THE SOLID STABILIZATION OF SOLUBLE WASTES GENERATED IN THE SOUTH AFRICAN FERROCHROME INDUSTRY

CF Maine · JP Smit · EW Giesekke

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Final Report to the Water Research Commission

by

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Council for Mineral Technology

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EXECUTIVE SUMMARY

Ferrochrome metal, used mainly in the manufacture of stainless steel, is produced from chromite ore, carbonaceous reducing agents (char, coke and coal) and fluxes (quartz, dolomite and limestone). The ferrochrome industry plays an important role in the South African economy by earning 4.5% of the country's foreign exchange and by employing about 28 000 people. It also generates solid wastes, ferrochrome slag and bag filter dust (BFD) during the production of ferrochrome metal. BFD contains toxic, carcinogenic Cr(VI) and thus poses a risk to health and the environment unless properly treated. It is estimated that the 10 local ferrochrome producers generate about 100 000 t of BFD per annum.

The high solubility of toxic Cr(VI), renders it very mobile, thus increasing the risk of potential contamination of natural water resources. Therefore proper treatment of the waste prior to its disposal is necessary. In view of the fact that South Africa's ferrochrome industry has the potential to contaminate water on a large scale there existed a need for a more systematic study regarding the nature of Cr(VI) contained in BFD and how it could be treated to minimize the threat this waste poses to health and the environment. In this study, the immobilization of BFD into cement-based and fired clay brick solid stabilized systems was extensively investigated. Further, the disposal of these products was evaluated by various leaching tests carried out according to the latest Department of Water Affairs and Forestry (DWAF) Guidelines in order to assess the extent to which the treated BFD poses a threat to the environment. This study also investigated the utilization of these solid stabilized products for potential commercial applications such as building materials. Estimates of production costs of these solid stabilized products, based on the findings of this study, were also made.

In view of the toxicity of chromate, the DWAF Guidelines require that the concentration thereof in leachates be measured accurately down to the parts per billion (ppb) level. In this study a spectrophotometric method using a 10 cm cell was used to measure the Cr(VI) concentration in solution accurately to 30 ppb. However, to conduct similar measurements of Cr(VI) concentrations below this level, the above method required improvement. It is suggested that utilizing a pre-concentration step involving the adsorption of chromate on activated alumina from very dilute solutions in an acid medium and then eluting a more concentrated solution in alkaline medium should be investigated. The Cr(VI) in this more concentrated solution could then be measured accurately by the conventional spectrophotometric method.

Water leaching studies on BFD indicated that the elution of Cr(VI) continues for a long time and is probably diffusion controlled. The formation of Cr(VI) in BFD arises from the oxidation by air of chromite fine dust particles in the bag filter in the presence of alkali. Condensation of volatile Si and Mg on the oxidized dust particles are thought to be responsible for the entrapment of Cr(VI) and the cause of the slow leaching thereof. In view of its formation by the above proposed mechanism, the leaching of Cr(VI) from BFD is always associated with salts reporting to the leachate. It was demonstrated that a once-off treatment of a BFD water slurry with ferrous sulphate or chloride reduces the bulk of chromium from the toxic hexavalent form to the trivalent form with the formation of a stable $Cr_xFe_{1-x}(OH)_3$ precipitate (where $x < 1$). This treatment is however, not a suitable method to achieve complete removal of Cr(VI) from BFD as it continues to leach in small quantities and therefore does not allow for the safe disposal of the treated waste. Other safer treatment options for BFD prior to disposal were therefore investigated.

One treatment option that was investigated was the production of cement-based solid stabilized products by mixing 9 per cent ordinary Portland cement (OPC), with water or brine, ferrochrome slag and electric arc furnace (EAF) slag, $FeCl_2$ and up to 15 per cent BFD. (The purpose of the addition of $FeCl_2$ and EAF slag to these mixes was to ensure the reduction of Cr(VI) contained in the BFD). These mixes were then poured in blocks and allowed to cure for different periods. Water leaching tests were conducted on whole and crushed, cured cement blocks. The percentage stabilization of Cr(VI) and salt were calculated based on the analyses of the water leachate and compared to those recorded for the individual components used to prepare the cement blocks. Complete Cr(VI) immobilization was observed in whole blocks and up to 99.7 per cent in crushed blocks. The mechanism of Cr(VI) immobilization in cured cement blocks was elucidated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). No Cr(VI) containing mineral phase could be identified in the cured blocks. However, SEM studies did indicate that a Ca-Mg-Al-silicate phase incorporates the Fe-Cr hydroxide formed as a result of the interaction between BFD, $FeCl_2$ and EAF slag. The presence of the latter two are deemed essential to ensure effective Cr(VI) immobilization in these systems.

It was also found that up to half of the salt, added to the cement blocks via BFD, was immobilized, as judged from the water leaching tests of crushed blocks. XRD indicated the presence of ettringite in these systems. This mineral phase is believed to be responsible for the sulphate immobilization. There was no evidence from the

corresponding energy dispersive spectrum (EDS) of this mineral phase that chromate was contained in the ettringite.

The observed compression strengths of these cured cement blocks make their use as building materials acceptable, according to the SABS specifications. The cost of cement and $FeCl_2$ needed to produce a 1000 standard size cement bricks amounted to R146.70, or R235/t of BFD treated in this manner. Due to the higher density of slag used in their manufacture, these cement bricks are heavier than ordinary ash bricks and may be more suitable as paving than building bricks.

The potential toxicity of cement blocks was evaluated according to the DWAF Guidelines, assuming a dumping rate of 2.7×10^5 kg/ha/month. This figure was based on the amount of BFD produced, the amount of BFD incorporated into the cement blocks and assuming each of the ten local ferrochrome producers has available a 30 ha dumping site. On the basis of the water leaching tests, only whole cement blocks are below the acceptable risk level (ARL) stipulated by DWAF for Cr(VI). However, on the same basis it was concluded that crushed cement blocks exceed the stipulated levels. Acid Rain and US EPA TCLP leaching tests on the crushed cement blocks indicate that no other potentially toxic components leach from these products. However, this depends on the final pH value of the leachate. At pH values less than 5, Mn, Zn and Pb levels in the leachate for crushed cement blocks do exceed the stipulated values according to the DWAF Guidelines.

The other BFD treatment option investigated was the production of clay bricks containing 50 per cent BFD, by firing at 1200 °C for 6 hours. Water leaching tests conducted on crushed fired clay bricks indicated that greater than 99 per cent of Cr(VI) and 90 per cent of salt were immobilized in these systems. Microprobe studies of fired clay bricks indicated that both chromate and salt are contained in a glassy Mg-Al-Fe-Si phase. Minimum firing temperatures of 750 and 1200 °C were required to achieve the abovementioned Cr(VI) and salt stabilization, respectively. Leaching tests conducted on crushed, fired clay bricks indicate that Cr(VI) and other elements are below the ARL values stipulated by the DWAF Guidelines. This is an improvement over the corresponding values obtained for crushed cement blocks. Leaching tests conducted on these systems as a function of pH confirmed that fired clay bricks are more effective in immobilizing Cr(VI) and other undesirable elements contained in BFD than cement blocks. It is also possible to incorporate a greater amount of BFD in fired clay bricks than in cured cement blocks. The cost per ton BFD treated in this manner was estimated at R190/t. This is cheaper than the

corresponding cost for cement blocks. Therefore the production of clay bricks appears to be the preferred route for treatment of BFD because of their minimal impact on health and the environment and their cost.

The local ferrochrome industry has lately been more inclined to recycle than dump the BFD. This is achieved by mixing BFD with fine chromite ore in the form of sintered briquettes heated at 1300 °C, or other related in-house developed technologies. The findings of this study confirms that this is the best available technology to immobilize the Cr(VI) contained in BFD and also the most cost effective treatment option. It would be necessary in the future to monitor the ground water in the vicinity of ferrochrome producers in order to confirm that in the long term, no Cr(VI) contamination occurs and this treatment option remains effective. For this reason it is recommended that an analytical method involving a pre-concentration step be developed for the accurate measurement of Cr(VI) concentration at a ppb level and be applied to the proposed ground water monitoring programme.

The solid stabilized products show potential for use as building materials, although the negative factors associated with using building materials made from toxic waste might limit their general use. Nevertheless, the technology developed would allow for the safe disposal of BFD in this form as landfill, an aspect that was not possible before. The technology developed in this study has indicated that toxic chromate, originating from BFD, can effectively be immobilized into cement blocks and fired clay bricks. The work has, therefore, made a contribution towards the development of waste minimization strategies needed for the disposal of this hazardous waste.

Further improvement of the immobilization of chromate in cement blocks may be achieved by increasing ferrous ion concentrations in mixes. It is recommended that this possibility be further investigated if the need arises in cases of chromate-containing wastes that cannot be easily recycled, e.g. electroplating sludges, waste paint and leather tanning wastes.

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LIST OF SYMBOLS, ACRONYMS AND ABBREVIATIONS

ARL	Acceptable Risk Level
BFD	Bag Filter Dust (Ferrochrome Production)
C-S-H	Calcium Silicate Hydrate
Cr(VI)	Chromate, Cr in the hexavalent oxidation state
Cr tot	Total Cr concentration, tri- and hexavalent-oxidation tates
DWAF	South African Department of Water Affairs and Forestry
EAF	Electric Arc Furnace
EDS	Energy Dispersive Spectroscopy
EEC	Estimated Environmental Concentration (ppb)
FeCr	Ferrochrome/Ferrochromium
ICDA	International Chromium Development Association
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infra Red
LC_{50}	median lethal dose, a statistical estimate to kill 50% of a given population of aquatic organisms
NMR	Nuclear magnetic resonance
OPC	Ordinary Portland Cement
ppb	parts per billion
ppm	parts per million
SABS	South African Bureau of Standards
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total dissolved solids
US EPA	United States Environmental Protection Agency
UV-VIS	Ultra-violet visible spectrometry
XRD	X-ray diffraction

1. INTRODUCTION

The South African Ferrochromium industry supplies nearly half of the world's requirement of chromium in the form of chromite ore and ferrochromium metal that is used mainly in the manufacture of stainless steel, chromium metal and chemicals. It was estimated that in 1996 this industry, situated mainly in the Northwest, Mpumalanga and Northern Provinces, employed about 28 000 people and contributed R5.2 billion (4.5%) to the South African foreign exchange earnings (Woods, 1996). This industry is expected to double every 14 years.

Ferrochromium metal is produced mostly in submerged arc, open top or closed furnaces where chromite ore, carbonaceous reducing agents (coal, char and coke) and fluxes (quartz, dolomite and limestone) are added. The products produced are ferrochromium metal, slag and dust. For open-top furnaces the dust is collected in a bag filter whereas for the closed furnaces, the dust is scrubbed with water in a venturi system which produces a sludge or slurry. According to Gericke (1995), the greatest risk to health and the environment from ferrochrome production lies in the toxic, carcinogenic Cr(VI), contained in the dust collected in the bag filter or in the sludge obtained from the gas cleaning system. This is particularly applicable to open top furnaces where Cr is oxidized to Cr(VI) or chromate in the off-gases. The sludge produced from closed furnaces also contains Cr(VI) but to a much lesser extent.

Due to the central role that the Cr(VI) or chromate containing wastes, bag filter dust (BFD) and sludge will play in this study, further details on the extent of local ferrochrome production and generation of BFD and other Cr(VI) containing waste were supplied by the local industry (Gericke, 1998) and are summarized in Appendix A. This indicates that there are currently 10 local ferrochrome producers, generating a total of 2.7 Mtpa ferrochrome, with 68 ktpa BFD and 28 ktpa of Cr(VI) containing sludge. Thus, the local ferrochrome industry generates about 100 ktpa of Cr(VI) containing wastes that need treatment or have to be stored in lined dams to prevent contamination of the environment.

In order to minimize the immediate impact of toxic BFD on the environment, it is added to water, treated with ferrous sulphate or chloride and pumped to lined dams for temporary storage. This treatment reduces the Cr(VI) to Cr(III) a non-toxic, essential micro-nutrient (Anderson, 1999). However, the addition of this reagent increases the salt load in the system. The lowering of pH as a result of this treatment

is remedied by the addition of lime that may remove some of the salts as gypsum. After settling, the clear water is recycled.

In view of the longer term threat that these soluble components (salts and chromate) in BFD, sludge and treated products may pose to the environment, there existed a need for a more systematic study and an evaluation of the various processing options available for the treatment thereof. This study was undertaken to address this need and the objectives of this investigation were as follows:

- To study the nature of Cr(VI) contained in BFD, how it is formed, leaches with water and the efficiency of the current treatment options.

- Optimization of the manufacture of solid stabilized products using BFD and other wastes generated in the production of ferrochromium to seek more long-term, permanent treatment options. This would involve using wastes available on site, *i.e.*, slag, clay and recycle water to produce cement blocks and fired clay bricks.

- Evaluation of the leachability of soluble salts and toxic components, Cr(VI) and other heavy metals, from the manufactured blocks and bricks by internationally accepted test procedures to assess their impact on the environment in the disposal thereof.

- Assessment of the solid stabilized products as potential materials of construction. Evaluation of the economics for the manufacture of these products.

It is likely that similar efforts may have partially been undertaken by the local industry. Gericke (1995) mentioned that efforts are underway by some of the local industry to recycle these ferrochrome wastes. However, it is unlikely that the results of these findings would be made available to the industry as a whole. Due to the importance of the ferrochrome industry to the local economy and bearing in mind that South Africa contains about three quarters of the world's reserves of Cr, the more systematic study outlined above was considered to be in the national interest. Results of the study would provide the means to minimize the threat these Cr(VI) containing wastes pose to the environment and natural water resources.

2. LITERATURE SURVEY

2.1 Health, Safety and Environmental Aspects of Chromium

Extensive documentation exists on chromium and the environment. Two excellent books have been published on this subject (Nriagu, *et al.*, 1988 and Langard, 1982). Both cover a wide range of topics, starting from the geochemistry, production and use of chromium containing products to their role in biology and impact on human health, animal life, atmosphere, and natural waters. In view of the toxicity and carcinogenic effects of Cr(VI) or chromates, it is understandable that books have been published that deal specifically with this aspect (Fairhurst, *et al.*, 1989 and Cross, *et al.*, 1997). In this regard it should also be noted that a more practical guide that provides an overview of the current legislation in the various countries and of the health, safety and environmental effects of chromium and its compounds has recently been published by Gericke, *et al.* (1998).

Table 1. Chromium Water quality standards (Gericke, et al., 1998)

Country	Type of water or effluent	Concentration, mg/l	
		Cr(VI)	Total Cr
France	General	0.1	0.5
	Cr processing		1.5
	Metal finish	0.1	3.0
Germany	Leather	0.05	1
	Metal/Chemical	0.1	0.5
Japan	Water	0.05	
	Plant public system	0.5	2.0
South Africa	Drinking	0.05*	0.1
	Max permissible limit		0.2
	Crisis limit		0.4
	Effluent discharge		0.5
United Kingdom	Drinking		0.05
United States	Fresh	0.01	0.18
	Salt	0.05	

*van der Merwe, 1996

In view of the fact that this study deals primarily with the potential threat that soluble components in Cr-containing metallurgical waste may pose to the local water resources, the water quality standards for Cr applicable in different countries are shown in Table 1.

In order to achieve and maintain the required low Cr concentrations in natural water resources the essential features of Cr chemistry pertaining to the environment have

to be understood. Excellent reviews are available that deal with this subject (Rai, *et al.*, 1989 and Richard, *et al.*, 1991). The important chemical processes that control Cr concentrations in the aqueous environment are: redox-transformations, precipitation-dissolution and adsorption-desorption reactions. Commonly occurring reductants, ferrous and organic matter, can easily transform the toxic, soluble Cr(VI) to the non-toxic Cr(III) form. The reverse reaction is not common in the environment. Only in the presence of manganese oxides is the reverse redox reaction possible under conditions expected in the environment. In the pH range of environmental interest, the trivalent form of Cr(III) generally forms insoluble $Cr(OH)_3$ or $(Cr,Fe)(OH)_3$ precipitates that allow for low Cr concentrations in water. Organic substances may interfere with the formation of these insoluble precipitates enhancing the mobility of Cr in water. The soluble chromates may be precipitated in the presence of Ba, forming insoluble $Ba(S,Cr)O_4$ solid solutions. Iron oxides are the most important adsorbents for chromate in the environment. On the basis of these reactions Bartlett (1991) has proposed a series of tests that can be used to monitor Cr in the aqueous environment and these will be applied in this study.

2.2 The Nature of Metallurgical Wastes Containing Chromium

As has already been mentioned, Gericke (1995) maintained that ferrochrome BFD poses the biggest threat to the environment due to the leachability of soluble chromate contained in these wastes. However, very little is known about the properties of these potentially harmful substances. As far as could be established the only study on the properties of ferrochrome BFD that appeared in the literature is by Cox, *et al.* (1985). They showed that 40 % of Cr contained in BFD is soluble and exists mainly as chromate and dichromate and is found predominantly in the sub-micron particles of the dust. They also found that the remainder of the chromium in the BFD is found in the larger particles as insoluble Cr_2O_3 in the form of chromite. It is the intention of this study to further elucidate the nature of ferrochrome BFD, particularly how it was formed, leaches with water and how it may be effectively treated.

Ferrochrome slag is the other solid waste generated by the local industry containing chromium. This waste does not leach soluble Cr and is not regarded as a threat to the environment (Gericke, 1995 and Coetzer, *et al.*, 1997). The acidity/basicity ratio of slags is defined as the ratio of the sum of the concentrations (weight percent) of $CaO + MgO$ to those of $SiO_2 + Al_2O_3$. Kilau *et al.* (1984) have demonstrated that

chromium-containing slags with $CaO:SiO_2$ greater than 2 (basic) are more likely to leach Cr. Most of the slag produced by the local industry is acidic in nature. However, it should be noted that Kornelius (1995) has indicated that other dusts collected from the local metallurgical industry (stainless steel, steel, ferro-silicon and ferro-manganese) also releases soluble Cr(VI) and other toxic components that would require treatment to prevent the contamination of the environment.

2.3 Treatment Options for Wastes Containing Chromates

Addition of ferrous ions is the most common treatment option to remove Cr(VI) from aqueous solutions. Eary and Rai (1988) have reviewed various aspects of this method. A more recent study on the kinetics of the reduction of Cr(VI) with Fe(II) has been undertaken by Pettine, *et al.* (1998). This reaction takes place over a wide pH range, from 6 to 11, and converts the soluble chromate to an insoluble $(Fe, Cr)(OH)_3$ precipitate. According to Gericke (1995), the local industry also adds ferrous sulphate or chloride, depending on the availability thereof, to a BFD-water slurry as a treatment option to minimize the leachability of Cr(VI) from this source. What needs to be established is how effective this treatment of BFD remains over the longer term.

In this regard it may also be of interest to point out that the treatment of Cr-containing solid waste has recently received considerable attention in the literature; Raghu, *et al.* (1989), Crosbie, *et al.* (1993) and Weng, *et al.* (1994). This is probably due to the general, greater awareness of environmental issues but also as a result of disposal problems encountered with a chromium ore residue, particularly in the states of New Jersey and Pennsylvania of the USA. These residues containing calcium chromates and associated products, originated from previous (1890-1964) chromium-mining operations where the ores were subjected to an alkaline roast to extract the soluble chromates. Although the residues are different from local Cr-containing BFD it may be useful to observe how the problem is addressed and to apply some of the ideas generated by these studies in the USA to local conditions. Of particular interest would be the design, evaluation and costing of different long-term, effective treatment options of these residues that ensure no further impact from them on the environment.

The possibility of incorporating waste containing soluble Cr(VI) in cement-based solid stabilized structures to ensure long-term immobilization of these toxic substances has been the subject of numerous studies. Since it is the intention in this

investigation to treat BFD in a similar manner, it is worthwhile to summarize some of the important findings of these studies.

