THE ASSESSMENT AND CLASSIFICATION OF INORGANIC MANGANESE CONTAINING WASTES

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W Pulles

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Water Research Commission

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Report to the
Water Research Commission

by

S Banister, B Zhao, SE Coetser and W Pulles

on behalf of

Pulles Howard & de Lange Incorporated

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The Steering Committee responsible for this project, consisted of the following persons:

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The researchers that were involved in this project are listed below.

Mr W Pulles (Project Leader)	:	Pulles Howard & De Lange Inc.
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Furthermore, in order for this initiative to be successful it also required collaboration from a number of pyro-metallurgical industries. Several people from the above stakeholder group assisted with our field studies and are thanked for their support and participation. They were: Deon Bessinger, Deon Zeelie, Leonie Reyneke (SEM) from Kumba Resources; Jannie Cronje, Jaco van Wyk from Samancor; Deon Allandale from Saldana Steel; Flip Heystek, Anton Gerber from Iscor – van der Bijl Park; Jan Eigenhuis from Manganese Metals Company and Cornel Scheepers from Alpha Cement.

EXECUTIVE SUMMARY

BACKGROUND

Off-gas dust collected from ilmenite smelting processes, as an air pollution control measure, is often classified as hazardous under Acid Rain Leaching Procedures (ARLP) due to its inorganic manganese content. It is believed that this stream may have a hazard rating that is inconsistent with its behaviour in the environment. This is often raised in respect to listing of manganese containing compounds as hazardous waste. Manganese is a naturally occurring, essential nutrient and its toxicity is related to its form and acceptable risk levels are arguably said to be set too low.

In this project, further characterisation research of this particular waste stream from a number of pyrometallurgical industries and pilot trails was conducted. Extensive leachability and characterisation studies, using a variety of techniques, were done. Furthermore, the need for and the use of a number of immobilisation treatment options were investigated since mobility and stability of the manganese links to bioavailability and therefore hazard risk posed to the environment. Certain process conditions were also compared in order to investigate means to minimise the risk posed by the waste, in the long term, when disposed of in a mono-landfill.

PROJECT AIMS

The main aims of the project are to establish whether the current methods employed for the hazard rating and classification of wastes containing manganese are appropriate, and whether, under specific conditions, other methods, which better represent the behaviour of such wastes, exist, or can be devised. Since it is not feasible to test the current methods and develop alternatives for the full range of manganese containing wastes which are produced in South Africa, a specific example based on pyro-metallurgically generated waste will be used to develop a generic approach to the management of inorganic manganese-containing wastes.

APPROACH FOLLOWED

A comprehensive literature search was undertaken to provide the theoretical background on manganese chemistry, its behaviour in the environment, toxicity as well as to investigate other alternative hazard characterisation methods. A number of pilot trails were conducted and samples collected of the off-gas dust under a variety of process conditions. Other industrial examples of this dust were also obtained. Together with the use of inorganic manganese standards in various solid forms, these samples were then characterised and compared. Each was subjected to a variety of leaching procedures (batch and column) and solutions to investigate the impacts on manganese mobility and what controls it. The effects were quantified and modelled.

FINDINGS

Detailed geochemical assessments of the off-gas dust, collected under oxidising conditions (post combustion and/or baghouse filters), showed that this provides conditions that produce more stable manganese compounds in the dust that is less available to the water phase or more stringent acid conditions. Under ARLP conditions it was found however that a greater proportion of manganese present in the “oxidised” dust is released as soluble manganese. This would however be decreased if post combustion was used.

Off-gas dust collected using wet scrubbers, under reducing conditions, contains manganese and other elements that are largely in a soluble form. The availability of the manganese to the water phase is however affected by a number of factors. This manganese can be rendered immobile by treating it with a number of chemicals like lime, calcite, desulphurisation slurry (CaO-CaS), ferric chloride and hypochlorite. Calcite, while having a slower reaction rate compared to lime, was shown to provide a more suitable long-term stabilisation measure for this dust, especially under stronger acidic conditions. Furthermore, higher liquid: solid ratios in the wet scrubber changed the hazard rating of the scrubber dust from one that could be delisted to one that had an EEC/ARL > 1.

Several other waste classification techniques were also assessed and they provided more insight into the reactive load, which is indicative of the bio-available or hazard risk component and the inert part of the waste stream. Furthermore, multiple extraction methods revealed trends with regard to behaviour of the dust sample over time and allowed for a fairly simple evaluation of the long- term effects of a number of treatment options.

PROPOSED CLASSIFICATION METHODOLOGY

A proposed process for assessing the hazard associated with inorganic manganese containing wastes is shown in the Figure below.

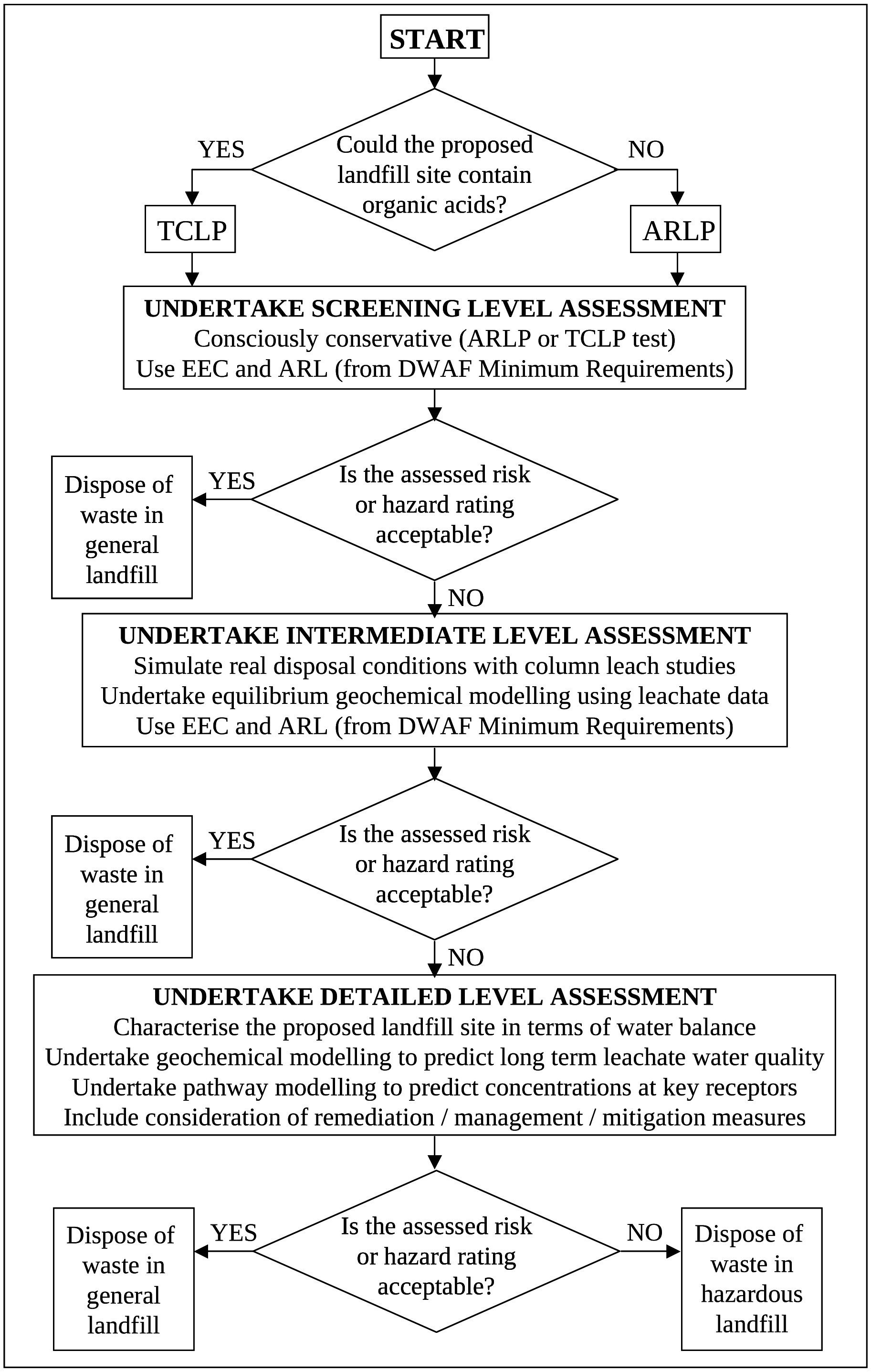
The proposed first step in the assessment process is to establish with absolute confidence whether or not the inorganic manganese containing waste will be disposed of in a landfill site that could contain organic acids. If there is a potential that organic acids may be present then the screening level test should be undertaken using both ARLP and TCLP tests. In interpreting the significance of the test results, use should be made of the EEC and ARL values set out in the DWAF Minimum Requirements.

If the results from the screening level assessment are within the conservative ARL and EEC values, then there is no need to undertake any further assessments and the regulatory process should be followed to obtain approval for disposal of the waste in a general landfill. If the results are negative then it will be necessary to move onto an intermediate level assessment.

In the intermediate level assessment, column leach studies are undertaken to replace the ARLP and/or TCLP tests, using landfill conditions that closely simulate the intended application. A geochemical assessment programme and equilibrium geochemical modelling should be undertaken using water quality data from the column study leachates. An assessment must be made to establish whether the proposed disposal conditions will lead to a stable waste and whether or not the column leach data can reasonably be used to assess long-term performance.

Use could still be made of the conservative EEC and ARL values set out in the DWAF Minimum Requirements.

If the results from the intermediate level assessment are within the conservative ARL and EEC values, then there is no need to undertake any further assessments and the regulatory process should be followed to obtain approval for disposal of the waste in a general landfill. If the results are negative then it will be necessary to move onto a detailed level assessment.



In the detailed level assessment, the following studies should be undertaken:

- Detailed characterisation of the proposed landfill site in terms of its water balance.

- Prediction of long-term leachate quality using kinetic geochemical models and evaluating the anticipated pH and redox conditions.
- Prediction of leachate flow, quality and load for the various remediation/management/ mitigation measures being considered.
- Detailed characterisation of the receiving environment (ground water and surface water) with modelling of the predicted water quality at key environmental / human receptors.
- Assessment of risk posed to environmental receptors based on local and international literature values for adverse risk.
- Conclusion as to whether waste should be disposed of in a general landfill or at a hazardous waste landfill site.

The process that has been followed must then be documented in a detailed report that presents all the collected data, assumptions, assessment process and results and that must then be submitted to the regulators for consideration and approval.

RESULTS AND DISCUSSION

The following conclusions can be drawn from this research project

Off-gas dust samples from smelter processes using ilmenite feed contain manganese in varying quantities. The level of inorganic manganese, although generally less than 15 % of the feed input balance, can result in the scrubber dust being classified as hazardous for disposal, based on ARLP results.

At a primary risk assessment level, it was found that a number of process conditions influence the ARLP results and the form of manganese found in the scrubber dust, which, ultimately affects its bio-availability and potential hazard to the environment.

In general it was found that off-gas collected in dry oxidizing environments could convert the manganese into a more stable form than is found under wet, reducing conditions. Despite this, it was found that a much higher manganese load is leached under ARLP conditions from the scrubber dusts that were collected under oxidising conditions (>100 mg/kg dust) compared to reducing conditions (<35 mg/kg dust). It must be noted that the inclusion of a post combustion chamber in the oxidising situation does significantly reduce the amount of soluble manganese in the “oxidized” dust.

It was also found that the liquid/solid ratio or water flow rate/temperature management in the wet scrubber is an important operational factor that affects the hazard risk assessment of Mn based on ARLP results and EEC calculations. Lower temperatures can significantly change the solubility of the manganese captured as dust from the furnace. Significant changes to the particle size distribution of the scrubber dust were also observed. The waste classification listing was lowered when the temperatures of the scrubber inlet were kept at 180 °C and 233 ℓ/hour scrubber water flow rate, compared to 114 °C and 393 ℓ/hour scrubber water flow rate. It must be noted that the temperatures are relative and not absolute. The measured temperature depends on the location of the thermocouple.

A number of possible immobilization techniques utilizing chemical additional precipitation methods were also evaluated, based on our literature search findings. It was found after an initial baseline study to determine optimum dosage ranges, that lime 5 %-10 % (w/v), calcite (37.5 % w/v), hypochlorite (9 % v/w) and a desulphurisation slag (10 %) from the smelter process could all significantly reduce the levels of soluble manganese under ARLP extraction conditions and the EEC/ARL ratio to <1 for delisting.

It was also seen that while calcite reacts slower than lime initially, in the long term it also provides alkalinity and buffering capacity to the waste to prevent leaching over time. This was also seen in the Multiple Extraction (MEP) results and geochemical modeling predictions. Dolomite was also considered as a good treatment option but due to impurities inherent in the product, it was found that it added rather than reduced manganese in the waste leachate. Dolomite may also contain other substances that could influence the potential pollution and toxicity of the treated waste. This needs to be checked before use. Moreover, burnt dolomite proved to have less contaminating manganese levels compared to raw dolomite.

The geochemical assessment and modelling of the dust showed that more chemical components, specifically manganese were leached out from the scrubber sample collected under reducing conditions (200 kW Trial 1) to the water phase than from the dust sample collected under oxidising conditions (1.5 MW Trial). This was also in line with the activity diagram analysis. Together with the chemical concentration analysis, it was concluded that the “oxidised: sample (1.5 MW dust) contains much less leachable metals as a whole, viz. manganese, cobalt, nickel and iron than in the “reduced” sample (200 kW Trial 1). Correspondingly, less minerals, specifically manganese-bearing minerals are less saturated (not precipitated) in the “oxidised” sample (1.5 MW) than in the “reduced” sample (200 kW). Alkalinity was also inherently higher in the 1.5 MW sample compared to the 200 kW WSD sample.

These finding all support the fact that it is better to store manganese-bearing wastes under oxidising conditions that results in formation of stable manganese-bearing minerals and eventually stabilises the manganese-bearing wastes.

Redox conditions in a scrubber dust waste disposal dump were also considered and three management options for the disposal of the wet-reduced scrubber dust and dry-oxidised scrubber dust were evaluated. The management options included the do-nothing approach, addition of calcite and addition of lime.

The following trends with time were observed in the oxidising (upper levels) and reducing conditions (lower and deeper) areas of the waste dump for the case study example. It must be noted that absolute values for manganese could not be predicted with certainty in this project, due to lack of certain critical data required for the kinetic modelling and the need to make informed (albeit unvalidated) assumptions.

Scrubber Dust collected under wet-reducing conditions

Disposal Option 1 – No treatment

During the first 15 years, pH increases in the dump (both reducing (deeper) and oxidising (surface) conditions) due to reaction of MnS. This increase would however still keep pH in the neutral to slightly alkaline range (pH <8). A slight decrease in pH due to the reaction of MnS in the wet scrubber dust was also observed (5-25 years) and this impacts by increasing the level of soluble manganese leached from the waste during this time period. Pyrolusite (MnO_2) a stable form of manganese can also dissolve rapidly when pH is less than 8. Manganese levels in solution were generally high in the dump (> 10mg/ℓ) for scrubber dust produced under reducing conditions but lowered (< 2 mg/ℓ) for “oxidised” baghouse dust.

Manganese levels in the wet reduced scrubber dust samples appear to fluctuate in the first 5 years (could increase or decrease depending on pH level and composition of the dust) but generally increase again over time if left untreated and can reach unacceptable risk levels. Oxidised scrubber dust however showed a decrease over time in the dump if left untreated and the sample tested did not produce hazardous levels of manganese.

Disposal Option 2 – Addition of lime

Manganese leaching from the waste can be controlled by treatment with lime. Lime, however, although it was most effective in the short term, was shown to have less benefit over the long term. Lime has a rapid and dramatic effect, neutralizing MnS and manganese is oxidised to form pyrolusite (MnO_2) and bixbyite (Mn_2O_3) primarily. Levels of manganese may however still exceed recommended maximum environmental limits using this method if scrubber dust is disposed under reducing conditions.

Disposal Option 3 – Addition of calcite

Addition of calcite to the scrubber dust also acts rapidly but was also shown to provide a better and more effective long-term solution to reducing the amount of Mn leached, especially in the reduced scrubber dust stored under reducing conditions.

Both lime and calcite addition were predicted to provide similar benefits when scrubber dust waste sample is stored under oxidising conditions. Sequential step extraction methods (SEP) were useful in indicating the proportions of reducible and oxidisable species in the waste and multiple extraction procedures (MEP) provided some clues to the long-term stability and effectiveness of various treatment methods over time that was supported by geochemical modeling predictions.

Inorganic manganese-containing wastes cannot all be classified into one category. The predominant form of manganese found in the waste plays a significant part in the assessing the hazard risk potential. Operational conditions used to collect the scrubber dust waste from the furnace can influence the type of manganese produced and its chemistry upon disposal. The impact of other trace metals and the chemistry over the long term also need to be considered and this is not always accurately reflected in ARLP-based classification methods.

CONCLUSIONS AND RECOMMENDATIONS

This project has demonstrated and concluded that the current methodology applied to the classification of manganese containing wastes is inappropriate as it does not consider the mineralogy and kinetic aspects of the waste in question.

It is therefore recommended that the existing methodology be revised and that the technical process described and presented in this report be implemented.

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1. INTRODUCTION

Many industrial processes today generate waste materials containing manganese (Mn) in some form. Waste streams or compounds of manganese, manganese dioxide or manganese chloride are considered hazardous material, with a hazard rating of 2 according to the "*Minimum Requirements for the handling, classification and disposal of hazardous waste*" as published by the Department of Water Affairs and Forestry (DWAF, 1998). Furthermore, the acceptable environmental risk concentration is given as 0.3 mg/l, and the amount that can be safely disposed of is 454 g/ha/month (DWAF, 1998).

The hazard rating determines the class of landfill at which the waste is disposed. In this case, manganese waste requires a H:H landfill site, where the requirements for the siting, investigation, operation and monitoring are the most stringent. The preferred technology for disposal of manganese-containing waste is recycling or immobilisation (e.g. micro-encapsulation or precipitation) and then land filling.

Waste classification test methods used in South Africa include the toxicity characteristic leaching procedure (TCLP) test and the acid rain leaching procedure (ARLP). Experimental work conducted by Pulles Howard and de Lange (PHD), on contract for a specific manganese-containing waste (PHD, 2000), showed that this element, due to its specific behaviour in these tests, might give results not consistent with its behaviour in the environment. As a result, it was found that there is a risk that some manganese wastes may have higher hazard classifications than is required for the protection of the water resource. This will lead to unnecessary high disposal costs, which is not in the interest of industry, the economy, or the environment.

In this project, further environmental characterisation research of inorganic manganese-containing waste streams, originating from pyro-metallurgical processes specifically, is carried out. Leachability, immobilisation and hazard potential of the constituent of concern is established in order to evaluate the environmental impacts of the waste at the disposal sites.

2. AIMS AND OBJECTIVES OF STUDY

The main aims of the project are to establish whether the current methods employed for the hazard rating and classification of wastes containing manganese are appropriate, and whether, under specific conditions, other methods, which better represent the behaviour of such wastes, exist, or can be devised. Since it is not feasible to test the current methods and develop alternatives for the full range of manganese containing wastes which are produced in South Africa, a specific example based on pyro-metallurgically generated waste will be used to develop a generic approach to the management of inorganic manganese-containing wastes.

In order to achieve this aim, the research components listed below were envisaged. To investigate the following:

a) The implication of manganese chemistry and geochemistry, its behaviour under various environmental conditions, and its application to the disposal of manganese-containing wastes;

b) The effects of a range of environmental factors on manganese mobility and behaviour;

c) The effects of selected pyro-metallurgical processes and/ or waste treatment technologies on the mobility of manganese in inorganic wastes;

d) Contamination levels associated with inorganic waste deposits known to contain manganese, and assess this relative to conventional classification methodologies for a specific case study;

e) The suitability of existing waste classification methods, with respect to manganese in inorganic waste deposits for a specific case study (viz. smelter scrubber dust), and develop, through experimental research, alternative methodologies, which may be appropriate under specific circumstances;

f) Various additives to immobilise manganese for testing in manganese containing waste materials on a theoretical basis for a specific case study, as well as the physical testing of such additives to specific wastes;

g) Devising and development of a comprehensive test methodology which may be applied to the classification of manganese containing wastes generated through pyro-metallurgical processes and disposal under a range of environmental conditions according to the findings of the research proposed in the above points. This will be applicable to inorganic wastes only.

3. METHODOLOGIES AND APPROACH

This section gives a brief description of the methodologies and approaches used during this study. The task outcomes, in terms of the final report structure, are illustrated in Figure 3.1.

The proposed work programme was as follows:

Task 1: Research of manganese chemistry and mineralogy

This component of the work was a desktop study which took the form of an in-depth literature survey that not only identified literature pertaining to traditional manganese chemistry and mineralogy, but also to geochemical and environmental observations and research relating to manganese. This component was aimed at qualitatively assessing the effect of environmental factors on inorganic manganese mobility.

Task **2: Validation and quantification of key environmental factors of manganese mobility**

This research was undertaken to validate the conclusions of the desktop study of environmental factors, which are considered to control manganese mobility, and to quantify these effects where possible using a specific case study.

Task 3: Testing of hypotheses through case studies

In view of the range of environmental factors, which can materially affect manganese mobility, the interaction of these factors was evaluated through a case study to verify hypotheses developed through tasks 1 to 3.

Task 4: Investigate effects of pyro-metallurgical processes on manganese mobility

A specific pyro-metallurgical process was identified, which generates manganese-containing wastes for the case study, and key components of this process that have the potential to affect manganese behaviour were also recognized. The process conditions considered for evaluation would include factors such as temperature, aeration, redox conditions, exposure to alkalinity, pH, exposure to other chemical/gaseous species, and residence time within these processes.

Task 5: Investigate methods to immobilise manganese

Waste treatment methodologies to immobilise manganese through process conditions and chemical additives for inorganic waste generated through a specific pyro-metallurgical process were identified. This was investigated through a desktop study and laboratory research using a specific pyro-metallurgical process as a case study.

Task 6: Investigate alternative waste classification methods

Current methods were evaluated and alternatives proposed based on experimental and theoretical findings for a specific case study.

a) This research assessed the suitability of the current use of the TCLP and Acid Rain Leach Procedure (ARLP) tests for the classification of manganese-containing wastes. These tests are intended to simulate worst-case conditions to be expected if wastes containing manganese are disposed in specific environments. The validity of these tests and their application in the range of environmental conditions that may be expected were tested against the findings of the above work in the context of a case study of manganese-containing waste originating from a pyro-metallurgical process.

b) It is proposed that current waste classification methods may be inappropriate under certain conditions. A range of waste generation methods, environmental factors and disposal options which may be applicable in certain cases and which may materially affect manganese mobility in ways that are not taken into consideration through these tests, may be identified and incorporated into other methods which reflect manganese behaviour in that specific environment. The development of such methods will require an integration of information obtained on manganese chemistry and mineralogy and various factors affecting manganese mobility, verified through experimental work and field examples.

Task 7: Prepare final project report

The findings of the project were documented in a research report submitted to the Project Steering Committee for final approval.

Table 3.1: Table illustrating the various phase outcomes of this study

Task	*Section Reference*	*Chapter*
Research of manganese • Chemistry • Mineralogy	Literature survey	Chapter 4
Validation and quantification of key environmental factors of manganese mobility	Geochemical modelling	Chapter 7
Testing of hypotheses through case studies	Scrubber dust characterisation	Chapter 6 Chapter 7
Investigate effects of pyro-metallurgical processes on manganese mobility • Pilot plant trials	Literature survey Liquid/Solid Ratio Dry vs Wet Off gas collectors Reducing vs Oxidising conditions Fe/Mn ratio	Chapter 4 Chapter 6 Chapter 7
Investigate methods to immobilise manganese • Inorganic Manganese Standards • Case Study • Iscor Pilot studies • Other Scrubber Dust Samples	Literature survey Batch tests Geochemical modelling	Chapter 4 Chapter 6 Chapter 7
Alternative waste classification methods	MEP, SEP, NEP	Chapter 8
Recommended methodology for classification of manganese containing wastes	Assimilation of research results	Chapter 9

4. LITERATURE SURVEY

4.1 GENERAL BACKGROUND

Manganese is ubiquitous in the environment. It is a naturally occurring substance found in many types of rocks (Lee, 1991) and is present in low levels in water, air, soil, and food (ATSDR, 1997).

Manganese is the twelfth most abundant element, by mass, in the earth's crust at approximately 1060 mg/kg (Lee, 1991). Manganese is described in the "*Encyclopedia of the Solid Earth Sciences*" (Kearey, 1993) as a group VII metallic element with atomic number 25. The most common oxidation states of manganese are the II and IV states. Its mass number is 54.938 g/mole and pure manganese is a silver-colored metal.

Manganese does not occur as a pure metal in the environment but combines with other substances such as oxygen, sulfur, and chlorine (Patty, 1981). These forms (called compounds) are solids that do not evaporate, but small dust particles of the solid material can become suspended in air. Manganese can change from one form to another (either by natural processes or by human activity), but it does not break down or disappear in the environment.

The aquatic chemistry of manganese is closely associated with that of iron chemistry. Both elements tend to behave synergistically in their dissolution from sediments under anaerobic conditions and re-precipitation under aerobic conditions. Manganese, however, once in solution, is more readily stabilized by complexation than iron is and is often difficult to remove from solution except at high pH where it precipitates as the hydroxide. Like iron, metallophilic bacteria can utilize manganese. Other water constituents and properties that govern the action of manganese in water are pH, redox potential, turbidity, suspended matter and the concentration of aluminium (DWAF, 1996).

Manganese can occur as inorganic or organic manganese. Only the inorganic manganese is discussed in this profile. The inorganic manganese includes those forms of the element such as dusts that are present in steel or battery factories as well as the combustion products from vehicles (ASDR, 2000).

4.2 ENVIRONMENTAL TRANSPORT, DISTRIBUTION AND TRANSFORMATION

The primary routes by which biota pick up contaminants are from the atmosphere and surface water. Manganese behaviour, in these components of the environment as well as others e.g. soil and groundwater, is discussed below.

4.2.1 Air

Elemental manganese and inorganic manganese compounds have negligible vapour pressures but can exist in air as suspended particulate matter derived from industrial emissions, burning of fossil fuels or the erosion of soils. More specifically, sources of airborne manganese include iron- and steel-producing plants, power plants, coke ovens, and dust from uncontrolled mining operations.

4.2

The fate and transport of manganese, in air, is largely determined by the size and density of the particles and the wind speed and direction. An estimated 80 % of the manganese in suspended particulate matter is associated with particles with a Mass Median Equivalent Diameter (MMED) of <5 µm, and 50 % of this manganese is estimated to be associated with particles that are <2 µm in MMED. (Note: Whether these data are for particles in urban or rural areas is unclear) (CICAD, 1999). Based on this data, the small particle size of manganese is within the respirable range, and widespread airborne distribution would be expected (WHO, 1981).

The size of manganese particles in the air tends to vary by source. Small particles dominate around ferromanganese and dry-cell battery plants, whereas larger particles tend to predominate near mining operations (WHO, 1999). Very little information is quoted as being available on atmospheric reactions of manganese (US EPA, 1984). Although manganese can react with sulphur dioxide and nitrogen dioxide, the occurrence of such reactions in the atmosphere has not been demonstrated. Manganese-containing particles are removed from the atmosphere mainly by gravitational settling or by rain (US EPA, 1984).

4.2.2 Water

Manganese from human-made sources can enter surface water, groundwater, and sewage waters. Small manganese particles can also be picked up by water flowing through landfills and soil. The transport and partitioning of manganese in water is controlled by the solubility of the specific manganese compound present. The range of processes controlling the transport and biogeochemical cycling of manganese in streams affects both nutrient availability and toxicity to ecosystems.

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In most waters (pH 4-7), Mn (II) predominates and is associated principally with carbonate, which has relatively low solubility (US EPA, 1984; Schaanning et al., 1988). The solubility of Mn (II) can be controlled by manganese oxide equilibria (Ponnamperuma et al., 1969), with manganese being converted to other oxidation states (Rai et al., 1986). In extremely reduced water, the fate of manganese tends to be controlled by the formation of the poorly soluble sulphide (US EPA, 1984). In groundwater with low oxygen levels, Mn (IV) can be reduced both chemically and bacterially to the Mn (II) oxidation state (Jaudon et al., 1989). Manganese is therefore a redox sensitive metal whose dissolved concentrations have been observed to undergo variations in streams (USGS 2003).

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Manganese cycling and transport in freshwater streams is also affected by light, but this is not well understood (Morgan, 1999). Scott *et al.* (2002) discuss the importance of both surface catalysed oxidation and photoreduction on the speciation of manganese in a mountain stream, which receives manganese-rich inflows from a wetland contaminated by acid mine drainage. They reported that rapid oxidation and precipitation of MnO_x was the dominant process and that light was found to promote oxidation and removal of manganese from the stream. This was presumably through a photosynthetically enhanced oxidation process. Other studies by showed that MnO_x in seawater is photoreduced in the presence of dissolved organic carbon and that the nature of the oxide is important in the overall rate of photoreduction and type of photoreductive mechanism used. The organo-manganese compound methylcyclopentadienyl manganese tricarbonyl (MMT) has been found to be persistent in natural aquatic and soil environments in the absence of sunlight, with a tendency

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to sorb to soil and sediment particles (Garrison et al., 1995). In the presence of light, photo-degradation of MMT is rapid, with identified products including a manganese carbonyl that readily oxidizes to manganese tetroxide (Garrison et al., 1995).

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In a number of cases, high levels of manganese in water (in excess of 1000 µg/litre) have been detected at US hazardous waste sites, suggesting that, in some instances, wastes from industrial sources can lead to significant contamination of water (ATSDR, 1997).

Manganese is often transported in rivers adsorbed to suspended sediments. Most of the manganese from industrial sources found in a South American river was bound to suspended particles (Malm et al., 1988).

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Manganese in water can also be significantly bio-concentrated (bioaccumulation) at lower trophic levels, e.g. bio-concentration factors (BCFs) of 10 000-20 000 for marine and freshwater plants, 2500-6300 for phytoplankton, 300-5500 for marine algae, 800-830 for intertidal mussels, and 35-930 for fish have been estimated (Folsom et al., 1963; Thompson et al., 1972). The high reported BCFs probably reflect the essentiality of manganese for a wide variety of organisms. Specific uptake mechanisms will exist for essential elements.

Heath (1999) conducted studies on metal levels of fish from the Crocodile River in South Africa, which is impacted by intensive urbanisation. He found BCFs, in various fish tissues compared to river water, to range from 4-790, with the highest BCF levels recorded in guts>gills>liver. High manganese in the gills can be ascribed to the fact that the gills are an excretion route for this metal, and intake of particulate matter, for example food and sediments, can be the result for high manganese levels recorded for the gut.

4.2.3 Soil

The chemical state of manganese and the type of soil determine how fast it moves through the soil and how much is retained in the soil. The tendency of soluble manganese compounds to adsorb to soils and sediments can be highly variable, depending mainly on the cation exchange capacity and the organic composition of the soil (Baes & Sharp, 1983; Kabata-Pendias & Pendias, 1984). The oxidation state of manganese in soils and sediments can be altered by microbial activity (Francis, 1985).

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Hydrous manganese oxides (Mn--OH^{o}) are almost ubiquitous in soils and sediments, which are not strongly reducing i.e. these forms of manganese in soil, do not dissolve in water containing oxygen. However when water percolates through soil, it is deprived of oxygen because the soil contains organic materials and aerobic organisms. In the absence of oxygen, manganese could then be reduced into soluble Mn^{2+} states (Kassim, 1994). Hydrous manganese oxides occur as coatings around silicate grains and as discrete grains of oxide mineral. The most common mineral forms of manganese in soils are two crystal forms of MnO_2, birnessite and vernadite.

4.2.4 Rock

Rocks with high levels of manganese compounds are mined and used to produce manganese metal. Manganese is mined as the ore pyrolusite (MnO_2), which is a secondary mineral formed by alkaline waters leaching manganese from igneous rocks and depositing it as MnO_2.

4.2.5 Environmental levels

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In South Africa (DWAF, 1996) the median concentrations of manganese in the environment are given as

- 8 µg/ℓ in fresh water, with a range of 0.02 – 130 µg/ℓ
- 1000 mg/kg in soils, and
- 0.2 µg/ℓ in seawater.

Manganese concentration in the mg/ℓ range can be found in anaerobic, bottom level waters, where manganese has been mobilized from the sediments.

The Agency for Toxic Substances and Disease Registry (ATSDR; 1997), in the United States, reported the average manganese levels in various media, as follows:

- levels in drinking water are approximately 4 µg/ℓ;
- average air levels are approximately 0.02 micrograms per cubic meter (µg/m^3);
- levels in soil range from 40 to 900 ppm (estimated mean of 330 mg/kg)
- the average daily intake from food ranges from 1 to 5 milligrams per day (mg/d).

Concentrations of manganese in surface water are usually reported as dissolved manganese. Total manganese might be a better indicator, because manganese adsorbed to suspended solids can exceed dissolved manganese in many systems, and the bio-availability of manganese in this form has not been established (NAS, 1977; US EPA, 1984). Accumulation of manganese in soil usually occurs in the subsoil and not on the soil surface (WHO, 1981).

4.3 HAZARD SUMMARY

4.3.1 Sources and potential exposure

The principal sources of manganese are from sedimentary deposits and thermal metamorphosed equivalents together with residual deposits.

Manganese is essential for normal physiological functioning in humans and animals, and exposure to low levels of manganese in the diet is considered to be nutritionally essential in humans. However, if manganese is mobilised to a significant extent it can have negative effects on ecological systems, particularly aquatic ecosystems. Manganese can also have adverse health effects on humans, but these occur at significantly higher concentrations than adverse effects on aquatic ecosystems. Chronic (long-term) exposure to high levels of manganese by inhalation in humans may result in central nervous system disorders (US EPA –Air toxics Website). People who work in factories where manganese metal is produced from manganese ore or where manganese compounds are used to make steel or other products are most likely to be exposed through inhalation to higher than normal levels of manganese.

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4.3.2 Toxicology - drinking water

Adverse aesthetic effects are the prime reason for limiting manganese concentrations in water used for domestic purposes due to taste and staining effects. The target drinking water quality guideline for manganese in South Africa is < 0.05 mg/ℓ, and is based on aesthetic considerations

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rather than toxicity criteria (DWAF, 1996a). Human health effects of manganese are only relevant at elevated concentrations. No adverse health effects are observed at concentrations below 5 mg/ℓ, and adverse health effects are rarely observed at concentrations up to 20 mg/ℓ. At higher concentrations chronic toxicity may occur as well as acute effects.

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4.3.3 Toxicology - aquatic ecosystems

Information on the acute and chronic effect of manganese on algae, invertebrates and vertebrates are very limited. The Chronic Effect Value (CEV), which is the concentration at which there is expected to be a significant probability of measurable chronic effects to up to 5 % of the species in the aquatic community, for manganese, is 370 µg/l. The acute effect value (AEV), which is the concentration above which there is expected to be a significant probability of acute toxic effects to up to 5 % of the species in the aquatic community, for manganese, is 1300 µg/l. The Target Water Quality Range for aquatic ecosystems is 180 µg/l (DWAF, 1996b).

4.4 PYRO-METALLURGY PROCESS DESCRIPTIONS

Pyro-metallurgy is a term used for processes carried out at relatively high temperatures, usually in furnaces, in which metalliferous material or metal is treated to prepare free metal, to purify or to refine free metal, or to prepare intermediate materials more suitable for use in preparing free metal (e.g. smelting; roasting of ores etc). Examples of metal industries utilising pyro-metallurgy processes include ferromanganese, ferrochromium, ilmenite, nickel laterite and zinc smelting systems. A combustible solid reductant (e.g., coke, coal or anthracite etc.) is generally used to fuel the process, while electricity supplied by electrodes is commonly used today to power the process in arc furnaces.

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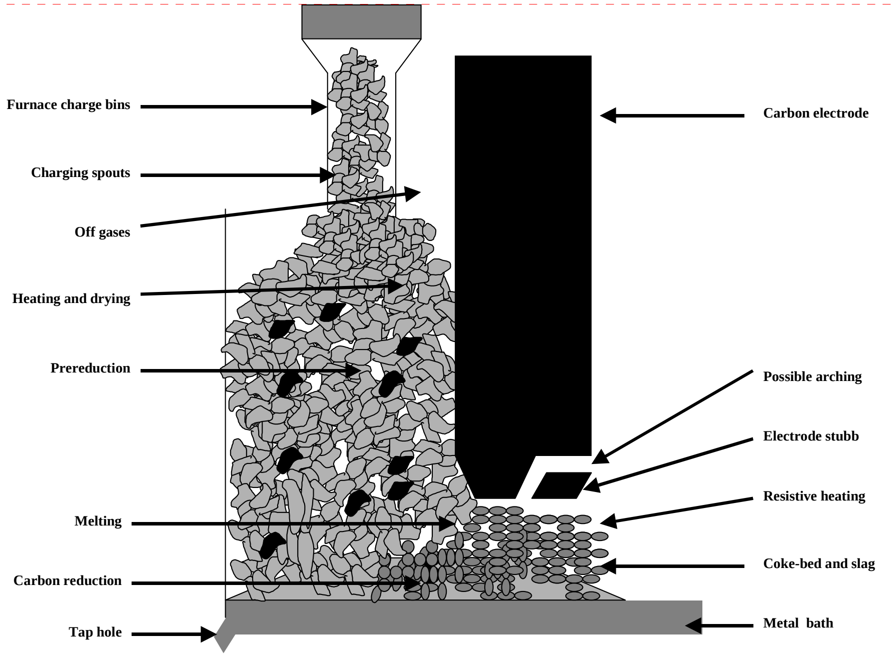

Figure 4.1: Sketch of the metallurgical system of a high carbon ferromanganese furnace

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The furnace consists of furnace zones, in which different phenomena take place (see Figure 4.1). In the upper parts of the furnace (denoted the pre-reduction zone), water evaporates and manganese and iron oxides, with high contents of oxygen, will be reduced by counter current carbon monoxide, and carbonates will decompose. In addition the Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) will take place in the pre-reduction zone. Carbon monoxide (CO) and carbon dioxide (CO2) are generated in the furnace from combustion of the auxiliary fuel (e.g. coal, oil contained in the scraps and decarburisation of some of the scrap). In higher temperature ranges, deeper down in the furnace, the reduction of the ore in the solid state continues. In the hearth of the furnace, the ore melts and reacts with carbon, forming metal. At the bottom, slag and metal are tapped from the slag/metal zone.

Several issues are important in operating a furnace. They include the electrical and metallurgical process within the furnace, balancing the current flow through the electrodes, avoiding furnace eruptions, maintaining a high production rate and maintaining the grade of the product (Pistorius and Geldenhuis, 2001).

Ninety five percent of manganese ores mined are used in the steel industry to produce very hard weathering alloys, of which ferromanganese and silicomanganese are the most important. Typically it is made by reducing the appropriate mixture of ferric oxide / ilmenite (Fe_2O_3/ $FeTiO_3$) and MnO_2 ores with carbon, in a blast furnace or an electric arc furnace. Some limestone is also added to remove silicate impurities as calcium silicate slag (Lee, 1991).

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Figure 4.2 below, represents the phenomena in the pre-reduction zone (upper parts of furnace) related to chemical species containing manganese.

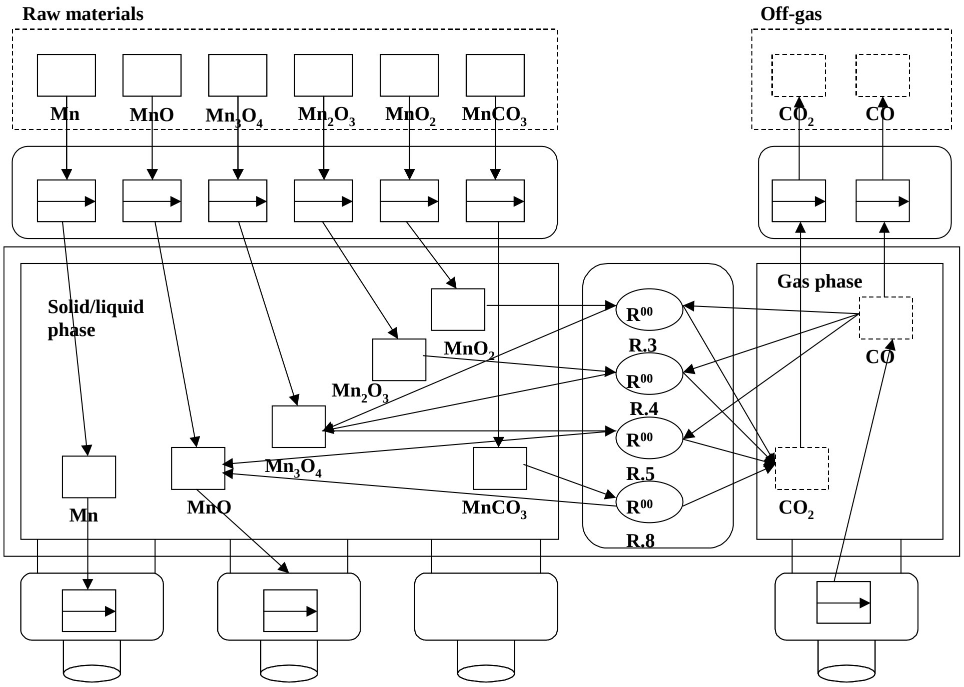

Figure 4.2: Manganese forms in the different zones of a furnace

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When MnO_2 is introduced to a smelter, it decomposes to Mn_3O_4 on the heating at 530 ºC (Lee, 1991). Mn_3O_4 has a spinel structure and consists of $Mn^{II}.Mn_2^{III}O_4$. The concentration / dissolution rate of manganese is thought to be controlled by the dissolution of Mn_3O_4 (PHD, 2000).

4.4.1 Smelter dust

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Primary emissions from the smelter / furnace include particulate matter and gases. Particulate matter, including metal oxides, is generated during the melting and refining phases and is exhausted from the furnace. The exhaust gases (off gas) from the carbothermic reduction process are typically collected from the furnace and cleaned by baghouses (fabric filters) or water scrubbers (Environment Canada, 1999) to reduce the air pollution potential. Particulate matter or " dust" collected in the filter or scrubber can therefore either be in a dry or wet (as a slurry) form.

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In this research project, the case study will focus on the manganese-containing scrubber dust collected from an ilmenite smelting process. The wet scrubber dust is recommended for delisting in terms of the Minimum Requirements (DWAF, 1998) as a general waste if disposed in a mono-landfill site. In addition disposal methods are recommended which are expected to effectively encapsulate and immobilise any potentially harmful contaminants. Wet scrubber dust containing manganese will be compared to dry scrubber dust samples.

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The dry collection of the dust exposes the dust to different chemical conditions than those expected in the wet scrubber of a production unit. The primary difference between wet and dry scrubber dust is that dry collection systems often include the use of a post-combustion chamber, in which CO gas is ignited to form CO_2 gas, and the fact that dust is collected in a dry form. Wet scrubber dust involves no post-combustion of the off-gas CO, and the dust is collected in a wet spray chamber equipped with water nozzles. The combustion of CO gas exposes the dust to temperatures not experienced in the wet scrubber system and will significantly alter the redox conditions in the off-gas stream. The combustion process may also combust any solid reductant in the off-gas, thereby artificially increasing the concentration of metals associated with the ilmenite feed in the off-gas dust.

