The Use Of The Waste Delisting Process - Case Study: The Management Of Ferrochrome Slag As A Construction Product In South Africa

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Submitted to the faculty of Natural Sciences in partial fulfillment of the requirements for the Magister in Environmental Management at the North-West University.

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ABSTRACT

Ferrochrome slag is a by-product from the production of ferrochrome, an essential component in stainless steel. World wide it is known that ferrochrome slags are been used mainly in the road and civil construction industries, and in producing refractories.

Slag management at ferrochrome producing companies has been influenced by the limited space available and financial cost implications of the slag dumps. In South Africa, according to the Department of Water Affairs and Forestry's minimum requirements, (DWAF, 1998), ferrochrome slag due to its quantity or volume on the disposal sites has been classified as hazardous, as it leaches Manganese (Mn) (33%) above the DWAF minimum environmental requirements acceptable levels. This rating of the slag has therefore put limitations on the use of slag commercially.

This paper investigates the various slag uses proposed which can impact positively on the management of the slag i.e. that would reduce its dumping loads and consequently its impact on the surrounding environment. The uses proposed for are brick and concrete making and road building.

The paper provides results for the proposed slag uses leaching potential, performs a risk assessment to determine its potential effect on the environment and human health as well as discusses the method used to delist the slag through the South African delisting process. Comments on the process from the DEAT are also provided.

**Keywords:** Ferrochrome slag, waste, delist, concrete, tar, bricks, road.
OPSOMMING

Ferrochroom slak is 'n by-produk in die produksie van ferrochroom, 'n belangrike komponent in die vervaardiging van vlekvrye staal. Dit is wereldwyd bekend dat Ferrochroom slak hoofsaaklik gebruik word in pad en siviele konstruksie industrieë, asook in die vervaardiging van vuurvaste materiale.

Die bestuur van slak by Ferrochroom vervaardigende maatskappye word beïnvloed deur die beperkte beskikbare spasie, asook finansiele koste implikasies van slakhope. In Suid Afrika, as gevolg van die hoë volume van ferrochroom slak op bergings areas, word slak geklassificeer as skadelik, aangesien dit hoë volume Mangaan deurlaat (Mn) (33%), wat bo die DWAF se minimum aanbevore aanvaarbare omgewingsvlakke is. Die klassifikasie van slak plaas daardeur beperkings op die kommersiële gebruik van slak.

Die verslag ondersoek die verskeie aanbevore gebruikte van slak wat die bestuur van slak positief beïnvloed, soos byvoorbeeld die hoeveelheid slak wat geberg word by spesifieke bergings areas, asook die impak daarvan op die direkte omgewing. Die volgende gebruikte van slak word aanbeveel, nl. vir die vervaardiging van stene, sement en die konstruksie van paaie.

Die verslag voorsien resultate vir die aanbevore gebruikte en die deursyfer potensiaal van slak. 'n Risiko analyse word gedoen om vas te stel wat die potensiele effek op die omgewing en menslike gesondheid inhou, asook die metode wat gebruik word om die slak te herklassificeer deur die Suid Afrikaanse herklassifiserings proses. Kommentaar van DEAT oor die proses word ook voorsien.

Sleutelwoorde
Ferrochroom slak, afvalmateriaal, herklassificeer, sement, teer, boustene, pad.
I would like to express my gratitude to my supervisor, Prof Kobus van der Walt, whose expertise, understanding, patience and persistence enabled me to complete my Masters. I appreciate his vast knowledge and skill in many areas, especially when assisting me in writing this dissertation.

I would also like to thank my family, Mom, Dad, Daniel and Matthew for the support they provided me through my entire life. In particular, I must acknowledge and thank my husband and best friend, Mark, for your love and encouragement.

In conclusion, I recognize that this research would not have been possible without the financial assistance of Samancor Chrome and express my gratitude to them.
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CHAPTER 1: INTRODUCTION

1.1 Background

Ferrochrome slag is a by-product from the production of ferrochrome, an essential component in stainless steel. Ferrochrome producing industries have been disposing their slag on slag disposal sites next to their furnaces for a number of years. These dumps depending upon their age and number of furnaces per site, can carry anything from 2.4 million to 21 million tons of slag.

According to the Department of Water Affairs and Forestry’s minimum requirements, (DWAF, 1998), ferrochrome slag due to its quantity or volume on the disposal sites has been classified as hazardous, as they leach Manganese (Mn) (33%) and Aluminum (AL) (50%) above the DWAF minimum environmental acceptable levels. This hazardous rating of the slag has put limitations on the use of slag, thereby reducing space available at the disposal sites and increasing financial cost implications for the ferrochrome industry, when reviewing rehabilitation and closure plans.

Internationally, ferrochrome slag is used commercially in the road and construction industries. In order for the slag to be commercially used in South Africa it had to be delisted. To achieve this, the following method was used:-

- Perform a literature review on ferrochrome slag, its uses internationally and the delisting process in South Africa and the United States of America
- Perform a South African Acid Rain (SAAR) test on the slag, to determine its leaching potential and hazardous rating in its original state.
- Decide upon the required uses of the slag for delisting and make products from slag i.e. bricks, concrete slab and tar mix.
- Perform a Toxicity Characteristic Leaching Procedure (TCLP) test or South Africa Acid Rain (SAAR) test on the slag products to determine the leaching potential and calculate the environmental load as per use requirements. For example, the number of bricks to be used in low cost housing development.
Motivate for use, if required and delisting by using the risk based approach to determine the effect on the environment or human health.