Kindness, *et al.* (1994) and later Allan, *et al.* (1995) have found that chromium-contaminated soil can be immobilized in solid stabilized structures using Portland and blended cements containing blast furnace slag. Similar results have been found for chromium-containing electroplating sludges (Csetenyi, *et al.*, 1997). Based on the analyses of pore fluids, water-, citric- and acetic acid leaches it was found that the efficiency of Cr(VI) immobilization improves with increasing blast furnace slag content in the mixes. Macias, *et al.* (1997) have also shown that exposure of these structures to extensive carbonation further improves the immobilization of Cr. In some instances based on the leaching tests results it was possible to achieve a concentration of Cr(VI) in the leachates less than 0.05 mg/l, signifying nearly complete immobilization of chromate in these cement-based structures.

A number of studies have also been undertaken to elucidate the mechanism of Cr immobilization in cement-based structures. The effective stabilization of Cr in structures made with blended cement containing blast furnace slag is mainly ascribed to the ability of the ferrous ions in the blast furnace slag to reduce Cr(VI) to insoluble Cr(III). For a similar reason, Zhang, *et al.* (1997) have found that the addition of ferrous sulphate to the cement-waste mix also contributes significantly to the immobilization of Cr in these solid stabilized products. However, an excess of ferrous ions results in a substantial retardation of cement hydration at early cure times. The possibility of chromate being incorporated into ettringite formed during the hydration of calcium aluminate phases in Portland cements could also be a means of decreasing the leachability of Cr(VI) from these structures (Auer, 1992). In this regard it may also be of interest to mention that Goske (1997) has been able to immobilize chromate into calcium aluminate cement-BFD mixes. He has demonstrated that the tricalcium aluminate hydrates formed, incorporate chromates and so decrease the leachability of Cr(VI) from these solid stabilized products.

Calcium silicate hydrate (C-S-H) is the main hydration product of ordinary Portland cement (OPC). It is therefore understandable that the interactions between C-S-H and chromium have been studied in some detail. Omotoso, *et al.*, (1995, 1998a and 1998b) and also Lin, *et al.*, (1996) have used X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), infra red (IR) and ^{29}Si nuclear magnetic resonance (NMR) to study these systems. For

effective detection of Cr in these systems, a 1M Cr(VI) solution was mixed with freshly prepared OPC. Under these circumstances $CaCrO_4.2H_2O$ was formed in a few minutes when the Cr/Ca ratio was greater than unity. Increasing the Ca concentration transforms this product to the partially soluble $Ca_2CrO_5.3H_2O$. Cr(VI) was also found to increase the condensation of C-S-H and the porosity thereof. Based on these observations there appears to be no prominent reaction or mechanism to suggest that a significant Cr(VI) immobilization can be expected in C-S-H systems. Whether the above reactions prevail under lower Cr(VI) concentrations as would be encountered in BFD-cement mixtures remains to be seen. On the other hand, for Cr(III)-doped C-S-H systems there is an indication that Cr is associated with silicate polyhedra as calcium-chromium(III)-hydroxide complexes (Omotoso, *et al*, 1996). This may be a possible mechanism for its immobilization. All these observations indicate that the most effective immobilization of Cr in cement-based systems are associated with a reduction of Cr(VI) to Cr(III) and then an incorporation of the latter into C-S-H.

The formation of vitrified products from Cr(VI) contaminated soil as highway construction aggregates were investigated by Meegoda, *et al.* (1997). Sand and carbon were added to the contaminated soil and fired to 1100 – 1400 °C to ensure reduction and vitrification. Leaching tests confirmed the effectiveness and immobilization of Cr(VI) in this treatment technology. It was demonstrated that the vitrification process resulted in the formation of a FeO or MgO chromium-containing spinel mixture that was embedded in a silicate network. In this regard it may also be of interest to note that Boucher, *et al.* (1997, 1995) registered two local patents where it was demonstrated that bricks of acceptable quality were produced when a mixture of ferrosilicon BFD (40% by mass), ferrochrome acid slag (30% by mass) and clay, was fired to 900 – 1250 °C for 5 hours. No leaching tests were conducted to determine whether any Cr contained in the slag would leach from the bricks. It is therefore the intention to subject ferrochrome BFD to similar tests to determine whether vitrification is a viable option for treatment and immobilization of the Cr(VI) contained in this waste.

Various leaching tests have been designed to assess whether the treated waste can safely be recycled and used as materials of construction or for other purposes. A review and assessment of the various leaching tests used for these purposes have been given by van der Sloot (1996). The South African Department of Water Affairs and Forestry (DWAF, 1998) has recommended that the US EPA (1990) Toxicity

Characteristics Leaching Procedure (TCLP) and Acid Rain test be used to evaluate potentially hazardous wastes with regard to their disposal. The TCLP leaching test is recommended where hazardous wastes are co-disposed with organic waste in a general waste dump. The Acid Rain test, on the other hand, is preferred where potentially hazardous wastes are mono-disposed in "dedicated" landfill sites, *i.e.*, only that waste is disposed of. For the local ferrochrome producers concerned with the disposal of BFD the latter option will probably apply. Further, it could be argued that in the case where it is the intention to use solid stabilized products made from hazardous wastes for specific applications, evaluation by the Acid Rain test would be more appropriate than the TCLP test. Whatever the case, the solid stabilized products containing BFD produced in this study will be evaluated by both test procedures. In order to gain a better understanding of the efficiency of the Cr immobilization process in these solid stabilized structures the specified tests could be extended over a wider pH range. In some instances it may also be appropriate to use more simple leaching tests, *i.e.*, the German DIN 38414 (1984) leaching test as a preliminary evaluation.

The information given in this literature review was used to plan the experimental programme to address the various objectives of this investigation. In view of the fact that some of the aims of this study were significantly different, it was decided for the sake of clarity, to present in this report the results and associated discussion of each objective in separate chapters. It was further decided to dispense with a separate chapter on experimental techniques and methods. Experimental detail will be introduced in the text when techniques are encountered for the first time. It is thereafter assumed that the reader is familiar with the experimental detail when it is again used on a later occasion. The last chapter of the report contains the overall summary and the main findings of the study and recommendations for future studies.

3. ANALYSES OF CHROMATE IN AQUEOUS MEDIA

The determination of Cr(VI) or chromate in aqueous media plays a crucial role in this investigation. Therefore this chapter is devoted to the assessment of the accuracy of this determination.

The Cr(VI) content in solution was determined by spectrophotometry with a Hewlett Packard 8452A Diode Array Spectrophotometer using 10 cm optical cells after addition of s-diphenyl carbazide in an acidic phosphate medium as recommended by

Bartlett (1991). The analytical wavelength of 542 nm was chosen for these measurements.

A solution containing 47.3186 mg/l Cr(VI) was prepared by dissolving 66.93 mg analytical grade $K_2Cr_2O_7$ into a 500 ml volumetric flask. This solution was diluted to prepare 14 standards of different concentrations ranging from 0.00946 to 0.23659 mg/l Cr(VI). These solutions were measured to construct a linear calibration graph with correlation coefficient of 0.99946 and uncertainty of 1.49 per cent. Another solution containing 61.6280 mg/l Cr(VI) was prepared by dissolving 87.17 mg $K_2Cr_2O_7$ in 500 ml water. This solution was diluted to prepare six solutions (labeled A to F) of different known Cr(VI) concentrations to assess the accuracy of the spectrophotometric measurement. For each solution 8 determinations of the concentration were made using different dilutions and these results are shown in Table 2.

It should be noted that for the more dilute solutions, A to D, larger variations were observed in the measured concentrations, particularly at higher dilutions. For dilutions smaller than 25 into 50 better agreement between the measured concentration values were observed. A statistical analysis of the measured concentrations was conducted for each solution, calculating the mean, standard deviation which is expressed both in real and percentage terms. These values are also shown in Table 2. A large standard deviation of 65 per cent was observed for the measurement of the concentration of solution A. This was primarily due to the large variations of measured concentrations recorded in this solution for dilutions larger than 25 into 50. For Cr(VI) concentrations larger than 0.03 mg/l the observed standard deviations were less than 6 per cent indicating that the measurement thereof was accurate and reliable. From these results it can be concluded that Cr(VI) concentrations can confidently be measured by this spectrophotometric procedure down to values of 0.03 mg/l although as a precautionary measure dilutions larger than 2 were generally avoided in the preparation of solutions for measurement by the spectrophotometric method in this report. This will be necessary only at very low concentrations (solutions A and B). The reliable measurement of Cr(VI) by the spectrophotometric method below 0.03 mg/l would require a preconcentration step as described by Pannain, *et al.*, (1995).

Table 2. Analyses of solutions of known Cr(VI) concentration

Solution	A	B	C	D	E	F
Dilution	Measured Cr(VI) concentration, mg/l					
5 into 50	0.05245	0.03189	0.05622	0.09370	0.15309	0.19520
10 into 50	0.02206	0.03733	0.05744	0.08776	0.15632	0.19578
15 into 50	0.01760	0.03697	0.05446	0.09315	0.15951	0.19939
20 into 50	0.01660	0.03423	0.05454	0.08718	0.15780	0.19927
25 into 50	0.01438	0.03707	0.05246	0.08198	0.15814	0.19747
30 into 50	0.01421	0.03634	0.05384	0.08427	0.15705	0.19594
40 into 50	0.01336	0.03461	0.05152	0.08427	0.15705	0.19595
45 into 50	0.01275	0.03346	0.05142	0.08370	0.15270	0.19518
Mean	0.02043	0.03524	0.05399	0.08715	0.15615	0.19677
Std Dev	0.01328	0.00199	0.00216	0.00430	0.00246	0.00173
	65%	6%	4%	5%	2%	1%
Expected	0.01233	0.03081	0.04622	0.07704	0.15407	0.21570
Difference	-66%	-14%	-!7%	-13%	-1%	+9%

The mean value of the measured concentration was also compared in Table 2 with the expected concentration and expressed as percentage difference, calculated according to the formula:

$$\frac{\text{(Expected) – (Observed)}}{\text{(Expected)}} \times 100$$

The largest difference is shown for the most dilute solution A and smaller differences are observed for the more concentrated solutions. The latter is ascribed to errors in weighing small masses of $K_2Cr_2O_7$ whilst the larger difference observed for solution A is ascribed to the inaccuracy in measurement of concentration at lower concentrations already mentioned above.

4. PROPERTIES AND TREATMENT OF FERROCHROME BAG FILTER DUST

In order to devise effective treatment options for BFD it was deemed necessary to first undertake a study of the nature of Cr(VI) in BFD. This was achieved by conducting water leaching tests, mineralogical investigations and chemical analyses on a variety of BFD samples collected in the local ferrochrome industry. The efficiency of the widely used treatment of BFD with ferrous ions was also critically examined. All this information was then used to design a more effective, and environmentally acceptable treatment option.

4.1 Collection of Samples

BFD from various local ferrochrome producers were collected:

- Two samples were obtained in August and October, 1996 from a ferrochrome producer in the Northwest Province using a semi-closed furnace. These samples will be referred to as A and B in the text below.

- Three samples were obtained from another ferrochrome producer in the Northwest Province in August 1995, December 1995 and May 1997. These samples will be referred to as C, D, and E, respectively, in the text below. All these samples were produced from a semi-closed furnace.

- Sample F was obtained from a ferrochrome producer in Mpumalanga Province in November, 1994, using a semi-closed furnace.

- Two samples were also obtained in June, 1996 from another ferrochrome producer in Mpumalanga Province. Closed furnaces were used in this operation and will be referred to as samples G and H in the text below.

As ores from different locations were processed, often by different means, it was considered that the BFD dust samples collected would also represent the wide variety of samples that are generated by the local ferrochrome industry.

4.2 Properties of Untreated Ferrochrome Bag Filter Dusts

4.2.1 Physical Properties

Ferrochrome BFD are fine, light powders. As an example, some of the physical properties of BFD samples B and E have been measured. The particle size of these solids was measured by laser diffraction using a Sympatec Helos particle size analyzer. The solids were dispersed in water and subjected to ultrasonics prior to measurement. A bimodal distribution of particle size was observed for both BFD samples with D_{10}, D_{50} and D_{90} values of 0.08, 0.71 and 3.65μm for sample B and 2.51, 13.23 and 15.21μm for sample E, respectively. The surface area of samples B

and E were 5.31 and 13.2 m^2/g, respectively, as measured by a Micromeritics ASAP surface analyzer with nitrogen gas at 77° K.

Table 3. Water Leaching of Untreated BFD (sample A)

Leaching Stage	Volume ml	pH	Time hours	Concentration, mg/l		Cr(VI) leaching rate, $mg.min^{-1}\ 10^3$
				Cr(VI)	TDS	
1	314	9.0	3.0	159.92	4684	278.97
2	340	10.3	3.0	28.98	870	54.74
3	325	10.5	2.0	11.08	410	30.01
4	380	11.1	3.0	6.46	340	13.64
5	360	10.2	2.0	2.49	160	7.47
6	405	11.0	15.5	1.74	170	0.76
7	365	10.6	3.0	0.76	100	1.54
8	400	10.6	15.5	0.86	130	0.37
9	400	10.6	6.0	0.64	120	0.71
10	430	10.8	24.0	1.17		0.35

4.2.2 Water Leaching Studies

Twenty grams of untreated BFD (sample A) were contacted with water at a solid:liquid ratio of 1:20 and agitated at room temperature with a magnetic stirrer for a fixed period. Thereafter the slurry was filtered and the pH, Cr(VI) concentration and total dissolved solids (TDS) of the filtrate were measured. (The pH of solution was measured with an ORION model 702A pH meter. The TDS was determined by gravimetry and the Cr(VI) concentration by spectrophotometry as described in chapter 3). This process was repeated 10 times, dispersing the filtered solids in fresh water at the same solid to liquid ratio but varying the contact time. The results of these measurements are shown in Table 3. These results indicate that initially, Cr(VI) and salts leach readily from BFD and that the amounts leached tailed off with increasing leaching stages. In stages 6, 8 and 10, the leaching was conducted for relatively longer periods and in these instances, relatively higher Cr(VI) and TDS concentrations were found. The leaching of Cr(VI) from BFD was also expressed as a rate in Table 3. These results indicate that a constant rate of Cr(VI) leaching may be approached in the later stages, suggesting that leaching is probably diffusion controlled. Complete removal of soluble components would require that consecutive leaching stages should increase in time with the square of the previous stage (Balzamo, *et al.*, 1996).

The accumulated amount of Cr(VI) and TDS leached from BFD (sample A) can be calculated from the data presented in Table 3 and these values are plotted in Figure 1 as a function of the accumulated time. The Cr(VI) and TDS values approach a constant value after an extensive leaching time (> 50 hours) and a number of stages.

A similar approach was used to calculate the accumulated amounts of Cr(VI) and TDS that can be leached from other BFD and these values are shown in Table 4. Substantial variation of accumulated amounts of Cr(VI) leached from different BFDs was observed. Samples A and B yielded relatively higher levels of Cr(VI) leached in comparison with C, D, E and F. Samples G and H contained very little soluble Cr(VI) that could be leached with water.

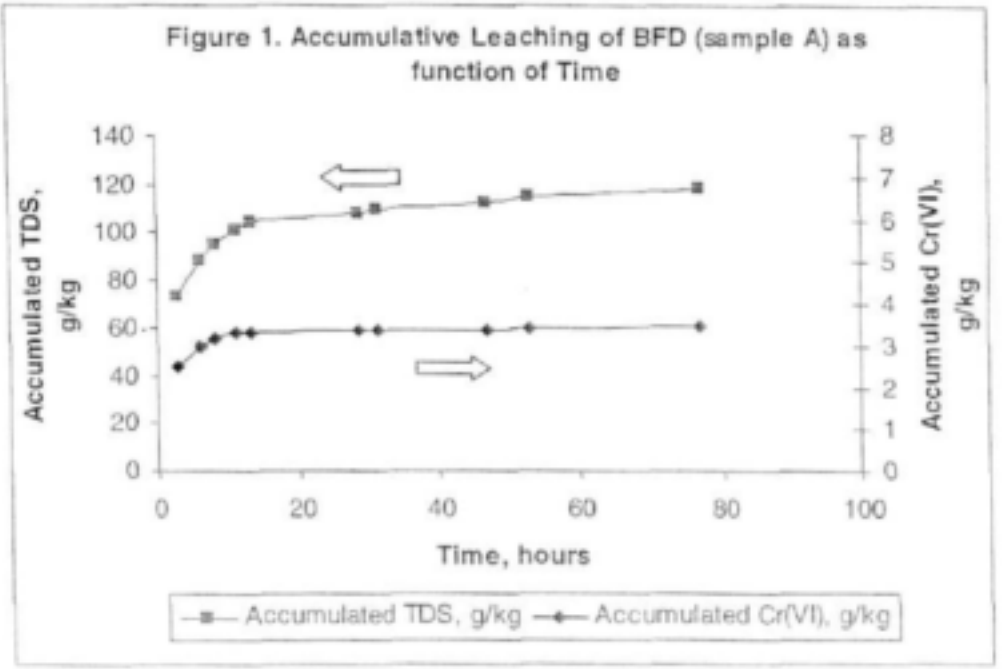


Figure 1 Accumulative Leaching of BFD (sample A) as Function of Time

It is to be expected that the magnitude of the amount of Cr(VI) leached depends primarily on the origin of the BFD and this may be directly related to the operating conditions and raw materials used in each operation. Furthermore it should be noted that for samples collected from the same operation, *i.e.*, C, D, and E, different leachable amount of Cr(VI) and TDS were observed. As these samples were collected at different times, differences in the type and amount of raw materials added to the furnace or air passing through the bag filter plant could all have played a role in causing these differences. Unfortunately this information was not available when the samples were collected. It was not always possible to determine the

associated amounts of leachable salts available in BFD. In these instances blank spaces appeared in Table 4. However, in the instances shown, there exists a correlation between the amounts of leachable salts with soluble Cr(VI) present in BFD. It should be pointed out that alkali roasting of chromite is a well established industrial practice to produce sodium chromate (Thompson, *et al.*, 1984) which depends on the amount of alkali, oxygen and temperature present during the process. The potential influence of the variability of these parameters on Cr(VI) formation in the bag filter during ferrochromium production will be investigated in the next section.

Table 4. Accumulated, leachable Cr(VI) and TDS from various BFD

BFD Sample	Mass g	Stages	Accumulated		Acc. Conc., g/kg	
			Time, h	L/S	Cr(VI)	TDS
A	20	10	77	183	3.455	118.58
B	40	9	100	88	5.502	
C	20	6	23	106	0.196	53.8
D	1000	10	20	67	0.119	33.4
E	50	5	5	200	0.672	91.10
F	30	1	3	3	0.028	
G	10	1	1	20	n.d.	
H	10	1	16	20	0.001	

n.d. not detected

More detailed chemical analyses of the leachates obtained when BFD samples, A, E and F were contacted with water are shown in Table 5. (The analyses of these solutions were conducted in the Analytical Science Division of Mintek. Na and K concentrations were determined by Atomic Absorption. Mg, Ca, Zn, Mn, Cd, B and Si concentrations were measured by Emission Spectroscopy. PO_4, Cl and SO_4 concentrations were determined by UV-VIS spectrometry, potentiometry and turbidimetry, respectively). Leachate A was obtained by combining 5 consecutive 1 hour water leaches of BFD sample A, each at a solid to liquid ratio of 40. Leachate E was obtained by combining the first two consecutive 12 hour water leaches at a solid to liquid ratios of 40 of BFD sample E. Leachate F was obtained by leaching sample F at a liquid to solid ratio of 20 for 2 hours. Also in this table are included the chemical analyses of return water (brine) collected from a ferrochrome producer in Northwest Province in May, 1997. The analyses of all the leachates, except the return water that has been treated with $FeSO_4$, contain toxic Cr(VI) above the permitted levels and clearly indicates that BFD would have to be stored in lined dams and could not be discharged into the natural water courses.