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The wet scrubber dust matrix, in our case study, predominantly consists of iron, titanium, aluminium and manganese with trace amounts of metals. Of main concern is the manganese content, which although high in terms of total content, has been found to be stable and is suspected to be in the form of rhodochrosite ($MnCO_3$) or pyrolysite (MnO_2) (PHD, 2000).

Important considerations in the hazard characterisation of the scrubber dust include stoichiometric ratio, scrubber inlet temperature and gas and liquid mass transfer rates (Bennett, 1997). The main disposal considerations for scrubber dust will be concerned with: pH, liquid to solid ratio; humidity; kinetics; acid-base reactions (alkalinity); redox reactions, particle size; adsorption and complexation (presence of other metals).

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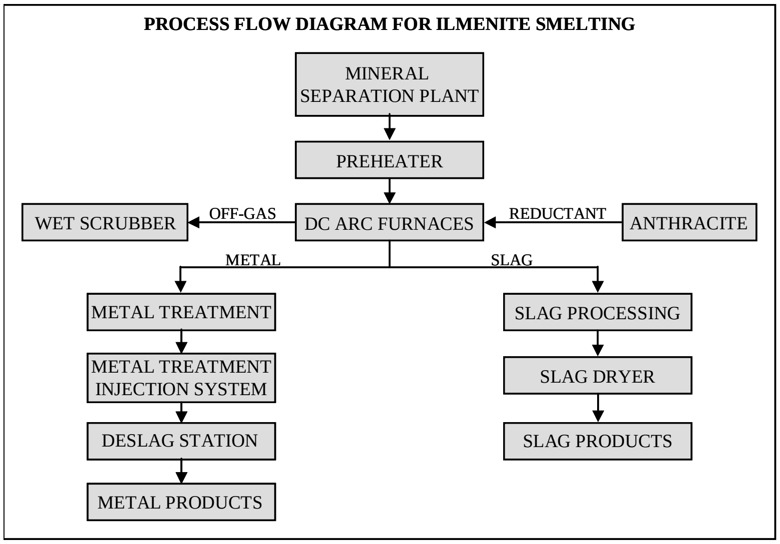

Figure 4.3: Simplified process flow diagram of the smelter process used as the case study

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4.5 HAZARDOUS WASTE IMMOBILISATION AND STABILISATION

Environmental problems are encountered if the concentrations of mobile substances available to organisms are either too low or too high. Measures to reduce pollutant levels in the bio-available, mobile phase fall under the following six categories:

- Breakdown, neutralization or decay;
- Concentration;
- Concentration;
- Dilution;
- Immobilisation;
- Stabilisation /Isolation; and
- Combination of options.

Immobilization is probably the most widespread mechanism in nature by which the risk to life of high concentrations of potentially hazardous substances is reduced. Immobilization can take the form of precipitation of an insoluble mineral, capture of an element in the lattice of insoluble mineral, or its adsorption on clays or zeolites. Physical forms of immobilization are the cementation of rocks, their recrystallization to a dense rock with low permeability, or in unusual cases the transformation into glass. In these last cases, immobilization is achieved because solutions can no longer enter and leach the rock under consideration (Emeritus *et al.*, 2002).

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Immobilization as an environmental option has met with considerable opposition from environmentalists and some environmental agencies. The main reason is that the pollutant is still present after immobilization, and it is feared that it will be set free again when there is a change in conditions at the disposal site. It is formally true that the pollutant is still present, and that it will be set free eventually after a long period of time, as no substance is perfectly insoluble. However, immobilization does serve the ultimate goal of environmental action: it guarantees that the concentrations of the pollutants in the mobile phase will not exceed certain safety limits, and that detoxification will proceed in a slow and orderly manner (Emeritus *et al.*, 2002*)*.

Stabilization / solidification is a treatment technology used to reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile or toxic form. Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents but may mechanically bind the waste into the monolith. Similarly, stabilization does not necessarily involve solidification, since precipitation and complexation are also mechanisms of stabilization.

4.5.1 Waste dumps/landfills

Manganese waste dump chemistry is dictated by both external and internal factors. External factors include rainfall, temperature and light, while internal factors include moisture content, oxygen content, temperature and all biological activities acting upon waste composition. High concentration of waste also increases the nature of threat to the environment.

Rainfall creates runoff and leachate from dumping sites, carrying fine waste and rock particles into the nearby surface or groundwater resources, thereby potentially affecting aquatic life by altering biochemical conditions and restricting food resources and habitat space. In addition, solutes within the immobile or slow flow region would tend to mix with the rapid flow region, especially as the concentration difference between the two regions develops. A rise in temperature can also influence reaction rates through an increase in kinetic energy. Most substances react faster with an increase in kinetic energy.

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Most substances react faster with an increase in kinetic energy. Furthermore, when wastes are exposed to atmospheric oxygen and light; oxidation, reduction and biochemical processes, through bacteria and fungi, are enhanced.

Internal factors influence the reactions (oxidation and reduction) that take place in the waste dump. They therefore control the solubility of un-dissolved waste materials, mobility, leachability and longevity of the waste (Michael, 2001).

The oxidation of the reactive minerals reduces the pH of the leachate. In addition, this in turn increases the solubility of metals in the wastes (Aubertin and Bussiere, 2001). Infiltrating rainwater can supply enough oxygen to the sub-surface regions of a waste dump for the continuation of these reactions to take place (Sengupta, 1993). However, during rainfall periods, lower infiltration pressure can result in lower reactivity of the waste inside the dump.

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Compaction, swelling capacity and grain size of the dumped materials will also control reaction rate and hence mobility of waste. In fine-grained waste material, reaction rate is faster due to larger exposed surface area (Sengupta 1993). Chemical parameters (e.g. pH, alkalinity, and kinetics) control solution and precipitation reactions between the fixed phase and the solvent water. They also control fixation of metal cation-anion complexes (Pero Des Potovic, 2000).

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4.5.2 Manganese immobilization and resolubilization

Treatment technology for the removal of manganese generally involves conversion of the soluble ions to an insoluble precipitate (oxides, hydroxides and Mn carbonate minerals). The precipitation of manganese in an aqueous system is complex because manganese can exist in many different oxidation states (+2; +3, +4; +6 and +7), complexes and chelated forms (Watzlaf, 1988). The formation of manganese complexes depends on oxidation states, pH, bicarbonate-carbonate-hydroxide equilibria and the presence of other materials.

4.5.2.1 Oxidation by Aeration

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Removal of manganese (oxidation from Mn^{2+} to Mn^{4+}) from water by natural or mechanical aeration and settling is a relatively slow process unless pH is raised above neutrality (Aziz and Smith, 1996) or more specifically above pH 9.4 (Ekenfelder, 1989). It has also been reported that even at high pH levels, organic matter in solution can combine with manganese and prevent its oxidation by simple aeration (Ekenfelder, 1989).

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Initially, the valence of manganese, in the air-oxidized precipitate (removed at high pH), lies between 2 and 3 (Mn_3O_4-hausmannite and β-MnOOH-feitknechtite, respectively). Both these minerals are eventually transformed into the more stable γ-MnOOH-manganite (Murray *et al*, 1985).

Since manganous ion (Mn^{2+}) has a low reactivity with oxygen and simple aeration is not effective below pH 9, addition of lime/ alkaline material to raise the pH, or the use of chemical oxidants in conjunction with coagulation and filtration, has also been employed for removal of manganese.

4.5.2.2 Oxidation by High-pH method

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The high pH method involves the addition of lime (CaO or $Ca(OH)_2$) or the addition of alkaline material e.g. sodium hydroxide (NaOH) or zeolite. Nichloas and Foree (1979) discussed using lime and sodium hydroxide to remove manganese from active mining waters and found that the reaction is pH dependent and proceeds very slowly below pH 8.5. Aziz and Smith (1996) discussed removal of manganese from water by filtration through low cost coarse media (e.g. crushed dolomite). Their results indicate that rough solid surfaces and the presence of carbonate in the limestone particle are beneficial in the precipitation of manganese in water. They reported manganese removal efficiencies of a 1 mg/ℓ manganese solution at a final pH of 8.5 with limestone of 95 %; crushed brick 82 %; gravel 60 % and aeration and settlement (no solid media) 15 %.

In the process of removing manganese by the high pH-precipitation method, other metals e.g. zinc, copper, lead, and mercury, can also precipitate as hydroxides and form complexes or chelates (Watzlaf, 1988). However, hydroxides of these metals are unstable and may resolubilise upon subsequent depression of pH (Peters and Ku, 1985). This means that if sludge is disposed of in or on a landfill, and exposed to reducing and moderately acid conditions, any manganese that resolubilises may need to be retreated at great expense. While it has been found that stability increased with age of the sludge (after three months), up to 50% manganese can resolubilise at pH 4.2 (Watzlaf, 1988).

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In this research project we will investigate the need for and addition of different carbonate sorbents (liming materials) to stabilize the manganese containing waste. Lime (CaO or $Ca(OH)_2$), calcite ($CaCO_3$) and dolomite (40-45 % $MgCO_3$ and 54-58 % $CaCO_3$) will be added to the waste and leachability of the immobilized waste compared. Generally calcite/ limestone ($CaCO_3$) is less reactive than lime (CaO) and dissolves at a much slower rate while maintaining basic conditions. Dolomite is more porous (and thus more reactive) and easier to handle. Neufield et al, (1996) found that dolomite yields a residue that is lower in pH than that produced from lime based sorbents that makes it particularly advantageous in stabilizing metal–laden waste solids.

The acid neutralizing capacity of “liming materials” is usually measured as the calcium carbonate equivalent (CCE). Pure calcite has a CCE of 100 %. Hydrated lime can typically have CCE from120-136 % while dolomitic limestone (concentration of $MgCO_3$ less than dolomite) has CCE of 75-108 %. Liming compounds that contain significant amounts of magnesium carbonate, calcium hydroxide, calcium oxide or magnesium oxide will have greater neutralizing power than the same weight of calcium carbonate.

4.5.2.3 Oxidation with Chemical oxidants

As an alternative to precipitation of manganese by the high-pH method, strong oxidizers such as permanganate, chlorine dioxide, hypochlorite or ozone can also be used. These chemicals oxidize manganese to pyrolusite ($Mn^{2+} \rightarrow MnO_2$). Knocke et al (1987) found that hydrogen peroxide was not effective for oxidizing manganese with high organic content. Sometimes alkali is added prior to the oxidants. It is also important to note that oxidants such as sodium hypochlorite (NaOCl) or potassium permanganate do not necessarily reduce concentrations of other metals e.g. copper, nickel and zinc (Watzlaf, 1988).

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Lundquist (1999) reported using a mixed oxidant solution produced by a device from MIOX Co. The oxidants are formed by passing brine (salt water) through an electrolytic cell, thus avoiding the handling of volatile substances such as chlorine gas and ozone. The results achieved were similar to those with sodium hypochlorite (NaOCl).

Kleinmann *et al* (1985) noted that manganese precipitated with excess alkalinity is easily resolubilised, while that precipitated with stronger oxidising agents (e.g. hypochlorite) is relatively stable. However, besides producing a more stable sludge, the primary disadvantage of using chemical oxidants is the increased cost compared to high pH methods and sensitive process control requirements.

4.5.2.4 Sorption

Manganese can also be removed by adsorption onto reactive surfaces. Ferric hydroxide ($Fe(OH)_3$) and manganese precipitates can provide surfaces for sorption of Mn^{2+}, which occurs at lower pH values than necessary for manganese removal as hydroxides or MnOOH. Morgan & Stumm (1964) showed that synthetic δ-MnO_2 had a zero point of charge at pH 2.8 in the absence of adsorbed ions other than H^+ and OH^-. At higher pH values, δ-MnO_2 was negatively charged and had a cation exchange capacity that increased with increasing pH. δ-MnO_2 adsorbs Mn^{2+} strongly, and approximately 1 mole of H^+ is released per mole of Mn^{2+} adsorbed. The capacity of δ-MnO_2 to adsorb Mn^{2+} was extremely high, in excess of 0.5 moles Mn^{2+} per mole of MnO_2 in the alkaline range.

Hydrous manganese oxides also have extremely high adsorption capacities and affinities for other heavy metals. McKenzie (1980) found that in general, metal ions are adsorbed in the order Pb > Cu > Mn > Co > Zn > Ni. Murray (1975) summarised the adsorption properties of δ-MnO_2 and demonstrated that there was significant adsorption of heavy metals at the point of zero charge, indicating that specific chemical forces are involved in the adsorption process in addition to electrostatic forces. He documented that the adsorption process is highly irreversible**.**

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Watzlaf (1988) tested the chemical stability of manganese and other metals (iron, nickel, copper, chromium and zinc) in acid mine drainage sludge. They found that in mine waters containing high concentrations of iron in relation to manganese (47:1) and other metals, manganese and other metals were removed at lower pH values than in mine waters with less iron (1:12). It is presumed that much of the manganese is removed by adsorption to ferric hydroxide. However, the sludge precipitated from the high iron water was less stable and found to go back into solution upon acidification. They also found that age increased the stability of the manganese in acid mine drainage sludge.

4.5.2.5 Biological processes

Microbial remediation efforts to remove manganese include designed wetlands, microbial bioreactors and pellets of mixed microbial cultures, rock filters or packed stone columns coated with algae or algae mats (Gordon and Burr, 1988). While manganese can be removed by plant uptake and bacteriological oxidation in wetlands, the processes can be easily disrupted through changes in conditions.

Manganese requires 0.29 mg of dissolved oxygen per milligram of manganese (II) thus exerting greater demand than iron (II) on a similar system. Hydrogen ions are produced at a rate of 0.036 mg per mg of Mn (II) oxidized, which indicates that the following reaction is pH dependent:

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$$2Mn^{2+} + O_2 + 2H_2O \quad \rightarrow \quad 2MnO_2 + 4H^+$$

As pH increases above 9, this reaction will increase in rate. However at lower pHs this reaction may take years to occur. Microbially, Mn (II) can be oxidized to Mn (IV) oxide to obtain energy for the cell. The black manganese oxide will encrust externally around the bacteria and produce a black slime. This process of manganese oxidation occurs in minutes, thus as seepage water travels through the wetlands or reactor there is ample time for the oxidation process by microorganisms to occur.

4.5.2.6 Other

Neufield *et al*. (1996) describe a dry clean coal technology system, whereby, a calcium based sorbent (usually slaked lime; limestone or dolomite) is injected directly into a furnace, ductwork, precipitator or scrubber vessel and produces powdered or granular by-products, as opposed to the slurries associated with traditional wet scrubber systems. All these processes produce a by-product, which is removed in the particulate control equipment. Dry by-products from lime or limestone injected into the furnace, such as in FBC systems, have neutralizing, sorptive and cementitous properties that make them interesting as potential reagents for hazardous waste stabilization because of their high free quicklime (CaO) and anhydrous calcium sulphate ($CaSO_4$) contents.

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4.6 HAZARDOUS WASTE CLASSIFICATION AND DISPOSAL

4.6.1 South African requirements

The Department of Water Affairs and Forestry (DWAF) have published a document called “ *Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste*” (1998) as part of their Waste Management Series. This document sets out a waste classification system where wastes are placed in two classes, General or Hazardous, according to their inherent toxicological properties. Hazardous wastes are further sub-divided according to the risk they may pose at disposal, using a hazard rating. In this way, less hazardous waste is distinguished from an extremely hazardous waste. Wastes with a hazard rating of 1 or 2 are very or extremely hazardous, while wastes with a hazard rating of 3 or 4 are of moderate or low hazard. The requirements for pre-treatment and disposal are appropriately set in accordance with the waste classification.

For a waste to be properly managed, its properties and the risk it poses must be fully understood. Hazardous waste is a waste that poses significant risk to the environment because of its toxic, chemical or physical properties. It, therefore, requires stringent technical control to ensure that it does not cause harm to man or to the environment.

Two factors are taken into account when assessing the risk posed by a hazardous substance in the waste. The Hazard rating is based on two factors, the amount of substance that is available to man and the environment (Estimated Environmental Concentration or EEC) which represents exposure and the inherent toxicological hazard of the substance (LC_{50} etc) which represents a specific effect or response.

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A waste is therefore given a Hazard rating using the following information:

Toxicity (LD_{50}), ecotoxicity (LC_{50}), carcinogenicity, mutagenicity, teratogenecity, persistence, environmental fate and estimated environmental concentration (EEC).

From this, the minimum requirements for disposal are derived e.g. certain wastes may not be landfilled and others must be pre-treated**.**

The Hazard Rating (HR) determines the class of Hazardous Waste Landfill at which the waste may be disposed. An H:h landfill may only accept Hazard Ratings 3 and 4. A H:H landfill may accept all four Hazard Ratings.

The EEC is calculated from the total amount of a hazardous substance in a waste stream which would be disposed of on one hectare of landfill, followed by a calculation of the resultant concentration in a body of water should the total amount of the hazardous substance leach to groundwater over an indefinite period of time. As such, it provides a worst-case scenario. The EEC is expressed as (ppb = µg/ℓ or µg/kg) = dose (g/ha/month) x 0,66. It is used to determine:

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- the amount of waste that can be disposed of within an acceptable risk;
- the maximum amount of a given hazardous substance in the waste that can be disposed of at a landfill site (Total Load); and
- whether a waste, initially regarded as hazardous, can be delisted and handled and disposed of as a general waste.

The EEC is always compared to 0,1 x LC_{50} of the specific hazardous substance in the waste, termed the Acceptable Risk Level. The Acceptable Risk Level is the concentration at which a substance would cause a mortality incidence of one in three hundred thousand in aquatic environment. It therefore represents the level at which a substance will have little adverse impact on the environment. When the EEC is higher than 0,1 x LC_{50}, then the waste retains its Hazard Rating. When it is lower, a HR1 waste remains HR1, but the other Hazard Ratings can delist and will be disposed of on a General Waste landfill with a leachate collection system (G:B+). A HR1 waste can only delist to a G:B+ landfill when the EEC is lower than 0,01 x LC_{50}.

Where there is a difference of opinion regarding classification or Hazard Rating, the results of tests or other proof may be submitted to the DWAF. Such tests would include the Toxicity Characteristic Leaching Procedure (TCLP) and the Acid Rain Leaching Procedure (ARLP). DWAF will use the test results to determine whether it is safe to delist the Hazardous Waste to a lower Hazard Rating or not. The information gained from classification and Hazard Rating must be applied in the handling of a Hazardous Waste, during collection, temporary storage and transportation. This is essential for safe disposal.

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4.6.1.1 Delisting

The fate of the waste stream is regulated by the most hazardous contaminant of which the EEC exceeds the Acceptable Risk Level (worse case scenario). But, hazardousness can be reduced, e.g., by treatment. The contaminant could be treated to a compound of which the EEC would fall within the Acceptable Risk Level. Treatment of a contaminant from one species to another (e.g. chloride to hydroxide or oxide) affects leachability and hence mobility in the environment. Tests can be carried out to prove that because of low mobility, the substance is of a less hazardous nature than that indicated. Tests recommended by DWAF to prove this would include the TCLP or the ARLP.

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4.6.1.2 Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP) was developed in the USA by the Environmental Protection Agency to measure a waste's leachability and hence the risk it poses to groundwater. It plays a major part in determining the Concentration Based Exemption Criteria used in the USA and Australia for the classification of wastes. In preference to this, South Africa has adopted the EEC, which is a method whereby the exposure of fauna to compounds of concern in the waste is estimated and quantified. The two approaches to waste classification, EEC and Concentration Based Exemption Criteria, have a number of important fundamental differences. In general, however, they lead to comparable values for the hazardousness of various wastes and waste streams. The TCLP can therefore be used to support or affirm the EEC.

The TCLP would be used when a waste is to be landfilled in a site that receives a variety of organic and inorganic wastes. The procedure simulates the dissolving action of the organic acid leachate formed in a landfill where Hazardous Waste has been co-disposed with General Waste. It can be used to determine the mobility of organics and inorganics in liquid, solid and multiphase wastes.

A sample of waste is extracted with either dilute acetic acid or an acetic acid and sodium acetate buffer over a period of 20 hours. The extraction fluid used will depend on the *in situ* alkalinity of the specific waste stream [USEPA, 1986]. The extract (simulated leachate) is analysed for the components of concern. If the components of concern are not known, a compositional analysis of the waste stream will be required before the procedure is performed. The procedure is based on the fact that different hazardous elements or compounds exhibit different solubilities under landfill conditions; for example, a waste containing mercuric chloride will exhibit a considerably different extraction result from one containing mercuric sulphide, which is extremely insoluble under normal conditions. It is important to note that the mobility of a particular identified hazardous element or compound will depend on its nature and composition. The procedure is therefore also particularly useful for evaluating the residues or products of wastes after solidification or other waste treatment technologies.

4.6.1.3 Acid Rain Leaching Procedure (ARLP)

The TCLP test was developed for cases where Hazardous Waste is co-disposed with organic waste, which could then generate organic acids. The organic acids could then mobilise pollutants, which would be of concern to the environment. In many cases, however, Hazardous Wastes are mono-disposed in "dedicated" landfill sites in which only that waste is disposed. Typical examples of such wastes would be the slags and sludges from mineral extraction and metal manufacturing industries. Leaching in such sites would more probably be due to "Acid Rain" than organic acids, and therefore the ARLP method is preferred to the TCLP method. The ARLP is based on the fact that carbon dioxide dissolves in rainwater, to form carbonic acid. The carbonic acid could mobilise organics and/or inorganics in the waste. The method thus entails the extraction of a sample of waste with a saturated solution of carbonic acid.

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4.6.2 International requirements

The United States Environmental Protection Agency (US EPA) identified several potential gaps in the adequacy and appropriateness of their hazardous waste characterization regulations. While the TCLP is most commonly used by the EPA and state agencies to evaluate the leaching potential of wastes and for determining toxicity, they recognized in their Hazardous Waste Characteristic Scoping Study (US EPA: Office of Solid Waste; 1996) that they needed to examine a broader array of leaching procedures in addition to the TCLP, to better predict environmental releases from various waste types and waste management conditions. Notable examples quoted were the inability of the TCLP to predict significant releases under highly alkaline conditions or to media other than groundwater or to serve as a leaching procedure for oily wastes. Other potential gaps identified related to toxicity, reactivity, etc. characteristic definitions. A number of alternative methods have been proposed to address these gaps.

4.6.2.1 Multiple extraction procedure (MEP)

The Multiple Extraction Procedure (MEP) is one test that the agency suggests may better simulate the long term leaching behaviour of alkaline wastes. The MEP involves an initial extraction with water and at least eight subsequent extractions with a synthetic acid rain solution. The MEP is intended to simulate 1 000 years of freeze and thaw cycles and prolonged exposure to a leaching medium. One advantage of the MEP over the TCLP is that the MEP gradually removes excess alkalinity in the waste. Thus, the leaching behavior of metal contaminants can be evaluated as a function of decreasing pH, where the solubility of most metals increases. Currently, the MEP is used in the Agency's de-listing program.

4.6.2.2 Synthetic acid precipitation leach test (SPLP)

The Synthetic Acid Precipitation Leach Test (SPLP) is considered by the Agency for evaluating the leaching of hazardous waste in industrial waste mono-landfills. The SPLP is similar to the TCLP, but the initial liquid-solid separation step has been eliminated and the acetate buffer extraction fluid has been replaced by a dilute nitric acid / sulfuric acid mixture (H_2SO_4: HNO_3, *60:40 w%, pH ±0.2*). The TCLP addresses co-management of industrial and non-industrial wastes in an organic acid environment, a scenario that does not match the disposal setting of many treated wastes, while the SPLP simulates disposal in an acid rain environment.

4.6.2.3 California waste extraction test (Cal WET)

The California Waste Extraction Test (Cal WET) is used to compensate for the low chelating activity of the acetate buffer used in the TCLP that may underestimate the ability of leachate containing chelating agents (ability to bind with and solubilise metal contaminants) to mobilize waste constituents.

The Cal WET was developed by the State of California to classify hazardous wastes. This test uses sodium citrate buffer as the leachate, a 10:1 liquid-to-solids ratio, and a testing period of 48 hours. Cal WET applies a soluble threshold limit concentration (STLC) as the regulatory standard. STLC standards for metal concentrations in the leachate are similar to those for the TCLP. Cal WET also develops a Total Threshold Limit Concentration (TTLC), which is equivalent to the Total Waste Analysis (TWA) procedure. Cal WET is a more aggressive test when compared to the TCLP. That is, Cal WET almost always extracts higher levels of contaminants, and the citrate buffer used in this test has greater chelation effect than the acetate buffer used in the TCLP.

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4.6.2.4 Other shortcomings of TCLP

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Other gaps identified include the fact that TCLP does not account for the oxidation/reduction reactions occurring in landfills. The addition of iron filings to stabilize foundry sand wastes seems to mask the potential leachability of lead by interfering with the TCLP. If metallic iron (iron filings) is added to the waste, the lead concentration in the TCLP extract may be decreased by an oxidation/ reduction reaction to levels below the lead TC level. If, however, the waste is placed in a landfill or surface impoundment, the iron oxidizes over time and loses its ability to further reduce the lead ions. This results in the leaching of lead to the environment.

4.6.2.5 Other leachability tests

Van Herck and Vandecasteele (2001) evaluated a sequential extraction procedure for the characterization and treatment of metal containing solid waste like fly ashes and blast furnace sludge and proposed an adapted procedure. The basic utility of selective sequential extraction is its use of appropriate reagents to release different heavy metal fractions depending on their form.

Fytianos *et al*. (1998) used a cascade-leaching test, at liquid to solid ratios (L/S) ranging between 5 and 100, to determine the leachability of heavy metals in fly ash from coal combustion processes in Greece. They found that the least leachable metals in fly ash were copper and manganese. All fly ash samples exhibited strong alkaline reaction, as indicated by pH values >11.75 at L/S = 10 and contact time of 10min. Manganese showed the least leachability in all samples. Leaching of manganese with maximum concentrations occurred at lower L/S ratios and then decreased with increasing L/S.

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Chang *et al.* (2001) compared three leachability tests viz. TCLP, Extraction procedure (EP) and the American Society for Testing and Materials methods (ASTM), for their ability to extract metals in chemical sludge and incineration bottom ash. They found that metal concentrations from TCLP≈EP>ASTM.

4.6.3 Suitability of current manganese classification systems

Recently the Manganese Committee of the Ferroalloys Association (TFA) opposed the proposal by the USEPA (2000) to add manganese to the group of hazardous constituents in Appendix VII and Appendix VIII, and the associated proposed treatment standards for manganese as a result. The proposed listings included as a hazardous waste, production of titanium dioxide non-wastewaters from the chloride-ilmenite process. In November 2001 the USEPA deferred any final action on all elements of the proposal related to manganese.

The contention is ongoing, and is based on a number of factors including a lower risk assessment level (3.3 mg/day) that implies that that manganese at higher levels is hazardous. It has been put forward that this is flawed, as manganese is not toxic in the usual sense of that word. Rather, manganese is an essential element in all biological systems, including plants, animals, and humans. Manganese is essential for normal neurological development and function. Accordingly, the hazard and risk assessment process for manganese must be inherently different, because fundamental assumptions normally present are not true. One typical assumption is that lower exposure assures a lower probability of adverse affect. In fact, at some point, for nutritionally essential substances, lower exposure results in greater probability of adverse effect.

They also argued that EPA's case for adding manganese to Appendix VIII is further weakened because EPA's survey reports and risk assessment do not reveal the form of manganese that was used in the agency's modeling or discuss how the different forms of manganese affect the potential for exposure. The issue of solubility and chemical form is a critical point. Inorganic manganese compounds are mostly solids and thus are most likely to exist as suspended particulate matter. The tendency of soluble manganese compounds to absorb to soils and sediments can be highly variable. The particle size and solubility associated with manganese compounds varies, and directly influences how and where they are deposited and absorbed (Rodier, 1955). For example, certain conditions favor the formation of manganese dioxide, which is insoluble in water at neutral pH (most water have a pH between 4 and 7 (USEPA 2001). Yet, TFA could find no account given to the critical factor of solubility in EPA's proposal and underlying risk assessment models. For example, in water or soil of pH greater than 8 or 9, the soluble divalent manganese ion is chemically oxidized to the insoluble tetravalent form (EPA Draft Health Assessment) Given that manganese compounds vary widely in solubility, this deficiency undermines the reliability of EPA's risk assessment because solubility is known to affect bio-availability and, therefore, hazard. Moreover, the TFA argued that the treatment standards proposed for manganese are not reasonable based on the amount of manganese present in the environment and because EPA did not account for dilution in the risk assessment model. Manganese in treated leachate and wastewaters will undergo both dilution and absorption prior to contact with groundwater aquifers or surface water bodies. Indeed, TFA also found no mention of EPA consideration of background levels in soils or in natural waters.

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4.7 MANGANESE CHEMISTRY AND GEOCHEMISTRY

4.7.1 Chemistry

Manganese belongs to group VIIA of the periodic table of elements, together with Technetium and Rhenium. It has an atomic structure of $3d^{5}4s^{2}$. Manganese shows the widest range of oxidation states i.e. -I, 0, I, II, III, IV, V, VI, and VII. Among them, the oxidation states of -I, I, III, V and VI are unstable. The most common oxidation states are the II and IV states. Mn (II) state is the most stable and Mn (II) ions exist in the solid, in solution and as complexes. The Mn (II) ion occurs at low redox potentials and low pH.

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Mn (II) salts are generally soluble, while the Mn (IV) state is generally insoluble and occurs predominantly in soils as the oxide MnO_2 (Lee, 1991). Nitrate, sulphate and chloride salts of manganese are fairly soluble in water, whereas oxides, carbonates ($MnCO_3$), phosphates ($Mn_3(PO_4)_2$), sulphides and hydroxides are less soluble (Lee, 1991).

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Low oxidation states are more basic and high oxidation states are more acidic. MnO and Mn_2O_3 are basic oxides and are ionic. MnO_2 is amphoteric and does not exist as Mn^{4+} ions. In alkaline solution Mn (II) readily oxidises to MnO_2. Mn (II) salts can easily be made from MnO_2

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$2MnO_2 + 2\,H_2SO_4 \rightarrow 2MnSO_4 + O_2 + 2H_2O$$

4.7.2 Mineralogy and geochemical occurrence

Commonly occurring minerals, which contain manganese, include pyrolusite (MnO_2), manganite ($Mn_2O_3.H_2O$), rhodochrosite ($MnCO_3$) and rhodonite ($MnSiO_3$). Manganese is not an essential constituent of any of the more common silicate rock minerals, but it can be substituted for iron, magnesium or calcium in silicate structures.

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4.7.3 Geochemistry

The ultimate disposal and subsequent chemical processes, which are expected to occur, are analogous to the geochemical processes, which occur in soils and rocks.

4.7.3.1 Reactivity

Manganese aqueous speciation and solubility

In most ground waters manganese exists principally in the reduced Mn^{2+} form, and in the absence of carbonate and sulphide species, the solubility is controlled by the metal hydroxide solid phase.

$$Mn(OH)_2 \rightarrow Mn^{2+}_{(aq)} + 2OH^-_{(aq)}$$

In an ideal solution the saturated equilibrium relationship is:

$$K_{s\,Mn} = [Mn^{2+}][OH^-]^2 = 10^{-12.9} \text{ at } 25^{o}C$$

These relationships differ in reality because of competing reactions in solution

$$Mn^{2+}_{(aq)} + OH^-_{(aq)} \rightarrow MnOH^+_{(aq)} \quad K = 10^{3.9}$$
$$Mn^{2+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Mn(OH)^-_{3\,(aq)} \quad K = 10^{8.3}$$

The solubility diagram of Mn^{2+} is presented in Figure 4.4 below. It can be seen that the minimum solubility of manganese occurs near pH 12. Since the pH of natural waters is near to neutral, one would expect to find fairly high levels of manganese. However, the presence of carbonate species affects the solubility of Mn^{2+} markedly as it precipitates as the sparingly soluble $MnCO_3$ under certain conditions (Figure 4.4).

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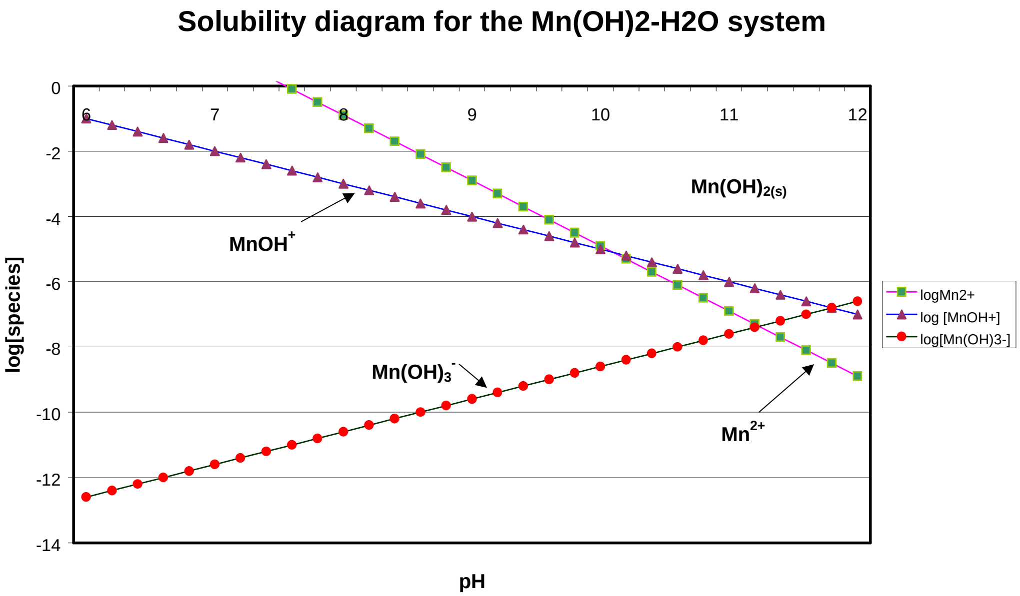

Figure 4.4: Solubility diagram for the $Mn(OH)_2$-H_2O system. The log [species (mole/l)] is plotted against pH

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The dependence of the solubility of manganese on carbonate concentration can be expressed through the following relationships:

$$Mn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Mn(OH)_{2\,(s)} \qquad K_{s\ Mn(OH)2} = 10^{-12.9} \text{ at } 25^oC$$

$$Mn^{2+}_{(aq)} + OH^-_{(aq)} \longrightarrow MnOH^+_{(aq)}$$

$$Mn^{2+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Mn(OH)^-_{3\,(aq)}$$

$$Mn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow MnCO_{3\,(s)} \qquad K_{s\ Mn(CO3)} = 10^{-10.4} \text{ at } 25^oC$$

$$\text{Log}\,[Mn^{2+}] = -10.4 - \log(a2) - \log C_T$$

$$\text{Log}\,[MnOH^+] = pH - 20.5 - \log(a2) - \log C_T$$

$$\text{Log}\,[Mn(OH)_3^-] = 3pH - 44.1 - \log(a2) - \log C_T$$

C_T = total equilibrium carbonic species concentration
a2 = ionization fraction of CO_3^{2-}

In the absence of carbonate or sulphide species, the solubility of manganese is controlled by the metal hydroxide solid phase. However, Figures 4.5 and 4.6 can represent the solubility of manganese in systems having some degree of carbonate alkalinity.

From Figures 4.5 and 4.6 it can be seen that the minimum solubility of $MnCO_3$ occurs near pH 10, and that for a given pH, the solubility of Mn (II) carbonate is inversely proportional to the equilibrium total carbonic species concentration.

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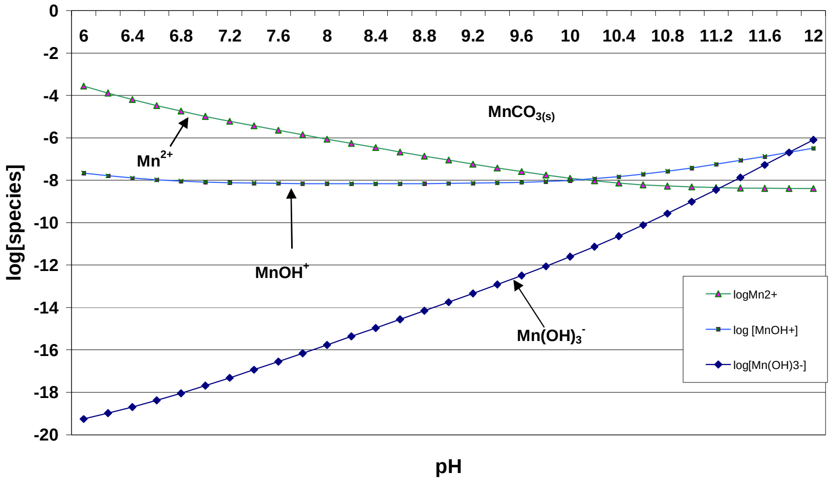

Figure 4. 5: Solubility Diagram for the $MnCO_3$-H_2O system. $C_T = 10^{-2}$M

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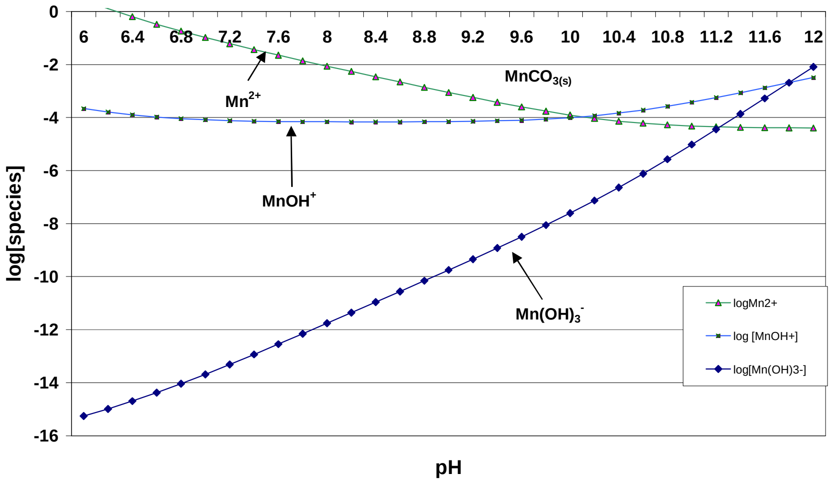

Figure 4.6: Solubility Diagram for the $MnCO_3$-H_2O system. $C_T = 10^{-6}$M

4.7.3.2 Oxidation of manganese

Thermodynamic Stability

Manganese is oxidized rapidly by air under strongly alkaline conditions. In moderately alkaline suspensions $Mn(OH)_2$ is oxidized by air to hausmannite (Mn_3O_4) and, after prolonged oxidation, to manganite, but further oxidation cannot be achieved under these conditions (Bricker, 1965).

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From the equation

$Mn^{2+} + H_2O + 0.5\ O_2 \rightarrow MnO_2 + 2H^+$ $\Delta G^o = -0.88$ kJ

The equilibrium constant, K, is calculated as 2.03, and pH = -0.5 log [Mn^{2+}] - 0.077 - 0.245 log[O_2].

The actual concentration of dissolved O_2 makes little difference to the Mn^{2+} concentration, which is thermodynamically unstable at pH 4 or higher. An example of the relationship between the stability of Mn^{2+} and pH, at concentrations of 0.18 mg/ℓ, is shown in Figure 4.7. However, the stability of Mn^{2+} solutions in the laboratory shows that the oxidation does not proceed at a measurable rate and is thought to be caused by a high activation energy for the oxidation reaction, or the high over potential required for the reduction of molecular O_2.

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Oxidation rates of Mn^{2+} in soils have been found to be proportional to the level of existing reactive manganese oxides in the soil, and it has been proposed that the oxidation is autocatalytic, involving specific adsorption of Mn^{2+} on existing manganese oxide surfaces. Hem (1963), Morgan and Stumm (1964), Wilson (1980), and Sung and Morgan (1981) also found that oxidation was catalysed by MnO_2 and lepidocrocite, and also by any fine particles in soils and waters.

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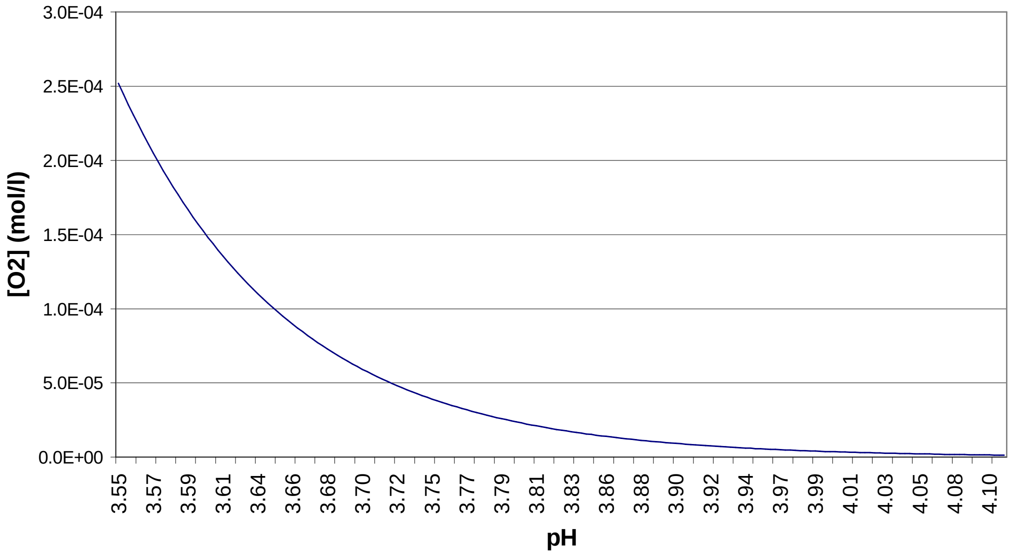

Figure 4.7: pH and [O_2] relationship to stabilise Mn^{2+} at < 0.18 mg/ℓ

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4.7.3.3 Mineral field stability

The Eh-pH diagrams (Figures 4.8 and 4.9) provide a useful device for illustrating the stability fields of the different manganese minerals in an aqueous environment as a function of redox potential and pH. Figure 4.8 has been constructed for typical atmospheric conditions and the relevant chemical equations used to construct the diagram are summarised in Table 4.1.

Figure 4.8 shows the stability fields of the various phases in the system Mn – O – C – H. This diagram was calculated for typical atmospheric conditions and the relevant chemical equations used to construct the diagram are summarised in Table 4.1. The stability field of rhodochrosite indicates that relative low carbon dioxide concentrations are required for this carbonate phase to precipitate. The prevailing pH and Eh conditions at the mining site are such that rhodochrosite

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will crystallise under ambient conditions, as depicted in Figure 4.8. However, Figure 4.9 shows that the stability field of rhodochrosite is extended to lower pH values with increased CO_2 partial pressure. Thus, these diagrams suggest that proper aeration of the waste material before placement would allow Mn^{2+} to be locked into the relative insoluble $MnCO_3$ (rhodochrosite). This provides an effective and economic means of limiting the liberation of manganese into the surrounding ecosystem.

