

# **ZINC RECOVERY FROM BAGHOUSE DUST GENERATED AT FERROCHROME FOUNDRIES**

by

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## **Zinc recovery from baghouse dust generated at ferrochrome foundries**

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### **Synopsis**

During the production of ferrochrome in electric arc furnaces, a dust is captured in baghouse filters as a means of air pollution control. This dust contains various metals such as chromium, zinc, iron, aluminium and magnesium. Due to the presence of hexavalent chromium in the dust, which is both toxic and carcinogenic, it requires disposal at a hazardous waste disposal site, entailing high cost. The possibility exists that these costs could be reduced if metals such as zinc can be recovered from the dust through, *inter alia*, leaching. Experiments were performed to determine suitable conditions for the leaching of zinc from such a baghouse dust. A two step leaching procedure was followed which prevented the formation of silica gel. The most favourable conditions for zinc extraction was with a sulphuric acid concentration of 336 g/l and an acid to dust ratio of 0,56. Under these conditions zinc was selectively leached with regard to iron and aluminium. The percentage recovery for zinc was 71,2 %, aluminium 1,8 % and iron 0,1 %. It was concluded that the second step (dilution) of leaching did not have a significant influence on the percentage extraction of metals from the dust.

Consideration of the chemical treatment cost of waste streams produced led to the conclusion that zinc recovery from baghouse dust is not an economically feasible project viewed in isolation. However, compared to disposal at a hazardous waste disposal site such as Holfontein, approximately R 467 054,00 per annum (based on a seven day week and baghouse dust production of 3 600 kg/day) can be saved.

**KEY WORDS:** Ferrochrome, baghouse dust, zinc, leaching, electrolytic precipitation, hydrometallurgy, solvent extraction, silica, chromium(VI), air pollution.

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### List of symbols

D	Distribution coefficient
HA	Concentration of acidic extractant in organic phase
$K_A$	Acidity coefficient of the extractant
$K_{ex}$	Extraction coefficient
$K_f$	Formation coefficient of the metal complex with the extractant
n	Charge on a metal ion
$P_{HA}$	Partition coefficient
$\rho_{Man}$	Partition coefficient of metal complex

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# Chapter 1

## Introduction

The wide use of stainless steel products, due to its resistance to corrosion and adverse conditions, has made the mining of chromite ore and the production of ferrochrome metals prevalent in South Africa today. Stainless steel consists of iron, chromium, nickel and other minor elements. The chromium in stainless steel come from ferrochrome and recycled stainless steel.

Ferrochrome is manufactured at ferrochrome foundries in electric arc furnaces. The feed to electric arc furnaces is chromite ore and can be presented as  $(\text{Fe,Mg})\text{O} \cdot (\text{Cr,Fe,AL})_2\text{O}_3$  (Kirk–Othmer, 1993). The chromium and iron react with carbon, charged to the furnace, and are reduced to form the metal product. Silica ( $\text{SiO}_2$ ) is also charged to the furnace as a fluidizing agent. The other metal oxides fed to the reactor, as part of the ore, are more volatile and a certain fraction of these metals evaporate, to be condensed again when the off gas is cooled (Stegemann, 2000). The silica also evaporates and condenses again (Omori, 1987). The condensed particles form a very fine dust that is captured in baghouse filters. The particles are very small and could enter the respiratory system of humans and animals. It also contains hexavalent chromium, which is toxic to humans and animals as well as being carcinogenic to humans (Nriagu and Nieboer, 1988).

The captured dust has to be disposed of in a safe and environmentally friendly manner. The  $\text{Cr}^{6+}$  is reduced to  $\text{Cr}^{3+}$  and precipitated as  $\text{Cr}(\text{OH})_3$  by raising the pH (Nriagu and Nieboer, 1988). The  $\text{Cr}(\text{OH})_3$  slag is a safe product to use as landfill because it is insoluble in water and is not toxic or carcinogenic. During disposal of the dust, the zinc and other metal oxides in the dust go to waste and can also pollute waterways.

At the Herculite ferrochrome foundry near Brits, approximately 3 600 kg dust is formed per day (Strobos and van Zyl, 1997). Due to the process of evaporation and condensation of the more volatile components, the concentration of some metal oxides like zinc and magnesium is increased above that of the slag composition. According to an analysis done by Rocklabs (Strobos and van Zyl, 1997), the dust contains, for example, 7,55 % zinc that relates to a total of 99,2 tons zinc per annum. No attempt is currently being made to extract any of the metals to offset the costs associated with the treatment and disposal of the baghouse dust.

The objectives of this investigation are to determine the optimum conditions for leaching of zinc from baghouse dust and to assess if treatment and disposal costs associated with this dust can be decreased due to recovery of zinc. The method of zinc recovery focuses on the hydrometallurgical route, which includes leaching, solution purification and metal precipitation. A process to purify the leached solution will be selected which will be evaluated based on published literature to determine if

the leaching process is feasible. The experiments were performed at laboratory scale. An economic evaluation to assess if savings will result will be presented.

Chapter 2 consists of a literature survey that addresses the raw material and the method of zinc recovery. Chapter 3 describes the experiments to determine leaching conditions and in Chapter 4 the results is discussed in terms of the optimum leaching conditions and economic implications. Chapter 5 contains concluding remarks regarding the optimum leaching conditions and economic feasibility and recommendations with regard to further test work.

# Chapter 2

## Literature Survey

The extraction of zinc from baghouse dust emanating from the ferrochrome industry is investigated in this dissertation. In order to plan the relevant laboratory experiments, information was gathered on the raw material utilised and general conditions for the recovery of zinc.

### 2.1 RAW MATERIAL

For better understanding of the experiments presented in this dissertation, it is important to know what the nature of the raw material utilised was, what compounds it consist of and what the characteristics and values of these compounds are.

The raw material is a baghouse dust emanating from the electric arc furnaces at Hernic ferrochrome foundry, situated near Brits in the North West Province. These furnaces are operated at temperatures in excess of 1500 °C (Nriagu and Nieboer, 1988). A typical analysis of this particular baghouse dust is given in Table 2.1.

**Table 2.1** Analysis of dust from Hernic ferrochrome foundry.

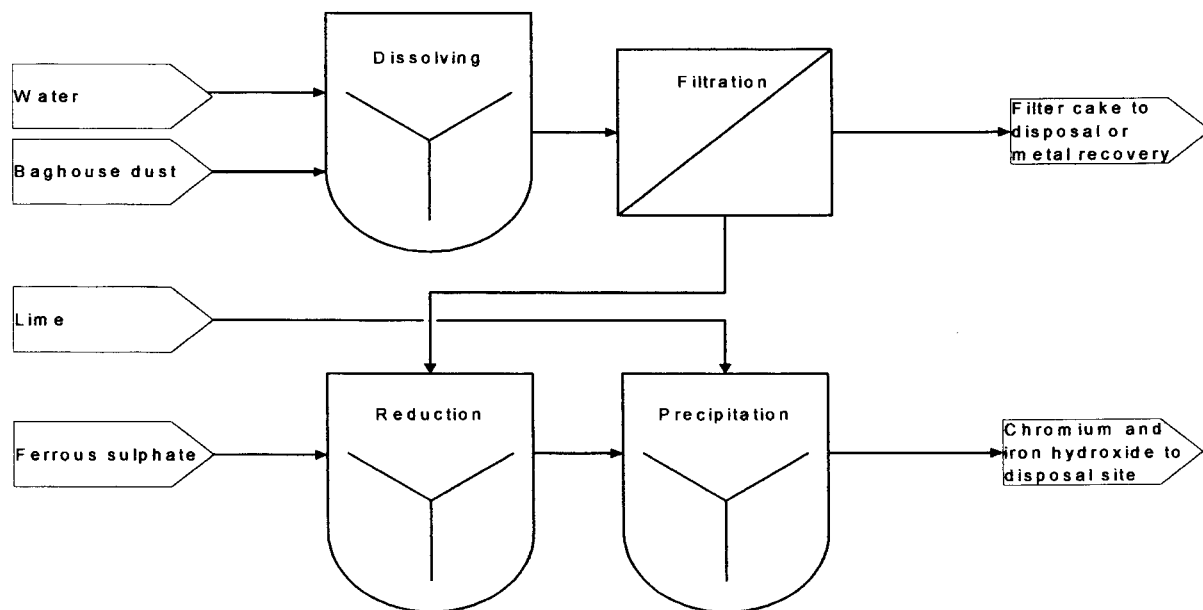
Component	Percentage
SiO <sub>2</sub>	45,21
Fe	2,33
Al	5,62
Mg	13,29
Na	5,94
K	3,06
Cr	3,18
S	3,4
Zn	7,55
Pb	0,123
Ga	0,035

A fraction of the chromium present is in hexavalent form. This form of chromium, depending on the relevant dosage, is both toxic and carcinogenic when ingested (Nriagu and Nieboer, 1988). Due to its high solubility in water, it can also pollute waterways through precipitation and seepage. This is the main reason the dust is removed from air streams emitted from ferrochrome foundries. In addition to chromium present in the dust, valuable compounds such as zinc (in the form of ZnO), aluminium (in the form of Al<sub>2</sub>O<sub>3</sub>) and gallium (in the form of GaO) are also present, and the extraction of these metals may be an additional incentive for treatment of the dust.

## 2.2 TREATMENT OF BAGHOUSE DUST

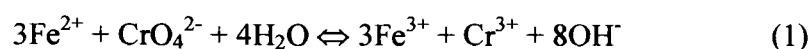
The baghouse dust removed from ferro chrome foundries in South Africa is normally disposed off on *ad hoc* disposal sites situated on the relevant foundry property. Prior to disposal the dust is usually treated with a ferrous compound (for example, ferrous sulphate) to reduce the hexavalent chromium present in the dust. A shallow layer of topsoil normally covers the disposal sites in an effort to prevent groundwater pollution through seepage. However, due to present and future environmental regulations, the above practice can no longer be accepted and alternative solutions are currently investigated in South Africa (Beukes *et al.*, 1999).

One such a solution was proposed by Strobos and Van Zyl (1997) and is shown in Figure 2.1. The first step for the treatment of the baghouse dust requires mixing it with water to dissolve all soluble compounds. The subsequent slurry is separated via filtration into solid (filter cake) and liquid (filtrate) phases. The filter cake can be either dumped at a waste disposal site or utilized for metal recovery. The utilization of the filter cake for recovering of valuable metals, and more particularly zinc, forms the basis of this dissertation and will be discussed in detail in Section 2.3. Although the treatment of the filtrate, to prevent contamination of natural waters, is not included in this dissertation, it is briefly outlined below to complete the overview on the treatment of baghouse dust.

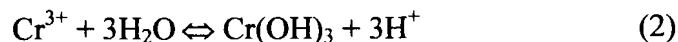


**Figure 2.1** Primary treatment of baghouse dust.

For the treatment of the filtrate, toxic hexavalent chromium can be reduced to its less toxic tri valent form, through the use of reducing agents described by Nriagu and Nieboer (1988). These include ferrous sulphate, sodiumbisulphate, sulphur dioxide, sodium hydrosulphate and sulphide waters. When ferrous sulphate is added to the filtrate, the following redox reaction will result (Nriagu and Nieboer, 1988):



The  $\text{Cr}^{3+}$  can then be immobilized by precipitating it as  $\text{Cr}(\text{OH})_3$ . The relevant hydrolysis reaction for  $\text{Cr}^{3+}$ , which takes place during hydrated lime dosing at a pH of between 6 and 9, is as follows:



The subsequent hydroxide can then be disposed of in a general landfill site, together with an excess of lime (Kirk-Othmer, 1993).

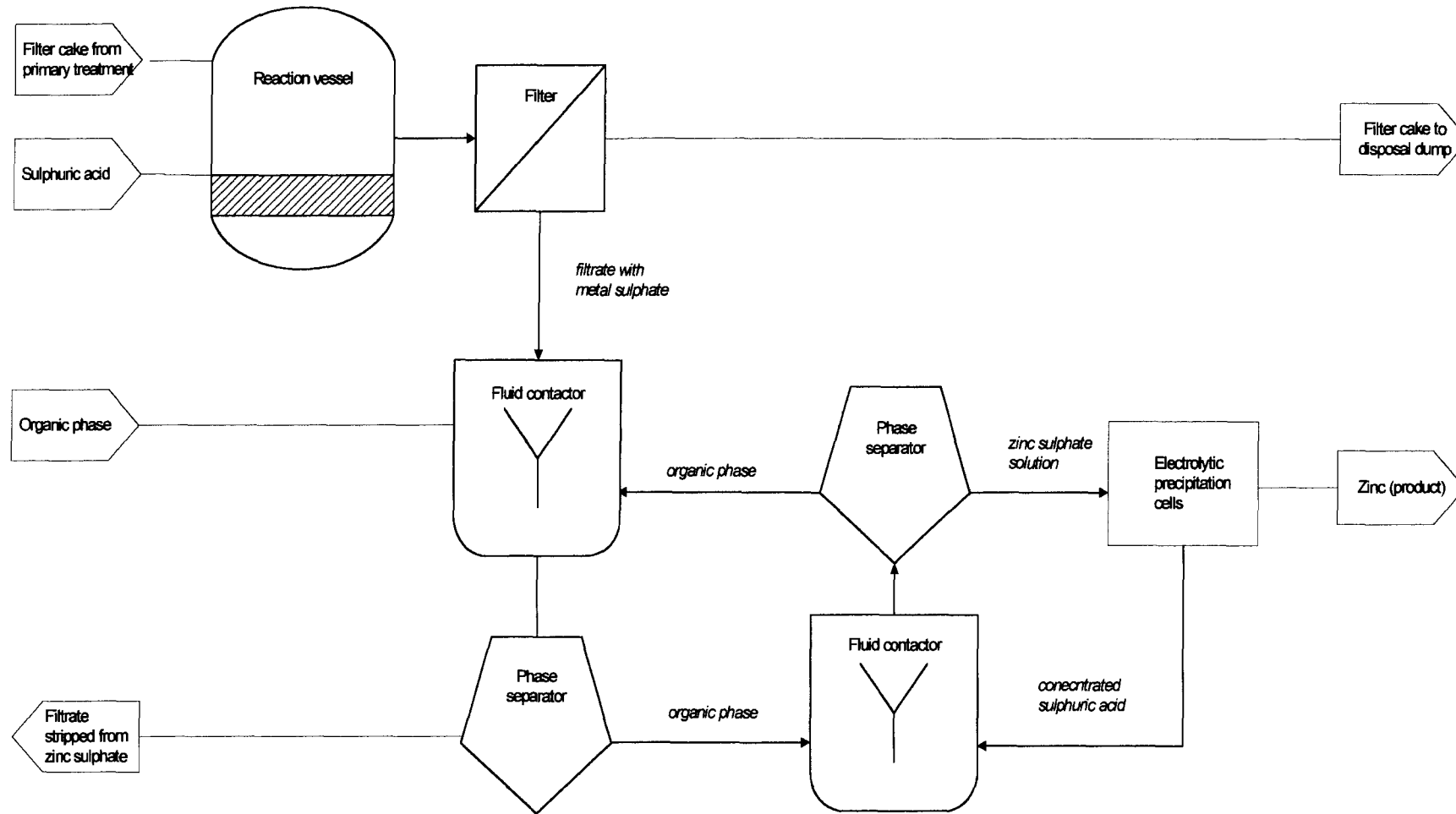
### 2.3 RECOVERY OF ZINC

The filter cake obtained from the filtration step in Figure 2.1 (primary treatment) contains the insoluble metal oxides that were initially present in the dust. Strobos and Van Zyl (1997) reported that approximately 10% (on a weight basis) of the initial baghouse dust is lost through dissolution and are subsequently separated from the dust as part of the filtrate. The most abundant compounds still present in the filter cake are silica, magnesium oxide, aluminium oxide and zinc oxide. Based on the relative simple process for the extraction of zinc from solid compounds (Evans and De Jonghe, 1991) and its high monetary value, this dissertation investigates the technical and economic feasibility of recovering zinc from these waste materials generated at ferrochrome industries.

Two different means of extracting metals from a raw material exist, namely pyro- metallurgy and hydrometallurgy. During pyro-metallurgy metal oxides react with carbon in the absence of oxygen to form  $\text{CO}_x$  and the metal. With hydrometallurgy the following processes take place: the metal oxide is dissolved with acid into an ionic form (leaching), the solution is refined (for example, through solvent extraction and stripping of the required metal), and the pure metal precipitated. Due to the environmentally clean and energy efficient nature of the hydrometallurgy method, as well as availability of reagents and laboratory equipment, it was decided to extract zinc by means of hydrometallurgy.

The extraction of zinc from the filter cake (obtained during primary treatment) through hydrometallurgy is schematically represented in Figure 2.2. The process can be divided into four stages, namely leaching, extraction, stripping and precipitation. During leaching, the sulphuric acid (commonly used in the extraction industry) reacts with the filter cake in a complete mixed reactor. The reactor contents are then filtered and the subsequent filtrate contains zinc and other elements such as iron, magnesium and aluminium. The filter cake from this secondary treatment, consisting of mainly silica and other undissolved metal oxides, is normally disposed of on a landfill site.