The results in Table 5 also indicate that thetreatment of BFD with $FeSO_4$ results in a higher salt load that is predominantly Na and K sulphate. Other components in the leachates are Ca, Mg and Cl. The components analyzed for comprise about 90%, or more, of the observed TDS. (It can be expected that in those instances where $FeCl_2$ is used in the treatment of BFD leachates, the chloride content of the return water would increase at the expense of the sulphate concentrations).

It can therefore be concluded from these water leaching studies on BFD that the leachable Cr(VI) is associated with alkali salts. A large proportion thereof is removed very rapidly when BFD is in contact with water but there is a smaller fraction of the soluble component that leaches very slowly at a rate that is probably diffusion controlled. Further, these results suggest that an effective treatment of the water leachable components in ferrochrome BFD should not only be concerned with the toxic chromate but should also consider the salts contained in these wastes.

Table 5. Chemical Analyses of BFD Water Leachates and Return Water

Component	Concentration, mg/l			
	BFD Leachate			Return Water
	A	E	F	
Cr(VI)	13	7.9	7.1	<1
Cr total	13	n.d.	7.5	<0.8
Na	84	206	208	973
K	70	74.5	290	1190
SO_4	245	806	502	7720
Mg	18	n.d.	3.3	1220
Ca	4.7	37.7	2.8	265
Zn	0.1	n.d.	<0.05	16
Cl	30	200	68	630
Mn	<0.01	n.d.	<0.01	9.8
Cd	<0.05	n.d.	<0.05	<0.05
B	<1	n.d.	<0.1	1.2
Si	5.3	n.d.	n.d.	18
PO_4	0.6	n.d.	n.d.	0.3
Total	470.7	1332.1	1093	12043
TDS	532	1570	1190	13267

n.d. not determined

Table 6. Chemical Analyses of BFD Samples

Sample	Chemical composition, percentage										Cr(VI)
	Cr_2O_3	SiO_2	Al_2O_3	FeO	MgO	C	ZnO	Na_2O	K_2O	MnO	g/kg
A	3.00	39.0	6.48	2.13	24.6	1.68	5.41	4.35	4.57	0.48	3.45
AL	2.53	39.4	6.96	2.04	26.1	1.74	5.29	1.31	2.18	0.50	
C	18.25	27.58	12.93	5.56	22.43	2.14	3.02	1.91	4.41	0.33	0.20
D	33.88	16.31	15.96	10.51	10.03	3.81	3.70	1.82	2.74	0.24	0.12
DL	35.35	17.06	15.88	10.65	9.20	3.74	3.94	0.90	2.16	0.24	
F	17.25	22.89	7.78	9.77	14.76	6.02	1.82			0.23	0.03
H	24.7	18.9	17.2	14.9	6.24	10.5	1.86	0.34	0.47	0.13	0.00

4.2.3 *Chemical Analyses of Untreated Bag Filter Dust Samples*

In order to elucidate the origin of Cr(VI) in BFD, the chemical analyses of samples A, C, D, F and H (see Table 6) were compared with their corresponding accumulated Cr(VI) concentrations listed in Table 4. Included in Table 6 are also the chemical analyses of dry, water leached samples A and D designated as AL and DL, respectively, to illustrate the influence of water leaching on the chemical composition thereof. (The chemical analyses of solids were conducted in the Analytical Science Division of Mintek. Methods similar to those described in the previous section were used. In addition, the C content in the solids was determined by the Leco combustion technique).

According to the results shown in Tables 4, the Cr(VI) content of these BFD samples, as indicated by water leaching studies, follow the sequence: A > C □ D > F > H. It was postulated in the previous section that the Cr(VI) content in BFD could be associated with the alkali content and oxidizing conditions in the dust extraction plant resulting in the formation of $NaCrO_4$. If it is assumed that a relatively higher C content in BFD is associated with low oxidizing conditions prevailing in the bag filter, then the results shown in Table 6 confirm this postulate. The low C and higher alkali content in BFD sample A should therefore promote high Cr(VI) levels in BFD. This trend was in fact observed in the chemical composition of the other BFD samples shown in Table 6. For sample H, the high C content and low alkali content should result in low Cr(VI) values, as is evident from the results shown in Table 4. Also the chemical composition of BFD samples AL and DL indicate that water leaching of these BFD samples decreases the alkali content contributing to the high salt content in the water leachates that are usually associated with Cr(VI) in these solutions. Further it should also be noted that the results shown in Table 6 indicate that the amount of Cr(VI) leached with water from BFD is not dependent on the amount Cr_2O_3 it contains. A large proportion of Cr in BFD is in the trivalent, non-toxic form.

4.2.4 *The Mineralogy of Ferrochrome Bag Filter Dust*

In a previous study, Coetzer (1996) reported the results of XRD and SEM analyses of BFD samples C, D and DL. The mineral phases that were identified in these BFD samples were: magnesiochromite $(Mg,Fe)(Cr,Al)_2O_4$, forsterite (Mg_2SiO_4), periclase (MgO), quartz (SiO_2) and cristobalite (SiO_2). The composition of magnesiochromite and forsterite phases were further elucidated by EDS and SEM. The greater

sensitivity of EDS over XRD identified the presence of small amounts of magnesium aluminium silicate ($Mg_3Al_2Si_3O_{12}$) and aluminium silicate (Al_2SiO_5) phases in the BFD samples.

An electron micrograph of BFD (sample D) indicated the presence of agglomerated composites of coarse and fine solid particles. EDS analyses of these particles showed that Cr, Fe, Mg, and Si are found in all the phases identified. The highest Cr_2O_3 concentration (46-49 per cent) was found in magnesiochromite, in all other phases, Cr_2O_3 concentrations of about 1 per cent were found. In no instance was there evidence of a decrease in Cr concentration upon water leaching the BFD sample (sample DL). Chromate appears therefore not to be associated with any particular mineral phase.

This mineralogical examination of BFD agrees with the overall chemical analyses reported in Table 6. The relatively high Mg and Si concentrations in BFD can be associated with the volatility of these elements during the smelting operation. These elements then more than likely condense on the dust particles as they cool in the bag filter used primarily for open-top or semi-closed furnaces. As further postulated in section 4.2.2, under these circumstances it is very likely that some of the Cr(III) in chromite dust is oxidized by air in the presence of alkali to Cr(VI). This occurs indiscriminately and is not associated with any particular mineral phase. The soluble Cr(VI) formed on the surface of the dust particles is easily removed by water when BFD is placed in contact with water. However, it is also possible that the Cr(VI) initially formed on the dust particles may be later coated by condensing Mg and Si in the cooler regions of the bag filter. It is expected that chromate trapped in this manner would be more difficult to leach when BFD is placed in contact with water.

The results shown in Tables 3 and 4 indicate that complete removal of Cr(VI) from some BFD by water leaching required long leaching periods (> 100 hours) and large liquid to solids ratios (>200) confirming this state of affairs. These conclusions differ to those given by Gericke (1995) who maintained that 24 hour leaching, at a liquid to solid ratio of 20 at a pH value of 2-6 are sufficient for complete removal of Cr(VI) from BFD during water leaching. These differences may be due to the type of BFD studied. Nevertheless, it is evident from the results presented in this report thus far that the removal of Cr(VI) from BFD by water leaching is a complex process and that this treatment option may not be the most effective and satisfactory long-term

solution. For this reason a number of alternative treatment options were investigated in this study and are discussed in sections which follow.

4.3 Bag Filter Dust Treated with Ferrous Ions

The most widely used treatment for the removal of Cr(VI) from aqueous medium is by the addition of ferrous ions (Eary, *et al.*, 1988). This practice is also widely used by the local ferrochrome industry for the treatment of BFD. This section examines, in more detail, the efficiency of this BFD treatment option. Of particular interest is the question of how effective the treatment is to inhibit the leaching of Cr(VI) from BFD in the longer term.

Thus water leaching studies were conducted on BFD (sample C) that was pre-treated with $FeSO_4$ at a Fe/Cr molar ratio of 30. The results for 7 consecutive water leaching stages of this treated BFD are shown in Table 7. In this pre-treatment a ten-fold excess of the required $FeSO_4$ was initially added and this caused the Cr(VI) concentration to be very low in the first five, short (1 hour) leaching stages. For longer leaching stages (6 and 7) Cr(VI) concentrations greater than 0.05 mg/l were observed. Only in stage 1 was an excess of Fe present in solution, measuring 212 mg/l (as measured by Atomic Absorption). During all the other stages no Fe was detected in solution. For the longer periods of leaching, the pH and salt content of the leachate increased. The treatment with $FeSO_4$ also resulted in a decrease of the pH values of the solution when compared to those shown in Table 3. The results shown in Table 7 clearly indicate that although the treatment of BFD with $FeSO_4$ is effective in the short term to prevent the leaching of Cr(VI), it is not effective in the longer term.

Table 7. Water leaching of a treated BFD (sample C) (Fe/Cr = 30)

Stage Number	Volume ml	pH	Time hours	Cr(VI) mg/l	TDS mg/l
1	375	6.65	1	0.00	3545
2	360	6.40	1	0.05	400
3	347	6.20	1	0.00	120
4	342	6.40	1	0.03	40
5	360	6.30	1	0.02	20
6	343	8.70	16	0.15	80
7	390	9.45	19	0.24	80

A precipitate of $Cr_xFe_{(1-x)}(OH)_3$ (Eary, *et al.*, 1988) where $x < 1$ is expected to be formed when a BFD slurry is treated with $FeSO_4$. It was necessary to establish whether the release of Cr(VI) observed in Table 7 for stages 6 and 7, over longer periods, originated from the Cr-Fe hydroxide precipitate that was formed or from the BFD. For this purpose a Cr-Fe hydroxide precipitate was formed by adding (at room temperature) 105ml of a 4566 mg/l Cr(VI) solution to 25g $FeSO_4.7H_2O$ dissolved in 300ml water. The precipitate formed was allowed to settle and washed with water by agitation with a magnetic stirrer for different periods. After each washing stage the solids were filtered and the filtrate analyzed for Cr(VI) and Fe content. The results of 6 consecutive water leaching stages of this precipitate for an accumulated time of 44 hours and a L/S ratio of 844 is shown in Table 8. These results indicate that in no water leaching stage was Cr(VI) leached from the Cr-Fe hydroxide precipitate. The results shown in Table 8 also indicate that the Fe concentration in the leachate decreases with increasing washing as the initial excess Fe is diluted. In the final washing stage, NaOH was added to increase the pH to a value of 6, however, even under these more alkaline conditions, there was no evidence that Cr(VI) was leached from the Cr-Fe hydroxide precipitate.

Table 8. Leaching of Cr-Fe hydroxide precipitate with water.

Stage	Time hours	Volume ml	pH	Concentration, mg/l	
				Cr(VI)	Fe
1	1.0	375	2.3	0.00	5818
2	1.83	376	2.6	0.03	566
3	4.08	343	2.5	0.00	65
4	1.67	350	3.0	0.00	1
5	15.92	410	3.2	0.00	1
6	19.25	365	6.0	0.00	0

The results shown in Table 8 suggest that the reduction of Cr(VI) with $FeSO_4$ is irreversible and is an effective treatment for removing Cr(VI) from solution although it contributes to the increase in the salt concentration of the treated water. Therefore the slow release of Cr(VI) observed in Table 7 from BFD treated with $FeSO_4$ more than likely originates from the BFD. A once-off treatment of BFD with $FeSO_4$ is not sufficient to reduce and immobilize the Cr(VI) that is slowly released from BFD over the longer term. In order to ensure that Cr(VI) is continually removed by this treatment ferrous ions would always have to be available in excess. For that reason BFD treated with $FeSO_4$ can not be disposed of and has to be retained in lined dams. It is therefore advisable that an alternative treatment for BFD would be required to address the longer term leaching of Cr(VI) and salt from BFD. An alternative

treatment option that could ensure the continual removal of Cr(VI) over a longer term will be discussed in the next section.

It should be pointed out that $FeSO_4$ is no more readily available locally and ferrochrome producers have used $FeCl_2$ instead. This reagent is as effective as $FeSO_4$ to remove Cr(VI) but more corrosive due to the presence of chloride. The use of alternative reducing agents (sulphite) to ferrous for removal of Cr(VI) was investigated by Beukes, *et al.* (1999). They found that in the acid pH range (< 6) sulphite reduction of Cr(VI) is comparable to Fe(II), however, the latter is effective over a significantly wider pH range, up to a pH value of 11 and therefore remains the preferred reagent.

4.4 Bag Filter Dust Treated with Reducing Slags

An improvement in the efficiency of $FeSO_4$ treatment of BFD would be achieved if ferrous ions were continuously available to chemically reduce the released Cr(VI) to Cr(III). This is possible if solids (iron, pyrite, magnetite) with Fe(II)-containing surfaces remain in contact with BFD. Blowes, *et al.*, (1997) and Petersen, *et al.*, (1997) have demonstrated that these mineral surfaces remove Cr(VI) from solution by an adsorption-reduction mechanism. Hence the treatment of BFD with iron-containing reducing slag was investigated. A further attractive feature of this option would be that these solid wastes, generated in the local metallurgical industry, are available at low or negative cost.

Table 9. Removal of Cr(VI) from solution in contact with ground EAF slag

Time	Percentage removals			
Mass of slag	**1g**	**2g**	**3g**	**4g**
1 hour	7.7	35.7	90.3	100.0
2 hours	6.5	38.7	85.5	
3 hours	6.6	54.6	88.7	
6 hours	18.0	59.9	88.6	
23 hours	18.2	76.4	90.2	
30 hours	23.7	72.5	87.8	

The percentage of Cr(VI) removed from 100ml of a 50 mg/l synthetic solution agitated in the presence of ground (2 minutes) EAF slag (ex Iscor, van der Bijl) are shown in Table 9 as a function of time and mass of material. In the presence of 1 and 2g of ground slag there is a gradual removal of Cr(VI) from solution over a period of 30 hours. In the presence of 3g of ground slag 90% Cr(VI) is removed within an hour

and this value remains practically constant for up to 30 hours of contacting. Contacting 4g of EAF slag with the synthetic solution removed all the Cr(VI) within 1 hour.

Based on these observations it can be estimated that about 1.25 mg Cr(VI) can be removed per gram of EAF slag. The mechanism of the Cr(VI) removal under these circumstances is presumed to be associated with the presence of wuestite (FeO) in the EAF slag as will be verified by mineralogical examination mentioned in the next chapter. The important feature of these experiments indicates that it may be beneficial to mix BFD with EAF slags to bring about the reduction of Cr(VI). This aspect will be investigated in the next chapter of the report where ferrochrome wastes (BFD and FeCr slag) are mixed with cement, $FeCl_2$ and EAF slag to produce solid stabilized products to immobilize the toxic soluble chromate contained in BFD.

5. FERROCHROME WASTE CEMENT-BASED SOLID STABILIZED PRODUCTS

One of the objectives of this study was to investigate the potential for immobilization of Cr(VI) contained in BFD by its incorporation into cement-based solid stabilized products. This is dealt with in detail in this chapter, and includes characterization of raw materials, manufacture and evaluation in terms of compressive strength, leachability and potential toxicity.

5.1 Materials

Ferrochrome BFD, slag, and brine were collected from a ferrochrome producer in the Northwest Province in June and December, 1998. EAF slag was obtained from Iscor, van der Bijl Park and ordinary Portland cement (OPC) was obtained from Lafarge Cement, Industria and Pretoria Portland Cement, Germiston.

5.2 Characterization of Solid Wastes

5.2.1 Chemical Composition of Solids

The solids used as starting materials in this study were characterized by chemical analysis conducted in the Analytical Science Division of Mintek using X-ray fluorescence, emission and atomic absorption spectroscopy. The EAF slag and solid

stabilized solids produced in this study were characterized by X-ray diffraction (XRD) with a Philips PW1140 Diffractometer using Co Kμ radiation. Solid stabilized products were also studied by scanning electron microscopy (SEM) using a LEOS440 Scanning Electron Microscope to obtain backscatter and secondary electron images. The particle size of solids in the range 0.1-875 μm was measured with a Sympatec particle size analyzer using laser diffraction. Solids with coarser particle size were measured by sieve analysis.

Table 10. Chemical Analyses of Solids (major components, > 0.1%)

Component	Composition, Percentage				
	FeCr slag	EAF slag	BFD	Cement1	Cement2
Na_2O	<2.7	<2.7	<2.7	128 ppm	0.1
MgO	7.5	3.3	23.2	2.48	3.3
Al_2O_3	12.7	3.4	4.5	4.47	3.3
SiO_2	53.5	15.4	47.1	21.2	22.9
P_2O_5	<0.1	0.9	<0.1	n.d.	
SO_4	0.2	0.5	5.7	n.d.	0.2
K_2O	0.2	<0.1	1.2	0.15	0.6
CaO	2.1	43.4	0.5	60.4	65.0
TiO_2	0.7	0.5	0.2	n.d.	
Cr_2O_3	12.6	0.3	8.0	<0.2	
Mn_2O_3	0.3	4.3	0.5	0.27	0.4
Fe_2O_3	9.4	27.2	4.3	2.61	3.8
Cl	<0.1	<0.1	1.0	n.d.	
ZnO	<0.1	<0.1	1.7	n.d.	
Ga	<0.1	<0.1	0.1	n.d.	
Total	99.2	99.2	98.0	91.6	100.5

n.d. = not determined

The chemical composition of FeCr and EAF slag, BFD and cement are shown in Tables 10 and 11. The major components (>0.1%) identified in the semi-quantitative scan are shown in Table 10 and the minor components are shown in Table 11. In all, 40 different components were identified. The sum of 14 major components (see Table 10) analyzed for and expressed in the oxide form, amount to >90%. The analysis of a local OPC (Cement1) together with the analysis of Cement2, which corresponds to a typical analysis of a South African OPC (Mantel, 1992), are included in Table 10. The similarities between the analyses of the two cements are evident. It is therefore assumed that the components not analyzed for in Cement1 are similar or of the same order of magnitude as for Cement2.

The analyses of FeCr slag (see Table 10) indicate that the major components are SiO_2, Al_2O_3, Cr_2O_3, Fe_2O_3 and MgO. The EAF slag consists mainly of CaO, Fe_2O_3 and SiO_2. This is in agreement with the XRD analysis of EAF slag. The presence of

larnite (Ca_2SiO_4) and wuestite (FeO) as major, and calcium silicate (Ca_3SiO_5) and $Ca_2Fe_2O_5$ as minor phases have been identified by this measurement. This indicates that most of the Fe in EAF slag is in the Fe(II) oxidation state. The major components in BFD are SiO_2, MgO and Cr_2O_3. The relatively high Mg and Si found in BFD can be associated with the volatility of these elements during the smelting operation which then condense on the dust particles as mentioned above in section 4.2.4.

Table 11. Semi-quantitative scan of solids (minor components, <0.1%)

Component	Concentration, ppm		
	FeCr slag	EAF slag	BFD
Co	<1000	<1000	<1000
Cl	773	320	10 000
V	644	518	282
Ni	272	11	617
Cu	27	26	117
Zn	250	709	14 000
Ga	23	<10	1 100
Ge	<10	<10	41
Se	<10	<10	13
Br	<10	<10	64
Rb	<10	<10	136
Sr	63	301	76
Y	13	26	87
Zr	170	71	317
Nb	<10	60	<10
Sn	<10	<10	16
Sb	<10	<10	20
Ba	66	379	23
La	<10	15	<10
Ce	13	42	<10
Pr	<10	<10	14
Ta	<10	<10	37
W	<10	35	90
Hg	<10	11	40
Tl	<10	<10	11
Pb	11	79	358
Bi	<10	<10	29
Th	<10	21	<10
U	<10	16	14

Analyses of the minor components (see Table 11) present in the solids were undertaken with the specific purpose of identifying potentially toxic and heavy metal components that could pose a threat to the environment. All solids contain trace amounts (> 250 ppm) of V and Zn. FeCr slag and BFD contain trace amounts of Ni but no significant amounts thereof are found in EAF slag. On the other hand, EAF slag contains trace amounts of Ba but this is not found in the other two solids. It should be noted that BFD contains trace amounts of Pb.