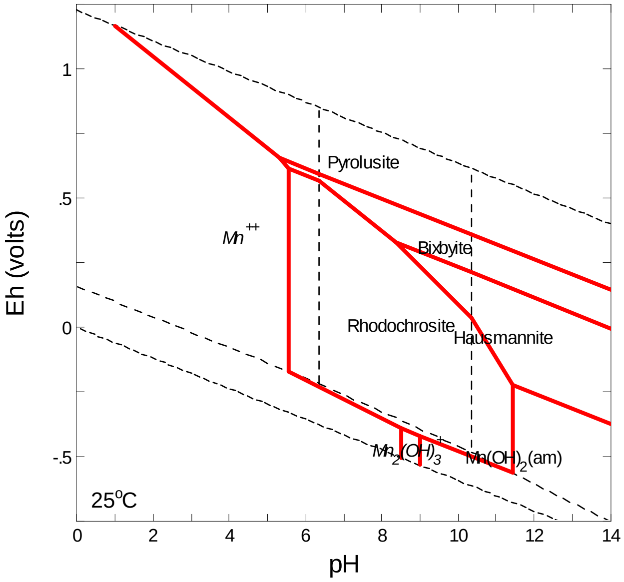

Figure 4.8: Eh – pH diagram depicting the stability fields of the relevant manganese phases under ambient conditions, i.e. T = 25°C, p = 1.013 bar, *a*[H_2O] = 1, *ƒ*[$CO_{2(g)}$] = 0.001

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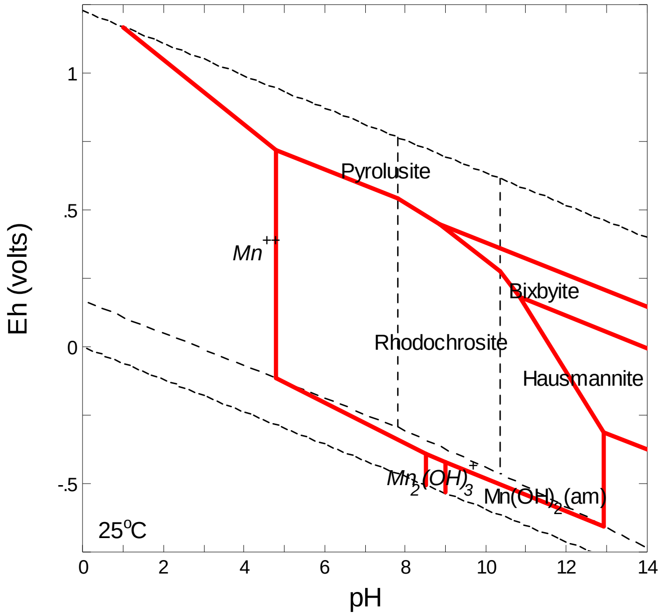

Figure 4.9: Eh – pH diagram depicting the stability fields of the relevant manganese phases under ambient conditions, i.e. T = 25°C, p = 1.013 bar, *a*[H_2O] = 1, *ƒ*[$CO_{2(g)}$] = 1.0

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Table 4.1: Summary of reactions used during the calculation of Figures 4.8 and 4.9

Species & Minerals	Reaction		Log K
Mn^{2+}	Mn^{2+}	$= Mn^{2+}$	0
MnO_4^-	$MnO_4^- + 5e^- + 8H^+$	$= Mn^{2+} + 4H_2O$	127.80
MnO_4^{2-}	$MnO_4^{2-} + 4e^- + 8H^+$	$= Mn^{2+} + 4H_2O$	118.41
$Mn(OH)_2$	$Mn(OH)_2 + 2H^+$	$= Mn^{2+} + 2H_2O$	22.20
$Mn(OH)_3^-$	$Mn(OH)_3^- + 3H^+$	$= Mn^{2+} + 3H_2O$	34.21
$Mn(OH)_4^{2-}$	$Mn(OH)_4^{2-} + 4H^+$	$= Mn^{2+} + 4H_2O$	48.29
$Mn_2(OH)_3^+$	$Mn_2(OH)_3^+ + 3H^+$	$= 2Mn^{2+} + 3H_2O$	23.90
$Mn_2OH_3^+$	$Mn_2OH_3^+ + H^+$	$= 2Mn^{2+} + H_2O$	10.56
$MnCO_3$	$MnCO_3 + H^+$	$= Mn^{2+} + HCO_3^-$	6.83
$MnHCO_3^+$	$MnHCO_3^+$	$= Mn^{2+} + HCO_3^-$	-1.27
$MnOH^+$	$MnOH^+ + H^+$	$= Mn^{2+} + H_2O$	10.59
Birnessite	Birnessite $+ 12e^- + 28H^+$	$= 8Mn^2 + 19H_2O$	269.68
Bixbyite	Bixbyite $+ 2e^- + 6H^+$	$= 2Mn^{2+} + 3H_2O$	50.19
Hausmannite	Hausmannite $+ 2e^- + 8H^+$	$= 3Mn^{2+} + 4H_2O$	61.32
Manganite	Manganite $+ e^- + 3H^+$	$= Mn^{2+} + 2H_2O$	25.41
Manganosite	Manganosite $+ 2H^+$	$= Mn^{2+} + H_2O$	17.93
$Mn(OH)_2$(am)	$Mn(OH)_2$(am) $+ 2H^+$	$= Mn^{2+} + 2H_2O$	15.30
$Mn(OH)_3$(c)	$Mn(OH)_3$(c) $+ e^- + 3H^+$	$= Mn^{2+} + 3H_2O$	31.93
Pyrolusite	Pyrolusite $+ 2e^- + 4H^+$	$= Mn^{2+} + 2H_2O$	41.56
Rhodochrosite	Rhodochrosite $+ H^+$	$= Mn^{2+} + HCO_3^-$	-0.24
Todorokite	Todorokite $+ 10e^- + 24H^+$	$=7Mn^{2+} + 15H_2O$	226.07

A comprehensive list of all important manganese reactions extracted from the PHREEQC Modelling package llnl data base is given in Appendix A.

4.8 CASE STUDY

4.8.1 Wet scrubber dust manganese immobilization

In a steel or ilmenite processing facility, the smelter feed stack can contain manganese either in the form of MnO_2 or in the form of impurities in ilmenite ($FeTiO_3$). Smelter dust originates in the furnace and forms part of the off-gas, it is transferred through ducts to a wet scrubber where it is removed from the off-gas into water.

It has been demonstrated (PHD, 2000) that either rhodochrosite or pyrolusite will form in the wet scrubber dust during the oxidation of Mn^{2+} in the smelter. However, considering the thermodynamic stability of Mn^{2+} as a function of pH it is reasonable to assume that MnO_2 will not be reduced to Mn^{2+} at pH > 4. Thus if WSD is pre-treated to ensure the full oxidation of Mn^{2+} to MnO_2 this would inhibit the mobilisation of Mn^{2+}.

Aeration of the manganese-compounds is a means to separate them from the system. It is put forward that the nature of the smelting process and subsequent wet scrubbing of the smelter dust may sufficiently aerate this material to immobilise the manganese in the dust. Past experiences indicate that this type of process does aerate the dust sufficiently to allow atmospheric CO_2 equilibration with the dust, thus resulting in the formation of rhodochrosite. Confirmation of this will be required once the process is in operation. The prevailing pH conditions within the mining site are pH > 6 and so MnO_2 is not expected to be reduced under these conditions.

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Furthermore, it is most likely that rhodochrosite would be the stable phase to form during the oxidation of Mn^{2+} under atmospheric conditions, together with a slight increase in pH.

In view of the above facts, it is unlikely that Mn^{2+} would be available for transport into the surrounding area. Instead, manganese would precipitate either as pyrolusite or as rhodochrosite. Both these phases are unlikely to dissolve under the prevailing conditions at the waste dump.

The mobility of manganese, which may be expected in the absence of the addition of stabilising material, may be assessed through analysis of the stability field diagrams (Figures 4.8 and 4.9). These fields confirm that at pH above 5.5 and under the expected range of redox potentials that may be expected in the mined area, rhodochrosite will be a very stable phase.

4.8.2 Disposal options and validation

It was proposed by others that wet scrubber dust (WSD) be disposed of with lime addition (PHD, 2000). This was questioned on the basis that the reasoning for the lime addition was not based on an analysis of the fate of the waste in the long term, in other words, the kinetic implications of the addition of lime were not considered. The discussions above serve to illustrate the point that the ultimate fate of manganese in a waste stream cannot be simply extrapolated from basic chemical tests but should take into account the complex chemistry of manganese in the natural environment. This section describes the considerations used in determining whether any chemical additives are necessary to stabilize manganese, and if so, which is the most appropriate additive.

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4.8.2.1 Lime addition

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The disposal of WSD with the addition of 10 % lime was proposed by Ockie Fourie Toxicologists (OFT), since it was found that on performing TCLP tests, with lime addition at 5 % lime increments, manganese became immobilized at 10 % lime addition. The same test was performed using ARLP, and immobilization of manganese was found to be effective at a 5 % lime addition. However, OFT recommended the use of TCLP test results and thus a 10% lime addition was recommended.

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PHD advised Ticor that this was not necessarily a valid approach to stabilizing manganese in the WSD since lime is highly reactive and may not stabilize manganese in the long term after lime is lost from the system (in other words, the kinetic behaviour of the two materials may differ substantially). In addition to this it was suggested that the possibility of manganese remaining immobile if disposed under certain conditions may exist and required further investigation. Furthermore, lime addition serves only to raise the pH, and immobilisation would thus be effected by the precipitation of $Mn(OH)_2$ and by promoting the oxidation of Mn (II) to MnO_2. However, under reducing conditions the manganese may become mobilized or the Mn^{2+} in the waste may not be oxidized to MnO_2 at all.

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It was proposed by PHD that the fate of manganese in the waste should be evaluated in order to determine whether the addition of a stabilizing material is in fact necessary and if so, whether lime is the most effective means of doing so.

The leach test results on which OFT based their conclusions are summarised below.

Acid Rain Test

– 0% Lime: 12.1 ppm Mn
– 5% Lime: < 0.05ppm Mn

TCLP Test

– 0% Lime: 24 ppm Mn
– 5% Lime: 26 ppm Mn
– 10% Lime: <0.05 ppm Mn

WSD will not likely be disposed in a site that contains organic wastes. Thus the ARLP appears to be the more appropriate test under the circumstances. However, due to the chemical interactions that occur between Mn^{2+} and CO_3^{2-}, the ARLP on a sample containing lime is considered inappropriate since the lime acts to neutralize the acidity of the acid rain extraction solution, and results in the precipitation of $MnCO_3$. The purpose of the ARLP is to simulate worst case conditions to which a waste may be exposed and would only have been valid in this case if lime was not expected to be relatively short-lived.

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4.8.2.2 Calcite / dolomite addition

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It was thought that if the addition of a stabilizing material was necessary, that this would best be achieved through the addition of either calcite or dolomite. This was decided for the following reasons:

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- These minerals are much less soluble than lime and would thus present a longer-term stabilization solution for manganese by increasing the pH of the system, thereby promoting the oxidation of Mn (II) to MnO_2. However, this is limited kinetically under reducing conditions and may pose a limitation if WSD is disposed in a reducing environment without prior aeration.
- They contribute significantly to the carbonate alkalinity of the system, and this alkalinity would increase with decreasing pH. Under reducing conditions, where MnO_2 may become reduced to Mn^{2+} thus mobilizing manganese, $MnCO_3$ precipitation may still be an effective immobilisation mechanism.
- Calcite is soluble at pH < 7.8, and deposits at pH higher than this. Thus the mixing of calcite with the smelter dust would ensure that the pH is buffered to pH > 7.8 and would dissolve to produce alkalinity at levels pH lower than this.

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4.8.2.3 No chemical addition

The lowest alkalinity and pH observed in ground water at the mining site is 20.1 mg/ℓ ($CaCO_3$) and 6.1, respectively. If the WSD were to be disposed in such a site, and in the absence of other geochemical processes, manganese would be expected to be mobilized to a significant degree. This can be indicated by the solubility diagram constructed for C_T = 1.1 x 10^{-3} M which will result at this alkalinity and pH (Figure 4.10). Manganese concentrations could reach 1.7x10^{-3}M (84 mg/ℓ) at pH 6.1.

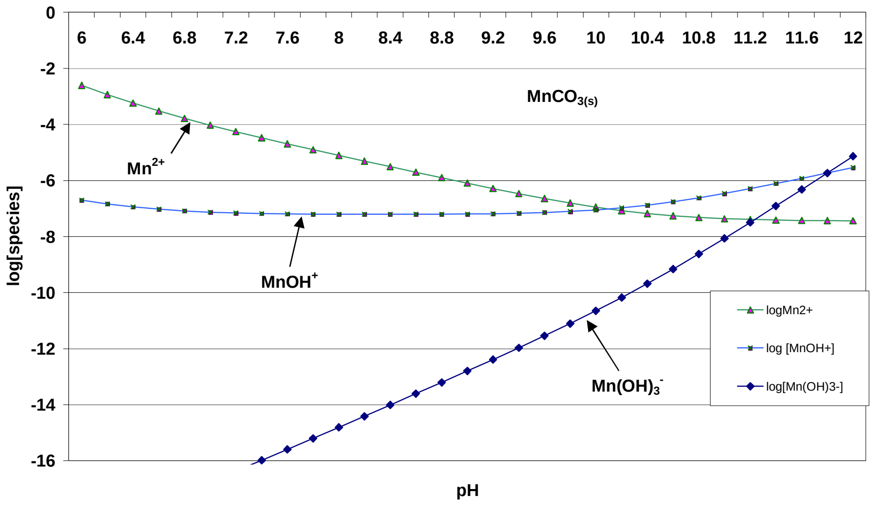

Figure 4.10: Solubility diagram for the $MnCO_3$-H_2O system. $C_T = 1.1 \times 10^{-3}$ M

It is clear from the above diagrams that either rhodochrosite or pyrolusite will form during the oxidation of Mn^{2+}. However, considering the thermodynamic stability of Mn^{2+} as a function of pH (Figure 4.10) it is reasonable to assume that MnO_2 will not be reduced to Mn^{2+} at pH > 4. Thus if WSD is pre-treated to ensure the full oxidation of Mn^{2+} to MnO_2 this would inhibit the mobilization of Mn^{2+}. Aeration of the manganese-compounds is the best manner to separate them from the system. However, the nature of the smelting process and subsequent wet scrubbing of the smelter dust may sufficiently aerate this material to immobilize the manganese in the dust. Past experiences indicate that this type of process does aerate the dust sufficiently to allow atmospheric CO_2 equilibration with the dust, thus resulting in the formation of rhodochrosite. Confirmation of this will be required once the process is in operation. The prevailing pH conditions within the mining site are pH > 6, and MnO_2 would not be expected to be reduced under these conditions.

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Furthermore, it is most likely that rhodochrosite would be the stable phase to form during the oxidation of Mn^{2+} under atmospheric conditions, together with a slight increase in pH.

In view of the above facts it is unlikely that Mn^{2+} would be available for transport into the surrounding area. Instead, manganese would precipitate either as pyrolusite or as rhodochrosite. Both these phases are unlikely to dissolve under the prevailing conditions at the waste dump.

The mobility of manganese, which may be expected in the absence of the addition of stabilizing material, may be assessed through analysis of the stability field diagrams (Figures 4.8 and 4.9). These fields confirm that at pH above 5.5 and under the expected range of redox potentials that may be expected in the mined area, rhodochrosite will be a very stable phase.

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4.8.2.4 Summary

The reduction / oxidation state of the environment will be predominantly controlled by the conditions in the residue dam or landfill. The conditions are expected to be mildly reducing as a result of continuous deposition of water on the surface. If manganese in a waste stream is in the form of rhodochrosite, it would already be in a reduced state and reducing conditions would thus not be expected to further mobilize this form of manganese.

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Adsorption reactions are expected to control the mobility of any metals since the residue dam will be constructed of clay and will be dominated by the residue dam matrix rather than from the specific waste stream, whether they be co-disposed or mono-landfilled on the dam. Adsorption reactions may occur in the presence of manganese and iron oxyhydroxides –if this mechanism were to play a role, this role would if anything be beneficial and would not lead to adverse effects in terms of generating toxic leachate (PHD, 2000).

5. EXPERIMENTAL RESEARCH PLAN

One of the primary objectives of this study was to provide scientific insight and comment on inorganic manganese speciation of pyrometallurgical scrubber dust and to infer how it behaves in the environment. A detailed environmental characterization of the manganese containing wastes from pyrometallurgical processes was carried out applying standard analytical techniques and leaching tests. Moreover, the factors impacting on metal leachability, viz. pH, liquid to solid ratio, kinetics, oxidation-reduction potential, complexation, and particle size were also investigated.

A number of methods can be used to predict the amount of manganese that leaches from a waste. This study employed batch and column leach studies, geochemical modelling using waste/soil characteristics and knowledge of manganese chemistry.

5.1 RESEARCH PLAN

A summary of the experimental plan is given in Figure 5.1.

5.2 METHODS

Various standards methods were used to assess the scrubber dusts and provide input data for the geochemical modelling exercise. A summary and brief description of the methods used in this project are provided in section 5.2.1.

5.2.1 Chemical characterisation of solid samples

5.2.1.1 Paste pH

Paste pH was performed on selected solid samples to determine the inert pH of the solid samples. Weigh off 1 g of sample and mix into 10 ml of distilled water. Wait for a period of 24 h and measure the pH of the sample (Sobek *et al.,* 1978).

5.2.1.2 Aqua reqia digestion and metal concentration determinations

Samples were submitted to Waterlab for aqua regia digestions (Method 3111B; APHA, 1998) whereafter total concentrations of selected metals where determined using inductively coupled plasma spectroscopy (ICP) (Method 3125; APHA, 1998).

5.2.1.3 Total solid and moisture content

Moisture content and total solid determinations, measured at 103°C, were conducted by a commercial accredited analytical facility (Waterlab; Horowitz, 1991).

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5.2.1.4 Loss on ignition

Loss on ignition at 1000 °C was determined at Waterlab (Horowitz, 1991).

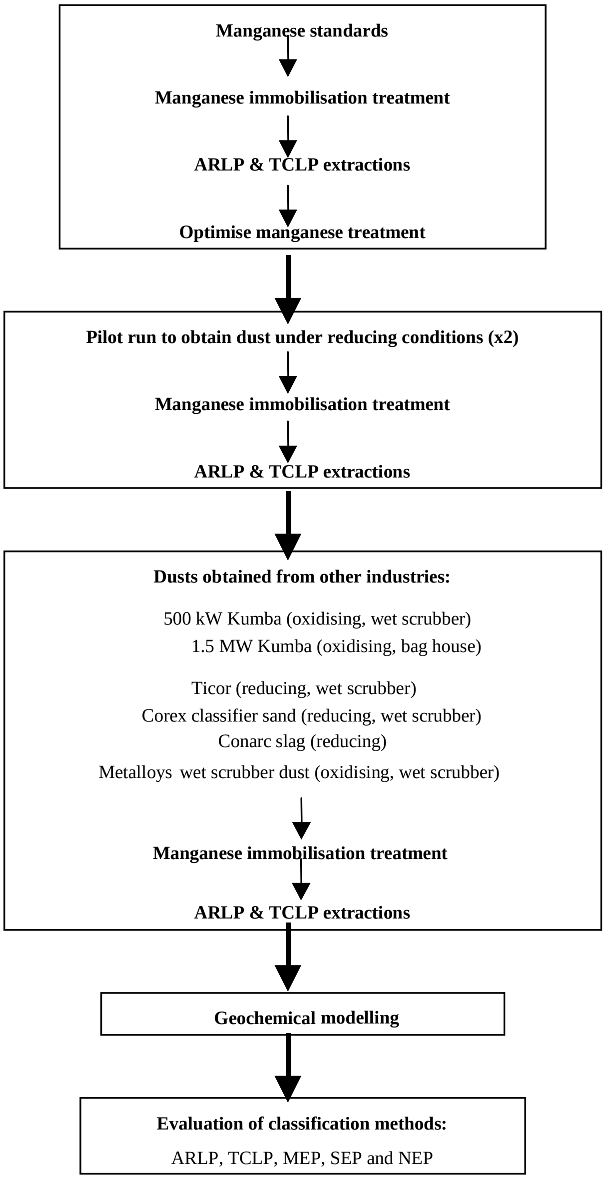

Figure 5.1: Flow diagram of the experimental research plan

5.2.1.5 Particle size analysis

Particle size distribution analyses of the scrubber dusts by (wet screening) were performed at Waterlab (Horowitz, 1991).

5.2.1.6 X-ray diffraction (XRD) and X-ray fluorescence (XRF)

Mineralogical analysis using XRD and XRF analyses were conducted on selected samples (Waterlab) to identify the manganese compounds associated with the dust. XRD and XRF analyses were also used as input data for modelling the long-term effects of the case study dusts and various treatment options.

5.2.1.7 Scanning electron microscopy (SEM)

SEM was performed on the scrubber dusts obtained from the 200 kW pilot run to determine the effect of the wet scrubber temperature on the types of manganese formed in the dust. Leonie Reyneke (Kumba Resources) was responsible for conducting SEM analysis, using the facilities at the University of Pretoria.

5.2.2 Chemical characterisation of liquid samples

5.2.2.1 pH

pH determinations were performed at the PHD Analytical Facility using a Zeiss pH/redox meter 300 (Method 4500-H^+B; APHA, 1998).

5.2.2.2 Alkalinity

Alkalinity determinations were performed at the PHD Analytical Facility as prescribed in Method 2320 B (APHA, 1998).

5.2.2.3 Electrical conductivity

Electrical conductivity was determined at the PHD Analytical Facility using a Yokogawa SC82 meter (Method 2510 B; APHA, 1998).

5.2.2.4 Sulphate concentration

Sulphate concentration determinations were performed at the PHD Analytical Facility using ion chromatography (Methrom 790, Swiss Lab) (Method 4020; APHA, 1998).

5.2.2.5 Metal concentrations

Metal concentrations of the liquid samples were determined at the PHD Analytical Facility using atomic absorption (Method 3111; APHA, 1998).

5.2.3 Hazard classification of the manganese wastes

A number of chemical extraction methods were used to classify the toxicity of the manganese containing wastes.

5.2.3.1 Acid Rain Leaching Procedure (ARLP)

The PHD Analytical Facility performed the extractions using carbonic acid prepared by Waterlab, in accordance with the waste classification series method published by DWAF (1998) (see Figure 5.2).

5.2.3.2 Toxicity Characteristic Leaching Procedure (TCLP)

The PHD Analytical Facility was responsible for the TCLP extractions according to the waste classification series method published by DWAF (1998) (see Figure 5.3).

5.2.3.3 Multiple Extraction Procedure (MEP)

MEP was performed at the PHD Analytical Facility (USEPA, 1986) to assess the long-term stability of the wastes to acid leaching. The wastes are subjected to leaching according to the Extraction Procedure Toxicity Test protocols and then the solids are re-extracted with a synthetic solution simulating acid rain conditions eight times (see Figure 5.4).

5.2.3.4 Sequential Extraction Procedure (SEP)

The modified three-step sequential extraction procedure as described by Coetzee *et al.* (1995) was used (see Figure 5.5). Speciation of the toxic elements contained in the wastes in soluble or readily available form (exchangeable, carbonate fractions or reducible fractions etc) is determined with the different extraction media.

5.2.3.5 Neutral Extraction Procedure (NEP)

The method protocol for ARLP was used for NEP extractions (DWAF, 1998), but the carbonic acid was replaced with acetate buffer (pH 4.2 – 4.5) supplied by Rochelle Chemicals (see Figure 5.6). This method is used by the Institute for Water Quality Studies (IWQS) as a preliminary leach assessment tool (personal communications- Philip Kempster).

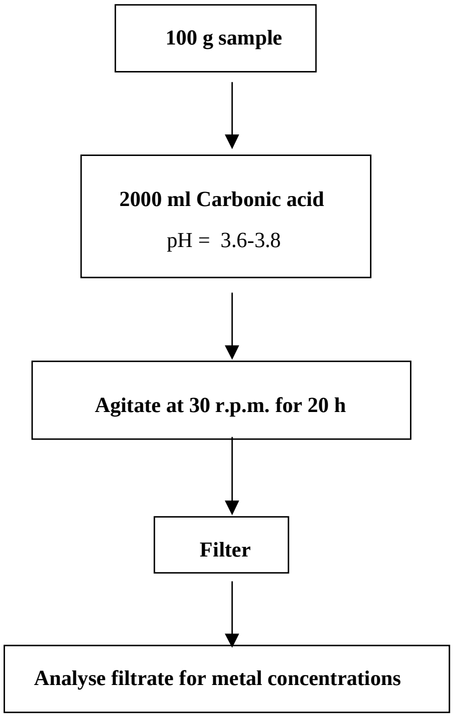

Figure 5.2: Schematic representation of the Acid Rain Leaching Procedure (ARLP)

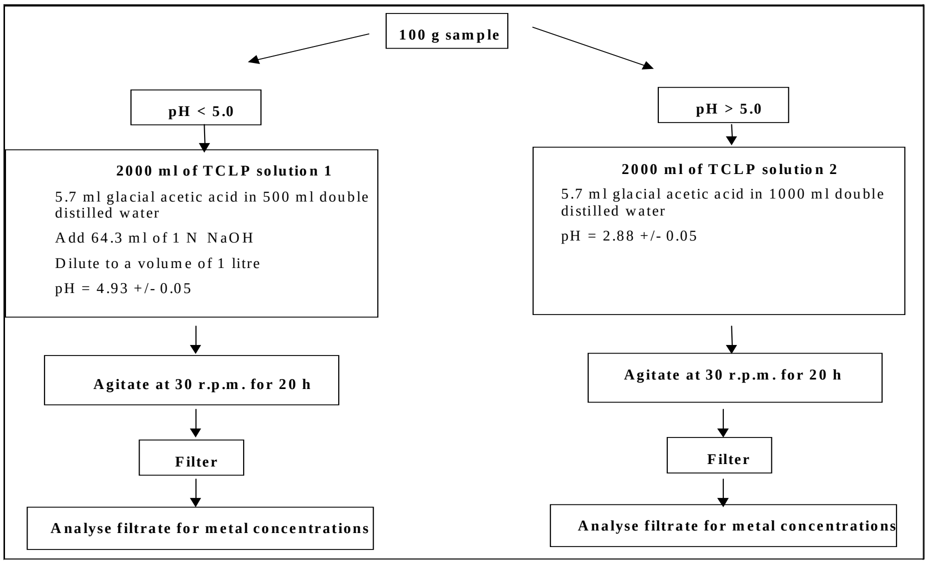

Figure 5.3: Schematic representation of the Toxicity Characteristic Leaching Procedure (TCLP)

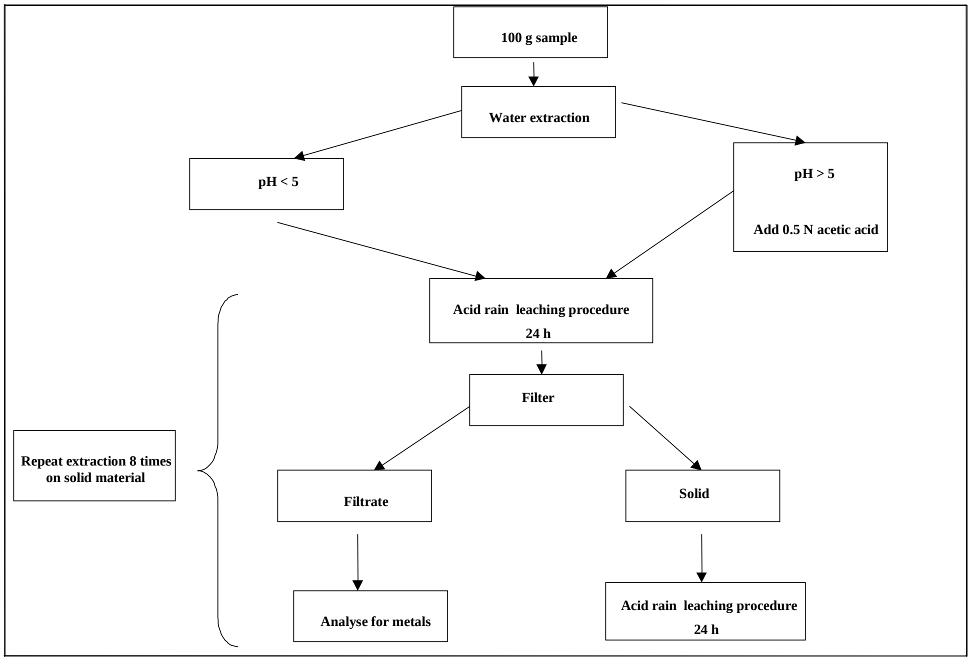

Figure 5.4: Schematic representation of the multiple extraction procedure (MEP)

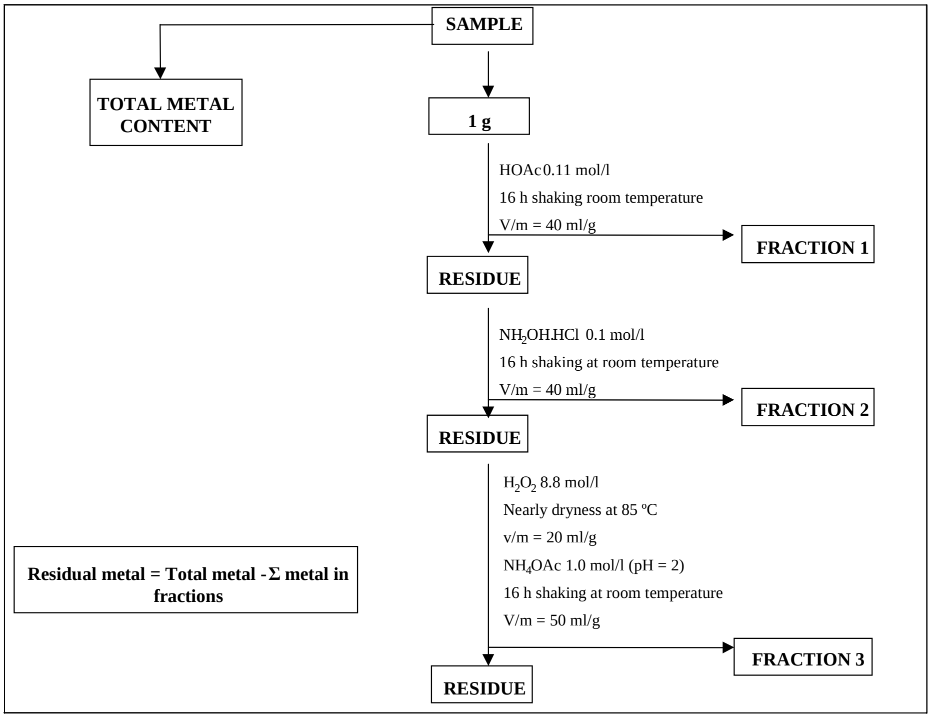

Figure 5.5: Schematic representation of the sequential extraction procedure (SEP)

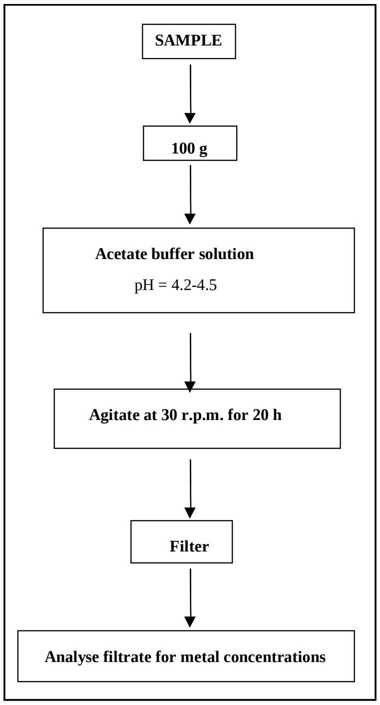

Figure 5.6: Schematic representation of the neutral extraction procedure (NEP)

5.2.3.6 Water leaching

One scrubber dust produced under oxidising conditions and one produced under reducing conditions were subjected to water leaching and analyzed for metal concentrations using atomic absorption (Horowitz, 1991). These results were used as input parameters for the geochemical model.

5.2.4 Scrubber dust and manganese immobilisation treatment

Batch tests were also conducted to examine the relative solubilities of manganese in samples untreated and immobilized with lime, dolomite and calcite or other selected stabilisation techniques (e.g. oxidisers).

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Samples were subjected to chemical treatment at different concentrations (refer Table 5.1). The chemical was manually mixed in with the sample and the mixture left for a period of 24 h before it was subjected to one of the extraction procedures (Section 5.2.3).

The following chemicals were investigated as treatment options to immobilise manganese:

- Lime (Ca (OH)$_2$ (Rochelle AR Grade, Batch #1401033 cc, Min 97%)
- Raw dolomite (Mg-CaCO$_3$) (provided by Iscor- Van der Bijl)
- Burnt dolomite (Mg-CaCO$_3$) (provided by Iscor- Van der Bijl)
- Calcite (CaCO$_3$) (Rochelle AR Grade, Batch #5600, Min 99.5%)
- Sodium hypochlorite (NaOCl) (Rochelle AR Grade, Batch #10092sh- 150g available chlorine per litre) (10-15%)
- Desulphurisation slurry (provided by Iscor - Van der Bijl).

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Lime, calcite and the desulphurisation slurry were sent to Waterlab for total manganese and iron determinations.

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<#>Raw dolomite (Mg-CaCO$_3$) (provided by Iscor- Van der Bijl)¶
<#>Burnt dolomite (Mg-CaCO$_3$) (provided by Iscor- Van der Bijl)¶
<#>Calcite (CaCO$_3$) (Rochelle AR Grade, Batch #5600, Min 99.5%)¶
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<#>Desulphurisation slurry (provided by Iscor - Van der Bijl).¶
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Table 5.1: Chemical treatment dosage applied

Chemical applied	**Concentration of chemical application (%) (w/v)**
No treatment	0.0
Lime	5.0
	10.0
Burnt Dolomite	5.0
Raw dolomite	5.0
Calcite	37.5
Sodium hypochlorite *(10-15 % solution)*	1.0 (v/v)
	9.0 (v/v)
Desulphurisation slurry	5.0
	10.0

The effect of the iron: manganese (Fe: Mn) ratio in the dust sample was also investigated. The addition of iron chloride in the ratio Fe: Mn 40:1 to the 200kW and 1.5 MW scrubber dust trail samples was evaluated under the various leaching procedures identified.

5.2.5 Geochemical modelling

Geochemical modelling of the case study scrubber dusts obtained under dry-oxidizing conditions and wet-reducing conditions was conducted. The aims of the modelling exercise were to assist in determining the effect of environmental and process conditions on stability and solubility of manganese containing waste i.e.

- Stability analysis of manganese species on activity-pH diagrams;
- Kinetic modelling of specific case study for long-term water quality prediction; and
- Risk assessment of identified management immobilisation strategies (Table 5.1) in the long term

ACT2 of the Geochemist's Workbench software was used to carry out manganese stability field analysis. REACT of the same package was used for kinetic modelling. PHREEQC version 2 was used for speciation of aqueous species in solution.

5.3 SAMPLES

Samples classified and characterised in this research project included:

- Inorganic manganese standards (pure form)
- Pilot plant study dust samples
    - 200kW furnace-wet scrubber (reducing conditions)
    - 500Kw furnace-wet scrubber (oxidising conditions)
    - 1.5 MW furnace-dry-baghouse (oxidising conditions)

- Other pyrometallurgical industry dust samples (full-scale):
    - Ticor - wet scrubber (reducing conditions)
    - Saldana Steel - Corex classifier sand – wet scrubber (reducing conditions)
    - Saldana Steel - Conarc slag (reducing conditions)
    - Metalloys – wet scrubber (oxidising conditions)

5.3.1 Inorganic Manganese Standards (pure form)

Standard manganese solutions representing the different forms of manganese of interest were prepared to determine the effect of different immobilisation methods on different pure forms of manganese.

The objectives of this section of the study were therefore to:

- select manganese immobilisation treatment options
- evaluate the suitability of the selected treatment options for manganese immobilisation
- determine the effect of the immobilisation treatment options on different forms of manganese.
- determine the concentrations at which chemical treatment options need to be applied to achieve effective manganese immobilisation.

The results obtained were then applied to the manganese containing samples obtained from both pilot studies and full-scale industries (Chapter 6).

- manganese chloride ($MnCl_2.4H_2O$; Analytical grade (AR); Batch: 23072MC; 99%)
- manganese carbonate ($MnCO_3$; AR grade; Batch: 08420LO; 99.9 %)
- manganese dioxide ($MnO_{2;}$ AR grade; Batch: 504088-032)

A standard manganese solution (1000 mg/ℓ as manganese) prepared using manganese chloride was also purchased from Rochelle Chemicals (AR grade; Batch 2241) and diluted to obtain a manganese concentration of 100 mg/ℓ.

Soluble manganese and iron determinations were performed on the standard manganese solutions prepared.

Distilled water (Electrical conductivity of 6.21 µS/cm) was used as a blank sample. Soluble manganese and iron determinations were performed on the distilled water.

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<#>Ticor – wet scrubber (reducing conditions)¶
<#>Saldana Steel - Corex classifier sand – wet scrubber (reducing conditions)¶
<#>Saldana Steel - Conarc slag (reducing conditions)¶
<#>Metalloys – wet scrubber (oxidising conditions)¶
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5.3.2 Case study samples- smelter scrubber dust

Both wet and dry scrubber dust were collected during pilot plant trials and analyzed. A full description of the analytical programme for these samples is attached as Appendix B.

5.3.2.1 Production of a wet scrubber dust sample under reducing conditions (200kW)

A pilot scale plant was commissioned with the intention of replicating the full-scale plant conditions as closely as possible. This included the removal of the post combustion chamber and the installation of a wet dust scrubbing system (Figure 5.7 and 5.8).

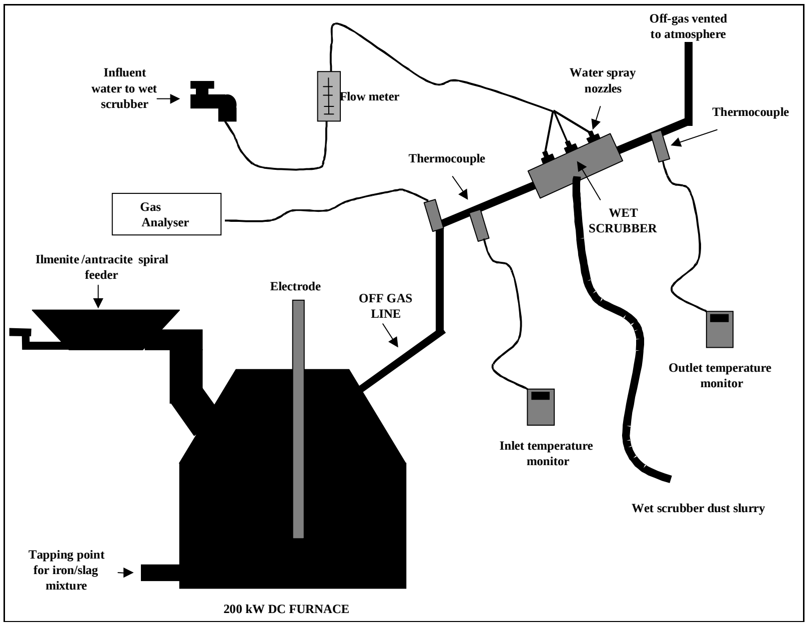

Figure 5.7: Schematic diagram of the experimental configuration used for the collection of wet scrubber dust

Figure 5.8: The 200 kW DC furnace

Two smelting trials were carried out in the 200 kW DC furnace located at the Kumba Pilot Plant facility in Pretoria West during November 2002. The first trial was operated under similar conditions to that used in April 2001 for the wet scrubber dust produced for PHD (Table 5.2). During the second trial, the effect of temperature of the wet scrubber was investigated by increasing the inlet water flow rate (2X) and thus cooling the dust down at a faster rate (Table 5.2). An iron heel was melted in the furnace at start-up. This was done to heat the furnace up, provide good electrical contact with the furnace anode and to provide a liquid bath to feed into. For both trials ilmenite (from Hillendale) and anthracite (from Zululand Anthracite Collieries) were used at a mass ratio of 10 ilmenite: 1.2 anthracite. The furnace was manually charged on a continuous basis.

Table 5.2: Trial design parameters of the two pilot runs

1.1 PARAMETER	**Trial 1**	**Trial 2***
Mass of ilmenite (kg)	80.0	100.0
Mass of anthracite (kg)	9.6	12.0
Duration of trial (min)	80.0	115
Temperature inside furnace (°C)	1650-1750	1650-1750
Average scrubber inlet temperature (°C)	180	114
Average scrubber outlet temperature (°C)	63.6	48.9
Water flow to scrubber (l/h)	220	393
Volume of scrubber effluent collected (l)	310	755

*Foaming occurred in the furnace and the trial was stopped for a period of 25 minutes before ilmenite/anthracite feeding commenced again.

The dust produced during the smelting process, together with the process gas (carbon monoxide), was then transported through the sealed off gas pipe (Figure 5.8 and Figure 5.9). A wet scrubber was installed into the off-gas pipe approximately 3 meters from the furnace. The wet scrubber was equipped with water spray nozzles. The dust was then collected as slurry using sample collection vessels for further processing.

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Figure 5.9: Off-gas line with wet scrubber

Thermocouples were located before and after the wet scrubber and temperature was logged at various intervals (Appendix C). A flow meter was inserted into the feeding line of the wet scrubber and water flow logged at various intervals (Appendix C).

Samples of the iron used for start-up, ilmenite, anthracite, a mixture of ilmenite and anthracite were obtained.

The wet scrubber effluent was discharged through a pipe into buckets. The buckets were filled until they overflowed, a sealing lid was then placed over the bucket and the lid was then taped to the bucket in an attempt to eliminate oxygenation during transportation. Half of the scrubber slurry obtained from each trial was sent to Waterlab for filtration and drying of the slurry while the other half was sent to the PHD Analytical Laboratory for flocculation.

The scrubber slurry was vacuum filtered using 0.45 µM membrane filters and the dust dried at 50 °C (Waterlab). Ferric chloride (42 %) was supplied by Ticor for flocculation and applied at a dosage rate of 10 mg/ℓ.

5.3.2.2 Pilot run – producing scrubber dust under oxidising conditions

Two other pilot plants, consisting of a 500 kW and a 1.5 MW smelter, respectively, were commissioned at the Kumba Test Facility for the production of scrubber dust under oxidising conditions (see Figure 5.10 and 5.11).

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Figure 5.10: 500 kW furnace

Figure 5.11: 1.5 MW furnaces

The 500 kW smelter was fed with 250 kg/h ilmenite and 32.5 kg/h anthracite during 13-18 October 2002. Temperatures in the smelter ranged between 1650 and 1750 °C while the temperature in the off-gas system averaged 250 °C. The off-gas line of the 500 kW smelter was connected to a wet scrubber and the dust collected as a wet scrubber dust slurry. The flow rate of the influent water to the wet scrubber was not measured.

A mixture of ilmenite and anthracite (ratio 100 kg ilmenite:12.6 kg anthracite) was used to feed the 1.5 MW smelter over a period of 14 days. This furnace is equipped with a combustion chamber where carbon monoxide is combusted using a pilot flame. The combustion output temperature averaged 1226 °C. From the combustion chamber the off-gas moved through the rest of the off-gas unit where it is cooled before entering the baghouse. The average temperature before the baghouse is 97 °C. The analysis programme for the 500kW and 1.5MW scrubber dust samples is provided in Appendix B.

