et al*, 1991a, 1991b). An indication of the dust amounts originating elsewhere and in other metallurgical processes can be obtained from the amounts reportedly originating per ton of product. These vary as follows:

* In steel production by electric arc furnaces (EAFs), 10-20 kg of dust is generated per ton of steel produced (Li and Tsai, 1993a; Barret *et al*, 1992; Hagni *et al*, 1991a).

* Non-electric furnaces in iron and steel production, like the blast furnace (BF), the basic oxygen furnace (BOF) and - in stainless steel production - the argon-oxygen decarburizing (AOD) vessel also contribute to the dust load. For example, Hagni *et al* (1991a and 1991b) state that over 10 million ton of BOF dusts are generated annually in the United States.

* In stainless steel production, the flue gases arising in the AOD process are, at least in some plants (see e.g. Kaas *et al*, 1984), cleaned together with those from the EAF. Even when collected separately, the two are sometimes combined before further treatment and disposal, as reported by Drabkin and Rissmann (1989) as part of a Waste Minimisation study for a specialty steel producer. However, the amounts of

dust from the AOD in this study were found to be less than an eighth of the total dust arisings.

* As discussed in the introductory paragraph to this chapter, no published information could be found on the amounts of dust originating from submerged arc furnaces in the production of ferrochromium. Commercial figures are available, but cannot be reported here for reasons of confidentiality.

* In the ferrosilicon industry, the dust amount can be much higher, ranging from 100 to 900 kg per ton of ferrosilicon (El-Nikhaily *et al*, 1989). This is explained by the formation of gaseous silicon oxide in the furnace, which then oxidises and condenses in the off-gases.

2.2.4 Mechanisms of Dust Formation

Any attempts to reduce the amounts of dust generated in metallurgical furnaces or to treat such dusts should be based on an understanding of the processes leading to their formation.

Dreisinger *et al* (1990) describe three mechanisms for the generation of dust in steel-making furnaces: (1) Atomization of liquid steel, followed by partial oxidation during solidification; (2) dusting of fine solids added in the form of fluxes and slag formers (e.g. CaO) and (3) fuming (evaporation) of volatile metals (e.g. Zn, Pb, Cd) with subsequent condensation, sometimes onto other dust particles.

Cox *et al* (1985), studying the distribution of chromium species in a Low Carbon ferrochromium dust, report similar findings: they distinguish between large angular particles chemically similar to chromite ore (representing dusting) and submicron particles forming "fluffy" aggregates (formed by evaporation and condensation). The atomization mechanism seems to be absent here.

2.3 TOXICITY OF STEEL PRODUCTION FURNACE DUSTS

2.3.1 Heavy Metal Content and Mobility

Emission control dusts and sludges from both ferrochromium and steel production have been declared hazardous wastes from specific sources - designated K091 and K061, respectively - by the United States Environmental Protection Agency (Federal Regulations, 1992). The

reason for the listing of dusts from steel production in electric furnaces is the leachability of the toxic elements Pb, Cd and Cr (Dreisinger *et al*, 1990). Correspondingly, the reason for declaring ferrochromium emission control dusts and sludges hazardous would have been, at least, the leachability of toxic chromium compounds.

In the hazard evaluation of solid wastes, it is their propensity to release toxic constituents that must be assessed. Therefore, if a material contains a toxic element or compound this does not have to indicate that the material must be regarded as hazardous. Of importance is the "bioavailability" or leachability of the toxic constituent. Laboratory extraction or leach tests are used to gain an understanding of the ease and extent of the mobilisation of toxins.

2.3.2 The Toxicity Characteristic Leaching Procedure

One such laboratory leach test, statutory in the USA for the evaluation of wastes (Albanese, 1990) and widely accepted elsewhere, is the Toxicity Characteristic Leaching Procedure (TCLP) developed by the US EPA.

The test consists of a batch extraction using a pH-buffered acetic acid lixiviant. The concentrations in the extract of 8 listed elements and 32 listed organics are used to determine whether a material must be classified as hazardous. The 8 elements and their maximum allowable concentrations (in ppm) in a TCLP extract are: Ag (5), As (5), Ba (100), Cd (1), Cr (5), Hg (0.2), Pb (5) and Se (1). The basis for these values could not be established but seem to be drinking water standards multiplied a hundredfold. For the organic constituents, toxicity levels and transport models were used to determine the regulatory levels (Albanese, 1990).

It has been argued that the TCLP takes no cognisance of the physical and chemical mechanisms whereby these heavy metals are released and that the use of acetic acid as lixiviant is not representative of leaching conditions in special metallurgical waste deposits like monofills (Drews and Mahote, 1994). Nevertheless, the method should provide a first-order assessment of heavy metal mobility and, thus, long-term liability for waste deposits.

In this respect, applications of the TCLP in metallurgy have been reported, e.g. to evaluate the leachability of a slag (Johansson and Löfgren, 1991) and to determine the effectiveness of a hydrometallurgical treatment of an arsenical copper smelter flue dust (Kunter and Bedal, 1992).

A working description of the TCLP, adapted to the testing of non-organics, is attached in Appendix A. A full description can be found in the Code of Federal Regulations (1992:66).

2.3.3 Leachability of Steel Production EAF Dusts

In a comprehensive study for the US Bureau of Mines, Law *et al* (1983) subjected dust samples from 32 different sources in the steel industry to the extraction procedure (EP) toxicity test, the predecessor of the TCLP. 29 of the dusts exceeded the limits for Pb, Cd and/or Cr. Eleven of the dusts were from stainless and alloy steel production: all of these failed the test.

It is interesting to note that none of the dusts from carbon steel production exceeded the limit for chromium.

Reports of similar studies on dusts from ferrochromium production could not be found. The only indication for mobility of chromium species in such dusts is inferred from the work of Cox *et al* (1985), who report that "roughly half of the total Cr in the primary smelter dust was [...] bioavailable".

2.3.4 The Long-Term Atmospheric Oxidation of Chromium

The TCLP and similar laboratory leach tests provide a measure of the immediate leachability and mobility of heavy metals. No cognisance is taken of long-term changes, which could turn a "harmless" material hazardous, or vice versa.

Chromium occurs mainly in two oxidation states in the natural environment, trivalent and hexavalent. Cr(VI) compounds are reported to be much more toxic and carcinogenic than Cr(III) compounds (Cox *et al*, 1985). It is known that some of the trivalent, less toxic, compounds can be oxidised by atmospheric oxygen to the hexavalent form. The rates of such reactions are slow with half-lives in the order of years, but finite, and thus relevant to waste deposits (Petersen and Petrie, 1993, quoting e.g. Saleh *et al*, 1989; Weijden and Reith, 1982; and Schroeder and Lee, 1975).

The mineral form of chromium, chromite, seems to be exempt from this oxidation reaction under normal conditions. Farrow and Burkin (1975) report that the oxidation reaction is slow even under the extreme conditions of high pH and elevated temperatures (250 °C). Viewed from another angle, the relative abundance of chromium in the earth's crust is such that if the oxidation of chromite were feasible, large amounts of hexavalent chromium should occur naturally. This is not the case: as Cox *et al* (1985) put it, "Cr^{6+} (is) present largely from anthropogenic processes".

Therefore, for waste materials containing chromium, it should not only be important to know the behaviour in a TCLP test, but also the amount and chemical form of non-leachable, but oxidisable trivalent chromium.

2.4 CHARACTERISTICS OF FERROCHROMIUM AND STEEL PRODUCTION FLUE DUSTS

The physical properties and chemical composition of ferrochromium and steel production furnace flue dusts are presented in the following sections. For steelmaking dusts, the discussion is largely based on the study conducted by the US Bureau of Mines (Law *et al*, 1983). The findings of Cox *et al* (1985) are used for ferrochromium furnace dust.

2.4.1 Particle size

The three mechanisms of dust formation (atomization, dusting and condensation) can be expected to be mirrored by the particle size distribution.

However, the extremely small size of the particles originating from atomization and condensation preclude particle size analysis by conventional methods. For example, Law *et al* (1985) simply state that "most of the particles are 1 μm or less in size". Analysis of micrographs obtained from scanning-electron microscopy provides the only means of determining particle sizes. Image analysis would allow this approach to be quantitative, but has not been reported in this context.

The qualitative electron microscopic analysis is exemplified by Van Craen *et al* (1983), who report that the individual dust particles from an EAF producing steel ingots from scrap "range in size from 0.01 to over 30 μm and (that) the agglomeration is common".

Cox *et al* (1985) are even less concise about the Low Carbon ferrochromium dust, describing "two main types of particles: small (largely submicron) particles forming "fluffy" aggregates and large, angular particles".

2.4.2 Density

Law *et al* (1983) determined the specific gravity of their 32 steelmaking dust samples in an ethanol pycnometer. The results ranged from 3.25 to 4.82 kg/dm^3.

The packing or apparent density, required for equipment sizing and similar engineering calculations, can be substantially lower and is influenced by factors such as surface charge and collection equipment. For example, the packing density of furnace dust from the ferrosilicon industry is 0.2 to 0.3 kg/dm^3 (El-Nikhaily *et al*, 1989), while the specific gravity of amorphous SiO_2 is approximately 2.2 kg/dm^3 (CRC Handbook, 1979:B-121).

2.4.3 Specific surface area

This parameter can be useful in the calculation of reaction kinetics.

In the study by the US Bureau of Mines on steelmaking dusts (Law *et al*, 1983), specific areas were determined by the BET method and ranged from 2.1 m^2/g to 8.1 m^2/g.

Ferrosilicon dusts have a specific area of 18 m^2/g to 22 m^2/g (El-Nikhaily *et al*, 1989).

These figures indicate that the particles can be regarded as nonporous: a spherical particle of diameter 0.1 μm and density 4.0 kg/dm^3 would have surface area of 3.14×10^{-14} m^2 and a volume of 5.24×10^{-22} m^3, resulting in a mass of 2.09×10^{-15} g and, hence, a specific surface area of 15 m^2/g. If the particle were porous, a significantly higher surface area would be expected.

2.4.4 Elemental composition

The chemical composition of EAF flue dusts can vary widely. The major elements are usually iron, zinc (introduced by galvanized scrap), chromium (when the source is a stainless steel furnace) and calcium. Statistics of the concentrations of these and other elements in 11 U.S. stainless steel EAF/AOD dusts, calculated from Law *et al* (1983), are shown in Table 2.2.

Of the minor and trace elements two groups are of importance: those that pose an environmental hazard and those that offer opportunities for resource recovery:

> The former group includes lead, cadmium and, possibly, other heavy metals such as mercury and selenium. Fluorides in EAF/AOD dusts ranged from 0.5% to 6.25%. [Figures from Law *et al*, 1983].
>
> The latter group is of significance only for dusts from stainless sources and includes nickel (0.15% to 3.3%) and molybdenum (0.02% to 1.5%).

Table 2.2: Elemental composition of stainless steel EAF dust (wt.%)
(calculated from Law *et al*, 1983)

Element	Min	Max	Median
Cr	1.53	17.7	7.76
Fe	21	45.5	28.7
Ni	0.15	3.34	1.62
Ca	1.76	8.3	4.98
Zn	0.9	11.1	3.9
Pb	0.23	2.24	0.91
Cd	0.006	1.79	0.032
S	0.05	1.08	0.33

The two ferrochromium dusts studied by Cox *et al* (1985) contained 5.5% and 10.9% chromium. No quantitative information was given on any of the other elements, but it was noted that the larger particles were chemically similar to chromite ore, while the smaller ones contained mainly Ca and Si.

2.4.5 Mineralogy

While the elemental analysis of the dusts helps with characterization, information on compounds and mineral phases is essential to predicting and understanding leaching behaviour, both into the environment and in a hydrometallurgical application.

Research in this regard has been reported by Hagni *et al* (1991a and 1991b) and by Li and Tsai (1993a and 1993b), in both instances on steelmaking electric arc furnace dusts. Hagni *et al* (1991b) have described the mineralogy of EAF dusts as "varied and interesting". Most particles were found to be polymineralic.

Iron, the major element in electric arc furnace dust from steelmaking, is generally present as hematite, magnetite and ferrites (of, e.g. zinc, manganese), but some ferrous oxide and metallic iron can also be distinguished.

Chromium, the element responsible for the hazard rating of the selected dusts, occurs mainly in the trivalent form in stainless steelmaking dusts. Data from Law *et al* (1983) shows that hexavalent forms make up between < 0.1% and 6.7% of the total chromium. Yet this small fraction is responsible for the hazard rating of the dusts. In the two ferrochromium dusts

studied by Cox *et al* (1985), the hexavalent forms made up 19% and 3.9% of the total chromium.

2.4.6 Surface enrichment

It is generally accepted that particulates originating from high temperature processes have enriched surface concentrations of volatile elements and compounds, which condense in the gas-cooling regime (see, e.g., Lee *et al*, 1975; Van Craen *et al*, 1983 and Cox *et al*, 1985).

Where these volatiles are toxic (e.g. Pb, Cd and hexavalent chromium), the significance of this mechanism is twofold: (1) small particles (which are more likely to escape particulate removal) contain higher concentrations of these substances and (2) enhanced concentrations of toxic substances are in immediate contact with the environment (e.g. in lung tissue following inhalation).

Laboratory leach tests, such as the TCLP, should, however reflect this increased toxicity. What is of importance, once again, is that the elemental composition alone does not provide enough information on environmental sensitivity.

2.5 TREATMENT OF CHROMIUM-CONTAINING FLUE DUSTS

From the above discussion it is evident why flue dusts such as those described should not be allowed to be released into the natural environment. Not only do the flue gases containing them have to be cleaned, but consideration must also be given to the fate of the dusts captured in emission control devices. An additional consideration is that such dusts can contain significant amounts of valuable materials (zinc, chromium, nickel and iron), which could be recovered, possibly profitably. Further processing, consisting of treatment and recovery, must be considered.

Treatment and recovery, however, only form part of the overall strategy of Waste Minimisation. The application of this strategy to the specific problem of metallurgical flue dusts is therefore explored in the following section.

2.5.1 Treatment in the Waste Minimisation Hierarchy

All of the strategies listed in Figure 1.1, except possibly elimination (which would require an alternative technology to produce steel), have been applied to a lesser or greater extent to EAF dusts in the steel industry, although generally not in the context of Waste Minimisation assessments. Examples of solutions falling into the last four categories (recycling, reuse, treatment and disposal) are given in the discussion on technologies for dust treatment and metal recovery in section 2.5.2. The significance of source reduction is graphically illustrated in Figure 2.1, which shows how the amount of dust from blast furnaces in the state of Northrhine-Westfalia (Germany) has been reduced over the years through improved operating practices and technical innovation.

In EAFs, source reduction can be achieved by new techniques such as bottom tapping, which reduces the amount of splashing (described by Schneider and Lünig, 1983). A consideration of the fundamental mechanisms of dust generation can also lead to improvements. De-zincing of scrap before melting would, for example, lead to less dust being produced by the volatilization mechanism. This consideration has led to the development of a de-zincing process by Metals Recovery Industries (MRI) in Hamilton, Ontario (Barcza and Nelson, 1990; Kola, 1993).

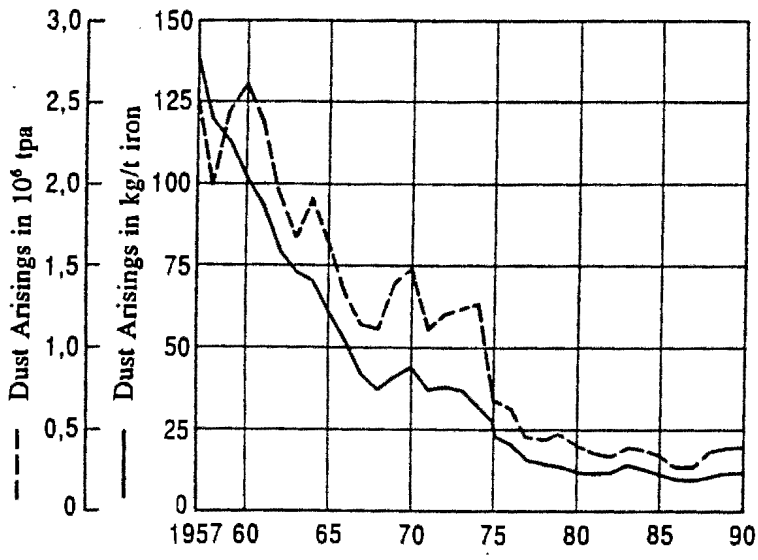


Figure 2.1: The Development of Blast Furnace Dust Arisings (from Philipp *et al*, 1992).

One formal Waste Minimisation assessment at a steel plant described in the open literature is that of Drabkin and Rissmann (1989). This assessment, carried out for a specialty steel producer in Butler, Pennsylvania, focused on the two hazardous wastes generated: EAF dust on the one hand and waste pickle liquors and rinse waters on the other. In fact, separate assessments were carried out for the two wastes, which originate only some 2 miles apart, with no thought given to concurrent treatment. The recommendations from the assessments were (1) that the K061 waste be stabilized by the addition of additives in an impermeable matrix to allow disposal in a non-hazardous landfill; and (2) that calcium fluoride be recovered from the waste pickle liquors (which originate from nitric and hydrofluoric acids) to reduce the amount of neutralized sludge requiring landfilling. It was acknowledged that the former solution did not embody waste reduction, but that it was "the only technically viable option available". In the latter proposal, no mention was made of the fate of the soluble nitrates in the neutralised liquor, which would continue to be "discharged to the outfall".

The Drabkin and Rissmann case study illustrates that the strategies available in the minimisation of wastes from steel plants are largely restricted to those starting with recycle. A certain degree of source reduction can be achieved by new furnace designs and by attention to housekeeping and maintenance, but ultimately a certain amount of dust is always generated. It is therefore not surprising that the focus of technology development for EAF dusts has thus been on these options. The recovery of valuable constituents, mainly zinc, chromium, nickel, molybdenum and iron either by direct recycle or by separate processing is an overriding theme, while treatment and disposal options have also been proposed. The following sections review some of the proposed and implemented technologies.

2.5.2 Technologies for Steelmaking Flue Dust Treatment and Metal Recovery

A comprehensive overview of different technologies for the treatment of steel plant dusts is given by Barcza and Nelson (1991). Kola (1993) also reviews the range of options available, declaring the problem of steel industry dust technically solved.

The discussion here mentions the range of options, but focuses mainly on the hydrometallurgical approach and on the PlasmaDust (TM) process. The former sets the scene for the experimental work reported in chapters 3 to 5, while the latter is presented as an example of the pyrometallurgical route, of which the environmental performance is to be assessed in chapter 7.

Biotechnology and disposal techniques are mentioned peripherally.

2.5.2.1 Preparatory processes

The very fine nature of smelter and furnace flue dusts makes them unsuitable for subsequent handling and treatment processes, particularly recycle to furnaces and similar thermal options. This can be overcome by agglomeration methods such as pelletizing (see e.g. Hanewald *et al*, 1991 or Schifferings, 1992:17) or briquetting, which is described for stainless steel dusts by Kaas *et al*, 1984.

The latter found that briquetting dusts with grinding swarf results in an increased strength of the briquettes. An ideal moisture content is 6-8%. Although they demonstrated the advantages of such briquettes, the most widely used process for the preparation of dusts for recycle remains the production of "green" pellets. In this process, dust is mixed with some 12% of water and caked on a spinning disc or in a drum, resulting in the formation of balls with $\pm$10-15 mm diameter (Hanewald *et al*, 1991). These may be air-dried. The adjective "green" refers to the absence of an oven-drying step.

Where the flue gas is cleaned by a wet scrubber, the necessity arises to dewater and, possibly, dry the sludge before it can be treated further. Schifferings (1992:4) described filtration, centrifugation and thermal drying operations with respect to sludges arising in steel works. In the bench-scale filtration of such sludges he obtained moisture contents of marginally less than 20%, while a large-scale trial produced cakes with a moisture content of 25%. These could be recycled to an EAF.

2.5.2.2 Hydrometallurgical processes

The reason for exploring a hydrometallurgical approach to EAF dust treatment was stated eloquently by Dreisinger (1990):

"Since the action of water seems to be naturally able to leach these metals (*Pb, Cd, Cr*) from the electric arc furnace dusts, it seems logical to consider hydrometallurgical treatment options for handling these waste products."

A hydrometallurgical operation consists typically of the following process steps: feed preparation, leaching, solid-liquid separation, solution purification and concentration, recovery from solution and liquid effluent treatment. This combination of unit operations can, potentially, be applied to dusts, which would represent a finely ground oxidic ore.

Barret *et al* (1992) described such a process to treat a carbon steel EAF dust, proceeding from work presented by Dreisinger *et al* (1990). The latter also tabulated different choices of leachant and the disadvantages of each (reproduced in Table 2.3). With the aims of recovering zinc for sale and isolating lead and cadmium from the dust residue, none of the tabulated leachants was considered suitable. Their chosen leachant was acetic acid, which effects good Zn, Pb and Cd recovery, while leaving most of the iron in the residue. The residue from Barret's process can be recycled to the arc furnace after pelletizing. This process (shown in Figure 2.2) produces a zinc rich sulphide (52 wt% Zn), which can be sold to a zinc producer. The acetic acid is regenerated with sulphuric acid, producing clean gypsum for sale. An acidic waste stream containing metal (Fe, Mg, Na, K) sulphates and chlorides is produced, "to be disposed by an effluent treatment facility". No economic assessment was presented for the process; the costs of the precursor process (Dreisinger *et al*, 1990) were claimed to be comparable to those of conventional pyrometallurgical processes, such as the Waelz kiln described below.

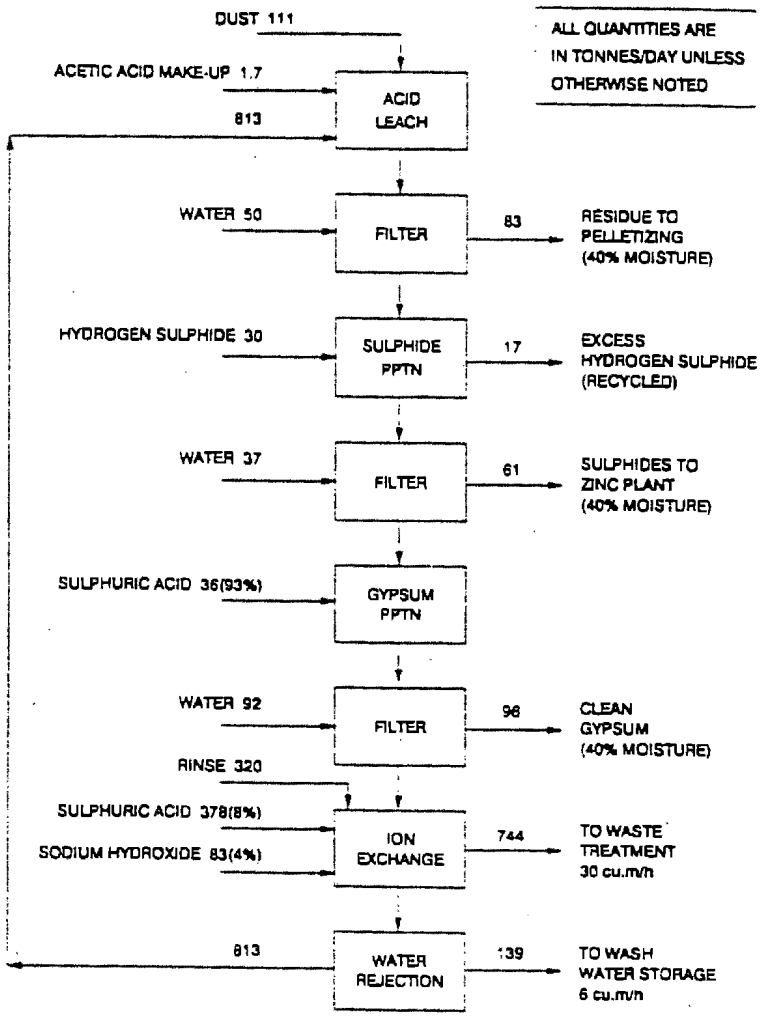


Figure 2.2: Proposed hydrometallurgical process for carbon-steel EAF dust (from Barret *et al*, 1992).

Table 2.3: Leachants and their disadvantages for carbon steel EAF dust treatment (adapted from Dreisinger *et al*, 1990)

Leachant	Disadvantages
NaOH	High reagent use. Incomplete Pb, Cd removal.
H_2SO_4 (pH 4-5)	Low Zn recovery. $PbSO_4$ in residue is toxic.
H_2SO_4 (pH < 2)	$PbSO_4$ in residue is toxic.
HCl (pH < 1)	Chlorine handling.
NH_3-$(NH_4)_2CO_3$	$PbCO_3$ in residue is toxic.

Barret *et al* (1992) claimed also that no hydrometallurgical processes are currently known to operate on EAF dust, and that some based on caustic leaching for zinc have been abandoned due to technical and economic problems. This lack of hydrometallurgical processes was explained by Neumeier and Adam (1988), who reported that for stainless steel dusts "physical separations and leaching tests proved impractical for segregating the metal values. The constituents were too intimately mixed for beneficiation separations and too refractory and too complex for selective leaching. Acid soluble constituents resulted in a high acid consumption." For carbon steel dusts, on the other hand, Barcza and Nelson (1990) reported that a commercial caustic-leach process is in operation at St.Florentine in France. According to Geutskens (1990) this process has been discontinued, as "the plant proved to be too inefficient in practice".

Fosnacht (1981) reviewed the use of leaching as a beneficiation process to remove "tramp" impurities like lead and zinc prior to recycling of the dust. According to this review, sulphuric acid, sodium hydroxide, hydrochloric acid and organic acids were studied in this respect. However, "most of the leaching methods have not proven to be economically attractive".

The idea of using spent pickling acid as leachant in a hydrometallurgical process has been investigated by Geutskens (1990), who reports high recoveries (98%) and selectivities (over iron) for zinc recovery from blast furnace dust preconcentrated in a hydrocyclone when leaching with waste hydrochloric pickle liquors under pressure. If developed, such a process would represent an ideal concurrent treatment of two waste materials; whether it can be extended to a stainless steel plant is a question requiring investigation.

According to the review by Kaltenhauser (1987), this idea of concurrent waste treatment has been implemented in practice to treat EAF dusts with spent acid wastes and slags. The aim of the process, in operation at Atlas Steel (location not mentioned), is to produce non-hazardous residues suitable for disposal.

2.5.2.3 Pyrometallurgical processes

Most technologies of choice for furnace flue dust treatment in the steel industry are thermal processes (for an overview see Kola, 1993; Barcza and Nelson, 1991 or McAloon, 1987). This is explained by the fact that such processes can simultaneously remove zinc, lead and cadmium by volatilization, reduce metal oxides and produce slags with predetermined characteristics. The objectives of recovery and treatment can thus be met simultaneously, if the slag can be made benign (i.e. non-leachable).

There is a considerable financial incentive to try to achieve such pyrometallurgical treatment by direct recycling: no major additional capital expenditure is required and the metallic values report directly to the final steel product. However, there are reservations to this approach:

1. Quality and operability problems are associated with the so-called "tramp elements": excessive Zn, Pb, P, S and Sn, to name the most important, in the feed to the electric arc furnace.

   Of these, zinc is the most abundant. In the furnace, it reports preferentially to the dust and, if this is recycled continuously, causes an increase in the dust amount, with attendant problems in the gas cleaning systems. In some cases the dust can be upgraded for sale as a zinc raw material by continued recycling with occasional or fractional purging of the Zn-enriched dust. In this approach, which is described in all of the review papers listed above, the value of the zinc-containing dust has to be balanced with the increased consumption of electricity in the furnace, which is due to additional energy

being consumed with every cycle in which zinc is volatilized (Ullrich and Schicks, 1991).

The maximum level of lead reported by Law *et al* (1983) was 2.2% for stainless steel dust and 3.8% for carbon steel EAF dust. The belief that lead can cause damage to furnace refractories if allowed to accumulate in the dust through recycling could not be verified directly. The recycling of briquetted dust to a stainless steel EAF at TEW (Krefeld, Germany) was terminated because of an increase in the levels of lead, zinc and alkali-earth metals in the melt (Schifferings, 1992:29).

Tin and especially sulphur and phosphorus must be limited in stainless steel as they adversely affect its properties through the formation of inclusions. It is common practice in ferrous metallurgy to determine sulphur and phosphorus values of all materials charged to production furnaces (see, e.g. analyses presented by Hanewald *et al*, 1991 or Johansson and Löfgren, 1991).

2. The fine nature of the dusts makes handling and return to the furnace difficult. Apart from pelletizing and briquetting, a number of solutions have been proposed. Two of these are to:
   - seal the dust in drums (Schifferings, 1992:27);
   - load the dust before the furnace is started up, covering it with other charges (Schifferings, 1992:29)

3. Provision must be made for a reductant and for increased energy consumption in the furnace.

Kaas *et al* (1984) reported an increase of 200-300 kg in the use of ferrosilicon when adding 1.5-2.0 t of briquettes consisting of 70% EAF/AOD dust to an 80 t EAF. On the other hand, oxygen savings were reported for some of the charges in which excess C and Si acted as reductants. A 20% increase in lime use was reported for the same experiment. These conditions resulted in 98% and 99% recoveries of the Cr and Ni, respectively, contained in the dust.

Neumeier and Adam (1988) added 10% coke breeze to a waste blend consisting of EAF and AOD dust, mill scale and grinding swarf, before pelletizing and reducing in an EAF. No additional ferrosilicon was required and slag volumes were normal; the recoveries of Cr and Ni were lower than those reported above but fell in the "normal range of recoveries" (Neumeier

and Adam, 1988) of these elements from scrap (> 90% for Cr, > 97% for Ni).

To melt and reduce metal oxides requires about three times the electrical energy needed to melt scrap (Kaltenhauser, 1987). This is illustrated by the figures in Table 2.4. It seems that the "typical" scrap figure reported by Boustead and Hancock (1982) is somewhat higher than the corresponding base case in the Neumeier and Adam (1988) plant trials (which was not reported).

Table 2.4: Reported EAF electrical energy requirements

Feed description	Metal	Energy consumption		Data source
	kg/(t feed)	MJ/(t metal)	MJ/(t feed)	
Scrap	934	1980	1849	Boustead and Hancock (1982)
Theory (100% "typical" dust)	543	8088	4392	Barcza and Nelson (1991)
87% waste mix (30% dust)	485	8330	4043	Neumeier and Adam (1988)
16% waste mix (ave 5 runs)	878	2040	1791	Neumeier and Adam (1988)

If the thermal treatment of dusts cannot be achieved by direct recycling, a separate fuel- or electrically-based process can be used. The review articles listed above describe a variety of both types. The former includes treatment in the Waelz kiln, the Rotary Hearth Furnace, the Flame reactor or, most recently, the Circulating Fluidised Bed (which has been described by Gudenau *et al*, 1992). The latter includes specially designed electric arc furnaces and plasma arc processes. An important consideration in every process is the production of a non-leachable slag (see e.g. Hanewald *et al*, 1991; McAloon, 1987; Johansson and Löfgren, 1990; and Schoukens *et al*, 1993).

Several companies and research organizations have built pilot scale (e.g. 1 MW) or commercial-size plasma furnaces for the treatment of steelmaking dusts. One process, mentioned often (e.g. by Kola, 1993; Barcza and Nelson, 1991; in Lead-Zinc '90 by Kola, 1990; Kaltenhauser, 1987 and McAloon, 1987) is the PlasmaDust (TM) process operated by SCANDUST at Landskrona in Sweden. It treats 30 000 tons per year of stainless steel dusts from various producers in Europe. The following process description is based on that of Johansson and Löfgren (1991), published by SCANDUST.

The PlasmaDust (TM) process consists of sections for raw material preparation, transport and injection, smelting, metal and slag handling, gas cooling and cleaning, and effluent treatment. A process flow diagram is shown in Figure 2.3 (overleaf).

The objectives of the process are to (1) recover the valuable stainless steel alloys (Cr, Ni, Mo) together with the iron for return to the steelmaker; (2) to produce a non-leachable slag and (3) to produce a zinc oxide rich sludge. With respect to the first objective, Ni and Mo recoveries in excess of 95% are reported; the Cr recovery is, however, significantly lower at 78%. Located on the outskirts of the town of Landskrona, the process is subject to stringent environmental demands on the stability of the slag product, liquid effluent concentrations and emissions to the air.

At the core of the process is the 12 m tall plasma shaft furnace powered by three 6 MW plasma generators. The dust-coal-sand mixture is injected with the plasma gas into the burners, while coke is continuously fed at the top of the shaft, keeping it filled. The metal oxides in the dust are reduced by carbon monoxide formed from the coke and tapped together with the slag from the bottom of the furnace. The volatile elements leave with the off-gases at the top of the furnace and are removed from these by a venturi scrubber. The gas (> 95% CO and H_2) is cleaned and a part is recycled as plasma gas, while the remainder is used as fuel gas in the driers and in a boiler for the municipal district heating system. A part of the venturi scrubber process water is discharged as saline effluent after the removal of dissolved metals and fluorides.

Flows of materials into and out of the process are shown in Table 2.5 (Appendix G). The system material balance closes to 96.3%, after some assumptions, as added to the table, were made to compensate for incomplete information. The element balances also close well for the metallic elements, but incomplete information on some of the other elements results in poor closures (e.g. Na, K, F, O, Si and Al). This emphasises the fundamental difficulty of accounting for pollutants by conventional mass-balancing: the flow of pollutants is often small in comparison to other process flows.

The energy requirements of the process are 2020 kWh per ton of dust for the plasma generators and 250 kWh per ton of dust for auxiliary uses. For comparison, the theoretical energy requirement for the reduction of one ton of "typical" low zinc alloy-steel dust was calculated by Barcza and Nelson (1991) to be 1220 kWh (= 4.39 GJ).

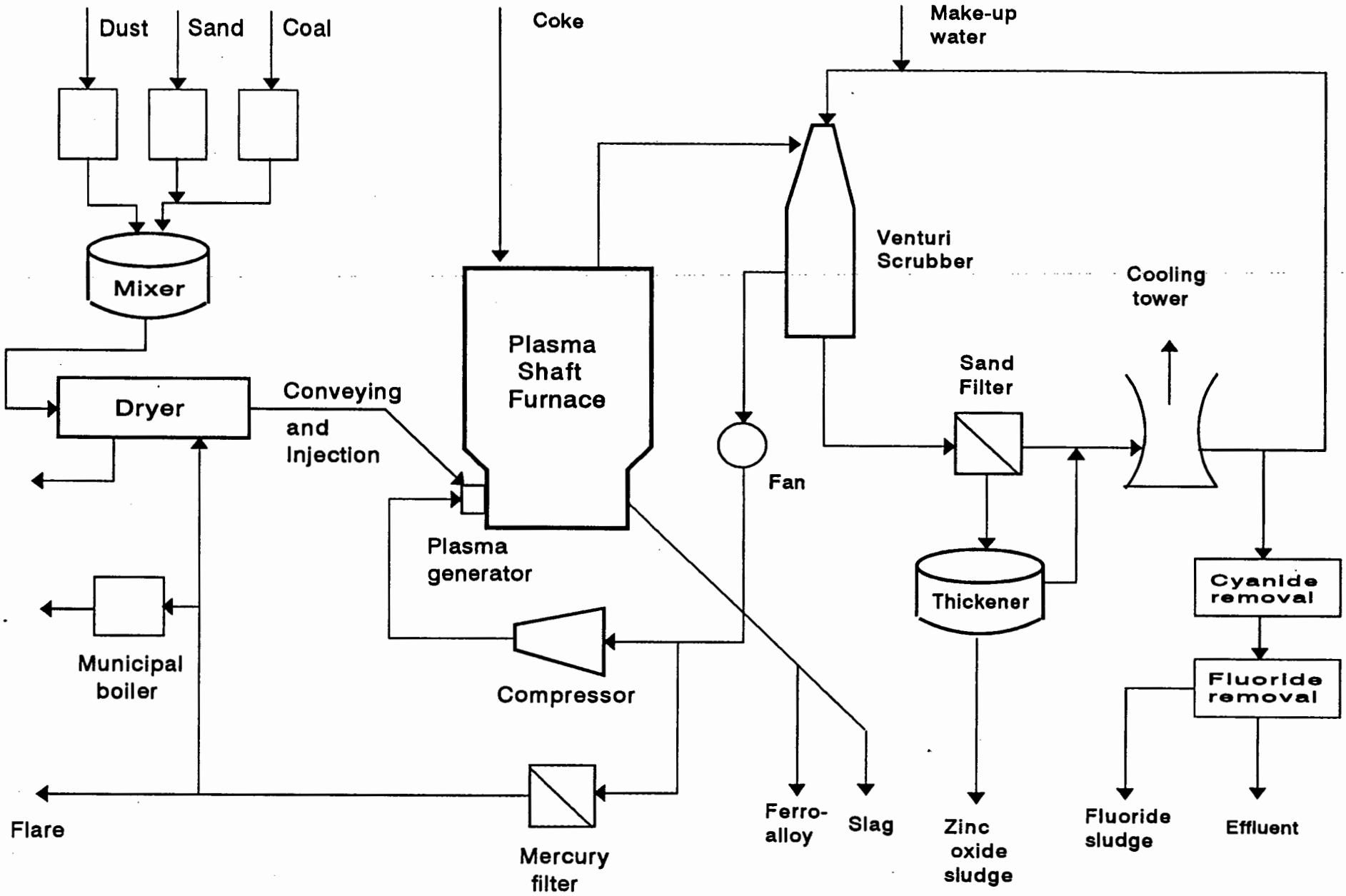


Figure 2.3: The PlasmaDust process

ScanDust charges a fee for the smelting of the dusts and returns the produced alloy to the steel companies. The value of the alloy is claimed to be higher in general than the smelting fee.

2.5.2.4 Biotechnological approaches

Biotechnology has not been applied on an industrial scale to the treatment of steelmaking dusts (Petrie and Paxton, 1993). However, at least two possible applications have been identified:

(i) Treatment of chromium (VI) containing wastes is possible by bacterial reduction. Apel and Turik (1991) tested three *Pseudomonas* species in batch cultures, identifying one which was resilient to hexavalent chromium and with which good reduction rates could be obtained for further process development.

(ii) The recovery of zinc from smelter dust was investigated by Burgstaller *et al* (1992). It was shown that the fungus *Penicillum simplicissimum* could solubilize 30 g/l of zinc from copper smelter dust in a bioreactor over a period of nine days.

Biotechnology has the advantages of low energy requirements and profitability at low turnover.

2.5.3 Disposal and Stabilisation/Solidification

The previous sections have discussed treatment in the context of recycle or recovery. In some instances, treatment is used in conjunction with disposal. This route has been proposed for EAF dusts, as discussed below:

Stabilization and Solidification techniques aim to alter the chemical and physical properties of a hazardous waste material to make it acceptable for disposal. Commonly, the aim is to produce a material which satisfies the TCLP requirements.

A common S/S approach in the steelmaking industry is to mix furnace flue dusts with portland cement and other binders. The aim is to immobilise the dust in a cementitious matrix; consequently binders may be used in quantities up to 30% of the dust weight. The solidified, leach resistant product can then be disposed when sufficient strength is reached after a few days' curing.

McAloon (1987) mentions the Chemfix (TM) process in this context, but does not elaborate whether it has been used on carbon or alloy steel dusts. Barcza and Nelson (1991) briefly describe the Super Detox (TM) and Roanoke (TM) processes, again without specifying the type of dust that these processes have been used on.

Research on the relationships between some of the performance parameters (leachability, compressive strength and permeability) of S/S products from hazardous wastes is currently in progress at the University of Cape Town. This work, carried out on ferrochromium smelter dust, augments the hydrometallurgical approach to dust treatment studied in this thesis.

2.6 CONCLUSION

In this chapter the origin, physical and chemical properties (including toxicity) and methods of treatment of chromium-containing flue dusts have been reviewed.