The next step, electrolytic precipitation (electrolysis), is the most common process utilized for the recovery of zinc from solutions in the metallurgy industry (Evans and De Jonghe, 1991). However, for successful recovery of zinc through electrolysis, substances that will interfere with the precipitation process will have to be removed to very low concentrations (Gill, 1980; Ritcey and Ashbrook, 1979). The above implies that a purification step is required to reduce the concentrations of interfering substances. However, in order to sustain a sufficient rate in the electrolytic precipitation cells, an optimum zinc concentration is also required. These criteria are addressed by solvent extraction; a process commercially used for the production of, *inter alia*, zinc sulphate solutions (Klocker *et al.*, 1997).

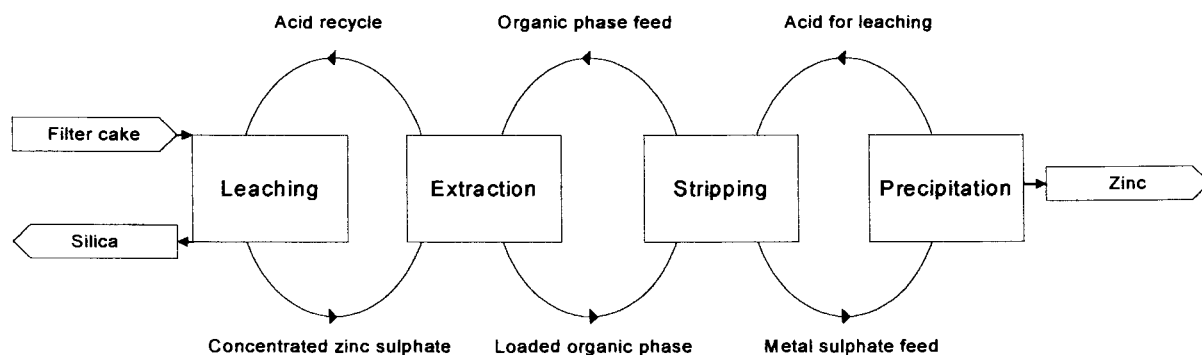


**Figure 2.2** Recovery of zinc through hydrometallurgy (secondary treatment of baghouse dust).

During solvent extraction the filtrate from the leaching step is treated with an acidic extracting agent, di(-2-ethylhexyl) phosphoric acid, dissolved in an organic carrier (n-heptane), and zinc ions are transferred from the aqueous to the organic phase. The organic and aqueous phases are then separated in a phase separation unit. The filtrate, depleted of zinc ions and enriched with  $H^+$ , can be recycled to the leaching step after neutralization and removal of excessive dissolved substances. During stripping the organic phase that was loaded with zinc ions during solvent extraction, is contacted with a concentrated sulphuric acid stream. Zinc ions are transferred from the organic to the aqueous phase, followed by separation of the two phases. Transfer of the ions between the two phases take place in complete mixed reaction vessels.

The subsequent concentrated zinc sulphate stream is then fed to the electrolytic precipitation cells. An electrical current is passed through the zinc sulphate solution causing the metal ions to be reduced to an oxidation state of zero, the elemental form of the metal. Through the precipitation of zinc in its elemental form, the zinc sulphate solution is converted to sulphuric acid that can be recycled to the solvent extraction unit. Ulman *et al.* (1998) summarised the above recovery of zinc to three circuits, as illustrated in Figure 2.3. The three circuits (linked by the leaching, extraction, stripping and precipitation stages) are:

- *The leaching circuit (LC):* the acid stream is recycled after treatment.
- *The solvent extraction circuit (SEC):* the organic phase is recycled and act as carrier of the zinc between the two aqueous circuits.
- *The electrolytic precipitation circuit (EPC):* the concentrated zinc sulphate solution is recycled after regeneration through contacting the depleted solution with the loaded organic phase.



**Figure 2.3** Extraction of zinc, viewed as three circuits, during secondary treatment of the baghouse dust.

In the following section, general principles applicable to leaching are discussed which will form the basis for the experiments.

### 2.3.1 Leaching with sulphuric acid

The rate of leaching is affected by a number of factors and optimum conditions for the extraction of zinc are determined thereby. This includes particle size, the nature of the solvent, temperature and agitation.

- Particle size influences extraction whereby smaller particle sizes result in greater interfacial area between the relevant solid and liquid. The diffusion path of the solute through the porous structure of the residual solids is also shorter. Small particles may, however, impede circulation of the liquid and separation of the particles from the liquid, making subsequent drainage of the solid residues more difficult. Even distribution of particle size is desired as this may lead to uniform time of extraction and minimal obstruction to solvent flow (Coulson and Richardson, 1996).
- The solvent should be a selective solvent and its viscosity should be sufficiently low for it to circulate freely. It was reported by Zeydabadi *et al.* (1998) that through varying the concentration of the sulphuric acid fed to the leaching step, and also the acid to raw material ratio, zinc could be leached out preferentially to other metals. The initial rate of extraction for all the components is the highest, due to the high concentration of the pure solvent. Therefore the initial quantities of material fed to the leaching vessel need to be controlled accurately, to ensure selection of zinc. The rate will decrease due to concentration gradients and changes in the viscosity of the solvent.
- An increase in temperature will increase the solubility of the materials that are being extracted, to give a higher rate of extraction. The diffusion coefficient will be expected to increase with temperature as well.
- Agitation (stirring) of the fluid is important because it prevents sedimentation and allows more effective use of the interfacial surface (Coulson and Richardson, 1996). An optimum rate for agitation can be obtained to the point where an increase in agitation rate does not increase the rate of extraction. This is due to the bulk concentration and the concentration at the surface of the solid being the same. The effect of bulk diffusion is then eliminated and if the particles are small, for example a powder, the rate of extraction can be accounted for by the rate of dissolution of the desired compounds.

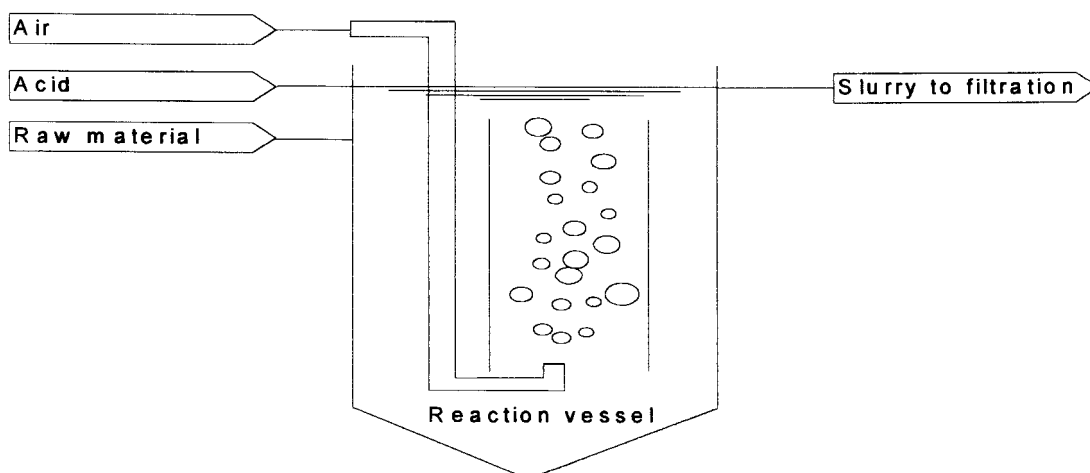
From large scale leaching operations, valuable information can be gathered about what the optimum conditions should be for the extraction of zinc. Commercially both batch and continuous processes are employed.

During continuous process leaching, zinc is leached through a two-step, counter-flow configuration. The zinc is leached at a temperature of approximately 95°C (Gill, 1980). It is practically difficult to increase the temperature above this because it is close to the boiling point of the liquid. To increase the temperature above this the system will have to be under increased pressure. The first contact step is with concentrated sulphuric acid of approximately 200 g/l. The reaction time is approximately two hours and the free acid concentration drops to 5 g/l. During this time, 50 to 75 percent of the soluble zinc present in the raw material is dissolved (Gill, 1980).



Batch process leaching of zinc oxide is not as commonly used as the continuous process, because of its smaller capacity. However, it does have certain advantages, for example, zinc ferrites ( $\text{ZnO-Fe}_2\text{O}_3$ ) which are formed during roasting and are insoluble during normal leaching, can be processed. The zinc ferrites are formed at temperatures in excess of  $650^\circ\text{C}$  that can easily be reached in electric arc furnaces where ferro chromium is produced. Therefore the batch leaching process will be more suitable for extraction of zinc from the dust formed in electric arc furnaces than, for example, leaching of zinc oxide formed through heating zinc sulphide. Another advantage is that each batch of the feed is individually treated and deviation from a standard feed's analysis can be accommodated (Gill, 1980). The heat of reaction of the decomposition of the ferrites raises the solution temperature to  $106^\circ\text{C}$ . A considerable amount of water is evaporated as steam and is removed via stacks.

In order to cause all the above-mentioned conditions to be met during leaching, the most suitable equipment has to be selected. Equipment used during leaching includes agitators and different types of leaching tanks. One precaution during agitation is to prevent high rates of agitation, which result in little movement of the solid particles relative to the liquid. Therefore agitation may be achieved by means of compressed air rather than mechanical stirrers. One example of a leaching vessel which accommodates agitation by compressed air, is a Pachuca leaching tank. Air is blown through a pipe, which enters the tank just above the solution level, and extends to the bottom of the tank where it opens. The air bubbles released from the pipe decrease the density of the slurry (see Figure 2.4). These leaching tanks are fairly efficient and used throughout the world (Coulson and Richardson, 1996). Tanks used for both batch and continuous leaching processes are the same.



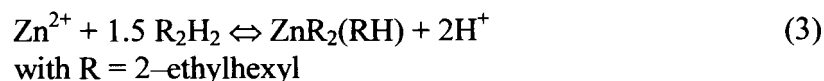
**Figure 2.4** A Pachuca leaching tank utilizing compressed air for agitation.

After leaching, the filtrate is treated *via* solvent extraction in order to:

- produce a product stream with mainly zinc sulphate and sulphuric acid with little other metal impurities, and
- to increase the concentration of zinc in the feed to the electrolytic precipitation plant.

### 2.3.2 Solvent extraction

During this process an organic solution (n-heptane), containing an optimum concentration of di-(2-ethylhexyl)-phosphoric acid (D2EHPA), is contacted with the filtrate produced in Section 2.3.1. Intensive mixing is required to establish sufficient contact between the organic and aquatic phases. Zinc is transferred from the aquatic to the organic phase through the following reaction (Klocker *et al.*, 1997):



D2EHPA is an acidic extractant and the extraction process entails the exchange of cations between the organic phase and the aqueous phase.  $\text{H}^+$  ions move from the organic to the aqueous phase and  $\text{Zn}^{2+}$  from the aqueous to the organic phase. The long carbon chains attached to the phosphorous acid prevent it from being dissolved in the aqueous phase and it thus remains in the organic phase (n-heptane). The effect of different parameters on the extraction can be quantified by the equation (Ullmann *et al.*, 1988: 6-45):

$$\log D = \log K_{ex} + n \log [\text{HA}] + n \text{pH} \quad (4)$$

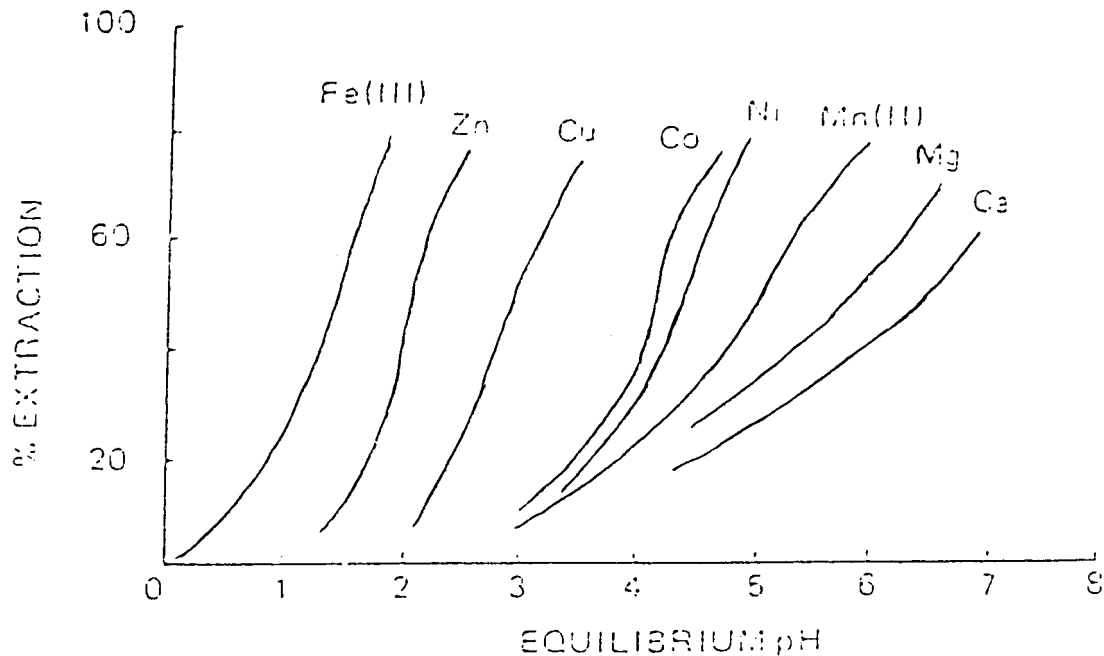
D is the distribution coefficient and  $K_{ex}$  is the extraction coefficient. HA is the concentration of the acidic extractant in the organic phase. A plot of log D against pH at constant reagent concentration should give a straight line with slope  $n$ , the charge on the metal ion. The extraction constant  $K_{ex}$  has the form (Ullmann *et al.*, 1988):

$$K_{ex} = p_{\text{HA}}^{-n} K_A^n K_f p_{\text{Man}} \quad (5)$$

It includes the partition coefficient  $p_{\text{HA}}$ , the acidity coefficient  $K_A$  of the extractant, the overall formation coefficient of the metal complex with the extractant  $K_f$  and its partition coefficient  $p_{\text{Man}}$ . The relative magnitude of  $K_f$  determines the amount of metal extracted at a defined reagent concentration and pH. Thus metals with high  $K_f$  values are extracted at lower pH than metals with lower  $K_f$  values (Ullmann *et al.*, 1988).

By changing the pH of the feed to the contact step between the organic and the aqueous phase, a specific ion can be extracted because different ions have different  $K_f$  values. For example, zinc is extracted at a pH between 1 and 2, while magnesium is extracted in the region of pH 5 to 7 (McKetta, 1984). This shows that a good selectivity of extraction between zinc and magnesium can be obtained. Figure 2.5 shows how zinc is preferentially transferred from the aqueous to the organic phases with respect to other metal ions in solution at different pH levels (McKetta, 1984).

Once the metal ions have been taken up into the organic medium, it can be stripped from the organic phase by contacting the organic phase with concentrated sulphuric acid (Zeydabadi *et al.*, 1997) and effluent from the electrolytic precipitation cells used for this purpose (Amer *et al.*, 1995). The concentrated acid solution becomes rich in zinc sulphate through intensive mixing with the organic phase.

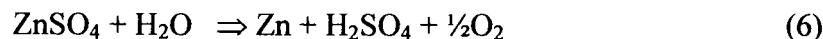


**Figure 2.5** Selective extraction of metals from sulphate media with D2EHPA at different pH levels.

The concentration of zinc in the feed to the electrolytic precipitation cells can be changed by adjusting the ratio between acid used for stripping and the organic phase (Evans and De Jonge, 1991). After stripping, the aqueous solution then forms the feed to the electrolytic precipitation plant.

### 2.3.3 Electrolytic precipitation

During electrolytic precipitation an electric current is passed through a zinc sulphate solution in electrolytic precipitation cells. This results in the conversion of zinc cations to zinc in an oxidation state of zero. Electrolysis must be started with an essentially neutral  $ZnSO_4$  solution, and the reaction takes place till approximately half the zinc is deposited. According to Rosenqvist (1983), the feed concentration of zinc to the precipitation plant should be approximately 50 to 150 g/l. The acid concentration increases to 100g  $H_2SO_4$  per litre. This solution is returned to the leaching plant or to the solvent extraction plant to be used as strip liquor (Amer *et al.*, 1995). The following reaction takes place during the precipitation:



The zinc accumulates at the cathodes and must be stripped every 24 to 48 hours. The cathodes are made from titanium and the anodes from lead-antimony or lead-silver alloy (Gill, 1980). The temperature must be kept constant at approximately 35 to 45 °C by circulating cooling water through lead coils placed in each cell. The current density should be approximately 20 to 40 amperes per square foot (0,09 m<sup>2</sup>) of cathode area. The theoretically required voltage is

approximately 2,35 V (Gilchrist, 1989), but in actual fact the voltage used is 3,25 to 3,5 V. This is due to current leakage throughout the electrical circuit.

Current leakage can also be due to other substances in the electrolyte solution (Gill, 1980; Ritcey and Ashbrook, 1979). Various negative effects can result through the presence of these ions, for instance, some of the ions can co-deposit with zinc, causing a decrease in the purity of the zinc product. The current efficiency and electrolyte resistivity can be negatively impacted. The characteristics of the zinc deposits can be altered causing it to either be spongy, beady or perforated. In Table 2.2 the concentrations of certain substances encountered in commercial plants and the possible effects on the quality of the deposited zinc are shown (Kirk-Othmer, 1996).