Table 5.3: Chemical analyses of some of the parameters obtained during the 500 kW and 1.5 MW trial runs (Results are similar for both)

Parameter	Analyses and concentration
Average ilmenite analysis	Fe_2O_3 = 51.10 % MnO = 1.24 %
Anthracite analysis	MnO = 0.09 %
Dust as % of ilmenite feed	3.95 %
Dust analysis	FeO = 26.16 % MnO = 3.5 %
Slag as % of ilmenite feed	51.81 %
Slag analysis	FeO = 10.57 % MnO = 1.69 %
Metal as % of ilmenite feed	33.32 %
Metal analysis	Fe = 98.89 % Mn = 0.041 %

5.3.3 Other pyrometallurgical industrial dust samples

Samples were obtained from three pyro-metallurgical production plants:

- Wet scrubber dust (Ticor)
- Corex classifier sand (Saldana Steel)
- Cornarc slag (Saldana Steel)
- Wet scrubber dust (Metalloys-Samancor).

The process details and dust classification data, where available, that were provided to the project team by these production companies are given in Appendix D.

The samples obtained from other industries were also subjected to TCLP and ARLP to characterize and classify the manganese and iron mobility of the samples (with and without treatment).

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<#>Corex classifier sand (Saldana Steel)¶
<#>Cornarc slag (Saldana Steel)¶
<#>Wet scrubber dust (Metalloys-Samancor).¶

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6. INORGANIC MANGANESE CONTAINING WASTE

6.1 CHARACTERISATION AND CLASSIFICATION OF INORGANIC MANGANESE CONTAINING WASTE

This chapter discusses the primary level risk assessment conducted for the scrubber dust waste stream samples. The waste can be termed “altered” which implies that there has been a mineralogical change from the natural state of the furnace feed materials.

The scrubber dust samples were analysed as required by the “ *Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste”* (DWAF, 1998). Both the ARLP and TCLP procedures were used. However, since this waste is inorganic in nature, the appropriate test procedure is the ARLP. Leachable elements (manganese and iron) concentrations were compared to the acceptable risk limits published by DWAF and the estimated environmental concentration evaluated (see Appendix E). This was calculated for the untreated sample and treated sample using various immobilisation chemical addition measures identified during the literature search (refer to Chapter 4).

6.1.1 Inorganic manganese standards (pure form)

In order to collect some baseline data, a number of pure inorganic manganese standards, representing the different forms of manganese of interest, were purchased. They included manganese chloride ($MnCl_2$), manganese dioxide (MnO_2), and manganese carbonate /rhodocrosite ($MnCO_3$).

100 mg manganese/ℓ solutions were prepared of each inorganic manganese compound. These solutions were then characterised by subjecting it to the ARLP and TCLP extraction procedures. Standards, with and without treatment to immobilise the manganese under acidic conditions, were tested. Immobilisation treatment chosen for this project included the addition of lime, dolomite (raw and burnt), calcite, hypochlorite and a desulphurisation slag (CaO-CaS). The latter, is another waste stream produced at the full-scale pyrometallurgical plant and if proved effective in stabilisation of manganese in the dust, could be mixed with the dust and provide an alternative integrated waste management option for the company.

Negative controls included in the ARLP extraction experiments showed that the raw dolomite released a significant amount of manganese (24.5 mg/ℓ) after ARLP extraction, which would be added to the sample. This was therefore not suitable to use to reduce the soluble manganese concentration of the scrubber dust sample to acceptable environmental concentrations. Burnt dolomite provided a much better dolomite option for stabilisation but was only really effective on $MnCl_2$ and $MnCO_3$ immobilisation and not on MnO_2 (residual 28 mg manganese/ℓ under ARLP conditions). It could be that the treatment period of 24 h was not adequate for burnt dolomite to immobilise the manganese as dolomite has a slower reaction rate than lime. Particle size analysis of the chemicals used for treatment were not determined and it could be that the dolomite used had a larger particle size than the other chemicals investigated as treatment options, therefore leading to a longer reaction period required for treatment.

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Figure 6.1 shows the results of ARLP extraction on the manganese level of the different inorganic manganese standards subjected to the chosen immobilisation methods. It is compared with TCLP extraction manganese results for MnO_2 and $MnCO_3$ (Figure 6.2). Based on these results (refer to Table 6.1), immobilisation of the three inorganic manganese types that resulted in manganese concentrations being reduced to acceptable risk levels of less than 0.3 mg/ℓ after ARLP extraction were: -

MnO_2 with lime (5 % w/w), hypochlorite (9 %) and CaO-CaS (10 %)
$MnCO_3$ with lime (5 %), hypochlorite (9 %) and CaO-CaS (10 %)
$MnCl_2$ with 5 % burnt dolomite, hypochlorite (9 %) and CaO-CaS (10 %)

Calcite (37.5 %) also significantly reduced the levels of soluble manganese remaining in all three standards solutions after ARLP extraction but not to levels below 0.3 mg/ℓ. Calcite was however able to perform better under TCLP extraction acid conditions (reduced soluble residual manganese to 7-17 mg/ℓ compared to the 5 % lime and 10 % desulphurisation slurry treatment regimes, which were very effective under ARLP conditions.

In comparison, 10 % lime and 9 % hypochlorite addition were the only methods of immobilisation tested that resulted in the acceptable risk performance level for manganese after ARLP and TCLP extraction (refer to Appendix C for full data result set).

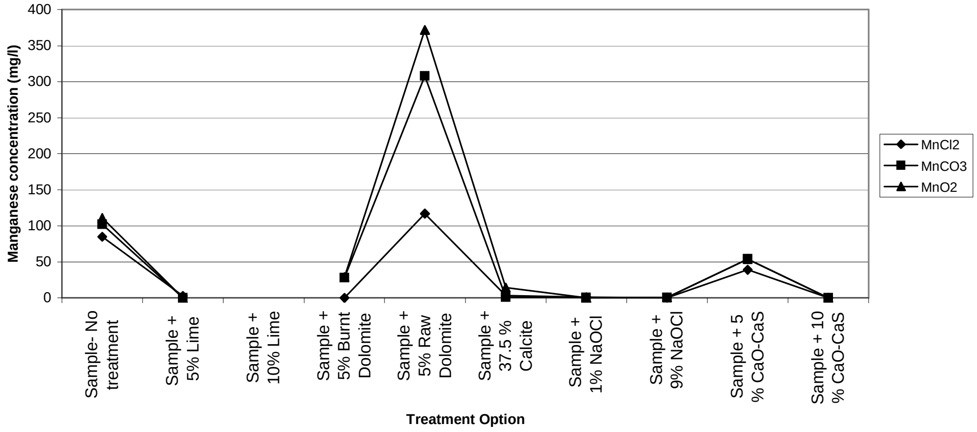


Figure 6.1: ARLP results for various inorganic manganese solutions –with and without treatment (not corrected)

Table 6.1: ARLP results for inorganic manganese standards

After ARLP Extraction	$MnCl_2$	$MnCO_3$	MnO_2	Mn
(corrected for negative control)	Manganese concentration (mg/ℓ)			
Sample	**80.4**	**97.0**	**106.3**	**95.6**
Sample + 5 % Lime	**1.77**	**<0.1**	**<0.1**	**<0.1**
Sample + 5 % Burnt Dolomite	**<0.1**	**0.2**	**26.4**	**3.27**
Sample + 5 % Raw Dolomite	**92.3**	**284**	**348**	**259**
Sample + 37.5 % Calcite	**1.18**	**<0.1**	**12.6**	**<0.1**
Sample + 1 % NaOC1	**<0.1**	**<0.1**	**<0.1**	**34.8**
Sample + 9 % NaOC1	**0.26**	**0.53**	**0.32**	**0.12**
Sample + 5 % CaO-CaS	**38.2**	**53.8**	**53.5**	**52.8**
Sample + 10 % CaO-CaS	**<0.1**	**0.12**	**0.14**	**1.65**

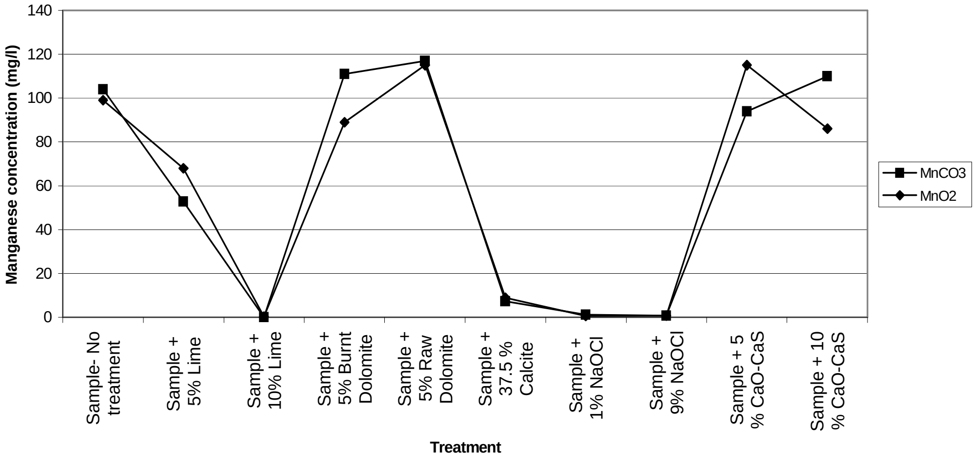
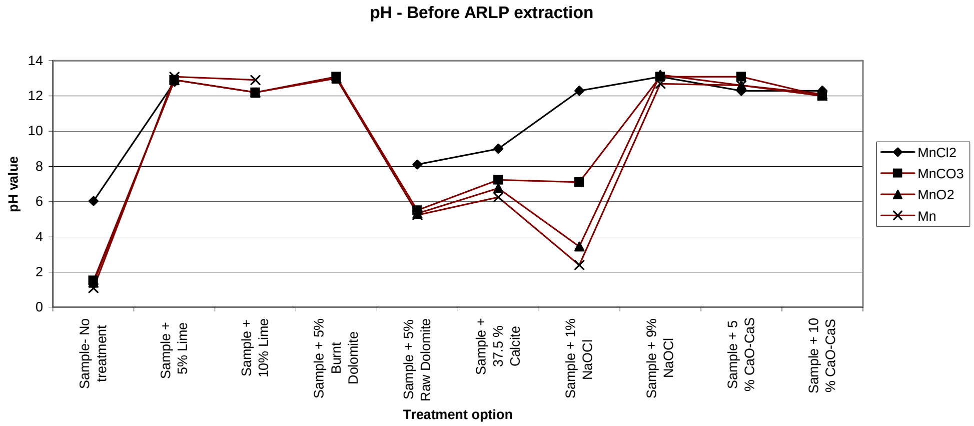


Figure 6.2: TCLP results for manganese dioxide (MnO_2) and manganese carbonate ($MnCO_3$) solutions –with and without treatment

pH measured before and after ARLP extraction, verify that the pH level in solution remained above 8 in samples treated with lime, calcite, NaOCl and 10 % CaO-CaS, thus ensuring a low soluble Mn leachate concentration (see Figure 6.3). However, when one examines the level of alkalinity (Table 6.2), which will provide long term buffering capacity for the waste sample, smaller increases were observed with addition of lime, but very large contributions are made by adding calcite. This will have a serious impact on the long-term stability of the treated waste sample in the environment as alkalinity is consumed with time (see verification in geochemical modelling results) and provides buffering capacity to fluctuations in pH.

Table 6.2: Alkalinity measured for the various manganese treatment options considered

Manganese standards	Alkalinity (average added as mg/ℓ $CaCO_3$)
Sample (manganese inorganic standard)	
Sample + 5 % lime	61818
Sample + 10 % lime	141797
Sample + 5 % burnt dolomite	7877
Sample + 5 % raw dolomite	14638
Sample + 37.5 % calcite	427211
Sample + 1 % NaOCl	2267
Sample + 9 % NaOCl	33071
Sample + 5 % CaO-CaS	4422
Sample + 10 % CaO-CaS	9007



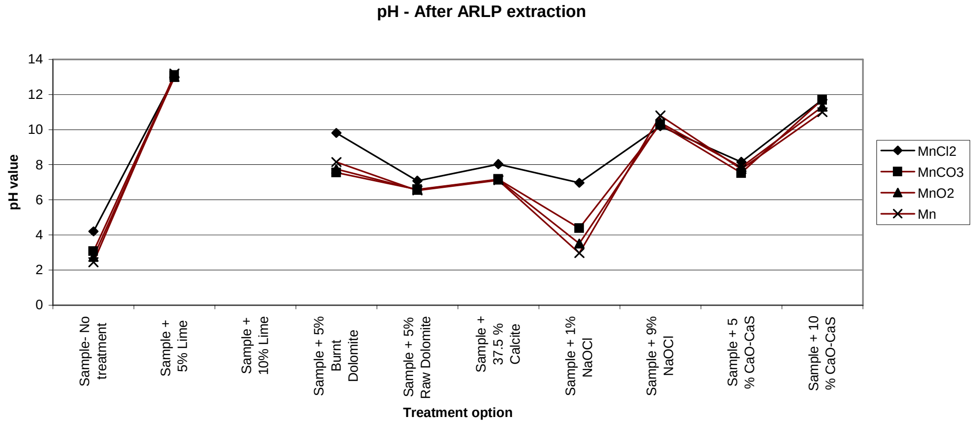


Figure 6.3: pH levels measured in solution before and after ARLP extraction of inorganic manganese standards- with and without treatment

6.1.2 Pyrometallurgical scrubber dust samples

6.1.2.1 Scrubber dust produced under reducing conditions (200 kW pilot plant trials)

The 200 kW trail runs produced a wet scrubber dust under reducing conditions. The results of the primary level, hazard risk characterisation leaching tests (DWAF, 1998) are provided in Tables 6.3 and 6.4. Trial 1 relates to the pilot plant run where inlet scrubber temperatures averaged 180 ˚C while Trial 2 was run at reduced inlet scrubber temperatures of 114 ˚C, by increasing the water flow rate through the scrubber.

Table 6.3: Paste pH results before and after the TCLP and ARLP extractions for the different 200 kW dust samples (No chemical treatment)

Sample	pH		
	Paste pH before ARLP	pH after ARLP	pH after TCLP
Scrubber dust - Trial 1 - filtered	9.35	8.90	5.10
Scrubber dust - Trial 2 - filtered	8.85	8.15	4.80

Table 6.4: Chemical analysis of the 200 kW scrubber dusts after TCLP and ARLP extractions (No treatment)

Sample	Metal concentrations after ARLP extraction (mg/kg)					Metal concentrations after TCLP extraction (mg/kg)	
	Mn	Fe	Al	Cd	Zn	Mn	Fe
Scrubber dust - Trial 1 - filtered	3.54	<0.05	17	1.00	3.02	1745	2804
Scrubber dust - Trial 2 - filtered	34	<0.05	<0.05	0.34	0.62	2298	2672

While a lower concentration of manganese was detected in the slurry for Trial 2 (Table 6.8), due to the increased dilution effect, the total amount of manganese captured was actually higher than Trial 1. Furthermore, the manganese found in the dust from Trial 2 was far more soluble under mildly acid conditions, seen by the almost ten fold increase in manganese (mg/kg) in the leachate after ARLP extraction (Table 6.4). This may be related to the different particle size profile of the two dusts (see Table 6.5) and predominant form of manganese produced in the scrubber. A larger proportion of particle sizes >0.71 mm was detected in scrubber dust from Trial 2. It is known for instance that manganese and iron oxides can exist as nodules, concretions, cement between particles or simply as coating on particles (Jenne, 1968). These oxides can act as scavengers for trace metals and can be unstable under certain acidic conditions and redox conditions i.e. low Eh.

Samples of the scrubber dust were also sent for SEM (scanning electron microscopy) analysis in an attempt to better understand the differences in composition or structure, but very little difference was observed (see Appendix F).

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6.6

A comprehensive analytical programme was conducted to characterise the various input and output waste streams from our case study furnace trials. This assisted in compiling a mass balance for manganese, which would contribute to evaluating the secondary risk level of the scrubber dust waste stream in terms of waste load.

Five key metal elements were measured to determine the relative metal composition profile in mg/kg of the raw materials (ilmenite, iron and anthracite) and solid material outputs (metal and slag) from the 200 kW furnace trials. The results are shown in Table 6.6. These metals were shown to pose a potential hazardous risk in earlier work carried out on wet scrubber dust from Ticor (PHD, 2001).

Table 6.5: Particle size analysis of the scrubber dusts (filtered)-200 KW pilot trials

Particle size distribution	**Trial 1 Scrubber dust (filtered) (g)**	**Trail 2 Scrubber dust (filtered) (g)**
Sample weight	100	50.02
1000 µm	0.66	11.06
710 µm	0.51	6.99
500 µm	0.81	7.42
300 µm	24.83	8.68
250 µm	11.24	3.18
150 µm	23.22	5.39
75 µm	25.04	6.06
<75 µm	13.66	0.64
Total	99.97	49.42

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Table 6.6: Chemical analysis of the solid materials

Sample	**Total iron (mg/kg)**	**Total manganese (mg/kg)**	**Total aluminium (mg/kg)**	**Total cadmium (mg/kg)**	**Total zinc (mg/kg)**	**Paste pH**
Iron metal used for start-up	28325	419	481	<1	135	ND
INPUT						
Ilmenite	79313	669	139	<1	97	ND
Anthracite	4838	199	2840	<1	113	ND
Ilmenite/Anthracite mixture	19888	499	490	<1	115	6.62
OUTPUT						
Iron (Trial 1)	632750	1132	2455	<1	126	ND
Slag (Trial 1)	172875	1944	1455	<1	114	ND
Iron (Trial 2)	92838	731	526	<1	106	ND
Slag (Trial 2)	56900	2546	1578	<1	117	ND

To assist with the input and output balance calculations, the wet scrubber inlet water quality (Table 6.6) was also analysed together with the scrubber dust slurry, filtered dust and filtrate (Tables 6.7, 6.8 and 6.9 respectively).

Table 6.7: Chemical analysis of the influent water to the wet scrubber

Analysis	Value
pH	6.77
Electrical conductivity (mS/m)	21
Alkalinity as $CaCO_3$ (mg/ℓ)	95
Sulphate concentration (mg/ℓ)	19
Sodium concentration (mg/ℓ)	10
Potassium concentration (mg/ℓ)	2.2
Calcium concentration (mg/ℓ)	20
Magnesium concentration (mg/ℓ)	5.4
Manganese concentration (mg/ℓ)	0.06
Iron concentration (mg/ℓ)	<0.05
Cadmium concentration (mg/ℓ)	0.02
Zinc concentration (mg/ℓ)	<0.05
Aluminium concentration (mg/ℓ)	<0.05

Table 6.8: Chemical analysis of the wet scrubber dust slurry

Analysis	Trial 1	Trial 2
Total manganese concentration (mg/ℓ)	4.5	1.5
Total iron concentration (mg/ℓ)	64	2
Total cadmium concentration (mg/ℓ)	0.033	0.029
Total zinc concentration (mg/ℓ)	1.97	0.15
Total aluminium concentration (mg/ℓ)	5.0	0.133
Total sodium concentration (mg/ℓ)	20	16
Total potassium concentration (mg/ℓ)	10	4.9
Total calcium concentration (mg/ℓ)	20	17
Total magnesium concentration (mg/ℓ)	20	12
Total solids @ 105 °C (mg/ℓ)	110	40
Moisture content (%)	100	100
pH	6.7	6.5
Electrical conductivity (mS/m)	39	32
Alkalinity as $CaCO_3$ (mg/ℓ)	166	152
Sulphate concentration (mg/ℓ)	30	18
Soluble sodium concentration (mg/ℓ)	19	14
Soluble calcium concentration (mg/ℓ)	15	14
Soluble magnesium concentration (mg/ℓ)	14	14
Soluble manganese concentration (mg/ℓ)	1.3	2.2
Soluble iron concentration (mg/ℓ)	<0.01	<0.01
Soluble cadmium concentration (mg/ℓ)	0.02	0.01
Soluble zinc concentration (mg/ℓ)	0.22	0.30
Soluble potassium concentration (mg/ℓ)	8.1	2.9
Soluble aluminium concentration (mg/ℓ)	0.23	0.28

Table 6.9: Analysis of the scrubber dusts

Chemical	Trial 1 Scrubber dust- filtered	Trial 2 Scrubber dust- filtered
Total manganese (mg/kg)	18538	20950
Total iron (mg/kg)	194125	200625
Total cadmium (mg/kg)	2.3	1.9
Total zinc (mg/kg)	6963	6450
Total aluminium (mg/kg)	13438	12313
Total sodium (mg/kg)	2036	1948
Total potassium (mg/kg)	2531	2811
Total calcium (mg/kg)	2794	2394
Total magnesium (mg/kg)	46925	44425
Total solids	50.16	49.62
Moisture content (%)	49.84	50.38
Loss of ignition	-0.87	-1.04

Table 6.10: Chemical analysis of the filtrates and supernatants of the wet scrubber slurry

Chemical	Filtrate (Trial 1)	Filtrate (Run 2)
Total iron (mg/ℓ)	0.18	0.17
Total manganese (mg/ℓ)	0.82	0.32
Total solids @ 105 °C (mg/ℓ)	<0.2	<0.2
Moisture content (%)	100	100
pH	8.6	8.3
Electrical conductivity (mS/m)	17	30
Alkalinity as $CaCO_3$ (mg/ℓ)	169	139
Sulphate concentration (mg/ℓ)	43	12
Sodium concentration (mg/ℓ)	18	14
Potassium concentration (mg/ℓ)	9.6	2.5
Calcium concentration (mg/ℓ)	23	17
Magnesium concentration (mg/ℓ)	17	14
Manganese concentration (mg/ℓ)	0.73	0.49
Iron concentration (mg/ℓ)	<0.05	<0.05
Cadmium concentration (mg/ℓ)	0.02	0.02
Zinc concentration (mg/ℓ)	<0.05	<0.05
Aluminium concentration (mg/ℓ)	0.18	<0.05

A mass balance was calculated and verified using the above information and support data provided by Ticor on the raw material solid composition. Figure 6.4 provides an illustration of the manganese mass balance for Trial 1, where approximately 4.6 % of the total manganese load input is recovered in the off-gas dust stream. Approximately 15 % of the manganese input was calculated as being recovered in Trial 2 scrubber dust stream.

A comparison of results for scrubber dusts collected from other 200 kW pilot trials conducted at the Ticor research facilities are shown in Table 6.10. Estimated Environmental Concentrations (EEC), calculated for the element manganese in the test samples, are also included.

EEC values were calculated, and the hazard classification has been performed, assuming a disposal area of 50ha and a mass flow rate of 2 000 t/month of wet scrubber dust (refer to Appendix E). It should be noted here that when the ratio of EEC/Acceptable Risk Level (ARL) is <1 (DWAF, 1998), a recommended delisting of the waste with regards to the specific component can be made.

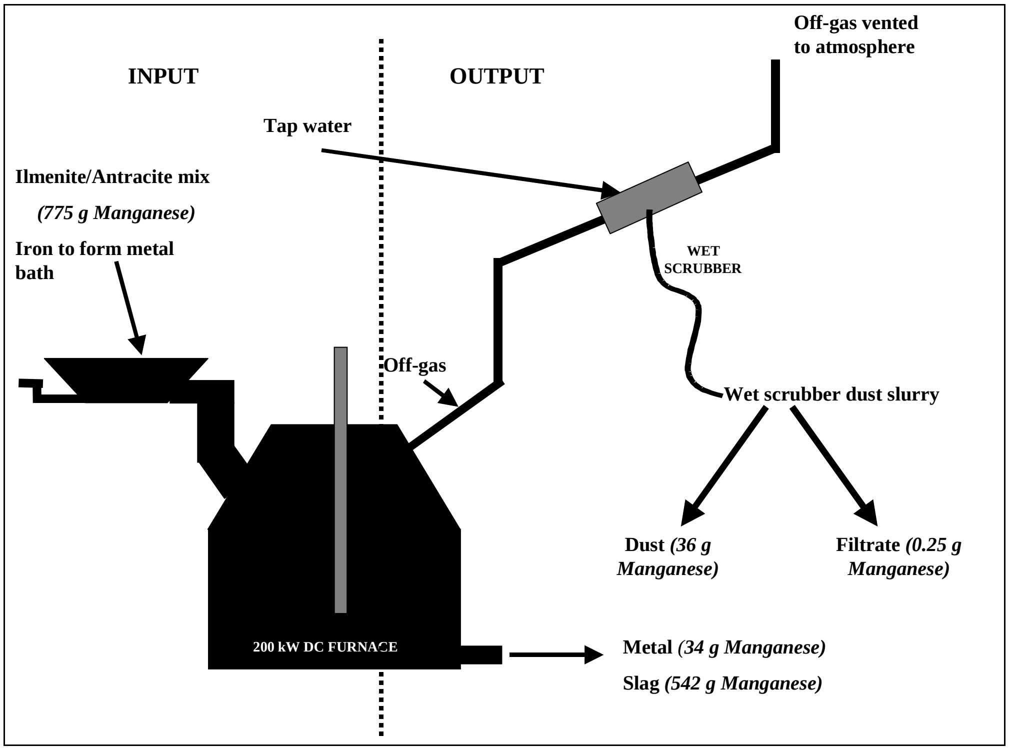

Figure 6.4: Manganese mass balance for 200 KW Furnace Pilot Plant Trial 1

Table 6.11: Comparison of manganese and leaching results for other similar test trials –wet reducing conditions, 200 kW furnace

Trial	Total manganese (mg/kg)	Manganese after ARLP (mg/kg)	EEC-(ARLP) (ppb)	EEC/AR
200 kW Trial 1 - 2003	18538	3.5	94	
200 kW Trial 2 - 2003	3750	34	898	3.0
200 kW Trial -April 2001	20974	2.4	62	0.21
200 kW Trial (DB270) - July 2001	-	33.0	873	2.9

It would appear from the data provided in Table 6.11 that the trial results can be grouped into two sets viz. Set 1: Trial 1 2003 and April 2001 and Set 2: Trial 2 2003 and July 2001. The difference between the two groups of test trials is the inlet water temperature and water flow rate through the wet scrubber. Set 2 trials were run with a water flow rate twice that for Set 1 which would provide for a faster cooling rate and water: solid ratio. This in turn affected the manganese load captured and the solubility of the manganese. ARLP and EEC results indicate that temperature management of the wet scrubber has a significant impact on the classification of the waste and delisting requirements

6.1.2.2 Scrubber dust produced under oxidising conditions (500 kW and 1.5 MW pilot plant trials)

Two samples of scrubber dust collected under oxidising conditions were tested. The 500 kW furnace off-gas was routed through a wet scrubber but the 1.5 MW furnace off-gas was routed through a post combustion chamber and the dust collected in a baghouse. A similar ratio of ilimenite/anthracite feed is used in all the pilot trials conducted and used for the research project. The results of the ARLP and TCLP extractions (DWAF, 1998) are presented in Table 6.12. Post combustion of the oxidised dust reduces the amount of manganese extracted or leached. Furthermore the amount of manganese leached under ARLP conditions is similar under TCLP conditions for this dry bag house dust. Post combustion therefore results in the formation of a relatively stable form of manganese based on TCLP and ARLP results. Wet oxidised dust samples however showed soluble manganese concentration approximately twice that of the dry baghouse dust under ARLP conditions (315 vs 118 mg/kg) and approximately twelve times the amount of manganese under TCLP conditions (2049 vs. 167 mg/kg) respectively.

Process conditions to capture and treat the off-gas dust therefore have an impact on manganese load and behaviour once it is disposed of in the environment. The post combustion unit, where CO is ignited to form CO_2, causes dust to be exposed to higher temperatures and alters redox conditions. It also combusts any solid reductant in off-gas thereby artificially increasing concentration of metals associated with ilmenite feed in the off-gas dust as compared to wet reducing conditions.

Table 6.12: Manganese and iron concentrations of the 500 kW and 1.5 MW scrubber dusts after TCLP and ARLP (No treatment)

Sample	pH			Metal concentration after ARLP (mg/kg)					Metal concentration after TCLP (mg/kg)	
	Paste pH before ARLP	pH after ARLP	pH after TCLP	Mn	Fe	Al	Cd	Zn	Mn	Fe
500 kW WSD Kumba	7.2	6.4	4.75	315	4.95	53	0.58	17.5	2049	13000
1.5 MW Kumba	8.6	5.9	3.95	118	200	31	0.24	74	167	3250

Chemical and mineralogical analysis results for the scrubber dusts obtained under oxidising conditions are provided in Table 6.13.

Scrubber dust from the pilot plant furnaces (using raw materials of ilmenite and anthracite from Ticor) showed high concentrations of other trace minerals of concern viz aluminium and zinc, with a hazard rating of 2 but manganese is the dominant HR2 metal of concern. These other trace metals may also play a significant role in the mineral complexes formed upon disposal of the waste and may affect the solubility and therefore risk posed to the environment by manganese.

Table 6.13: Analysis of the 500 kW and 1.5 MW scrubber dusts obtained under oxidising conditions

Chemical	500 kW	1.5 MW
Total Sodium (mg/kg)	780	621
Total Potassium (mg/kg)	1796	958
Total Calcium (mg/kg)	398	462
Total Magnesium (mg/kg)	7120	2958
Total Aluminium (mg/kg)	3338	988
Total Cadmium (mg/kg)	1.4	0.9
Total Iron (mg/kg)	1767	80475
Total Manganese (mg/kg)	14300	6813
Total zinc (mg/kg)	2325	2725
Moisture content (%)	20.46	0.05
Solids (%)	79.54	99.95
Loss of ignition	-0.13	-1.27

6.12

6.13 Other industrial samples

The leachability of scrubber dust samples containing manganese collected from other pyrometallurgical industries is provided in Table 6.14. These samples were taken from full-scale production facilities.

All these samples showed very low levels of soluble manganese under mild acidic conditions in the ARLP leachate ranging from 0.48 to 8.9 mg/kg manganese. Aluminium and zinc were also detected but at much lower concentrations compared to our pilot trial dusts. These differences may play a role in long term stability and also serves to illustrate the diversity and range of manganese containing wastes.

Table 6.14: Manganese and iron concentrations of the Ticor WSD, Corex classifier sand, Conarc slag and the Metalloys wet scrubber dust leachate after ARLP (No treatment)

Sample	pH after ARLP	Metal concentrations (mg/kg)				
		Manganese	**Iron**	**Aluminium**	**Cadmium**	**Zinc**
Ticor WSD	6.35	1.12	<0.05	ND	ND	ND
WSD Metalloys	7.75	0.48	1.08	93.5	8.87	5.81
Corex Classifier sand	10.55	8.92 *(1.6)	15.4	120	0.39	6.77
Conarc slag	9.75	0.48 *(0.09)	0.44	74.8	0.50	7.43

* ARLP results from company files

The leaching test results and EEC calculations given to us for the Conarc and Conex samples from in-house studies conducted by the respective companies, indicate that the manganese levels in the dust are less than the acceptable risk level and therefore would not be classified as hazardous. Our ARLP leachate results for manganese were found to be slightly higher than was provided but also result in an EEC level below the 300ppb risk limit.

6.2 MITIGATION OF POTENTIAL ENVIRONMENTAL IMPACTS

The third level of risk evaluation includes an investigation of the technologies to mitigate potential environmental impact. While the potential for manganese leaching varied in the scrubber dust samples tested, the ARLP results show that the dust samples could exceed the acceptable risk level concentration (EEC/AR > 1) and therefore may require immobilisation before disposal into the environment (Figure 6.5). The effect of a variety of chemical additions to immobilise the manganese and prevent it from leaching into the environment at significant levels, was pursued and is discussed.

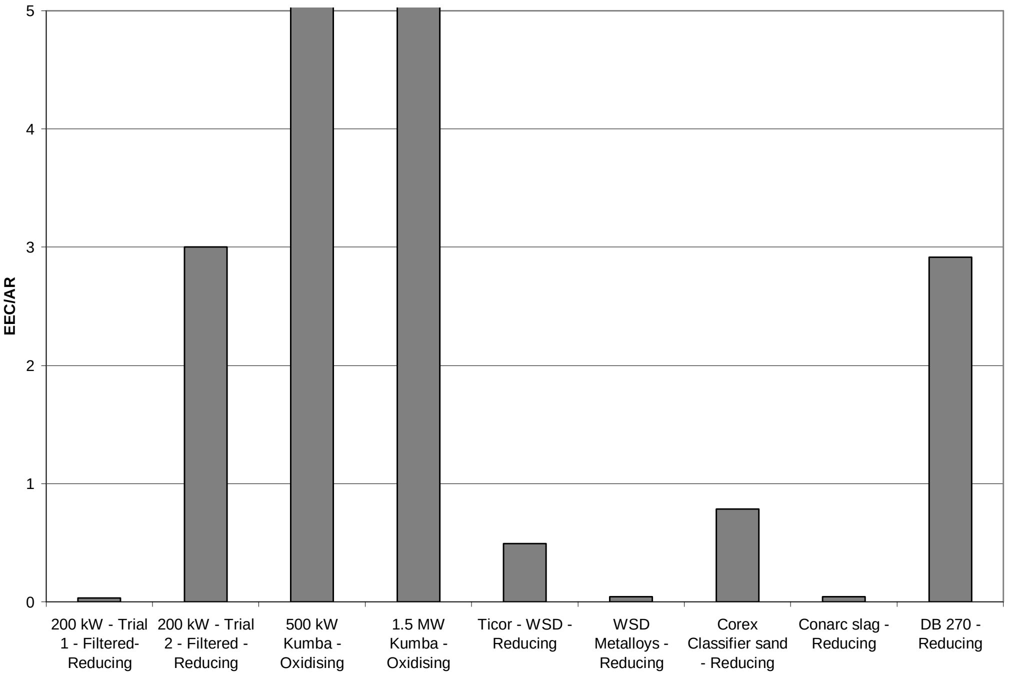

Figure 6.5: EEC/AR ratios for ARLP manganese for the different samples – no treatment

Based on the results obtained from immobilisation of the inorganic manganese solutions (pure form) (refer to section 6.1.1) all the scrubber dust samples were treated with the addition of lime, calcite, hypochlorite and the desulphurisation slurry. A summary of the manganese and iron concentrations found after ARLP and TCLP extractions (scrubber dust with treatment) is provided in Appendix C. Table 6.15 compares the soluble manganese remaining after treatment and acid extraction (ARLP) for the scrubber dust samples collected for this research product.

Table 6.15: Summary of manganese concentrations of the scrubber dust leachates, after ARLP (with and without treatment)

Treatment Option	**ARLP – Mn (mg/kg)**								
	200 kW - RUN 1 -	**200 kW RUN 2 -**	**500 kW KUMBA**	**1.5 MW KUMBA**	**Ticor - WSD**	**COREX CLASSIFIER SAND**	**CONARC SLAG**	**MET-ALLOYS-WSD**	**200 kW DB270**
Scrubber Conditions	Wet, Reduced	Wet, Reduced	Wet, Oxidised	Dry, Oxidised	Wet, Reduced	Dry, Reduced	Dry, Reduced	Wet, Oxidised	Wet, reduced
No treatment	3.54	34.1	315	118	1.12	8.9	0.48	0.48	33
5 % Lime	<0.01	<0.01	0.58	<0.01	0.12	1.0	0.2	<0.01	0.5
37.5 % Calcite	117	3.1	4.9	1.1	<0.05	0.38	0.2	7.8	3.8
9 % NaOCl	0.14	0.54	0.47	0.56	<0.05	1.4	0.38	<0.01	-
10 % CaO-CaS	0.08	0.52	-	-	<0.05	-	-	-	--

Five percent lime addition is shown to be effective in reducing the soluble manganese leached under mildly acidic conditions for most of the scrubber dusts tested and this agrees with data provided by Ockie Fourie Toxicologists (1997). However 5 % lime under TCLP conditions is not effective and it requires that the dosage be increased to 10 % (w/w) to reduce the risk factor (see Appendix E). Calcite performance fluctuated between the scrubber dust samples. This may have to do with the mixing of the calcite or error in analysis (in particular the results for 200 kW Run 1 and Metalloys appear erroneous). However, there was no scrubber dust sample left to repeat the test procedure for confirmation. The use of oxidants (9 % v/w) also provided an effective means to reduce the soluble manganese except for the dry reduced sample from Corex (Table 6.15). The results also indicate that the desulphurisation slurry at 10 % (w/w) can stabilise the manganese but should it be used and is co-disposed with the dust, its sulphur content may pose additional problems or risk to the environment. This was however not within the scope of this project to investigate further. It was found that all the applied treatment options could reduce the EER/AR ratio to <1 for delisting of the scrubber dust as hazardous (Figure 6.5).

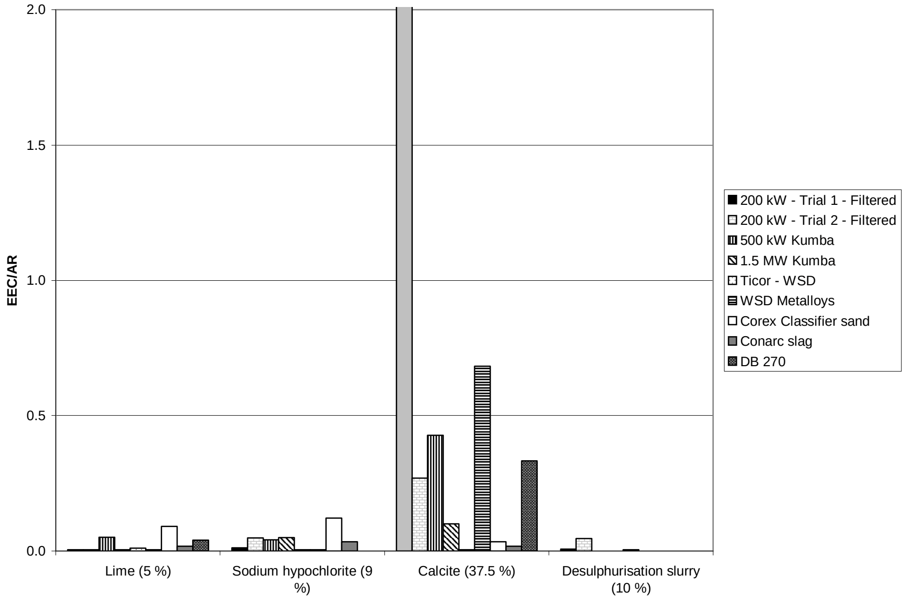

Figure 6.6: EEC/AR ratios for ARLP manganese for the different samples – after treatment

7. GEOCHEMICAL MODELLING

7.1 OBJECTIVES

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The objective of the geochemical modelling assessment was to determine the long-term effect of different chemical treatment options on the hazardous scrubber dust waste obtained from pyro-metallurgical industries. Geochemical modelling can assist in evaluating the real risks associated with the scrubber dust waste containing manganese as well as enabling comparative assessments of various waste management/stabilization options and their impact over time. Furthermore, the equilibrium modelling expanded on the theoretical geochemical data presented in the literature survey (see Chapter 4) by using actual column leach data from the dust sample.

7.2 BACKGROUND - SUMMARY OF MANGANESE CHEMISTRY

Aqueous manganese can be transported at standard conditions in the following forms (Liu et al., 1984):

- Anionic and complexes (group), e.g.CO_3^{2-}, HCO_3^-, CN^-, $PO4^{2-}$, Cl^-, OH^-, F^-, O^{2-}, SO_4^{2-}, NH_3^-;
- Colloids;
- Organic anionic complexes; and
- Micro particle suspensions.

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There are a number of anionic Mn^{2+} complexes occurring in the aqueous system (Table 7.1), which may explain the reason why manganese is so soluble and removable in various physico-chemical conditions.

Manganese or Mn^{2+} mineral phases are also abundant including complexes with Cl^-, F^-, SO_4^{2-}, PO_4^{2-}, NO_3^-, Se^{2-}, SeO_3^{2-}, AsO_4^{3-}, $V_2O_6^{2-}$, OH^-, and CO_3^{2-} while only a few minerals exist with manganese in oxidising states Mn^{3+}, Mn^{4+}, Mn^{6+}, and Mn^{7+}.

7.3 METHODOLOGY AND RESULTS

A detailed geochemical modelling exercise was conducted and included:

- Aqueous speciation and dissolution / precipitation of different mineral phases – stability analysis under a variety of conditions in terms of oxygen, redox potential and iron/manganese ratios without consideration of time scale (Stability analysis of manganese species on activity-pH diagrams).
- Kinetic modelling to predict the long-term water quality in terms of manganese, and pH when disposing of the waste in a mono-landfill. **(NB: Although Ticor scrubber dust waste was used, this mono landfill does not simulate the Ticor disposal facility where the waste is diluted with slimes before being deposited in a tailings dam. The mono-landfill is a worst-case scenario only containing scrubber dust material.)**

7.2

ACT2 of the Geochemist's Workbench software was used to carry out manganese stability field analysis while REACT of the same package was used for kinetic modelling. PHREEQC version 2 was used for speciation of aqueous species in solution. Water extraction (column leach) data of three different types of pyrometallurgical scrubber dust samples together with composition interpretation of geochemical data obtained by XRF, XRD and particle size analysis were used.

Table 7.1: Summary of manganese geochemistry (Huheey, 1974; LLNL database, Bethke, 1996)

Valence (manganese)	Aqueous	Minerals	
Mn^{3-}	$[Mn(NO)_3O]^{2-}$		
Mn^{2-}	N/A		
Mn^0	$[Mn(dipy)_3]$		
Mn++	$Mn(CN6)^{4-}$ $Mn(H_2PO_4)^+$ $Mn(HCO_3)^+$ $Mn(NO_3)^+$ $Mn(OH)^+$ $Mn(OH)3^-$ $Mn(OH)_3$- $Mn(OH)_4^{2-}$ $Mn(PO_4)^-$ Mn^{2+} $MnCl^+$ $MnCl_3^-$ MnF^+	MnCl MnF_2 $Mn(NO_3)_2$ $MnSO_4$ MnF_2 $MnCl_2$ $MnCl_2 \cdot H_2O$ $MnCl_2 \cdot 4H_2O$ $MnCl_2 \cdot 2H_2O$ $Mn(NO_3)_2$ $Mn_3(PO_4)_2$ $MnHPO_4$(c) $Mn_3(AsO_4)_2$ MnSe $MnSeO_3$ $MnSeO_3 \cdot 2H_2O$ MnV_2O_6 $Mn(OH)_2$ $MnSO_4$ $MnSO_4$ $MnCO_3$	
Mn^{3+}	$Mn[(CN)_6]^{3-}$ $Mn_2(OH)_3^{3+}$ $Mn(NH_3)^+$	$Mn(OH)_3$ $MnSeO_3 \cdot 2H_2O$	
Mn^{4+}	$Mn(NH_3)_2^{2+}$	$MnSeO_3$, MnO_2	
Mn^{5+}	$[MnO_4]^{3-}$ $Mn(NH_3)_3^{3+}$		
Mn^{6+}	$[MnO_4]^{2-}$	$BaMnO_4$(c)	
Mn^{7+}	$[MnO_4]^-$	Mn_2O_7	

* dipy - N-N chain

7.3.1 Selecting a disposal strategy

Addition of chemicals, e.g. $CaCO_3$ to the manganese-bearing system is a method for disposal and remediation of industrial wastes which is similar to treatment of acid rock drainage (ARD) as described by Gusek and Wildeman (1997). Addition of the chemicals to manganese-bearing waste is used for the generation of alkalinity, elevation of pH and precipitation of manganese in the waste. Removal of manganese by formation of MnO_2 is a general practice treatment of ARD for the remediation of high concentrations of manganese.