Table 12. Particle size distribution of solids

Size fraction Diameter, μm	Mass per cent		
	FeCr slag	EAF slag	BFD
< 1	0	0	21
< 25	3	26	99
< 50	11	37	100
< 75	22	45	100
< 100	31	52	100
< 250	50	75	100
< 500	65	95	100
< 750	68	95	100
< 1000	74	98	100
< 10 000	100	100	100

5.2.2 *Physical Characterization of Solids*

The particle size distributions of some of the solids used in this study are shown in Table 12. These results indicate that BFD is very fine and all the particles are less than 36 μm in diameter. EAF slag is coarser and the coarsest solids were those of FeCr slag, however, all solids are less than 10 mm in diameter.

5.2.3 *Water Leaching Tests*

In view of the high solubility of Cr(VI) and salts, water leaching tests were used as a measure to evaluate the degree of immobilization thereof in the solid stabilized products made in this study. For purposes of comparison, it was therefore also necessary to conduct similar tests on the materials used for their manufacture. Hence, these materials were leached with water for various periods to determine the amount of soluble salts (TDS) and chromate contained therein. These tests were conducted at room temperature, agitating 100g of crushed solids with 1000ml of water on a horizontal laboratory shaker. (A similar procedure is recommended by the German DIN 38414 leaching test). The results of these leaching tests are contained in Table 13. The total amount leached, expressed as the amount leachable per unit mass of solid, indicate that the leachability of soluble salts from these solids follows the order BFD > EAF slag > FeCr slag > OPC. Cr(VI) is only leached with water from BFD to a concentration of 1218.2 mg/kg. It should also be noted that all the leachates are strongly alkaline.

Table 13. Water soluble components in solids

Solid	OPC		FeCr slag		BFD			EAF slag	
Time	pH	TDS mg/l	pH	TDS mg/l	pH	Cr(VI) mg/l	TDS mg/l	pH	TDS mg/l
24h	11.88	2400	9.81	275	9.06	96.08	6555	12.28	1555
48h	12.06	2300	9.76	155	10.28	10.34	1245	12.17	595
72h			9.68	65	11.05	4.62	710	12.09	520
7d			8.34	170	10.52	10.78	745	11.97	785
Total g/kg		4.70		6.65		1.22	92.55		34.55

Results of the analyses of the major components in the water leachates are shown in Table 14. The leachates are designated by the solid leached and the duration of the leaching period, 24 or 48 hours. For longer leaching periods, 72 hours, 7 and 14 days, the leachates were combined for purposes of analyses and are designated by the solids name and "mix". In instances where the individual components of separate leachates rather than the combined leachates were analyzed, the mean values were calculated and the mean values are designated by * in Table 14. The OH concentrations in the leachates were calculated from the pH values shown in Table 13.

The sums of the components analyzed for were compared in Table 14 with the measured TDS values. In all instances, the sums of the components analyzed were less in the leachates than the observed TDS values. Efforts were made to identify these missing components, based on the chemical analyses of the solids shown in Tables 10 and 11. Hence the water leaching of EAF slag was repeated and the solutions re-analyzed for components: Al, Mg, Pb, Si, Zn, Ba and Sr. Only the latter two were present in significant quantities and are included in Table 14. These two components were also found in the leachates obtained from OPC. It may be possible that the missing components in the leachates could be CO_3 and HCO_3 or organic components, all of which were not analyzed for. Due to the high alkalinity of the leachates (see Table 13) and the long duration of leaching, it may be possible that CO_2 from the air was absorbed contributing to the presence of some of these components. This contention may be supported by analysis of the brine, the plant-recycle water obtained from the treatment of BFD with $FeCl_2$. These results indicate a satisfactory agreement between the sum of components analyzed for and the observed TDS value. Due to the relatively low pH value (7) of the brine the absorption of CO_2 should be less prevalent. The results shown in Table 14 indicate that the brine consists essentially of Na, K, Cl and SO_4.

Table 14. Composition of water leachates of solids

Leachate	Concentration, mg/l										
	Ca	K	Na	Cl	SO_4	OH	Ba	Sr	Cr(VI)	Sum	TDS
BFD24	50.3	490	1455	522	3268	0.2	n.d.	n.d.	96.1	5882	6555
BFD48	5.1	59.6	154	33	258	3.2	n.d.	n.d.	10.3	523	1245
BFD mix	1.7	44.7	129	2.5	63	10.1*	n.d.	n.d.	8.7*	260	733*
EAF24	481	31.8	10.8	18.5	5	324	n.d.	n.d.	0.17	871	1555
EAF mix	193	<1.0	<1.0	3	3	195*	n.d.	n.d.	0	394	671*
EAF24	804	11.0	40.8	3	<2	129	29.4	0.56	0	1018	1700
EAF48	505	1.24	3.4	<2	<2	135	19.2	0.18	0	664	1100
FeCr24	15.6	5.27	9.72	12	18	1.1	n.d.	n.d.	0	62	275
FeCr mix	6.26	.64	1.0	<1	3	0.5*	n.d.	n.d.	0	11	209*
OPC24	1060	52.2	26.5	<2	<2	129	48.0	7.95	0	1324	2400
OPC48	1050	14.7	9.8	<2	<2	195	42.2	2.10	0	1314	2300
Brine	378	1600	3805	5885	7111	0	n.d.	n.d.	0	18779	20453

n.d. not determined *Sum of the components

5.3 Manufacture of Cement Blocks

The masses of components used in the preparation of 16 different batches (A-P) of cement-mixes are shown in Table 15. In all mixes 620g of OPC was used, with variations in the masses of FeCr slag, BFD and EAF slag. The total mass of solids in each mix was 7 kg. The amounts of $FeCl_2$, brine or water used for each mix are also shown in Table 15. The compositions of additional 10 different mixes (Q-Z) are shown in Table 16. As before, the total mass of solids used in each mix amounted to 7 kg but in this instance the loading of BFD, EAF slag and $FeCl_2$ was increased. The role of Ba in the Cr(VI) stabilization was investigated by adding soluble $BaCl_2$ to two mixes (Y and Z). Only Rand Water Board water (no brine) was used to prepare the mixes shown in Table 16.

The various batches were mixed manually and then poured into plastic bottles and allowed to cure at room temperature, forming cylindrical blocks, 90mm in diameter and of equal height with an average volume of 570ml and 1.3kg cured, dry mass. Some of the mixes were also cast in 50mm x 50mm x 50mm cubic blocks and standard building bricks for compression strength tests. After curing for 7, 14, 28, 56

and 120 days, the blocks were dried for 2 hours at 120 °C to stop the curing process and then crushed to <10mm diameter and subjected to leaching tests.

Table 15. Composition of cement mixes

Mix No	Mass, g						
	Cement	FeCr	BFD	EAF	$FeCl_2$	Brine	Water
A	620	6170		210			1050
B	620	6170	210				1050
C	620	5960	210	210	8	1050	
D	620	5960	210	210	8		1050
E	620	5960	210	210		1050	
F	620	5960	210	210			1050
G	620	5750	210	420			1050
H	620	5540	210	630			1050
I	620	5960		420			1050
J	620	5960	420			1050	
K	620	5540	420	420	16	1050	
L	620	5540	420	420	16		1050
M	620	5540	420	420		1050	
N	620	5540	420	420			1050
O	620	5120	420	840			1050
P	620	4700	420	1260			1050

Table 16. Composition of additional cement block mixes

Mix No	Mass, g					
	Cement	BFD	EAF	FeCr	$FeCl_2$	$BaCl_2$
Q	620	630	630	5093	27	
R	620	630	630	5066	54	
S	620	630	630	5039	81	
T	620	840	840	4665	35	
U	620	840	1680	3790	70	
V	620	1050	1050	4236	44	
W	620	1050	2100	3142	88	
X	620	1050	2730	2512	88	
Y	620	630	630	5020		100
Z	620	1050		5230		100

Smaller (4x100g) cement blocks mixing 200g each of BFD and cement with water were also prepared. This was undertaken to enhance the X-ray diffraction (XRD) detection of significant mineralogical phases that may play a role in the Cr(VI) and salt stabilization process during curing. By increasing the addition of $Na_2Cr_2O_7.2H_2O$ to the mixes, blocks were produced that contain 0, 1, 5 and 9 per cent Cr(VI). These blocks were cured for 3, 7, 14 and 28 days at room temperature and then subjected to mineralogical examination using XRD and scanning electron microscopy (SEM).

Table 17. Compressive strength of cement blocks cured for 56 days

Mix Type	Compressive Force, N	Area of Blocks mm^2	Compressive Strength, Mpa
A	8107	2500	3.2
B	19246	2500	7.7
C	22127	2500	8.8
D	17591	2500	7.0
E	17049	2500	6.8
F	16052	2500	6.4
G	19515	2500	7.8
H	20184	2500	8.1
I	13041	2500	5.2
J	11231	2500	4.5
K	10512	2500	4.2
L	14571	2500	5.8
M	19928	2500	8.0
N	23431	2500	9.4
O	20156	2500	8.1
P	29568	2500	11.8
N	426087	23100	18.4
O	419984	23100	18.2
P	270176	23100	11.7

5.4 Compressive Strength of Cement Blocks

The compressive strengths of different cement blocks cured for 56 days were measured with a Tinius Olsen Press and are shown in Table 17. (These measurements serve as an important indicator of the extent to which the cement hydration reactions have taken place during curing of the solid stabilized products and whether they could potentially be used as building materials). Considerable variation in values of compressive strength was observed. This was probably due to the fact that it was only possible to produce one block of each mix type, allowing for only one measurement of the compressive strength. It should be pointed out that extensive studies regarding the compressive strength of cement bricks made from ferrochrome BFD, slag and various types of cement have already been reported on by Smit, *et al.* (1998). That study indicated that most of the bricks obtained the required compressive strength of 7 Mpa after 14 days curing and comply with the standards set by the South African Bureau of Standards (1984). Since it is evident that the required compressive strength can be achieved without any difficulty, these products could, in principle, be used as building materials. Because the present work concentrated more on immobilization of Cr(VI) and salts in these systems, smaller blocks were prepared using less material. Nevertheless, it should be noted that the observed compressive strengths of the larger bricks made from mixes N, O and P

(see Table 17) were of the same order of magnitude as those found by Smit, *et al.* (1998) in the previous study for similar materials.

5.5 Water Leaching of Cement Blocks

Water leaching of crushed cement blocks were used in this study as an indication of the degree of immobilization of soluble Cr(VI) and salt in these solid stabilized systems as a function of curing time. This approach was also used to study the immobilization of individual components of the salt in these systems. Further, whole cement blocks were also partially immersed in water to establish the effect on leaching of not crushing the materials.

5.5.1 Crushed Cement Blocks

The results of the water leaching tests conducted on crushed (<10 mm) cement blocks as a function of curing time (7-56 days) and for different leaching periods are shown in Table 18 (for mixes A and C) and Table 19 (for mixes H, K and P). The results of similar water leaching tests conducted on blocks obtained from the other 11 mixes, listed in Table 15, are shown in Appendix B. In all these tests, 100g of crushed cement blocks (< 10mm) were shaken for 24 hours with 1 liter of water on a horizontal laboratory shaker. After filtration, the wet residue was added to another liter of fresh water and subsequent cycles of leaching were carried out for 48 hours and again for 5 days. The results of these leaching tests indicate that there is generally a decrease in TDS in the leachates with increasing curing time of the blocks. Variations from this trend could be ascribed to inhomogeneous mixing of components during preparation of the mix and sampling of cured solids for the leaching tests. The differences in salt concentrations in the leachates between 7 and 14 days curing are not significant. Hence, leaching after 7 days curing was not regarded as significant and was discontinued.

Table 18. Water leaching of crushed cement blocks (Mixes A and C)

Mix No	Curing Time	Leaching Period	Leachate		
			pH	Concentration, mg/l	
				Cr(VI)	TDS
A	7 days	24 hours	12.24	0.000	1105
		5 days	12.16	0.000	585
	14 days	24 hours	12.38	0.002	1110
		48 hours	11.89	0.000	375
	28 days	24 hours	11.88	0.000	1040
		48 hours	11.18	0.000	570
	56 days	24 hours	11.98	0.016	936
		48 hours	11.43	0.046	421
C	7 days	24 hours	12.10	0.153	1041
		5 days	12.06	0.117	550
	14 days	24 hours	12.17	0.181	870
		48 hours	11.80	0.102	365
	28 days	24 hours	11.82	0.048	940
		48 hours	11.24	0.052	550
	56 days	24 hours	11.73	0.092	822
		48 hours	11.21	0.072	361

A similar trend can be observed for the Cr(VI) concentration in the leachates obtained from cement blocks cured for longer periods. Greater variations of Cr(VI) concentrations in the leachates as a function of curing time are observed in the leachates. The reasons for this are probably the same as those mentioned above for the observed variations in TDS values and are further accentuated by the greater sensitivity of the Cr(VI) concentration determination than the TDS values. (The results shown in Table 18 indicate that for Mix No A no Cr(VI) was found in the water leachates. This was expected as this mix contained no BFD, the source of Cr(VI). The low Cr(VI) concentrations observed after 56 days curing for Mix No A is probably due to contamination or small amount of Cr(VI) leaching from EAF slag as indicated in Table 14).

All the leachates were strongly alkaline as expected for cement based solids and the second leach was always lower in pH, Cr(VI) and TDS concentration than the first. No significant differences were observed in Table 18 between the 5 day and 48 hour leachates after 7 and 14 days curing. Hence the results in Table 19 contain only results for 24 and 48 hour leaching periods.

Table 19. Water leaching of crushed cement blocks (Mixes H, K and P)

Mix No	Curing Time	Leaching Period	Leachate		
			pH	Concentration, mg/l	
				Cr(VI)	TDS
H	14 days	24 hours	12.29	0.239	875
		48 hours	12.00	0.134	370
	28 days	24 hours	11.70	0.266	965
		48 hours	11.24	0.104	384
	56 days	24 hours	11.66	0.374	809
		48 hours	11.18	0.120	328
K	14 days	24 hours	11.95	0.307	935
		48 hours	11.78	0.119	550
	28 days	24 hours	11.41	0.182	902
		48 hours	11.13	0.070	385
	56 days	24 hours	11.43	0.159	776
		48 hours	10.99	0.052	322
P	14 days	24 hours	12.22	0.542	1050
		48 hours	11.56	0.291	440
	28 days	24 hours	11.69	0.672	973
		48 hours	11.57	0.236	389
	56 days	24 hours	11.24	0.182	831
		48 hours	11.56	0.125	413

The sum of the Cr(VI) and salts leached from a crushed cement block, cured for a specific period, was expressed in mg/kg and g/kg for Cr(VI) and TDS, respectively. These values were compared to the amounts of Cr(VI) and salt added for each mix and the percentage stabilization in the cured cement blocks was calculated. These results are shown in Tables 20 and 21 for cement blocks cured for 28 and 56 days, respectively. (The amounts of components added to each mix were determined from the mass of solids used to produce the mix, see Table 15, and the amounts that could be leached therefrom when these solids were leached with water, Table 13).

For cement blocks cured for 28 days the most effective Cr(VI) stabilization was observed with blocks made from mixes C, D, K and L (see Table 20). It is interesting to note that according to Table 15, in all these mixes $FeCl_2$ was added to promote the chemical reduction of Cr(VI). Ferrous ion was added in soluble form that allowed for extensive Cr(VI) reduction prior to cement hydration. In the absence of $FeCl_2$, Cr(VI) stabilization is also promoted with increasing EAF slag content in the mix. This is evident from the results shown in Table 20 for mixes F, G and H or N, O and P where the EAF slag to BFD mass ratio increases from 1 to 3. On the other hand, the poorest Cr(VI) stabilization was observed for blocks made from mixes B and J where no EAF slag or $FeCl_2$ was added.

Table 20. Cr(VI) and salt stabilization in cement blocks cured for 28 days

Mix No	Cr(VI), mg/kg			TDS, g/kg		
	Added	Leached	% Stabilized	Added	Leached	% Stabilized
A	0.00	0.0	0.0	11.06	16.10	-45.6
B	36.55	7.75	78.8	12.80	14.65	-14.4
C	36.55	1.00	97.3	17.82	14.90	16.4
D	36.55	1.53	95.8	14.75	15.15	-2.7
E	36.55	4.60	87.4	16.71	9.15	45.2
F	36.55	6.51	82.2	13.64	12.45	8.7
G	36.55	3.80	89.6	14.48	12.78	11.7
H	36.55	3.70	89.9	15.31	13.49	11.9
I	0.00	0.00	0.00	11.90	16.54	-38.3
J	73.09	24.15	67.0	18.45	12.94	29.8
K	73.09	2.52	96.6	22.35	12.87	42.4
L	73.09	3.14	95.7	19.28	10.91	43.4
M	73.09	22.05	69.8	20.12	14.02	30.3
N	73.09	19.91	72.8	17.05	12.88	17.8
O	73.09	14.63	80.0	18.73	12.15	35.1
P	73.09	9.08	87.6	20.40	13.62	33.2

The salt stabilization in crushed cement blocks, cured for 28 days are also included in Table 20. The poorest salt stabilization was observed for blocks made from mixes A and I where the least salt was added and no BFD was used. Increasing the salt content in the mixes improved its stabilization as is evident for cement blocks made from mixes E, K and L.

The Cr(VI) and salt stabilization in crushed cement blocks cured for 56 days are shown in Table 21. It should be noted that in general the Cr(VI) stabilization improved with curing from 28 to 56 days. Comparing the results for Cr(VI) stabilization in Tables 20 and 21, it can be noted that only for mixes C, G, H, and L was a decrease observed. This observation is different from the previous study (Smit, *et al.*, 1998) where a general decrease in Cr(VI) stabilization was observed with increasing curing time. This is probably due to the production of a less porous block in this study by using finer solids and the presence of EAF slag in the mix.

Table 21. Cr(VI) and salt stabilization in cement blocks cured for 56 days

Mix No	Cr(VI), mg/kg			TDS, g/kg		
	Added	Leached	% Stabilized	Added	Leached	% Stabilized
A	0.00	0.0	0.0	11.06	13.57	-22.7
B	36.55	7.45	79.6	12.80	10.35	19.1
C	36.55	1.64	95.5	17.82	11.83	33.6
D	36.55	1.15	96.9	14.75	10.68	27.6
E	36.55	1.32	96.4	16.71	10.20	38.9
F	36.55	2.55	93.0	13.64	9.77	28.4
G	36.55	7.20	80.3	14.48	10.49	27.5
H	36.55	4.94	86.5	15.31	11.37	25.7
I	0.00	0.00	0.00	11.90	13.11	-10.2
J	73.09	15.73	78.5	18.45	10.65	42.3
K	73.09	2.11	97.1	22.35	10.98	50.9
L	73.09	9.47	87.0	19.28	10.83	43.8
M	73.09	5.07	93.1	20.12	12.94	35.7
N	73.09	4.38	94.0	17.05	7.95	53.3
O	73.09	4.80	93.4	18.73	12.52	33.1
P	73.09	3.07	95.8	20.40	12.44	39.0

The stabilization of salt in crushed blocks cured for 56 days are also shown in Table 21. Again an improvement in salt stabilization was observed with increasing curing time. Only for mixes E and O was a small decrease in salt stabilization observed when comparing the results in Tables 20 and 21. The mechanism of salt stabilization and why it is so poor in blocks made from mixes A and I may be found in mineralogical examinations of the cured cement blocks and will be discussed to some extent later in the report.