Obtain comment from the DEAT on the motivation for the slag use.

1.2 Ferrochrome production history

Chromium was named after the Greek word "Chrōma" (χρωμα) meaning colour, because of the many colourful compounds made from it.

Chromium's history dates back thousands of years. Archaeologists found weapons that had been made of bronze and coated in chromium, in burial pits dating from the late 3rd century BC Qin Dynasty of the Terracotta Army near Xi'an. (Cotterell, 2004 )

The metal chromium was discovered in 1798 by Louis Nicolas Vauquelin. He concluded from his tests that he could isolate metallic chromium by heating the oxide in a charcoal oven. (Web elements, 2008)

Chromium was initially used in the 1800s as a component of paints and in tanning salts. Nowadays, it is used in the metal alloys industry to produce a Ferrochrome product, which is used in amongst other things for the production of stainless steel. A smaller amount is used in the chemical industry and refractory and foundry industries.

The development of the Charge Chrome industry was directly related to the developments in the alloy steel production technology. Chromium as a commercial metal is used as a medium for the introduction of chromium into steel. Chromium increases the hardness, strength, yield point, elasticity and resistance to corrosion, heat, acid, etc. Therefore, chromium is essentially used for the production of all varieties of stainless steels: Heat and Acid Resistant Steels; Structural, Tools and
other special categories of steels. Chromium steels are also used for the manufacture of ball and roller bearings.

According to DSIR (2005), “after initial experimentations and practices, during 1920’s to the 1930’s, followed by the alloy steel manufacturers using the Iron Ore and Chrome Ore process, the use of costly Low Carbon Ferro Chrome as the medium for introduction of additional chromium was established, during the 1940’s.”

This was followed in 1945, by the use of Ferro Chrome Silicon. The use of Low Carbon Ferro Chrome and Silico Chrome, for chromium addition, was continued till the 1960’s when, around 1964 the Vacuum Oxygen Decarburisation (VOD) and in 1968 the Argon Oxygen Decarburisation (AOD), respectively, were developed and commercialised in the Steel production plant. Then, in 1972 the CLU (Creusot-Loire Uddelohm) process was developed. These three processes, in particular the former two, ushered in a revolution in the alloy steel production technologies. With the advent of AOD and VOD technologies, the use of High Carbon Ferro Chrome, for introducing chromium into steel with much improved process economics, was established.”

Through the worldwide standardisation of these technologies, as well as the use of High Carbon Ferro Chrome - it was also established that Ferro Chrome, with even 50% chromium content, can be efficiently used in the production of stainless steels & other special alloy steels. This resulted in the arrival of Charge Chrome as the most economic and established medium of chromium addition to steels. Since the Charge Chrome production technology permits use of medium grade ores as well as high grade Ferro Chrome, the charge chrome was fast accepted by all chrome alloy producers of the world, in view of the fast depleting resources of high Cr /Fe ratio lumpy chrome ore.

1.3 What is ferrochrome slag?

Wikipedia (Wikipedia, 2007), states that a slag is a by-product of smelting ore to purify metals.
More specifically, ferrochrome slag is a by-product from the production of ferrochrome, which is an essential component in stainless steel production. (Lind et al, 2001)

1.4 The ferrochrome production process – How is slag produced?

The typical process by which ferrochrome and its by-product or waste slag is produced can be outlined as follows:-

Chrome ore is mined from underground and opencast mines. Two underground mining methods can be employed at Chrome mines; namely conventional scraper mining and trackless mechanised mining.

The conventional scraper method involves the ore being drilled and blasted, then scraped mechanically to loading points from where it is transported to shaft tips by locomotives and hoppers. From there it is hoisted to surface by conveyor belts installed in the inclined shafts.

In trackless mechanised mining the seam, which is contaminated by an internal waste parting, ore is drilled and blasted by conventional means. The blasted rock, consisting of some 70% chrome ore and 30% waste, is then loaded by load-haul-dump units and transported to conveyor loading points from where it is then hoisted from the mine workings. At these sections, about 19% of the chrome ore is left intact as pillars to stabilise the excavation and act as regional support. The mined chrome ore is transported to alloy plants for ferrochrome production.
The chrome ore is then added to the ferrochrome production furnaces, with other raw materials such as coal, coke, dolomite and quartzite for the production of ferrochrome. Within the furnaces an electric current, generated by means of carbon electrodes, melts the raw materials and reduces the chromium from the trivalent state in the ore to a zero valent state in the metallic form. The smelting point of the slag has to be higher than the metal smelting point, because metal is heated up by using the slag liquid phase. The densities of the liquid slag versus the metal allows them to be separated in the furnaces.

![Metal alloy being poured into casting bays.](image)

Niemelä and Kauppi, (2005) stated “Metal and slag are tapped from the furnace through the tap hole. The temperature of the slag in tapping slag is 1700°C and that of the ferrochrome is 1600°C.” The metal is cooled and solidified in casting bays. It is then crushed and screened into different size fractions to satisfy customer requirements.