7.3

During this study, the following treatment options were investigated:

- Lime (CaO);
- Calcite ($CaCO_3$); and
- Raw dolomite ($MgCO_3 \cdot CaCO_3$).

Lime (calcium oxide) or quicklime, is a white solid with a melting point of 2580 ^oC. It may be produced by burning limestone. Addition of lime into manganese-bearing wastes will enhance pH and result in manganese precipitation in the form of rhodochrosite and other manganese mineral phases.

Calcite (calspar) is a naturally occurring crystalline calcium carbonate ($CaCO_3$). Addition of calcite will produce an alkaline environment in the system enhancing the pH to ~ 8. The addition of calcite will be responsible for the formation of complexes, which will remain stable for a longer period than those formed through the addition of lime. This is due to the fact that lime has a much quicker reaction rate than calcite.

Raw dolomite or pearl spar, is a natural double carbonate of magnesium and calcium, $MgCO_3 \cdot CaCO_3$. Raw dolomite is a whitish solid that occurs in nature. The molecular weight of raw dolomite is 184.4g. Once again, the addition of dolomite to the aqueous system will enhance the alkalinity of the system.

7.3.2 Stability field analysis using geochemical modelling

The following systems were modelled by using ACT2 of the Geochemist's Workbench:

- H_2O-Mn system;
- H_2O-Mn-Fe-CO_2-S-Cl-NO_3 (NH_3) system;
- Addition of calcite, i.e. H_2O-Mn-Fe-$CaCO_3$;
- Addition of lime i.e. H_2O-Mn-Fe-CaO; and
- Addition of dolomite i.e. H_2O-Mn-Fe-$CaMg(CO_3)_2$;

A number of parameters can be plotted and analyzed in terms of activity diagrams against pH in the above mentioned systems. Six major factors were identified as most important in affecting manganese stability in aqueous systems. These factors can be measured and quantified in the field or laboratory. These factors are:

- Dissolved oxygen in solution ($O_2(aq)$)
- Oxygen in the gaseous form ($O_2(g)$);
- Redox potential in terms of Eh
- Redox potential in terms of paclet number (pe);
- Fe^{3+}/Fe^{2+} ratio; and
- Fe^{3+}/Mn^{2+} ratio.

7.3.2.1 H_2O-Mn system

The H_2O-Mn system refers to a water system with limited amounts of manganese species. The following input data were used during the geochemical modelling process (Figure 7.1; Tables 7.2 and 7. 3):

- H_2O (default a H_2O = 1.003); and
- a Mn^{2+} = 10^{-6}. This number is close to the total manganese mole concentration limit of 2.35×10^{-7} (8×10^{-6} g/l) in solution for fresh water according to the requirement of DWAF (1996).

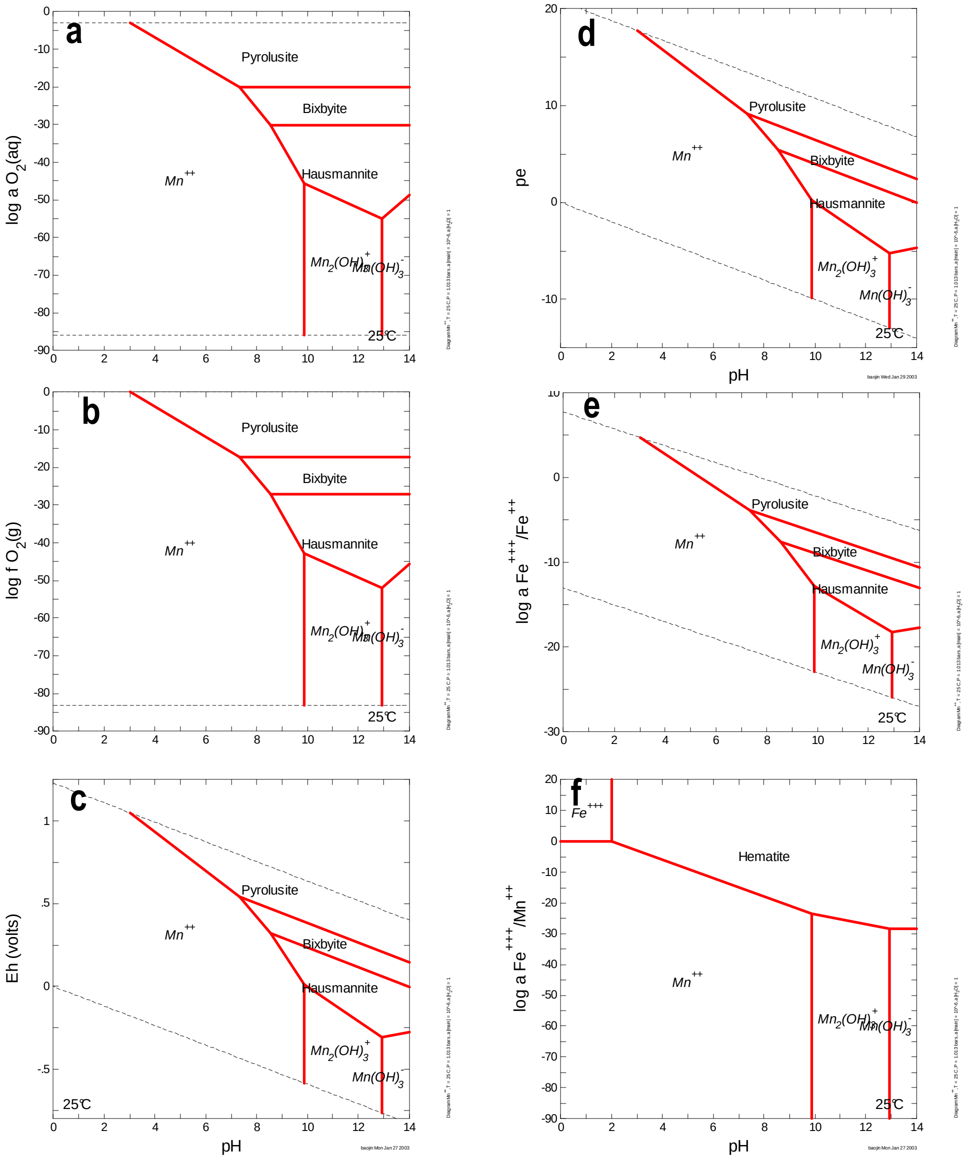

Figure 7.1: Stability fields for manganese in a H_2O-Mn system on log $fO_2(aq)$ (a), log $fO_2(g)$ (b), Eh (c), pe (d), Fe^{3+}/Fe^{2+} (e) and Fe^{3+}/Mn^{2+} (f) vs pH

The following results were obtained from the stability field analysis:

- Limited aqueous species occurring in the system are Mn^{2+}, $Mn_2(OH)_3^+$, and $Mn(OH)_3^-$ of which Mn^{2+} is dominating;
- Mineral phases occurring in the system are: pyrolusite (MnO_2), bixbyite (Mn_2O_3), hausmannite ($MnO\cdot Mn_2O_3$) and hematite (Fe_2O_3);
- Manganese is mostly stabilised above a pH of 10 where the manganese stability field is relative narrow;
- At the standard physico-chemical conditions (25 ^oC, 1 bar pressure, pH 7, Eh <0.5 volt; pe = 4; a $O_2(aq)$ is $2.30x10^{-5}$ and f $O_2(g)$ at 0.21), Mn^{2+} will be the dominant aqueous species and therefore manganese mobilizes easily, especially below a pH of 7.

7.3.2.2 H_2O-Mn-Fe-(Ca)-CO_2-S-Cl-NO_3 system

This system is based on the chemical analysis of the samples themselves, where the major components in the system were found to contain CO_2, Mn, Fe (Ca), S, Cl and NO_3 / (NH3). The input data used during modelling included:

- H_2O (default a H_2O = 1.03);
- a $Mn^{2+} = 10^{-6}$. This is in line with the DWAF's (1996) recommended maximum limit for fresh water where the concentration of total manganese in solution is $8x10^{-6}$g/l.
- f $CO_2(g)$ = 0.03. This is transferred to log f $CO_2(g)$ = -0.1523 at normal partial pressure;
- a $SO_4^{2-} = 10^{-6}$;
- a $Cl^- = 10^{-6}$; and
- a $NO_3^- = 10^{-3}$.

The following results were obtained from the stability field analysis (see Figure 7.2; Tables 7.2 and 7.3):

- The aqueous species occurring in the system are $MnSO_4$, $Mn(NH_3)_3^{2+}$, and $Mn(NH_3)_3^{2+}$, of which Mn^{2+} is in the form of $MnSO_4$.
- The mineral phases occurring in the system are: pyrolusite (MnO_2), bixbyite (Mn_2O_3), rhodochrosite ($MnCO_3$) and hematite (Fe_2O_3). Hausmannite ($MnO\cdot Mn_2O_3$) disappeared from the system; and
- Manganese is mostly stabilised above pH 8 where the manganese stability field is still relative narrow.

At the standard physico-chemical conditions (pH at 7, Eh <0.5 volt; pe = 4; and f $O_2(aq)$ at $2.3x10^{-5}$ and f $O_2(g)$ at 0.21), Mn^{2+} species are easily produced so that manganese in mineral forms is easily mobilized.

7.3.2.3 H_2O-Mn-Fe-$CaCO_3$ system

The addition of calcite ($CaCO_3$) to the system is the first management option considered. No oxidising-reducing reaction occurs in this process, but pH is increased dramatically due to formation of the dominating HCO_3^-. The manganese stability fields in mineral forms have therefore been drastically expanded to a pH of just about 7 from the original pH of 10. The following input data were used:

- H_2O (default a H_2O = 1.03);
- a $Mn^{2+} = 10^{-6}$; and
- a $CaCO_3$ = 1 Mole/*l*, i.e. 100 g/kg water.

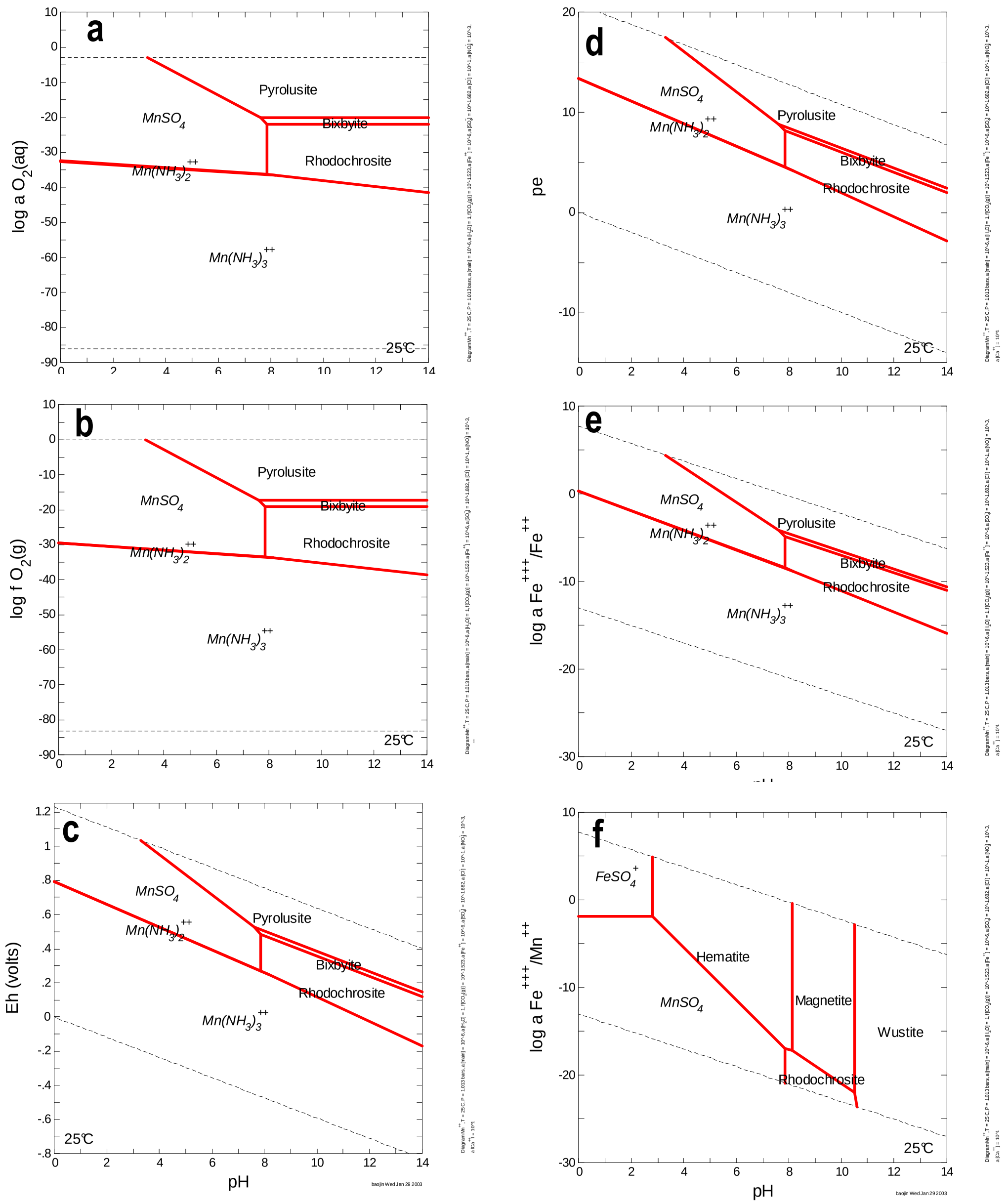

Figure 7.2: Stability fields for manganese in a H_2O-Mn-Fe-Ca-CO_2-S-Cl-NO_3- system on log fO_2(aq) (a), log fO_2(g) (b), Eh (c), pe (d), Fe^{3+}/Fe^{2+} (e) and Fe^{3+}/Mn^{2+} (f) vs pH

The following results were obtained from the manganese stability field analysis (Figure 7.3; Tables 7.2 and 7.3):

- Only manganese aqueous complex $MnHCO_3^+$ occurs in a relative narrow field in this system;
- A number of manganese mineral phases occur in the system. They include: pyrolusite (MnO_2), bixbyite (Mn_2O_3), rhodochrosite ($MnCO_3$), and hausmannite ($MnO \cdot Mn_2O_3$), together with hematite (Fe_2O_3), magnetite ($FeO \cdot Fe_2O_3$) and wustite ($Fe_{0.947}O$);
- Manganese is mostly stabilised above a pH of 7 and the manganese stability field is significantly increased;
- At the standard physico-chemical conditions, aqueous manganese species will not be produced in a significant amount. The addition of calcite will therefore be responsible for the effective stabilization of manganese in the manganese-bearing wastes.

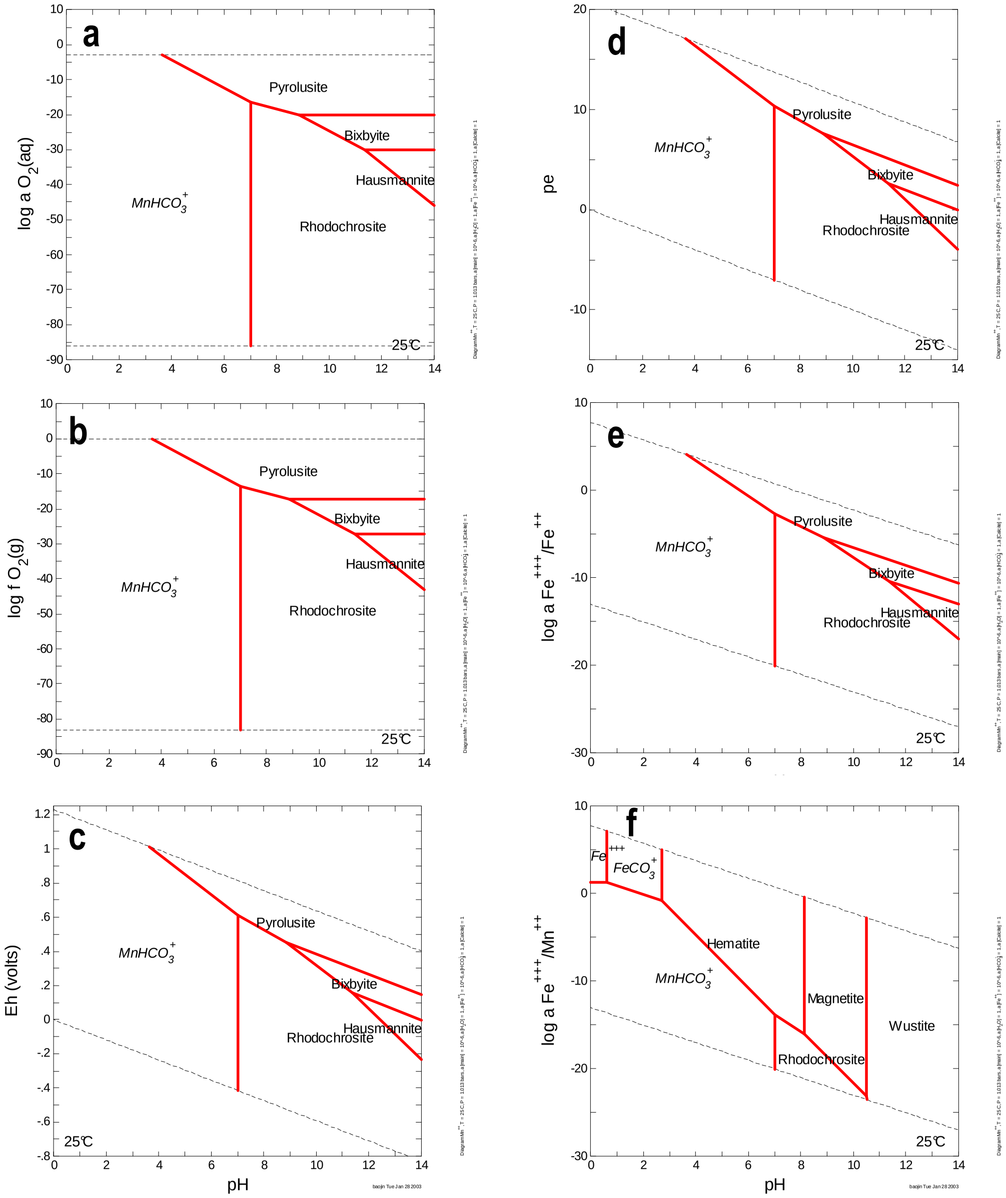

Figure 7.3: Stability fields for manganese in a H_2O-Mn-Fe-$CaCO_3$ system on log fO_2(aq) (a), log fO_2(g) (b), Eh (c), pe (d), Fe^{3+}/Fe^{2+} (e) and Fe^{3+}/Mn^{2+} (f) vs pH

7.3.2.4 H_2O-Mn-Fe-lime (CaO) system

The second management option investigated was the addition of lime (CaO) to the manganese containing waste. No oxidising and reducing reactions occur in this process and the pH is increased through the formation of Ca(OH). Therefore, the manganese stability fields have been dramatically increased at a neutral pH of 7. The following data were used as input to the model:

- H_2O (default a H_2O = 1.03);
- a $Mn^{2+} = 10^{-6}$; and
- a CaO (lime) = 1 Mole/*l*, i.e. 56 g/kg water.

The results obtained from the manganese stability field analysis with lime addition are similarly characterised by the following (Figure 7.4; Table 7.2 and 7.3):

- Mn^{2+}as the only aqueous species occurs in a relative narrow field in this system;
- The following manganese minerals occur in the system: pyrolusite (MnO_2), and rhodochrosite ($MnCO_3$) with a small field of bixbyite (Mn_2O_3) while two iron minerals occur in this system namely Ferrite ($CaO\cdot Fe_2O_3$) and wustite ($Fe_{0.947}O$);
- Manganese is mostly stabilised above a pH of 7 and the manganese stability field is significantly increased.

At the standard physico-chemical conditions, the system will not produce significant amounts of aqueous manganese species. In this case, addition of lime to the manganese-bearing wastes will be able to stabilize manganese. Lime addition is however not as good an option as the addition of calcite due to the fact that more $MnCO_3$ will precipitate due to addition of CO_3^{2-}. In addition, calcite reacts at a much slower rate than lime and is therefore a better treatment option to lime treatment for the stabilization of manganese-bearing wastes.

7.3.2.5 H_2O-Mn-Fe-Dolomite ($CaO_3\cdot MgCO_3$) system

The third management option considered is the impact of dolomite addition to manganese containing waste. Dolomite addition dramatically increased the manganese stability fields to just above neutral pH 7. The following input data was used:

- H_2O (default a H_2O = 1);
- a $Mn^{2+} = 10^{-6}$; and
- a Dolomite = 1 Mole/*l*, i.e. 186 g/kg water.

The results obtained from dolomite addition are quite similar to those obtained by calcite addition. The results obtained from the manganese stability field analysis can be summarized as follows (Figure 7.5, Table 7.2 and 7.3):

- Only $MnHCO_3^+$ occurs in a relative narrow field in this system;
- A number of manganese minerals occur in the system. These include: pyrolusite (MnO_2), and rhodochrosite ($MnCO_3$) with minor fields of bixbyite (Mn_2O_3) and Hausmannite ($MnO\cdot Mn_2O_3$). Three iron minerals occur in this system namely Hematite (Fe_2O_3), Magnetite ($FeO\cdot Fe_2O_3$) and wustite ($Fe_{0.947}O$); and

- Manganese is mostly stabilised above a pH of 7 and the manganese stability field significantly increased.

At the standard physico-chemical conditions, no significant amounts of aqueous manganese species will be produced in the system. In this case, addition of dolomite to manganese-bearing waste will be able to reduce mobility of manganese in solution. Table 7.2 summarizes relative concentrations of aqueous manganese species in the modelled systems. The major aqueous manganese species include Mn^{2+}, $Mn(NH_3)_2^{2+}$ and/or $Mn(NH_3)_3^{2+}$ with minor amounts of $MnHCO_3^+$, $Mn(OH)_3^+$ and/or $Mn(OH)_3^-$, Fe^{3+}, $FeCO_3^+$, and $FeSO_4^+$.

Table 7.3 summarizes the different manganese mineral phases in the modelled systems. The major manganese minerals are: pyrolusite, rhodochrosite, and hausmannite, with minor amounts of bixbyite, hematite, magnetite, wustite, and ferrite-Ca.

To stabilise Mn in mineral phases requires a higher pH (10) in the pure water system than these (pH 7 and 8) in other systems, e.g., addition of chemicals.

Table 7.2: Summary of aqueous species from equilibrium geochemical modelling results

Systems	**Mn++**	**$MnHCO_3$+**	**$Mn(OH)_3$+ $Mn(OH)_3$-**	**$Mn(NH_3)_2$ ++ $Mn(NH_3)_3$++**	**Fe+++**	**$FeCO_3$+ $FeSO_4$+**
H_2O-Mn	****	-	**	-	*	-
H_2O-Mn-Fe-Ca-CO_2-S-Cl-NO_3	****	-	-	****	-	*
H_2O-Mn-Fe-CaO_3	-	*****	-	-	*	*
H_2O-Mn-Fe-CaO	*****	-	-	-	*	-
H_2O-Mn-Fe-$CaCO_3 \cdot MgCO_3$	-	*****	-	-	*	*

Note: * trace; ** minor; *** major; **** dominating; ***** absolutely dominating

Table 7.3: Summary of mineral relative abundance in terms of stabilising field from equilibrium geochemical modelling results

Systems	**Pyrolusite**	**Rhodochrosite**	**Bixbyite**	**Hausmannite**	**Hematite Magnetite Wustite Ferrite-Ca**	**Stable field for pH >**
H_2O-Mn	***	-	**	***	*	10.0
H_2O-Mn-Fe-Ca-CO_2-S-Cl-NO_3	***	***	*	-	*	8.0
H_2O-Mn-Fe-CaO_3	***	****	**	**	*	7.0
H_2O-Mn-Fe-CaO	***	****	*	-	*	7.5
H_2O-Mn-Fe-$CaCO_3 \cdot MgCO_3$	***	****	**	**	*	7.0

Note: * trace; ** minor; *** major; **** dominating; ***** absolutely dominating

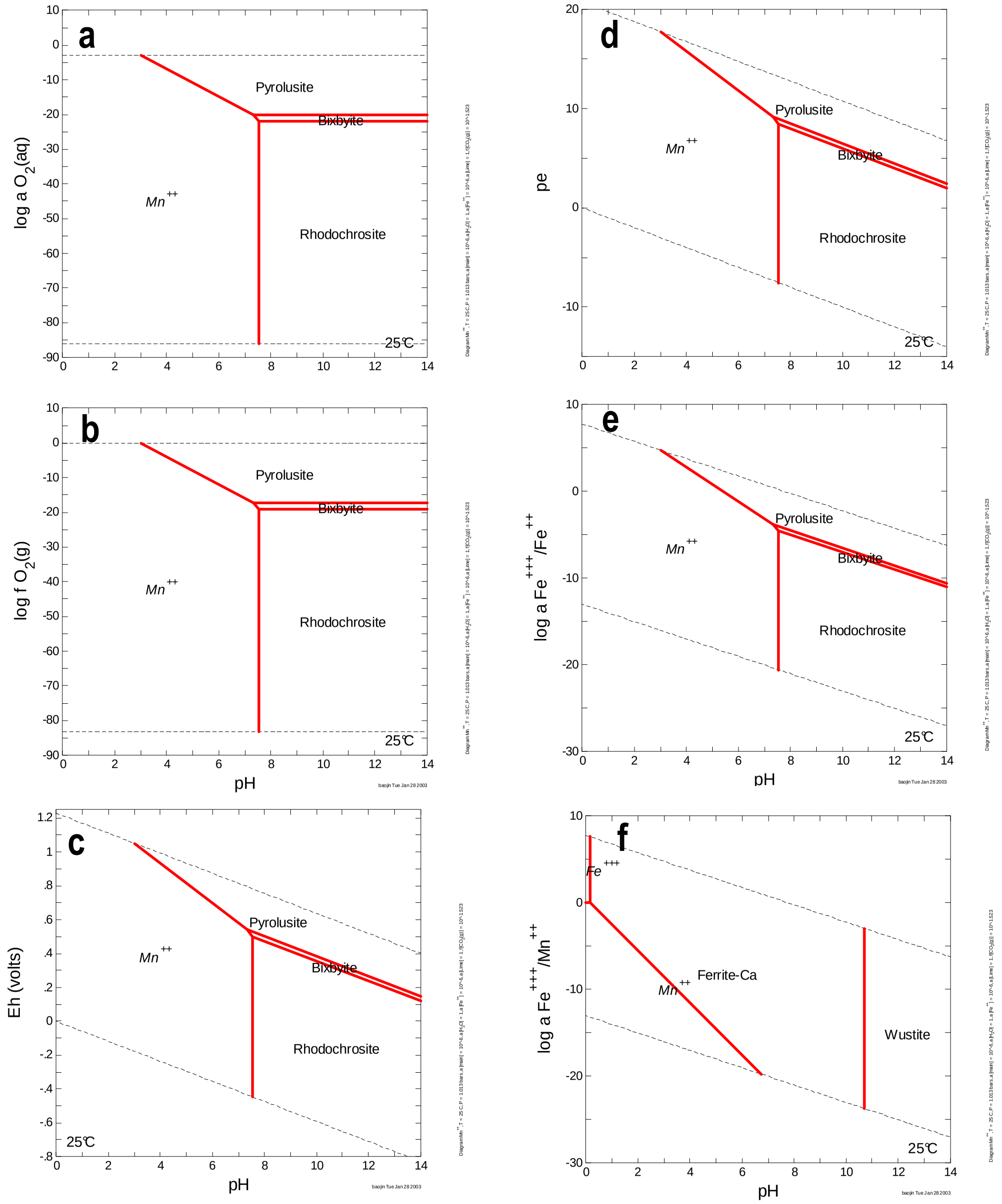

Figure 7.4: Stability fields for manganese in a H_2O-Mn-Fe-CaO (lime) system on log fO_2(aq) (a), log fO_2(g) (b), Eh (c), pe (d), Fe^{3+}/Fe^{2+} (e) and Fe^{3+}/Mn^{2+} (f) vs pH

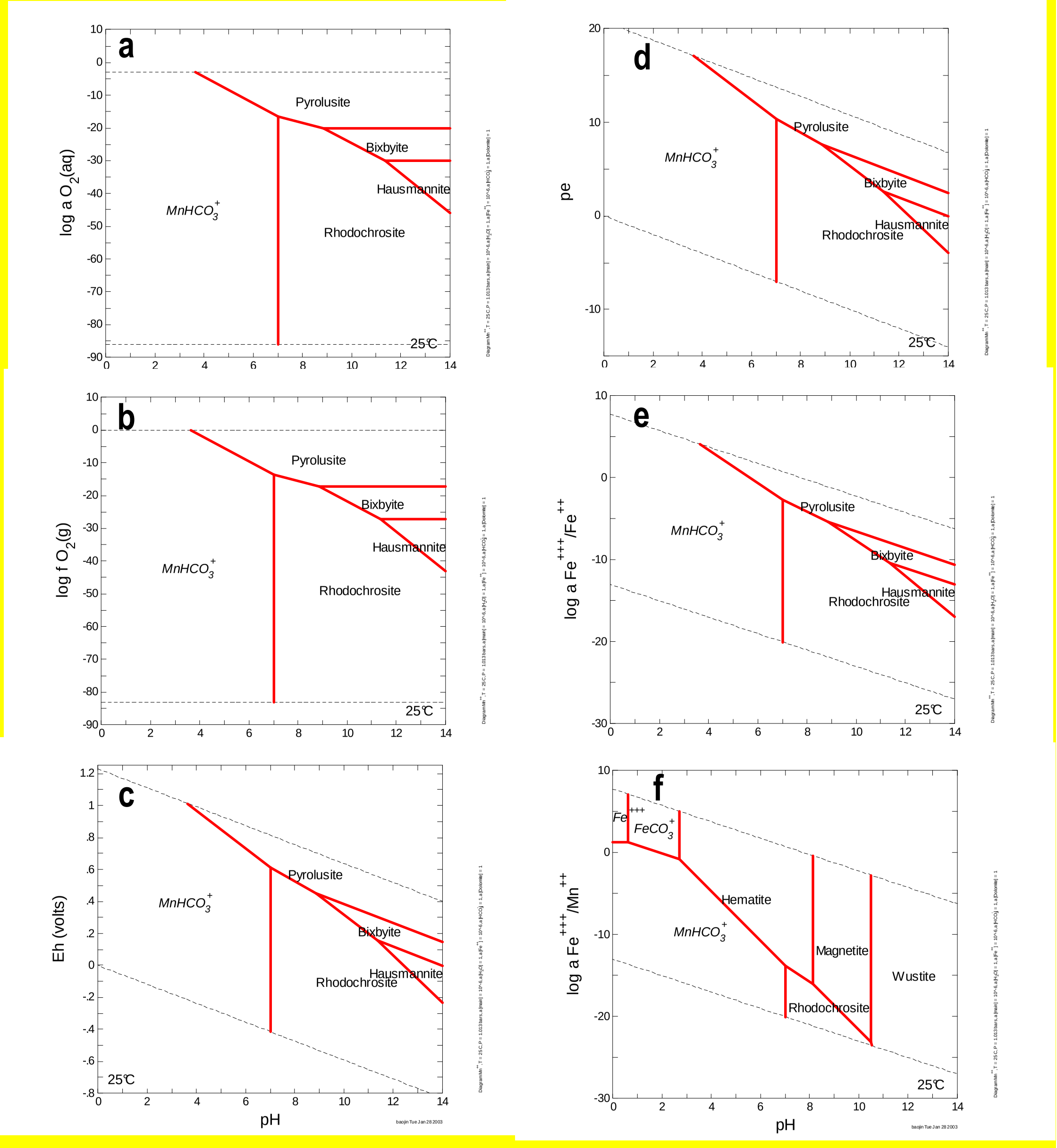

Figure 7.5: Stability fields for manganese in a H_2O-Mn-Fe-$CaMg(CO_3)_2$ system on log fO_2(aq) (a), log fO_2(g) (b), Eh (c), pe (d), Fe^{3+}/Fe^{2+} (e) and Fe^{3+}/Mn^{2+} (f) vs pH

7.3.3 Speciation using equilibrium modelling

Water extraction column leaching was performed on three scrubber dust samples (Horowitz, 1991):

- 200 kW pilot plant - wet scrubber dust (Trial 1) produced under reducing conditions;
- 1.5 MW pilot plant - baghouse dust produced under oxidising conditions; and
- Ticor full-scale facility-wet scrubber dust produced under reducing conditions.

This section deals with aqueous speciation and mineral saturation index analysis performed on the water quality data obtained from the leachates after extraction. The following need to be determined:

- Chemical concentrations;
- Mineral types;
- Mineral precipitation status; and
- The effect of the water chemistry and mineral saturation for the three samples.

7.3.3.1 Water quality from the original column leachates

The three leachates were analysed for water chemistry and the analytical results are listed in Table 7.4.

Table 7.4: Water quality data obtained after water extraction

Sample	**200 kW -Run 1 Pilot scale study (reducing conditions, Nov.02)**	**1.5 MW Pilot scale study (oxidising conditions, Oct. 02)**	**Ticor full-scale operation (reducing conditions, June 03)**
pH	7.45	8.15	7.05
Electrical conductivity (mS/m)	93.30	15.20	23.60
Total dissolved solids (mg/l)	700	114	198.375
Na (mg/l)	24.71	4.35	13.65
K (mg/l)	16.44	8.02	20.36
Mg (mg/l)	14.79	4.42	2.03
Ca (mg/l)	70.93	4.22	2.37
Fe_{total} (mg/l)	0.11	<0.05	<0.05
Al (mg/l)	2.50	1.84	1.36
Co (mg/l)	0.03	<0.05	<0.05
Cu (mg/l)	0.06	<0.05	0.05
Pb (mg/l)	<0.05	<0.05	<0.05
Ni (mg/l)	0.09	0.02	<0.05
Cd (mg/l)	0.03	0.02	N/A
Zn (mg/l)	0.29	0.32	1.03
Mn (mg/l)	0.09	<0.05	0.14
Cl (averaged) (mg/l)	1.191	0.861	5.52
F (avergaed) (mg/l)	4.956	1.783	2.45
Alkalinity as $CaCO_3$ (mg/l)	10.84	18.07	177.5
SO_4 (mg/l)	845	128	17.54

Redox potential was not measured for the column leachates as leaching was performed under oxidising conditions. The chemical water data were plotted in a histogram in order to compare the chemical compositions of the materials formed under different physico-chemical conditions (Figure 7.6). The following results were obtained:

- The quantity of metals leached from the 1.5 MW scrubber dust was lower than that leached from the 200 kW scrubber dust and the Ticor full operation sample. This indicates that more stable manganese minerals form under oxidising conditions, which corresponds with the activity diagram analysis;
- The total dissolved solids (TDS) leached from the 1.5MW scrubber dust sample (83 mg/ℓ) are much lower than the TDS leached from the 200 kW scrubber dust sample (437 mg/ℓ) and the Ticor full-scale operation sample (198 mg/ℓ).
- The concentrations of manganese, cobalt and copper leached from the 1.5 MW scrubber dust sample was below detection limit while small amounts of these metals were leached from the 200 kW scrubber dust sample (0.09 mg/ℓ) and Ticor full-scale operation sample (0.14 mg/ℓ) (Table 7.4).
- Nickel and cadmium concentrations leached from the 1.5 MW scrubber dust sample were lower than the amount leached from the 200 kW scrubber dust sample.
- Although more alkalinity was produced in the leachate of the 1.5 MW scrubber dust than in the leachate from the 200 kW scrubber dust sample, the highest alkalinity was found in the Ticor full-scale sample.

These results could be attributed to:

- The formation of more stable manganese minerals, e.g. pyrolusite, bixbyite and hausmannite in the 1.5 MW scrubber dust sample.
- The occurrence of more soluble manganese mineral phases in the 200 kW scrubber dust and the Ticor full-scale operation samples that can easily be leached by water.

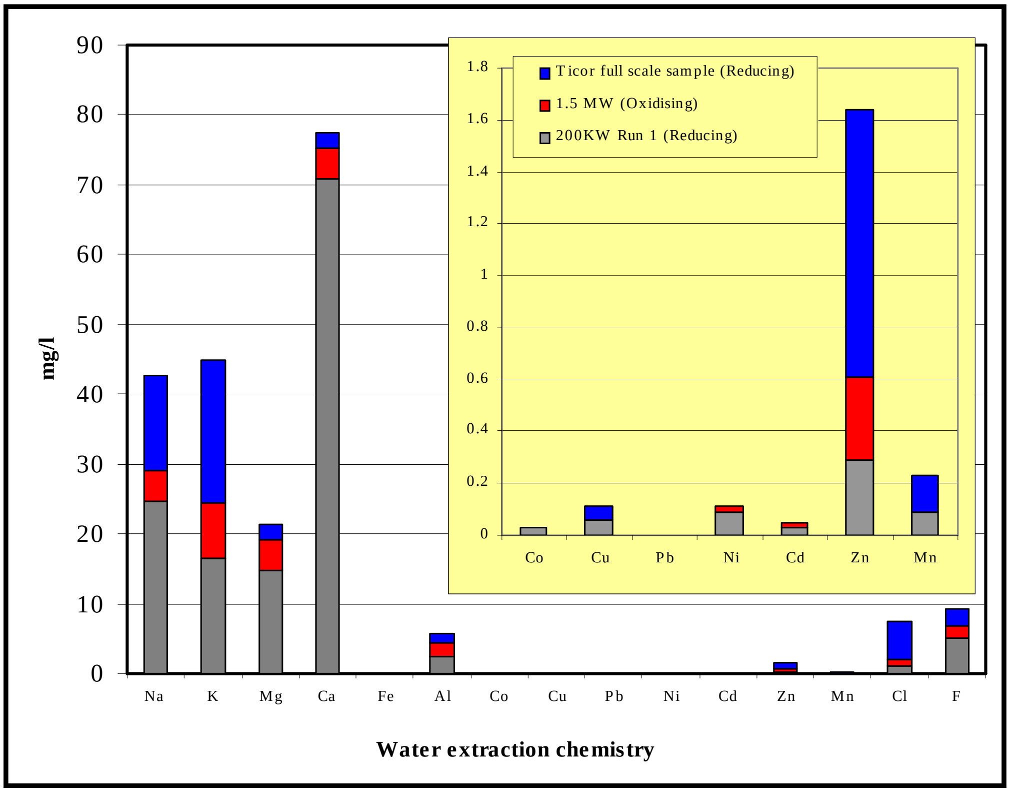

Figure 7.6: Water quality data for the metals for the water extractions performed on the 200 kW, Ticor full-scale operation, and 1.5 MW scrubber dust samples

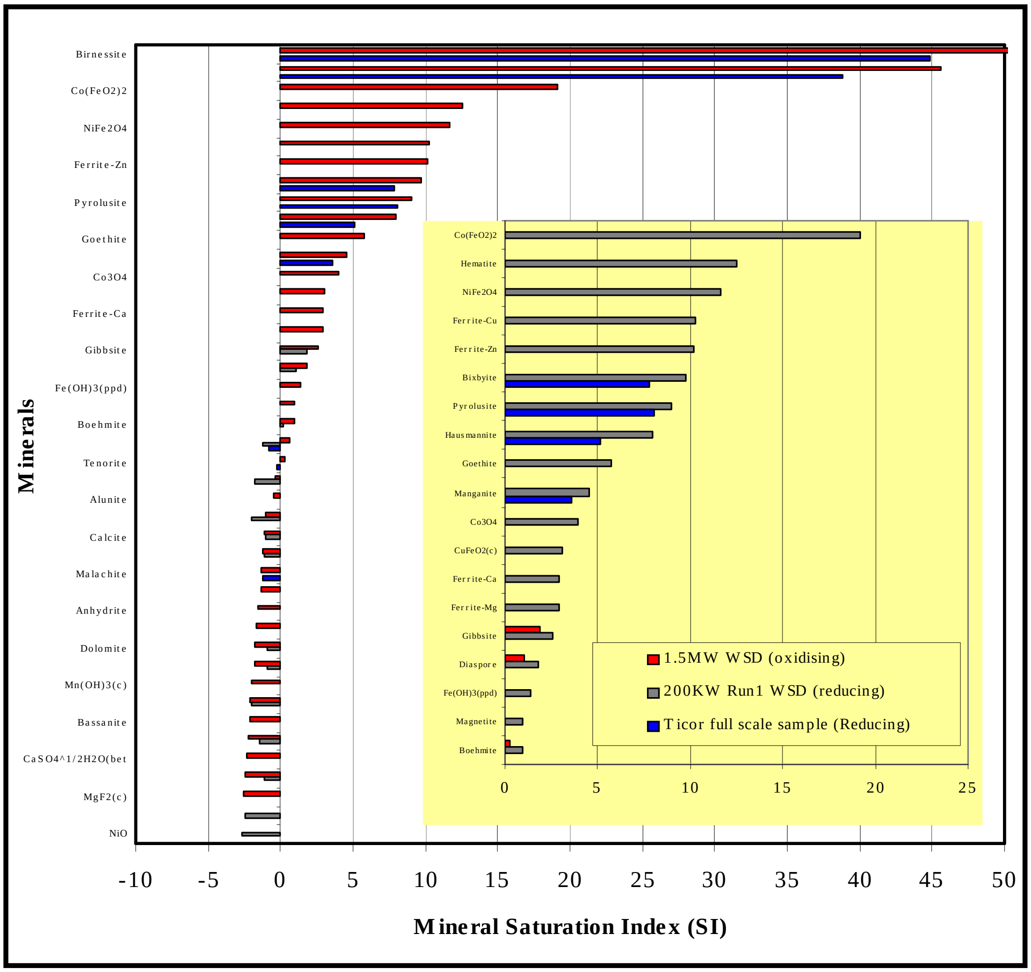

Figure 7.7: Mineral saturation index plot showing mineral supersaturation and undersaturation status of the scrubber dusts produced under oxidising and reducing conditions. The insert graph illustrates the mineral saturation index between 0 and 25.

7.3.3.2 Mineral saturation index (SI) analysis from equilibrium modelling results

The equilibrium model was developed using REACT of the Geochemist’s Workbench computer package. Initially, speciation and water chemistry equilibrium for the three different samples were performed using Phreeqc 2.0. The molality results of the water chemistry were used as input to the REACT in order to perform a full speciation. The mineral saturation index (SI) is plotted using histograms to demonstrate the possible variations between the different samples (Figure 7.7). Positive SI numbers indicates supersaturation while negative numbers indicate undersaturation. In the model, no precipitation was allowed in order to represent the current water system instead of equilibrium with solids.

The results obtained from the SI can be summarised as follow:

- Only small number of minerals (gibbsite, diaspore, corundum, hydrozincite) are supersaturated in the 1.5 MW scrubber dust sample while large amounts of minerals are supersaturated in the 200 kW and Ticor full-scale operation scrubber dust samples.
- No manganese-bearing mineral is supersaturated in the 1.5 MW scrubber dust sample while a number of minerals are supersaturated in the 200 kW and Ticor full-scale operation scrubber dust samples.
- Hausmannite, pyrolusite, bixbyite, the major manganese-bearing minerals are not supersaturated in the 1.5 MW scrubber dust sample but are supersaturated in the 200 kW and Ticor full-scale operation scrubber dust samples.
- Ferrite-Ca, $CuFeO_2$, Co_3O_4 ($CoO \cdot Co_2O_3$), manganite (MnOOH) and goethite (FeOOH), containing iron, copper and cobalt metals are not supersaturated in the 1.5 MW scrubber dust sample while they are supersaturated in the 200 kW and Ticor full-scale operation scrubber dust samples.