**Table 2.2** The influence of various ions on the electrolytic precipitation of zinc.

Impurity	Reported range, mg/l	Current efficiency	Characteristics of deposit	Comments
Germanium	0.005-0.2	Lowers	Spongy	Worse with cobalt
Tellurium	<0.001	Lowers	Uneven	Worse with cobalt
Selenium	<0.002	Lowers	Uneven	Worse with cobalt
Arsenic	0.003-0.02	Lowers	Corrugated	Worse with cobalt or germanium
Antimony	0.01-0.03	Lowers	Beady, poor adhesion	
Copper	0.05-0.2	Lowers		
Nickel	<0.01-0.5	Lowers	Holes	
Cobalt	0.03-2.0	Lowers	Holes	Reduces lead deposition
Tin	<0.02	Lowers	Filmy	
Iron	0.2-25	Lowers		May reduce anode corrosion
Cadmium	0.01-5			Deposits with zinc
Lead	1			Deposits with zinc
Thallium	0.5-5			Increases lead deposition,
Aluminium	10			Increases electrolyte resistivity
Magnesium	6.5-12 g/l			Increases electrolyte resistivity
Manganese	3-3.5 g/l			

The leaching step and the accompanying purification processes, such as solvent extraction, impact on the feed concentrations to the electrolytic precipitation plant. The quality of the feed to the electrolytic precipitation plant is directly influenced by the concentrations of metals in the product from the leaching plant. Ions can be carried over from the leaching circuit to the organic phase and again to the stripping acid if it is leached out from the dust initially (Zeydabadi *et al.*, 1997).

For this dissertation, leaching was studied through extensive laboratory experiments. Solvent extraction and electrolytic precipitation is discussed as part of this literature survey to provide criteria whereby the efficiency of the leaching process and the feasibility of zinc production from the waste product could be established.

# Chapter 3

## Experimental

Various experiments were performed in order to find the optimum conditions for leaching zinc (using sulphuric acid) from filter cake obtained from the filtration step of the primary treatment described in Chapter 2. These optimum conditions are dependant on the rate of leaching (of zinc), and are determined by a number of factors. These include, *inter alia*, particle size, rate of agitation, duration of leaching, temperature and the nature of the solvent (Coulson and Richardson, 1991). In the experiments conducted, the effect on the percentage extraction of various metals was determined when changing certain of the variables. All the experiments were batch experiments.

A two-step leaching procedure was followed to prevent the formation of silica gel. During leaching with sulphuric acid, the acid can act as a catalyst for the polymerisation of SiO<sub>2</sub> and form silica gel (Kirk-Othmer 1997). The formation of this gel makes it impossible to separate the silica and the dissolved substances by filtration. It is unclear why gel formation did not occur in this instance, but various factors can play a role, for example, salt concentration, pH and the presence of other metals such as iron. The presence of iron can, for example, retard the dissolution of silica (Kirk Othmer 1997).

The above two-step batch leaching experiments were performed with the apparatus and experimental set up described below.

### 3.1 APPARATUS AND EXPERIMENTAL SET UP

The apparatus used in the first step of leaching included:

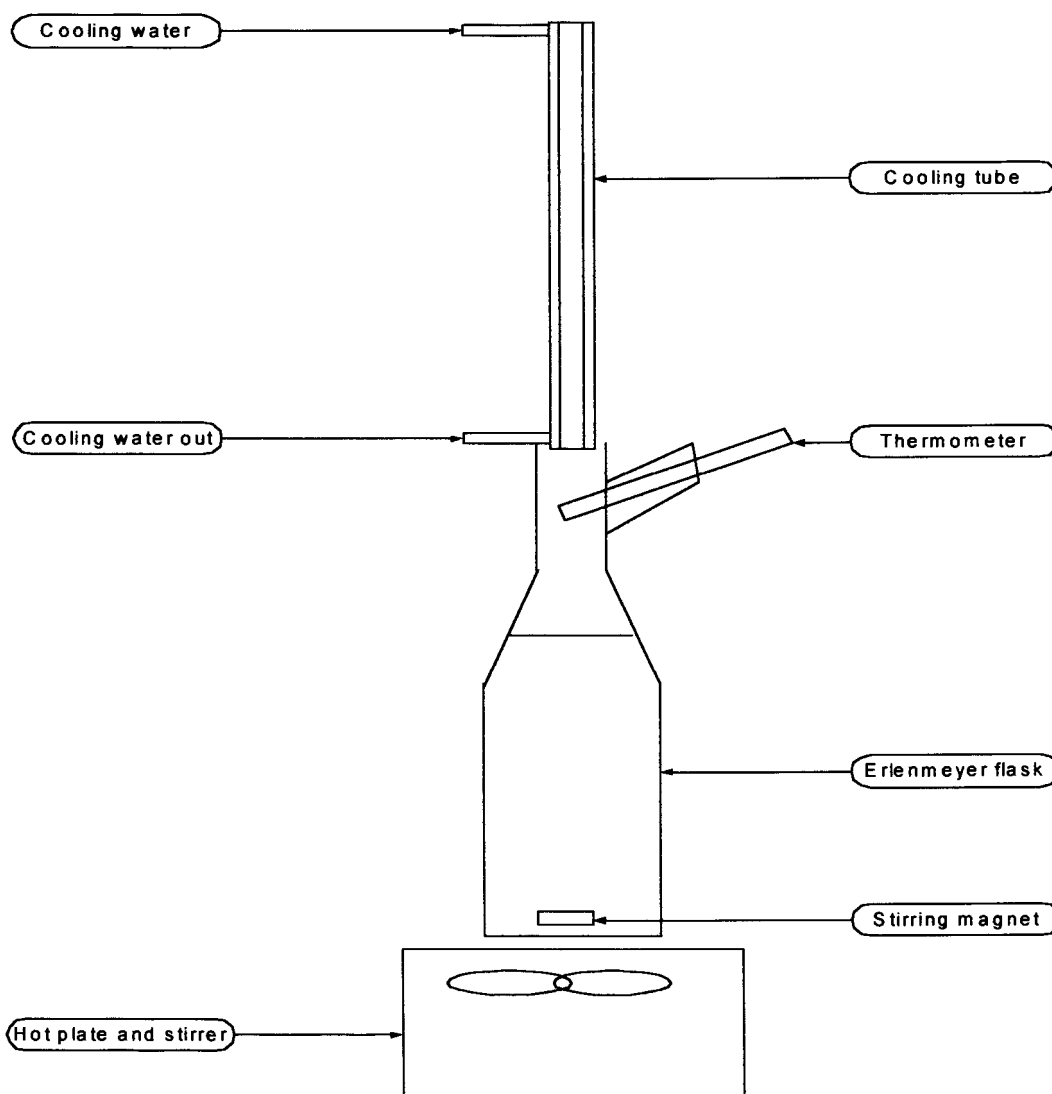
- a glass beaker,
- glass rod, and
- a measuring cylinder.

During the first step of leaching concentrated sulphuric acid was added to water and then added to the filter cake in a glass beaker. It was stirred while reacting for approximately 20 minutes. The second step of leaching, whereby the solution is diluted with distilled water, was performed with the following apparatus:

- Erlenmeyer flask,
- hot plate and magnetic stirrer (combined),
- magnet for stirring,
- cooling coil,
- Buchner filter,

- thermometer,
- pH meter, and
- an atomic absorption spectrophotometer.

The second step of leaching was performed in an Erlenmeyer flask placed on a hot plate to raise the temperature to 98 °C. The liquid was stirred with a magnetic stirrer. Any water vapour formed was condensed. A thermometer in the glass tube between the Erlenmeyer flask and the condenser measured the temperature of the water vapour. This experimental set up is illustrated in Figure 3.1 and shown in Figure 3.2.



**Figure 3.1** Schematic representation of the experimental set up for the second leaching step.

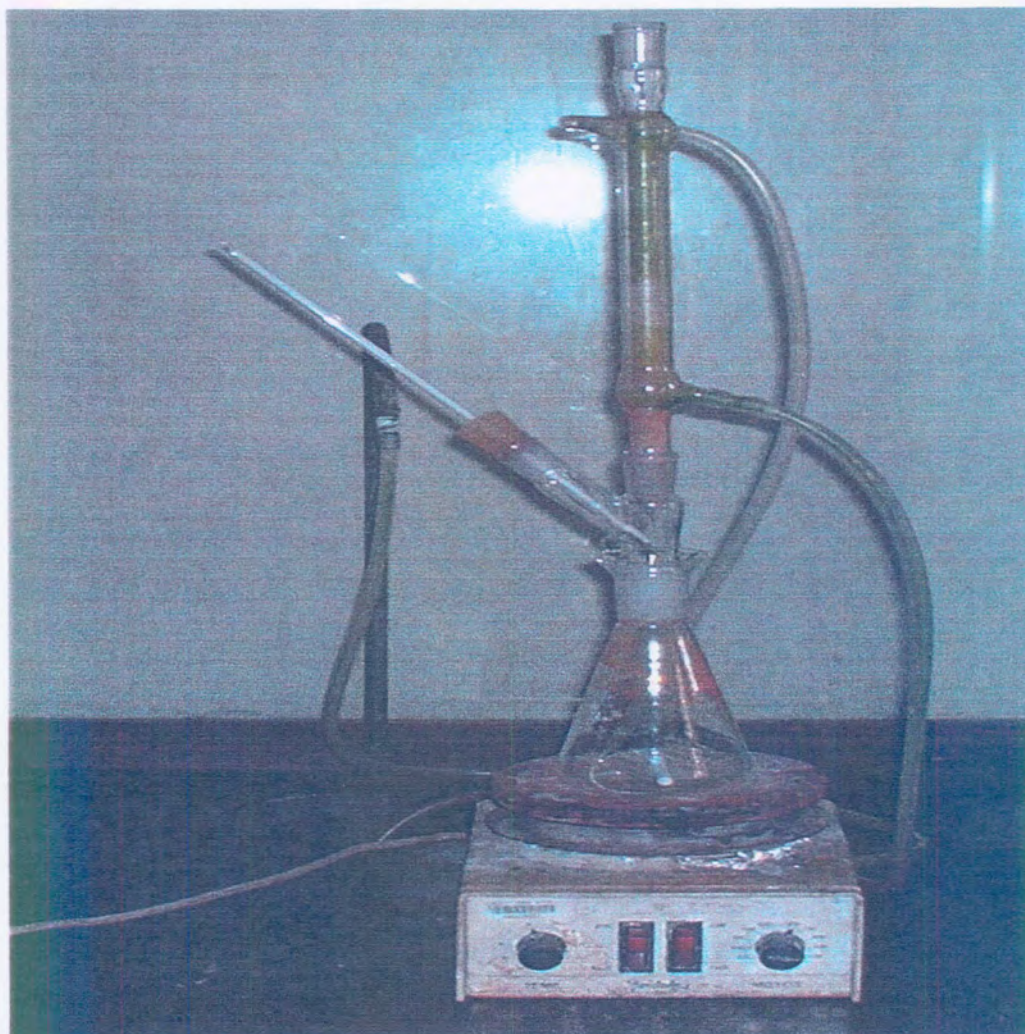


Figure 3.2 Picture of experimental set-up.

### 3.2 METHOD AND PLANNING

Since the filter cake is already in a powder form, no further attempt was made to change the particle size. As discussed by Coulson and Richardson (1991), particle size should be as small as possible, but not so small that drainage of the solid residues becomes difficult to achieve. The rate of agitation was kept constant for all experiments. The variables investigated were the duration of leaching, temperature at which leaching took place and the nature of the solvent.

After the first set of experiments was performed, results were questioned and the experiments repeated (see Chapter 4 for discussion). The conditions were slightly altered for the second set of experiments. The conditions for the second set of experiments will be given in brackets where the ranges of the variables are given.

During the concentrated acid leaching step, 30 (40) ml of distilled water were mixed with 20 ml of concentrated sulphuric acid (91 %) and added to 30 g of filter cake. This reaction mixture was stirred with a glass rod for 20 minutes.

In the second leaching step, a further 60 to 260 ml of distilled water were added to prevent diffusion limitations and saturation of the mixture from slowing down or stopping the dissolution reactions (Coulson and Richardson, 1991).

The reaction in the second leaching step took place in a 300-ml Erlenmeyer flask. A magnetic stirrer was used for agitation at a constant speed. Manual adjustment of the hot plate controlled the temperature of the reaction liquor after measurement of both the temperatures of the vapour and the reaction liquor with a thermometer. At completion of leaching, the slurry was filtered with a Buchner filter (Watman Nr 1 filter paper). After filtration, 50 ml of distilled water were used as wash water to remove any leach liquor still present in the filter cake.

The filtrate was analysed with an atomic absorption spectrophotometer to determine the concentration of zinc, iron, gallium, aluminium and magnesium in the filtrate. The percentage recovery for each metal extracted cake was calculated. The filter cake was dried and the weight of the filter cake determined.

For the different parameters investigated, slightly different reaction conditions were used that is summarised below.

### **3.2.1 Duration of leaching**

The effect of duration of leaching on the extraction efficiencies of various metals was evaluated by varying the duration of the second leaching step between 0 and 72 hours. All other conditions were kept constant, namely

- 30 g of filter cake,
- sulphuric acid concentration of 132 (151) g/l (based on initial charge of free acid),
- rate of agitation,
- volumes of 200 (160) ml water and 20 ml sulphuric acid, and
- temperature of 98°C.

### **3.2.2 Temperature during leaching**

The effect of temperature during leaching on the extraction efficiencies of various metals was evaluated by varying the temperature during the second leaching step between 25 and 98 °C (Gill, 1980). At 98 °C the reaction liquor was boiling and water had to be condensed. All other conditions were kept constant:

- duration of 24 hours,
- 30 g filter cake,
- sulphuric acid concentration of 132 (152) g/l (based on initial charge of free acid),
- rate of agitation, and
- volumes of 200 (160) ml water and 20 ml sulphuric acid.



### 3.2.3 Concentration of sulphuric acid

This variable was investigated by first of all keeping the acid to filter cake ratio constant (A) during the first step of leaching and changing the volume of water added for the second step. The volume of water added during the second step varied between 60 and 260 ml. The following variables were kept constant for each experiment (Zaydabadi *et al.*, 1998):

- duration of 24 hours,
- sulphuric acid concentration in second step 132 (152) g/l (based on initial charge of free acid),
- 30 g filter cake,
- rate of agitation, and
- temperature of 98 °C.

Thereafter (B) the mass of sulphuric added was varied between 8,37 and 33,5 g (Gill, 1980; Zaydabadi *et al.*, 1998) and therefore the acid to dust ratio from 0,28 to 1,12. Once again the duration, original mass of filter cake, rate of agitation and temperature were kept constant. In this case the volume of water added during the second step also remained constant at 200 (160) ml.

Table 3.1a and 3.1b summarise the experimental conditions for the first and second set of experiments for the different parameters investigated.

**Table 3.1a** Experimental conditions for the first set of experiments

<b>Parameter Investigated</b>	<b>Duration</b>	<b>Temperature</b>	<b>Concentration of H<sub>2</sub>SO<sub>4</sub> (A)</b>	<b>Concentration of H<sub>2</sub>SO<sub>4</sub> (B)</b>
<b>Experimental Conditions</b>				
Duration (hours)-2 <sup>nd</sup> step	0-72	24	24	24
Filter cake mass (g)	30	30	30	30
Acid to dust ratio	1,12	1,12	1,12	0,28-1,12
H <sub>2</sub> SO <sub>4</sub> concentration (g/l)-1 <sup>st</sup> step	662	662	662	414-662
H <sub>2</sub> SO <sub>4</sub> concentration (g/l)-2 <sup>nd</sup> step	132	132	106-208	69-132
Volume of water (ml) 2 <sup>nd</sup> step.	200	200	95-260	200
Temperature (°C) 2 <sup>nd</sup> step	98	25-98	98	98

**Table 3.1b** Experimental conditions for the second set of experiments

<b>Parameter Investigated</b>	<b>Duration</b>	<b>Temperature</b>	<b>Concentration of H<sub>2</sub>SO<sub>4</sub> (A)</b>	<b>Concentration of H<sub>2</sub>SO<sub>4</sub> (B)</b>
<b>Experimental Conditions</b>				
Duration (hours)-2 <sup>nd</sup> step	0-48	24	24	24
Filter cake mass (g)	30	30	30	30
Acid to dust ratio	1,12	1,12	1,12	0,28-1,12
H <sub>2</sub> SO <sub>4</sub> concentration (g/l)-1 <sup>st</sup> step	558	558	558	186-558
H <sub>2</sub> SO <sub>4</sub> concentration (g/l)-2 <sup>nd</sup> step	152	152	124-279	41-152
Volume of water (ml) 2 <sup>nd</sup> step.	160	160	60-210	160
Temperature (°C) 2 <sup>nd</sup> step	98	25-98	98	98

## Chapter 4

# Results and discussion

This chapter presents the results of the leaching experiments. It also discusses the further treatment required of the filtrate to produce a suitable feed for an electrolytic precipitation plant, waste streams produced and their required treatment, and the economic feasibility of zinc recovery from dust.

### 4.1 RESULTS OF THE LEACHING EXPERIMENTS

Results are graphically presented as the percentage extraction of metals in the dust against the value of a variable that was changed over a certain range. These ranges were determined by values in the literature (see Section 2.3.1 and Chapter 3) or by observations made during the execution of preliminary experiments. The exact values for these variables could not be determined from literature since there are no reported values for leaching conditions on bag house dusts. Percentage extraction was calculated from the concentrations of the metals present in the filtrate (produced after filtration of the leaching liquors) and concentrations reported in the bag house dust (Table 2.1).