The slag is air cooled and then further processed through a chrome recovery plant to remove the remaining chrome metal trapped in the slag. Once this has been completed the slag is deposited onto a slag disposal area on the site near the production furnaces. On an average day between 330 tons and 380 tons of slag can be produced from one ferrochrome furnace, which is 120 450 tons a year. Most slag disposal sites in South Africa are approximately 20 years old and have a minimum of 2.4 million tons of slag disposed on them, per furnace.
CHAPTER 2: FERROCHROME SLAG

2.1 Composition

The typical composition of the ferrochrome slags are 30% SiO$_2$, 23% MgO, 26% Al$_2$O$_3$ and 2% CaO. The chrome content in the slag is about 8% and the iron content 4% respectively. The slag also includes oxides such as Cr, Fe and calcium oxide. The chrome content of the slag is about 8% and the iron content 4% respectively. (Niemelä and Kauppi, 2005)

2.2 Ferrochrome slag classification

South Africa waste is controlled by a variety of acts and regulations, some of the important ones are listed below:-

- National Environmental Management Act (NEMA) no 107 of 1998
- Environmental Conservation Act (ECA) no 73 of 1989
- The Department of Water Affairs and forestry's (DWAF) - Minimum Requirements For The Handling, Classification And Disposal Of Hazardous Waste, Second Edition 1998
- Health Act no 63 of 1977
- Atmospheric Pollution Prevention Act no 45 of 1965, soon to be replaced by the National Environmental Management: Air Quality Act no 39 of 2004
- the National Water Act no 36 of 1998
- the proposed Waste Management Bill

The processed ferrochrome slag is termed as a waste, according to South African legislation. Waste is defined by the Environmental Conservation Act (ECA) no 73 of 1989 (ECA, 1989), as "any matter, whether gaseous, liquid or solid or any combination thereof, which is from time to time designated by the Minister by notice in the Gazette as an undesirable or superfluous by-product, emission, residue or remainder of any process or activity."
In terms of the Minimum Requirements For. The Handling, Classification And Disposal Of Hazardous Waste, Second Edition 1998, the Department of Water Affairs and Forestry was empowered to draw up a set of guidelines that would assist in the management of waste. This was achieved through the development of the Minimum requirements:-


Document 3: Minimum Requirements for the Monitoring of Water Quality at Waste Management Facilities.

Although DWAF was empowered to set up the guidelines, it is important to note that in terms of the draft Third Edition 2005 of the "Management of waste series", the Department of Environmental Affairs and Tourism (DEAT) is now identified as the lead department regarding wastes. (DWAF, 2005)

Within document 1 of the DWAF 2005 minimum requirements, waste is divided into two classes, General or Hazardous, according to their inherent toxicological properties. "Hazardous wastes are further subdivided, according to the risk that they may pose at disposal, using a hazard rating. In this way, a 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 of 4 are of moderate or low hazard." (DWAF, 2005)

"To determine whether a waste is hazardous a process has to be followed that will accurately test and analysed it, to identify its composition and concentration. The minimum requirements state that, “if a waste emanates from a certain industry, for example the medical, metal, agricultural or textile industry, it is probably hazardous.” (DWAF, 2005)

If the analysis confirms that a waste does contain hazardous substances (such as those listed in SANS 10228, the Basel Convention or the waste tables in the minimum requirements document), it should then be classified according to SANS
Thereafter a waste hazard rating is required. "In accordance with the Precautionary Principle, it is the most hazardous substance and its concentration that determines the class, the Hazard Rating, and hence the ultimate method of disposal of a waste or waste stream." (DWAF, 1998). The rating is determined by calculating the toxicity (LD50), ecotoxicity (LC50), carcinogenicity, mutagenicity, teratogenicity, persistence, environmental fate and Estimated Environmental Concentration (EEC) of the waste or its residue.

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

Hazard Rating 1 and 2: extreme and high hazard

Hazard Rating 3 and 4: medium and low hazard

From the definition given in the DWAF minimum requirements, since the ferrochrome slag is classified as a waste, and it emanates from a metal industry, one must assume that it is a hazardous waste. In addition to classifying and ranking hazardous waste, it is also important to determine the amount of the hazardous substance(s) that may leach and migrate from the waste disposal site, over an indefinite time. This concentration of hazardous substances is expressed as Estimated Environmental Concentration (EEC). The maximum amount of a given hazardous substance that can be safely landfilled, i.e., the Total Load, provides guidance on safe hazardous waste disposal levels at a specific landfill. The EEC that is calculated for a specific landfill must not exceed the Acceptable Exposure Levels as applicable for specific contaminants.

Therefore further tests in the form of Toxicity Characteristic Leaching Procedure (TCLP) and the South Africa Acid rain tests are done to determine its leaching potential, hazard rating and total load.

The South African EEC and total load calculations classified the ferrochrome slag, as it is stored in large quantities on the dumps, as a hazardous waste. It was seen to leach Manganese (Mn) (33%) and Aluminum (AL) (50%) above the minimum
requirements acceptable levels. With Mn been leached above the acceptable limits, this gives the slag a hazardous rating of H:H2.