The discussion has largely focused on dusts originating from steelmaking furnaces, since a large amount of research and development has been reported on these hazardous wastes. Little research seems to have been directed at other chromium-containing flue dusts such as those from ferrochromium production.

It was found that dusts containing valuable alloys (viz. Cr and Ni) are regularly treated by high-temperature reduction, producing a nonhazardous slag and a ferroalloy which is re-used in steel production. Hydrometallurgical treatment has been explored and, in a few cases, implemented, but is generally regarded as an inferior solution. The option of safe disposal is also practised in some instances. Only one formal Waste Minimisation assessment has been reported for a specialty steel producer: although both flue dusts and acidic waste streams were targeted in the assessment, the possibility of reducing waste by treating one with the other in a hydrometallurgical process was not identified. This prospect has been raised in at least two other references, but has to date not led to the development of a process which achieves a similar degree of resource recovery as the pyrometallurgical route.

A need has thus been identified to explore the hydrometallurgical treatment of dusts in a way that would allow the substitution of reagents with other wastes, particularly with acidic waste waters. This approach, which should be favoured by Waste Minimisation principles, is explored in the following chapters.

However, since the pyrometallurgical route for EAF dust treatment is generally favoured (both in practice and by listing as the BAT in some cases), the environmental merits of the Waste Minimising approach need to be demonstrated. A comprehensive approach, comparing the environmental burdens of either process, from cradle to grave, is best suited for this endeavour. Environmental Life Cycle Assessment provides a tool for such an approach. This technique is discussed and reviewed in chapter 6.

In the discussion, one pyrometallurgical process was selected to represent the thermal treatment route: known as the PlasmaDust (TM) operation, it is a plasma arc process used to treat furnace flue dusts from stainless steel production. A process flow diagram and mass balance have been presented for it. This process is compared in Chapter 7 by Life Cycle Assessment to the hydrometallurgical alternative, which is developed in the following three chapters.

3. CHARACTERISATION OF TWO CHROMIUM-CONTAINING DUSTS

3.1 INTRODUCTION: THE NEED FOR EXPERIMENTAL WORK

The review of treatment technologies for chromium-containing dusts in the previous chapter has identified a need to explore effective hydrometallurgical routes for their treatment. A principal aim for the research was shown to be the substitution of treatment reagents with suitable waste streams arising in close proximity to the dusts. In particular, the use of spent pickling acids was recommended.

Although substantial experimental findings have been published on the hydrometallurgical treatment of EAF dusts, the use of spent pickling acids for this purpose has only been addressed in the context of carbon steel. In this instance, Geutskens (1990) studied and recommended the leaching of blast furnace dust with spent hydrochloric pickling acids.

Furthermore, no published research could be found on any approach to the treatment of ferrochromium smelter dusts.

In order to develop a hydrometallurgical process for chromium-containing dusts, it was thus necessary to proceed experimentally. It was decided that a part of the experimental work should be directed at confirming the results published elsewhere, while the main thrust would address the deficiencies discussed above.

Two chromium-containing dusts were selected for the experimental work: they are the emission control dusts (captured in bagfilters) from (1) a Charge Chrome ferrochromium submerged arc furnace and (2) a stainless steel electric arc furnace (EAF) and argon-oxygen decarburizing (AOD) vessel. Both dusts were collected from the Middelburg site (South Africa) on which the Columbus Joint Venture, described by Johansson (1994), operates.

An important part of the experimental programme was a physical and chemical characterization of the two dusts. This was required not only to plan the experiments, but would also determine whether the two materials are comparable to those studied by other researchers. **The comparison was essential to extend the experimental findings to the ferrometallurgical industry in general.** In particular, it would justify the envisaged environmental performance comparison of two different processes.

The following sections describe the methods used to study the physical and chemical characteristics of the dust samples and the findings obtained from these studies. The leaching experiments are the subject of chapter 4.

3.2 APPEARANCE AND MICROSTRUCTURE OF THE DUSTS

The two dusts have strikingly different appearances. The colour of the ferrochromium smelter dust is best described as gunmetal-grey and its consistency as fluffy or cake-flour like. In contrast, the EAF/AOD dust is rust-brown, dense and sticky, staining all surfaces that it comes into contact with.

To obtain an understanding of the nature of the particles of which the dusts consist, they were studied under the S200 scanning electron microscope (SEM) of the Electron Microscope Unit at the University of Cape Town. Magnifications ranging from a few hundred to 40,000 were used. The samples were prepared by sprinkling the dust, using a laboratory spatula, onto microscope stubs coated with a mixture of glue and graphite.

Both dusts were found to consist largely of fluffy agglomerates of extremely fine spherical particles, ranging in size from an estimated 0.01 μm to about 1 μm.

The micrographs in Figure 3.1 (a) and (b) (Appendix F) show high-magnification views of such particles for the ferrochromium smelter dust. Of interest is also the edge of a larger, angular particle discernable in the bottom right corner of picture (a).

The micrographs in (c), (d), (e) and (f) depict the salient features of the EAF/AOD dust. The picture in (c) shows the three types of particle observed: large particles with angular or irregular shape, smaller spheroids ranging in diameter from 2 to 20 μm and the submicron "fluff". Picture (d) shows the spherical particle at higher magnification. In pictures (e) and (f) the surface detail of another spherical particle is shown at high magnifications. The group of spherical particles in (f) is the same seen in the bottom centre of (e).

The types of particle observed were linked to the mechanisms proposed for their formation in the following way:

* the large, angular or irregular-shaped particles represent "dusting" of feed materials (e.g. ores, fluxing materials) from the furnace.

* the larger spherical particles originate as liquid droplets atomized from the melt.

* the submicron-sized spherical particles are formed by the condensation of volatile components. As seen, they can occur as loosely bound fluff (probably formed in the baghouse) or condense onto the surfaces of other particles.

Elemental mapping by techniques such as energy-dispersive X-ray microanalysis (EDX) could help to verify these claims, but would constitute the subject of an entirely separate study.

3.3 SPECIFIC GRAVITY

The specific gravity of samples of the two dusts was measured with the aid of a Micromeritics Accupyc 1330 pycnometer. This instrument determines the free volume in a sample by measuring the amount of helium required to fill the previously evacuated sample chamber. By difference with the chamber volume, the volume of the sample is determined. The density is calculated from the weight of the sample divided by this volume. The results obtained for the two dusts were:

Table 3.1: Specific gravity of dust samples

	EAF/AOD dust	Ferrochromium dust
Specific gravity	4.22	2.63

In comparison to the figures presented in chapter 2, the ferrochromium smelter dust has a somewhat higher density than amorphous SiO_2, while the density of the EAF/AOD dust falls within the range reported by Law *et al* (1983) for EAF dusts.

3.4 PARTICLE SIZE ANALYSIS

The particle size distributions of the two dusts were established by laser diffraction using a Malvern 2600Ec analyser with the appropriate lenses. The lowest size range analyzed had an upper limit of 1.22 μm, which meant that no information on sub-micron particle size classification was available.

The particle size distributions for two samples of EAF/AOD dust and one sample of ferrochromium smelter dust (FSD) are shown in Figure 3.2. For both types of dust, the majority of particles would seem to occur in the submicron range. However, for ferrochromium dust in particular, a trimodal distribution is observed. This suggests the presence of three different mechanisms for the formation of this dust, each one having a characteristic particle size.

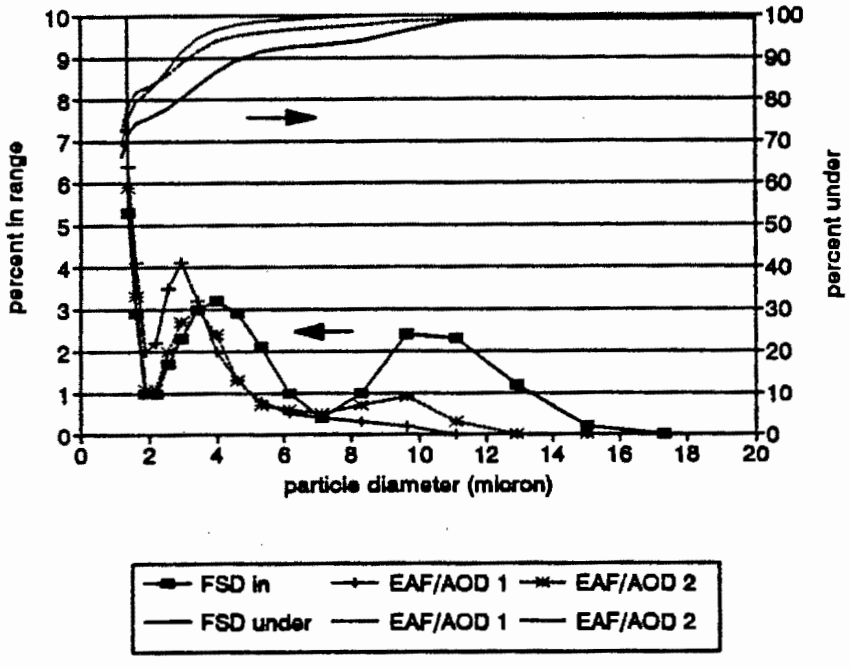


Figure 3.2: Particle size distribution of the dusts

3.5 ELEMENTAL ANALYSIS OF THE DUSTS

The elemental composition of the dusts was determined by two different methods. In the first, the dusts were completely dissolved and the elemental concentrations in solution were measured by Atomic Absorption Spectroscopy. The second method was quantitative X-ray fluorescence. Additionally, the sulphur content of the dusts was determined.

3.5.1 Analytical method

Some preliminary work indicated that neither dust could be completely dissolved in acid. Even Aqua Regia and hydrofluoric acid digest methods left undissolved residues.

It was thus decided to adapt a method recommended for chromite ore. The procedure is as follows: a 0.5 g sample is fused with 5 g of sodium peroxide over a Bunsen burner in a zirconium crucible. After cooling, the melt is crushed and washed into deionized water. 25 ml of 37% HCl is added to aid the dissolution. The solution is made up to 100 ml with deionized water.

Analysis of the solutions thus obtained was done by Atomic Absorption Spectroscopy on a Varian SpectrAA-30 spectrophotometer.

This method was applied to two samples of ferrochromium smelter dust and to three samples of EAF/AOD dust. The average elemental compositions of the two dusts, calculated from the concentrations found, are shown in Table 3.2. With the major elements Si and O not determined, neither composition adds to 100%.

Table 3.2: Elemental composition of dusts (wt.%)

Element	EAF/AOD dust	Ferrochromium smelter dust
Cr	11.5	1.80
Fe	29.7	0.57
Ni	2.10	0.02
Ca	5.59	4.80
Zn	1.58	6.49
Pb	0.52	0.058
Cd	0.004	0.0002
Mg	4.29	4.21
K	0.33	1.05
Ag (g/t)	28.0	4.0
Hg (g/t)	8.80	< 4.0
Mn	7.46	0.27
Mo	1.28	0.008
Ti	0.13	0.08
Sn	0.02	0.011
Cu	0.12	0.004

3.5.2 XRF analyses

The two dusts were also analysed for elemental composition by X-ray fluorescence at the Geochemistry Department of the University of Cape Town.

In the standard XRF procedure a spectrum is obtained by scanning a powder briquette of the sample and comparing this to the spectrum obtained for a standard material with a similar

matrix. In the analysis of the dusts, matrix effects had to be eliminated because of the lack of suitable standard materials. The structure of the sample was thus altered by a fusion technique. Synthetic standards prepared similarly could then be used to obtain quantitative data.

Lithium tetraborate was chosen as the flux. Fused disks were prepared from 0.5 g of sample and 5 g of flux. The sample had previously been ashed for 12 hours at 850 °C. Single element standards were prepared similarly, with the quantity of the standard chemicals adjusted to produce disks with suitable concentrations.

Computer-based quantitative interpretation of the XRF spectra obtained from the scanning of the disks gave the elemental compositions for the two dusts shown in Table 3.3. It has been assumed that the elements were present in the indicated oxide form.

Table 3.3: Major element compositions of dusts by XRF (wt.%)

Species	EAF/AOD dust	Ferrochromium smelter dust
Cr2O3	13.6	3.95
Fe2O3	42.8	1.69
Na2O	1.59	7.42
MgO	4.72	8.50
Al2O3	0.90	3.21
SiO2	7.45	54.4
P2O5	0.065	0.012
K2O	1.05	6.02
CaO	6.63	0.18
TiO2	0.09	0.06
MnO	9.78	0.61
NiO	2.80	0.02
ZnO	n.d.	n.d.
Total	91.4	86.1

n.d. = not detected

The totals obtained for the elemental compositions shown in Table 3.3 indicate that the major elements have largely been identified. Adding zinc oxide, which has not been determined, the totals should approach 93-95%, based on the zinc amounts found in the analytical approach.

From the compositions presented in Tables 3.2 and 3.3 it was concluded that the EAF/AOD dust is similar to those studied by Law *et al* (1983), falling into the ranges presented in Table 2.2 for all elements except cadmium, which was, nevertheless found in a comparable amount.

The ferrochromium smelter dust, on the other hand, is dominated by SiO_2, a feature not reported in the study by Cox *et al* (1985) on a ferrochromium smelter dust.

The elemental compositions determined by the two methods are fairly similar, with major discrepancies found for potassium (both dusts) and calcium and magnesium (ferrochromium smelter dust). These are attributed to sodium interferences in the AAS method and matrix effects in XRF (no fused disks were prepared for these elements).

3.5.3 Sulphur content determination

Sulphur content was identified as an important parameter for materials charged to steel production furnaces. Since sulphur was not determined in either of the two procedures described above, a separate analysis of sulphur content was performed.

The analyses were carried out on a Leco Sulphur Analyser determining total sulphur content by combustion to SO_2. The concentration of this compound in the gas stream is measured by infrared absorption.

The sulphur content of the ferrochromium smelter dust was found to be 2.6% and that of the EAF/AOD dust less than 0.01%. The latter is thus seen to differ from the values reported by Law *et al* (1983) shown in Table 2.2, with virtually no sulphur present.

3.7 CONCLUSION

From the physical and chemical characteristics determined in the preceding sections it was possible to draw conclusions on similarities and differences to the materials described in chapter 2.

(i) Ferrochromium smelter dust:

As discussed in chapter 2, only one article was found describing ferrochromium smelter dusts (Cox *et al*, 1985). Based on this description, the following similarities exist between the described dusts and the ferrochromium smelter dust characterised here:

* The microstructure appears to be similar, with submicron spherical particles and larger angular particles having been observed under the SEM.

* The smaller, spherical particles dominate in number.

* Significant amounts of bioavailable chromium are present; although the amount of chromium in the TCLP extract (0.53 mg/g dust) was much lower than the amounts of hexavalent chromium found in the two dusts (4.3 mg/g and 10.2 mg/g) studied by Cox *et al* (1983), the dust would still be classified hazardous.

The differences are:

* The amount of total chromium is lower at 1.8% compared to 5.5% and 10.9%.

* The amount of Si seems to be higher, although no figures were reported by Cox *et al* (1983).

From these findings it was concluded that ferrochromium dusts can be characterised by their microstructure and the presence of leachable chromium. Elemental compositions may differ.

(ii) Stainless steel EAF/AOD dust

This type of dust was found to exhibit the following similarities with materials described by other researchers:

* The same three types of particles as described by Dreisinger *et al* (1990) for EAF dust were observed.

* The majority of the particles occur in the submicron range.

* The specific gravity falls into the range reported for EAF dusts.

* The elemental composition is similar to that reported for stainless steel EAF dusts; generally the elemental concentrations fall into the ranges established by Law *et al* (1983). Moreover, most concentrations are similar to the medians in Table 2.2.

* The dust is hazardous as determined by the TCLP: chromium mobility alone being the reason as opposed to Cr, Pb and/or Cd being elements of concern in other cases.

No significant differences between the properties of this dust and those reported in the literature were found. It was thus concluded that the dust represents a "typical" stainless-steelmaking furnace flue dust.

4. EXPERIMENTAL DETERMINATION OF THE KEY PARAMETERS OF THE HYDROMETALLURGICAL PROCESS

4.1 INTRODUCTION

In the previous chapter the two chromium-containing flue dusts selected for the experimental work were characterized. It was concluded that they are similar to materials described in other published research and that they are, therefore, representative of the ferrochromium and the stainless steel industries.

The aim of the current chapter is to describe the experiments used to determine whether ferrochromium and stainless steel flue dusts can be treated hydrometallurgically. The experimental approach and the most important results are presented in the text of the chapter, with a description of the methods and complete lists of the results attached in Appendix B.

The results are then used in the following chapter to develop a description of a hydrometallurgical dust treatment process.

In support of this process development the experimental work addressed the following key parameters:

(1) Residue disposal: Can a "disposable" residue be produced from either dust?

(2) Residue recycle: Can a "recyclable" residue be produced from either dust?

(3) Reagents: What are the reagent requirements for a process meeting one of these requirements? Specifically, can a typical acidic waste stream be used?

(4) Byproducts and wastes: What amounts of other products, byproducts or wastes arise from a process meeting one of the above requirements?

To provide answers to these questions the dusts were leached with acid under different conditions and the leach residues were analysed from the disposal and the recycle perspectives. The rationale for exploring acid leaching was, as stated before, the frequent availability of acidic effluents from the same operation in which chromium-containing dusts arise.

Leaching in the context of the experimental work refers to the agitation of dust in a leachant slurry. The alternative, heap leaching, was considered impractical because the fine particle

size of the dusts would not only make containment of the dust on a heap difficult in practice, but would also result in low permeabilities with the wetted dusts acting like clay.

The chapter is divided into three major sections: the leaching experiments are described first, the disposal option is covered next and the recycle option is discussed last. Conclusions on the above questions and on the first hypothesis of the thesis are presented at the end of the chapter.

4.2 ACID LEACHING EXPERIMENTS

4.2.1 Justification for Leaching with Acid

In the discussion on treatment technologies for dusts in chapter two, leaching was identified as one of the unit operations of a typical hydrometallurgical process. In the treatment of carbon steel dusts it is the process step in which the valuable component (zinc) is separated from the "gangue".

It was also mentioned that hydrometallurgy was found to be unsuitable for the segregation of the metal values from stainless-steelmaking dusts. The main reasons for this finding were that neither physical beneficiation nor selective acid leaching was possible and that the acid consumption was high.

The aim of selective acid leaching would be to recover the valuable constituents of the dusts: for chromium-bearing dusts obviously the chromium, for stainless steel dust also the nickel and molybdenum. While the hexavalent chromium compounds and some trivalent chromium salts are water-, acid- or base-soluble, chromium oxide and particularly chromite are known for their refractory nature (see, e.g. Harvey and Hossain, 1987; or Farrow and Burkin, 1975). As discussed in chapter two, such refractory forms of chromium are dominant in flue dusts from ferrochromium and steel production.

Despite these difficulties, the hydrometallurgical approach was pursued, with acid leaching of the dusts as a central component. The reasons for this were that:

(1) Components that can leach from disposed dusts in a landfill situation are likely to dissolve in acids. It was therefore hypothesized that by contacting for relatively short times with acid, such components can be removed from the dusts, rendering the residues acceptable for disposal.

(2) Alternatively, acid leaching could serve as a means to remove tramp elements from dusts prior to direct recycling. As discussed in chapter two, attempts to recycle dusts directly to the EAF in stainless steel production have resulted in unacceptable levels of the tramp elements in the charge to the furnace.

(3) Acid, although contaminated, is often available from the pickling operations at steelworks either in the form of spent acid, or as dilute acidic rinse water. Both types need to be neutralized prior to disposal. If usable for the leaching of dusts, a high acid consumption could be desirable, resulting in savings on neutralizing chemicals.

4.2.2 Selection of Acids for Leaching

As stated in the first hypothesis in chapter 1, the objective of leaching the dusts with acid was to either (1) produce a residue which is acceptable for disposal, or (2) produce a residue which is acceptable for recycle.

This different approach could affect the choice of leachant and leaching conditions. Two acids were used in the experimental work: sulphuric and nitric. Sulphuric acid is, generally, available at low cost and nitric acid (although contaminated) is often available in stainless steel works from pickling operations.

The reservation of Dreisinger *et al* (1990) to the use of sulphuric acid, viz. that $PbSO_4$ in the leach residue is toxic (cf. Table 2.3), has been noted and is addressed in the interpretation of the experimental work.

The objectives of the leaching experiments were (i) to produce leach residues for toxicity tests and (ii) to analyse the leach residues and leachates. Different strengths of the two acids were evaluated.

4.2.3 Leaching Apparatus and Method

A 24 hour batch leach test with intermittent sample taking was used to evaluate the effects of acid strength and type.

The experimental apparatus and conditions, as well as the methods used for sampling, are described in Appendix B.

The leaching experiments were generally done in triplicate or quadruplicate to obtain a measure of experimental variability.

4.2.4 Leaching Conditions Studied

Apart from the effect of acid type on the two dusts, the main leaching condition studied was acid strength, with impurity of the acid a secondary issue. Other parameters such as temperature and solids concentration were ignored as the objective of the experimental work was to prove feasibility rather than to optimize conditions. Another parameter common in leaching experiments, particle size, was not applicable because the fine nature of the dust - cf. Figure 3.2 - made classification by size both irrelevant and difficult.

The dual objectives of acid leaching - disposal and recycle - were mirrored in the chosen acid strengths:

* Strongly acidic conditions (pH < 2) were desired to achieve rapid dissolution of the "problem" components: leachable chromium, lead and cadmium. In these experiments the dusts were slurried with acids of one normality.

* Selective leaching conditions were desired for the separation of tramp elements (Zn, Pb, S, P and Sn) from valuables (Cr, Ni, Mo, Fe). The difference in pH at the onset of precipitation of the hydroxides of Zn^{2+} (7.0) and Pb^{2+} (6.0) on the one hand and Cr^{3+} (5.3) on the other (Dean *et al*, 1972) suggested mild leaching conditions at a pH of approximately 5.5. A drawback of this approach is that tin (as Sn^{2+}) and nickel (as Ni^{2+}) report to the "wrong" phases. The extent and significance of this had to be determined.

The matrix of leaching experiments developed from these considerations is shown in Table B.1 in Appendix B.

Having noted the concerns of Dreisinger *et al* (1990) on the inability of sulphuric acid to remove lead, it was decided to also study the effect of sulphate contamination in nitric acid. The motivation for this was that if spent pickling acids or acidic rinse waters were to be used for acid leaching, cognisance would have to be taken of impurities. Nitric acid based pickling solutions might contain sulphates either from admixed sulphuric acid or from the concurrent treatment with other spent pickling solutions (containing, e.g. Na_2SO_4 (Johansson, 1994)).

The conditions selected for the added experiments were based on the results of the first experiments and are also shown in Table B.1.

4.2.5 Analysis of the Leachates

The samples collected from the above experiments were analysed for concentrations of Cr, Fe, Zn and Pb in all cases and additionally for Ni, Cd and Sn in the case of EAF/AOD dust. Speciation analyses were not undertaken. Volumes were recorded and a measure of the "free" or available acid was obtained. The total dissolved solids (TDS) concentrations were also measured. The methods used for analysis and the complete results are listed in Appendix B. The most pertinent findings are discussed in the following paragraphs:

(a) The elemental concentrations of the leachates (Table B.2, Appendix B) showed marked differences between the two dusts and, within each dust sample, between weakly and strongly acidic concentrations. Significant differences between sulphuric and nitric acids were observed only with respect to lead. Consistent readings could be obtained for the repeated experiments, this is illustrated by the graphs in Figure 4.1. The time dependence of element concentrations shows classical leaching behaviour only for Cr in EAF/AOD dust, and rapid initial dissolution to a plateau for Cr in ferrochromium smelter dust and lead and zinc in both dusts.

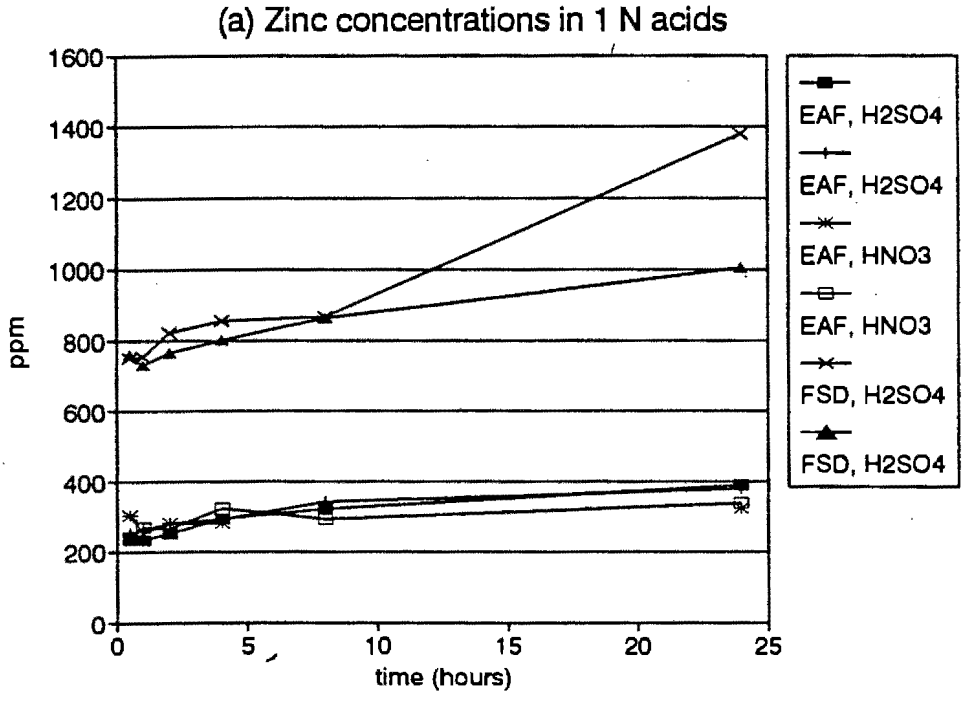
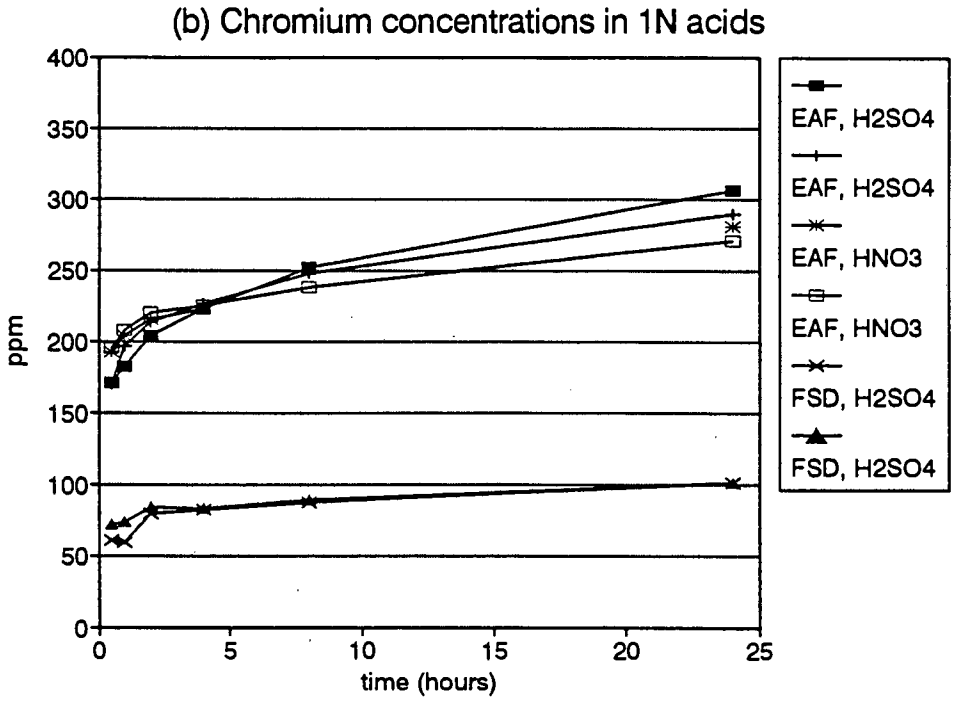


Figure 4.1: Metal concentrations in leachates



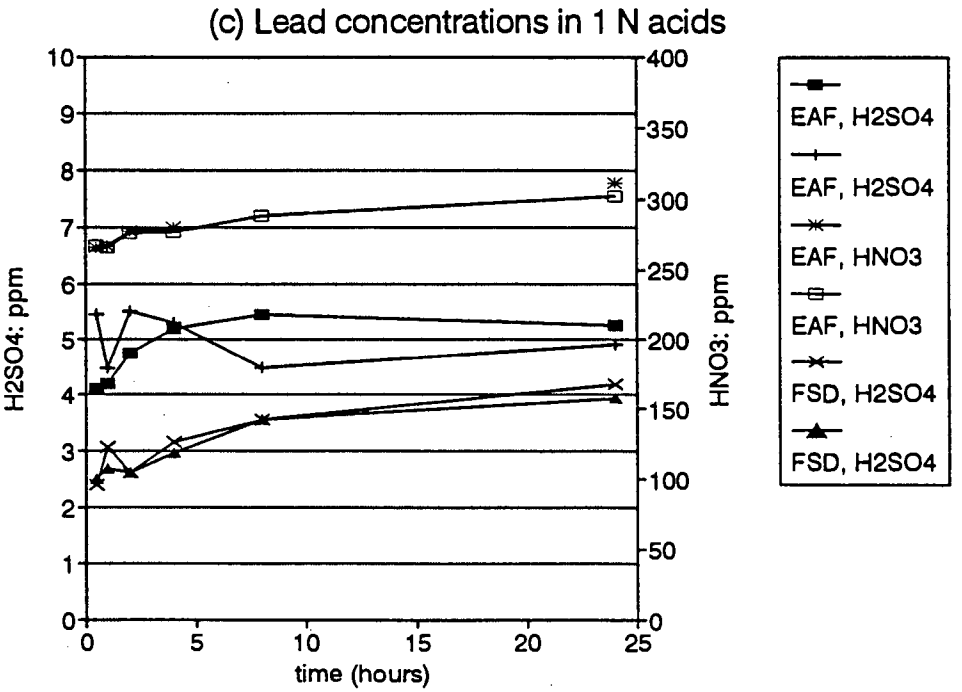


Figure 4.1 (continued): Metal concentrations in leachates

(b) The recorded filtrate volumes (Table B.2, Appendix B) were significantly lower than the amounts of leachant initially added. This was thought to be a consequence of evaporation and, to a limited extent, splashing from the open beakers.

(c) The free acid concentrations for the two dusts showed diverging behaviour with time: for the EAF/AOD dust they decayed exponentially with an asymptote at ± 70% of the original concentration, while for the ferrochrome smelter dust an initially fast but small drop was followed by a slightly increasing concentration of free acid. This is illustrated in Figure 4.2, which also shows that good reproducibility could be obtained for each set of experiments. The titrations also indicated that the nitric acid was only nominally 1 N, with an actual value of 1.26.

An explanation of the difference in acid consumption in the two dusts must be sought in the form of the easily soluble alkali and alkali earth metals, which are present in both dusts in relative abundance (cf. Figures 3.2 and 3.3). Indicative anion analysis showed large amounts of sulphates and chlorides originating from the ferrochromium dust. These salts do not consume acid on dissolution, whereas the oxides and hydroxides, believed to be the anionic form in EAF/AOD dust, do.

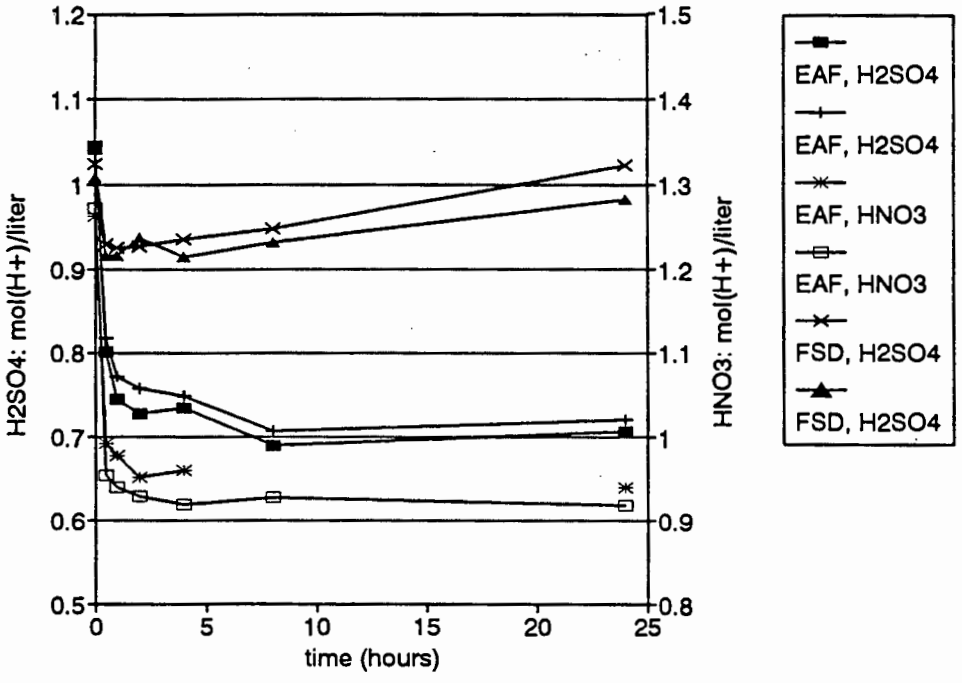


Figure 4.2: Free acid concentrations in leachates

(d) The interpretation of the TDS values with respect to leachable components of the dusts was obscured by the effects of the sulphates and nitrates. Unreacted nitric acid evaporated in the drying oven, resulting in markedly lower observed TDS values for the nitrate residues. Nevertheless, significantly lower TDS values were observed for the pH 5.5 leachates, as expected. In this category, no clear difference could be established between the TDS values of the two dusts. This was surprising, as the ferrochrome dust had a much lower acid consumption. It was concluded that this dust contained a higher fraction of water soluble constituents.

The TDS values indicated that processing of the leachates would require attention during the development of a process.

4.2.6 Analysis of the Leach Residues

All leach residues were collected from the filter and their wet weight recorded. Some were stored moist for toxicity testing, the others were oven-dried at 105 °C and the dry weight was recorded. From the wet and dry weights the moisture contents were calculated; they were between 20% and 25% for the EAF/AOD dust and between 31% and 33% for the ferrochromium smelter dust. The results are listed in Appendix B, Table B.3.

Four leach residues were selected for elemental analysis. The analysis was by the method described in chapter 3 and used on the original dusts. Each analysis was in triplicate. The elemental concentrations calculated for the four residues are listed in Appendix B, Table B.4.

The sulphur content of selected leach residues was also determined. The method used for the dusts (cf. section 3.5.3) was again employed. The results, tabulated in Appendix B, Table B.3 indicate that the sulphur content was negligible in all ferrochromium dust leach residues (compared to 2.6% S in the dust) and in all EAF/AOD residues, except that of the strong sulphuric acid leach, where a dramatic increase was seen. This is attributed to the precipitation of sulphates from the leach, probably with calcium and lead.

4.2.7 Material Balances for the Leaching Experiments

Material balances were used to confirm the accuracy of the experimental analyses. The principle of material balance closure stems from the conservation of matter: if the compositions and amounts of both the leachate and the leach residue are known, the mass balances can be "closed": for each element the difference between the original amount and the sum in the leachate and the residue is calculated and expressed as a percentage error.

This was done for the four experiments in which the elemental compositions of the leach residues were determined.

The range of closures obtained are shown in Table 4.1, with details tabulated in Appendix B, Table B.5. The consistently low closures for water are attributed to evaporation from the open beakers.

Table 4.1: Material balance closures of four experiments

Category	lowest (%)	highest (%)
Total solids	51.9 (92.3)	103.5
Water	86.9	88.4
Chromium	83.5	98.6
Iron	95.8	113.5
Zinc	86.6	102.6
Lead	85.3	116.0
Cadmium	87.8	102.1

The low closure for total solids in one of the experiments was explained by the evaporation of HNO_3 in the drying oven, resulting in an understated value for the TDS. From the titrations of the leachates from experiments 7 and 8, the amount of HNO_3 in this leachate was estimated to be 0.93 mol/l; multiplying by the leachate volume of 875 ml gave an amount of 51.3 g of HNO_3. Adding this amount to the residual solids closed the mass balance to 92.3%.

From the closures reported in Table 4.1, it was concluded that uncertainties of up to $\pm$ 15% remained over the compositions and amounts measured in the experimental work. This error margin was accepted as sufficiently low to draw conclusions on process feasibility from the experimental data.

4.3 TOXICITY OF THE LEACH RESIDUES

Some of the acid leaching experiments described in the previous section had the explicit objective to produce a "disposable" residue. The aim of this section is to present the results of the investigations on the residues from these experiments.

In the following subsections, the meaning of "disposable" is defined, the TCLP results for the leach residues are presented and the disposal option is discussed for each of the dusts.

4.3.1 A Definition of "Acceptable for Disposal"

A definition of "disposable" has not been provided up to this point: this is difficult because regulations and conditions for the safe consignment of wastes to a landfill may vary by site, region or country. In this work the example set by the Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of the United States, discussed in section 2.2.1, was followed, under which the landfilling of any hazardous waste was prohibited in that country. By the "TCLP rule" (Albanese, 1990) any waste material not passing the TCLP must, in that country, be regarded as hazardous.

The first criterion for "disposability" of dust residues in this work was thus defined as the ability to pass the TCLP. Since only chromium, lead and cadmium had been identified as problem elements in the dusts, the TCLP extracts would only be analysed for these three elements.

An added concern for chromium-containing waste materials was discussed in chapter 2: this is the possible atmospheric oxidation of trivalent chromium compounds to the more mobile and toxic hexavalent forms.

A second criterion for "disposability" was thus added: this is the absence of any chromium compounds which could oxidise in the residue to be disposed. This would be verified by identifying (through discussion) the chromium species in the residue.

4.3.2 Toxicity of Leach Residues by the TCLP

The residues from all strong (1 N) acid leaches were tested for toxicity by the TCLP in the same way as described for the dusts in chapter 3. With three or four residues available from each test, the TCLP could be done in triplicate. For interest, a single TCLP was done for the residue from the mild (pH 5.5) leaching of the ferrochrome smelter dust.

Table 4.2 shows the average values obtained in these TCLP tests. The results presented in chapter 3 on the raw dusts have been included for comparison. The full results, which are tabulated in Appendix B, show good reproducibility for all analyses, as confirmed by the standard deviations presented in Table 4.2.

Table 4.2: TCLP results for dusts and leach residues

TCLP results	pH	Cr (ppm)		Pb (ppm)		Cd (ppm)	
(a) Ferrochromium dust		ave	s.d.	ave	s.d.	ave	s.d.
original	6.28	26.5	0.40	<0.20	n.a.	n.a.	n.a.
treated with 1 N H2SO4	4.90	4.7	1.60	0.40	0.03	n.a.	n.a.
treated with 1 N HNO3	4.90	3.1	0.19	<0.20	n.a.	n.a.	n.a.
treated with HNO3, pH 5.5	5.25	6.4	n.a.	<0.20	n.a.	n.a.	n.a.
(b) EAF/AOD dust							
original	6.94	66.7	1.54	<0.20	n.a.	0.349	0.016
treated with 1 N H2SO4	4.81	0.7	0.03	21.0	2.71	0.011	0.003
treated with 1 N HNO3	4.86	<0.50	n.a.	<0.20	n.a.	n.d.	n.a.
TCLP limit:		5.0		5.0		1.0	

ave = average, s.d. = standard deviation, n.d. = not detected, n.a. = not applicable

The appearance of lead in the sulphuric acid leach residues confirms the findings of Dreisinger *et al* (1990) that $PbSO_4$ in the leach residue must be regarded as toxic. The almost complete absence of lead in the untreated dusts was somewhat more surprising. It could, however, be explained by the pH of the extracts: at pH 7 the lead(II) hydroxide should be insoluble, whereas at pH 4.9 this would not apply. The buffering capacity of the untreated dust thus ensured that lead did not report to the TCLP extract. Similar findings were reported for zinc in TCLP extracts by Drews and Mahote (1994).