The mass of the metals present in the filter cake (produced after primary treatment) used during leaching was calculated from Table 2.1 and the basis that 10 % of the mass is lost through dissolution of water soluble compounds in primary treatment (Strobos and van Zyl, 1997). The mass of the metals present in the filtrate was determined from the concentrations (analytically determined with the atomic absorption spectrophotometer) and the volume of filtrate produced (measured with a measuring cylinder). The percentage extraction is then the mass of a metal present in the filtrate divided by the mass of the relevant metal present in the filter cake used for leaching. All the experiments were performed in duplicate and the percentage extractions reported are the average of two identical experiments in each case. The results obtained during the duplication of experiments showed little deviation, as can be seen from the data presented in Appendices A and B.

The graphs presenting percentage extraction are indications of the success of an experiment with regard to selectivity and extent of leaching taking place, but do not give absolute values that can be used to evaluate the feasibility of the extraction process. In order to produce zinc by means of electrolytic precipitation cells, a minimum concentration of zinc must be present in the process stream, used as feed to these cells. The concentrations of other elements must also be within permissible levels (see Section 2.3.3). Therefore, the actual concentrations of the metals and the volumes of filtrate produced are presented in tabular form as well.

After the initial experiments were performed, no variation was seen in the zinc extraction efficiencies despite all the variations introduced during the second step of leaching. The experiments were then repeated with slightly different volumes of water utilised in the second step of leaching. Therefore, two sets of results are given for each variable that was investigated. In Appendices A and B the raw data for the two sets of experiments are reported.

Other than these reported results, visual observations were made that are now presented to further clarify the leaching experiments. Initially, when the concentrated sulphuric acid and water were mixed, the temperature of the mixture increased to approximately 100 °C. Directly after mixing the water and acid, the mixture was added to the filter cake and then stirred manually for 20 minutes. The temperature increased even further during this leaching step due to the exothermic reaction. For the second leaching step, the reaction mixture was diluted further. After the second leaching step, the slurry was filtered with a Buchner filter.

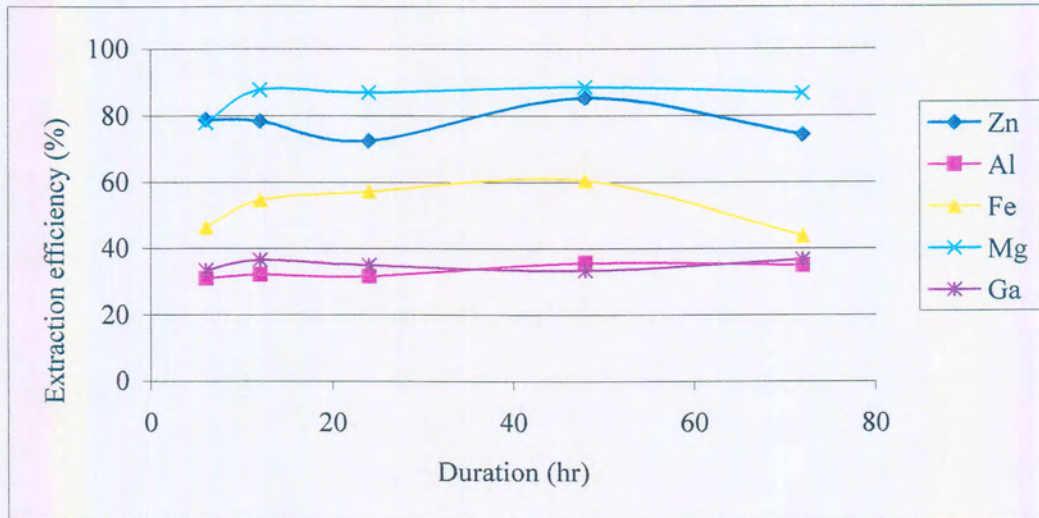
#### **4.1.1 Duration of leaching**

Conditions for the experiments that were performed to evaluate the duration of leaching are described in Section 3.2.1.

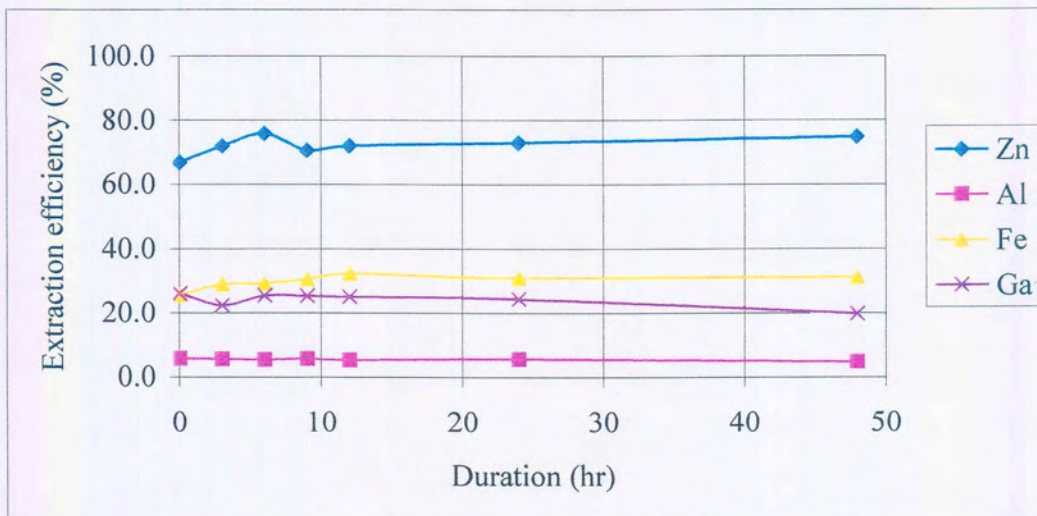
In Figures 4.1a and 4.1b the percentage extraction of zinc, aluminium, iron, magnesium and gallium are given. (In Figure 4.1b the extraction efficiency of magnesium is not shown. Very high readings of magnesium in the filtrate were obtained, due to the high dilution that was required to operate in the working range of the atomic absorption spectrophotometer.)

The graphs in Figures 4.1a (first set of experiments) and 4.1b (second set of experiments) indicate that the effect of duration on extraction efficiency is basically irrelevant. This is an indication that most of the leaching occurs during the first leaching step. In Table 4.1 the concentrations for the various metals are given for 6 hours duration of leaching (for both the first and second set of experiments). However, the concentrations of these metals in the filtrate are approximately the same despite a further increase in the duration of leaching in the second step.

Observations from Table 4.1 include the large decrease in aluminium concentration (from 1 677 mg/l to 333 mg/l) and the high value reported for magnesium. Approximately one third of the mass of the filter cake is also lost (compare final mass of 18,3 to 30 g of filter cake originally). The low pH of 0,86 indicates that there is excess free acid present in the filtrate. (The mass of filter cake was not determined in the first set of experiments and the pH was not determined in the second set.)



**Figure 4.1a** The effect of duration of leaching on extraction efficiency (first set of experiments).



**Figure 4.1b** The effect of duration of leaching on extraction efficiency (second set of experiments).

**Table 4.1** Concentration of metals in the filtrate for 6 hours leaching in the second step, for the first and second set of experiments.

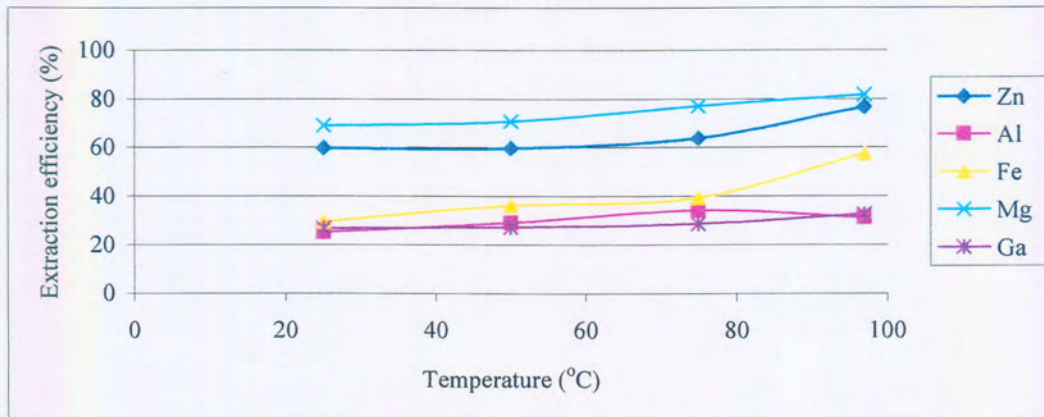
<b>Component</b>	<b>First set concentrations (mg/l)</b>	<b>Second set concentrations (mg/l)</b>
<b>Zinc</b>	7 675	8 209
<b>Magnesium</b>	11 934	30 420
<b>Aluminium</b>	1 677	333
<b>Iron</b>	1 259	1 021
<b>Gallium</b>	52	48
<b>Volume (ml)</b>	260	213
<b>Mass of Filter Cake</b>	-	18,3
<b>pH</b>	0,86	-

#### 4.1.2 Temperature of leaching

In Figures 4.2a and b the effects of temperature on the extraction efficiency are presented. From the graph in Figure 4.2a a marked increase can be seen in the extraction efficiency for zinc, iron and magnesium, above 70 °C. The results for these experiments compare well to those done for the duration of leaching, which were all performed at 98 °C.

Increase in efficiencies during leaching in the second step is not very clear for the second set (Figure 4.2b). The extraction efficiencies for zinc is high in all these experiments and thus it can be concluded that in this case the first step of leaching resulted in a more complete dissolution of the zinc. It should be noted that during the first step of leaching a slightly more diluted acid concentration was used in the second set of experiments. More acid would thus have been available for leaching of these metals as compared to when iron and aluminium are leached out at considerable amounts. See discussion on the effect of the nature of the solvent in Section 4.3.

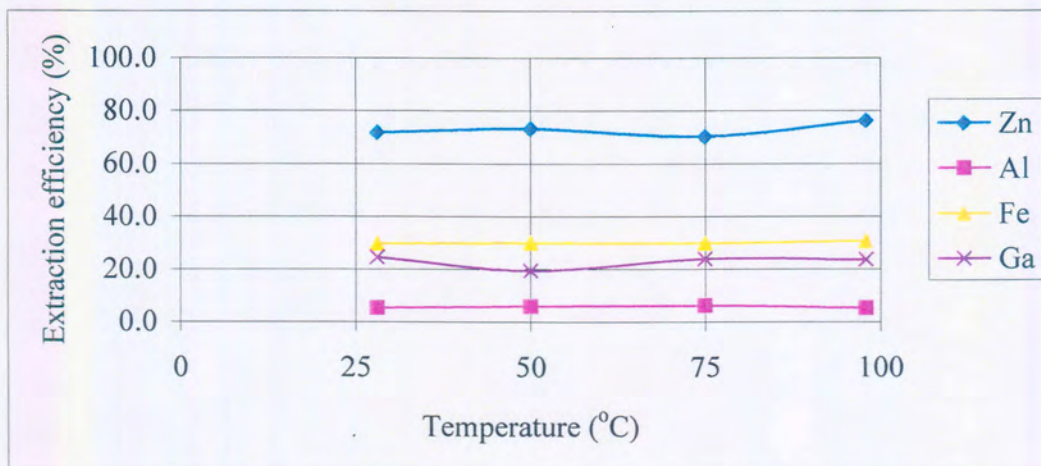
Tables 4.2a and b present the data from which the extraction efficiencies presented in Figure 4.2a and b have been calculated. The higher degrees of extraction at higher temperatures corresponds well with findings from Zeydabadi *et al.* (1997).



**Figure 4.2a** The effect of temperature of leaching on the extraction efficiency (first set of experiments).

**Table 4.2a** Concentrations in the filtrate of experiments on the influence of temperature.

Temperature (°C)	25	50	75	97
<b>Zinc</b>	7 907	7 827	8 468	6 885
<b>Aluminium</b>	1 893	2 222	2 644	1 615
<b>Iron</b>	1 155	1 388	1 414	1 385
<b>Magnesium</b>	15 230	15 505	15 848	11 693
<b>Gallium</b>	57	59	62	50
<b>Volume</b>	192	176	174	250
<b>PH</b>	0,6	0,5	0,5	0,6



**Figure 4.2b** The effect of temperature of leaching on the extraction efficiencies (second set of experiments).

**Table 4.2b** Concentrations in the filtrate of experiments on the influence of temperature.

Temperature (°C)	28	50	75	97
Zinc	7 257	7 885	7 703	8 027
Magnesium	28 079	28 242	31 237	31 673
Aluminium	330	383	419	351
Iron	855	971	1 145	1 091
Gallium	42	34	45	43
Volume (ml)	229	218	205	222
Mass of filter cake (g)	19,97	18,8	19	17

#### 4.1.3 Concentration of sulphuric acid

As described in Section 3.2.3, the effect of the concentration of sulphuric acid was evaluated by varying the amount of water added during the second leaching step and by varying the amount of acid added.

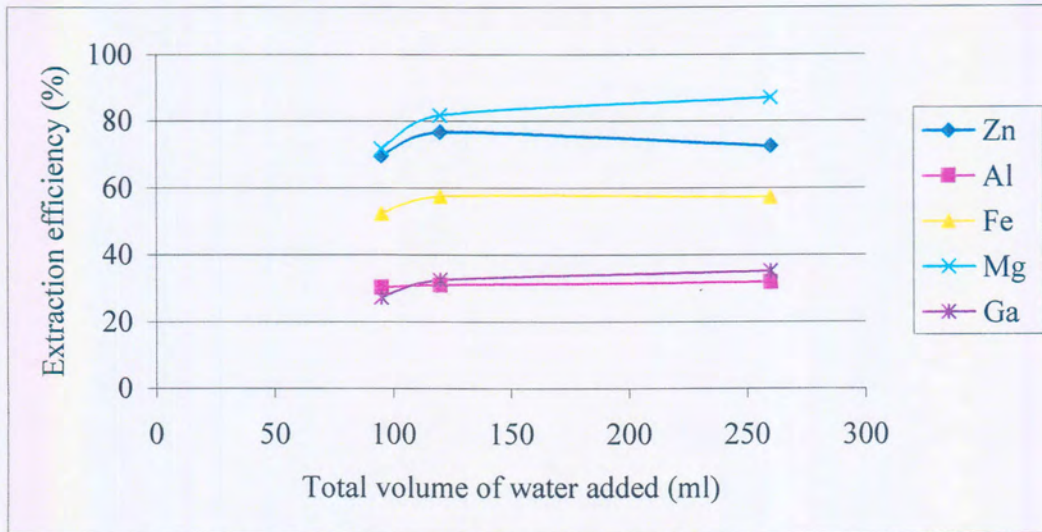
In Figures 4.3a and 4.3b the extraction efficiencies obtained for variable amounts of water added in the second leaching step are presented. In Figure 4.3a less extraction efficiency is observed for all the metals analysed, except for aluminium at lower volumes of water added.

In Figure 4.3b the same tendency was observed for all the metals where a higher extraction efficiency was observed with an increase in volume of water fed to the leaching reaction. This can be due to either of two reasons:

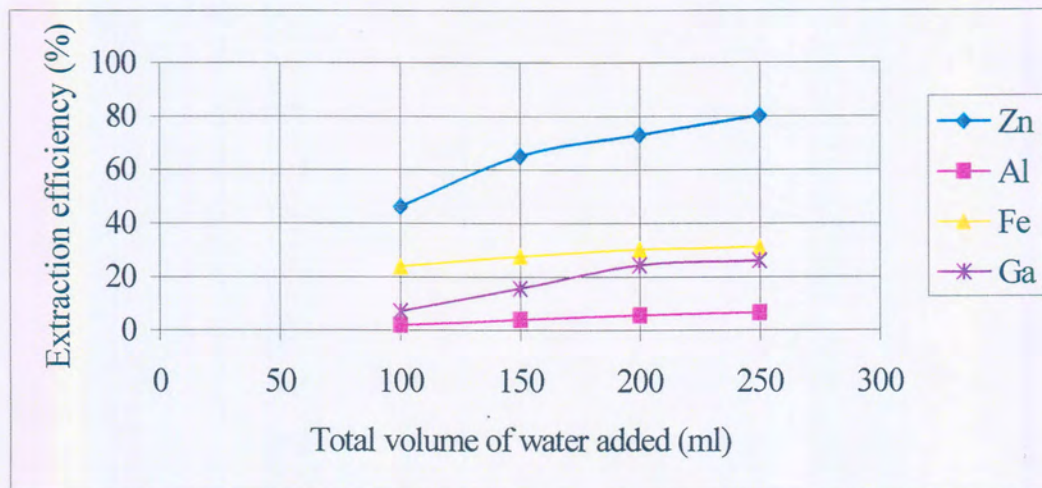
- better separation of dissolved substances due to less being present in the filtrate entrained in the filter cake, or
- inaccuracy of the atomic absorption spectro-photometer at high concentrations, giving lower readings than the actual readings.

It is not likely that a faster reaction rate, due to dilution factors in the second step, will have such a large influence on the process since from the previous results it seems that most of the leaching occurred in the first step of leaching.





**Figure 4.3a** The effect of the volume of water added during leaching on the extraction efficiency (first set of experiments).



**Figure 4.3b** The effect of the volume of water added during leaching on the extraction efficiencies (second set of experiments).