5.5.1.1 Solid stabilization of Individual Salt Components

The combined water leachates obtained from selected, crushed, cement blocks after 56 days curing, were analyzed for SO_4, Cl, Na, K, and Ca. These results are shown in Table 22 together with the OH and TDS concentrations obtained from Tables 18 and 19. OH concentrations were calculated form the corresponding pH values. For each of the leachates the sum of the individual concentrations does not amount to the observed TDS value indicating that there is another component that contributes significantly to the TDS. Presumably the omitted component is carbonate which unfortunately was not analyzed.

Table 22. Leaching of soluble components from crushed cement blocks cured for 56 days

Mix No	Concentration, mg/l						
	SO_4	Cl	Na	K	Ca	OH	TDS
A	15	2	9	7	317	104	679
C	69	53	67	31	165	47	592
H	24	9	47	18	245	52	568
K	115	68	95	41	124	31	549
P	54	13	71	31	167	46	622

Based on the analyses of leachates and the principles developed in the previous section, the amount of each component leached from the crushed cement block was compared to the estimated amount added to the original mix (see Tables 14 and 15). The percentage stabilization of each component was then calculated. These values are shown in Table 23 for SO_4, Cl and Na and in Table 24 for K and Ca. The results suggest that the anions SO_4 and Cl are more effectively stabilized in cement blocks than the cations Na, K and Ca. An explanation for these observations is given later in the report after the results of the mineralogical examination of the crushed cement blocks have been mentioned.

Table 23. SO_4, Cl and Na stabilization in crushed cement blocks cured for 56 days

Mix No	SO_4, g/kg			Cl, g/kg			Na, g/kg		
	Added	Leached	% Stab	Added	Leached	% Stab	Added	Leached	% Stab
A	0.27	0.30	-11.1	0.12	0.04	65.2	0.12	0.18	-44.0
C	2.44	1.38	43.5	1.56	1.06	32.1	1.30	1.34	-3.3
H	1.37	0.48	64.9	0.29	0.18	38.1	0.72	0.93	-29.6
K	3.54	2.30	35.1	2.13	1.36	36.1	1.88	1.90	-1.1
P	2.46	1.08	56.1	0.47	0.26	45.0	1.31	1.41	-7.4

Table 24. K and Ca stabilization in crushed cement blocks cured for 56 days

Mix No	K, g/kg			Ca, g/kg		
	Added	Leached	% Stab	Added	Leached	% Stab
A	0.17	0.14	20.9	2.60	6.34	-143.6
C	0.61	0.62	-0.6	2.67	3.30	-23.8
H	0.39	0.36	6.9	3.34	4.90	-46.9
K	0.82	0.81	0.5	3.04	2.48	18.3
P	0.60	0.61	-1.3	4.43	3.34	24.7

5.5.1.2 Cement blocks cured for 120 days

Some of the above cement blocks, after being cured for 120 days, were crushed and subjected to two successive 24 hours water leaching tests. The pH, Cr(VI) and TDS concentrations of the filtered leachates are shown in Appendix C. In all instances the pH and concentrations were lower for the second (48 hour) leaching stage. From

these results the mass of Cr(VI) and salts leached from solid stabilized product were calculated and compared to those originally added to the mix (see Table 15). This allowed for the calculation of the percentage Cr(VI) and TDS stabilization in the crushed cement blocks after 120 days curing. The results are shown in Table 25 and should be compared to corresponding values observed for the same blocks after 28 and 56 days curing that were given in Tables 20 and 21, respectively. In all instances, except for block N, it can be concluded that Cr(VI) stabilization improved even further on curing for 120 days when compared to those values observed for 56 days curing. The highest Cr(VI) stabilization of 99.1 per cent after 120 days curing, was observed for blocks K and L. In these instances the more effective Cr(VI) stabilization is probably associated with the $FeCl_2$ added to the original mix (see Table 15). On the other hand it should be noted that improved salt stabilization was only observed for blocks G an H after 120 days curing.

Table 25. Cr(VI) and salt stabilization in cement blocks cured for 120 days

Mix	Cr(VI), mg/kg			TDS, g/kg		
No	Added	Leached	% Stabilized	Added	Leached	% Stabilized
B	36.55	2.48	93.2	12.80	10.61	17.1
D	36.55	0.92	97.8	14.75	11.69	20.8
E	36.55	1.31	96.4	16.71	13.96	16.4
F	36.55	1.57	95.7	13.64	11.06	18.9
G	36.55	0.73	98.0	14.48	9.85	32.0
H	36.55	0.80	97.8	15.31	11.53	24.7
I	0.00	0.00	0.0	11.90	14.12	-18.7
J	73.09	4.28	94.1	18.45	12.82	30.5
K	73.09	0.69	99.1	22.35	13.11	41.3
L	73.09	0.64	99.1	19.28	10.94	43.3
M	73.09	4.55	93.8	20.12	10.64	47.1
N	73.09	9.91	86.4	17.05	9.70	43.1
O	73.09	3.41	95.3	18.73	12.54	33.0
P	73.09	3.32	95.5	20.40	14.12	30.8

5.5.1.3 Additional cement blocks

Additional cement blocks made with higher Cr(VI) and BFD loading than before were subjected to water leaching tests by the same method after 28 and 56 days curing. The results for these tests are shown in Appendix D and were used to calculate the Cr(VI) and salt stabilization values shown in Table 26. In spite of the fact that these blocks contained a higher Cr(VI) and BFD loading than before, excellent or even better stabilization was observed. It should be noted that for block U after 56 days curing (see Table 26) a 99.7 per cent Cr(VI) stabilization was observed for a Cr(VI) loading of 146.18 mg/kg. The highest Cr(VI) stabilization of 99.1 per cent in

previously prepared cement blocks was observed for blocks K and L (see Table 25) where the loading was half at 73.09 mg/kg. This suggests that even higher Cr(VI) loading could be considered without expecting a decrease in Cr(VI) stabilization. Therefore, the optimum Cr(VI) loading and stabilization in these types of cement blocks has apparently not yet been achieved.

Table 26. Cr(VI) and salt stabilization in additional cement blocks cured for 28 and 56 days

Mix No	Curing Period, d	Cr(VI), mg/kg			TDS, g/kg		
		Added	Leached	% Stab	Added	Leached	% Stab
Q	28	109.64	0.93	99.2	24.30	15.88	34.7
	56		5.73	94.8		14.81	39.1
R	28	109.64	1.00	99.1	28.13	16.91	39.9
	56		5.83	94.7		14.22	49.4
S	28	109.64	0.71	99.4	31.96	14.86	53.5
	56		4.48	95.9		14.88	53.4
T	28	146.18	1.48	99.0	28.85	16.72	42.0
	56		1.17	99.2		15.09	47.7
U	28	146.18	0.98	99.3	37.16	16.53	55.5
	56		0.42	99.7		18.37	50.6
V	28	182.73	10.65	94.2	33.54	21.42	36.1
	56		7.81	95.7		17.80	46.9
W	28	182.73	5.47	97.0	43.97	21.38	51.4
	56		10.27	94.4		19.94	54.7
X	28	182.73	4.75	97.4	46.48	23.43	49.6
	56		3.50	98.1		21.04	54.7
Y	28	109.64	8.58	92.2	34.66	16.78	51.6
	56		9.10	91.7		13.86	60.0
Z	28	182.73	33.71	81.5	37.30	16.45	55.9
	56		18.83	89.7		13.75	63.1

The poorest Cr(VI) stabilization shown in Table 26 was observed for blocks made from mix types Y and Z where $BaCl_2$ instead of $FeCl_2$ was used. Clearly the former is not as effective as the latter to promote Cr(VI) stabilization. These observations do not give credence to the postulate (Kersten, *et al.*, 1998) where a Cr(VI) coprecipitated solid solution with $BaSO_4$ could be invoked to explain its immobilization. On the other hand it should be noted that for the instances where $BaCl_2$ was added to the mix, the salt stabilization in the crushed cement blocks was the highest, larger than 60 per cent after 56 days curing (see Table 26). This would suggest that additional sulphate immobilization most probably occurred via $BaSO_4$ formation and was responsible for the higher values for TDS stabilization. Clearly further work would be needed to elucidate the mechanism of Cr(VI) immobilization in these systems and also to determine whether the optimum $FeCl_2$ addition has been achieved.

5.5.2 *Whole Cement Blocks*

Selected whole cement blocks that were cured for 56 days were partially immersed in 1 liter of water without any further agitation. After 7 days the water was replaced with fresh water and the blocks left partially immersed for a further 7 or 14 days. The results of measurements on the leachate after contact for 7, 14 and 21 days are shown in Table 27. The volumes of leachate decreased due to evaporation. Both the Cr(VI) and TDS concentrations of the leachate decreased with the time of immersion suggesting that no continual leaching took place and the Cr(VI) and salt were effectively retained in the solid stabilized product.

Table 27. Water leaching of cured whole cement blocks

Mix Type	Mass of Block, Kg	Immersion Time Days	Leachate			
			Volume Ml	pH	Concentration, mg/l	
					Cr(VI)	TDS
A	1.351	7	660	9.52	0.000	216
		14	740	9.19	0.000	83
C	1.240	7	720	9.25	0.000	370
		14	790	8.91	0.000	69
H	1.366	7	730	9.01	0.024	274
		14	810	8.92	0.000	79
K	1.360	7	720	9.30	0.064	349
		14	800	9.01	0.000	120
P	1.351	7	690	9.23	0.199	328
		14	800		0.011	109
S	1.353	7	585	9.10	0.024	598
		14	730	8.25	0.008	159
		21	730	8.60	0.012	172
U	1.315	7	540	9.46	0.038	784
		14	740	8.93	0.010	309
		21	780	9.09	0.010	358
W	1.232	7	650	9.89	0.024	685
		14	765	9.19	0.011	385
		21	815	9.27	0.014	216
X	1.247	7	630	9.88	0.011	715
		14	760	9.08	0.008	232
		21	800	9.15	0.007	198

Using these data, the mass of Cr(VI) and TDS leached from the blocks over 14 days was calculated and expressed as mass of component leached per kg of block. These values were compared to those of Cr(VI) and TDS added, and the percentage stabilization of Cr(VI) and salt was calculated. Results are shown in Table 28 and indicate that all the Cr(VI) and nearly 99% of the salts added were retained in the blocks though Cr(VI) and salt loads were increased by factors of 3 and 6 respectively. These Cr(VI) and salt stabilization values for whole blocks are

significantly larger than the corresponding data shown in Table 21 after 56 days curing for the crushed blocks. The significant improvement in salt stabilization observed for whole blocks is attributable to slower diffusion of salts from the larger blocks than the smaller(<10 mm) crushed material. Hence it is possible that whole blocks will effectively retain the undesirable components.

Table 28. Cr(VI) and salt stabilization in whole cement blocks

Mix Type	Cr(VI) mg/kg			TDS g/kg		
	Added	Leached	% Stab	Added	Leached	% Stab
A	0	0	0	11.061	0.151	98.6
C	36.55	0	100.0	17.820	0.259	98.0
H	36.55	0.01	100.0	15.312	0.193	98.7
K	73.09	0.03	100.0	22.348	0.347	98.4
P	73.09	0.11	99.9	20.400	0.232	98.9
S	109.64	0.015	100.0	31.96	0.344	98.9
U	146.18	0.021	100.0	37.16	0.496	98.7
W	182.73	0.019	100.0	43.97	0.600	98.6
X	182.73	0.010	100.0	46.48	0.503	98.9

5.6 Mineralogy of Cement Blocks

The objective of a mineralogical study of cured cement blocks was to identify the mineral phases responsible for the Cr(VI) and salt stabilization that was observed for these systems. Unfortunately a conventional XRD analysis of crushed, cured cement blocks was not successful in identifying the mineral phase responsible for the immobilization. This was primarily due to the fact that the observed XRD spectrum was dominated by solid crystalline phases present mainly in FeCr and EAF slag that was used in the manufacture of the cement block. It was impossible to identify the lesser mineral phases (< 4 mass percent) that could act as binder in the cementitious, immobilization reactions. For this reason 1:1 BFD to cement mixtures and also others doped with sodium chromate were prepared in order to enhance the presence of mineral phases that may be responsible for Cr(VI) and salt immobilization and allow for their detection by XRD and SEM.

The following mineral phases were identified by XRD (see Figure 2) in 1:1 cement : BFD mixtures cured for 7 and 56 days. Those phases originating form the BFD are: altered magnesiochromite $(Mg,Fe)(Cr,Al)_2O_4$, forsterite Mg_2SiO_4 and secondary chromite $Mg(Al_{1.5}Cr_{0.5})O_4$. The phases identified that originate from the cement hydration reactions are: Ca-silicates, portlandite $Ca(OH)_2$ and ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$. The other amorphous phases that may form during the

cement hydration curing reactions can unfortunately not be determined by XRD. Therefore the complete mechanism of Cr(VI) and salt immobilization in these structures can not be completely elucidated by XRD methods. Nevertheless, the observed phases can be used to elucidate some of the possible immobilization mechanisms.

In order to further identify the origin of Cr(VI) immobilization in cement blocks, 1:1 cement : BFD samples doped with $Na_2Cr_2O_7$, were prepared and examined by XRD. The X-ray diffractogram of such a cement block containing 5% Cr(VI) is shown in Figure 3. The only additional Cr(VI) containing phase identified was calcium chromate (chromatite). The solubility of $CaCrO_4$ is of the same order of magnitude as $CaSO_4$ (Kersten, *et al.* 1998) and is not expected to contribute significantly to Cr(VI) immobilization. These observations are similar to those recently reported by Omotso, *et al.* (1998a and b). Further information regarding the mineral phases responsible for effective Cr(VI) and salt immobilization that was observed in this report for the cement based systems were sought by SEM studies.

A SEM study of block L, cured for ~300 days, revealed an unique cluster of needle-like crystals assumed to be ettringite. A portion of the cluster of the crystals found in the electron back-scatter images is shown in Figure 4. Eight points on this image were selected for EDS-analyses that are contained in Table 29. Points 1, 2, 5 and 6 were selected as background whilst points 3, 4, 7, and 8 were within the needle-like crystals and show significant differences. There is relatively more SiO_2, MnO and FeO found for points 1, 2, 5 and 6 (background). The observed values suggest that these points are probably taken in the vicinity of EAF slag that contains predominantly more of MnO and FeO (see Table 10) than the other components used to produce block L. On the other hand, points 3, 4, 7 and 8 contains significantly more SO_3 and CaO. The presence of Al_2O_3 associated with CaO and SO_3 for these points strongly suggests that the crystals are more than likely ettringite. However, it should be noted that the analyses for points 3, 4, 7 and 8 shown in Table 29 for the crystals contain more CaO, Al_2O_3 and SO_3 than expected for ettringite. (Theoretical values expected for ettringite: CaO = 26.8%, Al_2O_3 = 8.1% and SO_3 = 19.1%). Uncertainty associated with standardless EDS analyses and the fact that the analyses were done on unpolished surfaces are probably responsible for the discrepancies.

Although the crystals shown in Figure 4 were unique and did not appear everywhere in block L, it is worth noting that the data shown in Table 29 indicate that no Cr_2O_3 was detected in association with any points, crystals or background. (EDS analyses can not distinguish between the different oxidation states of Cr). This would suggest that in this example Cr is not associated with ettringite and incorporation of Cr(VI) into ettringite may not be a mechanism of immobilization in these cement-based systems using OPC.

Optical microscopy of cured, cement blocks indicated the presence of a transparent film or varnish-like coating covering the surfaces of most of the particles. A secondary electron image of this amorphous, solid, gel-like substance together with rod-shaped crystals that developed during ageing (~300 days curing) for block L are shown in Figure 5. According to the EDS spectrum of this substance, also shown in Figure 5, the major elements contained by the gel-like substance are Ca, Mg, Al and Si, suggesting that it may be a Ca-Mg-Al-silicate. Significant to note is that Cr was also found in this gel-like substance and was always associated with Fe. Hence, it probably presents a Cr-Fe hydroxide, the reaction product when Cr(VI) is reduced with ferrous ions as described previously in section 4.3. It should also be noted that for mix L, $FeCl_2$ was added to remove Cr(VI) from BFD and that the resulting reaction product appears to be incorporated in the Ca-Mg-Al–silicate gel formed during curing of the cement block to bring about Cr(VI) immobilization.

5.6.1 Mechanism of Cr(VI) Immobilization in Cement Blocks

The mineralogical examination of cured cement blocks presented evidence suggesting that a mechanism for Cr(VI) immobilization in these systems is via the reduction of Cr(VI) with Fe(II). This is further confirmed by the fact that the highest percentage Cr(VI) stabilization observed in this study was reported for instances where $FeCl_2$ was directly added to the cement mixes (see results for blocks C, D, K, L, Q to X shown in Tables 20, 21, 25 and 26) prior to curing. In these instances the reduction of chromate by ferrous ions probably took place prior to the hydration of cement and its associated cementitious reactions. Under these circumstances it is possible that the added, acidic $FeCl_2$ may have induced lower localized pH values than those of 12 that were measured in these systems. It is therefore likely that the chemical reduction of chromate took place within the effective pH range quoted by Eary, *et al.* (1988) and Pettine, *et al.* (1998), The Cr-Fe hydroxide precipitate formed as a result of this reaction does not leach any Cr(VI), as demonstrated by the results

shown in Table 8, and when subsequently being incorporated into the Ca-Mg-Al-silicate gel presents an effective means of Cr(VI) immobilization in these systems.