It is however interesting to note that not all countries classify ferrochrome slag as hazardous or as a waste. A case in Finland was fought by Outokumpu Tornio Works, who were issued an IPPC permit in January 2002. In the permit the ferrochrome slag products were classified as waste after being sold traditionally as construction products. They appealed the waste interpretation to the Administrative Court. The Administrative Court upheld the waste interpretation in June 2004 (voting result 2 - 4 against Outokumpu Tornio Works). Finally, after almost four years since the beginning of the dispute, the highest administrative court in Finland, the Supreme Administrative Court issued its judgment on the issue on 23 December 2005 in Outokumpu Tornio Works favour.

CIRU (2007), reported that “The Supreme Administrative Court indicated that ferrochrome slag is a product. The decision was fairly extensively based on the facts from the scientific research conducted by CIRU:

"The mineralogical study on ferrochrome samples in the University of Oulu has shown that the decisive issue is not merely the content of detrimental substance in the material. The essential question is the form the detrimental substance and whether it can dissolve from the material in a meaningful extent to have environmental effects. A substance in a sparingly soluble form does not cause damage to biota or waterways. Any extra limiting measures are not reasonable for a product that has existed in the market for decades and that meets the environmental qualification criteria."

The Court justified this decision and interpretation with several arguments:

- "uninterrupted" process
- purposefully designed processes
- slag could immediately be processed into utilisable by-products
- favourable properties of the by-products create continuous strong demand
- the use of the products in accordance with their properties did not cause any hazard or harm to health or the environment
- sales prices covered or exceeded their manufacturing's costs
processing of slag into by-products was particularly profitable as this prevented the need to place the slag in a landfill.

generation of waste was reduced as the use of slag products replaced natural gravel reserves which contributed to sustainable development" (Ylimauna, 2006)

CIRU (2007), also reported that according to the solubility surveys reported by Paavo Ristola Oy in 2001 solubility of chrome from ferrochrome slag was low. A reason for this disparity of substance content and solubility was found in this research. It is based on the microstructure and mineralogical composition of slag.

However due to this South African hazardous rating process and the legislative requirements for hazardous waste ferrochrome slag has not been able to be used to its maximum potential in South Africa.
Chapter 3: ALTERNATIVE USES OF FERROCHROME SLAG

World wide it is known that ferrochrome slag is used mainly in the road and civil construction industries, and in producing refractories. Outokumpu (2007) reported that at their site in Tornio, Finland, over 60 000 tons of stainless steel slag and 315 000 tons of ferrochrome slag were sold and used as products in 2007 for building materials.

Wikipedia (2007), states that "Slag has many commercial uses, and is rarely thrown away. It is often reprocessed to separate any other metals that it may contain. The remnants of this recovery can be used in railroad track ballast, and as fertilizer. It has been used as a road base material and as a cheap and durable means of roughening sloping faces of seawalls in order to progressively arrest the movement of waves."

"The ferrochrome slag products are excellent materials to use in road construction, because the removal of the earth is reduced, that is the need of new material for road is 30-50% less than compared with natural sand and macadam for example. Water easily penetrates slag layers. (Niemelä and Kauppi, 2005) The ferrochrome slag is hard and stable and it is well suitable for demanding structures.

3. 1 Road construction

Extensive tests have been carried out on the physical properties of the ferrochrome slag from Vargon Alloys (Lind et al, 2001), and it was found to be highly suitable as road construction material.

The environmental impact of ferrochrome slag in road construction was investigated by B.B. Lind, A.-M. FaÈ iliman, and L.B. Larsson of the Swedish Geotechnical Institute in 2001, (Lind et al, 2001) They state that "leaching tests with salt seawater and pH-adjusted water reveal low leachability from the slag for most elements. Concentrations in the leachate from the slag are often in the same order as leaching from natural till sediments." They also determined that in road construction, "there
was a low migration of particles from the slag to the underlying soil; and that the leaching from the ferrochrome slag to the groundwater was low for the elements analysed, with the exception of potassium (K), which had a potential leaching capacity of around 16%, the leaching of chromium, nickel, zinc and other elements was just a few per cent."

In Australia and New Zealand, blast furnace, as well as steelmaking slags have been used in pavement construction as engineering fill, subbase and base. Examples of this use are to be found in the building of several freeways, heavy road network construction and the third runway construction at Sydney Airport. Both blast furnace and steelmaking slags have successfully been used in spray sealing and asphalt applications, but steelmaking slag is more commonly used as its better strength, abrasion and impact resistance make it particularly suitable for use in areas subjected to heavy vehicle loads and high shear stress.

"The world-wide move towards environmental improvement inevitably means increasing the utilisation of slag in order to minimise the extractive quarrying of primary aggregates thereby protecting more of our natural resources and landscape." (Euroslag, 2005)

In Delaware the USA, "since 1989, the Delaware Department of Transportation has paved State Route 1 with slag cement concrete—almost one million cu yd (764 555m³) of it. Running 51 miles (82 kilometres), the newly constructed road passes through two of the state's three counties.