In summary, more chemical components, specifically manganese were leached out from the 200 kW and Ticor full-scale samples produced under reducing conditions than from the 1.5 MW sample produced under oxidising conditions.

Coinciding with the chemical concentration analysis, it can be concluded that the oxidised sample (1.5 MW) contains less leachable metals, especially manganese, cobalt, nickel, copper and iron than the reduced samples (200 kW, Ticor full-scale operation). Less minerals, specificaly manganese-bearing minerals are saturated in the oxidised sample (1.5 MW) than in the reduced sample (200 kW, Ticor full-scale operation) at normal water conditions, i.e. close to neutral water.

7.3.4 Kinetic modelling to determine the effectiveness of waste treatment management options

The kinetic modelling was carried out on 3 options using the geochemical data and water quality data obtained from the 3 selected samples. Modelling was performed under both reducing and oxidising conditions. The following treatment options were investigated:

- Option 1 – No treatment;
- Option 2 - Addition of lime; and
- Option 3 – Addition of calcite.

The modelling was undertaken for a hypothetical mono-landfill site containing only scrubber dust material, i.e. this does not simulate the tailings dam system employed at Ticor for scrubber dust disposal where the waste is blended/diluted with normal tailings. The modelling was therefore undertaken for a worst case scenario.

7.3.4.1 Data input and assumptions

The water quality data sets obtained from the three scrubber dust samples (Table 7.4) were condensed to 10 % using the REACT model of the Geochemist's Workbench software package. This roughly represented the pore water quality of the three scrubber samples. The condensed water quality data was used as initial pore water quality in the kinetic geochemical modelling study.

7.3.4.2 Solid geochemistry of the scrubber dust samples

Table 7.5: Major chemical composition (wt%) of the scrubber dust samples determined by XRF

Analysis	200 kW scrubber dust-Run 1	1.5 MW scrubber dust	Ticor full-scale sample*
SiO_2	21.9	4.37	7.64
TiO_2	15.9	63.94	49.82
Al_2O_3	3.59	1.28	1.16
Fe_2O_3(t)	37.33	26.89	32.46
MnO	2.88	2.86	4.72
MgO	11.63	1.18	1.39
CaO	0.55	0.19	0.13
Na_2O	0.74	0.29	1.12
K_2O	0.32	0.36	1.2
P_2O_5	0.08	0.05	0.04
Cr_2O_3	0.74	0.15	0.16
L.O.I.	-0.12	-1.48	-0.6
TOTAL	95.53	100.08	100.47
H_2O-	0.79	0.12	0.7

* TiO_2 and Fe_2O_3(t) exceeded the upper limit of calibration.

In order to determine the mineralogy based on XRF and XRD analyses, the relationships between oxides and potential minerals are required. These are listed in Table 7.6.

The results can be summarised as follow:

- SiO_2 (Quartz, albite, muscovite, K-feldspar) are present in all three scrubber dust samples;
- For the major chemical composition TiO_2, possible minerals related to the 1.5 MW scrubber dust sample are pseudobrookite, rutile and ilmenite while titanomanetite or ilmenite and rutile are possible minerals related to the 200 kW and Ticor full-scale scrubber dust samples obtained under reducing conditions;
- Albite, muscovite and K-feldspar related to Al_2O_3 were identified in both the oxidised (1.5 KW) and the reduced (200 kW, Ticor full-scale operation) scrubber dust samples;
- Of the minerals related to Fe_2O_3, ilmenite and pseudobrookite were identified in the oxidised sample (1.5 KW) while titanomanetite was identified in the reduced samples (200 kW). Lepidocrocite occurred in the Ticor full-scale operation sample;

- Pyrolusite and bixbyite were identified as possible minerals related to MnO in the oxidised sample (1.5 KW), while alabandite and rhodochrosite were identified as a possible mineral related to MnO in the reduced samples (200 kW, Ticor full-scale operation).
- Carbonate minerals including siderite, cerussite were enriched in the 200 Kw Run1. Although, rhodochrosite was not detected by XRD in the sample, it should occur based on the Mn stability diagram (Figure 7.3) and the running condition of burning coal under reducing conditions. The Ticor full-scale sample was also produced under similar conditions, i.e. burning of coal and reducing condition so that they should also be enriched in carbonate minerals as in the 200 kW sample. It is also noticed that the 2A^o d-space was not allocated in the XRD analysis, which might be due to rhodochrosite. Therefore, Mn determined by XRF was assigned to rhodochrosite in the 200 kW scrubber dust sample and to rhodochrosite and pyrolusite in equal portions in the Ticor full-scale operation sample. Under oxidising conditions, Mn will be stable in the form of pyrodolusite and also no carbonate minerals were detected in the 1.5 Mw sample.
- CaO most probably occurs in apatite in both samples because P_2O_5 exists proportionally with CaO (Table 7.6); and
- Cr_2O_3 most probably occurs as chromite ($FeOCr_2O_3$) in both the reduced and the oxidised scrubber dust samples.

When evaluating the loss of ignition data, OH, Cl and F exist in both the 200 kW and Ticor full-scale operation and 1.5 MW scrubber dusts.

Table 7.6: Summary of possible minerals related to major chemical compositions

Analysis	**1.5 MW scrubber dust**	**200 kW scrubber dust**	**Ticor full-scale operation scrubber dust**
SiO_2	Quartz, albite, muscovite, k-feldpsar	Quartz, albite, muscovite, K-feldspar	Quartz, albite, muscovite, K-feldspar
TiO_2	Pseudobrookite, rutile, ilmenite	Titanomangnetite, rutile,	Ilmenite, rutile
Al_2O_3	Albite, muscovite, K-feldspar	Albite, muscovite, K-feldspar	
Fe_2O_3(t)	Ilmenite, pseudobrookite,	Titanomagnetite	Lepidocrocite (γ-FeO·OH)
MnO	Pyrolusite, bixbyite	Alabandite, rhodochrosite	Rhodochrosite, pyrolusite
MgO	Spinel magnesian ($MgO \cdot Al_2O_3$)	Spinel, magnesium ($MgOAl_2O_3$)	Spinel, magnesian ($MgOAl_2O_3$)
CaO	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)
Na_2O	Albite	Albite	Albite
K_2O	Muscovite, K-feldspar	Muscovite, K-feldspar	Muscovite, K-feldspar
P_2O_5	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)	Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)
Cr_2O_3	Chromite ($FeOCr_2O_3$)	Chromite ($FeOCr_2O_3$)	Chromite ($FeOCr_2O_3$)
L.O.I.	OH, F-, Cl-	OH, F-, Cl-	OH, F-, Cl-

7.3.4.3 Mineralogical data used for kinetic geochemical modelling

Table 7.7: Mineralogical data determined by XRD

Sample	Condition	Sid	Cer	Mas	Ala	Zin	TitM	Ilm	PseuB	Rut	Pyr	Le	Me	Rho*
200 kW scrubber dust – run 1	Reducing	6	2	36	7	16	15	9	-	3	-	-	-	-
1.5 MW scrubber dust	Oxidising	-	-	-	-	-	-	6	79	15	-	-	-	-
Ticor full-scale sample		-	-	-	-	-		46		24		17	13	-

Note: Sid – Siderite; Cer – Cerusite; Mas – Massicot; Ala – Alabandite; Zin – Zinkenite; TiM – Titanomagnetite; Ilm - Ilmenite; PsueB – Pseudobrookite; Rut – Rutile; Pyr – Pyrolusite; Le – Lepidocrocite (γ-FeO·OH); Me – Metal and or Alloy; Rho* - Rhodochrosite and its amount will be allocated and shown in modelling based on XRF data.

The ideal formulae for the listed minerals are:

Alabandite (MnS)
Cerussite ($PbCO_3$)
Ilmenite ($FeTiO_3$)
Lepidocrocite (γ-FeO·OH)
Massicot (PbO)
Pseudobrookite ($Fe_2O_3\cdot TiO_2$)
Pyrolusite (MnO_2)
Rhodochrosite ($MnCO_3$)
Rutile (TiO_2)
Siderite ($FeCO_3$)
Titanomagnetite ($TiO2\cdot FeO\cdot Fe_2O_3$)
Zinkenite ($Pb_9Sb_{22}S_{42}$).

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All these minerals were obtained from XRD analysis (Table 7.7) except pyrolusite and rhodochrosite that were estimated from XRF data (Table 7.5). The mineralogical data used was converted to grams per kilogram of water (g/kgw) (Table 7.8) and used as reacting minerals in the kinetic geochemical modelling based on the different moisture contents of the samples (in weight percent).

Table 7.8: Mineral composition (g/kg)

Sample ID	**Siderite (FeCO3)**	**Cerussite (PbCO3)**	**Pseudo-brookite (Fe2O3TiO2)**	**Massicot (PbO)**	**Zinkenite (Pb9Sb2S42)**	**Titabo-magnetite (TiO2FeOFe2O3)**	**Ilmenite (FeOTiO2)**	**Rutile (TiO2)**	**Pyrolusite***	**Rhodochrosite***
200 kW scrubber dust – Run 1	372	124	0	2232	992	930	0	186	-	264
1.5 MW scrubber dust	0	186	4898	0	0	0	372	930	598	-
Ticor full-scale operation scrubber dust based on 40wt% moisture	0	0	325	0	0	0	1150	600	72	96

Pyrolusite (MnO_2) and rhodochrosite were estimated from XRF data.

7.3.4.4 Recharge (rain) water quality and recharge rate

Pure rainwater was used as the only recharge water entering the system in the kinetic geochemical modelling. A recharge rate of 20 % and an assumed rainfall of 800 mm/yr were used for the kinetic modelling. The oxidising zone is unsaturated with water and its recharge rate of rainwater is estimated to be 0.40 kg per litre of pore water per year while the reducing zone is saturated with water and its recharge rate of rainwater is estimated to be 0.60 kg per litre of pore water per year.

7.3.4.5 Oxygen levels and assumption for height of dumps

Oxidising conditions refer to the top portion of the potential scrubber dump waste dump while reducing conditions refer to the bottom portion of the dump under the water table in a general landfill site.

The oxygen fugacity is assumed to be 10^{-15} to 10^{-20} at fixed level for the oxidised zone while it is assumed that no oxygen is present in the reduced zone.

A height of 10 m was assumed for both the oxidising zone (under oxidising condition) and reducing zone (under water table). This assumption was done to enable the estimation of the rainwater recharge in terms of per litre of pore water.

7.3.4.6 Mineral surface areas

Specific mineral surface areas (cm^2/g) were estimated from the particle size analysis (Waterlab). The estimation is based on the following formula:

$$\boxed{S=(6/d)/d_s*\lambda}$$

where:

S = True reactive area per volume, e.g., cm^2/g.
d = Diameter of the sphere, unit in length;
d_s = mineral specific density; and
λ = Surface roughness (true reactive surface area/equivalent smooth geometric surface area), dimensionless = 9 for this study.

The estimated specific surface areas ranged between 400 and 5000 cm^2/g (Table 7.9). The specific surface areas of calcite (5000 cm^2/g) is also estimated and used in the kinetic geochemical modelling.

Table 7.9: The estimated specific mineral surface areas (cm^2/g)

Mineral	**200 kW (Trial 1) - WSD**	**1.5 MW - Baghouse**	**Ticor full-scale - WSD**
Siderite	766	547	N/A
Alabandite	764	N/A	N/A
Cerussite	745	532	N/A
Pseudobrookite	750	536	4445
Massicote	408	291	N/A
Zinkenite	764	546	N/A
Titanomagnetite	766	547	N/A
Ilmenite	654	467	3873
Rutile	639	456	3785
Pyrolusite	766	547	4536
Calcite	5000	5000	5000

7.3.4.7 Mineral reaction rates

Most of the mineral reaction rates are not available in literature and most of them were estimated in a range between 1e^{-12} to 1e^{-17} mole/cm^2/s for this study.

7.3.4.8 Kinetic geochemical modelling

Three scrubber dust samples containing manganese (viz 200 kW wet scrubber dust and full-scale Ticor wet scrubber dust collected under reducing conditions and the 1.5 MW baghouse dust collected under oxidising conditions) were modelled. The effect of reducing and oxidising conditions that prevail in a waste dump for untreated and treated waste were predicted for a 100-year period. A number of models (18) were used and the results are presented in Figure 7.7 in terms of pH, and manganese in solution.

Option 1 – No treatment

Option 1 is defined as base case, i.e. no treatment. Figure 7.8 shows the modelled results in terms of pH (top) and Mn in solution (bottom). They are characterised by the following:

- The pH is mostly neutral except for the 200kW Run1 formed under reducing conditions where alkaline conditions up to 10.5 are expected after about 10 years. No clear trends for pH in reducing and oxidising environment can be seen;
- Higher levels of Mn^{2+} in solution were found under reducing conditions of the dump while manganese levels decrease under oxidising conditions for the sample 200 kW and Ticor full-scale operation scrubber dust samples.
- Although manganese concentrations are low under reducing conditions for the 1.5 MW scrubber dust sample, it is even less under oxidising conditions.

- For the first 10 years, pH increases to above 10 for the 200 kW scrubber dust sample under a reducing environment while pH is lower under oxidising conditions - most probably due to reaction of alabandite (MnS); and
- Mn concentration in solution is the highest, specifically in the first 10 years in 200 kW scrubber dust sample while it is the lowest in the 1.5 MW scrubber dust sample.

Option 2 – Addition of 1 mole of lime

Option 2 is defined as one of the management options. Figure 7.9 shows the disposal option 2 under addition of 1 mole of lime (CaO). The modelling results are characterised as follow:

- At first, pH rapidly increases to an alkaline range under both reducing and oxidising conditions in the dump. The addition of lime is responsible for the neutralisation of acid and also MnS;
- Addition of lime (CaO) will cause high pH in the solution and it therefore creates an alkaline environment. Manganese is mostly oxidised to pyrolusite (MnO_2) and bixbyite (Mn_2O_3); and
- Mn concentration is still the highest in 200 kW scrubber dust sample, but it is stabilises after the first 5 years under the reducing environment and becomes much lower under the oxidising environment.

Option 3 – Addition of 1 mole of calcite

Option 3 is defined as one of the best management options. Figure 7.10 shows the modelling results in terms of pH and Mn concentration in solution. The results are characterised by the following:

- At first, pH rapidly increases to an alkaline range of 7 and 11. This is true for both reducing and oxidising conditions in the dump due to addition of calcite and neutralisation of MnS. The pH is higher in the 200 kW and Ticor full-scale operation scrubber dust samples than in the 1.5 MW scrubber dust sample. This could be attributed to the high amounts of alabandite (MnS) found in the 200 kW scrubber dust; and
- Addition of calcite ($CaCO_3$) will increase the pH to alkaline levels in solution and achieve similar results of manganese removed to that removed by the addition of lime under the oxidising environment. The addition of calcite will however stabilise manganese over a longer period than treatment using lime.

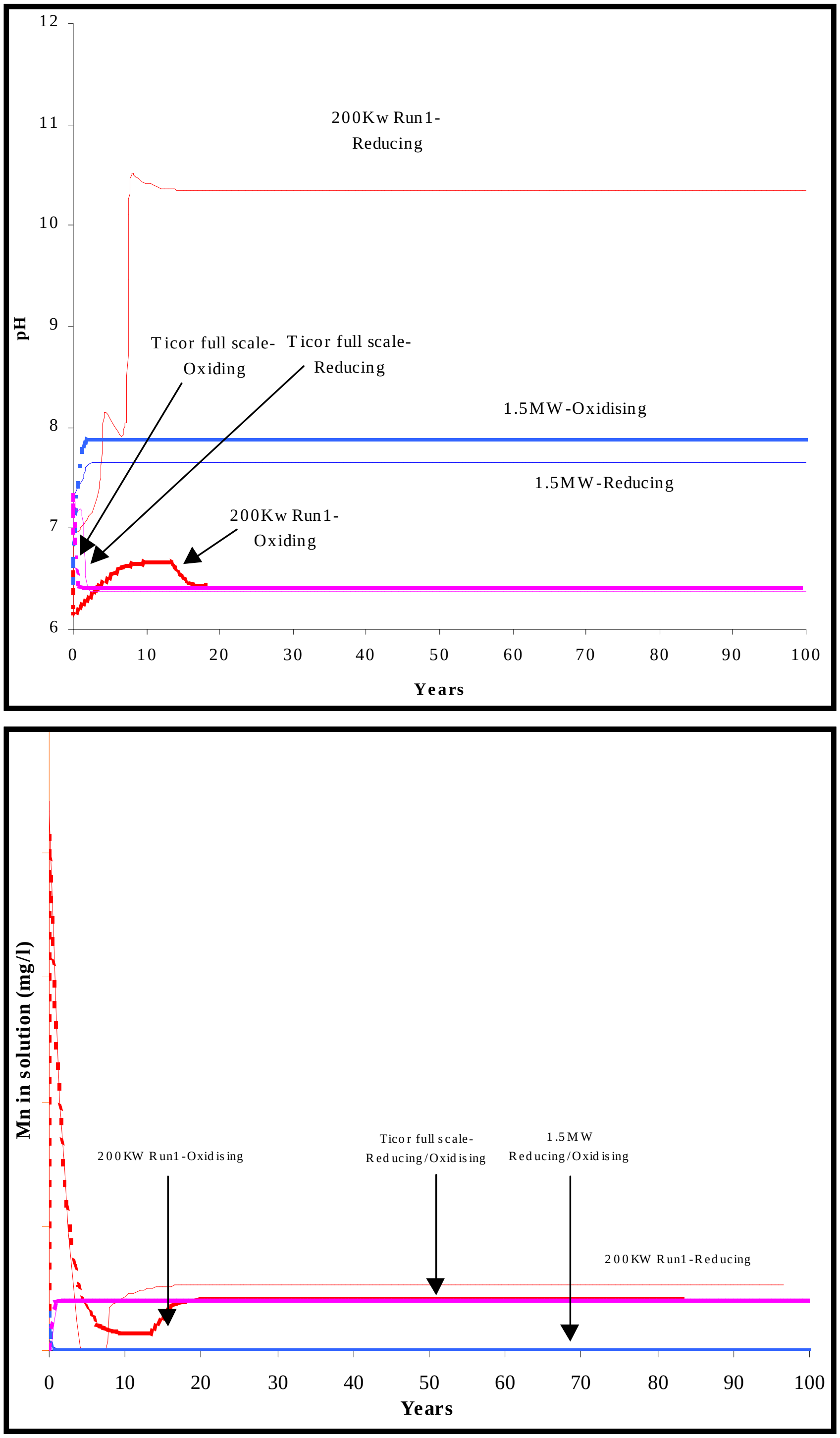

Figure 7.8: Disposal Option 1, no treatment: pH (top); and Mn in solution (bottom). Labels: -reducing, –oxidising, indicating the models were performed at reducing and oxidising conditions, respectively

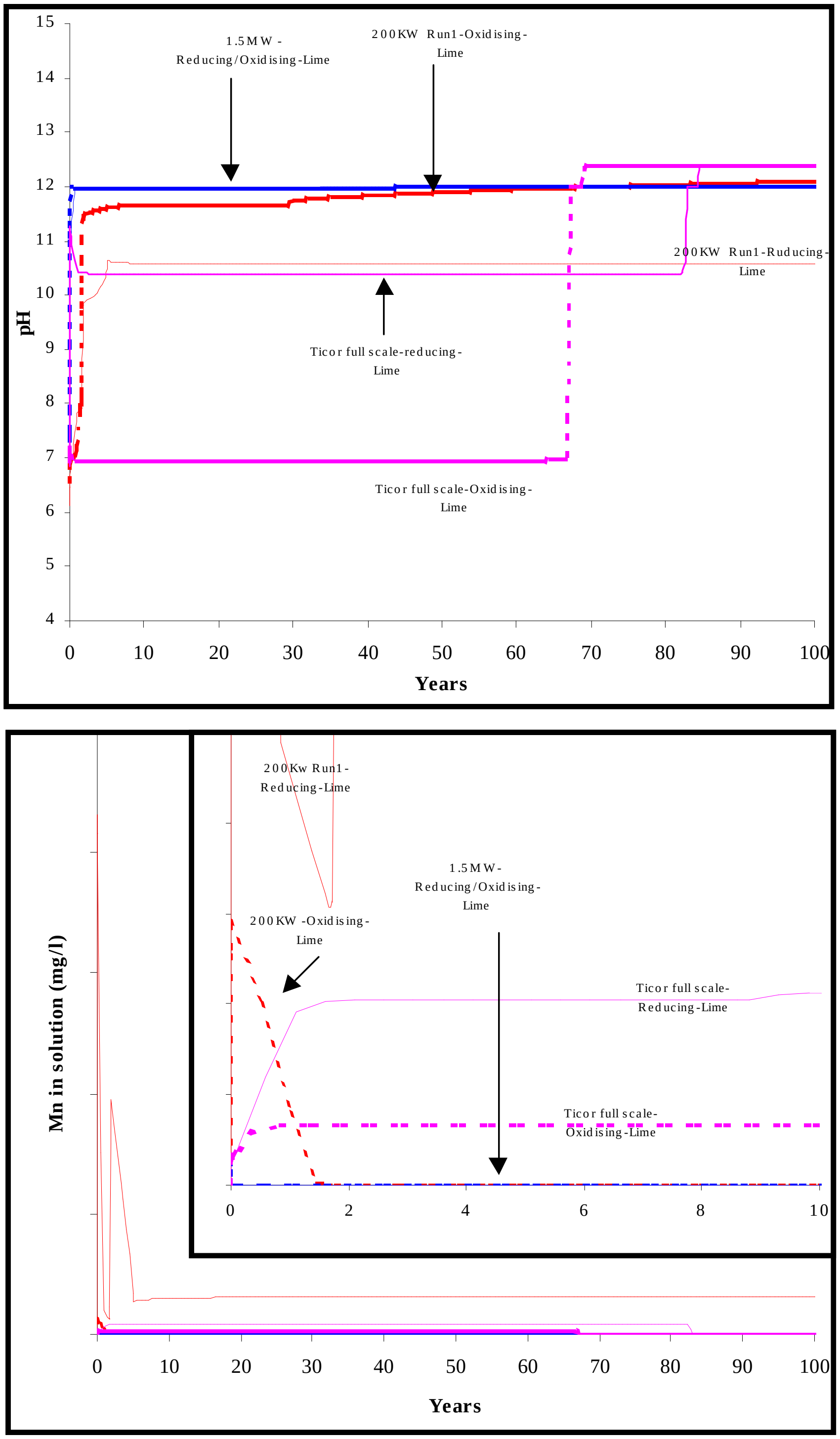

Figure 7.9: Disposal Option 2, addition of 1 mole of lime (CaO): pH (top); and Mn in solution (bottom). Labels: -reducing, –oxidising, indicating the models were performed at reducing and oxidising conditions, respectively; -Lime indicating addition of lime

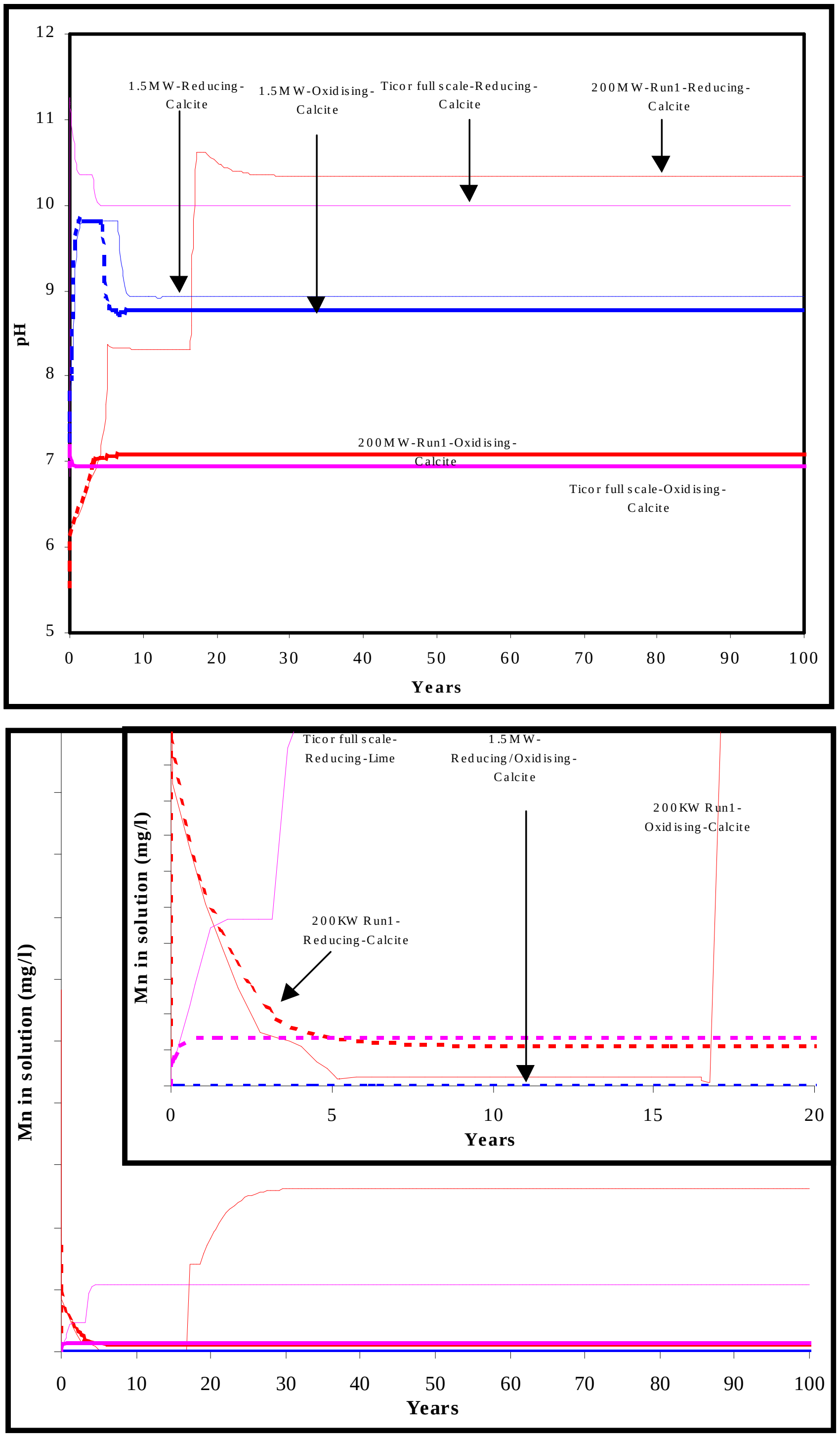

Figure 7.10: Disposal Option 3, addition of 1 mole of Calcite: pH (top); and Mn in solution (bottom). Labels: -reducing, –oxidising, indicating the models were performed at reducing and oxidising conditions, respectively; -Calcite indicating addition of calcite

Table 7.10 summarises the results from Water Extraction and Acid Rain Leach Test Procedure (ARLP) for the three samples. It is clear that the 200 kW Run1 and Ticor full-scale samples as Group 1 were produced under reducing conditions while the 1.5 MW sample as Group 2 was produced under oxidising conditions.

Mn concentrations obtained from Water Extraction and ARLP are characterised by the following:

- Mn concentrations in the Group 1 samples (200 kW Run1 and Ticor full-scale samples) are higher than in the Group 2 sample (1.5 MW sample) in the water extraction leachate, but there is not a significant difference between the two groups of samples;
- A reverse order for Mn concentrations occurs in the ARLP test results. Mn concentrations are much lower in the Group 1 (200 kW Run1 and Ticor full-scale samples) than in the Group 2 (1.5 MW sample). There is a significant difference between the two groups of the samples.

The reasons can be explained as follows:

- Carbonate minerals including siderite, cerussite were enriched in the 200 kW Run1. Although, rhodochrosite was not detected by XRD in the sample, it should occur in it based on the Mn stability diagram (Figure 7.3) and the running condition of burning coal under reducing conditions. The Ticor full-scale sample was also produced under similar conditions, i.e. burning of coal and reducing condition so that they should also be enriched in carbonate minerals as in the 200 kW sample. Under oxidising conditions, Mn will be stable in the form of pyrodolusite and also no carbonate minerals were detected in the 1.5 MW sample.
- XRF analysis (Table 7.5) indicates that MnO wt% in the two groups of the samples are not significantly different. In this case and based on the Mn stability diagram, Mn is similarly leachable from the two groups of samples under acid conditions, e.g. pH 3.6 – 3.8 (see Figure 7.3);
- Reaction of carbonate minerals in the Group 1 samples (200 kW Run1 and Ticor full-scale samples) in the Acid Rain solution will be able to enhance pH from acid to neutral or alkaline pH so that Mn will be stable. This can explain why Mn concentrations in the ARLP test are low in the two samples. In this case, it is quite similar to adding chemicals, e.g. calcite and lime to the system such that the alkaline pH will cause Mn mineral precipitation in the solution. However, no significant amount of carbonate minerals were formed under oxidising conditions in the Group 2 (1.5 MW sample) so that the pH in the ARLP will stay at acid conditions. n this case, Mn will be readily leachable due to the strong acid conditions;
- Based on the kinetic geochemical modeling results, there are some differences between the Group 1 and Group 2 samples. It is clear that Mn concentrations in solutions are higher in the Group 1 samples, but they are much lower in the Group 2 sample. However, there is not significant differences under the modelled conditions (reducing or oxidising) for the same samples (Figure 7.3) so that the original formation condition (reducing or oxidising) of the samples is very important to mineral formation and to the Mn leachability.
- If we consider the extreme conditions, e.g. at ARLP (pH 3.6 to 3.8), production of Mn WSD samples under reducing conditions is favoured more than under the oxidising conditions.

Table 7.10 Summary of Mn concentrations from water extraction, ARLP and modelling

Sample	Formation condition	Method	pH	Mn (mg/kg)
200 kW Run1	Reducing	Water Extraction	About 7	0.09
		ARLP	3.6	3.5
Ticor full-scale operation	Reducing	Water Extraction	A bout 7	0.14
		ARLP	3.6 – 3.8	1.12
1.5 MW	Oxidising	Water Extraction	About 7	<0.05
		ARLP	3.6 to 3.8	118

Table 7.11 summarises the kinetic modelling results of pH and Mn concentration (mg/ℓ) in terms of the following parameters:

- Three options in terms of base case (Option 1), addition of lime (CaO, Option 2) and of calcite ($CaCO_3$, Option 3);
- pH and Mn are averaged in periods of 0-5, 5-10, 10- 50 and 50 –100 years in order to compare the change over time;
- Formation conditions of the samples are reducing and oxidising; and
- Model conditions as reducing and oxidising scenarios.

Figure 7.11 is a set of histograms showing the summarised results from Table 7.10 in terms of samples (200 kW Run1 - top; Ticor full-scale operation - middle; 1.5 MW - bottom) and modelling conditions (reducing, oxidising).

Table 7.11: Summary of the kinetic modelled pH and Mn concentration (mg/ℓ)

Sample		**200KW WSD Run1**				**1.5MW WSD**				**Ticor full-scale operation**			
Condition for formation		**Reducing**				**Oxidising**				**Reducing**			
Model condition		**Reducing**		**Oxidising**		**Reducing**		**Oxidising**		**Reducing**		**Oxidising**	
Option	**Period (year)**	**pH**	**Mn**	**pH**	**Mn**	**pH**	**Mn**	**pH**	**Mn**	**pH**	**Mn**	**pH**	**Mn**
Option 1	0-5	7.1	102.3	6.4	67.6	7.5	0.3	7.6	1.4	6.6	14.0	6.6	15.5
	5-10	9.4	8.6	6.6	8.5	7.6	0.0	7.9	0.0	6.4	21.1	6.4	20.0
	10-50	10.3	26.1	6.4	19.1	7.6	0.0	7.9	0.0	6.4	21.1	6.4	20.3
	50-100	10.3	26.4	6.4	21.0	7.6	0.0	7.9	0.0	6.4	21.1	6.4	20.3
Option 2	0-5	8.2	85.1	9.3	0.7	11.4	0.0	10.7	0.1	10.3	2.8	7.0	1.1
	5-10	10.6	14.7	11.6	0.0	12.0	0.0	12.0	0.0	10.4	4.1	7.0	1.3
	10-50	10.6	15.5	11.7	0.0	12.0	0.0	12.0	0.0	10.4	4.2	7.0	1.3
	50-100	10.6	15.6	12.0	0.0	12.0	0.0	12.0	0.0	11.1	2.7	10.7	0.4
Option 3	0-5	6.6	7.4	6.6	4.5	8.9	0.0	8.8	0.0	10.4	3.9	7.0	1.1
	5-10	8.3	0.2	7.0	1.5	9.4	0.0	8.8	0.0	10.0	10.3	7.0	1.3
	10-50	9.7	16.4	7.1	1.1	9.0	0.0	8.8	0.0	10.0	10.8	6.9	1.3
	50-100	10.3	26.3	7.1	1.1	8.9	0.0	8.8	0.0	10.0	10.8	6.9	1.3

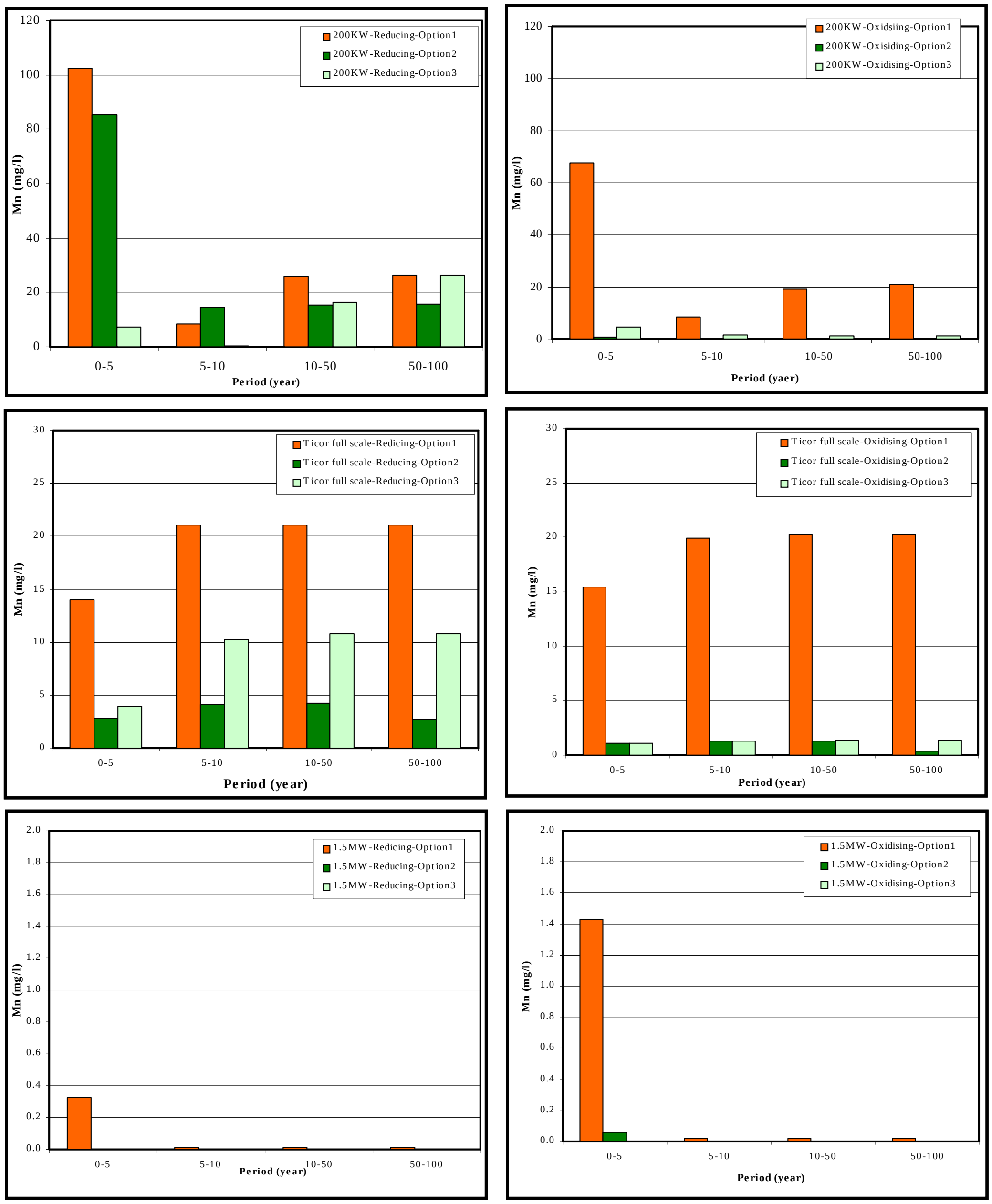

Figure 7.11: Histograms showing the summarised Mn concentration (mg/ℓ) in solution modelled in 3 options at reducing conditions (left), oxidising conditions (right) for 200Kw (top left/right), Ticor full-scale (middle left/right), 1.5MW (bottom left/right)

From the above presentation (Table 7.11, Figure 7.11), the results can be summarised as follows:

- Samples formed at reducing conditions clearly have much higher Mn in solution (Top, middle) than the sample formed at oxidising conditions;
- Addition of lime and calcite will stabilise Mn in the WSD;
- Mn concentration in solution is much higher in the reducing conditions (left histograms) than under the oxidising conditions (right histograms);
- Strong alkaline pH and oxidising conditions will be able to stabilise manganese wastes under normal conditions;

7.3.4.9 Sensitivity analyses of kinetic geochemical modelling input parameters

As discussed in the previous section, in the absence of data, a number of key assumptions had to be made regarding the data inputs for the kinetic geochemical modelling. Sensitivity analyses were performed, using the Ticor full scale samples at reducing conditions, in terms of mineral surface areas, mineral reaction rates, Mn mineral types and pH buffers. The results indicate that Mn concentrations in solution are:

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- very sensitive to pH, i.e. the higher the pH, the lower the Mn concentration in solution. This accords well with the modelling results for different management options and also accords well with the activity diagrams (Figures 7.1-5); and
- Mn concentrations in solution are less sensitive to mineral surface areas, mineral reaction rates.

7.4 CONCLUSIONS

The following conclusions can be drawn from the geochemical modelling study:

1. In both a pure water system (H_2O-Mn) and a more complex system (H_2O-Mn-Fe-CO_2-S-Cl-NO_3), the modelling results indicated that manganese is highly soluble and mobilizes in acidic, neutral, alkaline and even strong alkaline conditions. A variety of manganese aqueous species occur in these solution systems and most of the manganese-bearing minerals are only stable in a limited range of physico-chemical conditions, i.e. oxidising and strong alkaline (>pH 8-10) conditions. The modelling results indicate that manganese can be stabilized under a controlled oxidising and alkaline environment.

2. Three chemical treatment options were modelled geochemically. It was found that the addition of lime, calcite and raw dolomite would lead to:
    - Increased alkalinity of the aqueous system;
    - Enlarged manganese-bearing mineral stable fields; and
    - Effective removal of manganese from the solution by the creation of alkaline environment and improvement of the stable field of the manganese-bearing minerals.

3. When comparing the results obtained from water leaching for the scrubber dusts produced under oxidising and reducing conditions, it was found that more chemical components leached from the reduced samples than from the oxidized sample. This suggests that more stabilized manganese forms formed under oxidising conditions than under reducing conditions.

4. Kinetic modelling results where no chemical treatment was incorporated, indicated that more manganese would mobilise (under modelling conditions) under reducing than under oxidising conditions for all of the scrubber dust samples. Less manganese in solution was found for the scrubber dust sample produced under oxidising conditions than that for the scrubber dust samples formed under reducing conditions. A negative correlation between manganese concentration levels and pH was also found.

5. Kinetic modelling results where chemical treatment was incorporated indicated that both lime and calcite treatment will effectively reduce manganese levels in solution in a mono-landfill site under oxidising conditions Over the longer term, the concentration of manganese leached from the system will decline even further. However under reducing conditions, Mn concentrations will be much higher. Thus, lime and calcite addition will effectively stabilize manganese and reduce the risk involved with manganese-containing wastes.

From the above it can be concluded that:

- Strong alkaline pH and oxidising conditions will be able to stabilise manganese wastes;
- An oxidising and alkaline environment should be created for the landfilling of manganese wastes; and
- Addition of chemicals, e.g. lime, calcite, raw dolomite will be able to effectively reduce the manganese risk.

It should be noted that under acid conditions e.g. ARLP Test (pH 3.6) the leachability of Mn would be very different. As shown in the phase diagrams (Figures 7.1, 7.2, 7.3, 7.4, and 7.5), Mn will be soluble and unstable in solution and redox potential does not play a major role under acid conditions because Mn^{2+} is stable at all normal oxygen levels.

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8. EVALUATION OF METHODS FOR CLASSIFICATION OF MANGANESE CONTAINING WASTES

The ability to distinguish between the reactive load, which could be indicative of the bio-available or hazard risk component, and the inert part of a waste stream, is considered the most important requirement of an acceptable extraction procedure for waste classification

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Speciation extraction procedures can provide useful information with regard to the geochemical fate of trace metals under a variety of environmental conditions.

A number of alternative leaching procedures utilising a number of different leaching solutions were investigated including:

- Multiple extraction (MEP)
- Sequential extraction (SEP)
- Neutral extraction (NEP)

These methods were tested in an effort to gain more insight on three basic interaction types that would play an important role in the remobilisation of manganese viz. acid-base equilibria, reduction and oxidation reactions and with respect to MEP, behaviour over time.

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The different leaching procedures were tested on two different types of scrubber dust from our case study:

- 200 kW wet scrubber dust (Trial 1) – produced under reducing conditions
- 1.5 MW dry off gas dust – produced under oxidising (post combustion) conditions.

The percentage of total manganese leached from the various phase fractions and methods is shown in Table 8.1 and 8.2. The mobility of manganese from the scrubber dust samples collected under a variety of conditions as well as mixed together with lime or calcite is also shown. Furthermore, the effect of a high concentration of iron relative to manganese (Fe: Mn 40:1) in a sample is also reported.