4.3.3 A Discussion of the Disposal Option

A process designed to produce disposable residues from chromium-containing dusts would have the aim to solubilize all leachable forms of chromium, lead and cadmium (and any other heavy metals), thereby separating them from the residue which could then be disposed. [An alternative philosophy is embodied in the S/S approach (cf. section 2.5.2.5), which aims to immobilise the heavy metals]. The questions that had to be answered by the experimental work were listed in the introduction to the chapter and can be restated as follows:

* Can a residue be produced that satisfies the TCLP requirements?
* Is any chromium oxidisable by air in the residue?
* What are the minimum leaching conditions?
* What does the leachate contain and how is it treated?
* What is the amount and composition of the leach residue?

In the next two sections, these questions are discussed for the two dusts studied experimentally.

4.3.3.1 Disposal of Ferrochromium Smelter Dust Leach Residues

The TCLP results (Table 4.2) showed that chromium mobility results in a hazard rating for the ferrochromium dust. They also showed that filtered and washed residues from leaching with either sulphuric or nitric acid had much lower mobile chromium contents, bringing them within reach of "acceptable disposal", as defined above. Interestingly, the sulphuric acid leach residues showed increased lead mobility (although well within acceptable limits), which is explained by the conversion of lead oxide in the dust to lead sulphate in the residue.

Since both sulphuric and nitric acid reduced the toxicity of the dust, a sulphate contaminated spent nitric pickling acid should be usable for the treatment of this type of dust. The low acid consumption of the dust should, however, be noted.

Only a small fraction of the total chromium in the dust was leached by either acid. The leach residue therefore contained the same or a higher chromium content as the dust. The concern that this chromium could oxidise with time, forming mobile hexavalent species, needed to be addressed. Since the dust appeared to be similar to the one studied by Cox *et al* (1985), their findings could be used to discuss this concern. These findings were that the dust contains three forms of chromium: a non-leachable chromium oxide chemically similar to chromite ore, a soluble Cr^{3+} salt and

soluble hexavalent species. Since chromite is not oxidized by atmospheric oxygen, it could be concluded that as long as all of the trivalent chromium salt (which might be oxidisable) can be leached, long-term atmospheric oxidation should not be an issue. This remains to be confirmed: research at the University of Cape Town is currently addressing this issue. In any event, a procedure should be developed for determining what forms of chromium have been left in the residue, should this approach to treatment be considered in practice.

The leachates resulting from either acid were shown to be high in dissolved salts and also contained significant metal concentrations. Hexavalent chromium, as evidenced by the yellow colour of the leachates, is also present. Further treatment consisting of reduction, neutralization, metal precipitation and desalination would be required. Ultimately, a hazardous sludge containing heavy metals might still be produced: in this instance, at least a hazardous waste volume reduction would have been achieved.

4.3.3.2 Disposal of Stainless-Steelmaking Dust Leach Residues

The TCLP results (Table 4.2) showed that the amount of mobile chromium in this dust is unacceptably high. Treating with either sulphuric or nitric acid brought chromium mobility in the leach residues under control. However, the lead mobility in the sulphuric acid leach residue increased dramatically, making this leach residue unacceptable for disposal. Cadmium mobility in both leach residues was reduced, being below detection limits of 0.01 ppm for the nitric acid leach residue.

The disqualification of sulphuric acid as leachant for lead containing dusts emphasised the question whether sulphate contaminated spent pickling acids can be used in the treatment of such dusts. Nitric acid experiments with sulphate additions showed no reduction in lead removal for low concentrations of sulphates, but a strong reduction for heavily loaded solutions. Leach residues were not subjected to the TCLP, but with $\pm$ 70% of the lead left in the residue, these were expected to show similar trends to sulphuric acid leach residues. **This meant that spent pickling acids containing sulphates in the g/l range would not qualify for the treatment of lead containing EAF/AOD dusts under the disposal objective.**

If no sulphate-free waste acid is available, commercial grade nitric acid would have to be used for this treatment. In this case, the acid consumption of $\pm$ 6 mol/kg dust should be noted as an input requirement for the dust treatment process. [*Note: this figure is mentioned here in conjunction with the reasons stated in section 1.4.*]

The second concern for acceptable disposal - the chromium content of the residue - is addressed by the following considerations: Analyses of the leachates and residues (tabulated in Appendix B) showed that only $\pm 10\%$ of the chromium in the dust was leached, resulting in an increased chromium concentration in the leach residue. The chemical form of this residual chromium is not known and is critical for the long-term stability of the leach residue. Methods for determining it would, again, need to be developed, if the disposal option is to be pursued.

The leachates from either acid were characterized by high metal concentrations. These would have to be removed by neutralization and hydroxide precipitation prior to discharge as effluent.

4.4 RECYCLABILITY OF THE LEACH RESIDUES

While the previous section interpreted the experimental findings with respect to acceptable disposal of solid wastes, this section is concerned with the possibility of recycling such materials to the processes from which they originate.

Specifically, it was one of the aims of the leaching experiments to determine whether chromium-containing dusts can be treated by leaching to yield residues which are acceptable for recycle to metal production furnaces.

Similar to the previous section, a definition of what is meant by "acceptable for recycle" needs to be made. This definition is followed by a presentation of the relevant experimental results. The section is concluded by a discussion of the recycle option for each of the dusts.

4.4.1 A Definition of "Acceptable for Recycle"

The recycle of a waste material is given a higher preference than its treatment by the Waste Minimisation philosophy. As discussed in chapter 2, it is the first strategy to be considered after elimination and source reduction.

Also in chapter 2, it was mentioned that several attempts to recycle EAF/AOD baghouse dusts from stainless steel production to the EAF have been made. After finding a solution to the handling of such fine materials in the furnace environment, most programmes reported a build-up of deleterious elements in the recycled dust: zinc and lead were generally singled out. This accumulation led to the abandonment of the recycle strategy in favour of treatment

and recovery of chromium and nickel values in a separate, dedicated pyrometallurgical operation.

There are, thus, two criteria that a material must satisfy to be recycled to the EAF: (1) its physical structure must be appropriate for the furnace environment and (2) its chemical composition has to be sufficiently low in harmful and unwanted elements. Solutions have been reported for the former criterion; the focus of this experimental work has thus been on the latter.

The most comprehensive way of determining whether a leach residue would be acceptable for recycle to the furnace would be a full scale or pilot plant trial, in which the concentration in the dust of each unwanted element would be monitored. Since such trials are expensive, a theoretical prediction using computer simulation of the pyrometallurgical process, such as that developed by Jones (1989) for stainless steel production, might be favoured. Without access to either, worst case assumptions can be made to derive a definition of "recyclable".

This last approach was taken in the experimental work. The unwanted or "tramp" elements were identified as Zn, Pb, Sn, P and S.

For zinc, it was assumed that all the zinc in the furnace reports to the dust (see Ullrich and Schicks, 1991), but that increased zinc concentrations in the dust would not cause operability problems. (The range of zinc concentrations reported for EAF dusts lends credibility to these assumptions.) Still, a significant fraction of the zinc would have to be removed before recycling of the residue would become acceptable. This fraction was arbitrarily set at a third, which would mean that the zinc concentration in the dust would triple as a result of recycling, all other factors unchanged.

Similar assumptions were made for lead, except that the tolerated increase in its concentration in the dust was limited to a doubling because of the harmful effects on refractories. 50% or more of the lead would thus have to be removed to make a residue recyclable.

Tin, sulphur and phosphorus were merely identified as elements of concern: their behaviour in the leaching experiments was to be observed and recorded. The reasons for this were that all three report to either or both the metal and slag phases in the EAF and would thus not accumulate indefinitely as a result of dust recycling.

For the purposes of this work, a recyclable residue was thus defined as one in which a significant fraction of the tramp elements Zn (> 0.33) and Pb (> 0.5) has been removed, with a fractional removal of Sn, S and P also desirable.

4.4.2 Tramp Element Removal Efficiencies

The percentage removals achieved for Zn and Pb, as well as for some of the elements desired to remain in the residue (Cr, Fe, Ni), were calculated from the measured concentrations and are listed in Appendix B (Table B.6) together with an explanation of the calculations used.

The most important findings were that:

* good zinc removals (25% to 45%) could be achieved for either dust by leaching with either 1 N acid. They dropped to 5-10% when leaching at a pH of 5.5.

* complete lead removals could be achieved by leaching EAF/AOD dust with 1 N nitric acid, but virtually no lead was leached under any other conditions. For ferrochrome smelter dust, the figures were 12% (sulphuric) and 28% (nitric) for strong acid leaching with no lead removed at pH 5.5.

* small amounts of sulphates did not impact on the ability of nitric acid to remove lead, but at 14 g/l sodium sulphate caused lead recoveries to drop to a third of the original value.

* significant removals of iron (up to 17%) and nickel (up to 28%) occurred at the strong leaching conditions, but leaching at pH 5.5 dissolved no mentionable amounts. The differences were not as pronounced for chromium with 10% in the highest case and 1% in the lowest.

For tin, sulphur and phosphorus the following observations were made:

* Tin was only detected in the EAF/AOD dust. In the strong acid leachates from this dust small concentrations of this element were found, indicating that at least a partial removal could be achieved. The leachates at pH 5.5 contained no tin.

* Sulphur was only detected in the ferrochromium smelter dust. This sulphur could be virtually completely removed by all of the leach conditions studied. For the EAF/AOD dust significant sulphate precipitation into the leach residue was observed

when leaching with strong sulphuric acid. To what extent this phenomenon took place in sulphate-containing nitric acid was not determined.

* The XRF analyses showed the amounts of phosphorus in both dusts (cf. table 3.3). The analyses of sulphuric acid leach residues by the same analysis method showed much reduced P_2O_5 values for EAF/AOD dust (0.018%) and a slight reduction for ferrochrome smelter dust (0.009%).

These findings could then be applied to evaluate the option of leaching chromium-containing dusts and recycling the residues.

4.4.3 A Discussion of the Recycle Option

The specific questions that the experimental work had to answer in order to arrive at a conclusion on recycling were listed in the introduction to the chapter and can be restated as follows:

* Can a process be designed that removes sufficient amounts of Zn, Pb, Sn, S and P?
* What type of acid can be used?
* What are the minimum leaching conditions?
* What impurities must be avoided?
* What does the leachate contain?
* What is the amount, composition and moisture content of the leach residue?

The experimental results for the two dusts were interpreted as follows:

4.4.3.1 Recycling of Ferrochromium Smelter Dust Leach Residue

The low concentrations of chromium, nickel, molybdenum and iron in this dust were noted. They make recycling inherently unattractive. Chromium seemed to occur as chromite in the larger particles: a physical separation could thus be considered for the selective recovery of chromium from this dust. It should be noted that this would, however, not remove the bioavailable chromium, which according to the findings of Cox *et al* (1985), is located in the small, submicron particles.

The percentage removals of Zn and Pb in the 1 N acid approached values which would make this dust recyclable, although the effect of a low lead removal would

have to be studied. The sulphur could be almost completely removed, while a degree of phosphorus removal seemed to have occurred with sulphuric acid.

Leaching at pH 5.5 removed only a small fraction of the zinc and none of the lead.

Based on these results, only the stronger leaching conditions might produce an acceptable leach residue.

The leachates from this type of leach is dominated by a high salts content. It further contains the removed Zn and Pb as well as Cr (in the hexavalent form, as witnessed by the yellow colour) and Fe, but is strongly acidic. Further treatment of this leachate would commence with chromium reduction and neutralization. Metal precipitation and desalination would be essential before discharge as effluent.

4.4.3.2 Recycling of Stainless-Steelmaking Dust Leach Residue

The removals of Zn and Pb achieved by leaching with 1 N nitric acid were in excess of the required amounts. Tin was also at least partially leached, while sulphur was not present in the dust in significant amounts. A degree of phosphorus removal has been demonstrated with sulphuric acid.

Neither the leach at pH 5.5 nor the use of sulphuric acid resulted in lead dissolution. The results at pH 5.5 were surprising, as lead hydroxide should only precipitate at a pH of 6.0 according to Dean *et al* (1972).

Sulphates in nitric acid were found to reduce lead solubility by up to 70% when present in the g/l range. Significant amounts of lead could, however still be removed. Low sulphate concentrations (100s of ppm) had no effect in this regard.

Based on these results, leaching this type of dust for an hour with 1 N nitric acid would produce a recyclable leach residue. Spent pickling acids derived from nitric acid could be used, with a recognition of the impact of sulphate levels on lead solubility an sulphur levels in the leach residue.

The leachate from such an acid leach would contain large concentrations of iron, nickel and other metals as well as salts. To produce a reasonably concentrated zinc hydroxide sludge, which could be sold to the zinc industry as a raw material, an attempt should be made to leach more selectively. With good removals of zinc and lead obtained with 1 N acid, leaching at a pH of 3 or 4 might still result in good

removal of these and a much reduced iron concentration, since ferric hydroxide should precipitate in this pH range. To recover the zinc values, neutralization of the leachate with lime would be required followed by filtration or thickening of the resulting hydroxide sludge. Desalination might then be added before discharge of the remaining solution as effluent. Chromium reduction could be another processing step: the blue-green colour of the leachate does, however, indicate the predominance of the trivalent form.

4.5 CONCLUSION

This chapter has described the experiments which were designed to verify the hypothesis that chromium-containing dusts can be treated hydrometallurgically. The experimental findings have been presented and interpreted.

It has been shown that a ferrochromium smelter dust can be leached to yield a residue acceptable for disposal, but that the low metal values contained in the dust would make recycling unattractive. Nevertheless, should recycling be required, leaching could - with some qualifications - be used to prepare the dust for this.

For a dust from the furnaces of stainless steel production, leach residues could be produced which were acceptable both for disposal or recycle. The disposal option would require an investigation into the form of the remaining chromium.

The possibility of using sulphate contaminated nitric acid for the leaching was investigated and found to be practicable only for the recycle option. This means that spent pickling acids can, even if sulphate-contaminated, be treated concurrently with baghouse dust with due attention given to the fate of the sulphur.

The hypothesis that chromium-containing dust can be treated hydrometallurgically has thus been substantiated. It should, however, be noted that the chromium will tend to remain in the solid residue and that hydrometallurgical treatment should thus be seen as a pretreatment step to either metal recovery by smelting or to safe disposal.

5. DEVELOPMENT OF THE HYDROMETALLURGICAL PROCESS

5.1 INTRODUCTION

The findings of the experimental work described in the previous chapter supported the hypothesis that chromium-containing flue dusts can be treated by hydrometallurgical means to yield residues acceptable either for disposal or for recycle.

The experimental results are used in this chapter to develop a process description for the treatment of such dusts. The development of the process within this thesis is necessitated by the second hypothesis, which states that the environmental burdens of hydrometallurgical processing would be lower than those of pyrometallurgical treatment. To verify this claim, indications of the environmental impacts arising from both treatment processes are required. This exercise, in turn, requires an understanding of the nature of the two processes.

The pyrometallurgical process chosen for the comparison has been described in chapter 2. The material flows (reagents, products, effluents and wastes) and total energy requirements were identified from reports on the operation of the process. It is the aim of the current chapter to provide an equivalent description of the hydrometallurgical process. To enable this, the experimental results are first used to design a treatment process to flow diagram level. The material flows in each of the operations constituting the treatment process are then predicted. Finally, the energy requirements of the subprocesses are estimated and added to give the total process energy requirement.

The experimental work described in chapter 4 showed that both disposal and recycle options in the hydrometallurgical approach are technically feasible. However, the process design is based on the recycle option only; this makes the process functionally equivalent to the pyrometallurgical option. Also, only the stainless steel furnace dust is considered for the design: this is motivated primarily by the fact that no description for ferrochromium smelter dust treatment could be found to serve as the basis for a comparison.

The development of the process entails creating process flow diagrams, compiling material balances and estimating energy requirements. The last three sections of the chapter deal with these three topics.

5.2 SELECTION OF AN OPTION FOR FURTHER STUDY

It was shown experimentally that both chromium-containing dusts selected for the study could be treated to:

* yield residues meeting TCLP requirements (and could, thus, be disposed safely in a landfill subject to certain restrictions) and

* reduce tramp elements sufficiently to enable recycling of the residues.

However, the ferrochromium smelter dust did not contain significant amounts of valuable metals (Cr, Ni, Fe); this makes recycling inherently unattractive. Nevertheless, a decision to landfill it should be made only after weighing up all the known landfill disposal costs against the recycle option. The stainless-steelmaking dust, on the other hand, contained large fractions of metals valuable in steel production: the recycle option would seem to be preferable.

At this point, the first hypothesis, viz. that chromium-containing dusts can be treated by hydrometallurgical means, has been substantiated. Our attention now turns to the claim - stated in the second hypothesis - that such a process would be preferable to high-temperature treatment on the basis of environmental performance. The immediate predicament of this statement is that not one, but two different hydrometallurgical processes would seem to be preferable for the treatment of the two dusts.

However, as discussed in the introduction to this chapter, the lack of a suitably described treatment process for ferrochromium smelter dust to serve in the envisaged environmental comparison negates any further investigation on this type of dust in the context of this thesis.

The validation of the second hypothesis - by a comparative environmental assessment - is thus restricted to stainless-steelmaking dust. The recommended option for this type of dust is the use of acid leaching to prepare a residue acceptable for recycle to the electric arc furnace, with suitable treatment of the leachate.

In the following sections, the process for the "recycle option" for stainless-steelmaking dust is presented in more detail. Material flows and energy requirements are estimated; these estimates are required for the comparative environmental assessment, which is presented in chapter 7.

5.3 DESCRIPTION OF THE SELECTED PROCESS

It was argued in the conclusion to chapter 4 that the hydrometallurgical process to treat stainless-steelmaking dust is effectively only a pretreatment to allow recycling. The complete process thus consists of this pretreatment and of smelting of the residue in the EAF. Nevertheless, since the EAF is already a part of a conventional stainless steel producing operation, a "treatment" process, if built, would consist only of the hydrometallurgical dust beneficiation, its associated leachate treatment and disposal systems and a residue preparation plant, the function of which would be to agglomerate the residue to allow handling in the EAF (cf. section 2.5.2.1).

Any assessment of the process, be it economic or environmental, should, however, also take into account any changes that could occur in the operation of the EAF. Such changes, attributed to differences between the residue and normal EAF feed materials, could occur in electrical energy requirement, dust generation or amount of slag, to name just three examples.

A block flow diagram for the proposed dust treatment process is shown in Figure 5.1. Each of the three parts of the process is described in turn in the following sections.

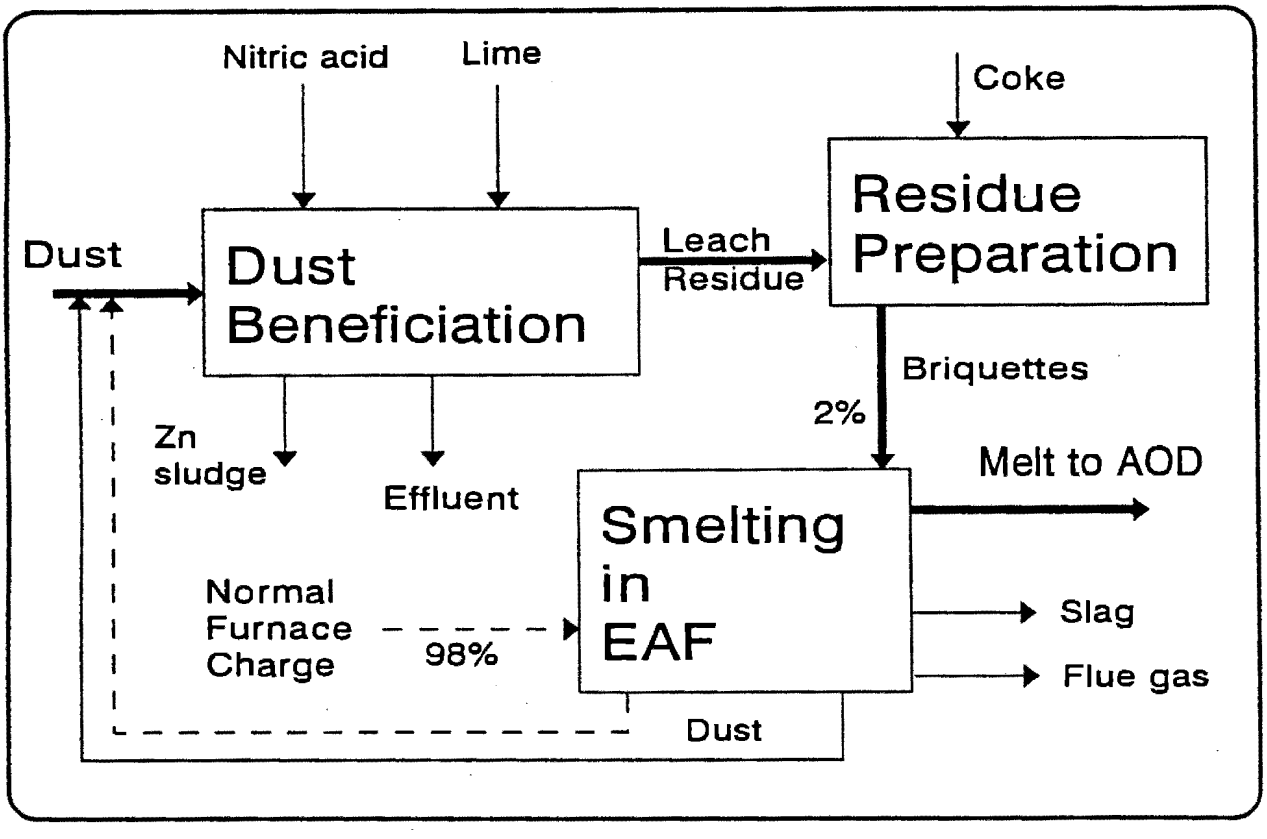


Figure 5.1: The "hydrometallurgical" process for the treatment of EAF/AOD dust

5.3.1 Description of the Hydrometallurgical Beneficiation Plant

A proposed process flow diagram for the beneficiation plant is shown in Figure 5.2. At the core of the process is the acid leaching of the chromium-containing dust. Spent pickling acid or acidic rinse waters from the pickling operations in stainless steel production can be used for this, provided that the effect of sulphate levels on lead removal and sulphur in the residue has been studied. A final pH sufficiently low to keep lead in solution is aimed for in leaching; from metal hydroxide solubility regimes (e.g. Dean *et al*, 1972) it is anticipated that this will lie between 3 and 5, which should result in most of the iron and trivalent chromium precipitating into the leach residue. If necessary this pH is achieved by the addition of slaked lime.

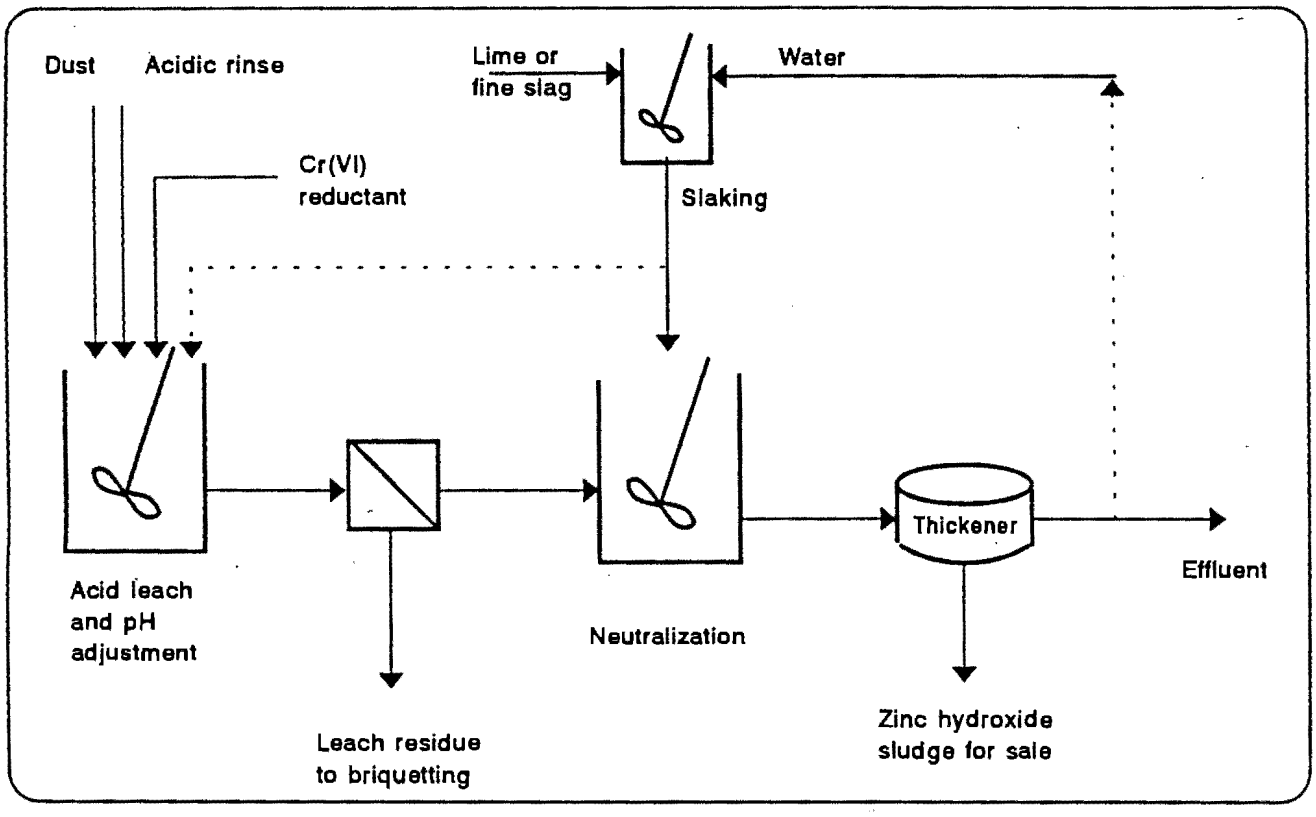


Figure 5.2: Process flow diagram for dust beneficiation

For the purposes of the assessment the leaching plant was assumed to be operated in batch mode. This is a reasonable assumption as the amount of dust to be processed from a normal stainless steel producer is relatively small. (A 500000 tpa steel plant would generate between 5000 and 10000 ton of dust per year). More importantly, the amounts and compositions of

dust and especially acid could vary significantly as both are waste products and therefore not controlled: batch plants are well suited to cope with such variations.

Acid leaching is followed by a separation of the leach residue from the leachate by filtration. The leach residue is sent to the residue preparation plant (shown in Figure 5.1).

The zinc and lead - and any other metals, except hexavalent chromium, in the leach residue - are precipitated as hydroxides by the neutralization of the leachate with slaked lime. A zinc-rich sludge is separated from the neutralized solution either by a thickener or by a second filtration.

If the neutralized solution contains hexavalent chromium, this should be reduced and precipitated as a hydroxide and added to the leach residue for return to the furnace. The remaining saline solution is either discharged as effluent or treated to recover salt mixtures and water for re-use. It will be assumed here that it can be discharged (as in the case study reported by Drabkin and Rissmann, 1989). This assumption is a simplification and not applicable to the situation where receiving water guidelines do not allow such a practice. Where more restrictive measures are in place, the recovery of the salts could be achieved by evaporation and crystallisation; their subsequent use or disposal would also have to be addressed.

5.3.2 Description of the Residue Preparation Plant

While the beneficiation plant makes the chemical composition of the dust acceptable for recycle, the function of the residue preparation plant is to alter its physical state. Any material charged to the EAF must be sufficiently dense to sink into the melt, strong enough to allow handling and storage, intimately mixed with the correct amount of reductant and relatively dry - as the generation of water vapour leads to decrepitation which, in turn, causes dusting - (Kaas *et al*, 1984).

The process most commonly used to prepare dusts for recycle is pelletizing. Kaas *et al* (1984) have argued that the density of dust pellets is insufficient to allow them to sink into the melt where they can react. Increased amounts of dust were observed from a furnace to which pellets were charged and the recycling process was therefore not effective. A briquetting process (discussed in section 2.5.2.1) was proposed by these researchers. This suggestion is followed here.

The briquettes are formed by pressing a mixture of the leach residue (moisture content adjusted), grinding swarf (cf. Table 2.1), binder and metallurgical reductant to about

25 kN/cm^2. The grinding swarf adds mechanical strength and increases the density; this is another example where the concurrent treatment of wastes is beneficial. Portland cement can be used as a binder. The selected reductant is coke breeze; the reasons for its use are discussed in section 5.3.3 below.

The proposed residue preparation plant (Figure 5.3) consists of a drier, a mixer and a briquetting press, together with the associated storage bins, hoppers and conveyors. The mixture to be briquetted should have a moisture content of 6-8% (Kaas *et al*, 1984).

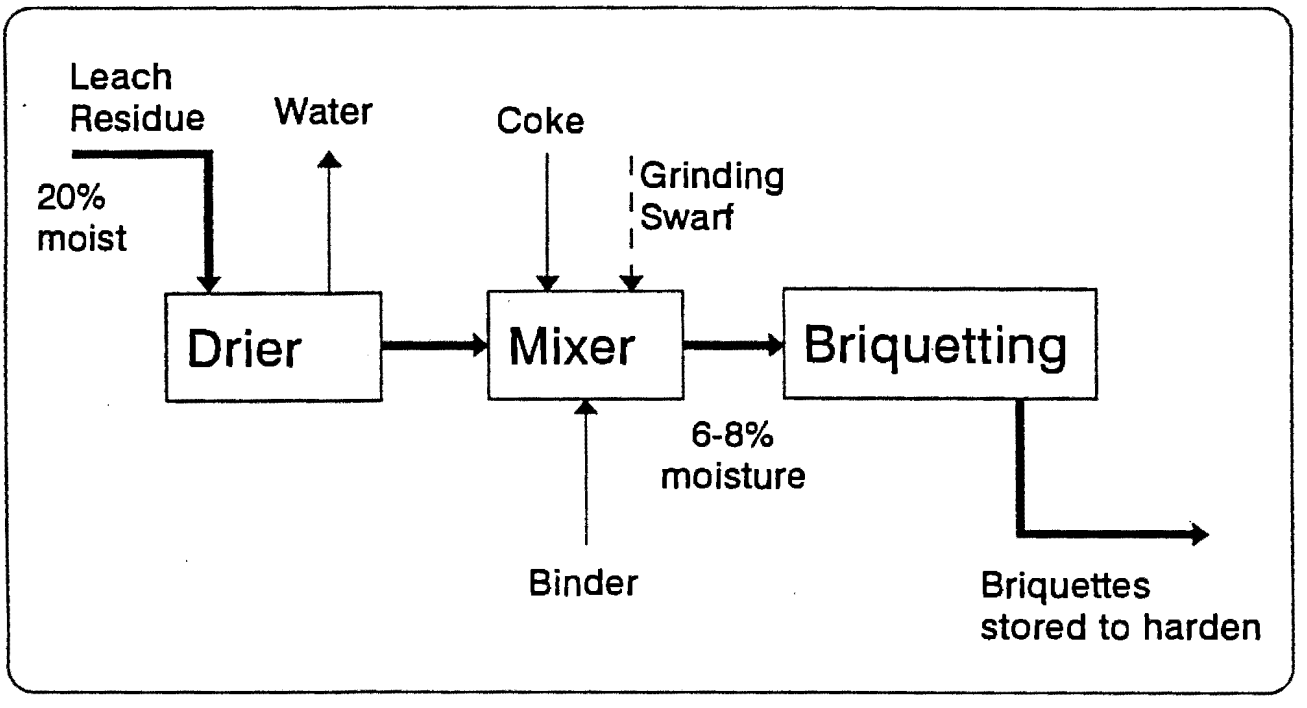


Figure 5.3: The Leach Residue Preparation Plant

5.3.3 Notes on Smelting in the Electric Arc Furnace

The prepared leach residue can be smelted in the EAF as a separate charge, producing a crude ferroalloy, or as part of the normal operation leading to the stainless steel product. As discussed in section 2.5.2.3, both approaches have been demonstrated with a mixture of furnace dusts, grinding swarf and mill scale. The latter method would seem preferable, as it has a lower overall energy consumption (it avoids the remelting of the crude ferroalloy), and utilises the EAF more efficiently. However, metallurgists' fears of product contamination favour the former (Kaas *et al*, 1984).

Here it is assumed that the residue can be smelted in the EAF during the normal operation. This is justified, because tramp elements are purposefully removed in the hydrometallurgical process. Further, Neumeier and Adam (1988) predicted that up to 20% of the scrap charge to the EAF could be replaced by a mixture of steel plant wastes. This is much higher than the 1-2% of the charge converted to dust. Recycling of a fraction of the dust should, therefore, not have a major influence on the operation of the EAF.

Furnace operating parameters that could change are:

* additions of reductants (e.g. coke or ferrosilicon) and slag basicity modifiers (e.g. limestone);

* electrical energy consumption;

* and slag, melt, flue gas and dust amounts and compositions. Attention must be paid to all elements which report primarily to the dust, as they are potentially brought into a closed system, if they cannot be separated in the leaching process. They would accumulate in the recirculating dust/leach residue and could cause quality, safety and operability problems.

A coal-based reductant is proposed for addition to the briquettes. As discussed in section 2.5.2.3, Neumeier and Adam (1988) found that a 10% coke breeze addition was effective for the reduction of a mixture of stainless steel plant wastes in an EAF. Ferrosilicon, which has also been shown to be effective, lowers the basicity of the EAF slag, which must be corrected by the addition of lime. The basicity (defined as the ratio of CaO + MgO to SiO_2) controls the equilibrium amount of chromium in the slag and, hence, the recovery of chromium to the melt.

Based on the findings of Neumeier and Adam (1988), it is assumed that the reduction of the dust residue contained in the briquettes can be achieved with additional coke only. The amounts of metal, slag, flue gas and dust have to be calculated: this is the subject of section 5.4.3.

5.4 MATERIAL BALANCES FOR THE SELECTED PROCESS

In this section, material flows - including those of reagents, products, effluents and wastes - are estimated for the three processes making up the proposed "hydrometallurgical" treatment process. The basis for all calculations is 1000 kg of dust.

(ii) Data collection: The data entered into PEMS for the beneficiation, briquetting and smelting processes is shown in Table 7.1 (Appendix G). (In the table, the REF. column contains the entered data; the CAL. column contains the amounts calculated after application of the allocation rules and balancing of the flows, cf. section 6.4.2.) Identical data sets have been used for the briquetting and smelting operations of the two configurations (nitric acid and spent pickling acid), but an imaginary co-product called "neutralised acid" has been added in the beneficiation process of the case employing spent pickling acid (shown in part (d) of Table 7.1). The reason for this is explained in the next section dealing with allocation. Each of the processes has been informed from the material balances and energy requirements described in chapter 5.

The other processes shown in Figure 7.3 derive their inputs from the PEMS database. The option of average European values has been used for electricity generation. The transportation of coke and nitric acid is assumed to be by electric rail over a distance of 200 km and for lime by truck of medium size for 50 km.

(iii) Allocation: The only by-product in the system is the zinc hydroxide sludge. It is treated as an open-loop output, meaning that it does not take a share of the system's environmental burdens away from the primary function, which is to treat the dust.

In the system using spent pickling acid an allocation problem arises from the concurrent treatment of waste from another system in the beneficiation process. This is addressed by allocating half of the environmental burdens of the dust beneficiation process to a byproduct, viz. neutralised acids. The approximately equal amount of dust (1000 kg) and nitric acid content (1260 kg) of the two wastes justifies this choice. It is acknowledged that more sophisticated allocation "rules" exist; they are, however, not explored here. The effect of this allocation can be seen from a comparison of sections (c) and (d) of Table 7.1, with the calculated burdens (CAL. column) being halved for the beneficiation process.

(iv) The inventory table, calculated by the PEMS computer model, is shown in Table 7.2 (Appendix G). The effect of using spent pickling acid rather than nitric acid, without making an allocation for the co-treatment of this waste, is also shown. The main differences between the three options are seen to be the total energy requirement, NO_x emissions and nitrates in the liquid effluent. The effect of the allocation decision is seen especially in this last item.

7.4.2 LCI of Dust Treatment in the Plasma-Shaft Furnace

(i) Subsystems definition: The primary subsystem is the PlasmaDust (TM) process, as shown in Figure 2.3. It is treated here as a single process, with streams 1 to 5 entering and streams 10 to 15 leaving.

Raw materials for the PlasmaDust (TM) process are sand, coal and coke: subsystems are defined for the extraction/production and transportation of each of these. Electricity generation forms another subsystem.

Of the streams leaving the PlasmaDust (TM) process, the slag, fluoride sludge and effluent are environmental outputs: while the slag can be deposited safely or even used in another economic activity, the sludge must be contained in a hazardous waste landfill.

The ferroalloy must be remelted in a stainless steel EAF, before it has the same form as the equivalent product in the hydrometallurgical process, this form being the molten feed to the AOD. The zinc oxide sludge leaves the system as an open-loop output and enters another economic system, viz. that of zinc production. Finally, the fuel gas produced in the PlasmaDust (TM) process is eventually converted to gaseous emissions. The system can be credited for the exported heat, which reduces environmental impacts elsewhere.

A process tree showing the subsystems and their connections is shown below.

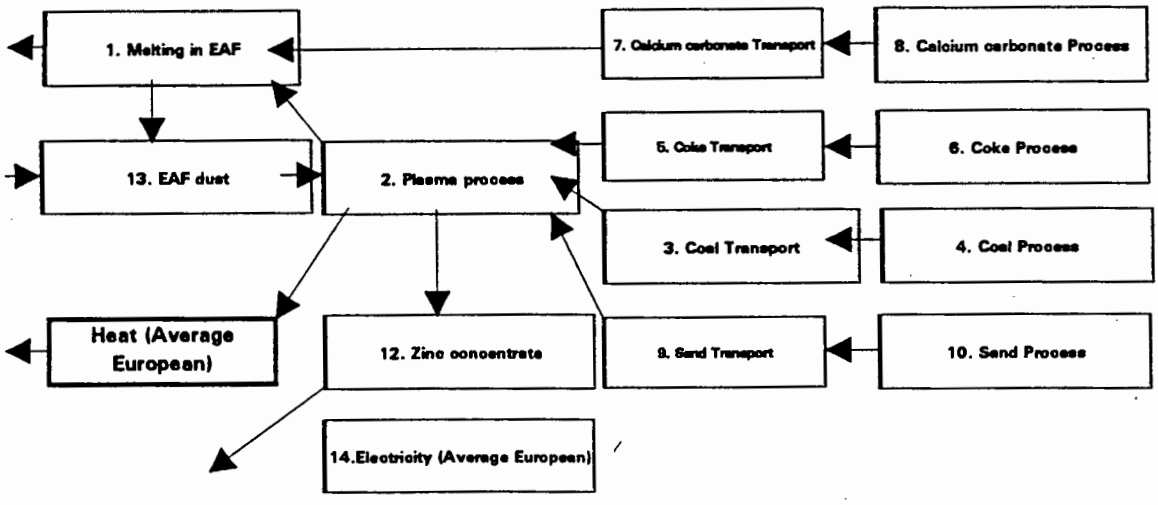


Figure 7.4: Process tree for pyrometallurgical treatment of EAF dust (produced from the PEMS template).

(ii) Data collection: The data entered into PEMS for the PlasmaDust (TM) process and for melting in the EAF are shown in Table 7.3 (Appendix G).

The PlasmaDust (TM) process is based on the material balance presented in Table 2.5 (Appendix G), with dust, mercury and cyanide emission data added from Johansson and Löfgren (1991). The net air consumption is based on the stoichiometric requirement for the combustion of the fuel gas. The material balance difference deviates by 20 kg from that in Table 2.5, the reason for this is that the components of the flue gas in that table do not add to the quoted total.