Jim Pappas, DelDOT's chief materials and research engineer, says slag cement has helped the state build roads that last. Mixes typically include 35% to 50% slag cement, and routinely exceed the specified minimum strength of 24 MPa (megapascal) (most are measured at 27.5 MPa or higher). Delaware was one of the first states to employ mixes with replacement rates as high as 50%, and the choice to innovate has paid off." (Slag cement, 2002)
Figure 3: State Route 1, built with 764 555m$^3$ of concrete, showcases slag cement concrete's durability

3. 2 Bricks

Ferrochrome slag has also been used for a number of years worldwide in the making of bricks, however not much information is available on this subject. These bricks are made from a mixture of concrete and slag at different recipes mixtures. This topic along with the use of slag in concrete for other purposes is discussed in more detail in point 3.3 below.

3. 3 Concrete

Samples of slag aggregate were tested by the Cement and Concrete Institute to determine the suitability of the slag for use in concrete and/or concrete masonry units. It was concluded that the samples met many of the requirements for aggregates for concrete products, but pop-outs and/or rust stains may occur on the surfaces of slag aggregated concrete products. (Goodman, 2003) These stains although found with the use of blast furnace slag are similar to the ferrochrome slag and are called greening is as a result of a complex reaction of sulphide sulphur in slag cement with other compounds in Portland cement.

"In most concrete made with blast furnace slag cement, the surface becomes light gray or white within hours after the concrete surface has been exposed to direct sunlight and air. If greening does occur, it usually appears within a week of concrete placement and typically disappears within a week, after oxidation starts. Surface greening diminishes as oxidation progresses and does not need to be treated." (Slag cement, 2002)

Gjørv et al, (1998) reported that ferrochrome slag was used as a hardener in the development of a fire proof concrete. The results of the test concluded that the
ferrochrome slag meet the requirements for use in the lining of facilities of iron and steel manufacturers. It also produced a better performance and required less expenditure than other concretes used.

Rossouw et al. (1981) analysed slag samples from a number of ferrochrome plants. They concluded that:

- it is possible to make good quality concretes with the chrome slag,
- mixes made with chrome slag aggregate, (both coarse and fine aggregate), tend to be slightly harsher than the control mixes made with norite coarse aggregate, pit sand and crushed quartzite sand. It was necessary to add natural sand to lean chrome slag aggregate mixes to achieve the same workability.
- chrome slags give mixes with strengths and permeabilities which compare favourable with the same properties of mixes with natural aggregates

The only potential negative environmental impact considered for the use of chrome slag as a cement aggregate, is that of the possible leaching of Cr (VI) from the aggregate (Broadhurst, 1997). This is not a major concern though due to the exhaustive tests done on the Charge Chrome slag by both Gencor Process Researchers and the Chemical Engineering Department of the University of Cape Town. (Broadhurst, 1997) Both the TCLP tests, as well as longer term lysimeter tests, have shown charge chrome slag, as produced from the submerge arc furnaces, to be environmentally inert.

Broadhurst (1997), concluded that there should not be objection to the slag being utilized as either a concrete aggregate, nor as a backfill material in other civil applications, including railway ballast.
CHAPTER 4: THE DELISTING OF HAZARDOUS WASTE

The delisting process in SA is still in its early stage compared to the delisting process in the USA who have been using this process for almost 25 years, and SA has not realised the full potential of this process.

4.1 Delisting in the USA

In the United States of American the Resource Conservation and Recovery Act, which guides EPA’s hazardous waste management programs, provides for a process to delist, a waste generated at a facility from the list of hazardous wastes. Their delisting process has been in place for almost 25 years. This delisting process is initiated by the generator (person who creates the waste), who prepares a petition for delisting the waste. The petition provides information about the waste, including its chemical composition, to demonstrate the rationale for delisting the waste. The petition is reviewed by the appropriate regulatory agency (either EPA or a state hazardous waste regulatory agency which has been authorized to grant delisting petitions) to determine whether the waste should continue to be listed as hazardous or not.

In a report published by the United States Environmental Protection Agency under the Resources Conservation and Recovery Act (RCRA), (USEPA, 2002), an evaluation of the outcomes and impacts of the hazardous waste delisting program over a 20 year period was investigated. It stated that this programme had a number of economic and to a lesser extent environmental positive impacts.

"Economically, the total administrative costs associated with this twenty year period of the delisting program ranged from $107 million to $226 million. The costs to petitioners is between 70-85% of that total. The costs of running the program, while large, were far outweighed by the cost savings achieved, however. From the inception of the delisting program through the year 2000, cumulative net cost savings attributable to the delisting program range between $1.2 billion and $2.4 billion. Even if no further delistings are ever granted, the delisting program will save over $105
million each year, from wastes that have already been removed from Subtitle C regulation." (USEPA, 2002)

Although a complete investigation of the waste that had been delisted was not done, the USEPA felt that these stream were not causing environmental problems.