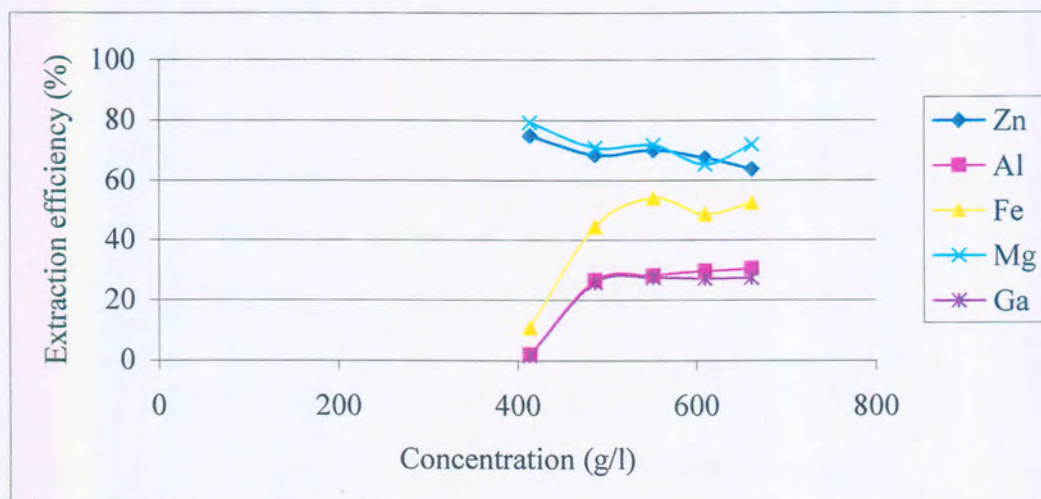
In Table 4.3b the concentrations for 100 and 200 ml of water added is shown as well as the volume of filtrate produced in each case (second set of experiments).



**Table 4.3b** Concentrations of metals in the filtrate of experiments performed with different volumes of water added.

Volume of water (ml)	100	200
Zinc	10 878	8 473
Magnesium	42 673	21 528
Aluminium	233	348
Iron	1 803	1 108
Gallium	25	46
Volume (filtrate) (ml)	100	216
Mass of filter cake		18,56

In Figures 4.3c and 4.3d the percentage extraction for variations in the amount of acid added is presented. In Figure 4.3c, the first data point (where 414 g/l of acid was used), indicates that selective leaching for zinc and magnesium can be achieved.



**Figure 4.3c** The effect of initial acid concentration (first step of leaching) on extraction efficiencies (first set of experiments).

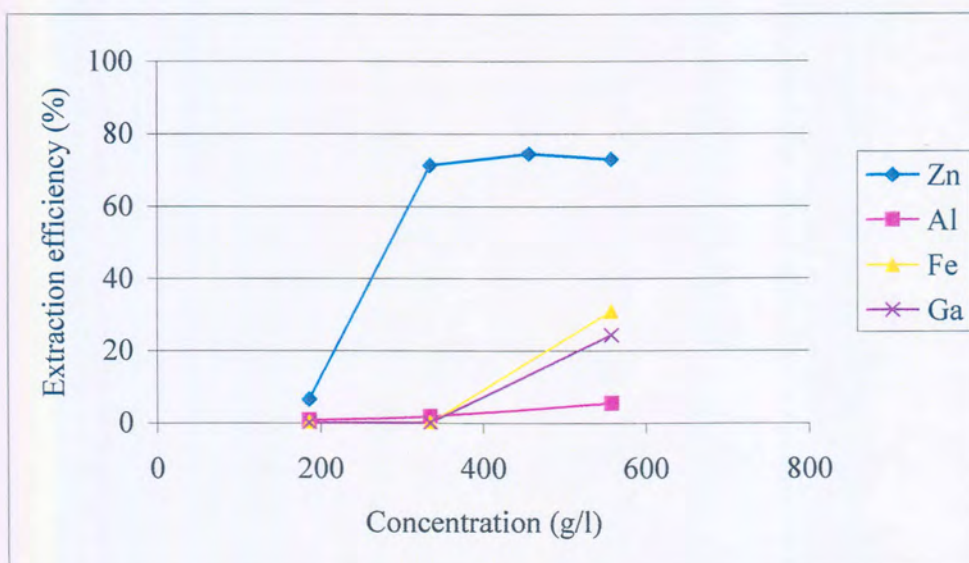
Table 4.3c gives the concentrations of the metals in the filtrate for this data point. The pH is also reported as approximately 3,2 to 3,5. This indicates that most of the free acid present was used in the reaction. The iron content was still relatively high (569 and 362 mg/l) and could still be detrimental to the extraction of zinc.

The results from the second set of experiments were more favourable than the first. In Figure 4.3d it can be seen that at low concentrations of 190 mg/l almost no extraction of all the metals was achieved, except for magnesium that is not shown here. At 336 g/l the percentage recovery for zinc was 71,2 %, aluminium 1,8 % and iron 0,1 %. Therefore, for all the leaching experiments performed, this data point represents the most favourable conditions for leaching of zinc.



**Table 4.3c** Concentrations of metals in the filtrate with an initial acid concentration of 414 g/l.

Component	Concentration (mg/l)	Concentration (mg/l)
Zinc	12 015	11 000
Aluminium	277	84
Iron	569	362
Magnesium	21 995	17 222
Gallium	4	4
Volume (ml)	150	176
PH	3,19	3,45



**Figure 4.3d** The effect of initial acid concentration (first step of leaching) on extraction efficiencies (second set of experiments).

In Table 4.3d the concentrations of all the metals that was used to calculate the percentage extractions presented in Figure 4.3d are given. At sulphuric acid concentration of 336 g/l, the zinc concentration is 9 628 mg/l and that for iron below the range where the atomic absorption photometer could detect it, but this is close to zero mg/l. For this experiment it can be seen that 184 ml of filtrate was produced for 30 g filter cake leached.

After evaluation of the influence of concentration of acid on the extraction efficiency, variations between the first and second set of experiments can be addressed. A comparison between Figures 4.1a and 4.1b shows that a greater percentage extraction of zinc, aluminium and iron was achieved in the first set of experiments, although the increase in extraction are greater for aluminium and iron than for zinc. Therefore, it can be seen that at these conditions there is a tendency to selectively leach zinc rather than aluminium and iron.

**Table 4.3d** Concentrations of metals in the filtrate with various initial acid concentrations.

<b>Initial concentration (g/l)</b>	<b>186</b>	<b>336</b>	<b>458</b>	<b>558</b>
<b>Zinc</b>	953	9 628	8 696	8 473
<b>Magnesium</b>	23 724	25 272		21 528
<b>Aluminium</b>	55	147		348
<b>Iron</b>	<100	<100		1 108
<b>Gallium</b>	0,3	5,5		46
<b>Volume</b>	196	184	211	216

The reason for the increased selectivity of leaching in the second set of leaching experiments can be explained by the concentration of acid used in the first step. In the first set of experiments 30 ml of water were used and in the second set 40 ml of water with 20 ml 91 % acid. This resulted in acid concentrations of 660 and 570 g/l respectively. Utilising a less concentrated acid led to increased selectivity for zinc, as also found by Zeydabadi *et al.* (1997).

In the following section the further processing of a process stream, such as that produced under these leaching conditions (336 g/l of acid in the first leaching step), to produce a suitable solution for electrolytic precipitation of zinc, will be addressed.

## **4.2 PRODUCTION OF A SOLUTION SUITABLE FOR ELECTROLYTIC PRECIPITATION**

The aim of leaching is to produce a zinc sulphate solution that is suitable for further treatment in electrolytic precipitation cells. The characteristics of such a zinc sulphate stream is:

- a zinc concentration of 50 to 150 g/l and
- minimal concentrations for other constituents, as discussed in Section 2.3.3.

When evaluating the results of the leaching experiments to these criteria, certain conclusions can be made. The concentration of sulphuric acid and the acid to dust ratio in the first step of leaching is critical to minimise the concentration of other elements in the filtrate. From the experiments performed the best results were obtained with 336 g/l and an acid to dust ratio of 0,56. This is, however, much higher than the theoretical value of approximately 0,2 required to leach for zinc

The amount of zinc present in the filtrate was 9 628 mg/l. This could vary with the amount of water used for dilution in the second step. The influence of the second step of leaching seems insignificant. Further experiments to clarify the second step of leaching and to optimize the selection of zinc in the first step of leaching have to be performed. Selectivity has to be optimised since aluminium is present in the filtrate at values of 145 mg/l. If present in the electrolyte solution it causes an increase in the electrolyte

resistivity, which in turn will cause a higher power requirement. Magnesium is present in values higher than 20 000 mg/l. This could also lead to increased electrolyte resistivity.

To address the low zinc concentration of the dust and to a reasonable extent the presence of other constituents in the dust, the processes of solvent extraction followed by stripping is discussed here. If we consider the solvent extraction in Figure 2.2, streams into this unit would be the filtrate produced after leaching and the D2EHPA in n-heptane (organic) stream. This solvent extraction process would consist of mixing tanks, followed by a phase separation stage. Streams leaving the process would be an organic stream, containing zinc as well as other metals that were extracted with zinc and an aqueous stream depleted of zinc. Besides the zinc, other elements such as trivalent iron will also be in the organic phase (see Figure 2.5, (McKetta 1984)). Virtually all the magnesium will, however, still be in the aqueous phase. This stream can be reused for leaching if it is treated in order to remove metals and sulphates. The treatment of polluted streams generated during treatment of baghouse dust and the disposal of solid waste will be discussed in Section 4.3.

After the solvent extraction stage follows the stripping stage. The feed streams to this stage are the organic phase (now loaded with zinc as well as other elements such as iron) and a sulphuric acid rich stream produced after leaching. In order to ensure the feed stream to the electrolytic precipitation cells have a zinc concentration of 50 to 150 g/l, an organic to strip acid ratio of approximately 10:1 has to be used (McKetta 1984). This would result in a zinc concentration of approximately 100 g/l.

### **4.3 WASTE STREAMS PRODUCED AND POSSIBLE TREATMENT**

If a treatment strategy for baghouse dust (as proposed in this dissertation) will be implemented, a number of waste streams will result. The most environmentally responsible approach would be to design the treatment process for zero liquid discharge. Therefore, no water would be consumed by the plant, except that which would be lost through co-disposal with sludge and evaporation.

During primary treatment, a stream of water will result that will contain all the soluble compounds in the dust. This will include chromate and sulphate associated with sodium, potassium and calcium. However, the chromate will then be addressed through reduction and precipitation as a hydroxide, as discussed in Section 2.2. The water produced after primary treatment could be reused as make-up water. However, a built up of salts to the saturation level will result and thus some water will have to be removed from the circuit. This water will be unfit for discharge into public streams and will have to be treated prior to reuse or discharge.

Since it will contain mono-valent ions (sodium and potassium), feasible treatment options could be membrane treatment such as reverse osmosis (Mallevalle *et al.*, 1996) or ion exchange. The resultant brine from the above processes will also have to be treated further through, for example, evaporation.

The solid residue (filter cake) produced after primary treatment is relatively safe to dispose. However, it does contain heavy metals such as zinc that could have a negative impact on ground water if it is leached out. This is a further motivation to recover the zinc from the baghouse dust. During the recovery process of zinc from baghouse dust, a magnesium sulphate rich stream will be produced. In order to maintain the policy of zero discharge, this stream will have to be treated and then reused.

One possibility would be to remove metals from the solution by precipitating it as hydroxide if the pH is raised. Magnesium will only precipitate at a pH of approximately 10,5 (Weast RC; 1971). To raise the pH to this value, sodium or calcium hydroxide can be used. If sodium hydroxide is used the advantage would be that the sodium sulphate will not co-precipitate with magnesium hydroxide. Pure magnesium hydroxide can be used as a neutralisation agent in water treatment, but could also have an application in the pharmaceutical industry (Kirk Othmer, 1996). The latter grade of magnesium hydroxide has a high monetary value of R20 to R30/kg (Crest Chemicals, 2001). If calcium hydroxide is used to raise the pH, some calcium sulphate will precipitate with the magnesium hydroxide. Calcium sulphate precipitates slowly, but given enough time and surface area, it will precipitate to the saturation level of approximately 1 350 mg/l sulphate in the absence of highly soluble ions, such as sodium and magnesium (Weast RC, 1971).

#### 4.4 ECONOMIC FEASIBILITY OF ZINC RECOVERY FROM BAGHOUSE DUST

Prior to addressing the costs of treatment associated with the proposed treatment strategies in this dissertation, the cost for disposal of a similar baghouse dust at Holfontein hazardous waste disposal site is presented. This cost will be on the basis of the dust being in the form of a sludge containing 25% moisture (mixing with water is required to prevent inhalation of small particles). The cost for transport to Holfontein is R 177,00/t and for disposal R 312,00/t (Waste Tech, 2001). Unit cost, purity and utilization efficiency for the different chemicals used for treatment of the dust at Holfontein are given in Table 4.4 (Crest Chemicals, 2001).

**Table 4.4** Unit costs, purity and utilization efficiency for chemicals as used in the calculations of cost (Crest Chemicals, 2001).

Chemical	Cost (R/t)	Purity (%)	Utilisation efficiency (%)
Ferrous sulphate	2 480,00	100	100
Lime	550,00	90	60
Sulphuric acid	90,00	98	-

In order to reduce the chromium in the baghouse dust to a hydroxide form, it is treated with ferrous sulphate and lime prior to disposal according to the following reactions (Section 2.2):



The costs associated with transport, treatment and disposal of the baghouse dust is calculated as follows:

Mass of solids for transport

$$= 3\,600 \times 1,25$$

$$= 4\,500 \text{ kg/day}$$

The transport cost per day

$$= 4\,500/1\,000 \times \text{R } 177,00$$

$$= \text{R } 796,50$$

Amount of chromium to be treated (Table 2.1)

$$= (3,18/100) \times 3\,600 \text{ kg/day}$$

$$= 114,5 \text{ kg/day}$$

Amount of ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )

$$= (\text{mass of chromium/molar mass of chromium}) \times \text{molar mass of ferrous sulphate}$$

$$\times \text{molar ratio}$$

$$= (114,5/52) \times 3 \times (277,8)$$

$$= 1\,835 \text{ kg/day}$$

Amount of lime required ( $\text{CaO}$ )

$$= (\text{moles of chromium} + \text{moles of iron}) \times \text{molar ratio} \times \text{molar mass of}$$

$$\text{lime}/(\text{purity} \times \text{utilization efficiency})$$

$$= (((114,5 / 52) + (1\,835 / 277,8)) \times (3 / 2) \times 56) / (0,6 \times 0,9)$$

$$= 1\,370 \text{ kg/day}$$

Amount of sludge formed

$$= \text{equivalent amount of ferric hydroxide} + \text{equivalent amount of chromium}$$

$$\text{hydroxide} + \text{equivalent amount of gypsum to lime added}$$

$$= ((1\,835/277,8) \times 107) + ((114,5/52) \times 103) + ((1\,370/56) \times 172)$$

$$= 5\,141 \text{ kg}$$

Mass of solids for disposal including 25% moisture

$$= (\text{dust} - \text{chromium} + \text{sludge}) \times 1,25 \text{ (moisture)}$$

$$= (3\,600 - 114,5 + 5\,141) \times 1,25$$

$$= 10\,783 \text{ kg/day}$$

The cost for treatment per day

$$= \text{cost of ferrous sulphate} + \text{lime}$$

$$= (R\ 2\ 480,00 \times 1\ 835)/1\ 000 + (R\ 550,00 \times 1\ 370)/1\ 000$$

$$= R\ 5\ 304,30/\text{day}$$

The disposal cost per day

$$= 10\ 783/1\ 000 \times R\ 312,00$$

$$= R\ 3\ 364,30/\text{day}$$

The total cost for disposal at Holfontein

$$= (R\ 796,50 + R\ 5\ 304,30 + R\ 3\ 365,30)$$

$$= R\ 9\ 466,10/\text{day based on } 3\ 600\ \text{kg/day production of baghouse dust.}$$

The cost for disposal at Holfontein is therefore

$$= R\ 3\ 455\ 126,50\ \text{per annum (based on a } 7\ \text{day week and production of } 3\ 600\ \text{kg baghouse dust/day).}$$

In contrast to disposal at Holfontein, the dust can be treated through primary treatment and leached with sulphuric acid to recover zinc. An economic evaluation of the proposed process can be subdivided into two sections, namely capital costs and operational costs. For the purpose of this evaluation of the process, only the operational costs, and more in particular the major chemical costs, will be evaluated.

The costs for this option can be split into three sections: primary treatment cost, revenue from zinc recovery and chemical costs for leaching and treatment of the waste stream with lime. For costing purposes the price for zinc is taken as \$815,00/ton at an exchange rate of R 8,55/ \$ (Business Report, 2001).

For primary treatment the chemical treatment cost is the same as for disposal at Holfontein, namely R 5 304,30/day.