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Table 8.1: Manganese leached from two different scrubber dust samples using a variety of extraction methods

		Total content of original sample (mg/kg)	Total % of manganese leached					
			Neutral extraction	ARLP	TCLP	Sequential extraction 1	Sequential extraction 2	Sequential extraction 3
200 kW run 1 scrubber dust (filtered)	**No treatment**	**18538**	**23**	**0.02**	**9.4**	**8.2**	**2.1**	**24**
	Ferric chloride	**18538**	**0.15**	**0.03**	**0.01**	**2.8**	**3.2**	**3.5**
	Lime (5 %)	**18538**	**21**	**<0.01**	**2.2**	**6.7**	**1.9**	**25**
	Calcite (37.5 %)	**18538**	**16**	**0.60**	**6.9**	**2.2**	**0.78**	**18**
1.5 MW Kumba sample	**No treatment**	**6813**	**3.0**	**1.7**	**2.4**	**2.9**	**1.5**	**0.50**
	Ferric chloride	**6813**	**0.05**	**0.05**	**0.04**	**1.6**	**0.64**	**0.21**
	Lime (5 %)	**6813**	**2.8**	**<0.01**	**1.6**	**2.2**	**1.5**	**0.34**
	Calcite (37.5 %)	**6813**	**1.7**	**0.02**		**0.6**	**0.82**	**0.58**

8.2

Selective-sequential extraction procedures assist in partitioning particulate trace metals into chemical forms likely to be released into solution. The following comments can be made on the selectivity of the extraction solutions tested:

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1. Acetic acid /acetate used in
   - TCLP (Glacial acetic acid, pH 2.9);
   - NEP (Acetate buffer solution, pH 4.2-4.5) and
   - SEP (0.11 M Acetic Acid)

   appears to be an efficient extractant to solubilise the manganese (~8-23 % of total) from the reduced scrubber dust sample (200 kW). This is significantly greater than that extracted by ARLP (0.02 %) which uses carbonic acid. Therefore, in a disposal system where acetic acid may be generated it is critical to apply one of the above tests. Conversely, in a disposal system where there is confidence that acetic or other organic acids will not be produced, use of any of the above tests could grossly overestimate the leachable manganese.
2. Acetic acid/acetate solutions also dissolve calcite and lime thus reducing the effectiveness of these chemicals to prevent leaching of soluble manganese. It would appear that a 5 % lime dosage is rendered almost completely ineffective in stabilising the manganese in the 200 kW reduced form dust sample. The addition of ferric chloride to the sample however would appear to be effective in immobilising the manganese to less than 0.2 % of the total under the same conditions.

3. The solubilisation of manganese from the scrubber dust obtained under oxidising process conditions (1.5 MW) by acetic acid was significantly lower (3 % of total Mn content) but again the effects of addition of lime or calcite were negated to varying degrees. The results of the mineral saturation index analysis, as part of the geochemical assessment (see chapter 7) infer that manganese containing minerals in the reduced scrubber dust sample are more soluble than those of the oxidised scrubber dust sample. 37.5 % (w/w) calcite addition would appear to reduce the soluble manganese levels by approximately 50 % in both samples under acetic acid extraction.

4. Step 2 of the SEP, which utilises hydroxylamine hydrochloride, is included in the protocol to bring reducible species into solution, particularly iron and manganese oxides. Results show approximate leaching of 2 % of the total manganese in this fraction unless treated with calcite (0.8 %) or by the addition of ferric chloride (<0.1 %).

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5. Hydrogen peroxide/ammonium acetate used in SEP Step 3 is designed to attack oxidisable matter. Mn (II) is an easily oxidisable metal. Depending on the oxidation state of manganese in the dust it could therefore either respond in Step 2 or 3. In our case, the highest extraction occurred in step 3 for the 200 kW reduced dust sample but in Step 1 and 2 for the 1.5 MW oxidised sample.

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It must be noted that these results are not selective enough to interpret results conclusively in terms of specific origin in a particular phase. However, a distinction can be made between adsorbed metals primarily reporting in step 1 (except those which form part of the calcite fraction or other substrate) that dissolves completely in acetic acid, and co-precipitated or incorporated metals.

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The recoveries in the individual steps for the multiple extraction procedure (MEP) are shown in Table 8.2. The MEP extraction procedure (see Table 8.2) is intended to simulate prolonged exposure to a leaching medium and gradually removes excess alkalinity in the waste. Extraction undertaken in the preliminary stage (Multiple Extraction-EP) shows a high level of manganese available to the water phase from the 200 kW reduced scrubber dust sample. This was also observed in the column leach tests used for geochemical modelling (see Chapter 7). Subsequent MEP solution extracts show a slight increase in the soluble manganese over time, but with the addition of lime and calcite it stabilises with time. There was still some significant release in the early extraction phases (first three phases) with lime and calcite, which may be linked to dissolution of these chemicals or the difficulty in getting a homogenous mix in practice. Total manganese MEP results (refer Table 8.2) show a benefit in using calcite over lime for stabilisation in the long term for both scrubber type samples. The presence of iron also reduced total manganese leached but was more pronounced with respect to the 200 kW reduced wet scrubber dust sample.

Table 8.2: Manganese leached from two different scrubber dust samples using the multiple extraction method

		Total content of original sample (mg/kg)	**Total % of manganese leached**									
			EP	**MP 1**	**MP 2**	**MP 3**	**MP 4**	**MP 5**	**MP 6**	**MP 7**	**MP 8**	**Total MEP**
200 kW scrubber dust (Trial 1 filtered)	**No treatment**	**18538**	**4.6**	**0.26**	**0.01**	**0.01**	**0.09**	**0.04**	**0.08**	**0.08**	**0.04**	**5.22**
	Iron chloride	**18538**	**1.7**	**0.11**	**0.02**	**0.01**	**0.04**	**0.05**	**0.02**	**0.04**	**<0.01**	**2.00**
	Lime (5%)	**18538**	**3.5**	**0.49**	**0.04**	**0.03**	**0.08**	**0.03**	**0.05**	**0.04**	**0.04**	**4.35**
	Calcite (37.5 %)	**18538**	**1.3**	**0.05**	**1.44**	**<0.01**	**0.01**	**0.01**	**0.01**	**0.02**	**0.01**	**2.87**
1.5 MW scrubber dust (Kumba sample)	**No treatment**	**6813**	**0.70**	**0.04**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.91**
	Iron chloride	**6813**	**0.49**	**0.03**	**0.03**	**0.03**	**0.01**	**0.02**	**0.02**	**0.01**	**0.02**	**0.66**
	Lime (5%)	**6813**	**0.40**	**0.03**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**0.01**	**<0.01**	**0.44**
	Calcite (37.5 %)	**6813**	**0.12**	**0.04**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**0.17**

All these extraction methods indicate (cannot provide actual particulate speciation) that the various manganese metals forms present in the scrubber dust would contribute to the level of pollution or variability in mobilisation content of the waste stream under fluctuating pH. Calcite has been shown to generally provide a better immobilisation management option for manganese compared to lime under a number of different leaching conditions. Scrubber dust produced under oxidising conditions contains manganese in a much more stable form as would be expected. The scrubber dust produced under wet, reducing conditions contains a significant amount of manganese that is soluble in the water phase and under mildly acidic conditions**.**

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9. RECOMMENDED METHODOLOGY FOR CLASSIFICATION OF INORGANIC MANGANESE-CONTAINING WASTES

Based on the research work undertaken in this project, and taking account of the "*Minimum requirements for the handling, classification and disposal of hazardous waste*" as published by the Department of Water Affairs and Forestry (DWAF, 1998), a recommended methodology for the classification of manganese-containing wastes has been proposed.

9.1 BACKGROUND ON MANGANESE CHEMISTRY AND BEHAVIOUR

The research undertaken as part of this project has given a detailed insight into the chemistry of manganese and its behaviour under various conditions that might apply in a waste disposal facility, specifically for manganese-containing waste generated through pyrometallurgical processes.

9.1.1 Manganese chemistry, geochemistry and stability analyses

Manganese chemistry is characterised by the following:

- It is capable of existing in a number of valence states (-3, +2, +3, +4, +5, +6, +7) although the Mn^{2+} form is most dominant in inorganic systems.
- Manganese exists in a limited variety of inorganic minerals.
- Manganese can only be stabilised under alkaline conditions.
- Under acidic conditions such as used in the ARLP and TCLP tests, manganese will always be leachable, regardless of whether reducing or oxidizing conditions prevail.

The ARLP and TCLP tests are therefore very stringent on manganese and will always leach out manganese – making them very conservative assessment tools.

9.1.2 Environmental controlling factors

Major environmental factors that affect the stability of manganese in water include the following:

- pH;
- oxidising or reducing conditions;
- enrichment of organic materials and wastes;
- mineral forms;
- CO_2 content;
- temperature;
- biochemical reactions;
- sorption by clay and hydroxides, e.g. hematite, goethite.

Manganese containing wastes produced by pyrometallurgical process are characterised by the following:

- Lack of organic materials due to its formation at high temperature >1650 ^{o}C;
- Slightly acid pH at 6.5 due to CO_2 buffer in the wet scrubber dust;

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- Depletion of soluble Mn due to production in a reducing environment created by burning coal; and
- Enrichment of carbonate minerals that will be more soluble than Mn oxides e.g. pyrolusite, bixbyite.

9.1.3 Stability analysis

Based on activity diagram analysis, the major factors affecting Mn stability include pH, redox conditions, and fugacity of CO_2. Mn is generally stabilised at alkaline, oxidising and enrichment of CO_2 (CO_3^{--}) conditions.

In this study, the wet scrubber dust samples were produced in reducing environments, although enrichment of CO_2 through the off-gas chamber causes precipitation of rhodochrosite ($MnCO_3$) and also other carbonate minerals, including iron, zinc, and lead carbonate, which have a fair amount of neutralising potential (NP) to increase the pH, and thereby prevent Mn from resolubilizing.

9.1.4 Remediation

The major remediation methods include:

- aeration/addition of chemical oxidants to create an oxidising environment;
- addition of neutralizing agents to create an alkaline environment to cause Mn precipitation; and
- other methods, e.g. physical and biological process.

In this research project, it is been shown that addition of chemicals to create an alkaline environment is sustainable in terms of long-term reduction of Mn concentration in solution.

9.2 PROPOSED HAZARD CLASSIFICATION METHODOLOGY

9.2.1 Generic risk-based assessment process

The proposed methodology is risk-based and incorporates the precautionary principle and the principle of demonstrable conservatism in the absence of site-specific information. However, the methodology makes provision for a lessening of the degree of conservatism as the level of detail of the investigation increases. Preference is also given to retaining test procedures that are known and established in South Africa, unless good scientific motivation exists to introduce new test procedures.

The general principles of a risk-based assessment procedure are shown in Figure 9.1 below. The process starts off with a consciously conservative assessment that uses simple and relatively inexpensive tests to produce a conservative and qualitative result. It is imperative that there is absolute confidence that the test results are conservative, as a successful (no hazard) outcome of this first screening level step can then confidently lead to the decision that there is no value in undertaking further testwork as a more realistic and detailed assessment will always lead to a lower assessed hazard. As conservative assumptions are replaced with more realistic assumptions and measured data, both the level of conservatism and the estimated risk decrease.

However, it is important to realize that a negative outcome (potential hazard) may not necessarily mean a real hazard as the negative outcome could simply be due to the ultra-conservative assumptions rather than a real hazard. For this reason, it would be necessary to move to an intermediate level (second tier) assessment where more realistic tests are undertaken under conditions that are more representative of the actual waste disposal conditions. Conservative assumptions could still be used to characterise the receiving environment and the assessment could be undertaken without incorporating remediation measures.

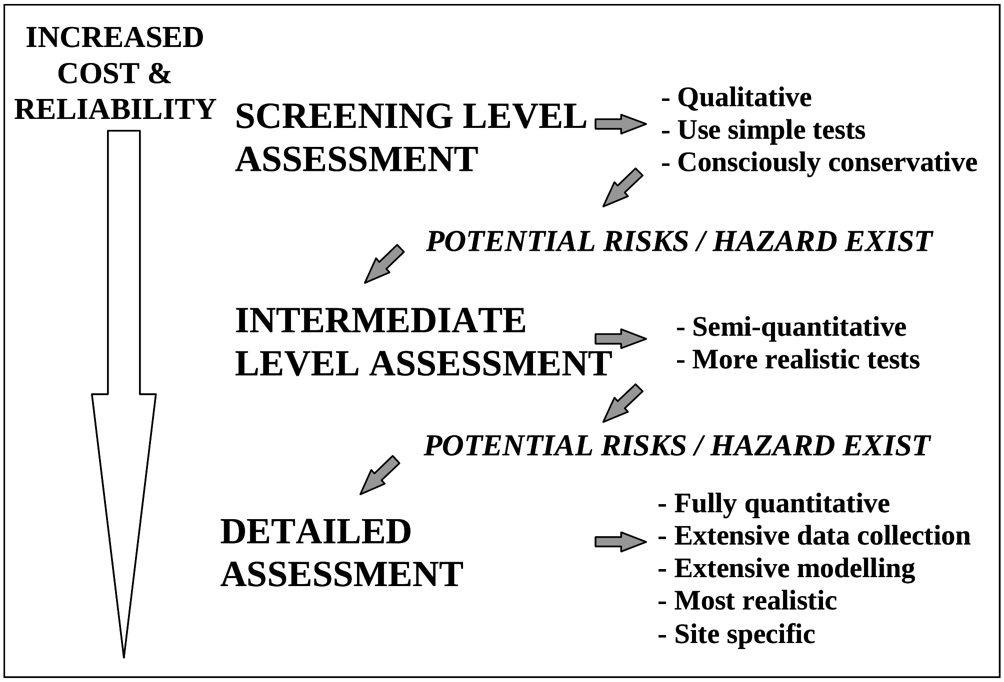

Figure 9.1: Schematic representation of the risk-based assessment procedure

If this intermediate level assessment still yields a negative result, the waste disposal strategy must then be subjected to a very detailed assessment process wherein any planned remediation measures are incorporated and site-specific environmental conditions are considered.

Although this proposed process might appear to be identical to that which is currently possible in terms of the DWAF Minimum Requirements Procedures, there is a very important distinction insofar as the intermediate and detailed assessments are not envisaged to be undertaken under the classification of a “delisting process”. Rather, the intermediate and detailed assessments flow naturally from the screening assessment and a final classification is only made once the complete process has been undertaken.

9.2.2 Specific process for classifying inorganic manganese-containing wastes

A proposed process for assessing the hazard associated with inorganic manganese containing wastes is shown in Figure 9.2 below.

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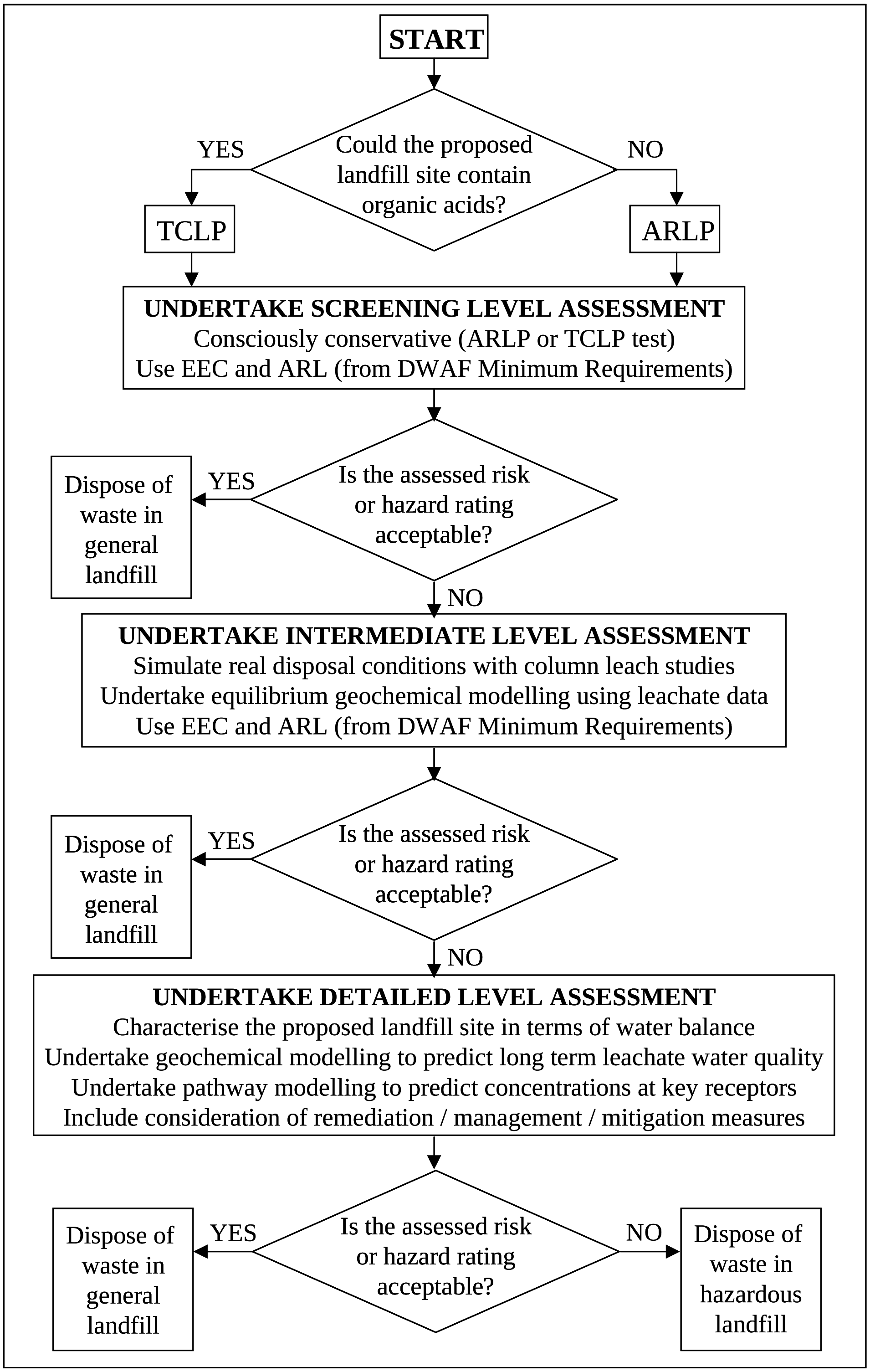

Figure 9.2: Proposed classification procedure for inorganic manganese-containing wastes

The proposed first step in the assessment process is to establish with absolute confidence whether or not the inorganic manganese containing waste will be disposed of in a landfill site that could contain organic acids. If there is a potential that organic acids may be present then the screening level test should be undertaken using both ARLP and TCLP tests. In interpreting the significance of the test results, use should be made of the EEC and ARL values set out in the DWAF Minimum Requirements.

If the results from the screening level assessment are within the conservative ARL and EEC values, then there is no need to undertake any further assessments and the regulatory process should be followed to obtain approval for disposal of the waste in a general landfill. If the results are negative then it will be necessary to move onto an intermediate level assessment.

In the intermediate level assessment, column leach studies are undertaken to replace the ARLP and/or TCLP tests, using landfill conditions that closely simulate the intended application. A geochemical assessment programme and equilibrium geochemical modelling should be undertaken using water quality data from the column study leachates. An assessment must be made to establish whether the proposed disposal conditions will lead to a stable waste and whether or not the column leach data can reasonably be used to assess long-term performance. Use could still be made of the conservative EEC and ARL values set out in the DWAF Minimum Requirements.

If the results from the intermediate level assessment are within the conservative ARL and EEC values, then there is no need to undertake any further assessments and the regulatory process should be followed to obtain approval for disposal of the waste in a general landfill. If the results are negative then it will be necessary to move onto a detailed level assessment.

In the detailed level assessment, the following studies should be undertaken:

- Detailed characterisation of the proposed landfill site in terms of its water balance.
- Prediction of long-term leachate quality using kinetic geochemical models and evaluating the anticipated pH and redox conditions.
- Prediction of leachate flow, quality and load for the various remediation/management/ mitigation measures being considered.
- Detailed characterisation of the receiving environment (ground water and surface water) with modelling of the predicted water quality at key environmental/human receptors.
- Assessment of risk posed to environmental receptors based on local and international literature values for adverse risk.
- Conclusion as to whether waste should be disposed of in a general landfill or at a hazardous waste landfill site.

The process that has been followed must then be documented in a detailed report that presents all the collected data, assumptions, assessment process and results and that must then be submitted to the regulators for consideration and approval.

10. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from this research project

Off-gas dust samples from smelter processes using ilmenite feed contain manganese in varying quantities. The level of inorganic manganese, although generally less than 15 % of the feed input balance, can result in the scrubber dust being classified as hazardous for disposal, based on ARLP results.

At a primary risk assessment level, it was found that a number of process conditions influence the ARLP results and the form of manganese found in the scrubber dust, which, ultimately affects its bio-availability and potential hazard to the environment.

In general it was found that off-gas collected in dry oxidizing environments could convert the manganese into a more stable form than is found under wet, reducing conditions. Despite this, it was found that a much higher manganese load is leached under ARLP conditions from the scrubber dusts that were collected under oxidising conditions (>100 mg/kg dust) compared to reducing conditions (<35 mg/kg dust). It must be noted that the inclusion of a post combustion chamber in the oxidising situation does significantly reduce the amount of soluble manganese in the “oxidized” dust.

It was also found that the liquid/solid ratio or water flow rate/temperature management in the wet scrubber is an important operational factor that affects the hazard risk assessment of Mn based on ARLP results and EEC calculations. Lower temperatures can significantly change the solubility of the manganese captured as dust from the furnace. Significant changes to the particle size distribution of the scrubber dust were also observed. The waste classification listing was lowered when the temperatures of the scrubber inlet were kept at 180 °C and 233 ℓ/hour scrubber water flow rate, compared to 114 °C and 393 ℓ/hour scrubber water flow rate. It must be noted that the temperatures are relative and not absolute. The measured temperature depends on the location of the thermocouple

A number of possible immobilization techniques utilizing chemical additional precipitation methods were also evaluated, based on our literature search findings. It was found after an initial baseline study to determine optimum dosage ranges, that lime 5 %-10 % (w/v), calcite (37.5 % w/v), hypochlorite (9 % v/w) and a desulphurisation slag (10 %) from the smelter process could all significantly reduce the levels of soluble manganese under ARLP extraction conditions and the EEC/ARL ratio to <1 for delisting.

It was also seen that while calcite reacts slower than lime initially, in the long term it also provides alkalinity and buffering capacity to the waste to prevent leaching over time. This was also seen in the Multiple Extraction (MEP) results and geochemical modeling predictions. Dolomite was also considered as a good treatment option but due to impurities inherent in the product, it was found that it added rather than reduced manganese in the waste leachate. Dolomite may also contain other substances that could influence the potential pollution and toxicity of the treated waste. This needs to be checked before use. Moreover, burnt dolomite proved to have less contaminating manganese levels compared to raw dolomite.

10.2

The geochemical assessment and modelling of the dust showed that more chemical components, specifically manganese were leached out from the scrubber sample collected under reducing conditions (200 kW Trial 1) to the water phase than from the dust sample collected under oxidising conditions (1.5 MW Trial). This was also in line with the activity diagram analysis.

Together with the chemical concentration analysis, it was concluded that the “oxidised: sample (1.5 MW dust) contains much less leachable metals as a whole, viz. manganese, cobalt, nickel and iron than in the “reduced” sample (200 kW Trial 1). Correspondingly, less minerals, specifically manganese-bearing minerals are less saturated (not precipitated) in the “oxidised” sample (1.5 MW) than in the “reduced” sample (200 kW). Alkalinity was also inherently higher in the 1.5 MW sample compared to the 200 kW WSD sample.

These finding all support the fact that it is better to store manganese-bearing wastes under oxidising conditions that results in formation of stable manganese-bearing minerals and eventually stabilises the manganese-bearing wastes.

Redox conditions in a scrubber dust waste disposal dump were also considered and three management options for the disposal of the wet-reduced scrubber dust and dry-oxidised scrubber dust were evaluated. The management options included the do-nothing approach, addition of calcite and addition of lime.

The following trends with time were observed in the oxidising (upper levels) and reducing conditions (lower and deeper) areas of the waste dump for the case study example. It must be noted that absolute values for manganese could not be predicted with certainty in this project, due to lack of certain critical data required for the kinetic modelling and the need to make informed (albeit unvalidated) assumptions.

a) Scrubber Dust collected under wet-reducing conditions

Disposal Option 1 – No treatment

During the first 15 years, pH increases in the dump (both reducing (deeper) and oxidising (surface) conditions) due to reaction of MnS. This increase would however still keep pH in the neutral to slightly alkaline range (pH <8). A slight decrease in pH due to the reaction of MnS in the wet scrubber dust was also observed (5-25 years) and this impacts by increasing the level of soluble manganese leached from the waste during this time period. Pyrolusite (MnO_2) a stable form of manganese can also dissolve rapidly when pH is less than 8.

Manganese levels in solution were generally high in the dump (> 10mg/l) for scrubber dust produced under reducing conditions but lowered (< 2 mg/l) for “oxidised” baghouse dust.

Manganese levels in the wet reduced scrubber dust samples appear to fluctuate in the first 5 years (could increase or decrease depending on pH level and composition of the dust) but generally increase again over time if left untreated and can reach unacceptable risk levels. Oxidised scrubber dust however showed a decrease over time in the dump if left untreated and the sample tested did not produce hazardous levels of manganese.

Disposal Option 2 – Addition of lime

Manganese leaching from the waste can be controlled by treatment with lime. Lime, however, although it was most effective in the short term, was shown to have less benefit over the long term. Lime has a rapid and dramatic effect, neutralizing MnS and manganese is oxidised to form pyrolusite (MnO_2) and bixbyite (Mn_2O_3) primarily. Levels of manganese may however still exceed recommended maximum environmental limits using this method if scrubber dust is disposed under reducing conditions.

Disposal Option 3 – Addition of calcite

Addition of calcite to the scrubber dust also acts rapidly but was also shown to provide a better and more effective long-term solution to reducing the amount of Mn leached, especially in the reduced scrubber dust stored under reducing conditions.

Both lime and calcite addition were predicted to provide similar benefits when scrubber dust waste sample is stored under oxidising conditions. Sequential step extraction methods (SEP) were useful in indicating the proportions of reducible and oxidisable species in the waste and multiple extraction procedures (MEP) provided some clues to the long-term stability and effectiveness of various treatment methods over time that was supported by geochemical modeling predictions.

Inorganic manganese-containing wastes cannot all be classified into one category. The predominant form of manganese found in the waste plays a significant part in the assessing the hazard risk potential. Operational conditions used to collect the scrubber dust waste from the furnace can influence the type of manganese produced and its chemistry upon disposal. The impact of other trace metals and the chemistry over the long term also need to be considered and this is not always accurately reflected in ARLP-based classification methods.

A proposed methodology for the assessment and classification of inorganic manganese containing wastes is presented in Chapter 9. This proposed process covers the assessment from an initial conservative screening level assessment through to a detailed site-specific quantitative assessment.

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APPENDIX A

CHEMICAL REACTIONS INVOLVING MANGANESE

Mineral	Chemistry	Reaction	log-k	Delta-h (kcal)
Mn^{+3} secondary master species		$Mn^{+2} = Mn^{+3} + e^{-}$	-25.51	25.8
MnO_4^{-} secondary master species		$Mn^{+2} + 4H_2O = MnO_4^{-} + 8H^{+} + 5e^{-}$	-127.824	176.62
MnO_4^{-2} secondary master species		$Mn^{+2} + 4H_2O = MnO_4^{-2} + 8H^{+} + 4e^{-}$	-118.44	150.02
Alabandite	MnS	$MnS + 1 H^{+} = + 1 HS^{-} + 1 Mn^{+2}$	-0.3944	-51
Birnessite	Mn_8O_{14}	$Mn_8O_{14}{:}5H_2O + 4 H^{+} = + 3 MnO_4^{-2} + 5 Mn^{+2} + 7 H_2O$	-85.5463	
Birnessite	Mn_8O_{14}	$MnO_2 + 4H^{+} + e^{-} = Mn^{+3} + 2H_2O$	18.091	< 0
Birnessite	Mn_8O_{14}	$MnO_2 + 4H^{+} + 2e^{-} = Mn^{+2} + 2H_2O$	43.601	
Bixbyite	Mn_2O_3	$Mn_2O_3 + 6 H^{+} = + 2 Mn^{+3} + 3 H_2O$	-0.9655	-958.971
Bixbyite	Mn_2O_3	$Mn_2O_3 + 6H^{+} = 2Mn^{+3} + 3H_2O$	-0.611	-15.245
Bixbyite	Mn_2O_3	$Mn_2O_3 + 6H^{+} = 2Mn^{+3} + 3H_2O$	-0.611	-15.245 kcal
Hausmannite	Mn_3O_4	$Mn_3O_4 + 8 H^{+} + 2 e^{-} = 3 Mn^{+2} + 4 H_2O$	61.03	-100.640 kcal
Hausmannite	Mn_3O_4	$Mn_3O_4 + 8 H^{+} = + 1 Mn^{+2} + 2 Mn^{+3} + 4 H_2O$	10.1598	-1387.831 kJ
Hausmannite	Mn_3O_4	$Mn_3O_4 + 8H^{+} + 2e^{-} = 3Mn^{+2} + 4H_2O$	61.54	-80.14
Manganese		$H_{fo}\,sOH + Mn^{+2} = H_{fo}\,sOMn^{+} + H^{+}$		
Manganite	MnOOH	$MnOOH + 3 H^{+} + e^{-} = Mn^{+2} + 2 H_2O$	25.34	
Manganite	MnOOH	$MnO(OH) + 3 H^{+} = + 1 Mn^{+3} + 2 H_2O$	-0.1646	
Manganite	MnOOH	$MnOOH + 3H^{+} = Mn^{+3} + 2H_2O$	-0.238	0
Manganite	MnOOH	$MnOOH + 3H^{+} + e^{-} = Mn^{+2} + 2H_2O$	25.34	
Manganosite	MnO	$MnO + 2 H^{+} = + 1 H2O + 1 Mn^{+2}$	17.924	-92.07
Mn_Vanadate	$Mn0.5VO_3$	$MnO.5VO_3 + 2H^{+} = 0.5Mn^{+2} + VO_2^{+} + H_2O$	2.45	-11.05
	$Mn_3(PO_4)_2$	$Mn_3(PO4)_2 = 3Mn^{+2} + 2PO_4^{-3}$	-23.827	2.120 kcal
	$MnCl_2{:}4H_2O$	$MnCl_2{:}4H_2O = Mn^{+2} + 2Cl^{-} + 4H_2O$	2.71	17.380 kcal
	$MnHPO_4$	$MnHPO_4 = Mn^{+2} + HPO_4^{-2}$	-12.947	
	MnS(Green)	$MnS + H^{+} = Mn^{+2} + HS^{-}$	3.8	-5.790 kcal
Nsutite	MnO_2	$MnO_2 + 4H^{+} + e^{-} = Mn^{+3} + 2H_2O$	17.504	0
Nsutite	MnO_2	$MnO_2 + 4H^{+} + 2e^{-} = Mn^{+2} + 2H_2O$	42.564	
Pyrochroite	$Mn(OH)_2$	$Mn(OH)_2 + 2 H^{+} = Mn^{+2} + 2 H_2O$	15.2	
Pyrochroite	$Mn(OH)_2$	$Mn(OH)_2 + 2H^{+} = Mn^{+2} + 2H_2O$	15.088	-22.59
Pyrolusite	MnO2	$MnO_2{:}H_2O + 4 H^{+} + 2 e- = Mn^{+2} + 3 H_2O$	41.38	-65.110 kcal
Pyrolusite	MnO_2	$MnO_2 = + 0.5 Mn^{+2} + 0.5 MnO_4^{-2}$	-17.6439	-520.031 kJ
Pyrolusite	MnO_2	$MnO_2 + 4H^{+} + e^{-} = Mn^{+3} + 2H_2O$	15.861	-29.18
Pyrolusite	MnO_2	$MnO_2 + 4H^{+} + 2e^{-} = Mn^{+2} + 2H_2O$	41.38	-65.11 kcal
Rhodochrosite	$MnCO_3$	$MnCO_3 + 1 H^{+} = + 1 HCO_3^{-} + 1 Mn^{+2}$	-0.1928	-212.521
Rhodochrosite	$MnCO_3$	$MnCO_3 = Mn^{+2} + CO_3^{-2}$	-10.41, -10.39	-2.079
Rhodonite	$MnSiO_3$	$MnSiO_3 + 2 H^{+} = + 1 H_2O + 1 Mn^{+2} + 1 SiO_2$	9.7301	-1319.422 kJ
Scacchite	$MnCl_2$	$MnCl_2 = + 1 Mn^{+2} + 2 Cl^{-}$	8.7785	-481.302 kJ
Tephroite	Mn_2SiO_4	$Mn_2SiO_4 + 4 H^{+} = + 1 SiO_2 + 2 H_2O + 2 Mn^{+2}$	23.0781	-1730.470 kJ
Todorokite	Mn_7O_{12}	$Mn_7O_{12}{:}3H_2O + 16 H^{+} = + 1 MnO_4^{-2} + 6 Mn^{+3} + 11 H_2O$	-45.8241	
	$BaMnO_4$	$BaMnO_4 = + 1 Ba^{+2} + 1 MnO_4^{-2}$	-10.09	
		$Mn^{+2} + 2X^{-} = MnX_2$		
		$H_{fo}\,wOH + Mn^{+2} + H_{fo}\,wOMn^{+} + H^{+}$		
	$MnCl_2$	$MnCl_2{:}4H_2O = Mn^{+2} + 2Cl^{-} + 4H_2O$	2.71	17.38
	MnS(Green)	$MnS + H^{+} = Mn^{+2} + HS^{-}$	3.8	-5.79
	$MnSO_4$	$MnSO_4 = Mn^{+2} + SO_4^{-2}$	2.669	-15.48
	$Mn_2(SO_4)_3$	$Mn_2(SO_4)_3 = 2Mn^{+3} + 3SO_4^{-2}$	-5.711	-39.06
	$Mn_3(PO_4)_2$	$Mn_3(PO_4)_2 = 3Mn^{+2} + 2PO_4^{-3}$	-23.827	2.12
	Mn_2Sb	$Mn_2Sb + 3H_2O = 2Mn^{+2} + Sb(OH)_3 + 7e^{-} + 3H^{+}$	61.0796	0
	MnSb	$MnSb + 3H_2O = Mn^{+3} + Sb(OH)_3 + 6e^{-} + 3H^{+}$	-2.9099	5.045
	$MnHPO_4(C)$	$MnHPO_4 = Mn^{+2} + PO_4^{-3} + H^{+}$	-25.4	0
	$Mn_3(AsO_4)_2{:}8H_2O$	$Mn_3(AsO_4)_2{:}8H_2O + 6H^{+} = 3Mn^{+2} + 2H_3AsO_4 + 8H_2O$	12.5	0
	MnSe	$MnSe + H^{+} = HSe^{-} + Mn^{+2}$	5.3508	-13.46
	$MnSeO_3$	$MnSeO_3{:}2H_2O + H^{+} = HSeO_3^{-} + Mn^{+2} + 2H_2O$	0.9822	2.03
	$MnSeO_3$	$MnSeO_3 + H^{+} = HSeO_3^{-} + Mn^{+2}$	1.21	0
$K_2Mn_3(FeCyanide_6)_2$	$K_2Mn_3(FeCyanide_6)_2$	$K_2Mn_3(FeCyanide_6)_2 = 12Cyanide^{-} + 2K^{+} + 3Mn^{+2} + 2Fe^{+2}$	-121.001	0
$K_8Mn_6(FeCyanide_6)_5$	$K_2Mn_3(FeCyanide_6)_5$	$K_8Mn_6(FeCyanide_6)_5 = 30Cyanide^{-} + 8K^{+} + 6Mn^{+2} + 5Fe^{+2}$	-293.685	0
	$Mn_2FeCyanide_6$	$Mn_2FeCyanide_6 = 6Cyanide^{-} + 2Mn^{+2} + Fe^{+2}$	-59.0272	0
	$MnCl^{+}$	$Mn+2 + Cl- = MnCl^{+}$	0.61	
	$MnCl_2$	$Mn+2 + 2Cl- = MnCl_2$	0.25	
	$MnCl_3^{-}$	$Mn+2 + 3Cl- = MnCl_3^{-}$	-0.31	
	$MnOH^{+}$	$Mn+2 + H_2O = MnOH^{-} + H^{+}$	-10.59	14.4
	$Mn(OH)_3$-	$Mn+2 + 3H_2O = Mn(OH)_3^{-} + 3H^{+}$	-34.8	
	MnF+	$Mn+2 + F- = MnF^{+}$	0.84	
	$MnSO_4$	$Mn+2 + SO_4-2 = MnSO_4$	2.25	3.37
	$Mn(NO_3)_2$	$Mn+2 + 2NO_3- = Mn(NO_3)_2$	0.6	-0.396
	$MnHCO_3$+	$Mn+2 + HCO_3- = MnHCO_3^{+}$	1.95	

Geochemistry: PHREEQC Modelling package llnl data base.

APPENDIX B:

B1: SAMPLING AND ANALYTICAL PROGRAMME-

Table B1: Analysis programme 200 kW samples

Sample	Analysis
Ilmenite/anthracite mixture	Paste pH, aqua regia digest and analyzed for Mn, Fe, Al, Cd and Zn
Ilmenite	Aqua regia digest and analyzed for Mn, Fe, Al, Cd and Zn
Anthracite	Aqua regia digest and analyzed for Mn, Fe, Al, Cd and Zn
Iron used for start-up	Aqua regia digest and analyzed for Mn, Fe, Al, Cd and Zn
Wet scrubber dust slurry (Trial 1)	Total solids, moisture content, pH, electrical conductivity, alkalinity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Wet scrubber dust slurry (Trial 2)	Total solids, moisture content, pH, electrical conductivity, alkalinity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Scrubber dust obtained from filtration (Trial 1)	XRD, XRF, total solids, moisture content, loss of ignition, particle size analysis, SEM Aqua regia digest and analyzed for Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Filtrate (Trial 1)	Aqua regia digest and analyzed for Mn and Fe Total solids, moisture content, pH, alkalinity, electrical conductivity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Scrubber dust obtained from flocculation (Trial 1)	XRD, total solids, moisture content and loss of ignition Aqua regia digest and analyzed for Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Supernatant (Trial 1)	Aqua regia digest and analyzed for Mn and Fe Total solids, moisture content, pH, alkalinity, electrical conductivity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Scrubber dust obtained from filtration (Trial 2)	XRD, total solids, moisture content, loss of ignition, particle size analysis Aqua regia digest and analyzed for Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Filtrate (Trial 2)	Aqua regia digest and analyzed for Mn and Fe Total solids, moisture content, pH, alkalinity, electrical conductivity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Scrubber dust obtained from flocculation (Trial 2)	XRD, total solids, moisture content, loss of ignition, particle size analysis Aqua regia digest and analyzed for Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Supernatant (Trial 2)	Aqua regia digest and analyzed for Mn and Fe Total solids, moisture content, pH, alkalinity, electrical conductivity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Influent to wet scrubber	pH, electrical conductivity, alkalinity, sulphate, Na, Ca, Mn, Mg, Fe, Cd, Zn, K and Al
Slag (Run 1)	Aqua regia digest and analysis for Mn, Fe, Al, Cd and Zn
Slag (Run 2)	Aqua regia digest and analysis for Mn, Fe, Al, Cd and Zn
Metal (Run 1)	Aqua regia digest and analysis for Mn, Fe, Al, Cd and Zn
Metal (Run 2)	Aqua regia digest and analysis for Mn, Fe, Al, Cd and Zn

ARLP and TCLP

The 200 kW smelter dusts obtained under reducing conditions were subjected to ARLP and TCLP in order to classify and characterize the samples in terms of manganese and iron mobilization. The scrubber dusts obtained after filtration were dried before extractions were performed while extractions on the flocculated scrubber dust were performed on “wet” samples due to the limited amount of dust obtained from flocculation.

The samples were also treated with immobilisation chemicals and the various extraction methods (discussed in Section 5.2) conducted on both untreated and treated dust samples.

B2: SAMPLING AND ANALYTICAL PROGRAMME - 500 KW AND 1.5 MW FURNACE PILOT TRIALS

Chemical characterisation of the pilot plant dusts obtained under oxidising conditions

The dust samples produced from the 500 kW and the 1.5 MW smelters were subjected to the following analyses:

- XRD, XRF and particle size screening (1.5 MW only)
- Aqua regia digestion and analyzed for sodium, potassium, calcium, magnesium, manganese, aluminium, cadmium, iron and zinc.
- Moisture content

ARLP and TCLP

The 500 kW and 1.5 MW dusts obtained under oxidising conditions were subjected to ARLP and TCLP in order to characterise and classify the dusts in terms of manganese and iron mobilisation. Samples were subjected to various chemical treatments before ARLP and TCLP were performed.

B3: OTHER EXTRACTION METHODS - EFFECT OF IRON 200 KW AND 1.5 MW FURNACE PILOT TRIALS

The 200 kW Trial 1 and 1.5 MW scrubber dust samples were subjected to several other leaching procedures - neutral extraction, multiple extraction and sequential extraction procedures. Samples with and without the addition of chemicals to immobilise the manganese were tested. Lime 5 % (w/w) and calcite 37.5 % (w/w) additions were made to these samples prior to extraction. Furthermore, the addition of ferric chloride in the ratio Fe:Mn 40:1 was done and the sample subjected to extraction procedures listed above. Leachates were analysed for manganese and iron.

B4: CHEMICAL IMMOBILISATION TREATMENT AND LEACHING OF SCRUBBER DUSTS

The following dusts obtained from the 200 kW pilot trials were subjected to chemical immobilisation treatment:

- Trial 1 scrubber dust obtained from filtration (Sample dried)
- Trial 2 scrubber dust obtained from filtration (Sample dried)

The following dusts or manganese containing wastes from other industries were subjected to chemical immobilisation treatment:

- 500 kW Kumba (Oxidising) (Wet sample)
- 1.5 MW Kumba (Oxidising) (Dried sample)

- Ticor wet scrubber dust (Reducing) (Wet sample)
- Corex classifier sand (Reducing) (Dried sample)
- Conarc slag (Reducing) (Dried sample)
- Metalloys wet scrubber dust (Oxidising) (Wet sample)

The following chemicals were investigated as treatment options to immobilise manganese:

- Lime
- Calcite
- Dolomite
- Sodium hypochlorite
- Desulphurisation slurry (Samancor).

The different scrubber dusts were subjected to different manganese immobilisation treatments (Table B2).

Table B2: Manganese immobilisation treatment options.

Chemical applied	Concentration of chemical application (%)
No treatment	0.0
Lime	5.0
	10.0
Burnt Dolomite	5.0
Raw dolomite	5.0
Calcite	37.5
Sodium hypochlorite	9.0
Desulphurisation slurry	5.0
	10.0

After mixing, samples were left for a period of 24 h, whereafter paste pH or pH was determined. The samples were then subjected to TCLP and ARLP. Soluble manganese, iron, aluminium, cadmium and zinc were determined on the leachate after ARLP extraction while only soluble manganese and iron concentrations were determined on the leachate after TCLP extractions.