Data for melting in the EAF has been restricted to energy and limestone requirements and dust generation. It is assumed that the PlasmaDust (TM) ferroalloy behaves like ferrous scrap, when remelted, except that no coke needs to be added because of the 5% carbon content of the ferroalloy. The figures for energy and limestone requirement are from Boustead and Hancock (1982).

All other processes derive their inputs from the PEMS database. Electricity generation uses the option of average European values. The transportation of sand is assumed to be by medium-sized truck over 50 km, while coal and coke are assumed to be transported by electric rail over a distance of 200 km. The assumptions for the transportation processes are the same as those made for the hydrometallurgical process.

(iii) Allocation: Only one process in the system calls for a decision on allocation: this is the PlasmaDust (TM) process itself, which generates saleable zinc and heat as byproducts.

The zinc oxide sludge can again be treated as an open-loop output, meaning that neither is the system held liable for any further emissions caused by use of the zinc, nor is the production of zinc allocated a share of the environmental interventions from the treatment of the dust.

On the other hand, the production of heat has to take such a share of the burdens, but deciding on the size of that share is complicated, as energy units have to be compared with mass units. Earnings from dust treatment and heat export could form a defensible basis for the decision. Economic data was, however, not available. Instead, it has been decided to credit the system for avoided emissions due to municipal heat not produced. The amount of heat is calculated from the calorific value of the fuel gas multiplied by an efficiency of conversion (50%) and a factor of 50% for heat actually

exported (since some is used internally in the driers and some of the fuel gas is burned in the flare). An overall conversion of 25% is thus used to calculate the amount of heat exported from the calorific value of the fuel gas: Eggels and van der Ven (1994) used the same value for an MSW incinerator.

(iv) The inventory table, containing results for a no-heat-credit and a 50%-heat-exported system is shown in Table 7.4 (Appendix G). It is seen that the configuration in which environmental credits are obtained for heat export has markedly lower values for energy use and gaseous emissions.

7.5 IMPACT ASSESSMENT FOR THE COMPARATIVE LCA

Proceeding from the inventory tables obtained for the hydro- and pyrometallurgical processes and their variations, an impact assessment can be performed. The following subsections show that the initial impact assessment uncovered a flaw in the allocation rules used in the inventory analysis phase. After addressing this, a revised impact assessment is presented.

7.5.1 The Initial Impact Assessment

The Problem Oriented Approach (discussed in chapter 6) was used, with all 10 impact categories available in the computer model included at first. It should be noted that the model is only tentative for human toxicity and aquatic ecotoxicity, owing to ongoing developments in the development of equivalency factors in these categories.

On inspection of the classification factors in the computer model it was found that the value for the human toxicity of chromium had been quoted incorrectly from the data source (Heijungs *et al*, 1992a). The value of 6.7, which is the human toxicological classification factor of chromium(III) for air (HCA), was replaced with 0.57, which is the HCW (equivalent factor for water) for chromium(III). The computer model did not allow a distinction to be made between the two valency states of chromium: with an HCW of 4100 for Cr(VI), this can be a serious shortfall.

Normalization, using the global factors incorporated in the model, was carried out as part of the impact assessment. Valuation was excluded, as no basis could be found for selecting a particular set of valuation factors. This meant that the results of the impact assessment had

to be presented graphically or as sets of numbers, since no single numerical result could be obtained.

The results of the impact assessment are shown numerically in Table 7.5 on the next page.

7.5.2 Inspection of the Initial Impacts

An inspection of the normalized impacts shows that they are dominated by nutrification impacts for the hydrometallurgical options, which are a hundredfold higher than any other impacts. Before any other comparisons can be made, these nutrification impacts have to be examined.

The environmental interventions classified in the computer model as contributors to nutrification are NO_x (0.13), nitrates (0.42), phosphates (1.0), ammonia (0.33) and COD (0.022). (The equivalency factors shown in brackets). In the inventory tables of the hydrometallurgical option (see Table 7.2), the amounts of ammonia and COD are zero, while phosphates and NO_x are two to three orders of magnitude lower than nitrates. The high values of the nutrification impact can, thus, be linked exclusively to the emissions of nitrates from the dust beneficiation plant.

In the case of nitric acid use, the nitrates are imported as part of the acid with the specific aim to treat the dust. However, in the case of concurrent treatment of dusts and spent pickling acids, the nitrates originate exclusively from the pickling acid. Even in the case of pyrometallurgical dust treatment, the spent pickling acid, and thus the nitrates, exist independently. This indicates that they should not fall within the boundary of the dust treatment system.

The allocation rule, whereby 50% of the environmental burdens of the dust beneficiation plant were allocated to pickling acid neutralization, is thus considered inapplicable. It seriously skews the environmental profile of the dust treatment process.

A better approach to allocation would consist of the separation of the environmental burdens of the dust beneficiation plant into three groups: those that can be traced to the dust (e.g. mercury and cadmium), those that can be traced to the pickling acid (e.g. nitrates) and those common to both (e.g. electrical energy requirements for the agitation of the leaching vessel). Allocation would then be by group, with a fractional approach optional for the third set.

PROBLEM ORIENTED REPORT

Non standard template used :- pemscr3.xls	Plasma treatment onsite	Plasma onsite with heat export	Treatment using nitric acid	Treatment using spent acid, no allocation	Treatment using spent acid, with allocation	Normalisation Factors (/E+9)
Fossil reserve depletion (Kg Oil)	214.5	183.3	383.9	161.9	131.8	[illegible]
Greenhouse - direct (Kg CO2)	2129.7	1999.5	2215.1	1690.7	1288.3	[illegible]
Greenhouse - Indirect (Kg CO2)	417.2	388.8	730.2	203.8	161.2	[illegible]
Ozone depletion (Kg CFC 11)	0.034	0.031	0.044	0.021	0.018	[illegible]
Acidification (Kg SO2)	22.4	21.2	28.0	15.0	12.0	[illegible]
Nutrification (Kg Phosphate)	1.3	1.2	527.7	526.1	263.2	[illegible]
Photochem. smog (Kg of Ethylene)	0.047	0.043	0.062	0.029	0.025	[illegible]
Human toxicity (Kg body weight)	26.3	24.8	33.8	18.3	14.9	[illegible]
Aquatic ecotoxicity (m3)	0.002	0.002	0.027	0.026	0.013	[illegible]
Landfill volume dm3	259.8	256.3	182.3	164.7	155.7	[illegible]

Normalised Results - % of the years production (x E+9)	Plasma treatment onsite	Plasma onsite with heat export	Treatment using nitric acid	Treatment using spent acid, no allocation	Treatment using spent acid, with allocation
Fossil reserve depletion	3.75	3.22	6.74	2.84	2.32
Greenhouse - direct	6.65	5.30	5.88	4.48	3.42
Greenhouse - Indirect	1.11	1.03	1.94	0.54	0.43
Ozone depletion	3.35	3.10	4.42	2.09	1.78
Acidification	7.85	7.41	9.78	5.23	4.19
Nutrification	1.80	1.67	705.55	703.28	351.89
Photochem. smog	1.25	1.16	1.66	0.78	0.66
Human toxicity	4.57	4.31	5.88	3.29	2.59
Aquatic ecotoxicity	0.00	0.00	0.00	0.00	0.00
Landfill volume	6.24	6.15	4.38	3.96	3.74

Table 7.5: Results of the initial impact assessment

7.5.3 The Revised Impact Assessment

To illustrate the effects of such an approach, a fourth life cycle inventory has been calculated for the hydrometallurgical process, with the nitrates in the dust beneficiation plant allocated as open-loop outputs, so that they fall beyond the system boundary. No allocation has been made for all remaining interventions in this process step, which results in an over-estimation of the environmental impacts of the process. The results are compared to those of the other hydrometallurgical options in Table 7.6 (overleaf).

The nutrification impact in the revised assessment is thus seen to be comparable in magnitude to that of the pyrometallurgical treatment. With the dominating effect of nitrates from pickling acid excluded from both systems, this is expected. The higher value for the hydrometallurgical system can be traced to the presence of phosphates from the dusts, a figure on which not much confidence could be placed (cf. chapter 4).

A graphical comparison of the two pyrometallurgical options with two hydrometallurgical process options (employing nitric acid and spent pickling acid, based on the revised assessment), is shown in Figure 7.5 (on the page after next). The nitric acid process, for which the nitrate problem remains, is seen to be the only process not comparable in the range of its normalised impacts. The impact categories of indirect greenhouse effect, photochemical smog and aquatic ecotoxicity are not shown on the graph.

7.6 DISCUSSION OF THE ENVIRONMENTAL PROFILES

7.6.1 Major Differences in the Environmental Profiles

From Figure 7.5, it can be seen that the environmental impact of the hydrometallurgical option using spent pickling acid is lowest in all categories except nutrification, where it is more than three times as high as that of the pyrometallurgical process. On the other hand, the hydrometallurgical process employing imported nitric acid for the leaching plant has the highest normalised impacts in all categories except landfill volume where it ranks second lowest at $\pm$ 70% of the requirement of the plasma process. The nutrification impact of this process is a 100 times higher than that of the second-ranked process in this category.

PROBLEM ORIENTED REPORT

Non standard template used :- pemscr3.xls	Nitric acid	Spent pickling acid, no allocation	Spent pickling acid, allocation by fraction	Spent pickling acid, nitrate allocation	Normalisation Factors (/E+9)
Fossil reserve depletion (Kg Oil)	384.9	161.9	131.8	161.9	[illegible]
Greenhouse - direct (Kg CO2)	2216.1	1690.7	1288.3	1690.7	[illegible]
Greenhouse - Indirect (Kg CO2)	730.2	203.6	161.2	203.6	[illegible]
Ozone depletion (Kg CFC 11)	0.044	0.021	0.019	0.021	[illegible]
Acidification (Kg SO2)	28.0	15.0	12.0	15.0	[illegible]
Nutrification (Kg Phosphate)	527.7	526.1	263.2	5.3	[illegible]
Photochem. smog (Kg of Ethylene)	0.062	0.029	0.025	0.029	[illegible]
Human toxicity (Kg body weight)	33.3	18.9	14.9	18.0	[illegible]
Aquatic ecotoxicity (m3)	0.027	0.026	0.013	0.026	[illegible]
Landfill volume dm3	152.3	164.7	155.7	164.7	[illegible]

Normalised Results - % of the years production (x E+9)	Nitric acid	Spent pickling acid, no allocation	Spent pickling acid, allocation by fraction	Spent pickling acid, nitrate allocation
Fossil reserve depletion	6.74	2.84	2.32	2.84
Greenhouse - direct	5.88	4.48	3.42	4.48
Greenhouse - Indirect	1.94	0.54	0.43	0.54
Ozone depletion	4.42	2.09	1.78	2.09
Acidification	9.78	5.23	4.19	5.23
Nutrification	705.55	703.28	351.89	7.02
Photochem. smog	1.66	0.78	0.66	0.78
Human toxicity	5.88	3.29	2.59	3.12
Aquatic ecotoxicity	0.00	0.00	0.00	0.00
Landfill volume	4.38	3.96	3.74	3.96

Table 7.6: Results of the revised impact assessment

The flows are estimated from scale-up of the experimental results, from information presented by other researchers on similar processes and from general chemical engineering principles.

In the estimation, the possibility is ignored that the dust amount and/or composition might change significantly through the proposed recycling. This is consistent with the first-order-assessment approach taken in the thesis. In section 5.4.4, the likely effect of recycling is estimated and shown to justify this approach.

5.4.1 Material Flows in the Beneficiation Plant

Table 5.1 (Appendix G) shows the material balance for the proposed dust beneficiation plant.

The dust composition is the same as that used in the PlasmaDust (TM) process (cf. Table 2.5), representing a typical baghouse dust from the EAF and AOD in stainless steel production. Because of the similarity of the dust studied experimentally with those from other producers, the results from chapter 4 can be extrapolated and used to predict the performance of the leach plant. A pure nitric acid leachant was used to simplify the calculations. If spent pickling acid or acidic rinse water were to be used, the effect on leaching extent (of, e.g. lead due to the presence of sulphates, cf. chapter 4) should be evaluated. Cognisance should also be taken of the possible precipitation of constituents of the spent acid or rinse water into the leach residue. CaF_2 (cf. section 2.5.1) and metal hydroxides should be mentioned in this respect.

A 1:20 solids to liquids ratio was assumed for the acid leach. The composition of the leach residue was calculated from the experimentally determined removals into the leachate (shown in Table B.6(i), Appendix B), with adjustments for Fe and Pb expected when targeting a final pH of between 3 and 4. For iron it was assumed that 90% of that found experimentally can be precipitated, while for lead 50% would remain in solution. These assumptions are explained in Appendix C. The amount of leach residue (dry matter) was adjusted from the 70% of the original dust found experimentally (average value obtained for experiments 7-10) by adding the additional iron and lead hydroxides expected.

The leach residue from the filtration was assumed to have a moisture content of 20% (the experimental average, cf. Table B.3(i), Appendix B, rounded off). For the zinc hydroxide sludge from the thickener a moisture content of 40% was used, this assumption is however seen to be trivial and only required in the context of the water balance (cf. Table 5.1).

Lime consumption was calculated from the neutralisation of all unreacted acid (a 30% consumption of acid during leaching was expected from the experimental results, cf. Table B.2(i), Appendix B) and the conversion of dissolved metals to the hydroxides. The concentrations of heavy metals in the effluent were assumed to be the same as those reported for the PlasmaDust (TM) process; this is justified by proposing the use of the same effluent treatment technique, viz. metal hydroxide precipitation by lime addition.

5.4.2 Material Flows in the Residue Preparation Plant

Table 5.2 (Appendix G) shows the predicted material flows in the residue preparation plant.

The amount of water to be vaporised in the drier is the difference of the water contained in the residue (which is 20% moist) and the briquettes (which are 6% moist).

The amount of coke is taken at 10% of the dry leach residue mass, following the example of Neumeier and Adam (1988). A better estimate would have to be found from a pyrometallurgical simulation (this topic is discussed in 5.4.3 below) or from plant trials.

No coke has been added for the reduction of the grinding swarf. Grinding swarf is only mentioned in the process for its ability to strengthen the briquettes when present as 30% or more of the final briquette mixture (dry basis), but is otherwise excluded from the system. The material flows resulting from smelting of the briquettes in the EAF (calculated in section 5.4.3 below) also ignore the presence of the grinding swarf. As shown by both Neumeier and Adam (1988) and Kaas *et al* (1984), grinding swarf can be recycled together with dust. However, the material flows calculated here are based on dust only, as this is the object of the assessment.

The amount of binder is estimated at 4% of the total mass, following demonstrations of successful briquetting and pelletizing with this amount (Neumeier and Adam, 1988; Kaas *et al*, 1984).

5.4.3 Material Flows for Smelting in the EAF

The distribution of the briquette components into the metal, slag, dust and gas phases in the furnace is ideally determined by pilot or full scale plant trials, or by simulation. A microcomputer simulation model for stainless steel production has been developed by Jones (1989), and this has been used by Barcza and Nelson (1991) to model the pyrometallurgical treatment of steel-plant dusts.

Without such a model, only a crude estimate of the material flows can be made, relying on theoretical considerations and on results published by other researchers (e.g. Ullrich and Schicks, 1991; Neumeier and Adam, 1988; Kaas *et al*, 1984).

The expected material flows resulting from the smelting of the briquettes in the EAF are shown in Table 5.3 (Appendix G). The assumptions made in the calculation of these values are listed and explained in Appendix C.

Increased dust emissions are expected from the smelting operation. Lee *et al* (1975) determined the particulate removal efficiency of a baghouse of a steel plant to be 99.89%. With 0.11% of the dust from the furnace escaping capture in the baghouse, dust emissions would be 0.047 kg for every 1000 kg of dust treated (cf. Table 5.3).

5.4.4 The Effect of Recycling on Dust Amount and Composition

In the calculation of the above material flows, an assumption was made that neither the amount nor the composition of the dust produced in the EAF would change with the recycling of the dust leach residue. This assumption formed the basis for calculating reagent amounts, predicted emissions and the energy estimates (in section 5.5, below) in the treatment process. It is the purpose of this subsection to evaluate this assumption.

The assumption is justified by the fact that the majority of the dust consists of metal oxides, which are reduced and added to the melt upon recycling. Kaas *et al* (1984) argue that, as long as the briquettes sink into the melt and have time to react, the dust amount should not be influenced by their presence.

On the other hand, the elements that report preferentially to the dust are removed from the system in the hydrometallurgical process. However, because this removal is only partial, a fraction of these elements is returned to the furnace only to report to the dust again. This is demonstrated in Figure 5.4 (overleaf) for the case of zinc, the most abundant of the volatile elements. The figure shows how the dust amount and composition with respect to this element would change. The magnitude of the change is inversely related to the removal efficiency in the leaching plant. However, even with the zinc concentration in the dust increasing by a factor of 2.5 in the described scenario, it would (at just under 6%) still fall into the range normally occurring in EAF dust (cf. Table 2.2).

In the calculation of the flows in figure 5.4 it was assumed that all the zinc fed to the furnace reports to the dust (worst case) and that 40% of the zinc fed to the leach plant is removed there. The calculations are based on 1000 kg of dust in the no-recycle scenario.

The assumption that neither dust amount nor composition will change by the proposed recycling of the leach residue is thus, even though incorrect, seen to be consistent with the objective of a first-order assessment.

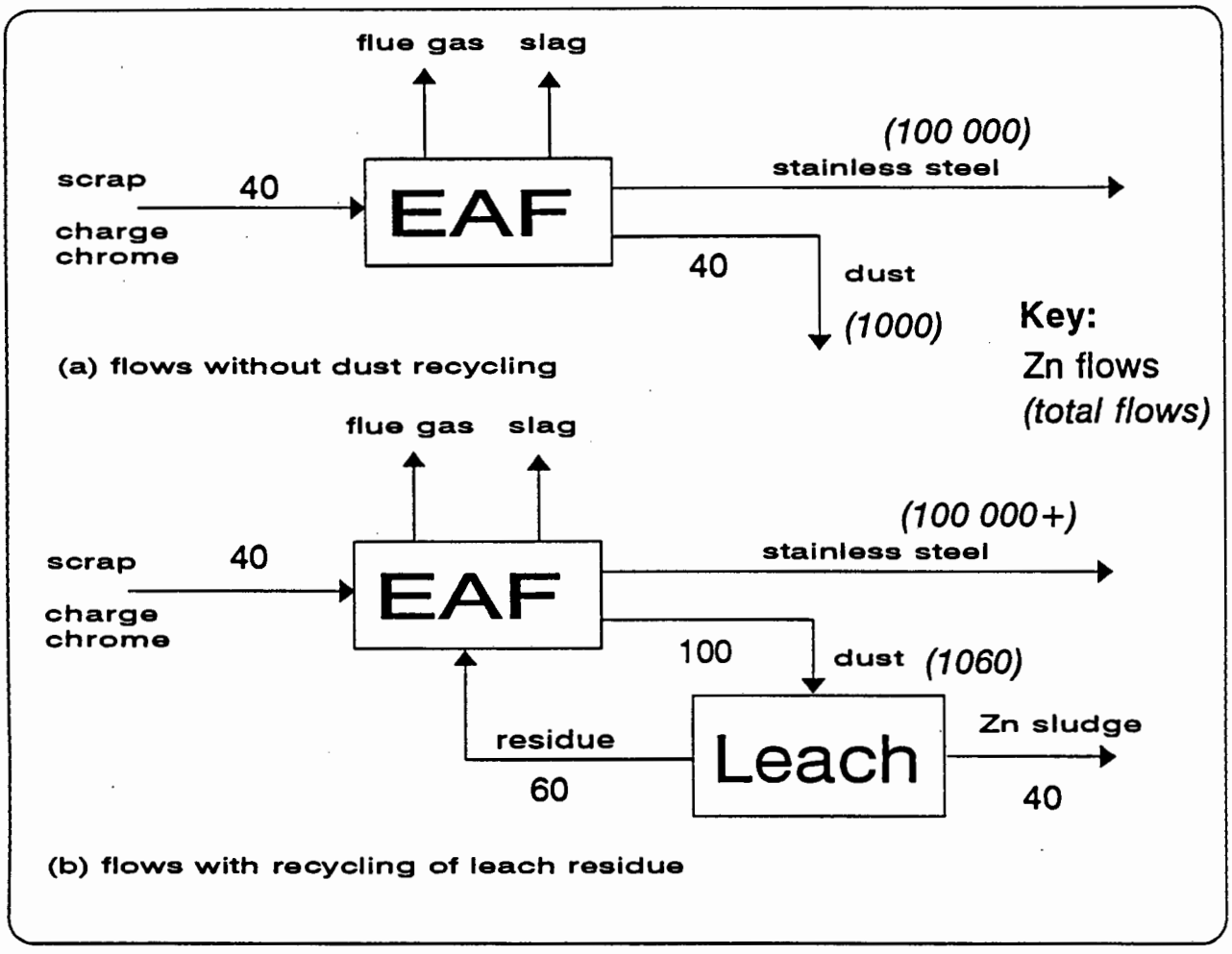


Figure 5.4: The effect of recycling on zinc flows

5.5 ENERGY REQUIREMENTS OF THE TREATMENT PROCESS

Process energy requirements are an important parameter in economic and environmental assessments. The total energy requirements of the "hydrometallurgical" process are estimated in the following sections to be 6550 MJ electricity and 480 MJ thermal energy per 1000 kg of dust treated.

The details of the methods used to arrive at these order of magnitude estimates for each of the three processes described above are given in the following three subsections.

The energy requirements were estimated from information presented by other researchers on similar processes, notably Barcza and Nelson (1990), Neumeier and Adam (1988) and Boustead and Hancock (1982), and from chemical engineering design principles, described by Coulson and Richardson (1983) and Perry and Green (1984). Energy balances internal to each process were not attempted.

5.5.1 Energy Use in the Dust Beneficiation Plant

Electrical energy would be required for dust conveying, agitation in the leaching and neutralization vessels, filtration (whether by pressure or vacuum), operation of the thickener (although minimal) and for the pumping of the various slurries. These energy requirements were estimated as follows:

* The dust conveying system was ignored, as it is strongly dependent on plant layout and would even be completely absent on a plant cleaning flue gases by a wet scrubber.

* Agitation energy uses in leaching and neutralization were calculated from a stirrer power rating and the time of reaction. The power rating was estimated from a correlation of Reynolds number and Power number, and the reaction time was predicted from the experimental results. Using this method, estimates of 1154 MJ per ton of dust were obtained for either process. The calculations are shown in Appendix D.

* The filtration energy requirement was also estimated in Appendix D. This was calculated from the pumping energy required to pass the leach slurry through a filter press. It was shown that at 35 MJ per ton of dust this is negligible compared to the agitation requirements.

* Pumping of the slurries should be against pressure gradients much smaller than those found in filtration; for a first order estimate the pumping requirements can, therefore, be ignored. Similarly, operation of the thickener rake should not contribute appreciable amounts to the process energy consumption.

The calculated energy requirements for this process summed to 2343 MJ. Allowing for a 10% addition from minor equipment, the estimate for electrical energy requirements in the beneficiation plant was 2580 MJ per ton of dust.

5.5.2 Energy Use in the Residue Preparation Plant

Unit operations in the preparation of leach residues for smelting which require electrical energy are the conveying of raw materials and briquettes, mixing of the raw materials, and briquetting. Additionally, thermal energy is required for the leach residue dryer. Estimations of these requirements follow:

* The heat needed to dry the 20% moist leach residue so that the briquetting mixture has a moisture content of 6-8% was estimated in Appendix D to be 478 MJ. It was also shown that a much larger amount of sensible heat (1890 MJ) could be recovered directly from the EAF flue gases arising together with 1000 kg of dust and that the total energy from the combustion of these flue gases would be of the order of 24 GJ. The drying operation could, thus, depend solely on this energy source, if this is not already used.

* The electrical energy required for the conveying of materials was ignored, as in the leaching plant.

* The mixing of the dried leach residue, binder and coke breeze is also likely not to be energy intensive. Perry and Green (1984:21-8) list some typical power requirements for mixers. Most mixer types require less than 25 hp (= 18.7 kW) for a capacity of 1.5 m^3 with typical mixing times of less than 15 minutes. Using these values, the electrical energy requirement of the briquette feed mixer was conservatively estimated at 16 MJ in Appendix D.

* The briquetting step, finally, was estimated to have an electrical energy requirement of 72 MJ. The calculations for this are, again, shown in Appendix D.

The energy requirements for the leach residue preparation plant are, thus, estimated as 170 MJ electricity (doubling the sum of the above for minor uses) and 480 MJ heat energy per ton of dust treated in the acid leach.

5.5.3 Energy Use for Electric Arc Furnace Smelting

Electric energy is converted into heat by the EAF which, in turn, melts the feed materials and provides the heat of reaction for the endothermic reduction of the metal oxides.

An estimate had to be made of the electricity required to smelt the briquettes: the figure reported by Neumeier and Adam (1988) and quoted in Table 2.4 was used, although it was

obtained for a system operating on a feed material containing only 30% dust. At 8330 MJ/t metal, this figure is ± 3% higher than the amount theoretically required to smelt a low-zinc alloy dust (calculated by Barcza and Nelson, 1991). It should, therefore, provide a reasonable starting estimate.

With a metal recovery of 456 kg for each ton of dust treated, the total smelting energy of the treatment process was estimated at 3800 MJ/t dust.

5.6 CONCLUSION

From the experimental findings, a process has been developed and described for the treatment and recycling of stainless-steelmaking furnace dust. Material flows and energy requirements in this process have been estimated.

The process makes use of imported nitric acid or spent pickling acid to leach tramp elements from the dust, leaving a residue which can be recycled to the electric arc furnace after being briquetted. A zinc and lead containing hydroxide sludge is produced as a byproduct, which is assumed to be saleable to the zinc industry as a raw material.

The described process is functionally equivalent to the PlasmaDust (TM) process described in chapter 2: the metallic components of the dust are recovered to stainless steel production, a benign slag is produced (here as part of the EAF operation) and a zinc hydroxide sludge is exported. Contaminated water arises in both processes: the amount here is, however, much larger. On the other hand, the PlasmaDust (TM) process has a higher energy requirement, but can export surplus heat to a municipal heating scheme.

Clearly, no preference in terms of environmental impacts can be expressed for either process at this stage. A systematic approach is required for this.

The next chapter describes Life Cycle Assessment, the method proposed for use in the environmental performance comparison.

6. ENVIRONMENTAL LIFE CYCLE ASSESSMENT AND ITS USE IN PROCESS DESIGN

6.1 INTRODUCTION

In the preceding chapters, a process was developed and described for the treatment of hazardous dusts arising in stainless steel production furnaces. Within the process, possible variations especially w.r.t. reagent sources have been noted. In particular, the use of spent pickling acid, another hazardous waste product from steel production, has been identified as a feasible alternative to purchased nitric acid.

A number of different waste management strategies can be applied to the problem of hazardous furnace dust. These have been reviewed in chapter 2. Special emphasis was placed on the option of thermal treatment, which is currently favoured in industrial practice.

It is the second objective of this thesis to determine whether the hydrometallurgical process thus developed is environmentally preferable to thermal treatment. A comparison of the environmental impacts, not limited to the treatment processes alone, but extended to all causally related activities, has been postulated as a means to establish this preference. In other words, a comparative "cradle-to-grave" assessment of the environmental impacts of both treatment options is required.

A procedure known as environmental Life Cycle Assessment (LCA) has been developed to conduct such "cradle-to-grave" studies. It has been selected in this thesis to execute the comparison between the two treatment processes.

The aim of this chapter is to present an overview of LCA, justifying its use for the proposed purpose. LCA is best known in relation to the debate over packaging materials and in the environmental assessment of consumer products. However, it is acknowledged to be a systems analysis tool (Huppes, 1994) and can thus be applied to evaluate the environmental profile of any suitably defined system, which could be based on a product, process or activity.

In the following sections, LCA is first introduced and set apart from other environmental management procedures. A review of the terminology used in systems analysis and LCA is presented next, followed by a detailed presentation of LCA methodology. Difficulties associated with the execution of LCAs in practice, and the possible applications of LCA are

then mentioned. Finally, the role that LCA can play in improved process design is investigated; in particular, its role in technology assessment is discussed.

The principles discussed in this chapter are then applied in chapter 7, where a comparative LCA to establish the environmentally preferred dust treatment process is presented.

6.2 LCA AND OTHER ENVIRONMENTAL MANAGEMENT TOOLS

As a result of the observed degradation of the natural environment, environmental strategists have over the last two decades developed a number of procedures, legal concepts and management systems to reduce the adverse effects of human activities on the environment. The following is a list of well-known such concepts:

Environmental Impact Assessment [EIA] and Risk Assessment [RA]; Best Practicable Environmental Option [BPEO]; Integrated Environmental Management [IEM]; Integrated Pollution Control [IPC]; Waste Minimisation; Environmental Management Systems (e.g. BS7750, SABS0251); and Responsible Care Initiatives.

While it is not the purpose of this work to discuss these concepts, it can be noted that all of them fail to address one or both of the following needs:

* a need exists to assess the environmental profile of "goods and services" in a holistic fashion and

* a need exists to quantify environmental impacts.

Environmental Life Cycle Assessment (LCA) originated in the late 1960's in energy studies and has, as a result of the above needs, undergone a strong revival in the last ten years (Christiansen, 1993). It has been defined as an aid which can "help us understand what the true environmental impacts are of products during their whole life cycle, from cradle to grave" (de Larderel, 1993). As such it differs from the list of environmental management tools and systems presented above: it is not site-specific, but rather attempts to quantify and aggregate all the environmental impacts associated with an economic system (such as a product) over its entire life cycle (Udo de Haes, 1993).

Formally, LCA has been defined by SETAC (the Society of Environmental Toxicology and Chemistry), which has co-ordinated much of the recent development of LCA, as follows:

"Life Cycle Assessment is a process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing extracting and processing of the raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal" (SETAC, 1993b:5).

6.3 DEFINITION OF TERMS USED IN SYSTEMS ANALYSIS AND LCA

As mentioned in the introduction to this chapter, LCA is considered a systems analysis tool. It is the purpose of this section to define some of the terms used in systems analysis and to show how they are used in LCA. In addition, terms specific to LCA are defined.

6.3.1 Systems Terminology

The development and interplay of complex technology and large economic and social structures in the twentieth century have given rise to a unifying approach to the analysis and design of systems. The "systems approach" to engineering and analysis is best exemplified by the expression "All Systems Go" originally associated with the launch of a space rocket (Jenkins, 1969). For such an event to achieve its objective, all the components of the system and its subsystems have to perform their designed function. Figure 6.1 shows what is meant by a system.

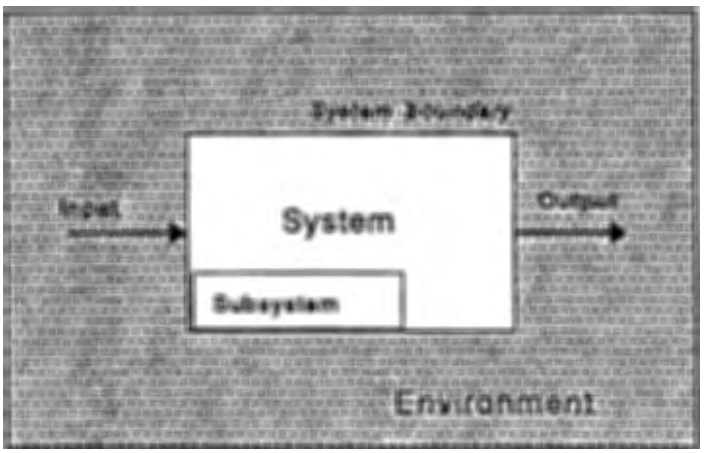


Figure 6.1: System and environment

Formally, a system is defined to be a collection of objects (components) connected by a relationship. The system is delineated from the remaining universe, defined as the environment, by the system boundary. Material and energy can cross the system boundary in the form of inputs and outputs. The conversion of inputs to outputs may be the function or objective of the system.

The concept of a system and its surroundings or environment is also used in thermodynamics, where, again, the environment is defined by exclusion.

6.3.2 Terms used in LCA

The concept of a system is used in LCA in the same way as described above. The unifying feature of the types of system studied in LCA is that the defining relationship is a function, usually in an economic context. In other words, the type of systems studied in LCA are those that provide goods or services.

The concept of environment as used in LCA is generally not as clearly defined as in systems analysis or thermodynamics. It is generally used in the context of the natural environment providing raw materials and receiving wastes, sometimes also called the biosphere.

This is illustrated by Figure 6.2 proposed by Guinée *et al* (1993a) in the context of a product system. However, Azapagic and Clift (1994) have used environment in the thermodynamic sense. From their discussion, the distinction between the two meanings is seen to be trivial when LCA is applied to whole systems (those having no interaction with other economic systems in the sense of Figure 6.2). As this is generally not the case, environment will be used in the colloquial sense of the natural environment in the following discussion.

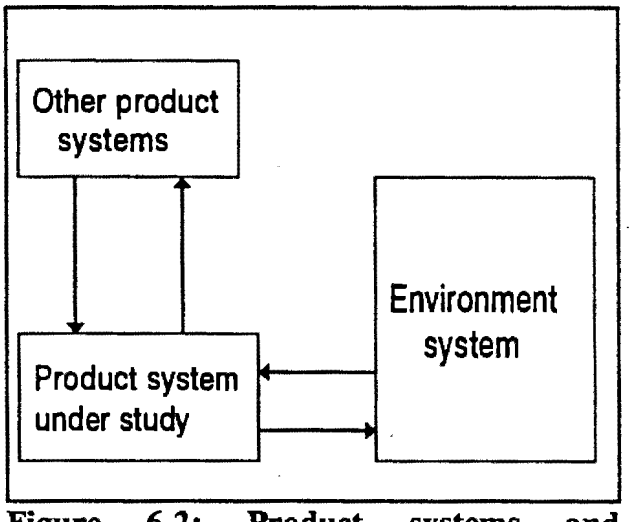


Figure 6.2: Product systems and environment (Guinée *et al*, 1993a)

To define other terms frequently used in LCA, Figure 6.3 (overleaf) is proposed. In conjunction with the schematic shown in it, the following terms apply in this thesis:

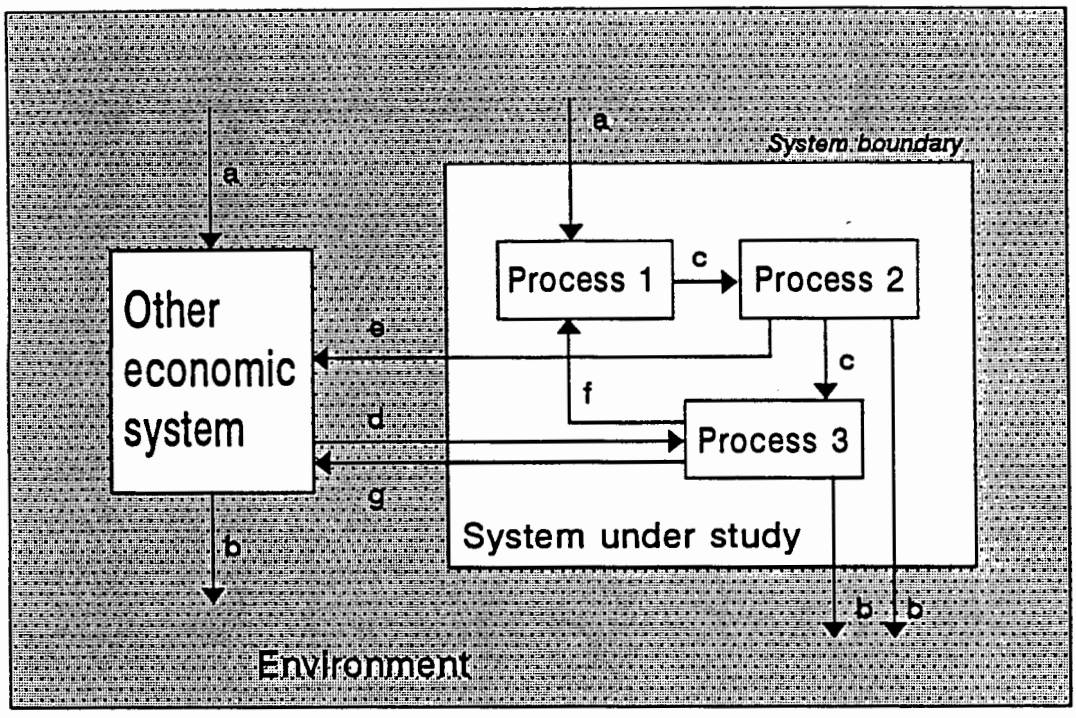


Figure 6.3: Schematic of a system in the context of LCA

* The system under study is the subject of a particular LCA.

* An economic system is the system under study or another system sufficiently similar to it to be the subject of a another LCA.

* A raw material or resource is a material existing in the environment and desired to be used in an economic system.

* Extraction: The transfer, depicted by (a) in Figure 6.3, of a raw material or resource from the environment into an economic system.

* Waste: a solid or liquid material arising in an economic system and purposefully transferred to the environment (as by (b) in Figure 6.3). The term effluent is used in the same sense for liquids.

* Emission: the transfer of materials other than those defined as waste (e.g. gases emitted intentionally or solids, liquids and gases emitted unknowingly) from an economic system to the environment, also shown by (b).

* Recycling is the activity shown by (f) or (e), whereby a material which would otherwise arise as a waste is returned to an activity within an economic system.

* Inputs (a, d, c and f) and outputs (b, c, e and f) are defined in the same sense as in systems analysis: a distinction is made between standard inputs and outputs [which relate to the environment, e.g. (a, b)], closed-loop flows [those not crossing the system boundary, e.g. (c, f)] and open-loop inputs and outputs [related to other economic systems, e.g. (d, e)].

* Environmental burden is the term used collectively for extracted raw materials, wastes and emitted substances, i.e. the standard inputs and outputs.

* The environmental impact is the effect caused in the environment by the environmental burdens.

* The cradle is that part of the environment from which raw materials are extracted, while the grave is that part of the environment which receives wastes and emitted substances.

6.4 A DESCRIPTION OF LIFE CYCLE ASSESSMENT

An LCA can be conceptual, qualitative, semi- or fully quantitative; it can be conducted on a single system or it can be comparative. It consists of four major components: the first, goal definition, dictating the scope in this respect. The other three parts are, as alluded to in the definition, inventory analysis, impact assessment and improvement assessment. Each of these steps is discussed in the following subsections. The discussion is largely based on the SETAC 'Code of Practice' (SETAC, 1993b). It should be borne in mind that LCA is still in a state of development and that consensus has not yet been reached on all issues.

6.4.1 Goal Definition and Scoping

(a) Purpose: LCAs can, potentially, become complicated and confusing: it is therefore important to clearly define the study purpose at the start of an LCA. This includes stating the reason(s) for the study and the intended use of the results. To direct the study a targeted audience may be specified. Identifying the participants in the study and the source of funding is considered good practice to assure the credibility of the results.

(b) Scope: The scope of the study needs to be defined clearly: this includes a definition of the system, its boundaries and the level of detail required in the study:

* The scope should be such that the stated purpose of the study can be realised.

* Ideally the system boundary should be drawn wide, but in comparative studies "processes and operations common to all alternatives can be omitted" (Clift, 1994).

* The data requirements (e.g. the type of environmental burdens to be considered), assumptions and limitations (such as geographic extent and time horizon) must be specified.

(c) Function: The function of the system needs to be defined clearly. Simultaneously, a functional unit is established. For example, in assessing different materials to package milk the function of the system is to package milk subject to specifications of hygiene and quantity, and the functional unit is defined in terms of an amount of milk (e.g. 1000 l) packaged in this way (Guinée *et al*, 1993a). The amounts of the different packaging materials (e.g. glass, carton) will vary, but will all result in the same required function. Specifying a functional unit reduces ambiguity, enables comparisons and clarifies the basis for the scope.