The amount of sludge to be transported and disposed, including 25% moisture

$$= 5\ 141 \times 1,25$$

$$= 6\ 426\ \text{kg/day}$$

The cost for transport and disposal of this sludge

$$= (R\ 177,00 + R\ 312,00) \times 6\ 426/1000$$

$$= R\ 3\ 142,30/\text{day}$$

The revenue from zinc recovery can be calculated as follows:

The amount of zinc leached out from experimental results (See Table 4.3d)

$$= \text{concentration of zinc} \times \text{volume of filtrate} \times \text{scale factor}$$

$$= 9,628\ \text{g/l} \times 0,184\ \text{l} \times 3\ 600/ 0,03$$

$$= 212,7\ \text{kg/day}$$

The revenue associated with this zinc

$$= 212,7\ \text{kg}/1000 \times \$\ 815,00 \times R\ 8,55/\ \$$$



$$= R 1\,482,20/\text{day}$$

The cost associated with sulphuric acid and lime is as follows:

The amount of sulphuric acid required for leaching

= acid to dust ratio x the amount of dust treated per day x recovery after primary treatment / purity (Note that approximately 10 % of the mass of the dust is lost through dissolution during primary treatment.)

$$= (0,56 \times 3\,600 \times 0,9)/0,98 = 1\,851 \text{ kg}$$

Assume that an equivalent amount of lime is added for neutralisation than the amount of acid added

= mass of sulphuric acid added x purity x molar mass of CaO/molar mass of sulphuric acid / (purity x utilization efficiency)

$$= (1\,851 \times 0,98 \times 56/98)/(0,9 \times 0,6)$$

$$= 1\,919 \text{ kg/day}$$

The cost for sulphuric acid

$$= R 90,00/\text{ton} \times 1\,851/1000$$

$$= R 166,60/\text{day}$$

The cost for lime

$$= R 550,00 \times 1\,919/1000$$

$$= R 1\,055,50/\text{day}$$

The total cost for this treatment option is therefore

$$= R 5\,304,30 + R 3\,142,30 + R 166,60 + R 1\,055,50 - R 1\,482,20$$

$$= R 8\,186,50/\text{day}$$

The cost is therefore R 2 988 072,50 per annum. However, compared to disposal at a site such as Holfontein, approximately R 467 054,00 per annum (based on a 7 day week and 3 600 kg dust produced per day) can be saved.

This treatment cost can possibly be further reduced, by either utilising the magnesium hydroxide produced during the treatment process in the water treatment industry or, using it in the pharmaceutical industry. The selective leaching for magnesium, as the results presented in Section 4.1 indicated, could therefore be a more viable option.

A further option would be to extract the gallium present in the dust. This has a much higher monetary value than the other metals in the dust. However, it was not leached out very effectively with sulphuric acid.

## Chapter 5

### Conclusions and Recommendations

From the leaching experiments performed it was concluded that zinc could effectively be leached from baghouse dust, with regard to iron and aluminium, using sulphuric acid. These findings were similar to those of Zeydabadi *et al.* (1997). However, it is not possible to selectively leach for zinc with respect to magnesium, but the opposite is possible.

Optimal extraction was obtained using a sulphuric acid concentration of 336 g/l and an acid to dust ratio of 0,56. These were the conditions for the first step of leaching with a duration of approximately 20 minutes. The percentage recovery for zinc was 71,2 %, aluminium 1,8 % and iron 0,1 %. The influence of the second leaching step on the percentage extraction of the various compounds was insignificant. Even despite all the variations of conditions in the second step of leaching, the extraction efficiencies were similar. It is recommended that further experiments be performed to optimise the first leaching step.

According to McKetta (1984), it would be possible to produce a zinc sulphate solution suitable for electrolytic precipitation, from the filtrate produced after leaching, through solvent extraction. Zinc produced through electrolytic precipitation could be sold at approximately \$ 815/t (Business Report, 2001). Due to the high chemical cost associated with the leaching and treatment of waste streams produced, it is not economically feasible to extract zinc from baghouse dust when addressed in isolation. However, should these costs be compared with the cost associated with disposing of the baghouse dust at a registered waste disposal site, this method for treatment will be viable. The cost for treatment and disposal of the dust at Holfontein has been calculated and amounts to R 3 455 126,50 per annum. The cost with zinc recovery amounts to R 2 988 072,50 per annum and therefore a saving of R 467 054,00 per annum (based on a 7 day week and 3 600 kg dust produced per day).

Another option could be if magnesium hydroxide of pharmaceutical grade (R20-30/kg) could be precipitated. The leaching experiments indicated that in the event of magnesium hydroxide production, it is possible to selectively leach for magnesium. This was achieved most effectively at a sulphuric acid concentration of 186 g/l and an acid to dust ratio of 0,26.

Finally, the possibility of extracting other elements, both upstream and downstream of the leaching step in the prescribed process, should be investigated. These may include, for example, gallium (for use in the superconductor industry) and potassium (for use in the fertilizer industry).

However, in the case of gallium, other leaching mediums (such as hydrochloric acid; Ulman, 1997) should be investigated as the present results based on sulphuric acid were not successful.

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## Appendix A

### Raw data for the first set of experiments

*(Volumes of water in first and second step (typically): 30 and 200 or 100 ml)*

**Table A.1** Conditions for the first set of experiments.

Number	Temperature (°C)	Duration (hr)	Volume acid added (ml)	Volume water added (ml)
1A	97	6	20	230
1B	97	6	20	230
2A	97	12	20	230
2B	97	12	20	230
3A	97	24	20	230
3B	97	24	20	230
4A	97	48	20	230
4B	97	48	20	230
5A	97	72	20	230
5B	97	72	20	230
6A	25	24	20	130
6B	25	24	20	130
7A	50	24	20	130
7B	50	24	20	130
8A	75	24	20	130
8B	75	24	20	130
9A	97	24	10	130
9B	97	24	10	130
10A	97	24	12,5	130
10B	97	24	12,5	130
11A	97	24	17,5	130
12B	97	24	17,5	130
12A	97	24	20	230
12B	97	24	20	230
13A	97	24	20	105
13B	97	24	20	105
14A	97	24	20	130
14B	97	24	20	130
15A	97	24	20	105
15B	97	24	20	105
16A	97	24	20	130
16B	97	24	20	130

**Table A.2** Concentrations of metals in filtrate after leaching (mg/l)\*.

Number	PH	Volume (ml)	Zinc	Alluminium	Iron	Magnesium	Gallium
1A	0,86	260	7 675	1 677	1 259	11 934	52
1B	0,84	284	6 841	1 554	1 119	11 006	49
2A	0,8	270	7 268	1 667	1 399	12 861	54
2B	0,8	288	6 780	1 605	1 329	12 277	53
3A	0,73	254	7 105	1 801	1 554	13 616	56
3B	0,71	253	7 187	1 749	1 596	13 822	57
4A	0,68	200	10 050	2 490	2 185	17 188	61
4B	0,77	282	7 980	1 821	1 442	12 895	53
5A	0,72	270	6 947	1 821	1 086	11 968	56
5B	0,71	288	6 367	1 729	1 103	12 826	52
6A	0,57	192	7 907	1 893	1 155	15 230	57
6B	0,56	192	7 667	1 842	991	13 547	57
7A	0,53	176	7 827	2 222	1 388	15 505	59
7B	0,54	194	8 288	2 233	1 345	15 093	61
8A	0,51	174	8 468	2 644	1 414	15 848	62
8B	0,57	218	7 847	2 243	1 388	15 642	57
9A	3,19	150	12 015	277	569	21 995	4
9B	3,45	176	11 000	84	362	17 222	4
10A	0,95	170	9 571	2 206	1 778	16 398	56
10B	0,96	218	8 203	1 732	1 456	13 204	53
11A	0,74	186	9 446	2 181	2 083	15 121	60
12B	0,75	198	8 783	1 975	1 848	14 715	57
12A	0,62	182	8 928	2 047	1 526	15 093	59
12B	0,61	189	9 218	2 161	1 638	12 723	60
13A	0,54	228	7 522	1 885	1 610	12 311	47
13B	0,58	255	6 926	1 691	1 428	11 521	45
14A	0,64	250	6 885	1 615	1 385	11 693	50
14B	0,61	259	8 160	1 842	1 764	13 925	55
15A	0,38	122	10 876	3 277	2 858	19 591	56
15B	0,4	140	10 485	2 835	2 241	16 157	57
16A	0,47	190	8 551	2 166	2 031	15 024	53
16B	0,44	178	8 736	2 316	2 213	16 054	54

\* Analysis for pH was done but not for mass of filter cake

**Table A.3** Percentage extraction efficiency of metals during leaching.

Number	Zinc	Alluminium	Iron	Magnesium	Gallium
1A	80	31	47	78	33
1B	78	31	46	78	34
2A	78	32	54	87	36
2B	78	33	55	88	37
3A	72	32	57	86	35
3B	73	31	58	87	35
4A	80	35	63	86	30
4B	90	36	58	91	37
5A	75	35	42	81	37
5B	73	35	46	92	37
6A	61	26	32	73	27
6B	59	25	27	65	26
7A	55	28	35	68	25
7B	64	30	37	73	29
8A	59	41	35	69	33
8B	68	27	43	85	24
9A	72	3	12	82	2
9B	77	1	9	76	2
10A	65	26	43	70	23
10B	72	27	45	72	28
11A	70	29	56	70	27
12B	70	28	52	73	28
12A	65	26	40	69	26
12B	70	29	44	60	28
13A	69	30	53	70	26
13B	71	30	52	73	28
14A	69	28	50	73	30
14B	85	34	65	90	34
15A	53	28	50	60	17
15B	59	28	45	57	19
16A	65	29	55	71	24
16B	62	29	56	71	24



**Table A.4** Analyses of zinc in the filtrates produced.

Number	Volume (ml)	Absorbance	Concentration (mg/l) x 0,5	Concentration (mg/l)	Mass (g)	Percentage extraction
1A	260	0,383	3 837	7 675	2,0	80
1B	284	0,342	3 420	6 841	1,9	78
2A	270	0,363	3 634	7 268	2,0	78
2B	288	0,339	3 390	6 780	2,0	78
3A	254	0,355	3 553	7 105	1,8	72
3B	253	0,359	3 593	7 187	1,8	73
4A	200	0,446	5 025	10 050	2,0	80
4B	282	0,350	3 990	7 980	2,3	90
5A	270	0,353	3 474	6 947	1,9	75
5B	288	0,324	3 183	6 367	1,8	73
6A	192	0,401	3 954	7 907	1,5	61
6B	192	0,389	3 834	7 667	1,5	59
7A	176	0,397	3 914	7 827	1,4	55
7B	194	0,420	4 144	8 288	1,6	64
8A	174	0,429	4 234	8 468	1,5	59
8B	218	0,398	3 924	7 847	1,7	68
9A	150	0,587	6 008	12 015	1,8	72
9B	176	0,538	5 500	11 000	1,9	77
10A	170	0,469	4 785	9 571	1,6	65
10B	218	0,403	4 102	8 203	1,8	72
11A	186	0,463	4 723	9 446	1,8	70
12B	198	0,431	4 392	8 783	1,7	70
12A	182	0,438	4 464	8 928	1,6	65
12B	189	0,452	4 609	9 218	1,7	70
13A	228	0,373	3 761	7 522	1,7	69
13B	255	0,344	3 463	6 926	1,8	71
14A	250	0,342	3 442	6 885	1,7	69
14B	259	0,404	4 080	8 160	2,1	85
15A	122	0,536	5 438	10 876	1,3	53
15B	140	0,517	5 242	10 485	1,5	59
16A	190	0,423	4 275	8 551	1,6	65
16B	178	0,432	4 368	8 736	1,6	62

**Table A.5** Analyses of aluminium in the filtrates produced.

Number	Volume (ml)	Absorbance	Concentration (mg/l) x 0,01	Concentration (mg/l)	Mass (g)	Percentage extraction
1A	260	0,161	16,8	1 677	0,44	31
1B	284	0,149	15,5	1 554	0,44	31
2A	270	0,160	16,7	1 667	0,45	32
2B	288	0,154	16,1	1 605	0,46	33
3A	254	0,173	18,0	1 801	0,46	32
3B	253	0,168	17,5	1 749	0,44	31
4A	200	0,240	24,9	2 490	0,50	35
4B	282	0,175	18,2	1 821	0,51	36
5A	270	0,175	18,2	1 821	0,49	35
5B	288	0,166	17,3	1 729	0,50	35
6A	192	0,182	18,9	1 893	0,36	26
6B	192	0,177	18,4	1 842	0,35	25
7A	176	0,214	22,2	2 222	0,39	28
7B	194	0,215	22,3	2 233	0,43	30
8A	218	0,255	26,4	2 644	0,58	41
8B	174	0,216	22,4	2 243	0,39	27
9A	150	0,023	2,8	277	0,04	3
9B	176	0,005	0,8	84	0,01	1
10A	170	0,202	22,1	2 206	0,37	26
10B	218	0,158	17,3	1 732	0,38	27
11A	186	0,210	21,8	2 181	0,41	29
12B	198	0,190	19,8	1 975	0,39	28
12A	182	0,197	20,5	2 047	0,37	26
12B	189	0,208	21,6	2 161	0,41	29
13A	228	0,171	18,8	1 885	0,43	30
13B	255	0,153	16,9	1 691	0,43	30
14A	250	0,146	16,2	1 615	0,40	28
14B	259	0,167	18,4	1 842	0,48	34
15A	122	0,300	32,8	3 277	0,40	28
15B	140	0,259	28,3	2 835	0,40	28
16A	190	0,197	21,7	2 166	0,41	29
16B	178	0,211	23,2	2 317	0,41	29

**Table A.6** Analyses of gallium for the filtrates produced.

Number.	Volume (ml)	Absorbance	Concentration (mg/l)	Mass (g)	Percentage Extraction
1A	260	0,170	52	0,014	33
1B	284	0,158	49	0,014	34
2A	270	0,176	54	0,015	36
2B	288	0,172	53	0,015	37
3A	254	0,182	56	0,014	35
3B	253	0,184	57	0,014	35
4A	200	0,198	61	0,012	30
4B	282	0,173	53	0,015	37
5A	270	0,180	56	0,015	37
5B	288	0,169	52	0,015	37
6A	192	0,217	57	0,011	27
6B	192	0,214	57	0,011	26
7A	176	0,223	59	0,010	25
7B	194	0,231	61	0,012	29
8A	218	0,220	62	0,013	33
8B	174	0,203	57	0,010	24
9A	150	0,021	4	0,001	2
9B	176	0,019	4	0,001	2
10A	170	0,200	56	0,010	23
10B	218	0,189	53	0,012	28
11A	186	0,213	60	0,011	27
12B	198	0,203	57	0,011	28
12A	182	0,215	59	0,011	26
12B	189	0,218	60	0,011	28
13A	228	0,173	47	0,011	26
13B	255	0,166	45	0,012	28
14A	250	0,181	50	0,012	30
14B	259	0,198	55	0,014	34
15A	122	0,204	56	0,007	17
15B	140	0,206	57	0,008	19
16A	190	0,192	53	0,010	24
16B	178	0,197	54	0,010	24

**Table A.7** Analyses of iron for the filtrates produced.

Number	Volume. (ml)	Absorbance	Concentration (mg/l) x 0,001	Concentration (mg/l)	Mass (g)	Percentage extraction
1A	260	0,113	1,3	1 259	0,33	47
1B	284	0,103	1,1	1 119	0,32	46
2A	270	0,123	1,4	1 399	0,38	54
2B	288	0,118	1,3	1 329	0,38	55
3A	254	0,134	1,6	1 554	0,39	57
3B	253	0,137	1,6	1 596	0,40	58
4A	200	0,179	2,2	2 185	0,44	63
4B	282	0,126	1,4	1 442	0,41	58
5A	270	0,129	1,1	1 086	0,29	42
5B	288	0,131	1,1	1 103	0,32	46
6A	192	0,137	1,2	1 155	0,22	32
6B	192	0,118	1,0	991	0,19	27
7A	176	0,164	1,4	1 388	0,24	35
7B	194	0,159	1,3	1 345	0,26	37
8A	174	0,167	1,4	1 414	0,25	35
8B	218	0,164	1,4	1 388	0,30	43
9A	150	0,069	0,6	569	0,09	12
9B	176	0,045	0,4	362	0,06	9
10A	170	0,150	1,8	1 778	0,30	43
10B	218	0,127	1,5	1 456	0,32	45
11A	186	0,246	3,1	2 083	0,39	56
12B	198	0,155	1,8	1 848	0,37	52
12A	182	0,180	1,5	1 526	0,28	40
12B	189	0,140	1,6	1 638	0,31	44
13A	228	0,138	1,6	1 610	0,37	53
13B	255	0,125	1,4	1 428	0,36	52
14A	250	0,122	1,4	1 385	0,35	50
14B	259	0,149	1,8	1 764	0,46	65
15A	122	0,227	2,9	2 858	0,35	50
15B	140	0,183	2,2	2 241	0,31	45
16A	190	0,168	2,0	2 031	0,39	55
16B	178	0,181	2,2	2 213	0,39	56