They concluded that "A program like delisting demonstrates its value in terms of reduction in economic losses, and concomitant improvement in human welfare." (USEPA, 2002)

In one case study the Westinghouse Savannah River Company petitioned to delist their hazardous and radioactive (mixed) waste, which originated from a wastewater treatment sludge generated during electroplating operations. To meet the EPA delisting treatment standards, the waste needed to be stabilized to control the leaching of hazardous constituents from the final waste form. They installed a Vitrification Treatment Facility to treat the waste producing a final vitrified waste in the form of glass ovoids (gems), which were stored in 71-gallon drums. The volume reduction of the hazardous waste of approximately 69% was achieved. This significantly reduces overall disposal costs, resulting in cost savings of approximately $7.0 million. Therefore a significant reduction in the environmental risk of the waste has also been achieved. (Westinghouse, 2002)

4.2 Delisting in South Africa

"In South Africa and the USA, delisting is when a hazardous compound in a waste moves from a specific risk group to a lower risk or 'non-risk' group. It does not become a non-hazardous compound, but the associated risk declines to a risk, which is smaller or acceptable." (DWAF, 2005)

In South Africa the process for delisting a hazardous waste involves the investigation into the EEC, where tests can be carried out to prove that, because of low mobility, the substance is of a less hazardous nature than that indicated. The tests used as was stated previously to prove this, would include the "Toxicity Characteristic Leaching Procedure" or the "Acid Rain" test.
Once tests results have been obtained, and one can prove that the EEC is lower than the Acceptable Risk Level, an application is made to the lead authority, DEAT, to motivate for the delisting of the specified hazardous waste. This delisting application follows a process whereby it is first reviewed and approved by the Department of Water Affairs and Forestry (DWAF), following this it is reviewed by DEAT and sent to the Chief Director of Waste Management for approval. For DEAT this process is relatively new, about 5 years.

The process to delist ferrochrome slag in South Africa entails the following:

1. Perform a South African Acid Rain (SAAR) test on the slag, to determine its leaching potential and hazardous rating in its original state, by using the SAAR test adapted from the USEPA 1311 method. (DWAF, 2005)

2. Decide upon the required uses of the slag for delisting and make products from slag i.e., bricks, concrete slab and tar mix.

3. Perform a Toxicity Characteristic Leaching Procedure (TCLP), following the approved Environmental Protection Agency method 1311, test on the slag products to determine the leaching potential and calculate the environmental load as per use requirements. For example, the number of bricks to be used in low cost housing development.

4. Motivate for use, if required and delisting by using the risk based approach to determine the effect on the environment or human health. A site specific risk based approach takes into account all site specific attenuation factors such as waste treatment, mode of site operation, climatic conditions and engineering attributes in the form of covers, liners and leachate interception.
CHAPTER 5: METHODS AND MATERIALS

As was previously discussed the Ferrochrome slag is only rated as hazardous due to its quantity or volume found in a specified area or dump.

It was determined to run leaching tests on the slag in its original state and on different types of slag products; i.e. bricks, concrete slab and tar / slag road mix which can be made and determine whether they will leach above the DWAF draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste and perform the EEC calculations.

5.1 Preparation and analysis of each product

The preparation and analysis for each product was carried out as follows by the CSIR:

5.1.1 Slag in its original state

The slag was crushed to a size less than 10mm and the South African Acid Rain (SAAR) test was performed the slag, to determine its leaching potential and hazardous rating in its original state.

5.1.2 Road construction

A slag, bitumen mix was prepared using the same ratio as is normally used for tar road construction. The tar mix was crushed to a size less than 10mm and subjected to a TCLP test due to the organic nature of tar. In order to be proactive and cover all aspects the leaching results were compared to the acceptable environmental risk level (AEL) as well as acceptable exposure to human health.

5.1.3 Bricks

Two different types of brick were made, the maxi and hollow brick, and these bricks were then crushed to a size less than 10mm and subjected to an acid rain test, due to there been no organics in the mix. Different building scenarios for the use of these bricks were developed as part of the delisting exercise. In order to be proactive and
cover all aspects the leaching results were compared to the acceptable environmental risk level (AEL) as well as acceptable exposure to human health.

5.1.4 Concrete

Concrete samples were prepared using the slag as aggregate. The concrete sample was also then crushed to a size less than 10mm and subjected to the Acid Rain test. In order to be proactive and cover all aspects the leaching results were compared to the acceptable environmental risk level (AEL) as well as acceptable exposure to human health.

5.2 TCLP and SAAR Method

In all cases the TCLP and Acid Rain testing were performed according to the SA guidelines found in the DWAF minimum requirements, as set out below:

5.2.1. TCLP Extraction: Extraction for analysis of contaminants:

1. Weigh out 100 gram of the dry waste, which passes through a 9.5 mm sieve, and quantitatively transfer it to the extraction bottle
2. Add two litres (21) of the appropriate TCLP solution (No. 1 or 2 as determined by preliminary evaluation) and close bottle tightly.
3. Rotate in agitation apparatus at 30 r.p.m. for 20 hours. Temperature of room in which extraction takes place should be maintained at 23 ± 2°C.
4. Filter through a glass fibre filter and collect filtrate. Record pH of filtrate.
5. Take aliquot samples from the filtrate for determination of metal concentrations.
6. Immediately acidify each aliquot sample with nitric acid to a pH just smaller than 2.7.
7. Analyse by AA or the other sensitive and appropriate techniques for different metals.
8. If analysis cannot be performed immediately after extraction, then store the acidified aliquots at 4°C, until analysis (as soon as possible).

5.2.2. SAAR Extraction: Extraction for analysis of contaminants:

Repeat 1 – 8 of the TCLP extraction method; Extraction for analysis of contaminants, as above, except for point 2, which must read:
o Add two litres (2l) of the Acid Rain Solution, as prepared, and close bottle tightly.