(d) Data quality: The required data quality (w.r.t., e.g. representativeness, age and accuracy) should be defined. To ensure transparency, methods to verify this quality should also be identified; these can take the form of audits and peer reviews.

(e) Transparency: Finally, it has been recognised that some of the decisions made in goal definition are inevitably arbitrary and must be clearly explained (Clift, 1994) so that the correct choices can be made in the procedures comprising the inventory analysis.

6.4.2 Inventory Analysis

The aim of the inventory analysis is to quantify all environmental burdens (extractions, wastes and emissions) and to present them in summarized form in an inventory table. The methodology for life cycle inventory (LCI) analysis is well defined: it proceeds from systems and subsystems definition to the drawing of process diagrams, and further to data collection, allocation (defined below) and to the calculation of the inventory table.

(a) Identification of processes: All the processes which contribute to the defined functional unit and which can be linked directly or indirectly to it by material or energy flows are identified. Their relationships are shown by a process flow diagram or process tree. All

ancillary materials and energy inputs are traced back to resource extraction. Any wastes produced in the main system or in the ancillary materials sequences are followed to final disposal. Flows which derive from or enter other product systems are identified as such. All transport steps are included. Interdependencies and loops are shown by the process flow diagram.

(b) Data collection: In the next step, input and output data for each individual process are collected and, for convenience, entered into a matrix. Material and energy balances should close for each process. It is important that the quality and source of data be consistent with the scope of the study. Variations and uncertainties should be noted. [In this case the sensitivity of the LCA result to such uncertainties and variations can be studied before conclusions for the study are drawn.]

(c) Allocation: Before the environmental burdens of the system can be calculated from the collected data, the allocation problem must be addressed: in its simplest form it arises when a system has more than one function, necessitating a decision to allocate the environmental burdens between the functions.

In general, the allocation problem can be linked to the presence of open-loop inputs and outputs, as defined in Figure 6.3. Three distinct cases of the allocation problem have been identified:

* a co-product exists (e.g. in the chlor-alkali industry), this is shown by (e) in Figure 6.3.;

* waste from another system is treated concurrently with waste from the system under study, this is illustrated by (d) in Figure 6.3;

* a material that would otherwise be classified as waste is recycled to another system; this case, known as open-loop recycling is illustrated by (g) in Figure 6.3.

Various approaches have been proposed to deal with allocation, but so far consensus has not been reached (Huppes and Schneider, 1994:preface). Some of the methods are based on objective characteristics (physico-chemical), while others use a causative (economic) approach. Weidema (1993c) states a strong case for allocation by economic aspects.

Azapagic and Clift (1994) have argued that this difficulty of solving the allocation problem arises from the modelling of incomplete systems. When considering whole systems (i.e. those with no open-loop inputs and outputs in the sense of Figure 6.3) the allocation problem can be solved completely by the principle of marginal variation.

Whatever method is chosen to deal with allocation, it is - once again - important that the approach is transparent.

(d) Inventory calculation: The completion of the inventory table takes place in three steps:

(1) the material and energy flows between the individual processes (the closed-loop flows) are adjusted so that the system performs to the specified functional unit (sequentially in the absence of loops, iteratively or by matrix methods in the presence of loops);

(2) the environmental inputs and outputs of each process are recalculated according to the allocation rules and the balanced flows; and

(3) each type of environmental input and output is summed to get the total burdens for the system.

The inventory table is a statement of the material and energy flows between the system and the environment and provides the first useful output of the LCA.

6.4.3 Impact Assessment

The list of environmental burdens contained in the inventory table can be used by itself to compare different configurations of a system, but the information that can thus be gained is limited. This stems from the observation that the amounts of the environmental burdens cannot be equated to the impacts that they have in the environment.

The impact assessment phase of LCA addresses the environmental effects of the material and energy uses and releases identified in the inventory table. In a non-comparative study, this phase could be used to identify those entries in the inventory table which lead to the largest adverse impacts, thus laying a foundation for the improvement assessment. In a comparative study it can be used to determine which of the studied system configurations has the lowest overall environmental impact. However, as is shown below, there is a subjective element to this endeavour.

The non-site-specific nature of an LCA makes it difficult, if not impossible, to carry out a conventional impact assessment. **The focus is therefore on the potential to do damage rather than on predicted damage itself** (Udo de Haes, 1993).

There are two approaches to impact assessment. The Problem Oriented Approach, which aggregates burdens according to their potential contribution to recognised environmental

effects or concerns, has been adopted by SETAC and will be discussed here. The medium oriented approach (also known as the Critical Volume Approach) compares burdens according to their principal media (air, water, land) and also identifies total energy consumption. [For air and water, each waste or emission (mass) is divided by the an environmental standard such as the maximum accepted concentration to arrive at the volume of the medium theoretically required to dilute the substance to the threshold value (see, e.g. Guinée *et al*, 1993a). For solid waste the occupied landfill volume is used as an impact indicator.]

The impact assessment consists of three steps: classification, characterization and valuation.

(a) Classification assigns each entry from the inventory analysis to one or more impact categories. Three general areas for protection are defined: these being resource depletion, human health and ecological health. The impact categories, and their relation to the general areas for protection, are shown in Table 6.1. The list is not exhaustive and may be adjusted, if deemed necessary by a specific situation. Again, reasons should be stated for the inclusion or exclusion of categories.

Table 6.1: **Impact categories in the Problem Oriented Approach** (adapted from SETAC, 1993b:24). + means a direct potential impact, (+) means an indirect potential impact.

Impact category	Resources	Human Health	Ecological Health
Abiotic resources	+		
Biotic resources	+		
Global warming		(+)	+
Ozone depletion		(+)	(+)
Human toxicity		+	
Ecotoxicity		(+)	+
Photochemical oxidants		+	+
Acidification		(+)	+
Nutrification			+
Land use			+

A school of thought argues for the inclusion of social welfare (including issues such as odour, noise, recreation, damage to buildings and agricultural/natural resource productivity) as a fourth category of concern (SETAC, 1993a); this would, however, turn LCA into more than an environmental tool. A method that includes social and economic aspects has been developed in Germany under the name 'Produkt-Linien-Analyse' (PLA); its practical application is, however, not favoured by the federal environmental agency (Umweltbundesamt, 1992:19). While the issues of equity and sustainability are important, it should be realised that including these into LCA would make an already complex procedure unmanageable.

(b) Characterisation quantifies, aggregates and (if desired) normalizes the impacts within the chosen impact categories. The result obtained from the characterisation step is a list of numbers corresponding to the impact categories shown, e.g. in Table 6.1. This is here referred to as the environmental profile of the system.

The quantification is achieved by means of equivalency factors: in each impact category each assigned intervention is multiplied by such a pre-determined factor. Equivalency factors have been calculated for a large number of substances contributing to global warming (e.g. with CO_2 as a reference the equivalency factor for methane is 11), ozone depletion, acidification, photochemical oxidant formation and nutrification (Heijungs, 1992a), but doubts exist over the application on a global scale for the last two. Development is still in progress on factors for human toxicity and terrestrial and aquatic ecotoxicity (see, e.g. Guinée and Heijungs, 1993). Preliminary factors have been published, again by Heijungs (1992a). The impact assessment will often require expert judgement.

The aggregation of all the impacts within each category is merely a process of summing.

The aggregates in each impact category can be normalized by dividing by the actual magnitude of all the impacts of that type in a certain region. Normalization provides a means of establishing to which environmental impacts the system contributes most. Normalization can also be on a global scale; for this purpose Guinée (1993) has published provisional global normalization factors.

(c) Valuation is the last step in the impact assessment procedure. Here, weighting factors are assigned to each impact category to allow a single environmental score to be calculated for the system.

Valuation **is a subjective procedure**, but the application of elements of decision theory can make the process more "rational and explicit" (SETAC, 1993b:26). Techniques for the rating

of alternatives and for reaching consensus, such as Saaty's Analytical Hierarchy Process (Zahedi, 1986), the Delphi Technique (Riggs, 1983) or the Nominal Group Technique (Delbecq *et al*, 1975) could allow for judgement both by experts and by interested and affected parties. Azapagic and Clift (1994) cite Clift *et al* (to be published) who found that Linear Programming provides a framework for valuation. Delmarco and Kniel (1994) used the principle of marginal analysis, but failed to demonstrate a basis for this approach.

Valuation, and indeed most of the impact assessment procedure, are not always necessary in an LCA. Improvements can often be made as a result of the inventory analysis alone.

6.4.4 Improvement Assessment

Contrary to the other sections of LCA, no methodology has been agreed upon yet for the improvement assessment. It is possibly the most difficult section to prescribe, as the nature of possible improvements can vary as widely as the purpose for carrying out an LCA.

This does not mean that LCA can not be used to identify improvement opportunities, but rather that intuitive approaches are used for this purpose.

Conceptually, improvement assessment should deal with "identification, evaluation and selection of options for environmental improvements" (SETAC, 1993b:26). As such, it could be informed from the inventory analysis, from a study of the inventory table (by methods such as dominance analysis and marginal analysis as discussed by Heijungs (1993a, 1993b)) or from the prioritisation of impacts during the impact assessment (Weidema, 1993b:89).

Another approach has been to include LCA in product design, rather than product design into LCA in the form of a methodology for improvement assessment. This approach is based on the premise that design and re-design of products and processes also involves aspects such as performance, cost, cultural and legal requirements (Keoleian, 1993). The US EPA has published a "Life Cycle Design Guidance Manual" (Keoleian and Menery, 1993) describing a systems approach to product design. In this approach, LCA is used to measure the environmental performance. It is proposed that any 'improved' system be assessed in a comparative LCA with the original. Only from the results of such a study would it be possible to conclude that environmental improvements have, indeed, been made.

6.5 LCA IN PRACTICE

As shown in the above discussion on the LCA method a comprehensive LCA has many facets and can, therefore, become complicated and time-consuming. The issue of data quality and applicability is also critical. The potential exists thus for accidental and intended misuse. The first can be avoided by using resources such as computer programs and databases, the second by standardization and (self)-regulation. As a result of developments on both of these fronts, LCA has been used extensively in practice.

6.5.1 Software tools for LCA

Miettinen (1993) gives an overview of software tools for LCA, listing 17 programs and discussing four packages in more detail. Many of these are undergoing continuing development. Some include databases, but according to several observers (e.g. Christiansen, 1993; Udo de Haes, 1993) publicly available databases need to be developed.

6.5.2 Standards for LCA

The SETAC 'Code of Practice', giving guidelines for LCAs, is an important development in the standardization of LCA methodology. Regulation is, however, currently left to practitioners themselves, with no standards organizations having developed official procedures to date.

6.5.3 Applications of LCA

Although the public interest in and expectations of LCA (at least in Europe) seem to be high, it should be remembered that the tool is still in a state of development. This is witnessed by the published literature: a study by the German Federal Environmental Agency quotes Rubik and Baumgartner (1991) who reviewed 280 citations and found that 60% of these were dealing with questions of methodology (Umweltbundesamt, 1992:21).

Nevertheless, Life Cycle Assessment has been applied extensively in practice. Udo de Haes (1993) reports three main groups of users: governments, companies and NGOs/consumers. Table 6.2 shows the reported applications by each of these groups:

Table 6.2: **Applications of LCA** (adapted from Udo de Haes, 1993)

Governments	Companies	NGOs/consumers
Certification	Product improvement	Purchase behaviour
Ecolabelling	Product design	Life style
Deposit systems	Company policies (purchase, waste, engineering, marketing)	Pressure group action against products, materials
Subsidy/tax	Information	
Energy policy	Advertisement	Actions directed at companies
Waste policy	Negotiations (with other companies, governments on, e.g., emission reduction alternatives)	Actions directed at government
Packaging policy		
Transport policy		

6.6 LCA AS A TOOL IN PROCESS DESIGN

An application of LCA in process design is not mentioned explicitly in Table 6.2 (Udo de Haes, 1993). This could be due to the fact that process engineering is already constrained by other environmental factors, these being technical and administrative in nature and that LCA is therefore not considered useful.

On the other hand, process design is often treated as a subsection of product design and might thus have been included in Table 6.2 by implication. For example, Udo de Haes (1993) mentions that companies have applied LCA aimed at single products to adapt in-house production processes and waste management systems, including reuse and recycling. It is certainly recognised that the environmental profile of products can often be improved by process modifications (Keoleian, 1993).

In this instance, the inventory analysis in LCA can be seen as an alternative to the information gathering stage of a Waste Minimisation audit; and the impact assessment as the motivation for such an audit.

Another interaction between LCA and process engineering and design can be expected from LCA providing a quantitative tool for the comparison of the environmental performance of systems. It can therefore be used for the evaluation and selection of alternative processes and technologies. This is the use of LCA in this thesis.

However, comparing finished designs does not satisfy the requirement of integrating environmental considerations into the earliest phases of design. Ideally, LCA, or aspects of it, should be incorporated into process synthesis. Methods to achieve this have not been described: the use of formal Waste Minimisation methodology as the improvement assessment of process-oriented LCAs is promising in this respect.

6.7 CONCLUSION

In this chapter, the environmental management tool known as Life Cycle Assessment, or LCA, has been described. The next chapter makes use of LCA to compare the environmental profile of the process proposed in chapter 5 to treat stainless steel EAF dust with that of the PlasmaDust (TM) process, which represents the technology of choice for European stainless steel producers.

The use of LCA as the preferred tool for the envisaged assessment is supported by the following concluding remarks on the discussion presented in this chapter:

* Although LCA is primarily used to assess the environmental profile of consumer products, it is a systems analysis tool and can thus also be applied to processes, as long as these can be suitably described in systems terms.

* In contrast to other environmental assessment methods, LCA addresses all the impacts associated with a system, commencing with the extraction of resources and ending with the disposal of wastes. It does this in an exact and quantitative way.

* In a comparative LCA simplifications resulting from the exclusion of all common aspects are allowed.

* Although the use of LCA for the comparison of technologies has not been reported before, no reasons could be found why LCA should not be usable in this respect.

7. LIFE CYCLE ASSESSMENT OF THE HYDROMETALLURGICAL PROCESS AND THE PYROMETALLURGICAL ALTERNATIVE

7.1 INTRODUCTION

In this chapter, the hydrometallurgical process to treat chromium-containing flue dusts - developed in this thesis - is compared to an existing process: treatment in a plasma-arc furnace. The comparison makes use of the tool of Life Cycle Assessment described in the previous chapter. The aim of the comparison is to substantiate the second hypothesis of the thesis, viz. that the hydrometallurgical process is preferable to a plasma process on the basis of environmental impacts over the entire life cycle.

The PlasmaDust (TM) process for the treatment of stainless steelmaking dusts has been described in chapter 2, section 2.5.2.3. The details of the hydrometallurgical process were described in chapter 5 to a level which allows a first-order assessment of the process to be conducted. Life Cycle Assessment methodology was reviewed and explained in chapter 6, where it was concluded that LCA is principally suited for the envisaged comparison.

The assessment was carried out with the aid of a Life Cycle Assessment Computer Model, which is introduced briefly in section 7.2. Only the input and output data for the study are presented in the main text of the chapter and in Appendices F and G. The complete inventories are contained on the computer disk in the sleeve in the back cover.

The remaining sections of this chapter follow the major components of a Life Cycle Assessment. The aim and scope of the LCA are defined first. Life Cycle Inventories for the two processes are presented next, followed by the comparative Impact Assessment. Finally, the findings of the study are discussed. There is no section dealing with Improvement Assessment. The contributions of LCA to improving the environmental profile of the hydrometallurgical process are discussed in the next and concluding chapter.

7.2 THE PEMS LCA COMPUTER MODEL

PEMS, the Pira Environmental Management System, is developed and marketed by Pira International, an "independent centre for research, consultancy, training and information services for the paper and board, packaging, printing and publishing industries", based in the UK. Environmental work at Pira is, however, "not specific to any one industry sector".

Quoting from the PEMS.2 User Manual (Pira, 1994): "PEMS is generic in its approach and can be used to conduct an LCA for any product, process or activity."

The program is executed on personal computers based on the *Intel 80386* or *80486* processor, making use of the *MS Windows* operating system and the spreadsheet *MS Excel*. It is coded in *MS Excel* macros and stores information in spreadsheet format. Databases containing life cycle inventories for a range of materials, energy production, transport and waste management are part of the software package. The "strength" of the software lies in its comprehensive databases.

The program can be used to conduct the inventory analysis and impact assessment phases of LCA. In this respect it adheres to the SETAC conventions and makes use of the latest published information.

PEMS is modular in nature: previously conducted studies and items from the databases can be used as building blocks for new studies. For this reason, the materials database contains "cradle-to-gate", rather than full life cycle inventories. LCAs are "closed" by adding options from the waste management, transportation and/or energy databases, as well as user-defined activities and processes.

The presence in the databases of materials such as coal, coke and lime, a number of country-specific electricity generation data and a range of options for the transportation of materials makes PEMS an ideal tool for the inventory analysis and impact assessment phases of the metallurgical LCA carried out in this thesis.

One material required for the assessment of the hydrometallurgical process, but not available in the materials database, was nitric acid. Delmarco and Kniel (1994) used process data from a nitric acid plant in Cape Town to create a PEMS LCA inventory for this material. Although the scope of this work was limited, it was decided to use their proposed inventory. The life cycle inventory for the base plant, as currently operating, was thus normalized to an output of 1000 kg of nitric acid and added to the materials database in PEMS.

7.3 GOAL DEFINITION FOR THE COMPARATIVE LCA

7.3.1 The Purpose of the LCA

(i) The reason for carrying out the LCA is to substantiate the second hypothesis of the thesis. This states that the hydrometallurgical process to treat chromium-containing flue dusts is preferable to an energy-intensive high temperature process, if all impacts in the life cycles of both processes are evaluated.

(ii) Intended use of results: The results of the LCA are expected to quantify, for a selected example, the relative merits of the recycle, re-use and recovery, and treatment options in the Waste Minimisation hierarchy (cf. Figure 1.1).

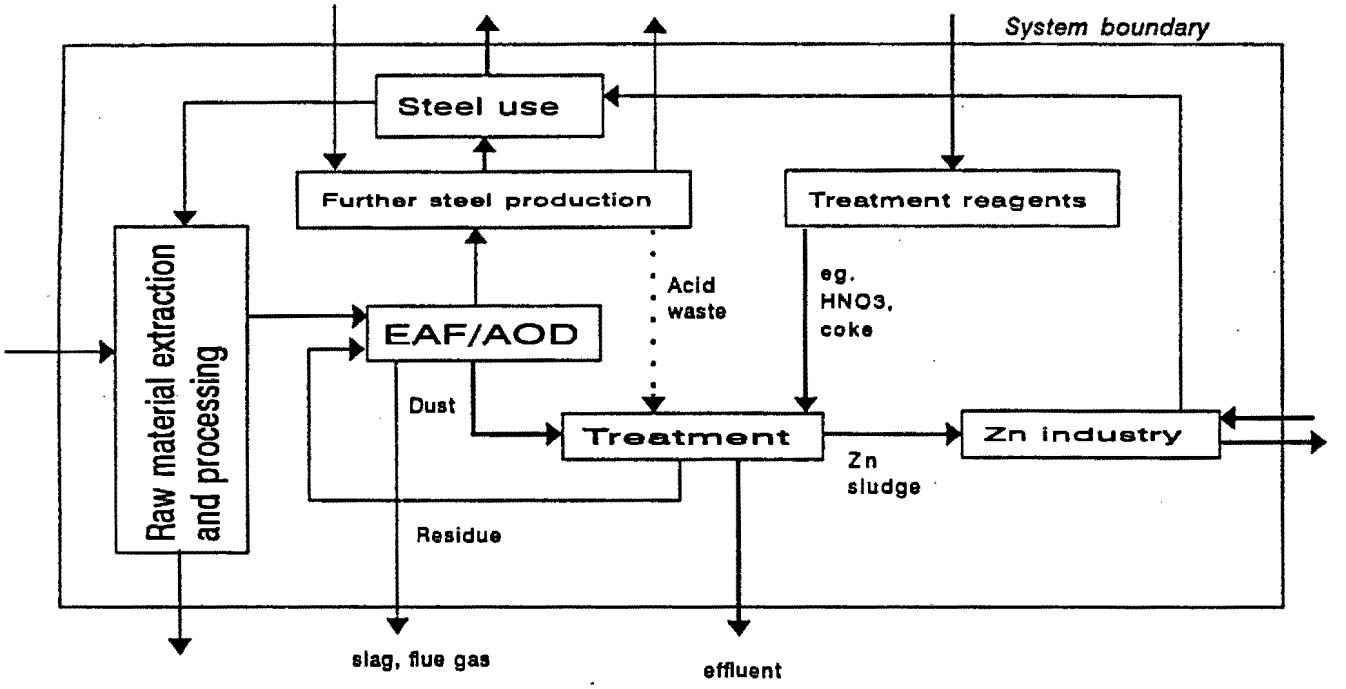
(iii) Target group: The results and method of the LCA are targeted at researchers with an interest in Waste Minimisation, Life Cycle Assessment and related environmental management topics.

7.3.2 The Scope of the LCA

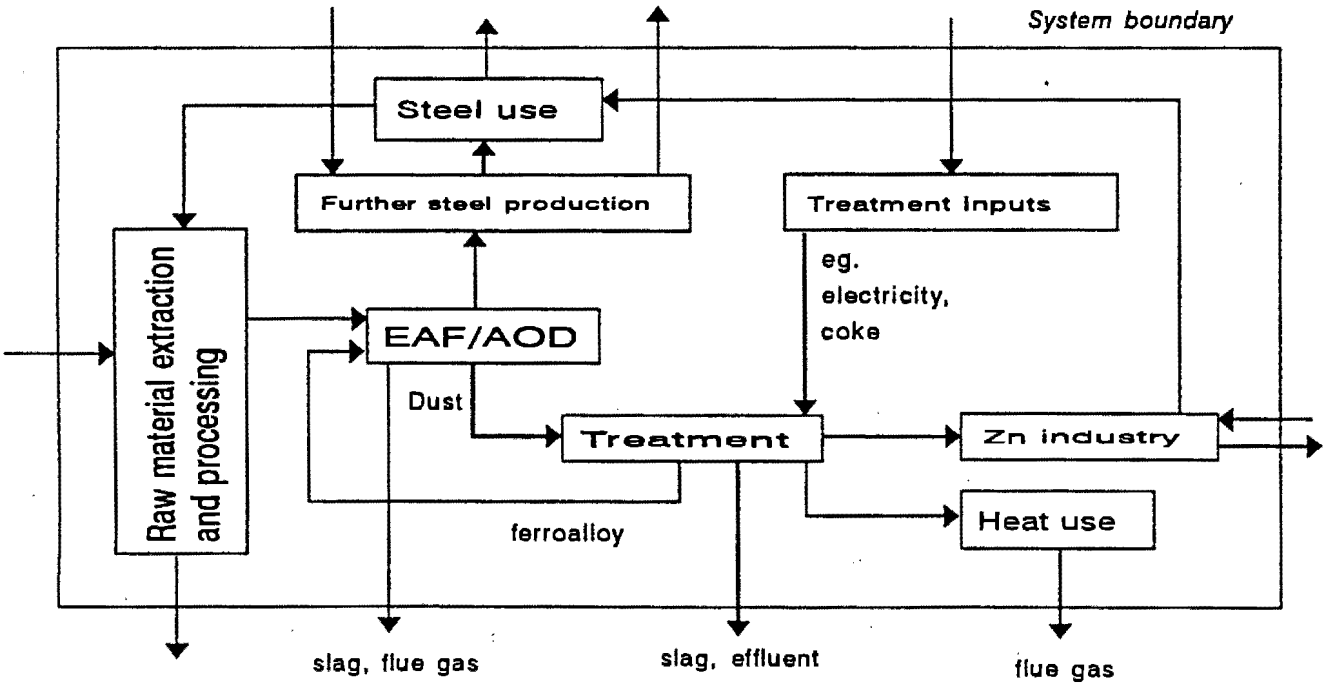
(i) Definition of system and boundaries: Two configurations of a system based on the treatment of chromium-containing dusts are assessed and compared in the study. Both have the function of treating the dusts, thereby recovering a chromium-rich ferroalloy into stainless steel. The first configuration is based on the hydrometallurgical process developed in this thesis, the second on the PlasmaDust (TM) process, which treats the dusts from several European stainless steel producers. Within the first option, the value of using spent pickling acid over imported nitric acid was to be quantified.

Parts (a) and (b) of Figure 7.1 (shown on the next page) depict the two system configurations in the context of the life cycle of dust treatment. These represent whole systems, with all inputs and outputs related only to the natural environment. The system boundary is thus drawn wide to include both the stainless steel and the zinc industry.

However, it is realised that assessments of the systems as shown in Figure 7.1 (a) and (b) would not only be extremely complex, but also without a clear focus on the dust treatment aspect. Therefore, the system to be studied is redefined with all aspects equivalent in the life cycles of both processes defined to lie outside the system boundary. This approach has been validated in chapter 6.



(a) hydrometallurgical dust treatment



(b) pyrometallurgical dust treatment

Figure 7.1: The dust treatment process and its life cycle

Figure 7.1 (c) shows the revised system. The generation of the dust, and use-reuse-disposal of the steel product are excluded as elements common to both configurations. For this, the EAF/AOD is broken down into two functional units: the furnaces as producing stainless steel (and the dust) are excluded from the revised system, while the EAF as used to complete the dust treatment is included. The former function is equivalent in both systems, while the feed materials in the latter differ.

The further use of the zinc sludge (120 kg per ton of dust arises in either system) should have identical consequences for both processes and this material therefore leaves the system as an open-loop output.

These simplifications exclude some other possibilities for solving the dust problem: notably the disposal and treatment-for-disposal options. The main reason for this is that no resources are recovered in these options and that the upstream components of the life cycle (e.g. ferrochromium production, scrap processing and electricity for the EAF) therefore change and can no longer be excluded.

The main implication of the simplifications is thus that no assessment can be made in this study of the environmental improvements derived from treating rather than dumping the dusts. On the other hand, life cycle methodology is currently poorly developed w.r.t. the assessment of disposed wastes. This aspect of LCA should be explored, with the work reported here providing data for a case study.

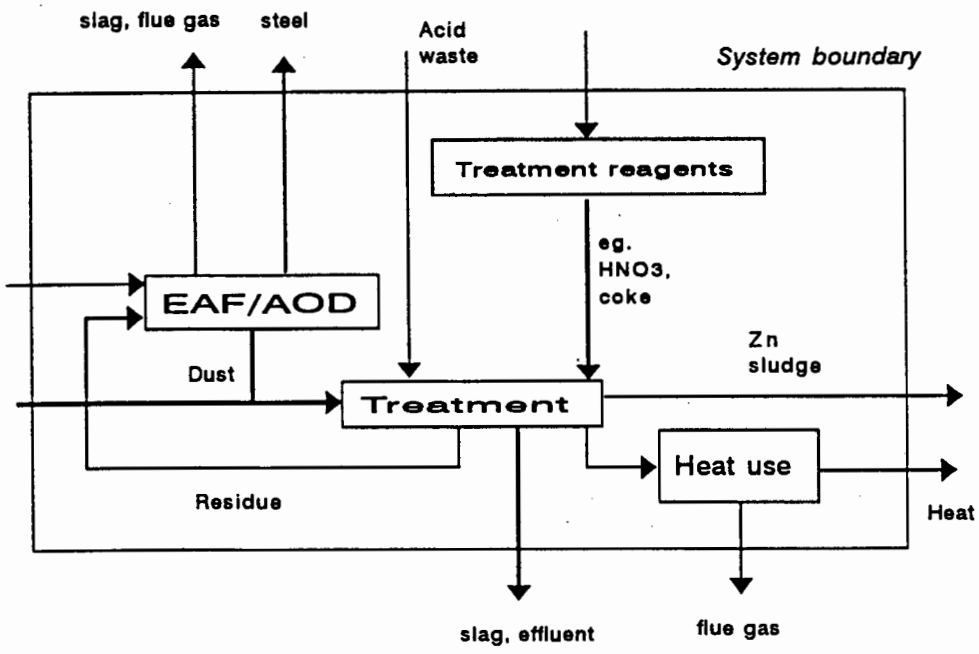


Figure 7.1 (c): Revised system for dust treatment

(ii) The level of detail of the LCA is such that the study can be called semi-quantitative: all major process flows and emissions are determined, but secondary items such as lubricants for process machinery, tire wear on vehicles or paper use in administrative functions are excluded. Capital equipment is also excluded from the assessment, which is consistent with LCA practice. These exclusions leave a degree of uncertainty in the interpretation of the results.

(iii) Data requirements: The types of environmental burden evaluated by the PEMS computer model are shown in the template in Figure 7.2 (Appendix F).

Data for the assessment phase (e.g. equivalency and normalization factors) is incorporated in the computer model. The sources of such data have been traced and verified by comparison with the originally published values, where possible.

Because of its subjective nature, valuation is not included in the assessment phase and valuation factors are, therefore, not required.

(iv) Assumptions and limitations:

1. Since the PlasmaDust (TM) process treats dusts from European stainless steel producers, it is assumed that the dusts originate in central Europe. It is further assumed that the dusts are treated at or close to the site of origin; this assumption excludes obscuring effects of transportation processes in the initial assessment.

2. This, in turn, assumes that the PlasmaDust (TM) process would have similar material and energy flows if it were situated in central Europe rather than in Scandinavia.

3. The data used for the PlasmaDust (TM) process consist of averages reported for its operation in 1990; that for the hydrometallurgical process of the estimates developed in chapter 5.

4. It is assumed that all material and energy inputs to the two processes are produced identically to those in the PEMS database.

(v) Matching scope and purpose: The scope, as defined above, should allow a conclusion to be reached w.r.t. the second hypothesis. This conclusion, evidently, is subject to the assumptions made and to the fact that the study is only semiquantitative.

7.3.3 The Functional Unit for the LCA

For the two systems to be comparable, they have to perform equivalent functions. These functions are: to treat chromium-containing metallurgical flue dust in such a way that all process residuals meet the TCLP criteria and that as much metallic value as technically feasible is recovered for re-use.

The basis for the comparison, i.e. the functional unit, is 1000 kg of dust treated to these specifications.

7.3.4 Data Quality in the LCA

(i) Required data quality: The data used in the LCA is required to reflect average annual per ton of dust process flows and emissions, or best predictable values, ideally accurate to within 10%.

(ii) Verification: All figures have to be from traceable, referenced sources or from experiment and prediction, as described in chapters 3 to 5 of this thesis. Additionally, the material balances have been shown to close to within 10% for both processes (cf. chapters 2 and 5).

7.4 LIFE-CYCLE INVENTORIES FOR THE COMPARATIVE LCA

7.4.1 LCI of the Hydrometallurgical Process

(i) Subsystems definition: Treatment of the dust and recovery of the metallic values contained therein - as developed in chapter 5 and shown in Figure 5.1 - occurs in the two primary subsystems: the hydrometallurgical beneficiation process and the reduction in the EAF. Briquetting of the beneficiated dust to prepare for smelting in the EAF is defined as a third subsystem.

The first process input to the hydrometallurgical process is spent pickling acid or fresh nitric acid: spent pickling acid would cross the system boundary, as it originates from another economic system, viz. steel production, and is thus treated as an open-loop input. On the other hand, subsystems need to be defined for nitric acid

production and transportation. Studying the effect of substituting nitric acid with spent pickling acid is an important objective of the assessment.

Other raw materials are required for the neutralization and the carbothermic reduction; they are limestone and metallurgical coke. Subsystems are defined for the extraction and transportation of each of these. Electricity generation forms another subsystem.

The portland cement binder added to the briquettes for strength is treated as an ancillary material, meaning that the environmental burdens of its production are ignored. This is justified by the relatively small amount required.

The only by-product of the system is the zinc hydroxide sludge. This enters another economic system and no further subsystems need to be defined for it.

The process tree illustrating the connections of these subsystems is shown in Figure 7.3.

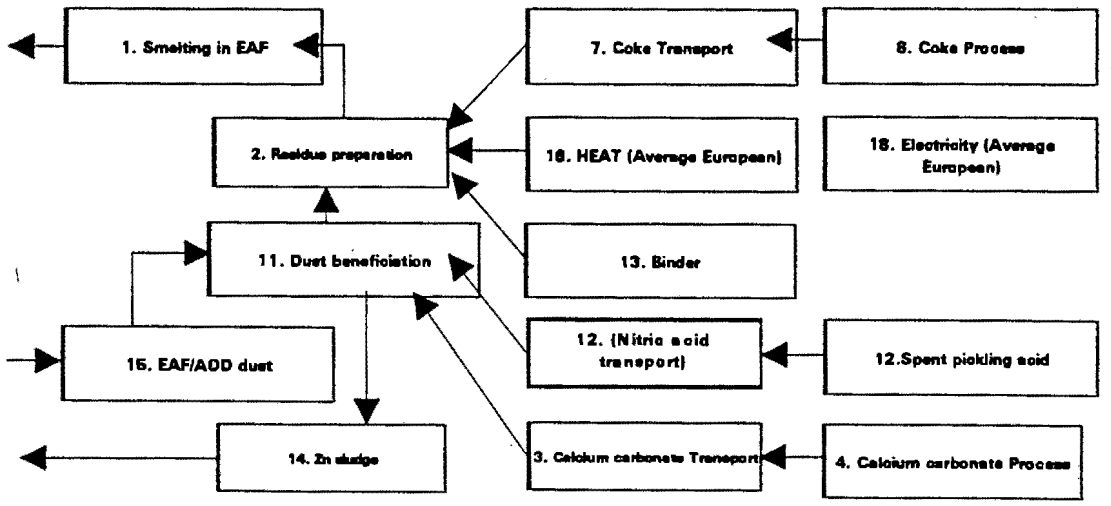
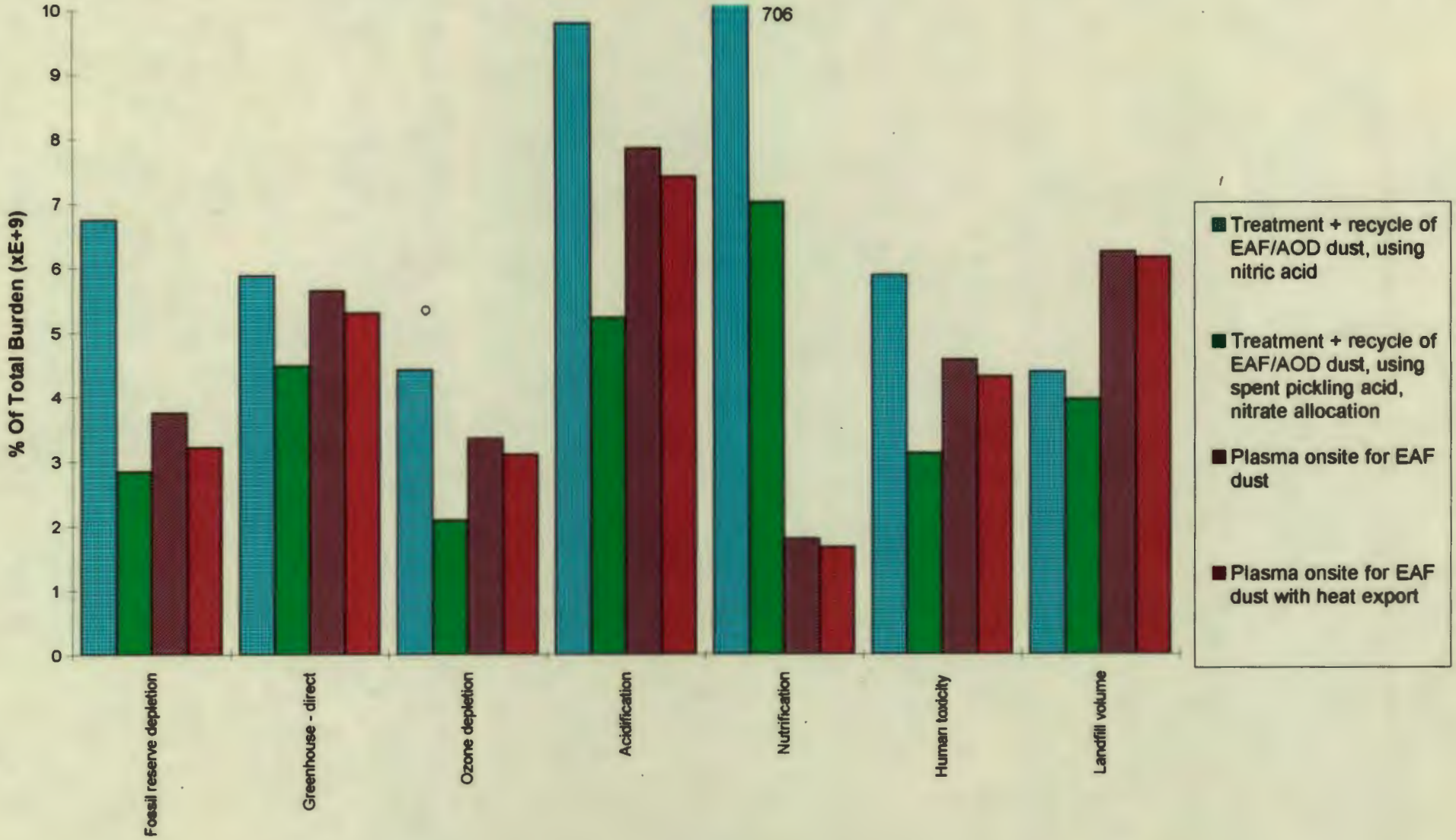


Figure 7.3: Process tree for hydrometallurgical dust treatment (produced from the PEMS template)

Figure 7.5: Impacts of alternative processes for the treatment of EAF/AOD dust



A first conclusion that can be drawn from the impacts in Figure 7.5 is thus that the hydrometallurgical process is only competitive with the pyrometallurgical route when informed by the Waste Minimisation guideline to use existing acidic waste streams for the dust treatment. However, before a conclusion can be reached on a preference between this option and the pyrometallurgical one, the sensitivity of the impacts to the numerous assumptions made and uncertainties encountered in the thesis has to be studied.

7.6.2 Sensitivity Analysis

Sensitivity analysis is a method used to study the effect of changes in input variables on output and is a useful tool to assess:

(1) the importance of the different input variables in terms of the effect that variations in these can have on the output;

(2) uncertainty in the values of the input variables: it can show which variables must be estimated more accurately; and

(3) stability of the output in the presence of unstable inputs.

A disadvantage of the PEMS computer model is that it does not make provision for sensitivity analyses. These have to be done by changing input data and studying the effect by repeating the impact assessment. Consequently, only a limited number of variations were studied for this LCA.

For the hydrometallurgical case, the following effects (highlighted in chapter 5 as uncertainties) were investigated:

* a change in the estimated energy requirement for the dust beneficiation plant. Variations of 50% were studied.

* the possibility of operating the leach residue drier on waste heat.

* a change in the amount of coke required in the smelting of the leach residue. Variations of 50% were, again, studied.

For the pyrometallurgical process, the studied effects, apart from that of heat export, were:

* a change in the process energy requirement. Since this requirement is well-known, a variation of 10% only was studied.

* a change in the location of the process. As the plant is situated in Sweden, swedish electricity generation was substituted for average European values. Simultaneously, transportation steps for the dust and the ingot product were defined, these being 500 km by electric rail each.

The motivation for this last change was to quantify the current European practice.

The questions that had to be answered from the sensitivity analysis were:

* Which parameters have the biggest influence on the environmental impacts?

* Which variations change the relative magnitudes of the impacts, making the pyrometallurgical process the preferred option?

Figures 7.6 and 7.7 (Appendix F) show the calculated variations in the impact profiles in the hydro- and pyrometallurgical dust treatment systems.

From these figures, it can be concluded that the effect of variations in the hydrometallurgical process are insignificant and that its impacts in all cases remain smaller than those of the pyrometallurgical base case. (Excluding the nutrification, which already in the base case exceeded the plasma equivalent). The biggest variations in impacts are caused by variations in the electricity estimate for the beneficiation plant.