**Table A.8** Analyses of magnesium for the filtrates produced.

Number	Volume (ml)	Absorbance	Concentration (mg/l) x 0,001	Concentration (mg/l)	Mass (g)	Percentage extraction
1A	260	0,360	12	11 934	3,10	78
1B	284	0,333	11	11 006	3,13	78
2A	270	0,387	13	12 861	3,47	87
2B	288	0,370	12	12 277	3,54	88
3A	254	0,409	14	13 616	3,46	86
3B	253	0,415	14	13 822	3,50	87
4A	200	0,513	17	17 188	3,44	86
4B	282	0,388	13	12 895	3,64	91
5A	270	0,361	12	11 968	3,23	81
5B	288	0,386	13	12 826	3,69	92
6A	192	0,456	15	15 230	2,92	73
6B	192	0,407	14	13 547	2,60	65
7A	176	0,464	16	15 505	2,73	68
7B	194	0,452	15	15 093	2,93	73
8A	174	0,474	16	15 848	2,76	69
8B	218	0,468	16	15 642	3,41	85
9A	150	0,653	22	21 995	3,30	82
9B	176	0,514	17	17 222	3,03	76
10A	170	0,490	16	16 398	2,79	70
10B	218	0,397	13	13 204	2,88	72
11A	186	0,673	23	15 121	2,81	70
12B	198	0,441	15	14 715	2,91	73
12A	182	0,452	15	15 093	2,75	69
12B	189	0,383	13	12 723	2,40	60
13A	228	0,371	12	12 311	2,81	70
13B	255	0,348	12	11 521	2,94	73
14A	250	0,353	12	11 693	2,92	73
14B	259	0,418	14	13 925	3,61	90
15A	122	0,583	20	19 591	2,39	60
15B	140	0,483	16	16 157	2,26	57
16A	190	0,450	15	15 024	2,85	71
16B	178	0,480	16	16 054	2,86	71

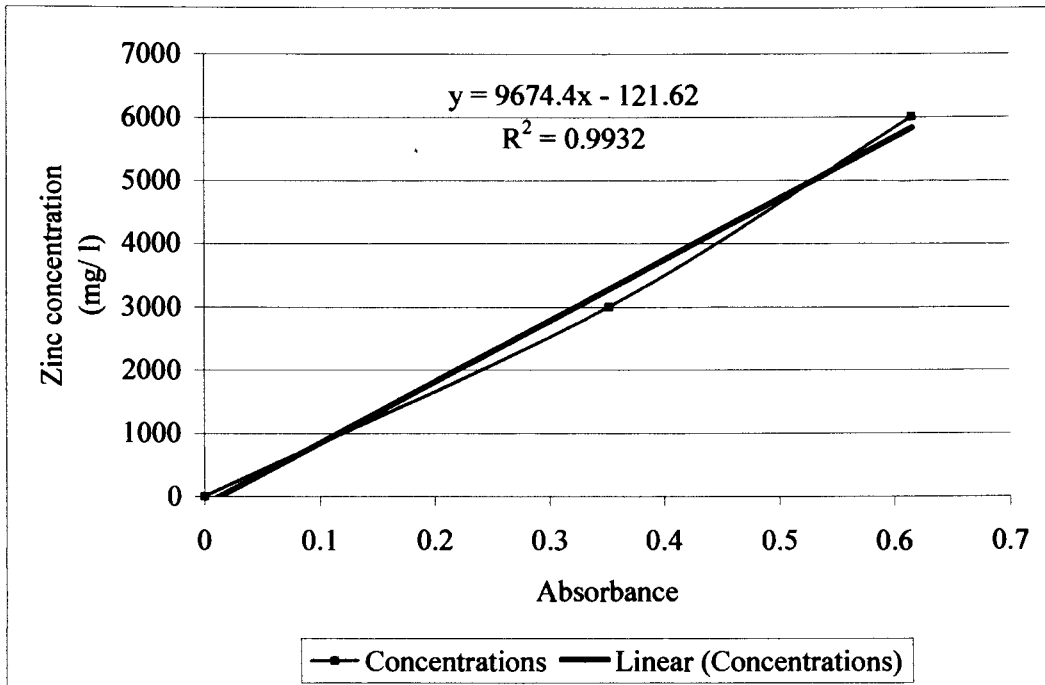


Figure A.1 Calibration curve for zinc concentration against absorbance.

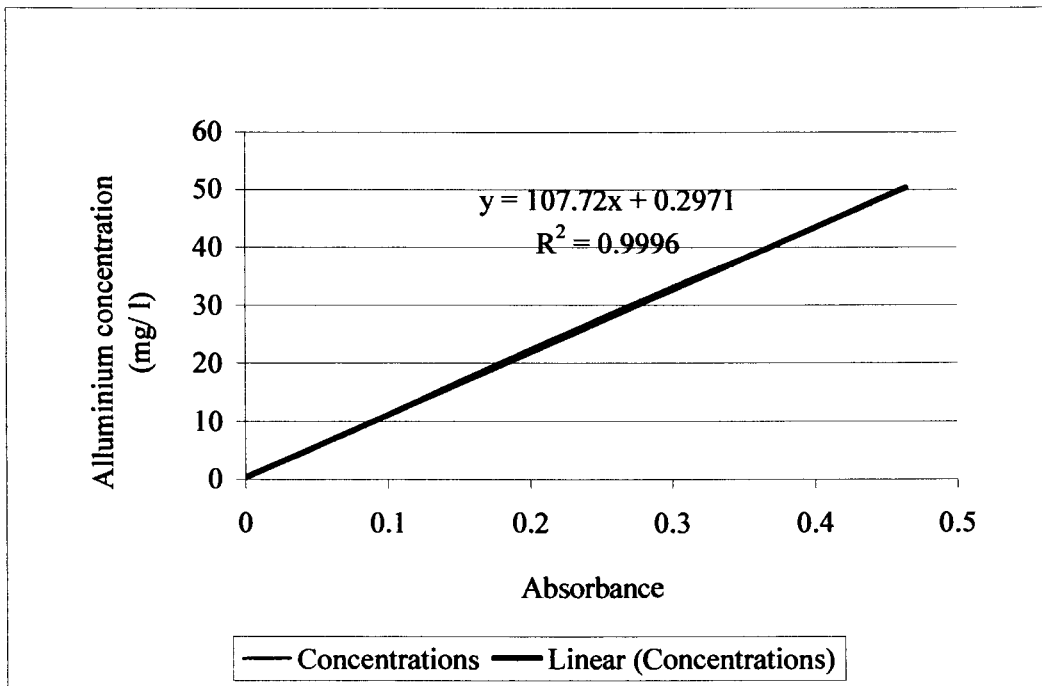


Figure A.2 Calibration curve for aluminium concentration against absorbance.

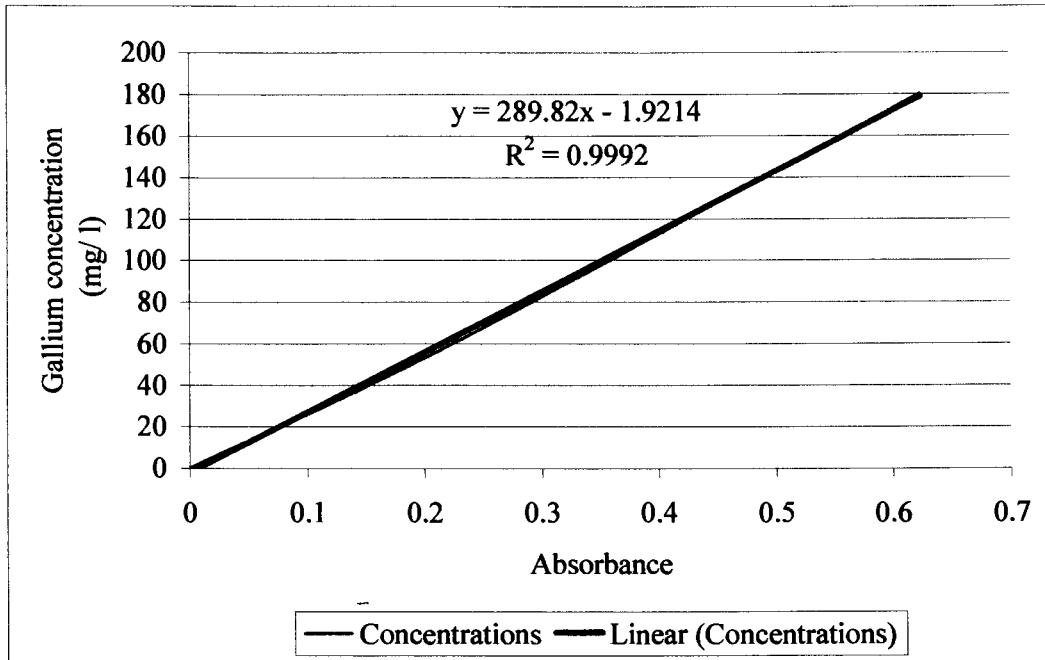


Figure A.3 Calibration curve for gallium concentration against absorbance.

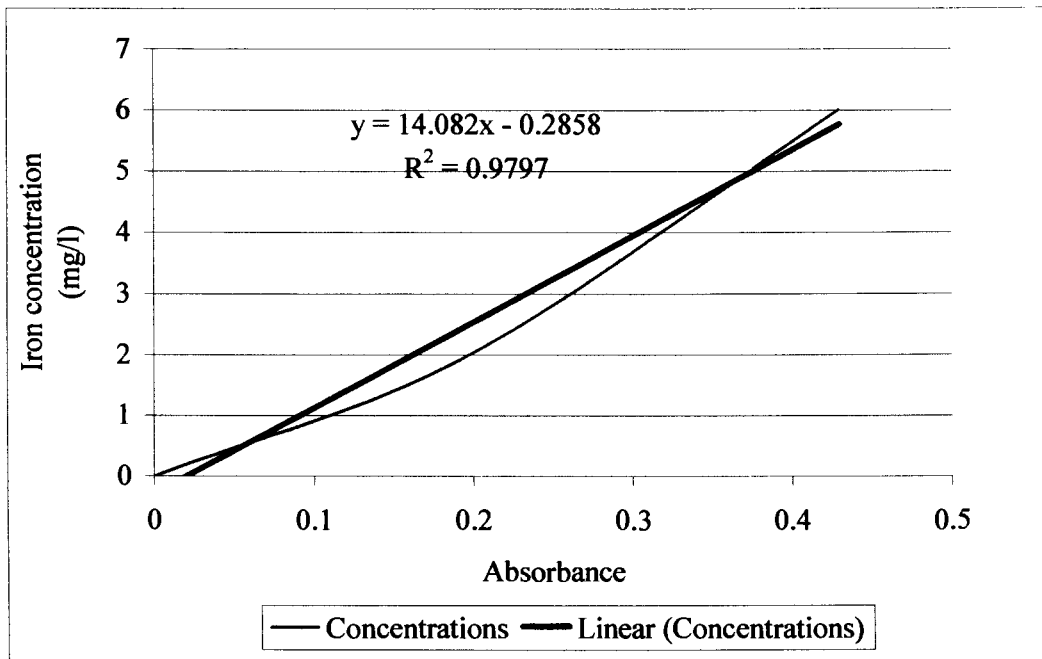
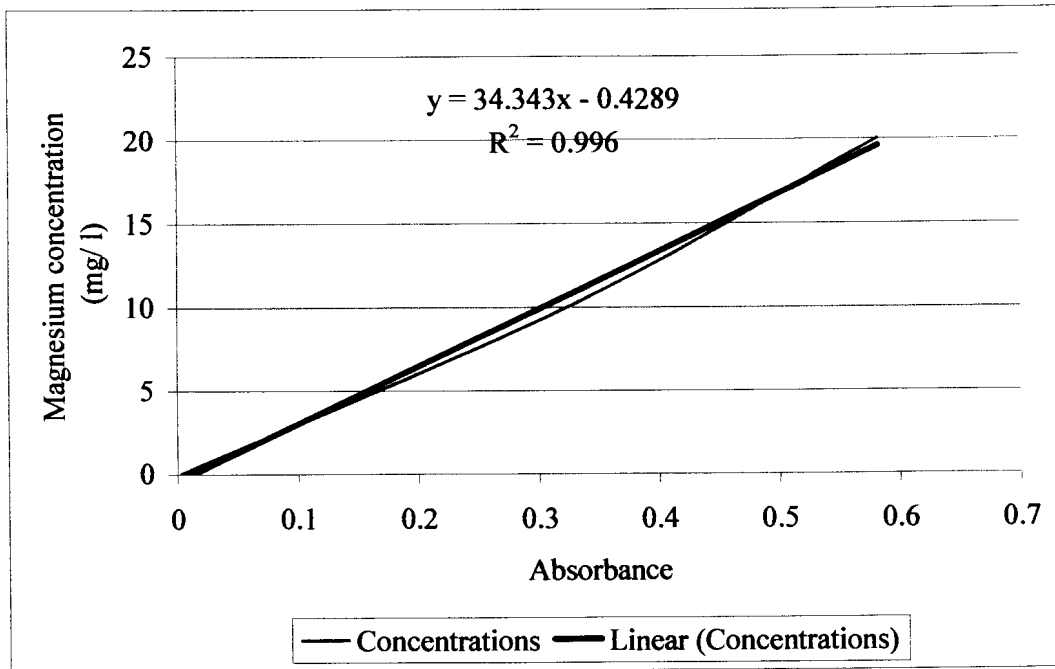


Figure A.4 Calibration curve for iron concentration against absorbance.



**Figure A.5** Calibration curve for magnesium concentration against absorbance.



## Appendix B

### Raw data for the second set of experiments

*(Volumes of water in first and second step (typically): 40 and 200 ml)*

**Table B.1** Conditions for the second set of leaching experiments.

Number	Temperature (°C)	Duration (hrs)	Volume acid added (ml)	Volume water added (ml)
17A	97	24	18,4	100
17B	97	24	18,4	100
18A	97	24	18,4	150
18B	97	24	18,4	150
19A	97	24	18,4	250
19B	97	24	18,4	250
20A	97	24	18,4	200
20B	97	24	18,4	200
21A	97	0	4,6	200
21B	97	0	4,6	200
22A	97	6	18,4	200
22B	97	6	18,4	200
23A	97	12	18,4	200
23B	97	12	18,4	200
24A	97	0	18,4	200
24B	97	0	18,4	200
25A	97	3	18,4	200
25B	97	3	18,4	200
26A	97	9	18,4	200
26B	97	9	18,4	200
27A	50	24	18,4	200
27B	50	24	18,4	200
28A	75	24	18,4	200
28B	75	24	18,4	200
29A	28	24	18,4	200
29B	28	24	18,4	200
30A	97	24	18,4	200
30B	97	24	18,4	200
31A	97	48	18,4	200
31B	97	48	18,4	200
32A	97	24	4,6	200
32B	97	24	4,6	200
33A	97	24	9,2	200
33B	97	24	9,2	200

**Table B.2** Concentrations of metals in filtrate after leaching (mg/l)\*.

Number	Mass of filter cake (g)	Volume of filtrate (ml)	Zinc	Alluminium	Iron	Magnesium	Gallium
17A	**	100	10 878	233	1 803	42 673	25
17B	**	110	11 068	244	1 716	37 445	30
18A	**	172	9 793	340	1 257	34 450	41
18B	**	156	10 022	316	1 364	38 153	36
19A	**	240	8 214	359	979	31 292	43
19B	**	264	7 681	363	884	31 346	41
20A	19	216	8 473	348	1 108	21 528	46
20B	19	228	7 966	352	1 062	30 910	44
21A	24	214	5 838	14	0	22 851	4
21B	24	313	5 047	32	0	18 985	3
22A	18	213	8 209	333	1 021	30 420	48
22B	18	233	7 682	333	1 016	28 024	45
23A	18	225	8 108	335	1 116	30 312	47
23B	18	212	8 372	333	1 712	31 455	47
24A	21	223	7 338	346	859	20 852	48
24B	21	228	7 480	368	905	28 623	47
25A	18	215	8 169	325	1 021	30 094	41
25B	18	230	7 986	365	992	29 222	41
26A	18	210	8 473	368	1 103	31 564	1
26B	18	214	8 169	374	1 137	32 544	1
27A	19	218	7 885	383	971	28 242	34
27B	19	224	7 601	369	1 145	25 356	38
28A	19	205	7 703	419	1 145	31 237	45
28B	19	217	7 824	390	1 062	31 401	48
29A	20	229	7 257	330	855	28 079	42
29B	19	221	7 682	330	1 215	29 331	47
30A	17	222	8 027	351	1 091	31 673	43
30B	17	207	8 574	334	1 145	33 851	47
31A	17	198	8 230	346	1 199	32 054	43
31B	18	183	10 216	346	1 344	34 940	42
32A	26	196	953	55	0	23 724	0
32B	26	206	669	56	0	23 995	0
33A	21	184	9 628	147	0	25 272	6
33B	21	176	10196	145	0	42 836	5
18A	**	**	953	55	0	23 724	0
18B	26	206	669	56	0	23 995	0
19A	21	184	9 628	147	0	25 272	6
19B	21	176	10 196	145	0	42 836	5

\* No analysis for pH was done.

\*\* Data were lost.