Figure 2. X-ray diffractograms of phases identified in BFD-cement blends after 7 and 56 days curing

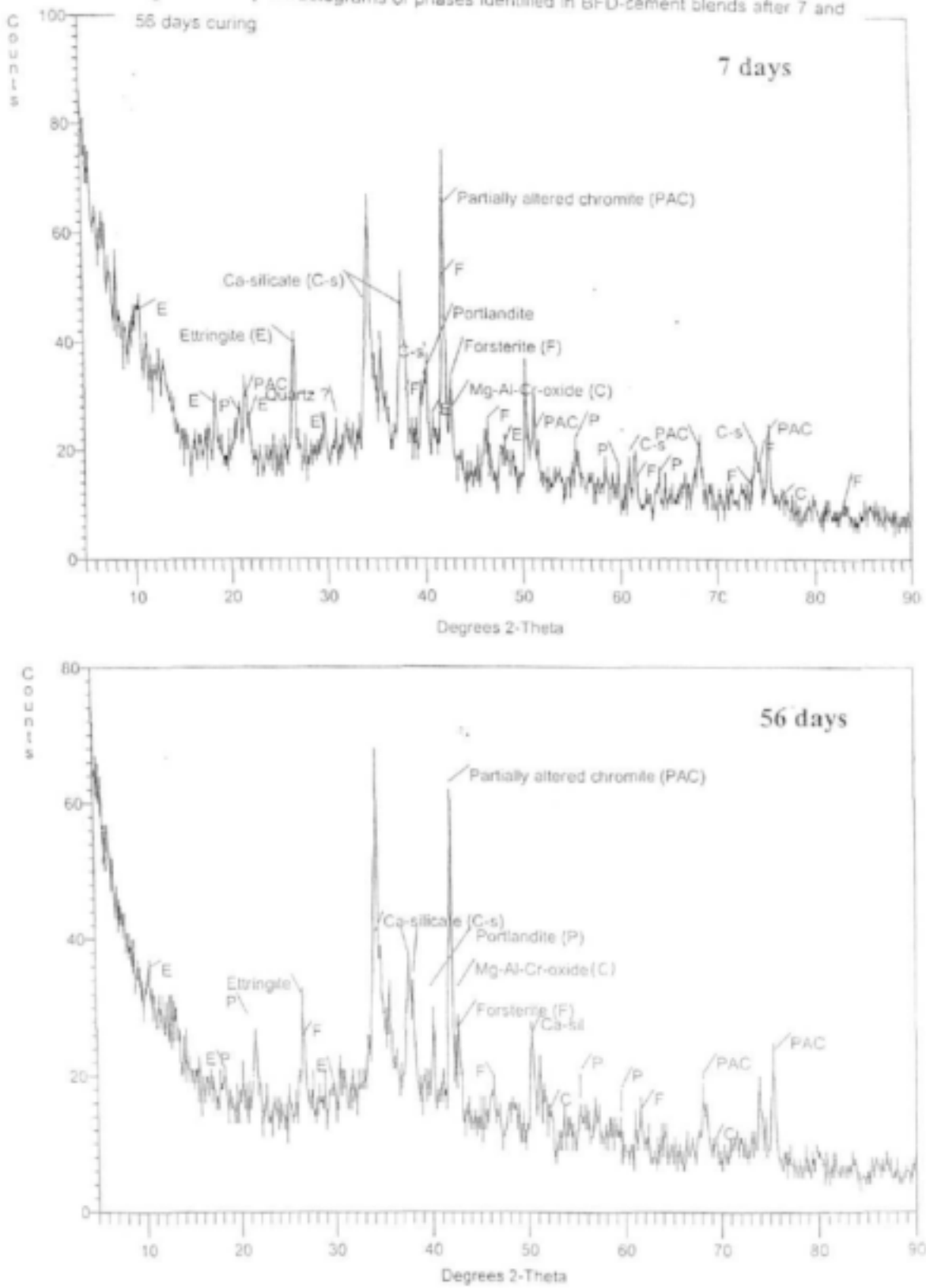


Figure 2. X-ray diffractograms of phases identified in BFD-cement blends after 7 and 56 days curing

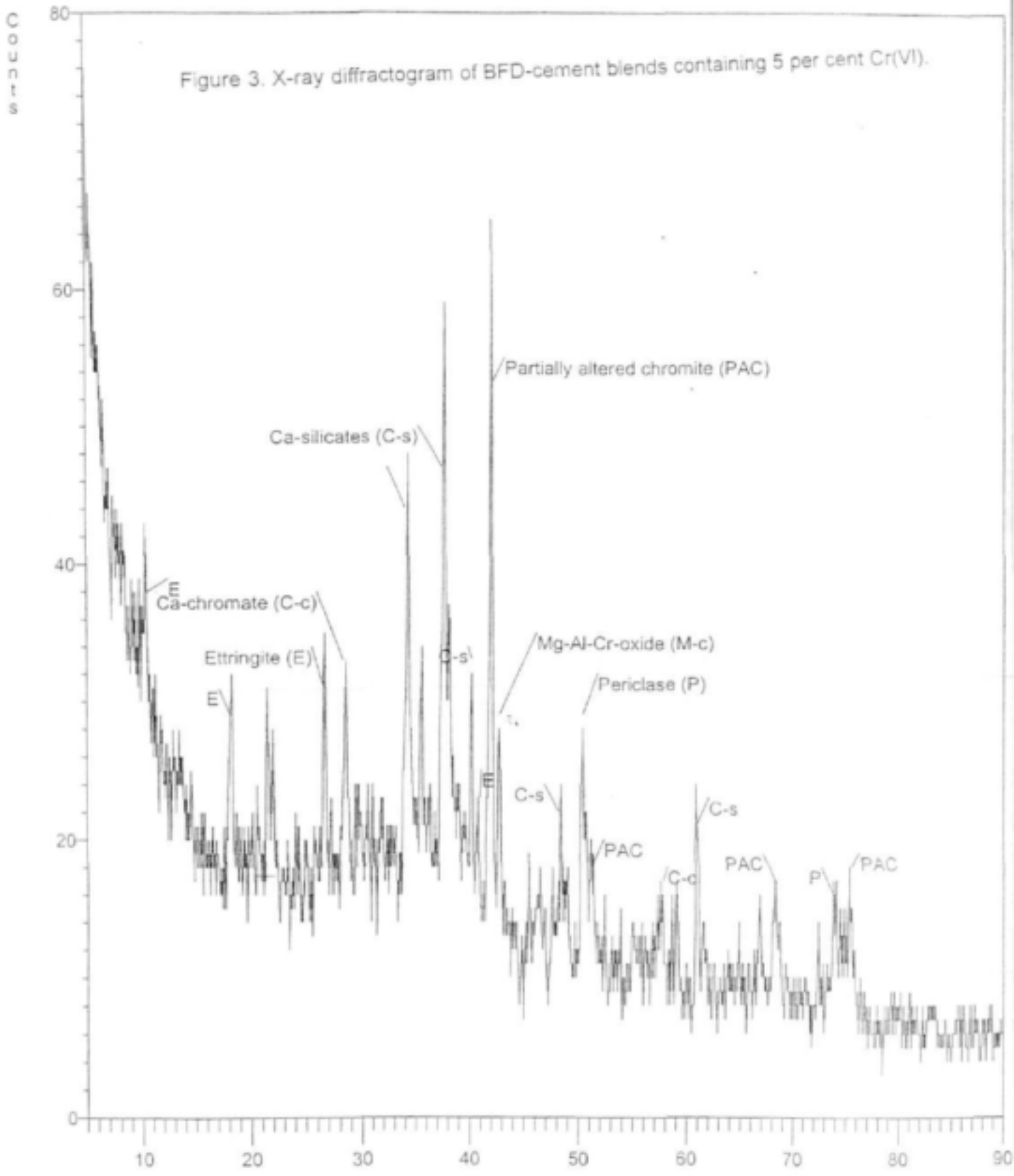


Figure 3. X-ray diffractogram of BFD-cement blends containing 5 per cent Cr(VI).

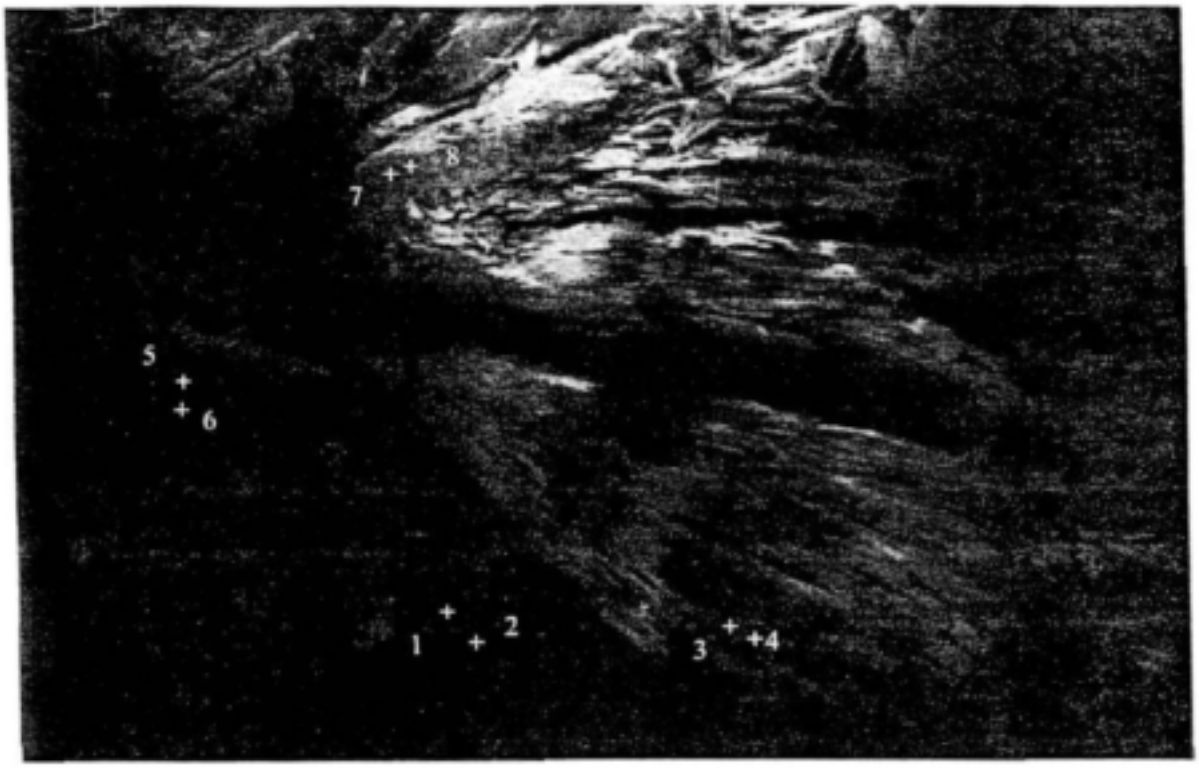
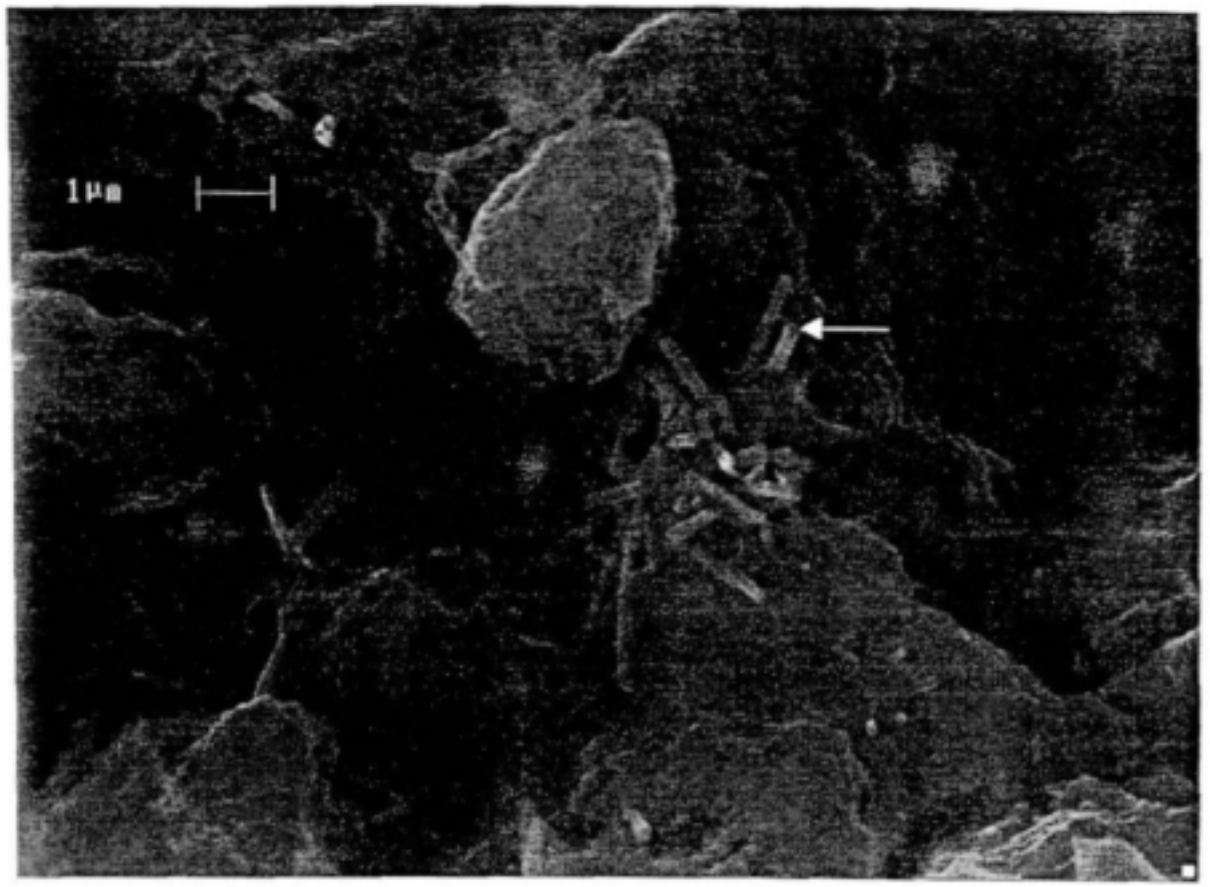


Figure 4. Back-scatter electron images of ettingrite crystals found in cement block L (approximately 300 days curing). The numbers on the image correspond to EDX-analysis indicated in Table 29. (Scale : - 5 micrometer.)

Table 29. Standardless EXD-analysis of an example of ettingrite and the EAF-substrate (Analyses obtained by SEM from cement block I – 300 days curing)

Label	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	MnO	FeO	Total
Point 1	4.7	0.5	19.7	17.9	1.2	1.3	3.2	1.7	28.2	7.3	85.7
Point 2	2.2	0.2	16.1	14.6	0.6	1.0	3.1	1.8	28.0	7.0	74.6
Point 3	3.2	0.3	14.7	0.4	30.2	0.1	38.5	0.2	0.3	0.4	88.4
Point 4	3.1	0.2	13.5	0.4	29.4	-0.1	38.4	0.0	0.9	0.3	86.2
Point 5	4.5	0.5	23.0	22.2	1.0	1.0	3.1	1.5	28.3	7.8	93.0
Point 6	4.8	0.7	26.2	26.2	0.8	1.2	2.9	1.7	25.4	7.6	97.3
Point 7	1.9	0.4	24.6	9.9	19.5	0.4	25.3	0.2	2.9	1.7	86.8
Point 8	0.4	0.0	12.6	2.0	22.3	0.1	33.8	0.0	0.8	0.6	72.7



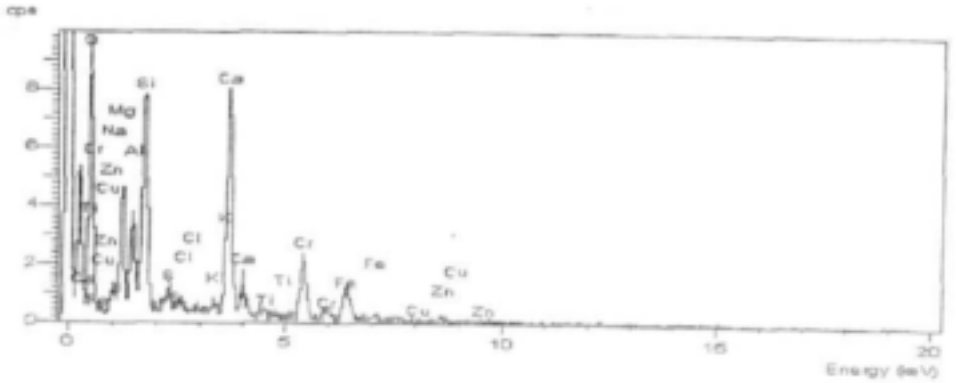


Figure 5. Secondary electron image of rod-shaped crystals of Ca-Mg-Al-silicate which developed from the rigid gel substrate. (Sample – cement block L, approximately 300 days curing.) The EDS-spectrum of the element ratios obtained is presented below. The position of analysis is indicated by the arrow in the top image

The addition of crushed EAF slag to the cement mixes also makes a contribution to the observed Cr(VI) immobilization in cured cement blocks. In cases where it was not added (mixes B and J) the poorest Cr(VI) stabilization was observed, see results in Tables 20 and 21, for 28 and 56 days curing, respectively. Conversely, where it was added and blocks were cured for 120 days, the highest Cr(VI) stabilization result was obtained. The observed removal of Cr(VI) by EAF slag (see results shown in Table 9) is likely due to the presence of the mineral wuestite (FeO) participating in a chromate adsorption-reduction mechanism as was observed for magnetite (Peterson, *et al.*, 1997).

It is postulated that particularly the chromate in BFD that leaches slowly and may not have been reduced with $FeCl_2$ could be immobilized by the wuestite contained in EAF slag. What is not certain is the extent to which the wuestite surface may become oxidized and passivated under the alkaline conditions prevailing in the cement block as was observed for magnetite. Results observed in this study suggest that this may not be too serious a limiting factor in the chromate reducing capacities of EAF slag. This aspect is examined further in this study in acid leaching experiments on the solid stabilized products.

The data presented in this report suggests that another proposed mechanism for chromate immobilization, by the formation of a $Ba(S,Cr)O_4$ solid solution seems less likely in these systems. The Cr(VI) stabilization observed for mixes Y and Z (see Table 26) where $BaCl_2$ was added deliberately was relatively poor. Neither were there ever any Ba-Cr combinations observed in the cured cement blocks studied by electron microprobe methods.

5.6.2 Mechanism of Salt Immobilization in Cement Blocks

The mineral ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, was observed by SEM (see Figure 4) in cement block L and also by XRD (see Figure 2) in cement-BFD mixtures. The presence of this mineral in the cured cement blocks prepared in this study suggests that this could be a mechanism by which sulphate ions are immobilized in these systems. This may be the reason for the observed SO_4 stabilization shown in Table 23. The improved salt stabilization observed in Table 26 for mixes Y and Z where $BaCl_2$ was added suggests that $BaSO_4$ formation in this instance may contribute to the SO_4 immobilization. However, this means of salt stabilization is probably only

applicable to cases where $BaCl_2$ is added. The Ba present in EAF slag (see Table 11) was probably not sufficient to have significantly contributed in other cases.

As calcium aluminate minerals were formed in the systems studied in this report it is possible that Cl analogues of ettringite, Friedel's salt, $Ca_2Al(OH)_6Cl.2H_2O$ (Taylor, 1997) could have been formed. If this were the case then this mineral could be responsible for the immobilization of Cl shown in Table 23. However, it should be noted that no evidence of Friedel's salt was found by XRD nor was there any Cl detected in the EDS spectrum (see Table 29) of ettringite shown in Figure 4.

The results shown in Tables 21 and 25 indicate an overall salt stabilization of 50 per cent or less in the systems studied. The reason for this relatively poor performance in comparison to Cr(VI) stabilization may be that these cement systems have no effective means of stabilizing Na and K as the results in Tables 23 and 24 clearly indicate. To improve overall salt stabilization, additives may be required that will immobilize these elements similar to the way that $FeCl_2$ immobilizes chromate. Alternatively, other systems may be sought as will be discussed later in this report.

5.7 Acid Leaching Tests on Crushed Cement Blocks

The success of the exercise to produce cement-based solid stabilization with chromate containing BFD is ultimately judged on the extent to which these products can safely be disposed of without posing a threat to health and the environment. For this purpose acid leaching tests were conducted on the crushed cement blocks employing techniques recommended in the recently published DWAF (1998) Guidelines. TCLP and Acid Rain leaching tests were used.

5.7.1 TCLP Leaching Tests

These tests were conducted according to the DWAF (1998) stipulated procedures. The analyses of leachates (determined by ICP-MS in the Analytical Science Division of Mintek) obtained from TCLP tests of different cement blocks are shown in Table 30. The final pH values of the leachates after 18 hours of agitation are also included in Table 30 as well as the maximum allowed concentrations of components stipulated by the US EPA for the TCLP test. None of the concentrations of the components in the leachates exceeded these stipulated values. No explanation can be offered why the final pH values of leachates of crushed blocks made from mixes N and P are

more acid than the others. Blocks made from mix P in particular (see Table 15) would be expected to produce a more alkaline leachate because they contain more EAF slag and a high concentration of free Ca. On the other hand it should be noted that the EAF slag is the waste with the highest Mn content (see Table 10). Hence the relatively larger amount of this component in the mixes N and P, coupled with the lower final pH values observed for these leachates, resulted in higher Mn concentrations being recorded in these instances (see Table 30). The same reason can be given for higher Ba concentrations observed in Table 30 for leachates from crushed blocks made from mixes N and P. EAF slag also contains the highest Ba content of all the wastes used to produce cement blocks.