For the pyrometallurgical dust treatment, the variations in impacts are also small, except for the changeover to Swedish electricity for the plasma process. Despite added environmental burdens from dust and ingot transportation, the impacts in this scenario drop sharply, for some impacts by more than 50%. This can be explained by the fact that a large proportion of Swedish electricity is generated from renewable energy, viz. by hydroelectric schemes. The PEMS database lists no burdens for this type of electricity generation; it certainly does not contribute to acidification, nutrification, the Greenhouse effect or fossil reserve depletion.

The remaining variations in the pyrometallurgical option were sufficiently small that none of its impacts dropped below those of the hydrometallurgical base case (excluding again the nutrification impact).

7.6.3 The Difference between Hydrometallurgical and Pyrometallurgical Treatment

From the results of the sensitivity analyses, it can thus be concluded that the relative magnitudes of the normalised impacts as shown in Figure 7.5 are not affected by uncertainty introduced at the process design stage in chapter 5.

The hydrometallurgical process employing spent acid can thus be seen to have marginally smaller environmental impacts in all categories except nutrification. The nutrification impact of this process is traced to the presence of phosphorus in the dust. The amount of this was measured only by one method and the chemical form has not been studied at all. No certainty exists thus over the precise magnitude of the nutrification impact. Its seriousness would have to be determined in the case of an industrial application of the hydrometallurgical process.

The preference for the hydrometallurgical process on the basis of environmental performance is, however, only valid as long as both processes use electricity from the same source. When the PlasmaDust (TM) process is assessed with clean electricity in its life cycle, this process becomes the preferred option.

This last observation establishes that the current European practice for the treatment of stainless-steelmaking furnace dusts is indeed the preferred option; also in relation to possible hydrometallurgical processing. As has been shown in chapter 5, the "hydrometallurgical" process also has a pyrometallurgical component, the energy requirement of which is only fractionally smaller than in thermal treatment. As long as this energy is supplied from a non-renewable and polluting source, all efforts to "clean up" the process are restricted.

7.7 CONCLUSION

In this chapter the comparative life cycle assessment of the hydrometallurgical process and the PlasmaDust (TM) process for the treatment of EAF/AOD dusts was presented.

From the LCA it was concluded that the hydrometallurgical process using imported nitric acid would perform worse environmentally than the currently preferred pyrometallurgical treatment route. However, if this process could be operated on an acidic waste stream also originating in stainless steel production, viz. spent pickling acid or acidic rinse water, it would have a marginally better environmental profile than the pyrometallurgical route. A qualification to the latter finding was that the nutrification impact of a phosphate containing waste stream from the hydrometallurgical treatment would have to be investigated in more detail.

With the latter finding, the second hypothesis of the thesis was substantiated. However, an important qualification should be added to it: The hydrometallurgical process is only preferable to pyrometallurgical treatment (on the basis of environmental impacts aggregated over the entire life cycle) if both processes operate on electricity from the same source. The effect of clean, renewable electricity dominates any environmental improvements that can be introduced by hydrometallurgical processing.

8. CONCLUSION

Three hypotheses were proposed for investigation in the introductory chapter. By way of experiment, discussion and calculation, arguments have been presented in the body of this thesis in support of these hypotheses. The findings are now summarized in the following sections. The difficulties encountered are also revisited and recommendations are made to address deficiencies.

8.1 THE HYDROMETALLURGICAL PROCESS: FEASIBILITY AND PREFERENCE

The first hypothesis in chapter 1 states that the hydrometallurgical treatment of chromium-containing dusts is technically feasible, while the second hypothesis deals with the perception that this route is environmentally preferable to the pyrometallurgical one. In support of these hypotheses, it was found that:

(1) Hydrometallurgical treatment is feasible as a preparatory step both for disposal or for recycling of a residue containing approximately 70% of the dust by weight. This was determined experimentally for ferrochromium smelter and stainless-steelmaking furnace dusts, which were deemed representative of flue dusts generated by the respective industries.

However, reservations remain about the forms of chromium in the residue (enrichment typically occurs) when considering the disposal option. These concern the possibility of long-term atmospheric oxidation leading to the remobilisation of the toxic hexavalent form of chromium.

The dissolved 30% of the dust can be split into a metal hydroxide fraction dominated by zinc - and thus possibly suitable as a raw material to the zinc industry - and a saline effluent. Depending on receiving water quality guidelines, desalination and safe disposal of the salts might be required for the latter.

(2) The hydrometallurgical process takes the form of an acid leach (nitric acid was found to be suitable) followed by neutralisation, precipitation and solid-liquid separation. Sulphuric acid leaching does not remove lead, another heavy metal found in the stainless-steelmaking dust. This disqualifies it for use in both the disposal and recycle scenarios for this dust. Nitric acid, when contaminated with sulphates, shows a reduced lead removal efficiency.

(3) The acidic effluents arising from the pickling operations in stainless steel production can, potentially, be used for the acid leaching of dust. A combination of nitric and hydrofluoric acid is normally used for pickling: as long as the amount of admixed sulphates from other effluents is controlled the spent acid or acidic rinse should be useful for dust treatment.

(4) The environmental profile of the hydrometallurgical process shows generally lower impacts than the pyrometallurgical process when spent pickling acid is used as a reagent, but markedly higher impacts when the production of nitric acid is incorporated into the assessment.

This result is not changed by the uncertainties introduced by estimates and approximations made in the process design. It is, however, subject to both processes deriving electrical energy from sources with similar environmental profiles.

In summary, treating chromium-containing dusts hydrometallurgically is both feasible and preferable, with both findings subject to qualifications.

8.2 FINDINGS ON THE USE OF LCA IN PROCESS DESIGN

Implicit in the statement of the second hypothesis was the assumption that LCA can be used to assess processes. With the current literature on LCA concentrating on its use in product-focused assessments, the study reported in this thesis explored some new ground in the application of LCA in the field of process engineering and design. The following findings can be reported:

(1) As presented in this thesis, LCA was used to assess a conceptually designed process and to compare its environmental profile to that of an existing process achieving an identical function. Using this method, the environmental impacts of the processes employed in the manufacturing of the reagents and the generation of electricity (an important process energy input) could be factored into the comparison. Similarly, environmental burdens associated with the transportation of materials could be accounted for. On the other hand, the assessment could be kept relatively simple by discounting all life cycle stages which were identical to both treatment processes.

LCA has thus been shown to be of use in technology assessment from an environmental performance perspective. Furthermore, it has been shown that such assessments can be made fairly early in process design, i.e. at the stage of conceptual design.

(2) Databases incorporated into the computer model used for LCA were found to be useful, allowing the contributions of upstream processes to be included with ease into the assessment. However, the number of processes available in the database is still a limiting factor. For example, data for nitric acid production is not contained in the database: fortunately a recently completed LCA could be cited for this purpose.

(3) The inclusion of processes involving the disposal of wastes (and hazardous wastes in particular) into the assessment was not possible, as long-term effects of such activities are poorly understood and not included in the database.

(4) It was found that the type of allocation method selected (applied to the case of concurrent waste treatment in this study) was critical to the result of the LCA. In this respect it was found that the best reflection of system performance is obtained by tracing each entry in the inventory table to its source and allocating accordingly. More sophisticated allocation rules need to be applied where such one to one correspondences can not be established.

(5) Finally, although only implicit to the presentation of the process design in chapter 5 and its assessment in chapter 7, LCA was in fact used in the design, especially to screen options. For example, the use of sodium hydroxide as a neutralising agent (instead of lime), which is technically feasible, was found to result in a large increase in fossil reserve depletion (amongst others): this was due to the large energy input required in the manufacture of this commodity. In practice, lime is preferred for reasons of cost: in this case, cost and environmental considerations (the latter extended to the life cycle) are seen to lead to the same result.

It can be concluded that LCA is a useful tool in the assessment of process design alternatives, particularly where the emphasis is on designing for minimum adverse environmental impact.

8.3 FINDINGS ON THE INTERACTION OF WASTE MINIMISATION AND LCA IN PROCESS DESIGN

The third hypothesis stated in the introduction originated from the proposal that formalised approaches to environmental management would assist in finding a better environmental solution. The hypothesis consists of three parts, which are discussed below:

(1) "Considerations of Waste Minimisation will lead to improvements in the process to be developed".

This has been shown to be the case, with the hydrometallurgical process using another waste stream as reagent having a significantly better environmental profile than the same process operating with imported acid.

In this case, it has thus been demonstrated semi-quantitatively that the strategy of reuse of a waste is preferable to treatment, as proposed in the Waste Minimisation hierarchy.

(2) "LCA will identify targets for the Waste Minimisation procedure..."

A formal Waste Minimisation audit was not conducted in this thesis. Only the principles of the approach, embodied by the Waste Minimisation hierarchy, were incorporated into the process design. The above statement can thus not be supported by any experiences made.

Nevertheless, the finding on the importance of electricity generation can demonstrate how LCA can inform an equivalent "Impact Minimisation" procedure: let us assume that the environmental impacts associated with the pyrometallurgical treatment (as determined in chapter 7) are deemed excessive. A systematic analysis of the inventory table will show that the majority of the impacts can be traced to electricity generation. At this point, a process generating not waste, but impacts, has been identified and the normal "Waste Minimisation" assessment phase can commence. This might lead to the recommendation of a process change, in this case from a fossil fuel generation system to a hydroelectric scheme.

(3) "Waste Minimisation will function as the improvement component of LCA".

Again, with no formal Waste Minimisation audit having been part of the thesis, this statement can not be substantiated by experience. However, the application of a Waste Minimisation principle - to re-use waste - led to a process with a significantly improved environmental profile. Whether this can be generalised remains to be shown: in particular, as Waste Minimisation usually operates only on a subsystem of the process targeted by LCA, there is no guarantee that local improvements will also be global. On the other hand, they might be amplified through the larger system.

In conclusion, the above arguments present sufficient evidence to support at least the proposal that formalised approaches to environmental management can contribute to improvements in

process design. Furthermore, it is believed that the support given to the statements contained in the third hypothesis warrants a further development of these ideas.

8.4 SOME GENERAL COMMENTS

With evidence having been presented in support of the hypotheses set out in the introduction, a number of general comments and conclusions can now be made:

* A criticism of this work might be that no consideration has been given to the economic feasibility of the process developed in chapter 5. This has intentionally been left out of the assessment. As stated in section 1.5 in the introduction, the value of the thesis should be seen in the discussion of environmental strategy and not in a recipe for dust treatment.

* The approach taken in this thesis w.r.t. the environmental impact assessment assumes that the process designer will want to assume responsibility for all the environmental impacts resulting from design decisions. While this is currently not accepted policy in large enterprises, there is every reason to believe that ethics will change as LCA gains acceptability as a metric for environmental assessment. Furthermore, it remains to be demonstrated whether this approach is in conflict with economic objectives.

* Finally, the strong influence that electricity generation was shown to have on the environmental profile reinforces the belief that while there might be "cleaner technology" in the current non-sustainable economy, "clean technology" can only be brought about by "clean" energy.

8.5 RECOMMENDATIONS

A number of difficulties were encountered and described in the process of gathering evidence to support the hypotheses around which this thesis has been built. To resolve these, the following recommendations are made:

* The chemical form of chromium in any leach residues prepared by methods described here and to be disposed should be determined. The likelihood of this chromium being oxidised by contact with air should also be assessed.

* Life Cycle Assessment methodology in general and computer databases in particular should be developed with respect to the assessment of the disposal of wastes. In this respect, some of the data contained in this thesis could be extracted to from a case study.

If the hydrometallurgical process to treat chromium-containing dust is to be developed further, the following should be undertaken:

* An economic feasibility study of this process;

* a detailed pyrometallurgical simulation for the return of the leach residue to the electric arc furnace;

* an investigation into the marketability of the zinc-containing metal hydroxide sludge produced as a byproduct.

Finally, it is recommended that consideration be given to the development of an "Impact Minimisation" procedure equivalent to Waste Minimisation but extended to the life cycle. It is proposed that such a procedure will form the basis for the improvement assessment part of Environmental Life Cycle Assessment, at least when applied in process engineering.

REFERENCE APPENDIX

Addis, B.J. (ed.) (1986)
Fulton's Concrete Technology, Portland Cement Institute, Midrand, South Africa.

Albanese, J.A. (1990)
TCLP Rule Promulgated by EPA, Plating and Surface Finishing, May 1990, pp.120-126.

Amer, A.M. (1991)
Processing of Ras-Shait chromite deposits, Hydrometallurgy, **28**, pp.29-43.

Atkinson, G.B. and L.J. Nicks (1985)
Leaching Aluminium-Superalloy Melts with Hydrochloric and Sulfuric Acids, Conservation and Recycling, **9**, 2, pp.197-209.

Azapagic, A. and R. Clift (1994)
Allocation of environmental burdens by whole system modelling - the use of linear programming, in Huppes and Schneider (1994), pp.54-60.

Barcza, N.A. and L.R. Nelson (1991)
Technology for the treatment of steel-plant dusts, Mintek Paper 8104, Mintek.

Barrera-Godinez, J.A., T.J. O'Keefe and J.L. Watson (1992)
Effect of ultrasound on acidified brine leaching of double-kiln treated EAF dust, Minerals Engineering, **5**, 10-12, pp.1365-1373.

Barret, E.C., E.H. Nenninger and J. Dziewinski (1992)
A hydrometallurgical process to treat carbon steel electric arc furnace dust, Hydrometallurgy, **30**, pp.59-68.

Basler and Hofmann (1974)
Vergleich der Umweltbelastung von Behältern aus PVC, Glas, Blech und Karton, Eidgenössisches Amt für Umweltschutz, Bern, cited by Udo de Haes, 1993.

Boustead, I. and G.F. Hancock (1982)
Energy and recycling in steel production systems, Resources and Conservation, **9**, pp.209-218.

Burgstaller, W., H. Strasser, H. Woebking and F. Schinner (1992)
Solubilization of Zinc Oxide from Filter Dust with Penicillium simplicissimum: Bioreactor Leaching and Stoichiometry, Environmental Science and Technology, **26**, 2, pp.340-346.

Canterford, J.H. (1985)
Hydrometallurgy: winning metals with water, Chemical Engineering, 92, Oct 28, pp.41-48.

Canterford, J.H. (1986)
Acid leaching of chromite-bearing nickeliferous laterite from Rockhampton, Queensland, Bull. Proc. Australas. Inst. Min. Metall, 291, 6, pp.51-56.

Christiansen, K. (1993)
Life Cycle Assessment in a Historical Perspective, Ch.1 in Environmental Assessment of Products, Weidema (1993a).

CRC Handbook (edited by Weast, R.C.) (1979)
Handbook of Chemistry and Physics, CRC Press, Florida.

Crittenden, B.D. and S.T. Kolaczkowski (1992)
Waste Minimisation Guide, The Institution of Chemical Engineers, Rugby, Warwickshire.

Clift, R. (1994)
Chairman's report session 3: Causality and allocation procedures, in Huppes and Schneider (1994).

Clift, R. and A. Longley (1994)
Personal communication.

Coulson, J.M., J.F. Richardson and R.K. Sinnot (1983)
Chemical Engineering: Volume 6 Design, Pergamon Press.

Cox, X.B., R.W. Linton and F.E. Butler (1985)
Determination of Chromium Speciation in Environmental Particles. Multitechnique study of Ferrochrome Smelter Dust, Environmental Science and Technology, **19**, 4, pp.345-352.

Dawson, M.F. and R.I. Edwards (1984)
An Alternative Route for the Production of Chromium Chemicals from Chromite, Mintek 50, Proceedings, vol. 2, Council for Mineral Technology.

Dean, J.G. et al (1972)
Removing Heavy Metals from Waste Water, Environmental Science and Technology, **6**, June.

de Larderel, J.A. (1993)
Environmental Life Cycle Assessment and its Applications, Journal of Cleaner Production, **1**, 3-4, p.130.

Delbeqc, A.L., A.H. van de Ven and D.H. Gustavson (1975)
Group Techniques for Program Planning, Glenview III, Scott, Foresman & Co.

Delmarco, K. and E. Kniel (1994)
Environmental Life Cycle Analysis - An evaluative tool for process design?, UCT Chemical Engineering Report.

Drabkin, M. and E. Rissmann (1989)
Waste Minimization Opportunities at an Electric Arc Furnace Steel Plant Producing Specialty Steels, Environmental Progress, **8**, 2, pp.88-96.

Dreisinger, D. (1990)
A challenge for the 1990s: The hydrometallurgical treatment of wastes and residues, Journal of Metals, January, 1990, p.27.

Dreisinger, D.B., E. Peters and G. Morgan (1990)
The hydrometallurgical treatment of carbon steel electric arc furnace dusts by the UBC-Chapparral process, Hydrometallurgy, **25**, pp.137-152.

Drews, S.C. and S.I. Mahote (1994)
Laboratory Leach Tests for Modelling Hazardous Waste Containment, UCT Chemical Engineering Report.

Eggels, P. and B. van der Ven (1994)
Allocation model in case of multiple waste handling, in Huppes and Schneider (1994), pp.143-148.

El-Nikhaily, A.E., M.A. El Zeky and M.A. Shahin (1989)
Microsilica dust in the ferrosilicon industry, CIM Bulletin, **82**, 923, pp.172-176.

Farrow, C.J. and A.R. Burkin (1975)
Alkali pressure leaching of chromium (III) oxide and of chromite mineral, Leaching and Reduction in Hydrometallurgy, Institute of Mining and Metallurgy, London.

Federal Regulations (1992)
Code of Federal Regulations, Title 40 - Protection of Environment, Part 260, U.S. Government Printing Office, Washington, 1992.

Fosnacht, D.R. (1981)
Recycling of Ferrous Steel Plant Fines, Iron and Steelmaker, **8**, 4, pp.22-26.

Geutskens, I.R. (1990)
Pressure leaching of zinc-bearing blast furnace dust, Lead-Zinc '90, edited by T.S. Mackey and R.D. Prengaman, The Minerals, Metals and Materials Society, pp.529-545.

Greig, J.A. (1987)
The effect of physical parameters on the pressure leaching of sphalerite concentrate, Separation Processes in Hydrometallurgy, edited by G. Davies, Ellis Horwood.

Gudenau, H.W., U. Härter, K.H. Peters, C. Bartels, A. Orth, E. Wallis and A. Kaune (1992)
Zirkulierende Wirbelschicht zur Aufbereitung von Stäuben, 2. Aachener Umwelttage, RWTH Aachen.

Guinée, J.B., H.A. Udo de Haes and G. Huppes (1993a)
Quantitative life cycle assessment of products. 1: Goal definition and inventory, Journal of Cleaner Production, **1**, 1, 3-13.

Guinée, J.B., H.A. Udo de Haes and G. Huppes (1993b)
Quantitative life cycle assessment of products. 2: Classification, valuation and improvement analysis, Journal of Cleaner Production, **1**, 2, 81-91.

Guinée, J. and R. Heijungs (1993)
A proposal for the classification of toxic substances within the framework of life cycle assessment of products, Chemosphere, **26**, 10, 1925-1944.

Hagni, A.M., R.D. Hagni and C. Demars (1991a)
Mineralogical Characteristics of Electric Arc Furnace Dusts, Journal of Metals, **43**, 4, pp.28-30.

Hagni, A.M., C. Demars and R.D. Hagni (1991b)
Mineralogy of Electric Arc Furnace (EAF) Dusts, EPD Congress '91, edited by D.R. Gaskell.

Hanewald, R.H., W.A. Munson, Jr. and D.L. Schweyer (1991)
Metal recovery from spent acid solutions and baghouse bags using the INMETCO process, in: Residues and Effluents - Processing and Environmental Considerations, edited by R.G. Reddy, W.G. Imrie and P.B. Queneau, The Minerals, Metals and Materials Society.

Harvey, W.W. and M.A. Hossain (1987)
Co-recovery of Chromium from Domestic Nickel Laterites, Journal of Metals, **39**, 1, pp.21-26.

Heijungs, R. (final editor) (1992a)
Environmental life cycle assessment of products - Guide, Centre of Environmental Science, Leiden.

Heijungs, R. (final editor) (1992b)
Environmental life cycle assessment of products - Backgrounds, Centre of Environmental Science, Leiden.

Huppes, G. (1994)
Chairman's report session 1: The issue of allocation, in Huppes and Schneider (1994)

Huppes, G. and F. Schneider (eds) (1994)
Proceedings of the European Workshop on Allocation in LCA, Centre of Environmental Science, Leiden.

Jackson, E. (1986)
Hydrometallurgical Extraction and Reclamation, Ellis Horwood.

Jenkins, G.M. (1969)
The Systems Approach, Journal of Systems Engineering, **1**, 1, Autumn 1969.

Johansson, B. and U. Löfgren (1991)
Operation of the ScanDust plant on stainless steel dust, published by ScanDust.

Johansson, S.E.E. (1994)
Columbus Joint Venture, XVth CMMI congress, Proceedings vol.2, edited by H.W. Glen, SAIMM, Johannesburg.

Jones, R.T. (1989)
Pyrosim (Pyrometallurgical process simulation software), Mintek, Johannesburg.

Kaas, W., E. Köhler, H.H. Borggrefe and K.D. Unger (1984)
Erzeugung und Verarbeitung armierter Filterstaubbriketts aus der Edelstahlerzeugung, Stahl und Eisen, **104**, 7, pp.357-362.

Kaltenhauser, R. (1987)
Recycling Furnace Dust, Iron and Steelmaker, March 1987, pp.23-26.

Keoleian, G.A. (1993)
The application of life cycle assessment to design, Cleaner Production, **1**, 3-4, pp.143-149.

Keoleian, G.A. and D. Menery (1993)
Life Cycle Design Guidance Manual. Environmental Requirements and The Product System, United States Environmental Protection Agency, EPA/600/R-92/226.

Kola, R. (1993)
Steel industry dust: solving of a problem by recycling, 4th International Scrap & Secondary Metals Conference, Metal Bulletin.

Kosson, D.S. (1988)
Opportunities for Research in Hazardous Waste Minimization, Environmental Progress, **7**, 3, pp.212-214.

Kroschwitz, J.I. and M. Howe-Grant (eds) (1993)
Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, volume 6, John Wiley and Sons, New York.

Kunter, R.S. and W.E. Bedal (1992)
Chloride-process treatment of Smelter Flue Dusts, Journal of Metals, December, 1992, pp.35-38.

Law, S.L., W.F. Lowry, J.G. Snyder and G.W. Kramer (1983)
Characterization of Steelmaking Dusts from Electric Arc Furnaces, RI8750, US Department of the Interior and Bureau of Mines.

Lee, R.L., H.L. Crist, A.E. Riley and K.E. Macleod (1975)
Concentration and size of trace metal emissions from a power plant, a steel plant, and a cotton gin, Environmental Science and Technology, **9**, 7, pp.643-647.

Legiec, I.A., C.A. Hayes and D.S. Kosson (1989)
Continuous Recovery of Heavy Metals from MSW Incinerator Ashes, Environmental Progress, **8**, 3, pp.212-216.

Li, Chung-Lee and Ming-Shing Tsai (1993a)
Mechanism of Spinel Ferrite Dust Formation in Electric Arc Furnace Steelmaking, ISIJ International, **33**, 2, pp.284-290.

Li, Chung-Lee and Min-Shing Tsai (1993b)
A crystal phase study of zinc hydroxide chloride in electric-arc-furnace dust, Journal of Materials Science, **28**, pp.4562-4570.

McAloon, T.P. (1987)
So Little Time, So Many Choices, Iron and Steelmaker, August 1987, pp.14-20.

Miettinen, P. (1993)
Software Tools in Life Cycle Assessment, Ch. 6 in Environmental Assessment of Products, Weidema (1993a).

Neumeier, L.A., and M.J. Adam (1988)
Recycling of stainless steelmaking dusts and other wastes, U.S. Bureau of Mines Information Circular, IC9195.

Nriagu, J.O. and E. Nieboer (eds) (1988)
Chromium in the Natural and Human Environments, John Wiley and Sons, New York.

Patterson, J.W. (1989)
Industrial wastes reduction, Environmental Science and Technology, **23**, 9, pp.1032-1038.

Perry, R.H. and D. Green (eds) (1984)
Perry's Chemical Engineers' Handbook, 6th edition, McGraw-Hill.

Petersen, J. and J.G. Petrie (1993)
Chromium Interconversions in Natural Environments - Potential Implications for Hazardous Leaching from Industrial Waste Landfills, UCT Chemical Engineering Report.

Petrie, J.G. and R.G. Paxton (1993)
Integrated technologies for treating liquid and solid wastes from ferrochrome and stainless steel production, unpublished.

Philipp, J.A. and H. Maas (1984)
Abfallwirtschaft in einem Hüttenwerk, Stahl und Eisen, 104, **8**, pp.403-407.

Philipp, J.A., H.P. Johann, M. Seeger, H.A. Brodersen and W. Theobald (1992)
Recycling in der Stahlindustrie, Stahl und Eisen, **112**, 12, pp.75-85.

Pira International (1994)
PEMS.2 - User Manual, 3rd edn., Pira International, Leatherhead, Surrey.

Resch, M.E. (1988)
Hazardous Waste Minimization Audits Using a Two-Tiered Approach, Environmental Progress, **7**, 3, pp.162-166.

Riggs, W.E. (1983)
The Delphi Technique: An Experimental Evaluation, Technological Forecasting and Social Change, **23**, pp.89-94.

Rubik, F. and T. Baumgartner (1991)
Evaluation of Eco-balances, IÖW, Heidelberg, cited by Umweltbundesamt (1992).

Saleh, F.Y., T.F. Parkerton, R.V. Lewis, J.H. Huang and K.L. Dickson (1989)
Kinetics of Chromium Transformations in the Environment, The Science of the Total Environment, **86**, pp.25-41.

Schifferings, C. (1992)
Recycling von Stäuben und Schlämmen der Edelstahlindustrie, Diplomarbeit, Fachhochschule Giessen-Friedberg.

Schneider, A. and H. Lünig (1983)
Umweltschutz im neuen Elektrostahlwerk Witten mit Bodenabstich-Lichtbogenofen, Stahl und Eisen, **103**, 3, pp.111-116.

Schoukens, A.F.S., F. Shaw and E.C. Chemaly (1993)
The Enviroplas process for the treatment of steel plant dusts, Journal of the SAIMM, **93**, 1, pp. 1-7.

Schroeder, D.C. and G.F. Lee (1975)
Potential Transformations of Chromium in Natural Waters, Water, Air and Soil Pollution, **4**, pp.355-365.

Sharma, T. (1990)
The Kinetics of Iron Dissolution from Chromite Concentrate, Minerals Engineering, **3**, 6, pp.599-605.

SETAC (Society for Environmental Toxicity and Chemistry) (1993a)
A conceptual framework for life-cycle impact assessment, SETAC, Pensacola.

SETAC (Society of Environmental Toxicology and Chemistry) (1993b)
Guidelines for Life-Cycle Assessment: A 'Code of Practice', SETAC, Brussels.

Sohn, H.Y. and M.E. Wadsworth (1979)
Rate Processes of Extractive Metallurgy, Plenum Press, New York.

Udo de Haes, H.A. (1993)
Applications of life cycle assessment: expectations, drawbacks and perspectives, Journal of Cleaner Production, **1**, 3-4, pp.131-137.

Ullrich, W. and H. Schicks (1991)
Aspekte zum Recycling von metallisch beschichtetem Stahl, Stahl und Eisen, **111**, 11, pp.85-92.

Umweltbundesamt (1992)
Ökobilanzen für Produkte: Bedeutung - Sachstand - Perspektiven, 38/92, Umweltbundesamt, Berlin.

van Craen, M.J., E.A. Denoyer, D.F.S. Natusch and F. Adams (1983)
Surface enrichment of trace elements in electric steel furnace dust, Environmental Science and Technology, **17**, 7, pp.435-439.

van der Weijden, C.H. and M. Reith (1982)
Chromium(III)-Chromium(VI) Interconversions in Seawater, Marine Chemistry, **11**, pp.565-572.

Weidema, B.P. (1993a)
Environmental Assessment of Products: A Textbook on Life Cycle Assessment, The Finnish Association of Graduate Engineers TEK.

Weidema, B.P. (1993b)
Quality Criteria for Life Cycle Assessments, Ch.5, in Environmental Assessment of Products, Weidema (1993a).

Weidema, B.P. (1993c)
Market aspects in product life cycle inventory, Journal of Cleaner Production, **1**, 3-4, pp.161-166.

Wentz, C.A. (1989)
Waste Minimization and Resource Recovery, Ch. 6, Hazardous Waste Management, McGraw-Hill.

Wentz, C.A., S-Y Chiu, L.J. Habegger, L.E. Martino and R.W. Peters (1988)
Design of a Tracking System for Hazardous Waste Minimization, Environmental Progress, **7**, 3, pp.155-161.

Zahedi, F. (1986)
The Analytic Hierarchy Process - A Survey of the Method and its Applications, Interfaces, **16**, 4, pp.96-108.

APPENDIX A

THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The following is a description of the experimental method adopted and used by UCT Chemical Engineering Department to determine the toxicity due to heavy metal mobility of treated and untreated wastes. It is based on the TCLP method of the United States Environmental Protection Agency (Federal Register, 1992:260 App.II).

The materials to be studied must be dry and the particle size must not exceed 9 mm.

If the sample is of a type not previously tested, so that its acidity/alkalinity is unknown, the following test is performed:

1. A 10 g sample is mixed with twenty times its weight of deionised water.

2. The mixture is placed on a magnetic stirrer for two minutes.

3.1 If pH of solution is < 5.0, the extraction fluid is made by adding 5.7 ml of glacial acetic acid to 500 ml deionised water, then adding 64.3 ml 1.0 N NaOH and diluting to 1 litre with deionised water.

3.2 If pH of solution is > 5.0, 3.5 ml 1.0 N HCl is added to the mixture. This is then slurried for 30 s, covered with a watchglass, heated to 50°C and held for 10 minutes. After cooling, the pH is measured.

3.2.1 If pH < 5.0 the extraction fluid is made as described in 3.1 above.

3.2.2 If pH > 5.0, the extraction fluid is made by diluting 5.7 ml glacial acetic acid with deionised water to a volume of 1 litre.

Samples for which the acidity/alkalinity can be expected to be similar to that of previously tested materials are immediately subjected to the main part of the TCLP, as described below.

4. A fresh sample to be extracted is placed with 20 times its weight of the extraction fluid into a *Schott* 2 l borosilicate glass bottle which is then agitated by end-over-end rotation for eighteen hours.

5. The slurry is filtered through Whatman's no. 1 filter paper using vacuum filtration. A sample is further cleaned by filtration through a 0.4 μm Millipore filter.

6. The pH of the filtrate is recorded.

7. If necessary, the filtrate is refrigerated before further analysis.

8. Samples are analysed for metal concentrations using Atomic Absorption Spectroscopy.

water, before drying at 105 °C and weighing. The wash water was kept separate from the leachate and was discarded.

A 50 ml portion of the leachate was further cleaned by filtration through a 0.4 μm Millipore filter, acidified with u10 ml of 1 N HNO_3 if the pH was above two and refrigerated before analysis.

B.1.2 The Matrix of Experiments

The factors that were investigated by the leaching experiments have been discussed in section 4.2.4. Table B.1 shows the set of experiments conducted to investigate the factors. The tests marked as "kinetic" had samples withdrawn at the specified time intervals.

Table B.1: Plan of the leaching experiments

Acid type	Strength	Volume*	Experiment numbers
EAF/AOD dust:		(ml)	
Sulphuric	1 N	1000 1250	1, 3 2, 4 kinetic
Nitric	1 N	1000 1250	7,8 kinetic 9, 10
	pH = 5.5	1000	5,6,11 (kinetic)
Ferrochrome dust:			
Nitric	pH = 5.5	1000	13,21,22
	1 N	1250	14,15,16
Sulphuric	1 N	1500 1250	17, 19 kinetic 18, 20
Added experiments:	(EAF/AOD)		(nitric acid)
Light Na_2SO_4	1 N	1000	S3, S4
Strong Na_2SO_4	1 N	1000	S1, Ŝ2

* This is the volume of leachant added at the start. The dust amount for all experiments was 1/20th of this, in gram.

The conditions selected for the added experiments were based on the initial results obtained. As discussed in section 4.2.5, it was found that virtually complete lead removal could be achieved by leaching the dusts with 1 N nitric acid, while both sulphuric acid leaching and nitric acid leaching at pH 5.5 liberated no lead. The experiments with 1 N nitric acid were thus repeated with light (0.001 N) and strong (0.1 N) sodium sulphate additions. These experiments were terminated after 12 hours.

B.2 ANALYSIS OF THE LEACHATES

B.2.1 Elemental concentrations

Elemental concentrations were determined by Atomic Absorption Spectroscopy on a Varian SpectrAA-30 spectrophotometer. Where necessary, the samples were diluted with deionized water to fall within the calibration ranges of the different elements. The percentage relative standard deviations (%RSD) reported by the instrument were in the range of 0.1 to 1.5. Generally, readings with low %RSDs (<5%) could be obtained down to 10% of the lowest calibration standard. Readings lower than these values were reported as < "value"; and as n.d. (not detected) if there was no observable difference from the reading for a blank.

The complete results are listed in Table B.2.

B.2.2 Filtrate volumes

The filtrate volumes were recorded with the aid of a 1 l measuring cylinder with an accuracy of $\pm$ 7.5 ml. As can be seen from the results in Table B.2, they were significantly lower than the amounts of leachant initially added. This was thought to be a consequence of evaporation and, to a limited extent, splashing from the open beakers.

B.2.3 Unreacted acid

A measure of the free or unreacted acid - also shown in Table B.2(I) - was obtained for the experiments in which 1 N acids were used for leaching. This was done by titration of a 5 ml sample diluted to 100 ml with distilled water against 0.1 N NaOH to a pH of 2.0. This endpoint was chosen, because the precipitation of any metal hydroxides (which commences

approximately at pH 2.5) would also consume NaOH. The amount of NaOH required to neutralize from pH 2 was determined for the acid leachant solution alone and was added as a constant to the titration volumes. All titrations were carried out in duplicate.

B.2.4 Measurement of the TDS values

The total dissolved solids (TDS) concentration was measured by evaporating 5 ml of sample in a drying oven at 105 °C and recording the weight of the residue. Each measurement was duplicated and the mean relative deviation from the mean was 2.4%. The TDS values are also listed in Table B.2.

B.3 THE CALCULATION OF PERCENTAGE REMOVALS

In the calculations for the final leachates (those collected by filtration after 24 hours) the percentage dissolution was defined as the product of the element concentration and the leachate volume (including the filter cake moisture) divided by the product of the initial dust amount and the element concentration in the dust. For the intermediate samples the leachate volume was equated to the sample volume (50 ml) and the initial dust amount was taken as the product of the ratio of sample to initial leachant volume and the initial dust amount.

The calculated percentage removals are shown in Table B.6.