**Table B.3** Percentage extraction of metals during leaching.

Number	Zinc	Alluminium	Iron	Magnesium	Gallium
17A	44	2	23	92	6
17B	49	3	24	89	8
18A	67	6	28	127	17
18B	63	5	27	128	14
19A	79	9	30	162	25
19B	81	10	30	178	26
20A	73	8	31	100	24
20B	73	8	31	152	24
21A	50	0	0	105	2
21B	63	1	0	128	2
22A	70	7	28	139	25
22B	72	8	30	140	26
23A	73	8	32	147	26
23B	71	7	47	143	24
24A	65	8	25	100	26
24B	68	8	26	140	26
25A	70	7	28	139	22
25B	73	8	29	145	23
26A	71	8	30	143	1
26B	70	8	31	150	0
27A	69	8	27	132	18
27B	68	8	33	122	21
28A	63	9	30	138	23
28B	68	8	30	147	25
29A	66	8	25	138	24
29B	68	7	34	139	26
30A	71	8	31	151	23
30B	71	7	30	151	24
31A	65	7	30	136	21
31B	75	6	32	138	19
32A	7	1	0	100	0
32B	6	1	0	106	0
33A	71	3	0	100	2
33B	72	3	0	162	2

**Table B.4** Analyses of zinc in the filtrates produced.

Number	Absorbance	Concentration (mg/l) x 0,5	Concentration (mg/l)	Mass in filtrate (g)	Percentage extraction
17A	0,580	5 439	10 878	1,1	44
17B	0,590	5 534	11 068	1,2	49
18A	0,523	4 897	9 793	1,7	67
18B	0,535	5 011	10 022	1,6	63
19A	0,440	4 107	8 214	2,0	79
19B	0,412	3 840	7 681	2,0	81
20A	0,418	4 236	8 473	1,8	73
20B	0,393	3 983	7 966	1,8	73
21A	0,288	2 919	5 838	1,2	50
21B	0,249	2 524	5 047	1,6	63
22A	0,405	4 105	8 209	1,7	70
22B	0,379	3 841	7 682	1,8	72
23A	0,400	4 054	8 108	1,8	73
23B	0,413	4 186	8 372	1,8	71
24A	0,362	3 669	7 338	1,6	65
24B	0,369	3 740	7 480	1,7	68
25A	0,403	4 084	8 169	1,8	70
25B	0,394	3 993	7 986	1,8	73
26A	0,418	4 236	8 473	1,8	71
26B	0,403	4 084	8 169	1,7	70
27A	0,389	3 943	7 885	1,7	69
27B	0,375	3 801	7 601	1,7	68
28A	0,380	3 851	7 703	1,6	63
28B	0,386	3 912	7 824	1,7	68
29A	0,358	3 628	7 257	1,7	66
29B	0,379	3 841	7 682	1,7	68
30A	0,396	4 013	8 027	1,8	71
30B	0,423	4 287	8 574	1,8	71
31A	0,406	4 115	8 230	1,6	65
31B	0,504	5 108	10 216	1,9	75
32A	0,047	476	953	0,2	7
32B	0,033	334	669	0,2	6
33A	0,475	4 814	9 628	1,8	71
33B	0,503	5 098	10 196	1,8	72

**Table B.5** Analyses of aluminium in the filtrates produced.

Number	Absorbance	Concentration (mg/l)	Percentage extraction
17A	0,188	233	2
17B	0,196	244	3
18A	0,261	340	6
18B	0,244	316	5
19A	0,284	359	9
19B	0,287	363	10
20A	0,267	348	8
20B	0,270	352	8
21A	0,020	14	0
21B	0,034	32	1
22A	0,256	333	7
22B	0,256	333	8
23A	0,258	335	8
23B	0,256	333	7
24A	0,266	346	8
24B	0,282	368	8
25A	0,250	325	7
25B	0,280	365	8
26A	0,291	368	8
26B	0,296	374	8
27A	0,303	383	8
27B	0,292	369	8
28A	0,330	419	9
28B	0,308	390	8
29A	0,254	330	8
29B	0,254	330	7
30A	0,278	351	8
30B	0,265	334	7
31A	0,274	346	7
31B	0,274	346	6
32A	0,052	55	1
32B	0,053	56	1
33A	0,120	147	3
33B	0,118	145	3

**Table B.6** Analyses of gallium for the filtrates produced.

Number	Absorbance	Concentration (mg/l)	Mass in filtrate (g)	Percentage extraction
17A	0,040	25	0,003	6
17B	0,047	30	0,003	8
18A	0,058	41	0,007	17
18B	0,052	36	0,006	14
19A	0,138	43	0,010	25
19B	0,131	41	0,011	26
20A	0,145	46	0,010	24
20B	0,140	44	0,010	24
21A	0,017	4	0,001	2
21B	0,014	3	0,001	2
22A	0,154	48	0,010	25
22B	0,143	45	0,010	26
23A	0,143	47	0,010	26
23B	0,144	47	0,010	24
24A	0,146	48	0,011	26
24B	0,143	47	0,011	26
25A	0,065	41	0,009	22
25B	0,064	41	0,009	23
26A	0,003	1	0,000	1
26B	0,002	1	0,000	0
27A	0,050	34	0,007	18
27B	0,056	38	0,009	21
28A	0,138	45	0,009	23
28B	0,146	48	0,010	25
29A	0,062	42	0,010	24
29B	0,145	47	0,010	26
30A	0,063	43	0,010	23
30B	0,145	47	0,010	24
31A	0,067	43	0,008	21
31B	0,066	42	0,008	19
32A	0,003	0	0,000	0
32B	0,003	0	0,000	0
33A	0,020	6	0,001	2
33B	0,019	5	0,001	2

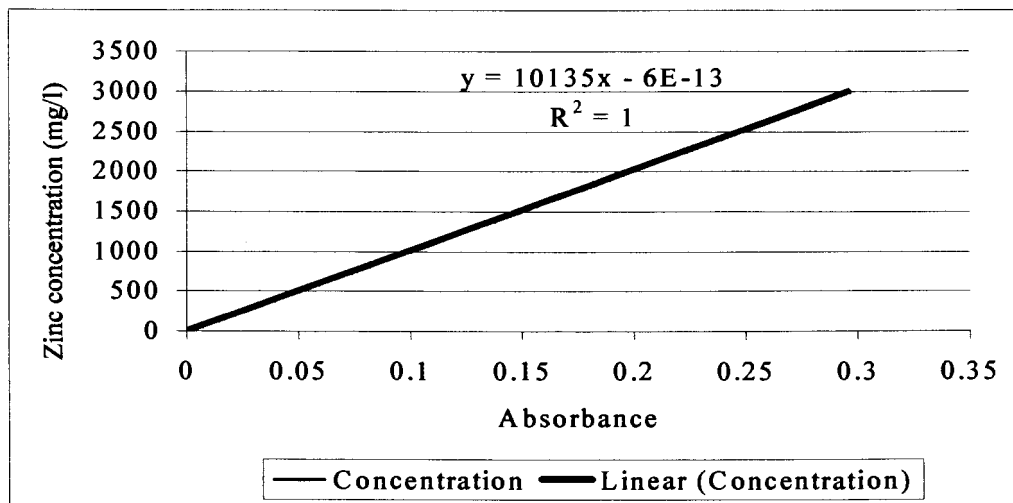
**Table B.7** Analyses of iron for the filtrates produced.

Number	Absorbance	Concentration (mg/l) x 0.05	Concentration (mg/l)	Mass in filtrate (g)	Percentage Extraction
17A	0,458	90	1 803	0,2	23
17B	0,437	86	1 716	0,2	24
18A	0,326	63	1 257	0,2	28
18B	0,352	68	1 364	0,2	27
19A	0,259	49	979	0,2	30
19B	0,236	44	884	0,2	30
20A	0,29	55	1 108	0,2	31
20B	0,279	53	1 062	0,2	31
21A	0,022	0	0	0,0	0
21B	0,013	0	0	0,0	0
22A	0,269	51	1 021	0,2	28
22B	0,268	51	1 016	0,2	30
23A	0,292	56	1 116	0,3	32
23B	0,436	86	1 712	0,4	47
24A	0,23	43	859	0,2	25
24B	0,241	45	905	0,2	26
25A	0,269	51	1 021	0,2	28
25B	0,262	50	992	0,2	29
26A	0,289	55	1 103	0,2	30
26B	0,297	57	1 137	0,2	31
27A	0,257	49	971	0,2	27
27B	0,299	57	1 145	0,3	33
28A	0,299	57	1 145	0,2	30
28B	0,279	53	1 062	0,2	30
29A	0,229	43	855	0,2	25
29B	0,316	61	1 215	0,3	34
30A	0,286	55	1 091	0,2	31
30B	0,299	57	1 145	0,2	30
31A	0,312	60	1 199	0,2	30
31B	0,347	67	1 344	0,2	32
32A	0,012	0	0	0,0	0
32B	0,011	0	0	0,0	0
33A	0,022	0	0	0,0	0
33B	0,017	0	0	0,0	0

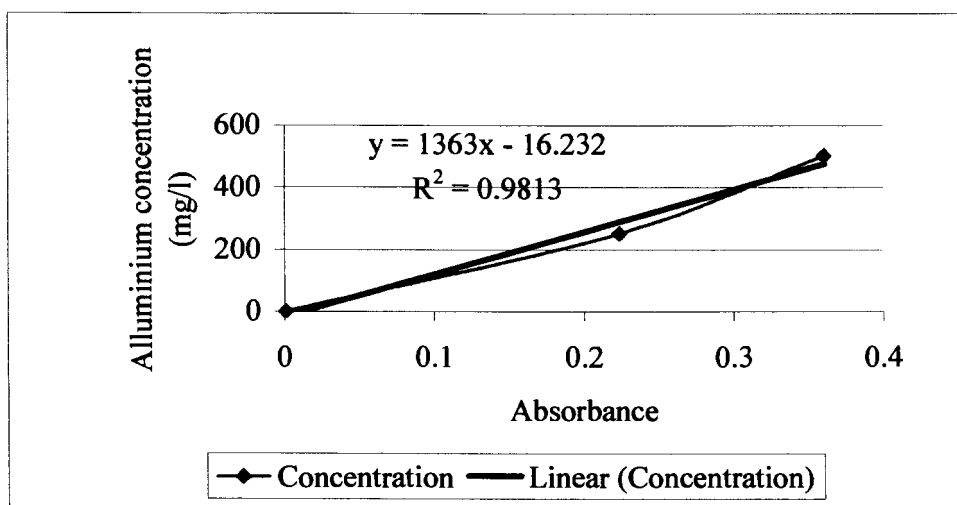
**Table B.8** Analyses of magnesium for the filtrates produced.

Number	Absorbance	Concentration (mg/l) x 0,001	Concentration in filtrate (mg/l)	Mass in filtrate (g)	Percentage extraction
17A	0,803	21,3	42 673	4,3	92
17B	0,707	18,7	37 445	4,1	89
18A	0,652	17,2	34 450	5,9	127
18B	0,72	19,1	38 153	6,0	128
19A	0,594	15,6	31 292	7,5	162
19B	0,595	15,7	31 346	8,3	178
20A	0,609	16,1	21 528	4,7	100
20B	0,587	15,5	30 910	7,0	152
21A	0,439	11,4	22 851	4,9	105
21B	0,368	9,5	18 985	5,9	128
22A	0,578	15,2	30 420	6,5	139
22B	0,534	14,0	28 024	6,5	140
23A	0,576	15,2	30 312	6,8	147
23B	0,597	15,7	31 455	6,7	143
24A	0,547	14,4	20 852	4,7	100
24B	0,545	14,3	28 623	6,5	140
25A	0,572	15,0	30 094	6,5	139
25B	0,556	14,6	29 222	6,7	145
26A	0,599	15,8	31 564	6,6	143
26B	0,617	16,3	32 544	7,0	150
27A	0,538	14,1	28 242	6,2	132
27B	0,485	12,7	25 356	5,7	122
28A	0,593	15,6	31 237	6,4	138
28B	0,596	15,7	31 401	6,8	147
29A	0,535	14,0	28 079	6,4	138
29B	0,558	14,7	29 331	6,5	139
30A	0,601	15,8	31 673	7,0	151
30B	0,641	16,9	33 851	7,0	151
31A	0,608	16,0	32 054	6,3	136
31B	0,661	17,5	34 940	6,4	138
32A	0,533	14,0	23 724	4,7	100
32B	0,46	12,0	23 995	4,9	106
33A	0,747	19,8	25 272	4,7	100
33B	0,806	21,4	42 836	7,5	162





**Figure B.1** Calibration curve for zinc concentration against absorbance.



**Figure B.2** Calibration curve for aluminium concentration against absorbance.

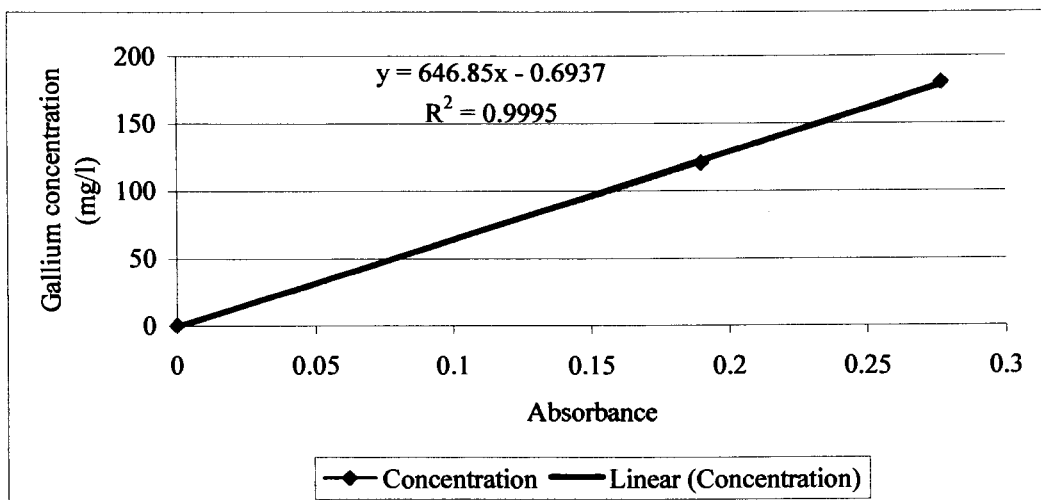


Figure B.3 Calibration curve for gallium concentration against absorbance.

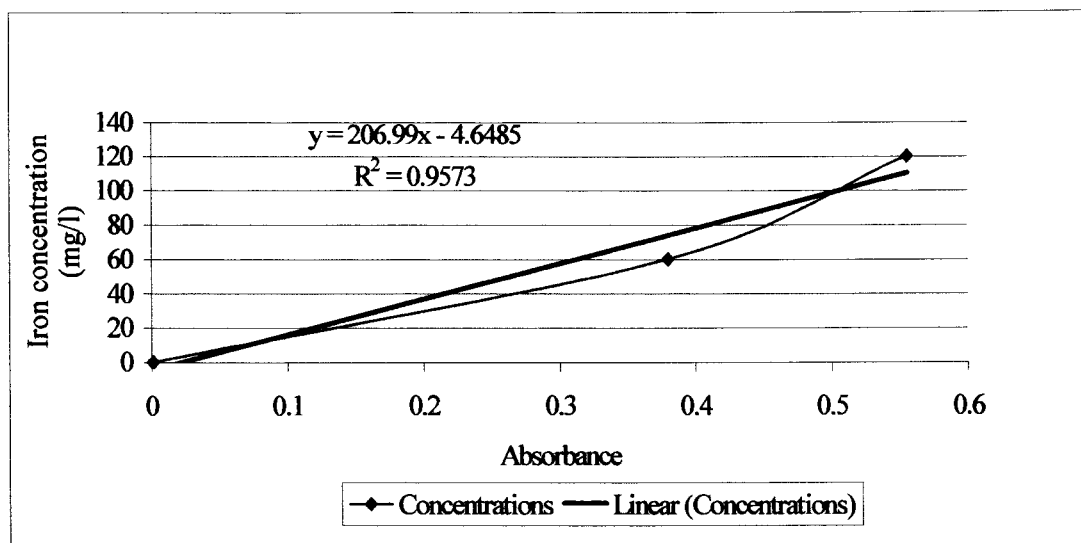
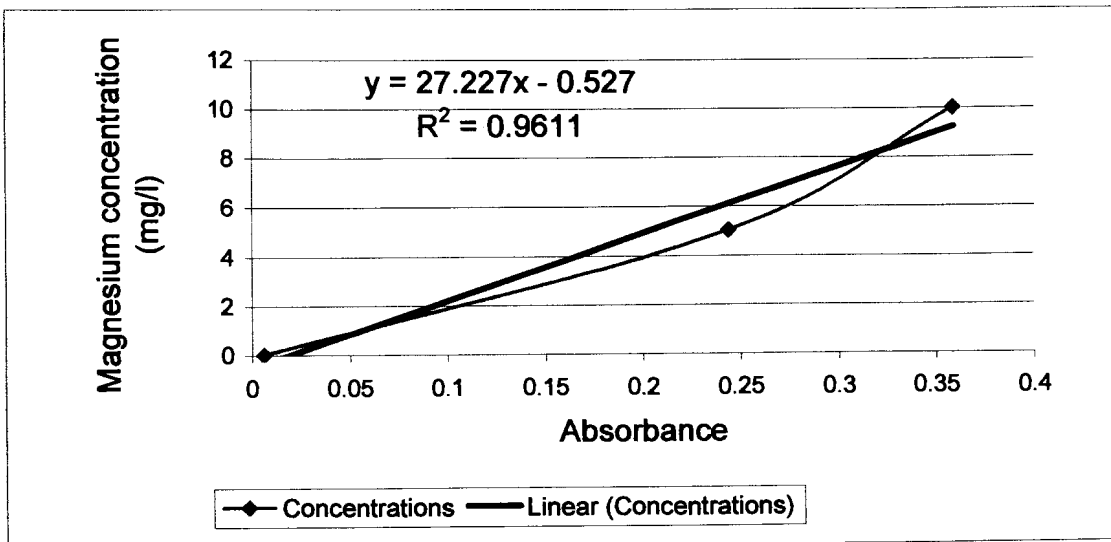


Figure B.4 Calibration curve for iron concentration against absorbance.



**Figure B.5** Calibration curve for magnesium concentration against absorbance.