APPENDIX C
ANALYSIS DATA AND MEASUREMENTS

Table C.1: Temperatures measured at inlet and outlet of the wet scrubber during trial 1 using thermocouples (A constant flow rate of 220 ℓ/h was applied using a flow meter)

Wet scrubber inlet temperature		Wet scrubber outlet temperature	
Time	**Temperature (°C)**	**Time**	**Temperature (°C)**
12h30	170	12h30	61
12h45	174	12h45	60
12h55	190	12h55	69
13h05	179	13h05	65
13h15	186	13h15	62
13h25	184	13h25	67
13h35	175	13h35	61

Table C.2: Temperatures measured at inlet and outlet of the wet scrubber during trial 2 using thermocouples and flow rate of influent water to wet scrubber

Wet scrubber inflow (ℓ/h)		Wet scrubber inlet temperature		Wet scrubber outlet temperature	
Time	**ℓ/h**	**Time**	**Temperature (°C)**	**Time**	**Temperature (°C)**
14h38	300	14h38	146	14h38	79
14h45	350	14h55	133	14h45	83
14h47	400	15h14	96	14h55	55
15h05	380	15h17	95	15h05	51
15h10	390	15h30	104	15h06	47
15h12	400	15h34	107	15h10	46
15h14	410	15h45	104	15h12	45
15h16	420	15h50	104	15h14	44
15h40	400	16h03	118	15h15	43
15h59	430	16h13	124	15h16	42
16h04	440	16h25	122	15h17	42
				15h18	41
				15h30	46
				15h32	49
				15h34	43
				15h37	38
				15h45	43
				15h50	42
				15h59	48
				16h03	48
				16h10	49
				16h13	47
				16h25	53

Table C3: Total manganese and total iron concentrations of the chemicals used for immobilisation treatment

	Manganese concentration (mg/kg)	**Iron concentration (mg/kg)**
Lime	0.29	<0.25
Calcite	0.65	<0.25
Desulphurisation slurry	<0.25	<0.25

Table C4: Soluble manganese and iron concentrations (mg/ℓ) of the distilled water and the standard manganese solutions

SOLUTION	**Manganese concentration (mg/ℓ)**	**Iron concentration (mg/ℓ)**
Distilled water	0.03	<0.01
Manganese chloride	99.94	<0.01
Manganese carbonate	97.99	<0.01
Manganese oxide	104.06	<0.01
Rochelle manganese standard solution	100.34	<0.01

Table C5: Inorganic Manganese standards- Manganese and iron concentrations (mg/ℓ) after 24 h of treatment, after ARLP and TCLP (not corrected for blanks)

Sample	**Type of treatment**	**Before extractions**		**After ARLP extractions**		**After TCLP extractions**	
		[Mn] mg/ℓ	**[Fe] mg/ℓ**	**[Mn] mg/ℓ**	**[Fe] mg/ℓ**	**[Mn] mg/ℓ**	**[Fe] mg/ℓ**
Distilled water	No treatment	ND	ND	4.53	2.82	2.57	<0.05
	Lime (5 %)	ND	ND	1.09	1.27	5.97	4.48
	Burnt Dolomite (VDB) (5 %)	11.8	78.5	0.96	<0.05	21.3	9.18
	Burnt Dolomite (VDB) (5 %) (Repeat)	ND	ND	0.42	2.95	8.37	19.5
	Raw dolomite (VDB) (5 %)	121	5.84	24.5	19.5	276	112
	Calcite (37.5 %)	ND	ND	1.77	<0.05	2.21	2.99
	Sodium hypochlorite (10-15 % solution) (1 %)	ND	ND	2.27	5.01	0.63	10.5
	Sodium hypochlorite (10-15 % solution) (9 %)	3.52	26.5	0.10	3.71	1.69	<0.05
	Desulphurisation slurry (5 %)	0.32	<0.05	0.41	<0.05	9.88	160
	Desulphurisation slurry (10 %)	ND	ND	ND	ND	ND	ND
$MnCl_2$	No treatment	ND	ND	84.9	<0.05	99.8	1.44
	Lime (5 %)	ND	ND	2.86	<0.05	23.8	2.52
	Burnt Dolomite (VDB) (5 %)	ND	ND	ND	ND	ND	ND
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	<0.05	<0.05	73.7	27.7
	Raw dolomite (VDB) (5 %)	2660	<0.05	117	19.6	407	290
	Calcite (37.5 %)	ND	ND	2.95	1.02	16.8	3.62
	Sodium hypochlorite (10-15 % solution) (1 %)	ND	ND	0.70	9.02	1.94	10.1
	Sodium hypochlorite (10-15 % solution) (9 %)	183	21.3	0.36	3.24	0.93	<0.05
	Desulphurisation slurry (5 %)	<0.05	<0.05	38.7	<0.05	139	444
	Desulphurisation slurry (10 %)	1.88	<0.05	58.4	218	0.22	<0.05
	Desulphurisation slurry (10 %) Repeat	ND	ND	<0.05	<0.05	119	830

Table C5 (Continued): Inorganic Manganese standards- Manganese and iron concentrations (mg/ℓ) after 24 h of treatment, after ARLP and TCLP (not corrected for blanks)

Sample	Type of treatment	Before extractions		After ARLP extractions		After TCLP extractions	
		[Mn] mg/ℓ	[Fe] mg/ℓ	[Mn] mg/ℓ	[Fe] mg/ℓ	[Mn] mg/ℓ	[Fe] mg/ℓ
$MnCO_3$	No treatment	ND	ND	102	<0.05	104	<0.05
	Lime (5 %)	0.19	<0.05	<0.05	<0.05	52.8	<0.05
	Lime (10 %)	<0.05	<0.05	ND	ND	<0.05	<0.05
	Burnt Dolomite (VDB) (5 %)	<0.05	<0.05	28.0	17.1	42.0	8.84
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	0.62	14.8	111	47.8
	Raw dolomite (VDB) (5 %)	2668	375	308	<0.05	117	147
	Calcite (37.5 %)	ND	ND	1.10	15.0	7.28	<0.05
	Sodium hypochlorite (10-15 % solution) (1 %)	11.5	0.34	0.48	<0.05	1.23	0.24
	Sodium hypochlorite (10-15 % solution) (9 %)	186	33.1	0.63	2.62	0.76	<0.05
	Desulphurisation slurry (5 %)	0.29	<0.05	54.2	15.5	94.2	236
	Desulphurisation slurry (10 %)	2.36	<0.05	0.39	<0.05	57.8	335
	Desulphurisation slurry (10 %) Repeat	ND	ND	0.12	<0.05	110	646
MnO_2	No treatment	ND	ND	111	<0.05	99.1	<0.05
	Lime (5 %)	<0.05	-1.39	<0.05	<0.05	67.4	<0.05
	Lime (10 %)	0.34	<0.05			0.33	<0.05
	Burnt Dolomite (VDB) (5 %)	0.17	-6.65	28.6	16.4	88.6	8.54
	Burnt Dolomite (VDB) (5 %) repeat	ND	ND	25.1	<0.05	94.5	37.8
	Raw dolomite (VDB) (5 %)	3236	491	372	<0.05	115	213
	Calcite (37.5 %)	ND	ND	14.4	14.6	8.85	<0.05
	Sodium hypochlorite (10-15 % solution) (1 %)	2.46	0.35	<0.05	<0.05	0.59	<0.05
	Sodium hypochlorite (10-15 % solution) (9 %)	189	31.7	0.42	2.96	0.77	<0.05
	Desulphurisation slurry (5 %)	0.74	-5.18	53.9	21.5	115	129
	Desulphurisation slurry (10 %)	2.19	<0.05	0.27	<0.05	85.8	313
	Desulphurisation slurry (10 %) Repeat	ND	ND	<0.05	<0.05	113	763
Rochelle Manganese standard	No treatment	ND	ND	100	<0.05	91.8	<0.05
	Lime (5 %)	ND	ND	<0.05	<0.05	11.8	<0.05
	Burnt Dolomite (VDB) (5 %)	0.35	-6.66	6.24	16.0	99.6	24.9
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	1.13	<0.05	94.5	29.5
	Raw dolomite (VDB) (5 %)	2631	780	284	<0.05	123	144
	Calcite (37.5 %)	ND	ND	1.51	15.1	8.07	<0.05
	Sodium hypochlorite (10-15 % solution) (1 %)	581.50	0.42	37.1	<0.05	0.01	<0.05
	Sodium hypochlorite (10-15 % solution) (9 %)	11.9	42.7	0.22	17.1	0.85	<0.05
	Desulphurisation slurry (5 %)	0.88	<0.05	53.3	20.7	108	228
	Desulphurisation slurry (10 %)	1.67	<0.05	0.20	<0.05	110	637
	Desulphurisation slurry (10 %) Repeat	ND	ND	3.10	<0.05	84.3	389

Table C6: Inorganic Manganese standards - pH and alkalinity after 24 h of treatment, after ARLP and TCLP

Sample	Type of treatment	Alkalinity mg/ℓ $CaCO_3$	pH before extraction	pH after ARLP	pH after TCLP
Distilled water	No treatment	6.44	6.24	3.84	3.47
	Lime (5 %)	32390	12.9	12.7	5.24
	Burnt Dolomite (VDB) (5 %)	16157	12.4	12.1	3.68
	Burnt Dolomite (VDB) (5 %) (Repeat)	ND	ND	7.85	4.35
	Raw dolomite (VDB) (5 %)	29655	10.3	7.35	4.44
	Calcite (37.5 %)	359288	9.48	8.18	6.71
	Sodium hypochlorite (10-15 % solution) (1 %)	847	12.4	6.97	3.73
	Sodium hypochlorite (10-15 % solution) (9 %)	38390	13.1	10.1	4.42
	Desulphurisation slurry (5 %)	7836	13.0	11.6	3.69
	Desulphurisation slurry (10 %)	ND	ND		
$MnCl_2$	No treatment	6.44	6.03	4.21	3.39
	Lime (5 %)	49335	12.8	13.0	5.13
	Burnt Dolomite (VDB) (5 %)	ND	ND	ND	ND
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	9.80	3.40
	Raw dolomite (VDB) (5 %)	14764	8.10	7.09	4.60
	Calcite (37.5 %)	359288	9.01	8.03	6.69
	Sodium hypochlorite (10-15 % solution) (1 %)	3807.38	12.3	6.97	3.47
	Sodium hypochlorite (10-15 % solution) (9 %)	36893	13.1	10.2	4.36
	Desulphurisation slurry (5 %)	5445	12.3	8.16	3.67
	Desulphurisation slurry (10 %)	11798	12.3	11.7	4.05
	Desulphurisation slurry (10 %) Repeat	ND	ND	11.4	4.45
$MnCO_3$	No treatment	ND	1.52	3.07	5.05
	Lime (5 %)	55427	12.9	13.1	4.70
	Lime (10 %)	145200	12.2	ND	12.0
	Burnt Dolomite (VDB) (5 %)	6164	13.1	7.56	3.84
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	7.40	4.00
	Raw dolomite (VDB) (5 %)	15881	5.50	6.59	4.35
	Calcite (37.5 %)	484275	7.23	7.18	6.19
	Sodium hypochlorite (10-15 % solution) (1 %)	726	7.10	4.39	2.88
	Sodium hypochlorite (10-15 % solution) (9 %)	39358	13.1	10.3	4.39
	Desulphurisation slurry (5 %)	3399	13.1	7.53	3.80
	Desulphurisation slurry (10 %)	5445	12.0	11.7	4.25
	Desulphurisation slurry (10 %) Repeat	ND	ND	11.2	4.40
MnO_2	No treatment	0.00	1.40	2.76	4.92
	Lime (5 %)	54459	12.9	13.0	4.80
	Lime (10 %)	138394	12.2	ND	11.8
	Burnt Dolomite (VDB) (5 %)	6428	13.0	7.75	3.80
	Burnt Dolomite (VDB) (5 %) repeat	ND	ND	7.35	4.00
	Raw dolomite (VDB) (5 %)	16562	5.31	6.57	4.44
	Calcite (37.5 %)	74843	6.76	7.15	6.21
	Sodium hypochlorite (10-15 % solution) (1 %)	0.00	3.45	3.51	4.87
	Sodium hypochlorite (10-15 % solution) (9 %)	40195	13.2	10.4	5.11
	Desulphurisation slurry (5 %)	38607	12.6	7.86	3.49
	Desulphurisation slurry (10 %)	8168	12.1	11.3	4.15
	Desulphurisation slurry (10 %) Repeat	ND	ND	11.6	4.40

Table C6 (Continued): Inorganic Manganese standards - pH and alkalinity after 24 h of treatment, after ARLP and TCLP

Sample	Type of treatment	Alkalinity mg/ℓ $CaCO_3$	pH before extraction	pH after ARLP	pH after TCLP
Rochelle Manganese standard	No treatment	0.00	1.09	2.45	5.04
	Lime (5 %)	88050	13.1	13.2	4.98
	Burnt Dolomite (VDB) (5 %)	11041	12.9	8.15	4.03
	Burnt Dolomite (VDB) (5 %) Repeat	ND	ND	7.40	3.50
	Raw dolomite (VDB) (5 %)	11344	5.24	6.54	4.33
	Calcite (37.5 %)	490439	6.25	7.12	6.20
	Sodium hypochlorite (10-15 % solution) (1 %)	0.00	2.40	2.97	4.89
	Sodium hypochlorite (10-15 % solution) (9 %)	15849	12.7	10.8	4.16
	Desulphurisation slurry (5 %)	19303	12.6	7.75	3.60
	Desulphurisation slurry (10 %)	10618	12.0	11.0	4.30
	Desulphurisation slurry (10 %) Repeat	ND	ND	7.35	4.35

Table C.7: 200 kW Pilot trial – pH, manganese and iron concentrations (mg/ℓ) after 24 h of treatment, after ARLP and TCLP

Sample	Type of treatment	Paste pH before extractions	pH after ARLP	pH after TCLP	After ARLP extractions		After TCLP extractions	
					[Mn] mg/kg	[Fe] mg/kg	[Mn] mg/kg	[Fe] mg/kg
Run 1 DRD (filtered)	No treatment	9.35	8.90	5.10	3.54	<0.05	1745	3387
	No treatment (Repeat)	ND	ND	ND	ND	ND	1134	898
	Lime (5%)	ND	12.0	6.25	<0.05	<0.05	826	17.2
	Lime (5%) (Repeat)	ND	ND	ND	ND	ND	2.70	<0.05
	Lime (10%)	ND	ND	4.85	ND	ND	50.9	120
	NaOCl (9 %)	ND	10.7	4.55	0.14	5.07	9.25	7.62
	Calcite (37.5 %)	ND	8.20	4.75	117	422	1272	7604
	CaO-CaS (10 %)	ND	11.7	12.5	0.08	<0.05	1.83	<0.05
Run 2 DSD (filtered)	No treatment	8.85	8.15	4.80	34.1	<0.05	183	3508
	Lime (5%)	ND	12.1	6.00	<0.05	<0.05	1430	159
	Lime (10%)	ND	ND	4.85	ND	ND	94.7	1.38
	NaOCl (9 %)	ND	10.8	4.55	0.54	2.08	5.33	6.72
	Calcite (37.5 %)	ND	7.40	4.70	3.06	19.3	1317	10024
	CaO-CaS (10 %)	ND	11.8	12.4	0.52	1.56	4.43	11.9

Table C.8: 500 kW and 1.5 MW Pilot Trials –pH, manganese and iron concentrations (mg/ℓ) after 24 h of treatment, after ARLP and TCLP

Sample	Type of treatment	pH			After ARLP extraction					After TCLP extraction	
		Paste pH before ARLP	pH after ARLP	pH after TCLP	Mn (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Fe (mg/kg)
500 kW WSD Kumba	No treatment	7.20	6.40	4.75	315	4.95	52.7	0.58	17.5	2049	13000
	Lime (5%)	ND	12.2	5.15	0.58	0.00	ND	ND	ND	181	922
	Sodium hypochlorite (9 %)	ND	10.7	ND	0.47	0.00	ND	ND	ND	ND	ND
	Calcite (37.5 %)	ND	6.95	ND	4.86	0.00	ND	ND	ND	ND	ND
1.5 MW Kumba	No treatment	8.55	5.90	3.95	118	200	30.8	0.24	74.4	167	3250
	Lime (5%)	ND	12.1	5.50	0.00	0.00	ND	ND	ND	106	1389
	Sodium hypochlorite (9 %)	ND	10.8	ND	0.56	0.00	ND	ND	ND	ND	ND
	Calcite (37.5 %)	ND	7.90	ND	1.14	0.00	ND	ND	ND	ND	ND

Table C.9: Samples obtained from other industries – pH, manganese and iron concentrations (mg/ℓ) after ARLP and TCLP

Sample description	Type of treatment	After ARLP extraction						After TCLP extraction		
		pH	Mn (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	pH	Mn (mg/kg)	Fe (mg/kg)
Ticor wet scrubber dust	No treatment	6.35	5.6	<0.05	ND	ND	ND	5.70	15.60	4156.80
	Lime (5%)	11.3	0.12	<0.05	ND	ND	ND	11.15	0.12	<0.05
	Lime (10%)	11.3	<0.05	<0.05	ND	ND	ND	11.25	0.20	<0.05
	Calcite (37.5 %)	8.65	<0.05	<0.05	ND	ND	ND	ND	ND	ND
	Desulphurisation slurry (10 %)	11.05	<0.05	<0.05	ND	ND	ND	ND	ND	ND
	Sodium hypochlorite (9%)	10.75	<0.05	<0.05	ND	ND	ND	ND	ND	ND
WSD Metalloys	No treatment	7.75	0.48	1.08	93.5	8.87	5.81	ND	ND	ND
	Lime (5%)	11.3	<0.05	<0.05	ND	ND	ND	ND	ND	ND
	Calcite (37.5 %)	7.15	7.76	0.22	ND	ND	ND	ND	ND	ND
	Sodium hypochlorite (9%)	10.7	<0.05	<0.05	ND	ND	ND	ND	ND	ND
Corex Classifier sand	No treatment	10.6	8.92	15.4	120	0.39	6.77	ND	ND	ND
	Lime (5%)	11.3	1.04	<0.05	ND	ND	ND	ND	ND	ND
	Calcite (37.5 %)	6.90	0.38	<0.05	ND	ND	ND	ND	ND	ND
	Sodium hypochlorite (9%)	10.7	1.38	<0.05	ND	ND	ND	ND	ND	ND
Conarc slag	No treatment	9.75	0.48	0.44	74.8	0.50	7.43	ND	ND	ND
	Lime (5%)	11.4	0.20	<0.05	ND	ND	ND	ND	ND	ND
	Calcite (37.5 %)	10.0	0.20	<0.05	ND	ND	ND	ND	ND	ND
	Sodium hypochlorite (9%)	8.90	0.38	<0.05	ND	ND	ND	ND	ND	ND

Table C.10: DB270 – pH, manganese and iron concentrations (mg/ℓ) after ARLP

Type of treatment	Paste pH	pH after ARLP	pH after TCLP	After ARLP extraction		After TCLP extraction	
				Mn (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Fe (mg/kg)
No treatment	8.25			33.1	0.00	1159	5380
Lime (5%)	8.25	12.0	8.55	0.45	0.00	27.8	13.4
Lime (10%)	8.25	11.7	12.3	0.63	0.00	0.45	13.4
Calcite (37.5 %)	8.25	8.25	ND	3.78	0.00	ND	ND

Table C.11: Total metal concentrations after aqua regia digestion of the original samples

	200 kW -Run 1 - Filtered	200 kW -Run 2 - Filtered	Kumba - 500 kW	Kumba - 1.5 MW	Ticor WSD
Total manganese (mg/kg)	18538.00	20950.00	14300.00	6813.00	15843.00
Total iron (mg/kg)	194125.00	200625.00	176750.00	80475.00	137038.00
Total cadmium (mg/kg)	2.30	1.90	1.40	0.90	2.15
Total zinc (mg/kg)	6963.00	6450.00	2325.00	2725.00	10495.00
Total aluminium (mg/kg)	13438.00	12313.00	3338.00	988.00	2688.00
Total sodium (mg/kg)	2036.00	1948.00	780.00	621.00	2173.00
Total potassium (mg/kg)	2531.00	2811.00	1796.00	958.00	5548.00
Total calcium (mg/kg)	2794.00	2394.00	398.00	462.00	566.00
Total magnesium (mg/kg)	46925.00	44425.00	7120.00	2958.00	4183.00

Table C.12: Total solids, moisture content and loss of ignition of the original samples

	200 kW -Run 1 - Filtered	200 kW -Run 2 - Filtered	Kumba - 500 kW	Kumba - 1.5 MW	Ticor WSD
Total solids	50.16	49.62	79.54	99.95	9.95
Moisture content (%)	49.84	50.38	20.46	0.05	90.05
Loss of ignition	-0.87	-1.04	-0.13	-1.27	0.60

Table C.13: XRD and XRF results of the original samples

	200 kW -Run 1 - Filtered	200 kW -Run 2 - Filtered	Kumba - 500 kW	Kumba - 1.5 MW	Ticor WSD
XRD – Siderite	6.00	3.00	-	-	-
XRD – Cerrusite	2.00	3.00	-	-	-
XRD – Massicot	36.00	-	-	-	-
XRD – Albanite	7.00	2.00	-	-	-
XRD – Zinkenite	16.00	-	-	-	-
XRD – Titanomagnetite	15.00	29.00	-	-	-
XRD - Ilmenite	-	9.00	17.00	6.00	46.00
XRD – Pseudobrookite	-	-	54.00	79.00	-
XRD - Rutile	3.00	5.00	22.00	15.00	24.00
XRD - Magnetite	-	-	7.00	-	-
XRD - Lepidocrocite	-	-	-	-	17.00
XRD – Metal and/or alloy	-	-	-	-	13.00
XRD - 2.0a – Not allocated	14.00	48.00	-	-	
XRF - SiO_2	21.90	ND	ND	4.37	7.64
XRF - TiO_2	15.90	ND	ND	63.94	49.82
XRF - Al_2O_3	3.59	ND	ND	1.28	1.16
XRF - Fe_2O_3(t)	37.33	ND	ND	26.89	32.49
XRF - MnO	2.88	ND	ND	2.86	4.72
XRF - MgO	11.63	ND	ND	1.18	1.39
XRF - CaO	0.55	ND	ND	0.19	0.13
XRF - Na_2O	0.74	ND	ND	0.29	1.12
XRF - K_2O	0.32	ND	ND	0.36	1.20
XRF - P_2O_5	0.08	ND	ND	0.05	0.04
XRF - Cr_2O_3	0.74	ND	ND	0.15	0.16

Table C.14: Particle size distribution (%) of the original samples

Particle size	200 kW - run 1 filtered	200 kW - run 2 - filtered	Ticor WSD
1000 µm	0.66	22.38	0.00
710 µm	0.51	14.14	0.00
500 µm	0.81	15.01	0.00
300 µm	24.84	17.56	0.00
250 µm	11.24	6.43	0.29
150 µm	23.23	10.91	0.38
75 µm	25.05	12.26	0.67
< 75 µm	13.66	1.30	98.66

Table C.15: Results of the water extractions performed on selected samples incorporated into the geochemical model

Sample	200kW - Run 1 - Filtered	Kumba – 1.5 MW	Ticor WSD
Sulphate (mg/ℓ)	845.08	128.31	17.54
Chloride (mg/ℓ)	1.19	0.86	5.52
Fluoride (mg/ℓ)	4.96	1.78	2.45
Aluminium (mg/ℓ)	2.50	1.84	1.36
Calcium (mg/ℓ)	70.93	4.22	2.37
Cobalt (mg/ℓ)	0.03	<0.05	<0.05
Copper (mg/ℓ)	0.06	<0.05	<0.05
Cadmium (mg/ℓ)	0.03	0.02	ND
Iron (mg/ℓ)	0.11	<0.05	<0.05
Potassium (mg/ℓ)	16.44	8.02	20.36
Magnesium (mg/ℓ)	14.79	4.42	2.03
Manganese (mg/ℓ)	0.09	<0.05	0.14
Sodium (mg/ℓ)	24.71	4.35	13.65
Nickle (mg/ℓ)	0.09	0.02	<0.05
Lead (mg/ℓ)	<0.05	<0.05	<0.05
Zinc (mg/ℓ)	0.29	0.32	1.03
Alkalinity as mg/ℓ $CaCO_3$	10.84	18.07	177.50
pH	7.45	8.15	7.05
Conductivity (mS/m)	93.30	15.20	23.60

APPENDIX D:

OTHER PYRO-METALLURGICAL SCRUBBER DUST SAMPLES PROCESS DESCRIPTIONS AND QUALITY DATA

Figure D1 depicts the processes involved with the Corex process where the classifier sand was obtained. Iron Ore (Fe_2O_3), coal, coke and fluxes (limestone, dolomite and quartz) are the input materials in the smelter. The temperatures of the smelter range between 1500 and 1700 °C while the temperature of the off-gas is around 1100 °C. Dust is formed under reducing conditions and treated with a wet scrubber. The slurry is then sent to a settling pond where the classifier sand was collected (Figure D1).

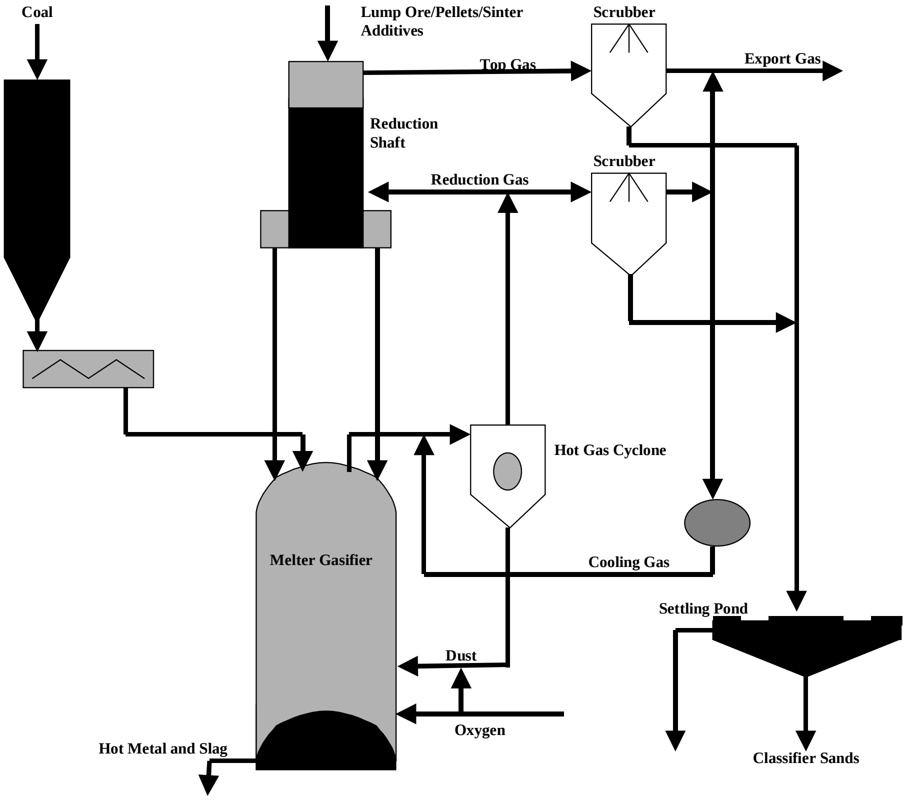

Figure D1: The Corex Process.

The Conarc Process uses a twin-shell alternating current arc furnace to produce low carbon steels from Corex-liquid iron, granulated iron and reduced iron from the Midrex Plant. These charge materials contain very low levels of residual elements and therefore the waste products (slag and dust) will be environmentally safer than the waste products from a conventional arc furnace. A de-oxidising agent is charged through the charging hole in the main roof. Aluminium, ferro-silicon, or a mixture of the two materials may be used as a de-oxidisation agent. An initial pre-charge of lime and burnt dolomite is done, to ensure that the basicity of the slag that is present in the furnace is higher than 1.5. The burnt dolomite is added to prevent excessive refractory wear by the very acid slag present. Saldana Steel previously performed ARLP tests on the Corex classifier sand and on the Cornarc slag. The results of these tests are presented in Table D1, Table D2 and Table D3.

Table D1: Metal concentrations of Corex Classifier sand after ARLP

Element	Acceptable risk (ppb)	Concentration in stream (mg/kg)	EEC (ppb)
Aluminium	10 000	0.26	8.58
Arsenic	430	Not detected	
Barium	7 800	0.09	2.97
Lead	100	0.01	0.33
Zinc	700	Not detected	
Fluoride	1 500	0.3	9.9
Cadmium	31	Not detected	
Chromium	4 700	Not detected	
Copper	100	Not detected	
Iron	9 000	37.62	1242.46
Mercury	22	Not detected	
Manganese	300	1.59	52.47
Nickel	1 114	Not detected	

The limiting element in determining the quantity of waste disposed of per month is manganese occurring at 1.59 mg/kg. Thus the amount of Corex Classifier Sand that can be disposed of per month is as follows:

$$\text{Dose (g/ha/month)} = \frac{\text{Acceptable risk}}{0.66} = \frac{300\text{ ppb}}{0.66} = 454.55\text{ g/ha/month}$$

The quantity of waste, therefore is 1 715.28 t/month over the 6 ha that are currently in use.

Table D2: Chemical analysis of the Conarc slag as supplied by Saldana Steel

Parameter	**Value**
Moisture @ 110 °C	0.12
Total Sulphur (S) % m/m	0.02
Sulphide Sulphur (S) % m/m	0.011
Sulphate Sulphur (SO_3) % m/m	0.02
Silica % m/m	14.67
Calcium % m/m	25.85
Magnesium % m/m	5.40
Aluminium % m/m	3.17
Sodium % m/m	0.038
Copper % m/m	0.003
Zinc % m/m	<0.001

Table D2 (Continued): Chemical analysis of the Conarc slag as supplied by Saldana Steel

Parameter	**Value**
Manganese % m/m	0.71
Iron % m/m	24.49
Nickel % m/m	<0.002
Chromium % m/m	0.031
Cadmium % m/m	<0.0025
Vanadium % m/m	0.053
Strontium % m/m	0.19
Tin % m/m	0.042
Barium % m/m	0.15
Carbon % m/m	0.13
Phosphorous % m/m	0.53
Titanium oxide % m/m	0.48
Arsenic mg/kg	<0.0002
Fluoride % m/m	<0.003

Table D3: Metal concentrations of Corex Slag after ARLP

Element	**Acceptable risk (ppb)**	**Concentration in stream (mg/kg)**	**EEC (ppb)**
Aluminium	10 000	0.59	951.87
Arsenic	430	Not detected	
Barium	7 800	0.12	193.6
Lead	100	Not detected	
Zinc	700	0.05	80.67
Fluoride	1 500	0.1	161.33
Cadmium	31	Not detected	
Chromium	4 700	Not detected	
Copper	100	Not detected	
Iron	9 000	0.24	387.2
Mercury	22	Not detected	
Manganese	300	0.09	145.2
Nickel	1 114	0.01	16.13

The limiting element in determining the quantity of waste disposed of per month is manganese occurring at 0.09 mg/kg.

Thus the amount of Conarc slag that can be disposed of per month is as follows:
454.55 g/ha/month

and the quantity of waste therefore 45 455 t/month over the 9 ha that are currently under use.

The third sample was obtained from Samancor from the Meyerton Works (Metalloys Wet Scrubber Dust). Figure D2 gives a schematic diagram of the process involved with the production of Ferro Manganese. Manganese ore, coal and coke are smelted in an Arc furnace at 1100 °C and manganese alloy, slag and off-gas produced. The off-gas is produced under oxidising conditions and can be collected in dry from using a bag filter or the off-gas can be sent through Venturi Scrubbers. The average temperature in the off gas system is 350 °C and the water used in the Venturi scrubbers is recycled and therefore not measured. The sludge water produced is then stored in the sludge dams. The sample tested by PHD was taken from the sludge dam indicated on Figure D3 as X.

Samancor supplied PHD with chemical analyses performed on the sludge dams. The average values of the chemical parameters are given in Table D4.

Table D4: Average chemical analyses of the Samancor sludge dams

Chemical parameter	**Value**
Calcium concentration (mg/ℓ)	1.40
Magnesium concentration (mg/ℓ)	9.00
Sodium concentration (mg/ℓ)	3149
Potassium concentration (mg/ℓ)	4503
Manganese concentration (mg/ℓ)	1.04
Sulphate concentration (mg/ℓ)	2037
Nitrogen as ammonia (mg/ℓ)	65.0
Nitrogen as nitrate (mg/ℓ)	23.4
Chloride concentration (mg/ℓ)	1248
Phenol concentration (mg/ℓ)	837724
Phosphor concentration (mg/ℓ)	28.7
Electrical conductivity (mS/m)	2127
pH	9.19

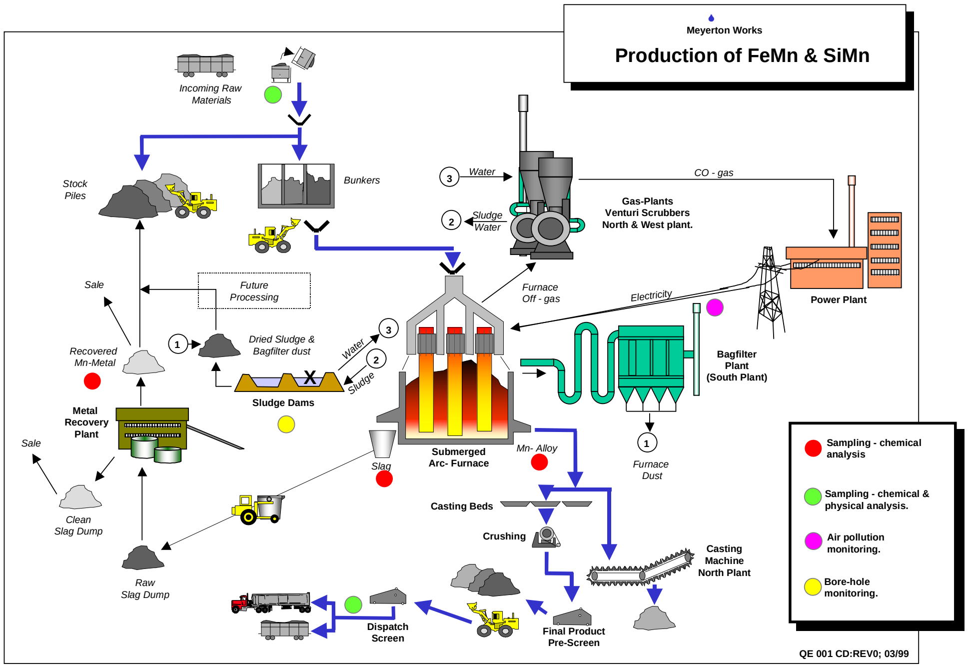

Figure D3: Schematic diagram of the production of ferromanganese at the Meyerton Works indicating where the wet scrubber dust sample was obtained with the symbol X

Table D5: Chemical characteristics of the samples obtained from other industries

	Corex classifier sand	Metalloys wet scrubber dust
XRD-Calcite	7	-
XRD-Dolomite	38	-
XRD-Hematite	51	-
XRD-Sylvite KCl	-	28
XRD-Aphthitalite - $K_{3}NaSO_{4})_{2}$	-	58
XRD-Hausmanite - $Mn_{3}0_{4}$	-	5
XRD-Halite	-	6
XRD-Quartz	4	2
Total Sodium (mg/kg)	400	133177
Total Potassium (mg/kg)	849	176263
Total Calcium (mg/kg)	86044	11379
Total Magnesium (mg/kg)	35877	6796
Total Aluminium (mg/kg)	2333	4113
Total cadmium (mg/kg)	2.6	7.6
Total Iron (mg/kg)	211463	6659
Total Manganese (mg/kg)	110	70899
Total Zinc (mg/kg)	48	1296
Moisture content (%)	14.49	98.81
Solids (%)	85.51	4.19
Loss of ignition	20.55	12.02

Table D6: Particle size analyses (%) of the Corex classifier sand and the Metalloys wet scrubber dust.

Particle size	Corex classifier sand	Metalloys wet scrubber dust
1000 µm	9.45	0.00
710 µm	8.51	0.00
500 µm	10.57	0.00
300 µm	17.72	0.00
250 µm	7.77	0.00
150 µm	21.68	0.00
75 µm	19.05	0.23
<75 µm	4.58	99.54

APPENDIX E

HAZARDOUS WASTE CLASSIFICATION

Table E.1: Acceptable risk and estimated environmental concentrations of manganese (ARL = 0.3 ppm) for the different samples disposed in a 50 ha landfill site at a disposal rate of 2 000 tons/month, based on ARLP and TCLP tests

Type of treatment	Sample	Sample description	After ARLP					After TCLP				
			Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL	Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL
No Treatment	200 kW - Trial 1 - Filtered	Reducing	0.34	13.60	8.98	0.03	YES	1745	69800	46068	153.56	NO
	200 kW - Trial 2 - Filtered	Reducing	34.10	1364	900.24	3.00	NO	183.00	7320	4831	16.10	NO
	500 kW Kumba	Oxidising	315.00	12600	8316	27.72	NO	2049	81960	54094	180.31	NO
	1.5 MW Kumba	Oxidising	118.00	4720	3115	10.38	NO	167.00	6680	4409	14.70	NO
	Ticor - WSD	Reducing	5.60	224.00	147.84	0.49	YES	15.60	624.00	411.84	1.37	NO
	WSD Metalloys	Oxidising	0.48	19.20	12.67	0.04	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	8.92	356.80	235.49	0.78	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	0.48	19.20	12.67	0.04	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	33.10	1324	873.84	2.91	NO	1159.00	46360	30598	101.99	NO
Lime (5 %)	200 kW - Trial 1 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	826.00	33040	21806	72.69	NO
	200 kW - Trial 2 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	1430.00	57200	37752	125.84	NO
	500 kW Kumba	Oxidising	0.58	23.20	15.31	0.05	YES	181.00	7240	4778	15.93	NO
	1.5 MW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	106.20	4248	2803	9.35	NO
	Ticor - WSD	Reducing	0.12	4.80	3.17	0.01	YES	0.12	4.80	3.17	0.01	YES
	WSD Metalloys	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	1.04	41.60	27.46	0.09	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	0.20	8.00	5.28	0.02	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	0.45	18.00	11.88	0.04	YES	27.80	1112	733.92	2.45	NO
Lime (10 %)	200 kW - Trial 1 - Filtered	Reducing	ND	ND	ND	ND	ND	50.90	2036	1344	4.48	NO
	200 kW - Trial 2 - Filtered	Reducing	ND	ND	ND	ND	ND	94.70	3788	2500	8.33	NO
	500 kW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Ticor - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	0.20	8.00	5.28	0.02	YES
	WSD Metalloys	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Conarc slag	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DB 270	Reducing	0.63	25.20	16.63	0.06	YES	0.45	18.00	11.88	0.04	YES
Sodium hypochlorite (9 %)	200 kW - Trial 1 - Filtered	Reducing	0.14	5.60	3.70	0.01	YES	9.25	370.00	244.20	0.81	YES
	200 kW - Trial 2 - Filtered	Reducing	0.54	21.60	14.26	0.05	YES	5.33	213.20	140.71	0.47	YES
	500 kW Kumba	Oxidising	0.47	18.80	12.41	0.04	YES	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	0.56	22.40	14.78	0.05	YES	ND	ND	ND	ND	ND
	Ticor - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	1.38	55.20	36.43	0.12	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	0.38	15.20	10.03	0.03	YES	ND	ND	ND	ND	ND

Table E.1 (Continued): Acceptable risk and estimated environmental concentrations of manganese (ARL = 0.3 ppm) for the different samples disposed in a 50 ha landfill site at a disposal rate of 2 000 tons/month, based on ARLP and TCLP tests

Type of treatment	Sample	Sample description	After ARLP					After TCLP				
			Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL	Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL
Calcite (37.5 %)	200 kW - Trial 1 - Filtered	Reducing	117.00	4680	3088	10.30	NO	1272.00	50880	33581	111.94	NO
	200 kW - Trial 2 - Filtered	Reducing	3.06	122.40	80.78	0.27	YES	1317.00	52680	34769	115.90	NO
	500 kW Kumba	Oxidising	4.86	194.40	128.30	0.43	YES	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	1.14	45.60	30.10	0.10	YES	ND	ND	ND	ND	ND
	Ticor - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	7.76	310.40	204.86	0.68	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	0.38	15.20	10.03	0.03	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	0.20	8.00	5.28	0.02	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	3.78	151.20	99.79	0.33	YES	ND	ND	ND	ND	ND
Desulphurisation slurry (10 %)	200 kW - Trial 1 - Filtered	Reducing	0.08	3.20	2.11	0.01	YES	1.83	73.20	48.31	0.16	YES
	200 kW - Trial 2 - Filtered	Reducing	0.52	20.80	13.73	<0.05	YES	4.43	177.20	116.95	0.39	YES
	500 kW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Ticor - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Conarc slag	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table E.2: Acceptable risk and estimated environmental concentrations of iron (ARL = 9 ppm) for the different samples disposed in a 50 ha landfill site at a disposal rate of 2 000 tons/month, based on ARLP and TCLP tests

Type of treatment	Sample	Sample description	After ARLP					After TCLP				
			Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL	Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL
No Treatment	200 kW - Trial 1 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	3387	135474	89413	9.93	NO
	200 kW - Trial 2 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	3508	140334	92620	10.29	NO
	500 kW Kumba	Oxidising	4.95	198.00	130.68	0.01	YES	13000	520000	343200	38.13	NO
	1.5 MW Kumba	Oxidising	199.60	7984	5269	0.59	YES	3250	130000	85800	9.53	NO
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	177.50	7100	4686	0.52	NO
	WSD Metalloys	Oxidising	1.08	43.20	28.51	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	15.40	616.00	406.56	<0.05	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	0.44	17.60	11.62	0.00	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	<0.05	<2.00	<1.32	0.00	YES	5380	215180	142019	15.78	NO
Lime (5 %)	200 kW - Trial 1 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	17.23	689.20	454.87	<0.05	YES
	200 kW - Trial 2 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	158.84	6354	4193	0.47	YES
	500 kW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	922.10	36884	24343	2.70	NO
	1.5 MW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	1389	55544	36659	4.07	NO
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	<0.05	<2.00	<1.32	0.00	YES
	WSD Metalloys	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	<0.05	<2.00	<1.32	0.00	YES	13.40	536.00	353.76	0.04	YES
Lime (10 %)	200 kW - Trial 1 - Filtered	Reducing	ND	ND	ND	ND	ND	120.07	4803	3170	0.35	YES
	200 kW - Trial 2 - Filtered	Reducing	ND	ND	ND	ND	ND	1.38	55.20	36.43	0.00	YES
	500 kW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	<0.05	<2.00	<1.32	0.00	YES
	WSD Metalloys	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Conarc slag	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DB 270	Reducing	<0.05	<2.00	<1.32	0.00	YES	13.40	536.00	353.76	0.04	YES
Sodium hypochlorite (9 %)	200 kW - Trial 1 - Filtered	Reducing	5.07	202.80	133.85	0.01	YES	7.62	304.80	201.17	0.02	YES
	200 kW - Trial 2 - Filtered	Reducing	2.08	83.20	54.91	0.01	YES	6.72	268.80	177.41	0.02	YES
	500 kW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND

Table E.2 continued: Acceptable risk and estimated environmental concentrations of iron (ARL = 9 ppm) for the different samples disposed in a 50 ha landfill site at a disposal rate of 2 000 tons/month, based on ARLP and TCLP tests

Type of treatment	Sample	Sample description	After ARLP					After TCLP				
			Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL	Total content (mg/kg)	Waste (g/ha/m)	EEC (ppb)	EEC/ ARL	EEC< ARL
Calcite (37.5 %)	200 kW - Trial 1 - Filtered	Reducing	421.70	16868	11133	1.24	NO	7604	304176	200756	22.31	NO
	200 kW - Trial 2 - Filtered	Reducing	19.29	771.60	509.26	0.06	YES	10024	400946	264624	29.40	NO
	500 kW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	0.22	8.80	5.81	0.00	YES	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	Conarc slag	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	DB 270	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
Desulphurisation slurry (10 %)	200 kW - Trial 1 - Filtered	Reducing	<0.05	<2.00	<1.32	0.00	YES	<0.05	<2.00	<1.32	0.00	YES
	200 kW - Trial 2 - Filtered	Reducing	1.56	62.40	41.18	0.00	YES	11.89	475.60	313.90	0.03	YES
	500 kW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	1.5 MW Kumba	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Kumba - WSD	Reducing	<0.05	<2.00	<1.32	0.00	YES	ND	ND	ND	ND	ND
	WSD Metalloys	Oxidising	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Corex Classifier sand	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Conarc slag	Reducing	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

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