Table B.2(i): Results of leach runs with 1 N acid

1. EAF/AOD dust

(a) 1.0 N sulphuric acid

Sample	free acid (mol/l)	leachate (ml)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Fe (ppm)	Ni (ppm)	Sn (ppm)	TDS (ppm)
1		868	328	420	4.91	1.278	2960	341	4.4	70080
2.0	1.04									
2.1	0.80	50	171	237	4.12					66320
2.2	0.74	50	183	235	4.20					65450
2.3	0.73	50	204	255	4.74					67070
2.4	0.74	50	223	298	5.20					66720
2.5	0.69	50	252	322	5.46					66730
2.6	0.71	860	306	392	5.25	1.27	2890	330	4.0	69510
3		880	296	382	5.09	1.252	2900	322	4.0	70530
4.0	1.04									
4.1	0.82	50	170	255	5.45					
4.2	0.77	50	197	264	4.48					
4.3	0.76	50	214	281	5.51					
4.4	0.75	50	227	295	5.30					
4.5	0.71	50	248	343	4.50					
4.6	0.72	875	290	380	4.91	1.246	2865	321	3.8	70240

(b) 1.0 N nitric acid

7.0	1.26									
7.1	0.99	50	193	305	266					
7.2	0.98	50	204	255	267					
7.3	0.95	50	216	283	278					
7.4	0.96	50	223	282	280					
7.5		30								
7.6	0.94	905	281	326	312	1.186	2335	312	3.5	37070

shaded = not determined

Table B.2(i) [continued]

Sample	free acid (mol/l)	leachate (ml)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Fe (ppm)	Ni (ppm)	Sn (ppm)	TDS (ppm)
8.0	1.27									
8.1	0.95	50	196	241	268					
8.2	0.94	50	208	270	266					
8.3	0.93	50	220	269	276					
8.4	0.92	50	225	326	277					
8.5	0.93	50	238	294	288					
8.6	0.92	905	271	341	302	1.16	2295	295	3.5	35490
9		868	286	364	315	1.216	2380	308	3.3	36910
10		875	285	371	316	1.203	2285	308	3.6	35580

(c) 1.0 N nitric acid with sulphates

S1			267	323	108		2035	258		51040
S2			269	330	109		2060	261		52210
S3			256	313	303		1860	247		34230
S4			254	324	296		1840	247		34980

2. Ferrochrome smelter dust

(a) 1.0 N sulphuric acid

17.0	1.02									
17.1	0.93	50	61.1	755	2.4					70410
17.2	0.93	50	60	757	3.06					70710
17.3	0.93	50	80	824	2.61					71020
17.4	0.94	50	82.6	854	3.16					70260
17.5	0.95	50	88.2	868	3.56					73930
17.6	1.02	1015	101.4	1378	4.19		56.9			81640
18		1065	104.7	1018	4.12		55.9			78250

shaded = not determined

Table B.2(i) [continued]

Sample	free acid (mol/l)	leachate (ml)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Fe (ppm)	Ni (ppm)	Sn (ppm)	TDS (ppm)
19.0	1.01									
19.1	0.92	50	72	762	2.51					
19.2	0.92	50	74.5	733	2.68					
19.3	0.94	50	84.2	769	2.62					
19.4	0.92	50	83.6	804	2.95					
19.5	0.93	50	89.6	864	3.56					
19.6	0.98	1055	101.5	1005	3.94		54.2			78730
20		1085	94.6	930	4.14		52.5			76440

(b) 1.0 N nitric acid

14		1125	107.3	959	9.30		46.2			27060
15		1095	108.5	953	9.26		46.8			28510
16		1065	107.4	968	9.56		47.7			28910

shaded = not determined

Table B.2(ii): Results of leach runs at contant pH

1. EAF/AOD dust

Sample	leachate (ml)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Fe (ppm)	Ni (ppm)	Sn (ppm)	TDS
5.1	50	65.8	75.6	<0.2			2.52		6130
5.2	50	67.0	59.2	<0.2			2.88		6840
5.3	50	69.1	75.8	<0.2			3.96		8140
5.4	50	71.5	80.8	<0.2			5.4		9400
5.5	775	75.0	89.4	<0.2	0.31	0.96	8.4	n.d.	10690
6.1	50	59.0	28.1	<0.2			1.44		
6.2	50	64.7	49.6	<0.2			2.4		
6.3	50	69.0	55.4	<0.2			3.36		
6.4	50	71.4	56.0	<0.2			4.44		
6.5	690	81.2	87.4	<0.2	0.28	0.72	8.52	n.d.	11110
11.1	50	59.2	37.6	<0.2			1.44		
11.2	50	61.3	42.0	<0.2			1.92		
11.3	50	62.5	48.0	<0.2			2.52		
11.4	50	65.4	66.2	<0.2			3.84		
11.5	768	68.5	50.8	<0.2	0.18	0.96	5.88	<2.5	9060

2. Ferrochrome smelter dust

13	890	33.2	384.2	<0.2		0.48	0		11150
21	887	29.6	357.0	<0.2		0.72	0		10630
22	888	27.0	332.2	<0.2		0.84	0		11310

Notes: shaded = not measured, n.d. = not detected

Table B.3(i): Residues from leaching with 1.0 N acid
Amounts, moisture and sulphur contents

Residue	No.	Dust mass (g)	Wet cake (g)	Dry cake (g)	% Moisture	% Sulphur
EAF/AOD	1	50	50.2	38.1	24.1	
sulphuric	2	50	51.4	39.6	23.0	4.6
acid	3	50	49.6			
	4	50	50.5	38.5	23.8	
	mean	50	50.4	38.7	23.6	
EAF/AOD	7	50	44.6	35.3	20.9	
nitric	8	50	43.3	34.4	20.6	
acid	9	50	41.9			
	10	50	43.7	34.8	20.4	< 0.01
	mean	50	43.4	34.8	20.6	
Ferrochrome	17	62.5	66.1	44.4	32.8	
sulphuric	18	62.5	66.0	44.8	32.1	< 0.01
acid	19	62.5	66.0	44.7	32.3	
	20	62.5	64.6			
	mean	62.5	65.7	44.6	32.4	
Ferrochrome	14	62.5	67.3	45.1	33.0	
nitric	15	62.5	67.1	45.0	32.9	< 0.01
acid	16	62.5	65.8			
	mean	62.5	66.7	45.1	33.0	

Table B.3(ii): Residues from leaching at constant pH
Amounts, moisture and sulphur contents

Residue	No.	Wet cake (g)	Dry cake (g)	Moisture content (%)	Sulphur content (%)
EAF/AOD	5	47.0	37.1	21.1	
dust	6	47.7	36.8	22.9	
	11	51.7	40.3	22.1	< 0.01
	mean		38.1	22.0	
Ferrochrome	13	59.8	40.9	31.6	
smelter	21	61.0	41.4	32.1	< 0.01
dust	22	59.7	40.9	31.5	
	mean		41.1	31.7	

Table B.4: Composition of leach residues (wt.%)

Element	Residual 10	Residual 11	Residual 18	Residual 21
Cr	14.6	11.1	1.85	1.77
Fe	35.1	30.8	0.7	0.8
Ni	3.5	3.1	0.0	0.0
Ca	0.0	0.0	0.0	0.0
Zn	1.39	1.43	5.4	6.4
Pb	0.070	0.572	0.069	0.070
Cd	0.002	0.003		

shaded = not determined

Table B.5: Material Balances for Leaching Experiments

		Experiment Number							
		10		11		18		21	
Category		comp.	mass (g)	comp.	mass (g)	comp.	mass (g)	comp.	mass (g)
(1) Solids (dry)									
Dust in:	g		50		40		62.5		50
Acid in:	(g/l)	77.0	77.0	77.0	6.6	49.0	61.3	77.0	2.4
Filter cake:	g		34.8		40.3		44.8		40.9
TDS:	(ppm	35580	31.1	9060	7.0	78250	83.3	10530	9.4
Closure	%		51.9		101.4		103.5		96.1
(2) Water									
Acid in:	ml		1000		886		1250		1031
Leachate:	ml		875		768		1065		887
Cake moisture:	ml		8.9		11.4		21.2		19.6
Closure	%		88.4		88.0		86.9		87.9
(3) Chromium									
in dust:	(%)	11.5	5.73	11.5	4.584	1.80	1.12	1.80	0.90
in leachate:	(ppm	285	0.25	68.5	0.05	104.7	0.11	29.6	0.03
in residual:	(%)	14.6	5.09	11.1	4.47	1.85	0.83	1.77	0.72
Sum out:			5.35		4.52		0.94		0.75
Closure	%		93.3		98.6		83.8		83.5
(4) Iron									
in dust:	(%)	29.7	14.83	29.7	11.87	0.57	0.36	0.57	0.29
in leachate:	(ppm	2285	2.02	0.7	0.00	55.9	0.06	0.7	0.00
in residual:	(%)	35.1	12.20	30.8	12.41	0.70	0.31	0.79	0.32
Sum out:			14.22		12.41		0.37		0.33
Closure	%		95.8		104.6		104.1		113.5
(5) Zinc									
in dust:	(%)	1.58	0.79	1.58	0.63	6.49	4.06	6.49	3.25
in leachate:	(ppm	371	0.33	88.4	0.07	1018	1.11	357	0.32
in residual:	(%)	1.39	0.48	1.43	0.58	5.37	2.41	6.36	2.60
Sum out:			0.81		0.64		3.51		2.92
Closure	%		102.6		102.0		86.6		90.1
(6) Lead									
in dust:	(%)	0.52	0.26	0.52	0.21	0.06	0.036	0.06	0.03
in leachate:	(ppm	316	0.28	<0.2	0.00	4.1	0.000	<0.2	0.00
in residual:	(%)	0.07	0.02	0.57	0.23	0.07	0.031	0.07	0.03
Sum out:			0.30		0.23		0.031		0.03
Closure	%		116.0		111.7		85.3		98.5
(7) Cadmium									
in dust:	(%)	0.004	0.002	0.004	0.002				
in leachate:	(ppm	1.203	0.001	0.258	0.000				
in residual:	(%)	0.002	0.001	0.003	0.001				
Sum out:			0.002		0.002				
Closure	%		87.8		102.1				

Table B.6(i): % recoveries into the leachate with 1 N acid

1. EAF/AOD dust

(a) 1.0 N sulphuric acid

Sample	Cr	Zn	Pb	Cd	Fe	Ni
1	5.0	46.1	1.6	57.8	17.3	28.2
2.0	0.0	0.0	0.0	0.0	0.0	0.0
2.1	3.0	29.9	1.6			
2.2	3.2	29.7	1.6			
2.3	3.6	32.2	1.8			
2.4	3.9	37.7	2.0			
2.5	4.4	40.7	2.1			
2.6	4.6	42.7	1.7	56.9	16.8	27.0
3	4.5	42.6	1.7	57.4	17.2	27.0
4.0	0.0	0.0	0.0			
4.1	3.0	32.3	2.1			
4.2	3.4	33.4	1.7			
4.3	3.7	35.6	2.1			
4.4	4.0	37.3	2.0			
4.5	4.3	43.4	1.7			
4.6	4.4	42.1	1.6	56.8	16.9	26.7

(b) 1.0 N nitric acid

7.0	0.0	0.0	0.0			
7.1	3.4	38.5	101.5			
7.2	3.6	32.3	101.8			
7.3	3.8	35.8	106.1			
7.4	3.9	35.7	107.0			
7.5						
7.6	4.4	37.3	107.7	55.9	14.2	26.9

Table B.6(i) [continued]

Sample	Cr	Zn	Pb	Cd	Fe	Ni
8.0	0.0	0.0	0.0			
8.1	3.4	30.4	102.2			
8.2	3.6	34.1	101.5			
8.3	3.8	34.1	105.5			
8.4	3.9	41.3	105.7			
8.5	4.2	37.2	110.1			
8.6	4.3	39.0	104.4	54.7	14.0	25.4
9	4.3	39.9	104.3	55.0	13.9	25.4
10	4.4	41.1	105.7	54.8	13.5	25.6

2. Ferrochrome smelter dust

(a) 1.0 N sulphuric acid

17.0	0.0	0.0	0.0		
17.1	6.8	23.3	8.3		
17.2	6.7	23.3	10.6		
17.3	8.9	25.4	9.0		
17.4	9.2	26.3	10.9		
17.5	9.8	26.7	12.3		
17.6	9.2	34.5	11.8		16.1
18	9.9	26.7	12.2		16.6
19.0	0.0	0.0	0.0		
19.1	8.0	23.5	8.7		
19.2	8.3	22.6	9.3		
19.3	9.4	23.7	9.1		
19.4	9.3	24.8	10.2		
19.5	10.0	26.6	12.3		
19.6	9.5	26.1	11.5		15.9
20	9.1	24.9	12.4		15.9

(b) 1.0 N nitric acid

14	10.7	26.6	29.0		14.5
15	10.6	25.7	28.1		14.3
16	10.2	25.4	28.2		14.2

Table B.6(ii): % recoveries into the leachate with constant pH

1. EAF/AOD dust

Sample	Cr	Zn	Pb	Cd	Fe	Ni
5.1	1.1	9.6				
5.2	1.2	7.5				
5.3	1.2	9.6				
5.4	1.2	10.2				
5.5	1.0	8.8		12.7	0.0	0.6
6.1	1.0	3.6				
6.2	1.1	6.3				
6.3	1.2	7.0				
6.4	1.2	7.1				
6.5	1.0	7.6		10.0	0.0	0.6
11.1	1.0	4.8				
11.2	1.1	5.3				
11.3	1.1	6.1				
11.4	1.1	8.4				
11.5	0.9	4.9		7.3	0.0	0.4

2. Ferrochrome smelter dust

13	3.3	10.5			0.1	
21	2.9	9.8			0.2	
22	2.7	9.1			0.3	

APPENDIX C

ESTIMATION OF MATERIAL FLOWS IN THE DUST TREATMENT PLANT

This appendix provides additional information on the calculation of material flows in the hydrometallurgical dust treatment process.

C.1 ASSUMPTIONS MADE IN THE CALCULATION OF MATERIAL FLOWS FOR THE DUST LEACHING PROCESS

Calculation of leachate and leach residue amounts and compositions

A model of the leaching system was developed from the experimental results, assuming that these can be transposed to any "typical" EAF/AOD dust, in particular to the type treated in the PlasmaDust process. This assumption was justified by the finding that the dust studied experimentally can be regarded as representative of the stainless steel sector.

The acid for leaching was 1 N nitric, which is neutralized with hydrated lime (10% calcium hydroxide, by mass) to a pH of 3.5 after leaching, adding iron (and possibly lead) hydroxide, as well as calcium fluoride to the leach residue.

In conjunction with Table 5.1, the following apply:

* The amount of water in the leachate is the sum of the water added with the nitric acid and the water produced in the acid neutralisation reactions.

* To calculate the amounts of the metal species in the leachate, the averages for experiments 7-10 were used for Cr, Zn, Cd and Ni; for iron it was assumed that by adjusting the final pH its removal could lowered to 10% of the experimental values, while for lead a removal of 50% was assumed to account for this pH adjustment. Half the Mn, Hg (their hydroxides precipitate at highish pH) and S, none of the Sn, Mo, Si and Al and all the Mg, K, Na, Cl and P were assumed in the leachate. For fluorine, it was assumed that 90% of the original amount would report to the residue, mainly as CaF_2 precipitate. The Ca in the leachate was calculated correspondingly, assuming that the fluoride is the only form precipitating. The non-water oxygen content of the leachate was derived from the amounts of N, S and P.

* A computer program to predict chemical speciation like, eg. MINTEQA2, could be useful to predict the distribution between dissolved and precipitated phases.

* The amounts of all species, except water, in the residue were calculated from the differences between the totals added (in dust, acid and lime) and the amounts in the leachate. Their total differed by 10.8% from the dry residue mass (predicted from the experimental work and the assumptions pertaining to iron and lead), which was considered reasonable for the crude assumptions.

C.2 ESTIMATION OF MATERIAL FLOWS FROM SMELTING OF THE BRIQUETTES IN THE EAF

This section contains information used in the calculation of the material flows in Table 5.3. The feed to the furnace consists of the briquettes from Table 5.2.

The amount of each element in the briquettes is calculated by summing the amounts in the leach residue (Table 5.1), the coke breeze and the binder. The composition of coke breeze has been assumed to be the same as that of the coke in the PlasmaDust process (Table 2.5). The elemental composition of the binder (Portland cement) was calculated from information presented by Addis (1986:14) for typical South African portland cement and came to Si - 11%, Ca - 46%, Al - 2.5%, Fe - 1.7%, O - 35% and S - 1.3%.

The fraction of the metals in the briquettes reporting to the melt were taken as 98% (Fe), 90% (Cr), 98% (Ni) and 95% (Mo). These values are based on the assertion by Neumeier and Adam (1988) that in their plant trials (where 14-19% of the furnace charge consisted of a mixture of wastes) the metal recoveries fell into the normal operating range. These recoveries are similar to those reported for the INMETCO process (Hanewald et al, 1991), which is a two-stage operation employing a rotary hearth furnace and an EAF to recover metallics from chrome and nickel containing wastes. 60% of Mn is recovered into the metal in this product.

The amounts of carbon, silicon, sulphur and phosphorus in the melt are estimated as 3.8%, 0.1%, 0.2% and 0.05%, respectively; these are the values reported for the INMETCO process (Hanewald et al, 1991).

It was then assumed that 1% of all non-volatile elements and 100% of the volatiles (Zn, Pb, Cd, Hg, Na, K, Cl) in the furnace feed report to the dust, together with stoichiometric oxygen to form the lowest valency oxides. This is, of course, a gross simplification, but represents a worst-case scenario. An exception was made for fluorine, for which Johansson and Löfgren (1991) estimate 10% reporting to the dust in another high-temperature process.

The remaining carbon and all hydrogen are assumed to report to the gas phase as carbon monoxide and hydrogen. The amount of oxygen in the gas phase is calculated stoichiometrically.

The balance of all elements, except oxygen, is then assumed to be present in the slag. The oxygen in the slag is, again, calculated stoichiometrically (taking into account that sulphur is present in the slag as a sulphide). The amount of slag so determined is 210 kg, which is slightly higher than the 197 kg calculated for a theoretical system by Barcza and Nelson (1991). The slag composition is similar to that reported for the INMETCO process, although too high in SiO2 and chromium.

Under these assumptions the material balances for all elements except oxygen should, and do, close exactly. The poor closure for oxygen is directly linked to the amount of coke added to the briquettes. If more coke were added, more oxygen would be found in the flue gas as CO, improving the closure for this element. However, if the briquettes are added as a minor component to an EAF operating on the normal mixture of scrap and charge chrome, the excess carbon in the furnace would reduce the metal oxides in the leach residue. A benefit of this is that less oxygen is required in the AOD to lower the carbon content, as reported by Kaas et al (1984).

APPENDIX D

ENERGY REQUIREMENTS IN THE HYDROMETALLURGICAL PROCESS

The purpose of this appendix is to estimate energy requirements for the various unit operations used in treating and recycling a chromium-containing dust.

The estimates are to be order-of-magnitude quantities, sufficiently accurate to inform whether a unit operation is a critical contributor to overall energy consumption.

D.1 ENERGY REQUIREMENTS OF STIRRED TANKS

Two unit operations in the dust beneficiation plant require the agitation of a slurry for prolonged periods: these are leaching (estimate 2 hours, 1 for leaching and 1 for pH adjustment) and neutralization (2 hours assumed). It is assumed that each occurs in batch mode in a 30 m^3 vessel agitated by a top-mounted turbine-type impeller (recommended for large-scale solids suspension by Perry, 1984:19-6). The power drawn by the stirrers needs to be estimated in order to calculate the energy consumption.

Correlations for impeller power use in stirred vessels can be found in standard Chemical Engineering texts. Such correlations take into account the configuration of the system (impeller and vessel diameter, type of impeller and presence of baffles), operating characteristics (impeller revolutions) and slurry properties (density and viscosity). A graphical representation of such correlations is shown in figure 19-13 in Perry's Chemical Engineers' Handbook (Perry, 1984).

Assuming the following values for the design variables,

impeller diameter (D_a) = 1.86 m [60% of tank diameter]
tank diameter = 3.1 m
tank height = 4.1 m
impeller speed (N) = 1 s^{-1} (60 rpm)
fluid density (ρ) = 1200 $kg.m^{-3}$
fluid viscosity (μ) = 0.002 Pa.s (double that of water)

the Reynolds number

$$N_{Re}=\frac{D_a^2 N\rho}{\mu} \quad \text{.....(C.1.1)}$$

is calculated to be 1.1E+6.

This corresponds to a turbulent regime (even a gross error in the viscosity estimate would not change this). From figure 19-13 in Perry and figure 10.59 in Coulson and Richardson (1983), a power number of 3 can be assumed to be conservative.

From the expression for the power number,

$$N_P=\frac{P}{\rho N^3 D_a^5} \quad \text{.....(C.1.2)}$$

the power transmitted by the impeller shaft can be calculated to be 80.1 kW. Assuming an efficiency of 50% for energy conversion in the electric motor, the motor rating would have to be 160 kW.

Either stirred tank, running for 2 hours, would then have an energy requirement of 1154 MJ.

The power requirement is highly sensitive to both the impeller diameter and the impeller speed: decreasing the impeller diameter to 1 m (40% of tank diameter) reduces the energy requirement for the leaching tank to 152 MJ; decreasing the impeller speed to 50 rpm (impeller staying at 1.5 m) reduces it to 668 MJ.

D.2 ENERGY REQUIREMENTS FOR FILTRATION

After acid leaching of dusts, the slurry is separated into a leach residue/precipitate and a filtrate. The energy requirement for this unit operation must be estimated.

It is assumed that the filtration occurs in a constant flow filter, with the flow provided by a positive displacement pump. The power used by the system is the product of the pressure head, the flow rate and the pump and motor efficiencies; the energy use is obtained by integrating with respect to the time of operation.

Positive displacement pumps provide constant flow against any head smaller than the pump's relieve valve setting and have efficiencies between 50% and 90% (Perry, 1984:6:12).

The pressure head consists of frictional losses in pipes, static head differences and the resistance of the filter cake and medium. The first two will be neglected here. The pressure drop in an incompressible filter cake - at constant flow rate - increases linearly with time, as shown by equation D.2.1:

$$\Delta P = \frac{Q^2 \alpha \mu W}{A^2} t \qquad \text{.....(c.2.1)}$$

where Q = flowrate of filtrate (m^3/s)
P = pressure drop (Pa)
A = area of filter (m^2)
W = mass solids per volume filtrate (kg/m^3)
t = time (s)
α = specific filter cake resistance (m/kg)
μ = viscosity of slurry (Pa.s)

The thickness of the filter cake is calculated from the amount of the solids, the filter area, the cake porosity (ϵ) and the solids density (ρ_s) by equation D.2.2:

$$L = \frac{WQt}{A(1-\epsilon)\rho_s} \qquad \text{.....(C.2.2)}$$

Selecting a filter area of 50 m^2, a flow rate of 20 m^3/h, a maximum pressure drop of 1000 kPa and using values of 40, 1.9×10^{11} (determined indicatively) and 0.002 for W, α and μ, respectively, it can be shown (using equation A.2.1) that 27 m^3 of slurry (equivalent to the treatment of 1 ton of dust) can be filtered under constant flow rate conditions; the final pressure difference is 898 kPa and the filter cake thickness is calculated from equation A.2.2 to be 0.9 cm.

The pumping power is given by $P = dP \times Q = dP_f/t_f \times t \times Q$. Integrating from $t=0$ to $t=t_f$, gives $W = \frac{1}{2}\, dP_f \times Q \times t_f$.

Assuming pump and motor efficiencies of 70% and 50%, the motor energy requirement is calculated to be 34.6 MJ.

D.3 THERMAL ENERGY REQUIREMENT FOR RESIDUE DRYING

The material balance for the residue preparation plant shows that 103 kg of water must be removed from the residue obtained when 1000 kg of dust is leached.

The theoretical energy required for the drying operation is calculated from (1) the enthalpy difference of the liquid water and 50% moist (assumption) air at 25°C on the one hand and the air-vapour mixture at 60°C and 70% relative humidity. (These values are convenient assumptions that should result in an order of magnitude estimate for the drying operation), and (2) the heat added to the solids and the remaining water:

1. A psychrometric chart (like those shown in figs 12-1 to 12-3 and 20-11 in Perry, 1984) can be used to determine the amount of air and the enthalpies. The moisture content of the incoming air is 0.01 kg/kg of dry air; in the leaving stream it is 0.099 kg/kg dry air. To evaporate 103 kg of water (Table 5.2) thus requires 1156 kg of dry air. The enthalpy of the incoming air is 50 kJ/kg dry air, that of the added water is calculated to be 9.3 kJ/kg dry air and that of the leaving air is 320 kJ/kg dry air. The enthalpy difference comes to 261 kJ/kg dry air; multiplying by the 1156 kg of dry gives a heat requirement of 301 MJ.

2. For every 103 kg of evaporated water, 852 kg of residue and 89 kg of water are heated from 25°C to 60°C (no phase change). Assuming that the solid behaves like magnetite (for which an average heat capacity of 0.67 kJ/kg.K can be calculated between 25°C and 60°C from data given in Perry (1984:3-131)), the heating of the solid would require 20.1 MJ. [If the solid were hematite, this value would be 19.9 MJ.] The enthalpy of liquid water at 60°C is 107.89 Btu/lb, that for liquid water at 25°C is 45.04 Btu/lb (Perry, 1984:3-237); the difference is 62.85 Btu/lb (= 146.2 kJ/kg); multiplying with 89 kg, a value of 13.0 MJ is obtained. The total for the heating of the solid is, thus, estimated at 33.1 MJ, which is minor compared to the actual drying requirement.

Indirect rotary driers (heated generally by steam) achieve thermal efficiencies of 70-90% (Perry, 1984: 20-39). Assuming a thermal efficiency of 70%, the dryer energy requirement becomes 335/0.7 = 478 MJ.

This heat could be provided from steam; alternatively, the sensible and combustion heat of the EAF flue gases could be utilised. 1000 kg of EAF dust arises as a result of the production of 100 t of stainless steel. Simultaneously, ± 2200 kg of flue gas arises (Jones, 1989:126). Assuming this gas to consist of pure carbon monoxide (heat capacity

6.6+0.0012T cal/K/mol, with T in Kelvin) and that sensible heat can be recovered only during cooling from 1000°C to 250°C, the amount of heat available is calculated to be 5563 cal/mol (= 23277 J/mol). 2200 kg of carbon monoxide is 78.6 kmol: the available heat is thus 1893 MJ. This sensible heat could thus be utilised directly.

Additionally, the heat of combustion of carbon monoxide could be utilised in a furnace. This is 2414.7 kcal/kg (= 10103 kJ/kg); multiplying out gives 22230 MJ. The total available heat is estimated at ± 24 000 MJ.

The potential exists therefore to operate the drier on heat obtained from the flue gases of the EAF, if this heat is not already harnessed in the steel production.

D.4 ESTIMATION OF MIXING ENERGY REQUIREMENT

Assuming that a mixer with a capacity of 1.5 m^3, a power requirement of 25 hp (= 18.7 kW) and a mixing time of 15 minutes (resulting in a cycle time of 30 minutes, with charging and discharging) can be found (these are typical values from Perry, 1984:21-8), and assuming a solids filling density of 1500 kg/m^3, resulting in a throughput of 4500 kg/h, the energy requirement per kg of feed is calculated as 0.015 MJ.

To mix the 1086 kg of dried leach residue, binder and coke breeze would then require 16.2 MJ of electrical energy.

D.5 ESTIMATION OF WORK AND ENERGY FOR BRIQUETTING

The estimation of the briquetting energy requirement is based on the description of a briquetting process by Kaas et al (1984), who made briquettes from stainless steel furnace dusts and grinding swarf.

Again, only an order of magnitude estimate of energy consumption is required.

A briquetting pressure of 25 kN/cm^2 was reported to result in briquettes with sufficient strength and density. The work required theoretically for the forming of the briquettes can be calculated in two ways: from fundamental considerations of specific area and pressure - multiplied to give force - and depth of compression (giving distance); or from the equipment specification of the rolling press given in Table 1 of the paper by Kaas et al (1984).

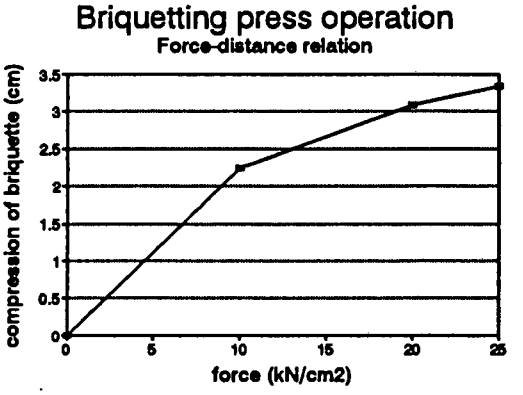
Both approaches are shown in Figure D.1 (overleaf). In the first, the theoretical work should be estimated from the area under the curve of the force-distance diagram; taking the product of final force and distance results in a conservative estimate, which accounts crudely for machine efficiency.

Allowing for a 50% efficiency of the conversion of electrical into mechanical energy, the energy required for the briquetting of 941 kg of leach residue, 85 kg of coke and 60 kg of binder is estimated at 72 MJ.

Figure D.1: Estimation of briquetting press work load

Approach 1: fundamentals

Final density	2500	kg/m3	from ref.
Initial density	1500	kg/m3	assumed
Pressure	250000	kN/m2	from ref.
Briquette height	0.05	m	unimport
Specific surface	0.008	m2/kg	calculate
Initial height	0.083	m	calculate
Specific work	67	kJ/kg	calculate
Total work	73	MJ	calculate



Approach 2: from rolling press specifications

Roll diameter	0.65	m	from ref.
circumference	2.04	m	from ref.
rpm	10		from ref.
distance/hour	1225.2	m/h	calculate
Force	350	kN	from ref.
Work/hour	428827	kJ/h	calculate
Briquettes/hour	6500	kg/h	from ref.
Specific work	66.0	kJ/kg	calculate
Total work	73	MJ	calculate

APPENDIX E

COMPUTER FILENAMES FOR THE LCA MODEL ON DISK

The 5.25" computer disk in the back cover contains the LCA inventories described in chapter 7. These were created with the aid of the April 1994 release of PEMS.2, operated under *MS Excel* version 5. The inventories have been compressed into the file LCINV.ZIP using the program *pkzip*. If "unzipped" (using *pkunzip.exe*, also on the disk), the following files should be found:

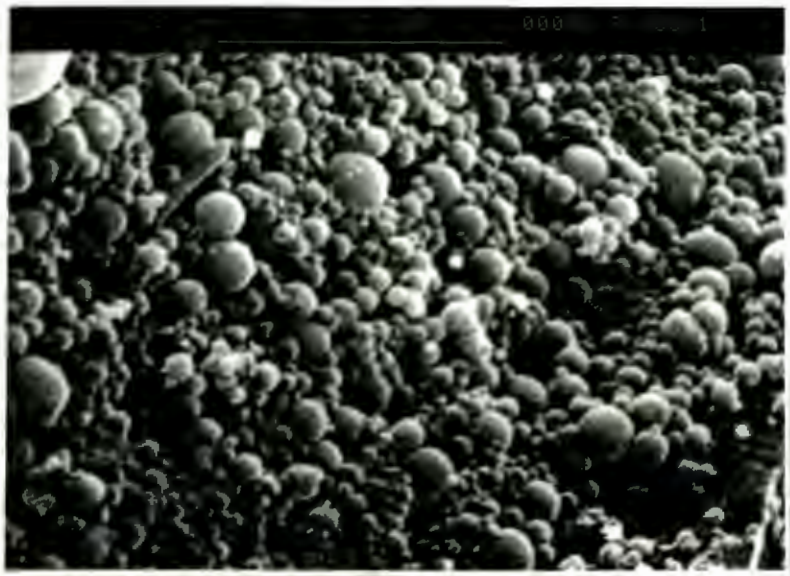
Plasma2.XLS	Plasma treatment on site, with no credits granted for heat exports
Plasma3.XLS	Plasma treatment on site, with credits for the export of heat
Plasma4.XLS	Plasma treatment at the remote location, using Swedish electricity
Wetpro81.XLS	Hydrometallurgical process using nitric acid
Wetpro83.XLS	Hydrometallurgical process using spent pickling acid, nitrates allocated by fraction
Wetpro84.XLS	Hydrometallurgical process using spent pickling acid, no allocation
Wetpro85.XLS	Hydrometallurgical process using spent pickling acid, nitrates allocated to another system

Additionally, variations on Plasma3.XLS and Wetpro85.XLS are included. These are the inventories that are summarised by Figures 7.6 and 7.7.

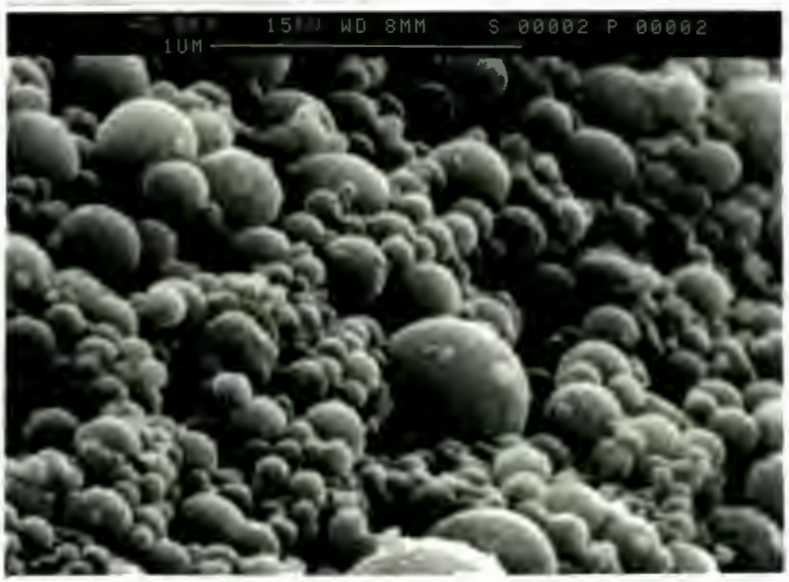
Note: These files can be viewed using *MS Excel*, however to edit them, PEMS is required.

APPENDIX F: FIGURES

Figure 3.1: Micrographs of Dusts



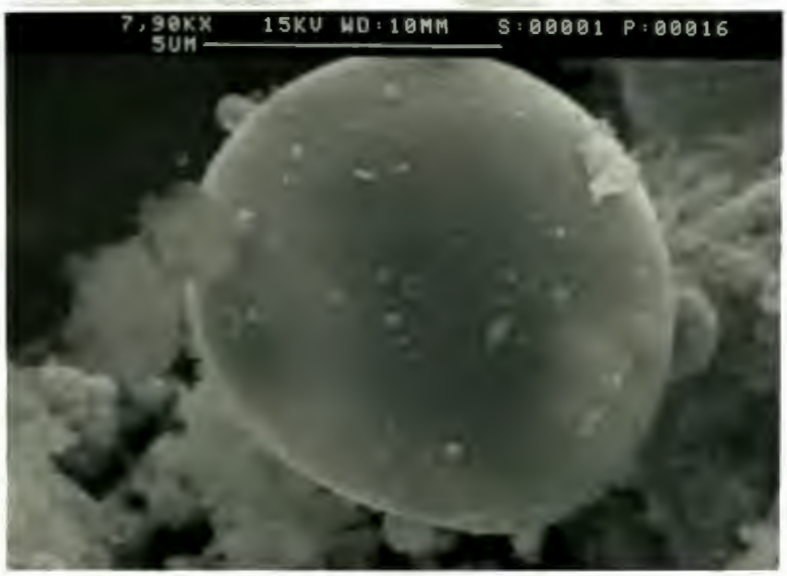
(a) Ferrochromium smelter dust (x 20 200)



(b) Ferrochromium smelter dust (x 43 800)

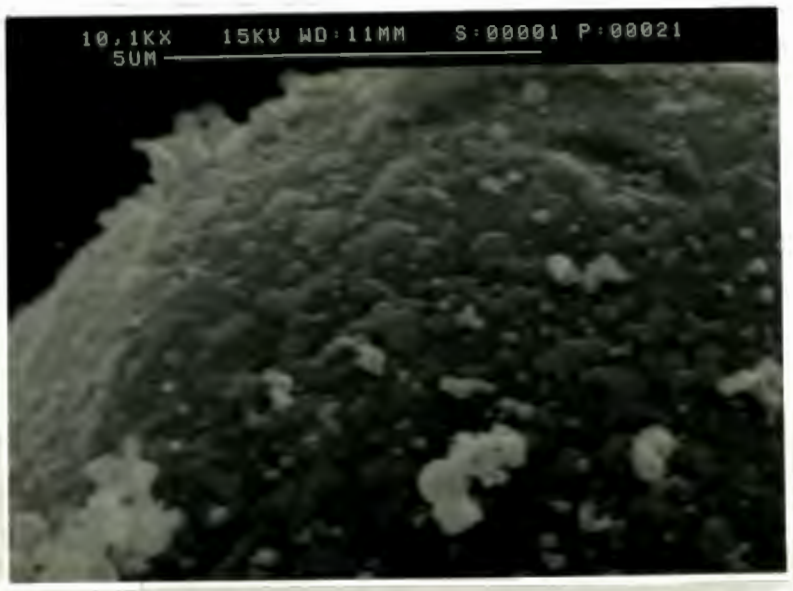
Figure 3.1 (continued): Micrographs of Dusts

(c) Stainless steel EAF/AOD dust (x 2 360)



(d) Stainless steel EAF/AOD dust (x 7 900)

Figure 3.1 (continued): Micrographs of Dusts



(e) Stainless steel EAF/AOD dust (x 10 100)

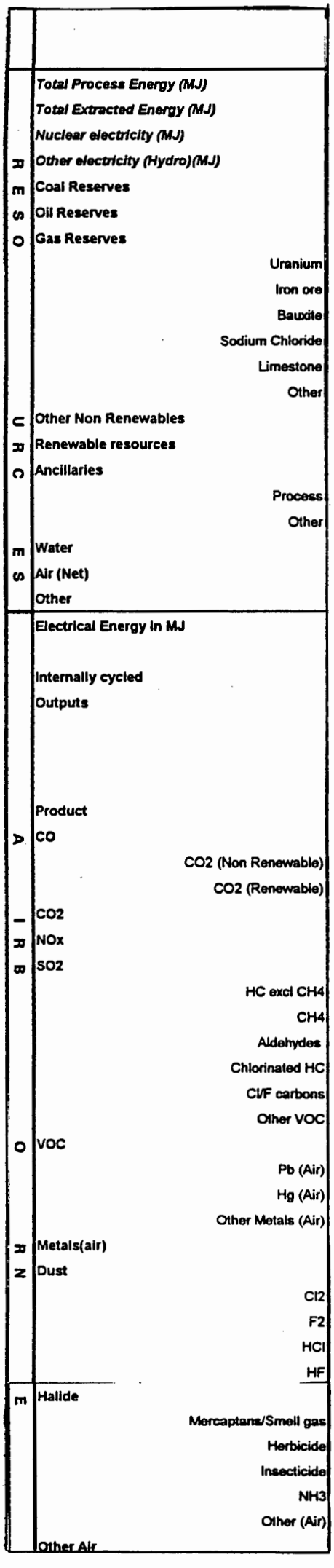
(f) Stainless steel EAF/AOD dust (x 39 800)

Figure 7.2: PEMS Data Categories

(a) Summary

INPUTS (CLOSED LOOP) (MJ)		
		(kg)
INPUTS (STANDARD)		
	Total Process Energy (MJ)	
	Total Extracted Energy (MJ)	
RESOURCES	*Nuclear Electricity (MJ)*	
	Other/Hydro Electricity (MJ)	
	Coal Reserves	
	Oil Reserves	
	Gas Reserves	
	Othar Non Renewables	
	Renewable Resources	
	Ancillaries	
	Water	
	Air (Net)	
	Open Loop Inputs	
OUTPUTS (CLOSED LOOP) (MJ)		
		(kg)
OUTPUTS (STANDARD)		
	Co Product	
	Molten ferroalloy	
AIRBORNE	CO	
	CO2	
	NOx	
	SO2	
	VOC	
	Metals(air)	
	Dust	
	Halides	
	Other Air	
WATER	Waste water	
	Metals(water)	
	TDS	
	TSS	
	Oils & Greases	
	Miscellaneous	
	COD	
	BOD	
MISC	Landfill weight	
	Open Loop Outputs	
	Other Solid	
	Landfill Volume (dm3)	
MASS BALANCE		

(b) Detail


RESO
Total Process Energy (MJ)
Total Extracted Energy (MJ)
Nuclear electricity (MJ)
Other electricity (Hydro)(MJ)
Coal Reserves
Oil Reserves
Gas Reserves
Uranium
Iron ore
Bauxite
Sodium Chloride
Limestone
Other
URC
Other Non Renewables
Renewable resources
Ancillaries
Process
Other
ES
Water
Air (Net)
Other
Electrical Energy in MJ
Internally cycled
Outputs
Product
A
CO
CO2 (Non Renewable)
CO2 (Renewable)
I
CO2
R
NOx
B
SO2
HC excl CH4
CH4
Aldehydes
Chlorinated HC
Cl/F carbons
Other VOC
O
VOC
Pb (Air)
Hg (Air)
Other Metals (Air)
R
Metals(air)
N
Dust
Cl2
F2
HCl
HF
E
Halide
Mercaptans/Smell gas
Herbicide
Insecticide
NH3
Other (Air)
Other Air

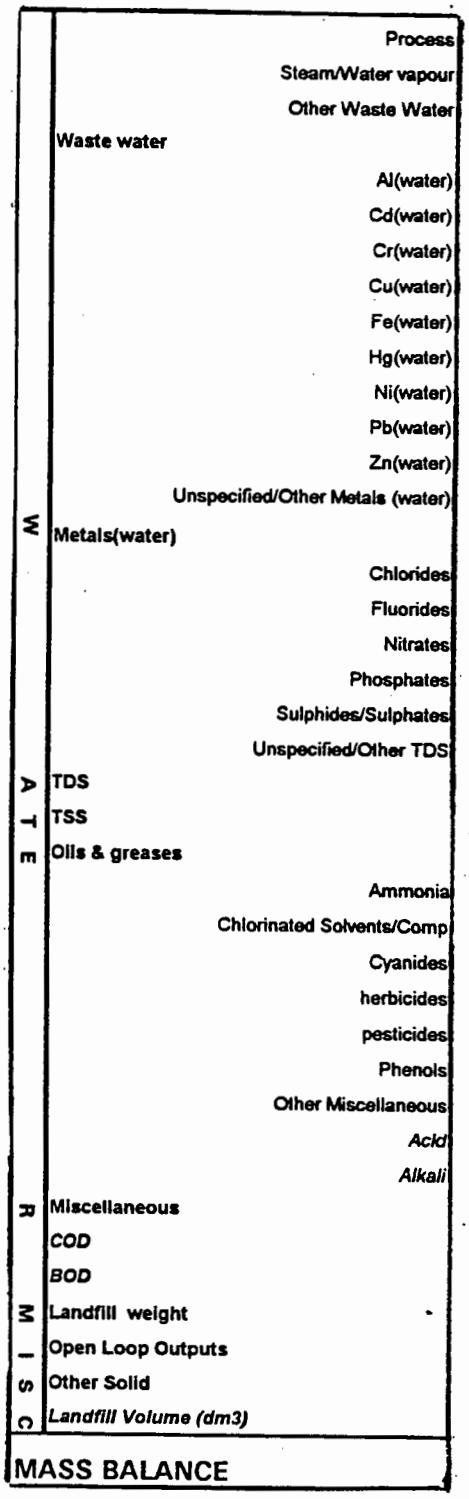

Process
Steam/Water vapour
Other Waste Water
Waste water
Al(water)
Cd(water)
Cr(water)
Cu(water)
Fe(water)
Hg(water)
Ni(water)
Pb(water)
Zn(water)
Unspecified/Other Metals (water)
W
Metals(water)
Chlorides
Fluorides
Nitrates
Phosphates
Sulphides/Sulphates
Unspecified/Other TDS
A
TDS
T
TSS
E
Oils & greases
Ammonia
Chlorinated Solvents/Comp
Cyanides
herbicides
pesticides
Phenols
Other Miscellaneous
Acid
Alkali
R
Miscellaneous
COD
BOD
W
Landfill weight
I
Open Loop Outputs
S
Other Solid
C
Landfill Volume (dm3)
MASS BALANCE

Figure 7.6: The effect of variations on the impacts of the hydrometallurgical process