Table 30. TCLP test results on crushed cement blocks after 56 days curing

Mix	Final	Concentration, mg/l									
No	pH	V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
A	11.12	<0.1	<0.1	<0.1	<0.5	<1.0	0.67	<0.05	0.26	<0.05	<0.05
C	10.39	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	0.23	<0.05	0.34
H	11.00	<0.1	0.26	<0.1	<0.5	<1.0	<0.1	<0.05	0.24	<0.05	0.15
K	10.43	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	0.23	<0.05	<0.05
N	6.42	<0.1	<0.1	16.5	<0.1	<1.0	<0.1	<0.1	0.88	<0.1	<0.05
P	7.17	<0.1	<0.1	23	<0.1	<1.0	<0.1	<0.1	0.86	<0.1	0.71
TCLP			5		5	1	5	1	100	0.2	5

5.7.2 *Acid Rain Leaching Tests*

The pH values and the analyses of the leachates obtained from Acid Rain leaching tests after 20 hours agitation are shown in Table 31. Cr was the only component that was detected in the leachates above the analytical detection limit. This was observed for leachates obtained from crushed cement blocks made from mixes H, K, N and P. Generally, lower metal concentrations were observed in the leachates obtained from crushed cement blocks for Acid Rain (see Table 31) than for TCLP (see Table 30) leaching tests. This observation demonstrates the fact that the leachability of metal components from solid stabilized products depends not only on the final pH value of the leachate but also possibly on the medium of extraction. This aspect will be investigated in more detail in the following section in both nitric and acetic acid media. These leaching conditions are more severe than in the TCLP and Acid Rain tests. However, this would allow for a more stringent evaluation of the potential environmental impact of the solid stabilized product and hopefully would also give a clearer distinction between the efficiency of immobilization of undesirable wastes for different solid stabilized systems.

Table 31. Acid rain test results on crushed cement blocks after 56 days curing

Mix No	Final pH	Concentration, mg/l									
		V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
A	6.33	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
C	5.82	<0.1	<0.1	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	0.08
H	6.19	<0.1	0.12	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
K	5.84	<0.1	0.12	<0.1	<0.5	<1.0	<0.1	<0.05	<0.05	<0.05	<0.05
N	6.02	<0.1	0.21	<0.1	<0.1	<1.0	<0.1	<0.1	<0.05	<0.1	<0.05
P	5.94	<0.1	0.14	<0.1	<0.1	<1.0	<0.1	<0.1	<0.05	<0.1	<0.05

5.7.3 Nitric and Acetic Acid Leaching Tests

The concentrations of V, Cr, Mn, Zn, Pb and Cd in the leachates as a function of pH in nitric acid medium for cured, crushed cement blocks made from mixes D, J and O are shown in Table 32. Results of similar tests and those using acetic acid medium are shown in Table 33 for cured, crushed cement blocks made from mix M. For Cr, both the total Cr and Cr(VI) concentrations are reported. The difference between these values is ascribed to the concentration of the non-toxic Cr(III). The results shown in Tables 32 and 33 indicate that the concentrations of Cr tot, Mn, Zn and Pb increase with decreasing pH value of the leachates. On the other hand, no significant changes in V, Cr(VI) and Cd concentrations were observed in the leachates as a function of pH.

Table 32. Nitric acid leaching test results on crushed cement blocks D, J and O

Mix No	Final pH	Mequiv /g	Concentration, mg/l						
			V	Cr tot	Cr(VI)	Mn	Zn	Pb	Cd
D	11.49	0.00	0.02	0.12	0.00	0.01	<0.01	<0.01	<0.01
	3.95	1.13	<0.01	0.03		2.4	2.9	<0.01	<0.01
	2.16	2.25	<0.01	2.5		13	11	0.10	<0.01
	1.96	3.38	<0.01	4.0		12	13	0.24	<0.01
	1.46	4.73	<0.01	4.9	0.01	16	13	0.40	<0.01
J	11.34	0.00	0.04	0.41	0.35	0.05	0.02	<0.01	<0.01
	7.67	1.13	0.03	0.38	0.60	0.3	0.04	<0.01	<0.01
	3.43	2.25	0.03	1.4	0.01	4.9	19	0.08	<0.01
	2.77	3.38	<0.01	4.6	0.01	6.2	22	0.40	<0.01
	1.45	4.73	0.15	6.9	0.12	8.0	26	0.6	<0.01
O	10.98	0.00	<0.1	0.20	0.11	<0.1	0.15	<0.05	<0.02
	5.62	1.13	<0.1	<0.1	0.02	4.8	7.6	<0.05	<0.02
	3.46	2.25	<0.1	2.1	0.01	19	40	0.09	<0.02
	2.91	3.38	<0.1	6.0	0.05	27	44	0.24	0.02
	2.38	4.50	<0.1	9.8	0.07	41	50	0.38	<0.02

In an attempt to establish the origin of the observed metal in the leachates, their concentrations were correlated with the quantities (see Table 15) of wastes used to prepare the mixes and their analyses (see Tables 10 and 11). For the observed Mn

concentration in the leachates shown in Tables 32 and 33 in the nitric acid medium such a correlation was possible. The Mn concentration in the leachates at the lowest pH value follows the order: O>M>D>J and this is also the order of the amount of EAF slag added to the mixes. Since the EAF slag contains the most Mn in the wastes used to compose the mixes, it is more than likely that the increasing Mn concentration measured in the leachates at lower pH values originates from this source.

Table 33. Nitric and acetic acid leaching test results on crushed cement block M

Acid	Final pH	Mequiv /g	Concentration, mg/l						
			V	Cr tot	Cr(VI)	Mn	Zn	Pb	Cd
HNO_3	10.71	0.00	<0.1	0.51	0.1	0.21	0.67	<0.05	<0.02
	8.60	0.113	<0.1	<0.1	0.00	0.27	<0.1	<0.05	<0.02
	4.22	0.225	<0.1	0.12	0.07	10	25	<0.05	<0.02
	3.68	0.338	<0.1	3.8	0.12	24	59	0.14	<0.02
	2.49	0.45	<0.1	11	0.08	33	68	0.38	0.02
Acetic	11.38	0.00	<0.02	0.25	0.18	<0.1	<0.1	<0.02	<0.02
	6.60	1.075	<0.02	<0.1	0.00	3.7	3.6	0.03	<0.02
	5.45	2.149	<0.02	0.37	0.00	12	17	<0.02	<0.02
	4.93	3.224	0.03	1.3	0.00	15	22	<0.02	<0.02
	4.68	4.298	0.03	2.4	0.00	17	23	0.40	<0.02
	4.37	6.447	0.11	3.6	0.00	21	27	0.07	<0.02

A similar correlation to establish the origin of the observed increase in Cr tot concentration in nitric acid medium in the leachates with decreasing pH values is not so obvious. The Cr tot concentration in the leachates at the lowest pH values follows the sequence: M>O>J>D. The wastes with the highest Cr content used to prepare the mixes was FeCr slag and BFD. The amount of FeCr slag used in the mixes follows the order: J=D>M>O and for the BFD used the order was: M=O=J>D, neither fully conforming to the observed decrease in Cr tot concentration. Unfortunately the Fe concentration in the leachate was not measured in these tests. It should be pointed out that only for mix D was $FeCl_2$ added to immobilize the Cr(VI). It is not certain whether this addition of ferrous chloride for mix D is responsible for the low Cr tot measured in the corresponding leachate. On the other hand it is interesting that the observed Cr(VI) concentration in the leachates remains constant and is not affected by the pH value thereof. Therefore, it can be concluded that the increased leaching of Cr from cement stabilized solids at lower pH values arises from the extraction of the non-toxic Cr(III) and not from the Cr(VI) that was immobilized. Hence the original objective of cement-based solid stabilization to immobilize Cr(VI) has been achieved even with leachates of lower pH values. However, under these conditions other undesirable components in the wastes now start to appear in the

leachates, indicating that the other wastes used to achieve this objective have to be subjected to further scrutiny.

The observed increase in Zn concentration towards lower pH values, shown in Tables 32 and 33, for the leachates in nitric acid medium follows the order: M>O>J>D. The waste with the highest Zn content used to prepare the cement blocks was BFD. The quantities used follow the order: M=J=O>D which unfortunately does not fully conform to the observed sequence of observed Zn concentrations. So it must be concluded that Zn from other sources than the BFD contributed to the observed concentrations in the leachates towards lower pH values. Similar conclusions can be made for the origins of Pb concentrations observed in Tables 32 and 33 for nitric acid leachates towards lower pH values. The Pb more than likely originates from the BFD, the waste containing the most Pb, however, to account for the observed Pb concentrations, contributions from other Pb-containing wastes may also have to be considered.

Since an acetic acid medium was used in the TCLP test the leaching of cement blocks M with both nitric and acetic acids was undertaken and results are shown in Table 33 as a function of pH. Due to the buffering action of acetic acid it is not possible to conduct leaching tests in this medium to the same low pH values as for nitric acid. Comparing the metal concentrations, shown in Table 33 in different media for the same pH values, indicates that similar amounts of Cr(VI), Zn and Pb report to the leachates. However, the results in Table 33 indicate that more V and Cr tot tend to leach in the acetic- than the nitric acid medium.

5.8 Potential Toxicity of Cement Blocks

The results of the above leaching tests were used to evaluate the potential toxicity of the cement blocks in accordance with the recently published DWAF (1998) Guidelines. According to these Guidelines the acceptability of disposal of hazardous wastes is based on the relationship between the acute ecotoxicity of a substance, expressed as LC_{50} (mg/l) and the Estimated Environmental Concentration (EEC) expressed in ppb. LC_{50} = median lethal dose, is a statistical estimate of the amount of chemical which kills 50 per cent of a given population of aquatic organisms under standard conditions. EEC represents the exposure as a result of a hazardous substance in the treated waste should it enter into the environment. EEC (ppb) = dose (g/ha/month) x 0.66. The results of the leaching tests are used to calculate the

EEC if information about the area of the dumping site and the rate of delivery of waste thereto is available. It is assumed that if the EEC is a tenth of LC_{50} the waste has a limited effect on the environment and this is regarded as the Acceptable Risk Level (ARL). Listed in Table 34 are, according to the DWAF Guidelines, the values for the Hazard Rating, ARL and Allowed Disposal Rate for the elements/components, shown by the TCLP and Acid Rain tests in the previous sections, that may leach from crushed cement blocks.

Table 34. Hazardous Waste Classification of Certain Elements (DWAF, 1998)

Element/ Compound	Hazard Rating	ARL mg/l	Allowed Disposal Rate (g/ha/month)
As	2	0.43	651
Ba	3	7.8	11818
Cd	1	0.031	47
Cr(III)	3	4.7	7121
Cr(VI)	1	0.02	30
Na dichromate	2/3	1.5	2272
Pb	2	0.1	151
Mn	2	0.3	454
Hg	1	0.022	24
Ag	3	2	3030
Se	2	0.26	394
V	3	1.3	1970
Zn	2	0.7	1061

The Hazard Rating assigned to a substance depends on the LC_{50} value. For values < 1 a Hazard Rating of 1 is given; for LC_{50} < 10 a Hazard Rating of 2 is a assigned and further for every increase by a factor of 10 in LC_{50} values, the Hazard Rating increases by one unit. From the leaching tests conducted, Cr(VI) is the most hazardous substances found in the cement-based stabilized products made in this study. The other elements with Hazard Rating of 1, Cd and Hg, do not feature in the TCLP and Acid Rain leaching tests (see Tables 30 and 31). It is therefore obvious that the toxicity of the prepared cement-based solid stabilized products would firstly be judged on the extent by which the Cr(VI) has been immobilized in these systems. It should also be noted that according to the DWAF Guidelines (see Table 34) sodium dichromate has a higher Hazard Rating than Cr(VI). The results presented in chapter 4 indicated that the Cr(VI) contained in ferrochrome BFD is in a sodium chromate form so it may be argued that the higher Hazard Rating and ARL concentrations should apply to this study rather than the more stringent Cr(VI) data listed in Table 34. Nevertheless, both criteria would be used in the evaluation of the cement-based solid stabilized products prepared in this study.

Table 35. Chromate Toxicity of Cement-Based Products

Mix No	Curing time days	Block type	Leaching time days	Mass kg	Cr(VI) conc mg/l	Volume ml	Cr(VI) leached mg/kg	EEC ppb	
								Cr(VI)	$Na_2Cr_2O_7$
H	56	whole	7	1.366	0.024	730	0.0128	2.27	6.05
K	56	whole	7	1.360	0.064	720	0.0339	6.00	17.21
U	56	whole	7	1.315	0.038	540	0.0156	2.76	7.92
X	56	whole	7	1.247	0.011	630	0.0056	0.99	2.84
K	56	crushed	1	0.100	0.159	1000	1.5900	281.7	807.3
K	120	crushed	1	0.100	0.069	1000	0.6900	122.2	350.3
U	56	crushed	1	0.100	0.028	1000	0.2800	49.6	142.2
X	56	crushed	1	0.100	0.20	1000	2.0000	354.3	1015.4
Cr(VI)				0.100	0.017	1000	0.1690	20*	
Nodichromate				0.100	0.448	1000	4.448		1500*

* DWAF ARL limits

The chromate toxicity of some whole and crushed cement blocks were evaluated as shown in Table 35. This was based on the water leaching data for whole (see Table 27) and crushed (see Appendices C and D) cement blocks. These values were used to calculate the amount of Cr(VI) leached per kg of block, crushed or whole. (The spectrophotometric method used to measure the Cr (VI) in water leaching is specific for Cr(VI). The acid leaching tests conducted on these materials, see Tables 32 and 33, indicated that the Cr(VI) concentration in the leachate is independent of the pH. Hence the water leaching test results on these materials may be regarded as an adequate and sensitive test for assessing the influence of Cr(VI) on the environment). To convert the water leaching test results to the corresponding EEC values, the data on the dosage of waste to the dumpsite, expressed in g/m/ha, would be required. To obtain a realistic figure the following assumptions were made: The estimated total annual production of Cr(VI) containing BFD and sludge was shown in Appendix A estimated to be 96624 tpa. There are 10 local ferrochrome producers and assuming each has at their disposal a 30 ha dumpsite where slag and cement-based BFD products could be dumped. The cement-based products made in this study contain 6 to 15 per cent BFD, an average of 10 percent is assumed. Using this information it seems reasonable to assume a dumping rate of 2.684×10^5 kg/ha/month for cement-based products made from ferrochrome BFD and slag. With this assumption the EEC values (ppb) for Cr(VI) were calculated from the water leaching data and are shown in Table 35. For cement-based products to pose no risk to health and the environment the calculated EEC must be less than the ARL value both expressed in ppb units.

For all the whole cement blocks, the EEC values for Cr(VI) are less than the 20 ppb stated in Table 34 for the ARL value. Therefore, based on the assumptions made, whole cement blocks pose no risk. This suggests that whole blocks could safely be dumped or be used as landfill. On the other hand for the crushed cement blocks, the Cr(VI) EEC values calculated from the leaching data are all larger than the ARL value and therefore the product still poses a risk and cannot be dumped. Hence cement blocks should be strong to limit the extent of their crushing during dumping.

Since sodium dichromate contains 34.89 per cent chromate, the Cr(VI) EEC values for whole and crushed cement blocks were converted to the corresponding $Na_2Cr_2O_7$ values. These EEC values are also shown in Table 35. The highest calculated sodium dichromate EEC value, 1015 ppb, was reported for crushed cement blocks made from mix X. This is below the ARL value (1500 ppb) quoted in Table 34 for $Na_2Cr_2O_7$. Therefore, all the calculated EEC sodium dichromate values are less than the acceptable ARL value as stipulated by the DWAF Guidelines. Based on this assessment, both the whole and crushed cement-based solid stabilized products containing BFD pose no risk to health and the environment. This is in contrast to the conclusions reached on the evaluation based on the Cr(VI) EEC values where only the whole cement blocks were acceptable.

The results in Table 35 also contain theoretical chromate concentration limits for the leachate, beyond which under the stipulated experimental leaching conditions, the product would pose a risk to the environment. For Cr(VI) this was 0.017 mg/l and for sodium dichromate 0.448 mg/l. The Cr(VI) concentrations in the leachates shown in Tables 18 and 19, Appendices B, C and D mostly fall within these limits, particularly for those blocks cured for more than 28 days. The majority of blocks cured for a shorter period, produced leachates containing Cr(VI) outside these limits, thus indicating that curing time is important to achieve the desired Cr(VI) immobilization in these systems.

The TCLP and Acid Rain tests for cement-based solid stabilized BFD (see Tables 30 and 31) under sufficiently alkaline conditions (pH >10) produced no metal concentrations except Cr higher than the ARL values given in Table 35. However if leaching was conducted under more acidic conditions, Cr(III), Mn, Zn and Pb concentrations are observed in the leachate that exceed the ARL values listed in Table 34. Mn and Zn showed the largest deviations. This emphasizes that that the above cement-based treatment of BFD is only effective under alkaline conditions. On

the other hand, conducting leaching tests under more acidic leaching conditions, outside the normal scope of the testing procedure, is useful to compare the efficiency of immobilization of different solid stabilized systems as will be discussed later in the report.

It can therefore be concluded that by producing cement-based products incorporating BFD, a plausible disposal option has been found for the local ferrochrome industry for handling this toxic waste. However, in view of some of the assumptions made in this evaluation, particularly with regards to actual disposal rates of these cement-based solid stabilized systems, this conclusion should be re-examined for each individual application. The potential toxicity analysis of these products also suggested that it would be necessary to produce strong cement blocks to minimize crushing during disposal and ensure sufficient alkalinity therein to prevent leaching of other toxic constituents in the waste.

5.9 Potential for Commercialization and Utilization

The compressive strength of cement blocks made with BFD, EAF and FeCr slag (see Table 17) complied with the SABS specifications. Standard stock bricks of dimension 22.3 x 10.8 x 7.6 cm^3 could therefore be made using the mixes shown in Tables 15 and 16 and used for various building applications. Based on the masses of materials used in mix W or X, assuming that the cost of production is only that of cement (R200/t) and of $FeCl_2$ (R1400/t), the cost to produce 1000 bricks of this type would be R146.70. This price compares favourably with that currently paid in the industry of R150-200 per 1000. The bricks are relatively heavier than normal building bricks, density 2.27 g/cm^3 and are probably more suitable for use as paving bricks. Transport costs would also have a bearing on the feasibility of a commercial venture of this nature. The negative stigma associated with utilizing a treated toxic waste as a building material would have to be overcome. Whether this can be achieved remains to be seen and more work would be required to adequately demonstrate that these cement blocks pose no threat to the environment or health in the short or longer term. Special precautions would also have to be taken to ensure the safety of workers during brick making, wearing the appropriate safety equipment to eliminate their exposure to BFD before it is safely immobilized.

The economics of the waste treatment process can be evaluated in another way if the cement blocks were to be manufactured solely for disposal of BFD. Using the

composition of mixes W and X and the same costs of cement and $FeCl_2$ mentioned above, it would cost R235/t of BFD treated in this manner. This cost is comparable to the current R250/t disposal cost for hazardous waste charged by Enviroserve, a local industrial waste management company. If so desired, the whole cement blocks would not pose a threat to the environment and could be safely used as landfill. Thus, as a result of this study, a process has been developed that provides a safer disposal option for ferrochrome BFD.

6. FERROCHROME WASTE FIRED CLAY BRICKS

The immobilization of Cr(VI) containing BFD into fired clay bricks was another solid stabilization option considered in this study. The results of this investigation are reported in this chapter along similar lines to those of the previous chapter dealing with cement-based systems.

6.1 Materials

Clay used in the manufacture of fired clay bricks was obtained from a brick manufacturer in the vicinity of a ferrochrome producer situated in the North West Province. The chemical composition of the clay is given in Table 36. Mineralogical analysis of the clay by XRD indicated the presence of minerals: illite (K-Al-Silicate) found in the clay fraction, quartz in the non-magnetic fraction and in the small magnetic fraction, iron oxides, ilmenite and chromite were found.