5.3 Calculations of the EEC

Each products leaching results were subjected to the EEC calculations to compare them against the AEL. The 'fixed-scenario' approach to the determining the EEC applies as a general rule. The EEC calculations is based on the fixed scenario risk assessment and is expressed as \( \text{EEC(} \text{ppb} \text{)} = \text{dose (} g/\text{ha/month} \text{)} \times 0.66 \). The 0.66 is derived from the ratio of the substance in a weight of underground body of water.

\[
\text{EEC(} \text{ppb} \text{)} = \frac{A \text{ (waste load/ha of land/month)}}{B \text{ (weight of underground body of water)}}
\]

Where A: Waste in g/ha x size of drainage basin x percentage (unity) which may leach into the groundwater.

Where B: Surface area of body of water x average depth x weight of water

Where dose represents the total amount in grams of the substance in the waste to be disposed of, on one hectare of the disposal site per month.
CHAPTER 6: RESULTS

When reviewing the results of the leaching tests, the main challenge for determining whether the slag product was a concern to the environment or not, was to determine its potential to enter a water source and create some form of pollution. The leaching potential and risk-based approach results were as set out below and submitted to the DEAT for comment.

6.1 Leaching and risk based approach results

6.1.1 Slag in its original state

The slag results showed that it had the potential to leach Mn above the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. The results of the slag were calculated as having a hazard rating of 2 for slag disposed of in large quantities on a slag dump. It must be noted that the Hazard rating 2 compound delists when the estimated environmental concentration (EEC) is < Acceptable Risk Level. I.e. smaller stockpiled quantities for the slag reduces the EEC and therefore allows the slag to delist. See Appendix 1 for slag results.

6.1.2 Road construction product

A slag, bitumen mix results showed that it had the potential to leach Al above the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. However, it must be noted that Al did not leach from the original slag material when the acid rain test was performed on the slag before mixing it with the bitumen.

Two assumptions were drawn from these results:

1. There was a chemical reaction between the slag and bitumen mobilized the Al; or
2. The tar was leaching the Al. No tests were done on the tar alone to determine if this was the case.
The risk based approached reviewed the potential for the tar / slag mixture to breakdown and reach in large enough quantities a water source. This would not be easily done as the mixture solidifies and becomes extremely hard making it difficult to breakdown. However according to the tests on the slag alone, it was determined that the slag could be used as a base material for road construction, as it did delist for use as base material using the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. The results and the risk based approach followed are shown in Appendix 2.

6.1.2 Cement and concrete aggregates product

The scenario used for the determination of the hazard rating was based on the assumption that a 1 ha portion of land would be evenly covered with concrete. The elements that did not delist according the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste in the scenario were Mn, Al, Na, K and Mg. However, delisting of this product could be motivated for, by using the risk based approach.

The risk based approached reviewed the potential for the concrete material to breakdown and reach in large enough quantities a water source. Concrete becomes more stable over time and in so doing would fix the highlighted elements into the concrete. It can therefore be assumed that the associated risk of using the slag in this application will also decrease over time due the increased stability of the concrete. The impact of the mentioned elements on the environment will be insignificant due to the extremely low risk of them reaching the aquatic environment while fixed in the concrete.

These results and the risk based approach followed, determined that the slag could be used in concrete, as it posed no threat to the environment or human health. The results and the risk based approach followed are shown in Appendix 3.

6.1.3 Brick manufacturing product

Three building scenarios as proposed in the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste
(DWAF, 2005) were developed for the two types of bricks used. These scenarios were for medium, high and high density low cost housing.

Constituents that does not delist for brick manufacturing were Fe, Na, K, Mg based on the draft third edition of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. In this case the elements did not delist based on human health exposure limits. The results and the risk based approach followed are shown in Appendix 4. However again a risk based approach was conducted to reviewed the potential for the brick material to breakdown and reach in large enough quantities a water source.

Being used in the manufacturing of bricks, the human health exposure will be limited to skin contact, via various control measures and protective equipment requirements, and in the worst case scenario, occasional direct ingestion of very small portions of the total brick mix by children. Taking into consideration that the pH of saliva varies between 6.9 and 6.5 it is highly unlikely that these elements would be mobilized to an extent that it will have a negative health effect.

These results and the risk based approach followed, determined that the slag could be used in brick making, as it posed no threat to the environment or human health.

6.2 DEAT response to the results and risk based approached

The above results and risk based approach was approved by the DEAT and the slag was delisted for the above uses. See Appendix 5 for letter of delisting from the DEAT. Conditions set in the letter were that the historical slag dumps at the various sites had to be permitted with an ECA Section 20(1) permit, before the slag could be sold from these dumps and that the DWAF forward their comments to the DEAT directly.
CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

The delisting process in South Africa has not been fully investigated or utilized by companies to determine how to better manage their hazardous waste, and should be investigated. In America this process has been in use for over 20 years and has proven to be valuable for the reduction in economic losses and improvement in human and environmental health.