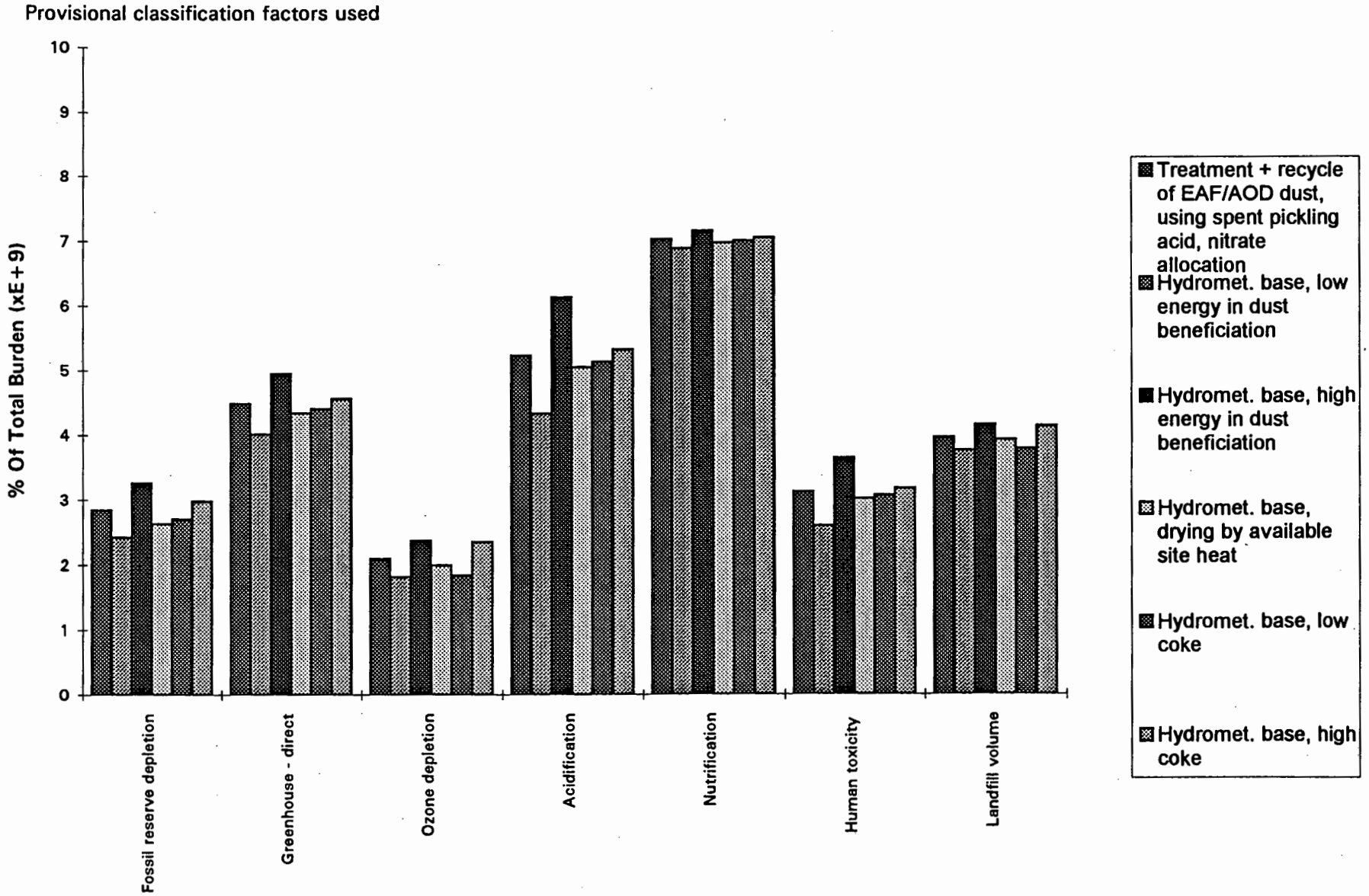
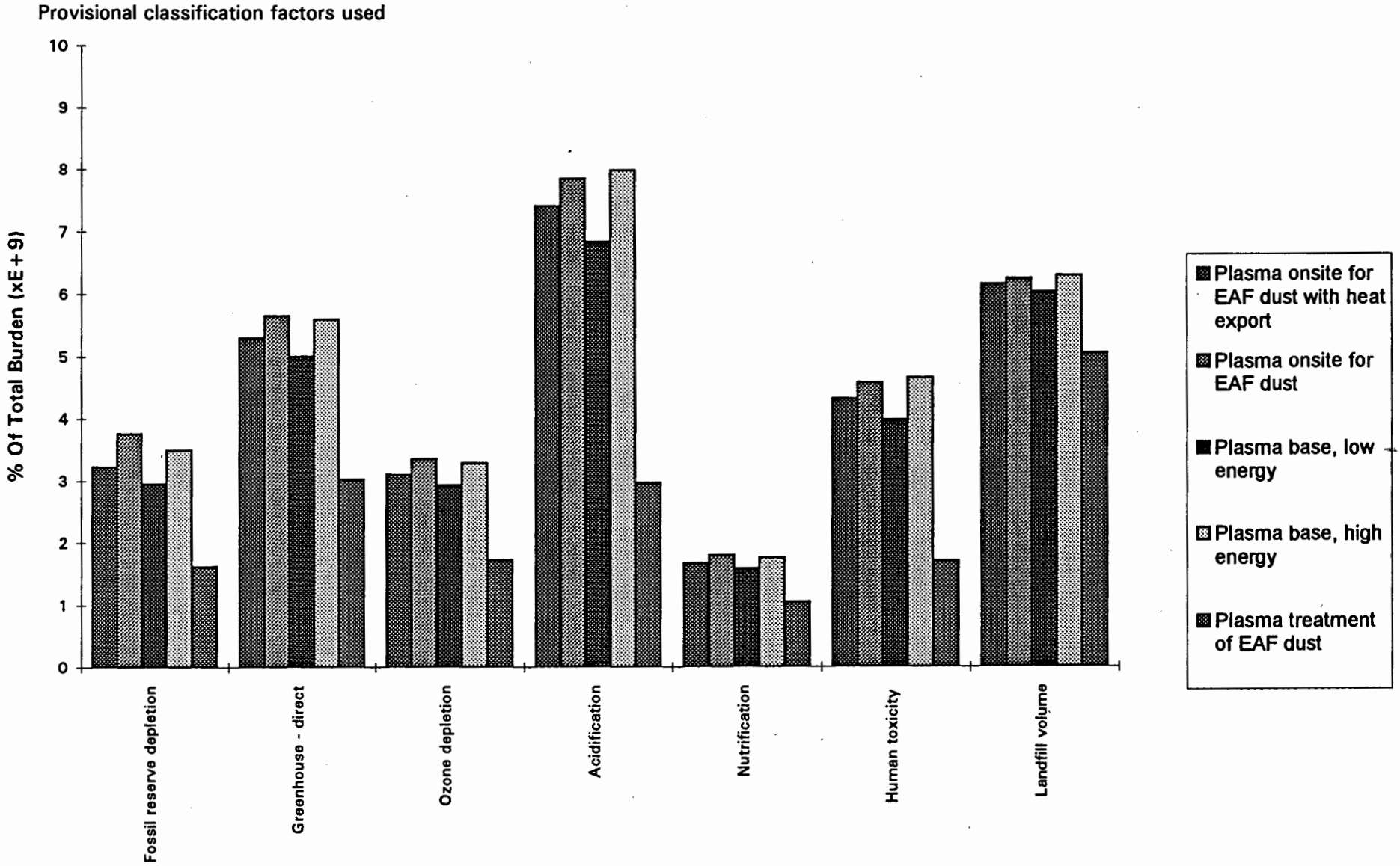


Figure 7.7: The effect of variations on the impacts of the pyrometallurgical treatment of dust



APPENDIX G: TABLES

Table 2.5: Material Flows in the PlasmaDust process

(relative to 1000 units of dust)

Component	STREAM 1 Dust		2 Sand		3 3 Coal		4 4 Coke		5 Water	
	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow
SiO2	9		50		6.1		9.0			
Al2O3	2				2.4		3.6			
CaO	8		50		0.30		0.45			
MgO	3				0.24		0.35			
H2O					2.9	1.2			100	1043
Element										
Fe	31.8	318			0.3	0.13	0.5	1.1		
Cr	11.3	113			0.2	0.09	0.3	0.7		
Ni	2.9	29								
Mo	0.5	5								
Mn	1.5	15								
Si	4.2	42	23.4	7	2.9	1.14	4.2	9.3		
Al	1.1	11	0.0	0	1.3	0.51	1.9	4.2		
Ca	5.7	57	35.7	11	0.2	0.09	0.3	0.7		
Mg	1.8	18	0.0	0	0.1	0.06	0.2	0.5		
Na	1.4	14								
K	1.2	12								
Zn	4.0	40								
Pb	0.8	8								
Cd	0.03	0.3								
Hg	0.0005	0.005								
Cl	0.7	7								
F	0.5	5								
C	0.8	8			70.3	28	84.6	186		
O	31.1	311	40.9	12	16.1	6.4	7.1	16		
S	0.4	4.2			0.6	0.2	0.83	1.8		
N		0.0			4.1	1.6				
H		0.0			1.1	0.4				
Minimum		1000		20		40		220		1043
Maximum		1000		40		40		220		1043
Average		1000		30		40		220		1043

Component	10 Ferroalloy		11 Slag		12 Zn sludge		13 F sludge		14 Effluent		15 Fuel gas		TOTAL IN	TOTAL OUT	DIFF.	% CLOSURE
	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow				
SiO2			30		?											
Al2O3			7													
CaO			29													
MgO			10													
H2O					35	42	35	1.2		1000			1044.4	1043.2	1.2	99.9
Element																
Fe	65	302	3	9.8									319.4	312.0	7.4	97.7
Cr	19	88	5	16.3					1E-05	0.0001			114.0	104.6	9.4	91.7
Ni	6	28	0.15	0.49					2E-06	0.00002			29.4	28.4	1.0	96.7
Mo	1.1	4.9											5.1	4.9	0.3	95.0
Mn	3	14											14.7	14.0	0.7	95.0
Si	0.5	2	14.0	46									59.5	47.9	11.6	80.5
Al			3.7	12									15.3	12.0	3.2	78.8
Ca			20.7	67			33.3	1.2					68.7	68.5	0.2	99.8
Mg			6.0	20									18.6	19.6	-1.0	94.7
Na									0.7	7.0			14.0	7.0	7.0	50.0
K									0.6	6.0			12.0	6.0	6.0	50.0
Zn			0.01	0.03	33	40			8E-06	8.0E-05			40.0	39.6	0.4	99.1
Pb			0.0005	0.0016	6.6	7.9							8.0	7.9	0.1	99.0
Cd			0.0002	0.0007	0.25	0.30			3E-07	3.0E-06			0.3	0.3	0.0	99.2
Hg									5E-08	5.0E-07	4.4E-07	2.13E-06	0.0050	0.0000	0.0050	0.1
Cl									0.7	7.0			7.0	7.0	0.0	100.0
F			0.6	2.0			31.7	1.1	0.002	0.02			5.0	3.1	1.9	61.6
C	5	23			?						40.7	198	222.2	221.2	1.0	99.5
O			35.2	114	8.1	10					54.7	266	344.9	389.7	-44.8	87.0
S	0.02	0.1		6.2		0.1							6.3	6.3	-0.1	98.5
N											0.33	1.6	1.6	1.6	0.0	100.0
H											0.09	0.4	0.4	0.4	0.0	100.0
Minimum		400		400		100		2		1020		446	2323	2368	-45.0	98.1
Maximum		530		250		140		5		1020		526	2343	2471	-128.0	94.5
Average		465		325		120		3.5		1020		486	2333	2420	-86.5	96.3

Table 2.5: Material Flows in the PlasmaDust process

Notes

1. Average values for SS dust from Law et al (1983)
2. Calculated from components; Ni, Mn, Zn as MeO, Fe, Cr as Me2O3, Na, K as oxides
3. Jones (1989:Appendix A), data is probably for hard coal
4. Jones (1989:Appendix A)
5. Assumed to make up the balance
6. Kola (1990) states that the fuel gas is more than 95% CO and H2.
7. Backcalculated metal from ferroalloy, recover Fe 95%, Cr 78%, others 95%
8. Assume that 99% of these metals report to the gas phase and are recovered in the Venturi scrubber.
9. Assume that 99% of the sulphur reports to the slag and that the remainder is recovered in the scrubber.

Table 5.1: Material flows for the dust beneficiation process

(relative to 1000 units of dust)

	STREAM														
Component	1 Dust		2 Acid		3 Residue		4 Lime		5 Water		6 Zn sludge		7 Effluent		IN	OUT	CLOSURE
	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	ppm	Flow			
H2O		0		19540	19.0	192				5998	40	48		25604	25538	25844	98.8
Element																	
Fe	31.8	318.2			31.1	314					3.7	4.4	0	0	318	318	100.0
Cr	11.3	113.3			10.7	108					4.1	4.9	0.1	0.00256	113	113	100.0
Ni	2.9	29.4			2.2	22					6.3	7.6	0.02	0.00051	29	29	100.0
Mo	0.5	5.1			0.5	5					0.0	0.0	0	0	5	5	100.0
Mn	1.5	14.7			0.7	7					6.1	7.3	0	0	15	15	100.0
Si	4.2	42.1			4.2	42					0.0	0	0	0	42	42	100.0
Al	1.1	10.6			1.0	11					0.0	0	0	0	11	11	100.0
Ca	5.7	57.2			0.5	5	54.1	360			0.0	0	16118	412.7	417	417	100.0
Mg	1.8	18.1			0.0	0					0.0	0	707	18.1	18	18	100.0
Na	1.4	14.0			0.0	0					0.0	0	547	14.0	14	14	100.0
K	1.2	12.0			0.0	0.0					0.0	0	469	12.0	12	12	100.0
Zn	4.0	40.0			2.4	24					13.1	15.7	0.08	0.00205	40	40	100.0
Pb	0.8	8.0			0.4	4					3.3	4.00	0	0	8	8	100.0
Cd	0.030	0.3			0.0134	0.135					0.1380	0.17	0.003	7.7E-05	0	0	100.0
Hg	0.0005	0.005			0.0002	0.003					0.0021	0.0	0.0005	1.3E-05	0.0050	0.0050	99.7
Sn	0.017	0.17			0.0168	0.170					0.0000	0.0	0	0	0	0	100.0
P	0.15	1.49			0.0000	0.000					0.0000	0.0	58.1	1.5	1	1	100.0
Cl	0.7	7			0.000	0.00					0.000	0.0	273	7.0	7	7	100.0
F	0.5	5			0.4	4.5					0.0	0.0	19.5	0.5	5	5	100.0
C	0.8	8			0.8	8					0.0	0.0	0	0	8	8	100.0
O	32.5	325		960	30.4	307		288			21.8	26.1	37834	969	1574	1302	82.7
S	0.14	1.4			0.1	1					0.0	0.0	27.3	0.7	1	1	100.0
N	0	0.0		280	0.0	0					0.0	0.0	10936	280	280	280	100.0
H	0	0.0		20	0.2	2		18			1.4	1.6	0.006	0.00	38	4	10.6
Minimum		1000		20800		961		666		5998		120		27319			
Maximum		1000				1057											
Average		1000		20800		1009		666		5998		120		27319	28464	28447	99.9
dry	103.1	1031	0.0	1260	85.7	865	54.1	666	0.0	0	60.0	72	66988	1715			
wet	103.1	1031	0.0	20800	104.8	1057	54.1	666	0.0	5998	100.0	120		27319			

Table 5.2: Material flows for the residue preparation process

(relative to 1000 units of dust in the beneficiation plant)

	STREAM											
Component	1	Residue	2	Vapour	3	Coke	4	Swarf	5	Binder	6	Briquettes
	Mass %	Flow	Mass %	Flow	Mass	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow
H2O	19.0	192	100	102	0	0	0	0	0	0	6	91
Other	85.7	865			100	86	100	408	100	60	94	1419
Total		1009		102		86		408		60		1510

Table 5.3: Material distribution for smelting of briquettes in the EAF

Baghouse efficienc 99.89 % Dust emissions: 0.047 kg (relative to 1000 units of dust in the beneficiation plant)

	STREAM													
Componen	1 Briquettes		2 Metal		3 Slag		4 Dust		5 Flue gas		IN	OUT	DIFF.	BALANCE
	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow	Mass %	Flow				
SiO2					36.8	88								
Al2O3					16.3	39								
CaO					4.6	11								
MgO					19.2	46								
H2O	0.00	Flow									Flow	0	0	ERR
Element														
Fe	31.01	314	67.4	307	1.3	3.1	7.1	3.1			313.7	313.7	0.0	100.0
Cr	10.85	110	21.7	99	4.1	9.9	2.5	1.1			109.8	109.8	0.0	100.0
Ni	2.18	22	4.7	22	0.1	0.2	0.5	0.2			22.1	22.1	0.0	100.0
Mo	0.51	5	1.1	4.9	0.1	0.2	0.1	0.1			5.1	5.1	0.0	100.0
Mn	0.73	7	1.0	4.4	1.2	2.9	0.2	0.1			7.3	7.3	0.0	100.0
Si	4.16	42	0.1	0.46	17.2	41.2	1.0	0.4			42.1	42.1	0.0	100.0
Al	2.06	21			8.6	20.7	0.5	0.2			20.9	20.9	0.0	100.0
Ca	0.78	8			3.3	7.8	0.2	0.1			7.9	7.9	0.0	100.0
Mg	2.77	28			11.6	27.8	0.6	0.3			28.1	28.1	0.0	100.0
Na	0.02	0			0.0	0.0	0.4	0.2			0.2	0.2	0.0	100.0
K	0.00	0			0.0	0.0	0.0	0.0			0.00	0.00	0.00	ERR
Zn	2.40	24			0.0	0.0	55.0	24.3			24.3	24.3	0.0	100.0
Pb	0.40	4			0.0	0.0	9.1	4.0			4.0	4.0	0.0	100.0
Cd	0.01	0			0.0	0.0	0.3	0.1			0.135	0.135	0.000	100.0
Hg	0.00	0			0.0	0.0	0.0		-0.01	2.5E-03	0.003	0.003	0	100.0
Sn	0.02	0			0.1	0.2	0.0	0.0			0.170	0.170	0.000	100.0
P	0.000	0	0.05	0.23	-0.1	-0.2	0.0	0.0			0.000	0.000	0.000	ERR
Cl	0.00	0			0.0	0.0	0.0	0.0			0.00	0.00	0.00	ERR
F	0.44	5			1.7	4.1	1.0	0.5			4.50	4.50	0.00	100.0
C	0.79	8	3.8	17.3	0.0	0.0	0.2	0.1	46.0	-9	8.0	8.0	0.0	100.0
O	37.56	380			39.0	93.5	20.7	9.1	64.0	-13	380.0	90.1	******	23.7
S	2.77	28	0.2	0.91	11.2	26.8	0.6	0.3			28.0	28.0	0.0	100.0
N	0.15	2			0.6	1.5	0.0	0.0			1.503	1.503	0	100.0
H	0.24	2			0.0	0.0	0.1	0.0	-12.0	2.4	2.4	2.4	0.0	100.0
Minimum						197								
Maximum	-													
Average		1012		456		240		44		-20	1012	720	-291	71.2
dry		1010	100.0	456	100.0		100.0	44	100.0	-20				
wet		1010												

Table 7.1: PEMS input data for the hydrometallurgical option

Treatment + recycle of EAF/AOD dust, using nitric acid		(a) 1. Smelting in EAF			(b) 2. Residue preparation			(c) 11. Dust beneficiation			(d) 11. Dust beneficiation		
		NOTE	REF.	CAL.	NOTE	REF.	CAL.	NOTE	REF.	CAL.	NOTE	REF.	CAL.
INPUTS (CLOSED LOOP) (MJ)		Electricity (Avera	3800.000	3800.000	Electricity (Avera	170.000	170.000	Electricity (Aver	2580.000	2580.000	Electricity (Aver	2580.000	1290.000
					HEAT (Average E	480.000	480.000						
(kg)		Briquettes	1102.000	1102.000	Calcium carbonat			CaCO3	900.000	900.000	Calcium carbona	900.000	450.000
		(excl. swarf)			Dolomite			Acid	1260.000	1260.000	Acid	1260.000	630.000
					Coke	86.000	86.000	EAF/AOD dust	1000.000	1000.000	EAF/AOD dust	1000.000	500.000
					Coal								
					Leach residue	1009.000	1009.000						
INPUTS (STANDARD)					Binder	60.000	60.000						
	Total Process Energy (MJ)		3800.000	3800.000		650.000	650.000		2580.000	2580.000		2580.000	1290.000
	Total Extracted Energy (MJ)												
RESOURCES	*Nuclear Electricity (MJ)*												
	Other/Hydro Electricity (MJ)												
	Coal Reserves												
	Oil Reserves												
	Gas Reserves	○											
	Uranium												
	Iron ore												
	Bauxite												
	Sodium Chloride												
	Limestone												
	Other												
	Other Non Renewables												
	Renewable Resources												
	Ancillaries												
	Process							Acid + lime +	25700.000	25700.000	Acid + lime + hy	25700.000	12850.000
	Other							hydration					
	Water								25700.000	25700.000		25700.000	12850.000
	Air (Net)	02 saving!	-47.400	-47.400									
	Open Loop Inputs												
OUTPUTS (CLOSED LOOP) (MJ)		(MJ)											
(kg)		(kg)											
OUTPUTS (STANDARD)		EAF/AOD dust	44.000	44.000				Zn sludge	120.000	120.000	Zn sludge	120.000	60.000
	Co Product										neutr. acid	1009.000	
	Molten ferroalloy	Molten ferroalloy	456.000	456.000	Briquettes	1102.000	1102.000	Leach residue	1009.000	1009.000	Leach residue	1009.000	1009.000
AIR	CO												
	CO2 (Non Renewable)	from C in flue gas	231.000	231.000				lime hydration	396.000	396.000	lime hydration	396.000	198.000
	CO2 (Renewable)												
	CO2		231.000	231.000					396.000	396.000		396.000	198.000
	NOx												
	SO2												
	HC excl CH4												
	CH4												
	Aldehydes												
	Chlorinated HC												
	Cl/F carbons												
	Other VOC												
	VOC												
	Pb (air)												
	Hg (air)		0.003	0.003									
	Other Metals (air)												
	Metals(air)		0.003	0.003									
	Dust		0.047	0.047									
	Cl2												
	F2												
	HCl												
	HF												
	Halides												

Table 7.1: PEMS input data for the hydrometallurgical option

	Treatment + recycle of EAF/AOD dust, using nitric acid	(a) 1. Smelting in EAF			(b) 2. Residue preparation			(c) 11. Dust beneficiation			(d) 11. Dust beneficiation		
	Mercaptans/Smell gas												
	Herbicide												
	Insecticide												
	NH3												
	Other (Air)												
	Other Air												
	Process							in effluent	25604.000	25604.000	in effluent	25604.000	12802.000
	Steam/Water vapour	from H in flue gas	21.600	21.600		102.000	102.000						
	Other Waste Water	initial	91.000	91.000									
	Waste water		112.600	112.600		102.000	102.000		25604.000	25604.000		25604.000	12802.000
	Al(water)												
	Cd(water)								0.000	0.000		0.000	0.000
	Cr(water)								0.003	0.003		0.003	0.001
	Cu(water)												
	Fe(water)												
	Hg(water)								0.000	0.000		0.000	0.000
	Ni(water)								0.001	0.001		0.001	0.000
	Pb(water)												
	Zn(water)								0.002	0.002		0.002	0.001
	Unspecified/Other Metals (water)												
WATER	Metals(water)								0.005	0.005		0.005	0.003
	Chlorides								7.000	7.000		7.000	3.500
	Fluorides								0.500	0.500		0.500	0.250
	Nitrates								1240.000	1240.000		1240.000	620.000
	Phosphates								4.597	4.597		4.597	2.298
	Sulphides/Sulphates								6.300	6.300		6.300	3.150
	Unspecified/Other TDS							cations	456.800	456.800	cations	456.800	228.400
	TDS								1715.197	1715.197		1715.197	857.598
	TSS												
	Oils & Greases												
	Ammonia												
	Chlorinated Solvents/Comp												
	Cyanides												
	herbicides												
	pesticides												
	Phenols												
	Other Miscellaneous												
	Acid												
	Alkali												
AIR	Miscellaneous												
	COD												
	BOD												
SOLIDS	Landfill weight		210.000	210.000									
	Open Loop Outputs												
	Other Solid												
	Landfill Volume (dm3)	ass. 2 kg/m3	105.000	105.000									
	MASS BALANCE		0.950	0.950		-49.000	-49.000		15.798	15.798		-993.202	-496.601

WETPRO81.XLS - (20/9/94) /2
WETPRO81.XLS - (20/9/94) /2

Table 7.2: Life cycle inventories for the hydrometallurgical process

		Nitric acid	Spent acid, no allocation	Spent acid, allocation by fraction
RESOURCES	*Total Process Energy (MJ)*	2.64E+04	1.55E+04	1.24E+04
	Total Extracted Energy (MJ)	2.89E+04	1.80E+04	1.50E+04
	Nuclear electricity (MJ)	2.25E+03	2.03E+03	1.62E+03
	Other electricity (Hydro)(MJ)	1.56E+03	1.41E+03	1.12E+03
	Coal Reserves	5.28E+02	4.21E+02	3.57E+02
	Oil Reserves	1.06E+02	6.72E+01	5.28E+01
	Gas Reserves	1.59E+02	3.00E+01	2.44E+01
	Uranium	0	0	0
	Iron ore	0	0	0
	Bauxite	0	0	0
	Sodium Chloride	3.00E-02	0	0
	Limestone	0	0	0
	Other	1.02E+03	1.02E+03	5.10E+02
	Other Non Renewables	1.02E+03	1.02E+03	5.10E+02
	Renewable resources	3.08E+01	1.93E+01	1.56E+01
	Ancillaries	1.27E-01	1.26E+03	6.30E+02
	Process	2.65E+04	2.60E+04	1.31E+04
	Other	2.60E+04	3.21E+03	2.49E+03
	Water	5.25E+04	2.92E+04	1.56E+04
	Air (Net)	4.90E+03	7.15E+02	5.87E+02
	Other	1.46E+03	1.37E+03	8.15E+02
WASTE	Electrical Energy in MJ			
	Internally cycled			
	Outputs			
	Product	456	456	456
AIR	CO	2.06E+00	8.22E-01	6.63E-01
	CO2 (Non Renewable)	2.12E+03	1.64E+03	1.25E+03
	CO2 (Renewable)	3.67E+01	2.29E+01	1.86E+01
	CO2	2.15E+03	1.67E+03	1.27E+03
	NOx	1.81E+01	5.03E+00	3.98E+00
	SO2	1.52E+01	1.14E+01	9.15E+00
	HC excl CH4	0	0	0
	CH4	0	0	0
	Aldehydes	0	0	0
	Chlorinated HC	0	0	0
	Cl/F carbons	0	0	0
	Other VOC	8.84E+00	4.19E+00	3.55E+00
	VOC	8.84E+00	4.19E+00	3.55E+00
	Pb (Air)	5.50E-04	1.19E-04	1.08E-04
	Hg (Air)	2.50E-03	2.50E-03	2.50E-03
	Other Metals (Air)	6.17E-04	1.39E-04	1.27E-04
	Metals(air)	3.67E-03	2.76E-03	2.74E-03
	Dust	2.55E+01	2.54E+01	1.28E+01
	Cl2	3.00E-02	7.02E-03	6.03E-03
	F2	0	0	0
	HCl	5.31E-02	1.22E-02	1.12E-02
	HF	6.40E-03	1.48E-03	1.35E-03

Table 7.2: Life cycle inventories for the hydrometallurgical process

		Nitric acid	Spent acid, no allocation	Spent acid, allocation by fraction
E	Halide	8.95E-02	2.07E-02	1.85E-02
	Mercaptans/Smell gas	6.98E-02	1.36E-02	1.24E-02
	Herbicide	0	0	0
	Insecticide	0	0	0
	NH3	1.79E-02	1.39E-02	1.20E-02
	Other (Air)	2.94E+03	4.62E+01	3.91E+01
	Other Air	2.94E+03	4.62E+01	3.91E+01
	Process	2.58E+04	2.56E+04	1.28E+04
	Steam/Water vapour	2.61E+02	1.25E+02	1.25E+02
	Other Waste Water	2.61E+04	3.68E+03	2.86E+03
	Waste water	5.22E+04	2.95E+04	1.58E+04
	Al(water)	0	0	0
	Cd(water)	7.74E-05	7.71E-05	3.86E-05
	Cr(water)	2.56E-03	2.56E-03	1.28E-03
	Cu(water)	0	0	0
	Fe(water)	0	0	0
	Hg(water)	1.30E-05	1.30E-05	6.50E-06
	Ni(water)	5.10E-04	5.10E-04	2.55E-04
	Pb(water)	0	0	0
	Zn(water)	2.05E-03	2.05E-03	1.03E-03
	Unspecified/Other Metals (water)	1.10E-01	5.91E-02	5.02E-02
W	Metals(water)	1.15E-01	6.43E-02	5.28E-02
	Chlorides	7.00E+00	7.00E+00	3.50E+00
	Fluorides	5.00E-01	5.00E-01	2.50E-01
	Nitrates	1.24E+03	1.24E+03	6.20E+02
	Phosphates	4.60E+00	4.60E+00	2.30E+00
	Sulphides/Sulphates	6.41E+00	6.37E+00	3.20E+00
	Unspecified/Other TDS	4.68E+02	4.65E+02	2.35E+02
A	TDS	1.73E+03	1.72E+03	8.65E+02
T	TSS	3.18E-01	2.48E-01	2.15E-01
E	Oils & greases	2.76E-02	1.29E-02	1.02E-02
	Ammonia	0	0	0
	Chlorinated Solvents/Comp	0	0	0
	Cyanides	1.12E-03	2.18E-04	1.99E-04
	herbicides	0	0	0
	pesticides	0	0	0
	Phenols	0	0	0
	Other Miscellaneous	2.12E-01	2.72E-02	2.70E-02
	Acid	2.12E-06	0	0
	Alkali	0	0	0
R	Miscellaneous	2.13E-01	2.74E-02	2.72E-02
	COD	0	0	0
	BOD	5.17E-02	4.21E-02	4.19E-02
M	Landfill weight	2.72E+02	2.58E+02	2.51E+02
I	Open Loop Outputs	5.87E+02	3.03E+02	2.26E+02
S	Other Solid	2.74E+02	2.21E+02	1.84E+02
C	*Landfill Volume (dm3)*	1.82E+02	1.65E+02	1.56E+02
MASS BALANCE		-31.66	-31.75	-544.3

Table 7.3: PEMS input data for the pyrometallurgical option

Plasma onsite for EAF dust		(a) 1. Melting in EAF			(b) 2. Plasma process			(c) 2. Plasma process		
		NOTE	REF.	CAL.	NOTE	REF.	CAL.	NOTE	REF.	CAL.
INPUTS (CLOSED LOOP) (MJ)		Electricity	1849.000	859.738	Electricity	8172.000	8171.554	Electricity (Swed	8172.000	8171.554
								Municipal heat	-1166.897	-1166.833
(kg)		Alloy ingot	1000.000	464.975	Coal	40.000	39.998	Coal	40.000	39.998
		CaCO3	64.813	30.136	Coke	220.000	219.988	Coke	220.000	219.988
					CaCO3			CaCO3		
					Sand	30.000	29.998	Sand	30.000	29.998
					EAF/AOD dust	1000.000	999.945	EAF/AOD dust	1000.000	999.945
INPUTS (STANDARD)										
	Total Process Energy (MJ)		1849.000	859.738		8172.000	8171.554		7005.104	7004.721
	Total Extracted Energy (MJ)									
RESO	*Nuclear Electricity (MJ)*									
	Other/Hydro Electricity (MJ)									
	Coal Reserves									
	Oil Reserves									
	Gas Reserves									
	Uranium									
	Iron ore									
	Bauxite									
	Sodium Chloride									
	Limestone									
	Other									
URCES	Other Non Renewables									
	Renewable Resources									
	Ancillaries									
	Process					1043.000	1042.943		1043.000	1042.943
	Other									
	Water					1043.000	1042.943		1043.000	1042.943
	Air (Net)				to combust gas	267.200	267.185	to combust gas	267.200	267.185
	Open Loop Inputs									
OUTPUTS (CLOSED LOOP) (MJ)		(MJ)								
(kg)		(kg)								
OUTPUTS (STANDARD)		EAF dust	15.000	6.975	Zinc concentrate	120.000	119.993	Zinc concentrate	120.000	119.993
	Co Product									
	Molten ferroalloy	Molten ferroalloy	985.000	458.000	Alloy ingot *	465.000	464.975	Alloy ingot *	465.000	464.975
AIR	CO									
	CO2 (Non Renewable)	ex CaCO3	28.518	13.260		726.000	725.960		726.000	725.960
	CO2 (Renewable)									
	CO2		28.518	13.260		726.000	725.960		726.000	725.960
	NOx				?	4.271	4.271	?	4.271	4.271
	SO2				?			?		
	HC excl CH4				?			?		
	CH4				?			?		
	Aldehydes									
	Chlorinated HC									
	Cl/F carbons									
	Other VOC									
	VOC									
	Pb (air)				?			?		
	Hg (air)				?	0.000	0.000	?	0.000	0.000
	Other Metals (air)									
	Metals(air)					0.000	0.000		0.000	0.000
	Dust					0.069	0.069		0.069	0.069
	Cl2									
	F2									
	HCl									
	HF									
	Halides									

Table 7.3: PEMS input data for the pyrometallurgical option

	Plasma onsite for EAF dust	(a) 1. Melting in EAF			(b) 2. Plasma process			(c) 2. Plasma process		
	Mercaptans/Smell gas									
	Herbicide									
	Insecticide									
	NH3									
	Other (Air)									
	Other Air									
	Process					1000.000	999.945		1000.000	999.945
	Steam/Water vapour					3.600	3.600		3.600	3.600
	Other Waste Water									
	Waste water					1003.600	1003.545		1003.600	1003.545
	Al(water)									
	Cd(water)					0.000	0.000		0.000	0.000
	Cr(water)									
	Cu(water)					0.000	0.000		0.000	0.000
	Fe(water)									
	Hg(water)					0.000	0.000		0.000	0.000
	Ni(water)					0.000	0.000		0.000	0.000
	Pb(water)									
	Zn(water)					0.000	0.000		0.000	0.000
	Unspecified/Other Metals (water)									
W	Metals(water)					0.000	0.000		0.000	0.000
	Chlorides					7.000	7.000		7.000	7.000
	Fluorides					0.020	0.020		0.020	0.020
	Nitrates									
	Phosphates									
	Sulphides/Sulphates									
	Unspecified/Other TDS				cations	13.000	12.999	cations	13.000	12.999
A	TDS					20.020	20.019		20.020	20.019
T	TSS									
E	Oils & Greases									
	Ammonia									
	Chlorinated Solvents/Comp									
	Cyanides					0.000	0.000		0.000	0.000
	herbicides									
	pesticides									
	Phenols									
	Other Miscellaneous									
	Acid									
	Alkali									
R	Miscellaneous					0.000	0.000		0.000	0.000
	COD									
	BOD									
W	Landfill weight	ex CaCO3	36.295	16.876		328.500	328.482		328.500	328.482
I	Open Loop Outputs									
S	Other Solid									
O	*Landfill Volume (dm3)*					164.250	164.241		164.250	164.241
	MASS BALANCE					-67.261	-67.257		-67.261	-67.257

Table 7.4: Life cycle inventories for the plasma treatment

		Onsite, no heat credit	Onsite, 50% heat exported
RESOURCES	*Total Process Energy (MJ)*	2.00E+04	1.83E+04
	Total Extracted Energy (MJ)	2.73E+04	2.56E+04
	Nuclear electricity (MJ)	2.73E+03	2.73E+03
	Other electricity (Hydro)(MJ)	1.89E+03	1.89E+03
	Coal Reserves	7.17E+02	6.97E+02
	Oil Reserves	7.48E+01	5.99E+01
	Gas Reserves	3.39E+01	2.42E+01
	Uranium	0	0
	Iron ore	0	0
	Bauxite	0	0
	Sodium Chloride	0	0
	Limestone	0	0
	Other	6.42E+01	6.42E+01
	Other Non Renewables	6.42E+01	6.42E+01
	Renewable resources	2.27E+01	1.79E+01
	Ancillaries	7.33E-03	6.36E-03
	Process	1.66E+03	1.65E+03
	Other	4.19E+03	3.91E+03
	Water	5.84E+03	5.56E+03
	Air (Net)	1.37E+03	1.28E+03
	Other	1.59E+03	1.58E+03
	Electrical Energy in MJ		
	Internally cycled		
	Outputs		
	Product	458	458
AIRBORNE	CO	1.02E+00	8.30E-01
	CO2 (Non Renewable)	2.06E+03	1.93E+03
	CO2 (Renewable)	2.71E+01	2.14E+01
	CO2	2.08E+03	1.95E+03
	NOx	1.04E+01	9.60E+00
	SO2	1.52E+01	1.45E+01
	HC excl CH4	0	0
	CH4	0	0
	Aldehydes	0	0
	Chlorinated HC	0	0
	Cl/F carbons	0	0
	Other VOC	6.70E+00	6.20E+00
	VOC	6.70E+00	6.20E+00
	Pb (Air)	2.59E-06	-2.35E-04
	Hg (Air)	3.00E-04	3.00E-04
	Other Metals (Air)	3.04E-06	-2.76E-04
	Metals(air)	3.06E-04	-2.11E-04
	Dust	1.13E+00	1.06E+00
	Cl2	1.02E-02	8.30E-03
	F2	0	0
	HCl	2.67E-04	-2.42E-02
	HF	3.22E-05	-2.93E-03

Table 7.4: Life cycle inventories for the plasma treatment

		Onsite, no heat credit	Onsite, 50% heat exported
E	Halide	1.05E-02	-1.89E-02
	Mercaptans/Smell gas	2.98E-04	-2.70E-02
	Herbicide	0	0
	Insecticide	0	0
	NH3	2.45E-02	2.37E-02
	Other (Air)	7.85E+01	7.63E+01
	Other Air	7.85E+01	7.63E+01
	Process	1.12E+03	1.03E+03
	Steam/Water vapour	3.63E+00	1.08E+00
	Other Waste Water	4.71E+03	4.52E+03
	Waste water	5.83E+03	5.55E+03
	Al(water)	0	0
	Cd(water)	3.00E-06	2.86E-06
	Cr(water)	0	0
	Cu(water)	1.20E-04	1.20E-04
	Fe(water)	0	0
	Hg(water)	5.00E-07	5.00E-07
	Ni(water)	2.00E-05	2.00E-05
	Pb(water)	0	0
	Zn(water)	8.00E-05	8.00E-05
	Unspecified/Other Metals (water)	9.71E-02	9.15E-02
W	Metals(water)	9.73E-02	9.18E-02
	Chlorides	7.00E+00	7.00E+00
	Fluorides	2.00E-02	2.00E-02
	Nitrates	0	0
	Phosphates	0	0
	Sulphides/Sulphates	9.92E-02	9.82E-02
	Unspecified/Other TDS	2.67E+01	2.61E+01
A	TDS	3.38E+01	3.32E+01
T	TSS	4.44E-01	4.29E-01
E	Oils & greases	1.44E-02	1.14E-02
	Ammonia	0	0
	Chlorinated Solvents/Comp	0	0
	Cyanides	1.05E-04	-3.33E-04
	herbicides	0	0
	pesticides	0	0
	Phenols	0	0
	Other Miscellaneous	6.55E-02	6.24E-02
	Acid	0	0
	Alkali	0	0
R	Miscellaneous	6.55E-02	6.20E-02
	COD	0	0
	BOD	1.02E-01	9.72E-02
W	Landfill weight	4.22E+02	4.19E+02
I	Open Loop Outputs	4.88E+02	4.77E+02
S	Other Solid	3.59E+02	3.49E+02
C	*Landfill Volume (dm3)*	2.60E+02	2.56E+02
MASS BALANCE		-66.60	-66.61