World wide it is known that ferrochrome slag is used in the road and civil construction industries. It is a good alternative to using the quarry material of primary aggregates and thereby adds to the protecting more of our natural resources and landscape. In the case of Ferrochrome slag the delisting process has been used to effectively demonstrate that the slag can be delisted for use in the construction industry. Based on a leaching results and risk based approach taken, the delisting for applications in brick manufacturing, as concrete aggregates and for road construction purposes could be motivated. However it is recommended that more research is needed to determine whether the leaching of the Al is attributed to the chemical reaction of the slag and bitumen or the tar itself.

The method by which the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste subscribe to determine whether a material is hazardous or not, may capture a large amount of wastes which are not necessarily risky. It is recommended that the methodology be reviewed to determine its effectiveness and how accurate the results it gives are.

Delisting is a good waste management technique to be used for reduction in economic losses, and qualitative improvement in the environmental and human welfare.

The challenge is to realise the value of our waste and harvest its resources, creating a better environment for all that live in it.
REFERENCES


CIRU, 2007 Outokumpu, CASE: Outokumpu Chrome Oy. Downloaded in 2008 for Cases section. Email: (http://cirucentre.fi/cases/outokumpu) Centre for industrial residue utilisation, pl 4300, 90014 oulu yliopisto, puh. 08 553 2574, Fax. 08 553 2339.


DSIR, 2005 The Department of Scientific and Industrial Research. Email: (http://dsir.nic.in/reports/techreps/lsr079.pdf)


Ylimauna, Juha, (Juha.Ylimaun@outokumpu.com), 2006 Discussion of slag Email to Heather Booysen (heather.Booysen@samancorcr.com) 13 January 2006
Appendix 1: SAAR results for slag in its original state
# Certificate of Analysis

**Client:** Heather Booysen  
**Sample Description:** Leachate  
**Sample Id:**  
**No. of Samples:** 4  
**Date Received:** 19/05/2006

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**Signed:** Callie Adlem (Chemistry) : Head of Laboratory  
**Date:** 02/06/2006
Appendix 2: Slag / tar mix scenario results
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<th>Hazard Rating</th>
<th>Class</th>
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**Values:**
- CML: Categorical Minimum Limit
- CML: Categorical Maximum Limit
- DL: Detection Limit
- Class: Hazard Class
- CML: Categorical Minimum Limit
- CML: Categorical Maximum Limit

**Environmental Data:**
- **CML:** Categorical Maximum Limit
- **CML:** Categorical Minimum Limit
- **DL:** Detection Limit
- **Class:** Hazard Class

**Table Data:**
- **Volume (L):** 200.000
- **Volume (L):** 200.000
- **Volume (L):** 200.000
- **Volume (L):** 200.000
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- **Volume (L):** 200.000
- **Volume (L):** 200.000
- **Volume (L):** 200.000
- **Volume (L):** 200.000

**Reference:**
- **EHR:** Environmental Hazard Rating (mg/kg)
Appendix 3: Building scenario calculations for slag bricks
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</tr>
<tr>
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</tr>
<tr>
<td>2 Area of building</td>
</tr>
<tr>
<td>3 Area of property</td>
</tr>
<tr>
<td>4 Buildings per hectare</td>
</tr>
<tr>
<td>5 Bricks per building</td>
</tr>
<tr>
<td>6 Brick mass per hectare</td>
</tr>
<tr>
<td>7 Mass per water/month</td>
</tr>
<tr>
<td>8 Mobility test</td>
</tr>
<tr>
<td>9 Pathway/Exposure scenario</td>
</tr>
<tr>
<td>10 Receptor risk assessment</td>
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<tr>
<td>11 Benchmark environment</td>
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<td>13 Reference dose from literature (RFD)</td>
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Appendix 4: Slag / concrete scenario results
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**Notes:**
- SCC: Standardized Common Quantities
- Date: Date of analysis

**Additional Information:**
- This analysis is part of a suite of measurements for a waste material.
Appendix 5: Delisting approval letter from the DEAT
CSIR
Natural Resources and the Environment
P. O. Box 395
PRETORIA
0001

Attention: Dr. S. Oeloise

SAMANCOR CHROME SLAG CLASSIFICATION AND DELISTING FOR USAGE ON TAR ROAD, CEMENT AND BRICK MAKING

This Department approves the delisting of the Samancor waste streams as applied for by the CSIR on behalf of Samancor in their submission “SAMANCOR CHROME SLAG Classification and Delisting, October 2006”

This approval is subject to:

(a) Submission of the letter of approval from the Department of Water Affairs and Forestry (DWAF), to the Department of Environmental Affairs and Tourism. This Department has already approached DWAF in this regard. (DEAT has received a copy of the delisting approval letter sent to CSIR by DWAF)

(b) The delisted material not being used in any downstream application prior to the approval of a section 20(1) permit in terms of the Environment Conservation Act, 1989 (Act 73 of 1989) for the storage of the Samancor Chrome Slag and subject to the conditions therein.

If you have any queries, please do not hesitate to contact the Department.

Yours sincerely,

[Signature]

De Pam Yako
DIRECTOR GENERAL
Department Environmental Affairs and Forestry
Letter signed by Mr. Leon Bredenhann
Designation: Deputy Director; Permitting
Date:

cc. H. Booyse
SAMANCOR
Middelburg Ferrochrome
Private Bag X251846
Middelburg
1050