Table 36. Chemical Composition of Clay

	Percentage Composition								
Compo-sition	CaO	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	Cr_2O_3	MnO	Fe_2O_3
	0.71	64.7	13.4	1.47	0.43	1.42	<0.2	0.15	8.05

6.2 Manufacture of Fired Clay Bricks

Different masses of clay, BFD, salts and coal (see Table 37) were mixed in a mechanical mixer with a minimum amount of water (20 % by mass of total solids). The compositions of 11 different batches are shown in Table 37. The mix was then pressed into a compact brick with dimensions 42mm x 78mm x 115mm using a Tinius Olsen Press at 25 kN. Thereafter the bricks were allowed to dry at room temperature for a week before heating in a kiln, where the temperature was increased from 25 to 1200 °C over 48 hours, kept at constant temperature for 6

hours, and then cooled to room temperature for 48 hours. The influence of temperature on effective stabilization of Cr(VI) and salts was investigated on 12 clay bricks produced with composition corresponding to mix number 11. In this instance two bricks were heated at a time to various temperatures, ranging from 550 to 1050 °C for 6 hours in a Labcon furnace.

Table 37. Composition of Mixes Used in the Manufacture of Fired Clay Bricks

Mix Number	Mass, grams						
	Clay	BFD	Coal	$K_2Cr_2O_7$	NaCl	Na_2SO_4	Dry Brick
1	400	400	0	0	0	0	800
2	400	400	0	1	0	0	801
3	400	400	0	2	0	0	802
4	400	400	0	4	0	0	804
5	400	400	0	0	10	10	820
6	400	400	0	0	20	20	840
7	400	400	0	0	40	40	880
8	800	0	0	0	10	10	820
9	800	0	0	0	20	20	840
10	800	0	0	0	40	40	880
11	400	400	24				824

6.3 Water Leaching Tests of Crushed, Fired Clay Bricks

As discussed in the previous chapter, the degree of Cr(VI) and salt immobilization in the solid stabilized systems can be effectively measured by conducting water leaching tests on the crushed materials. Results of experiments conducted on different clay bricks fired at 1200 °C and then on bricks fired at different temperatures are discussed.

6.3.1 Clay Bricks Fired at 1200 °C

Clay bricks that were fired at 1200 °C were crushed and leached with water for various periods. (Compositions of the different mixes that were used in the manufacture of the bricks were given in Table 37). The pH values, and Cr(VI) and TDS concentrations that were measured for the leachates after 1 and 4 days of continuous agitation are shown in Table 38. The Cr(VI) and salt concentrations in the water leachates obtained from crushed, fired clay bricks are significantly lower than those observed for crushed, cured cement blocks (see Tables 18, 19 and Appendices B, C and D). In this regard, it should also be noted that fired clay bricks contained 50 per cent BFD whilst cured cement blocks contain only a maximum of 15 per cent BFD. Furthermore in some mixes additional Cr(VI) as ($K_2Cr_2O_7$) and salts

were added during the manufacture of the clay bricks (see Table 37) to further increase the chromate and salt load. Notwithstanding the higher Cr(VI) and salt load in fired clay bricks these components appear to be more effectively immobilized in this method than in cured cement blocks.

Table 38. Water Leaching of Clay Bricks Fired at 1200 °C

Mix Type No	Leaching Period, days	Leachate		
		pH	Concentration, mg/l	
			Cr(VI)	TDS
1	1	9.23	0.031	63
	4	9.42	0.015	85
2	1	9.19	0.132	75
	4	9.60	0.077	38
3	1	9.57	0.148	75
	4	9.86	0.004	35
4	1	8.77	0.208	83
	4	9.35	0.025	30
5	1	9.24	0.235	58
	4	9.53	0.070	33
6	1	9.34	0.247	325
	4	9.28	0.001	140
7	1	9.35	0.117	380
	4	9.39	0.000	150
8	1	8.78	0.001	450
	4	8.94	0.000	100
9	1	8.34	0.002	205
	4	8.73	0.000	95
10	1	7.83	0.007	515
	4	8.34	0.000	70

On the basis of the water leaching tests on fired clay bricks, (Table 38) the percentage Cr(VI) and TDS stabilization was calculated using the same procedure as for the cured cement blocks. These values are shown in Table 39 for the 10 different types of clay bricks that were fired at 1200 °C. High Cr(VI) stabilization (>99.5%) was observed even with a four fold increase in Cr(VI) addition to the mix. Good salt stabilization values (>90%) were also observed, except for mix number 8 where no BFD and the least amount of salt was added. By contrast, for mix number 7 with a more than 3-fold increase of salt addition, a salt stabilization of 96% was achieved. The remarkable results shown in Table 39 justifies that further work be conducted on the mechanism of salt and Cr(VI) stabilization in these systems. One aspect that was investigated further was the influence of firing temperature on the extent of Cr(VI) and salt stabilization.

Table 39 Stabilization of Cr(VI) and Salt in Crushed Clay Bricks Fired at 1200 °C

Mix No	Cr(VI), mg/kg			TDS, g/kg		
	Added	Leached	% Stab	Added	Leached	% Stab
1	609	0.58	99.9	46.275	1.675	96.4
2	1050	2.19	99.8	47.466	1.375	97.1
3	1489	1.52	99.9	48.653	1.300	97.3
4	2365	2.42	99.9	51.020	1.275	97.5
5	594	3.15	99.5	69.537	1.000	98.6
6	580	2.48	99.6	91.690	4.650	94.9
7	554	1.17	99.8	132.977	5.300	96.0
8	0.0	0.01	0	24.390	5.500	77.4
9	0.0	0.02	0	47.619	3.000	93.7
10	0.0	0.07	0	90.909	5.850	93.6

6.3.2 Clay Bricks Fired at Various Temperatures

Clay bricks (mix 11, Table 37) were fired at various temperatures and after cooling to room temperature were leached with water. The pH, Cr(VI) and TDS concentrations in the leachates obtained from these tests (for 24 and 48 hour periods) are shown in Table 40 for bricks fired at 550 to 1050 °C. The results indicate that the Cr(VI) and salt concentrations in the leachate decreases for bricks fired at temperatures greater than 750 °C. The results for the bricks fired at 950 °C need to be reinvestigated as unexpected increases in Cr(VI) and salt concentrations were observed in this leachate and in this instance there was also no significant decrease in the subsequent leachate, for 48 hours, as was observed for the other cases.

The sum of the masses of components leached were calculated and compared to the amount of components added. These values were then used to determine the percentage Cr(VI) and salt stabilization in the clay bricks fired at different temperatures. Results shown in Table 41 indicate that the salt rather than the Cr(VI) stabilization is more sensitive to the clay brick firing temperature. At a 550 °C firing temperature, 96% of Cr(VI) but only 31% of the salts are stabilized. Above 750 °C, greater than 99% of Cr(VI) is stabilized in the clay bricks. Even the bricks fired at 950 °C, for which results are presumed suspect, a Cr(VI) stabilization greater than 99% was observed. The results in Table 41 indicate that if salt stabilization values comparable to those shown in Table 39 were desired, a firing temperature close to 1200 °C would be required. This study has not investigated the optimum firing time required to achieve satisfactory salt stabilization.

Table 40. Water Leaching of Clay Bricks Fired at Different Temperatures

Firing Temperature °C	Leaching Period Hours	Leachate		
		pH	Concentration, mg/l	
			Cr(VI)	TDS
550	24	9.02	2.433	2853
	48	9.83	0.062	238
650	24	8.61	2.027	1908
	48	9.48	0.093	119
750	24	8.08	0.182	2003
	48	9.37	0.00	180
850	24	7.75	0.145	1648
	48	9.39	0.00	123
950	24	8.91	0.272	949
	48	8.80	0.224	901
1050	24	9.22	0.060	628
	48	9.66	0.031	67

Table 41. Cr(VI) and Salt Stabilization in Clay Bricks Fired at Different Temperatures

Temp °C	Cr(VI), mg/kg			TDS, g/kg		
	Added	Leached	% Stab	Added	Leached	% Stab
550	591.4	42.95	95.8	44.93	30.91	31.2
650	591.4	21.20	96.4	44.93	20.27	54.9
750	591.4	1.82	99.7	44.93	21.83	51.4
850	591.4	1.45	99.8	44.93	17.71	60.6
950	591.4	4.96	99.2	44.93	18.5	58.8
1050	591.4	0.91	99.8	44.93	6.95	84.5

6.4 Mineralogy of Fired Clay Bricks

As for the case of cement-based systems, the mineralogy of fired clay bricks was investigated to establish the mechanism of Cr(VI) and salt stabilization observed in these materials. An electron microprobe (EMP) analysis was conducted on BFD and fired clay bricks using a JEOL 733 superprobe (batch 4). The results of this investigation are given in Appendix E for both BFD and fired clay bricks. For BFD, two high chromium-bearing phases, a spinel and a chromium glass, both with varying composition were identified. The other minor mineralogical phases mentioned by Coetzer (1996) were also found in this study. In the fired clay brick, chromium was found in large spinel particles, small Cr-spinel and Cr-glass particles and in a solid solution phase. It is proposed that the latter amorphous glassy Mg-Al-Fe-Si phase incorporating Cr_2O_3 (0.8 to 2.1%), MnO (0.2 to 0.5%), ZnO (3.6 to 5.0%), Na_2O (6.2 to 7.8%), SO_3 (up to 2.1%) and K_2O (1.7 to 2.8%) is responsible for the observed immobilization of Cr in the fired clay bricks. The presence of sulphur in this glassy phase could be an indication that the chromate, accompanied by its reduction, was incorporated into this phase. Similarly, this phase is also responsible for the effective

salt immobilization observed in fired clay bricks as indicated by the results shown in Table 39.

6.5 Acid Leaching Tests on Crushed, Fired Clay Bricks

These tests were conducted in order to evaluate the impact these materials may have on health and the environment according to the DWAF Guidelines (1988).

6.5.1 TCLP Leaching Tests

Crushed, fired clay bricks obtained from mixes 1, 4, 7 and 10 (see Table 37) were subjected to the TCLP leaching procedure (US EPA 1990). The solids were agitated for 19 hours in extraction fluid no. 1 with an initial pH value of 4.98. The final pH value of the fluid after agitation was not recorded. The TCLP leachate was analyzed for the eight US EPA stipulated elements together with Mn and V. The results of the analyses of the leachates are shown in Table 42 together with the maximum allowed values stipulated for the US EPA TCLP test and the ARL values stipulated by DWAF. The concentrations of the elements in the leachates were significantly less than stipulated by the US EPA. However, the concentrations in Table 42 for Cr, Mn and Pb for some mixes exceed the DWAF recommended ARL values.

Table 42. TCLP leaching test results on fired clay bricks

Mix No	Concentration, mg/l									
	V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
1	<0.05	<0.1	0.13	<0.027	<1	<0.05	<0.02	0.11	<0.01	0.14
4	<0.05	0.14	1.7	<0.027	<1	<0.05	<0.02	0.25	<0.01	<0.05
7	<0.05	0.17	0.11	<0.027	<1	<0.05	<0.02	0.13	<0.01	<0.05
10	<0.05	<0.1	0.99	<0.027	<1	<0.05	<0.02	0.13	<0.01	<0.05
TCLP		5		5	1.0	5	1.0	100	0.2	5
ARL	1.3	0.02	0.3	0.43	0.26	2	0.031	7.8	0.022	0.1

6.5.2 Acid Rain Leaching Tests

Acid Rain leaching tests were conducted on selected crushed, clay fired bricks. The results of the chemical analyses of 10 different metal concentrations in the leachates of these tests are shown in Table 43. The leachates contain only V, Cr, Mn and Ba in detectable quantities. In all instances the concentrations of V and Ba are below the DWAF recommended ARL values (see Table 34). This also applies for Mn except for fired clay bricks made from mix no 10. This result requires further investigation as the

components used in this mix (see Table 37) contained no BFD suggesting that the Mn originated only from the clay. However, no detectable Mn was observed in the other leachates from the fired clay bricks. Low Cr concentrations, fractionally higher than the DWAF recommended ARL values, were found in the leachates. These Cr concentrations were also lower than the corresponding values observed in similar tests conducted on cured cement blocks (see Table 31). These observations confirm the previous findings that fired clay bricks are superior to cured cement blocks in their ability to immobilize chromate. The next section investigates this further.

Table 43. Acid Rain leaching tests on selected crushed clay bricks

Mix No	Concentration, mg/l									
	V	Cr	Mn	As	Se	Ag	Cd	Ba	Hg	Pb
1	0.01	<0.003	0.016	0.005	<0.02	<0.04	<0.004	0.011	<0.02	<0.02
4	0.123	0.039	0.023	<0.004	<0.02	<0.04	<0.004	0.013	<0.02	<0.02
7	0.012	0.043	0.019	<0.004	<0.02	<0.04	<0.004	0.019	<0.02	<0.02
10	<0.002	<0.003	0.535	<0.004	<0.02	<0.04	<0.004	0.017	<0.02	<0.02

6.5.3 Nitric Acid Leaching Tests

These results are shown in Table 44 for fired clay brick batches 4 and 10. For crushed fired clay bricks made in batch 4, containing 50% BFD, the V, Cr, Mn, Zn and Pb concentration in the leachate increases with decreasing pH. However, the concentrations of the ions measured in these leachates are considerably lower than for the corresponding tests for cement blocks shown in Tables 32 and 33. This confirms the previous observations that fired clay bricks are fired more effective in immobilizing these ions. The leaching tests for fired clay brick batch no 10, that contains no BFD, indicate no Cr and Pb and smaller amounts of V and Zn reporting to the leachates than for batch no 4. The same amount of Mn is found in the leachates for both batches 4 and 10. This suggests that the Mn observed in the leachate originates form the clay and not from the BFD. On the other hand, all the Cr and Pb observed in the leachate from batch 4 and a large proportion of the Zn and V originated from the BFD used to produce the fired clay brick.

Table 44 - Nitric acid leaching test results of clay fired bricks

Batch No	Final pH	Mequiv /g	Concentration, mg/l					
			V	Cr	Mn	Zn	Pb	Cd
4	8.28	0.00	0.44	0.1	<0.1	<0.1	<0.02	<0.02
	4.84	0.041	0.13	<0.1	0.24	0.93	<0.02	<0.02
	4.25	0.102	<0.1	<0.1	0.66	0.63	0.08	<0.02
	4.23	0.143	<0.1	0.1	0.84	0.97	0.02	<0.02
	3.66	0.204	<0.1	0.16	1.2	1.3	0.08	<0.02
	3.37	0.306	0.16	0.26	1.5	2.0	0.07	<0.02
	2.34	0.407	0.29	0.25	1.7	1.5	0.09	<0.02
10	6.93	0.00	<0.1	<0.1	0.50	<0.1	<0.02	<0.02
	4.28	0.204	<0.1	<0.1	1.1	0.25	<0.02	<0.02
	2.04	0.407	0.1	<0.1	2.2	0.17	<0.02	<0.02

6.6 Potential Toxicity of Fired Clay Bricks

The results from water, TCLP and Acid Rain leaching tests on crushed, fired clay bricks were used to evaluate the potential toxicity of fired clay bricks. The evaluation was based on the DWAF (1998) Guidelines and followed the same approach that was used previously in this investigation to evaluate cured cement blocks (see section 5.8). For fired clay bricks made with BFD the dumping rate was estimated to be 5.368×10^4 kg/ha/month, a fifth of that assumed to be applicable to cement blocks. This was due to the fact that the fired clay bricks incorporated 50 per cent BFD whereas the corresponding figure for cement blocks was only 10 per cent. Based on these assumptions, the amount of toxic component leached per kg of crushed fired clay brick was calculated from the leaching test. Results are shown in Table 45 for selected cases together with the corresponding EEC (ppb) values.

Table 45. Toxicity evaluation of crushed, fired clay bricks

Element	Mix No	Leaching		Mass Kg	Conc mg/l	Vol ml	Amount leached mg/kg	EEC ppb
		Time hours	medium					
Cr	1	24	water	0.100	0.031	1000	0.31	11
	5	24	water	0.100	0.235	1000	2.35	83
	7	24	water	0.100	0.117	1000	1.17	41
	7	19	TCLP	0.100	0.17	2000	3.4	120
	4	20	Acid Rain	0.100	0.039	2000	0.78	28
Mn	4	20	Acid Rain	0.100	0.023	2000	0.46	16
	4	19	TCLP	0.100	1.70	2000	34.0	1205
	7	19	TCLP	0.100	0.11	2000	2.20	78
	10	20	Acid Rain	0.100	0.535	2000	10.7	379
Pb	1	19	TCLP	0.100	0.14	2000	2.8	99
V	4	20	Acid Rain	0.100	0.123	2000	2.46	87
Ba	4	19	TCLP	0.100	0.25	2000	5.0	177

For evaluation of Cr(VI) toxicity in crushed, fired clay bricks, the results for water leaching (see Table 38), Acid Rain (see Table 43) and TCLP (see Table 42) tests were used to calculate the EEC values. All these values were larger than the DWAF Guidelines permitted value of 20 ppb except for those calculated from a water leaching test on mix no 1. On the other hand, the EEC values, estimated for crushed, fired clay bricks, are generally lower than those obtained for crushed cured cement blocks shown in Table 35. Thus, although water leaching tests on whole, fired clay bricks were not conducted, Cr(VI) toxicity of fired clay bricks is expected to be less than that for cured cement blocks. The chromate immobilization originating from BFD in fired clay bricks would therefore be more effective than in cured cement-based systems and would be the preferred route for disposal of BFD. Further, the improved associated salt stabilization and the ability to incorporate more BFD in the fired clay bricks are additional reasons why this system would be preferred over the cement-based system. The costs of these options are compared in the next section.

Other toxic components in fired clay bricks were evaluated and these results are also shown in Table 45. In one instance, Pb was detected in the TCLP leachate (see mix no 1, Table 42). The corresponding EEC value was calculated to be 99 ppb, just below the permitted value of 100 ppb according to the DWAF Guidelines. For Mn, conflicting data were found in Table 45. Of the four cases presented, two EEC values were below and two above the permitted value of 300 ppb. It is not possible to conclude from these data the reasons for these discrepancies. This matter would have to be investigated further at a later stage. Instances where V and Ba were detected in the leachate yielded EEC values of 87 ppb and 18 ppb, respectively. These were considerably lower than the permitted values of 130 ppb and 7800 ppb for V and Ba, respectively, permitted by the DWAF Guidelines. The toxicity evaluation of crushed fired clay bricks shown in Table 45 confirms that disposal of BFD by this system is promising and can at the moment, be regarded as the best technology available for immobilization of the toxic components contained therein.

6.7 Potential for Commercialization and Utilization

The major cost in the production of fired clay bricks is the energy (coal) required to fire them to 1200 °C for 6 hours. According to Gilbert (1999) 380 kWh are required to heat 1 ton of clay from 25 to 1200 °C. Assuming a 10 per cent thermal efficiency this would cost R570/t if electricity at 15c/kWh is used. If on the other hand, coal is used to fire the clay bricks, the fuel cost would amount to R95/t of bricks produced. These

figures can be compared with the cost of clay bricks used as building material, quoted at up to R500 per 1000 bricks depending on transport costs. Expressed per ton of BFD treated, the energy costs to produce fired clay bricks would amount to R190 as half of the bricks consist of BFD. This cost compares favourably to the R235/t quoted previously to treat BFD via the manufacture of cement blocks and the cost of R250/t charged by a local industrial waste management company for disposal of the hazardous waste Therefore, both economic and performance evaluations indicate that the disposal of BFD via fired clay bricks is the preferred treatment option.

7. CONCLUSIONS AND RECOMMENDATIONS

The overall objectives of this study have been met and various options for the treatment of toxic chromate containing BFD have been devised and evaluated in terms of cost and potential environmental impact. The nature of ferrochrome BFD has been elucidated by leaching and mineralogical studies and has indicated that Cr(VI) continues to leach from BFD when in contact with water. Evidence was presented to suggest that the formation of chromate in BFD is associated with alkali and oxidizing conditions prevailing in the dust extraction system used in the production of ferrochrome. The treatment of an aqueous slurry of BFD with ferrous sulphate or chloride has been shown to be effective in the short term to remove Cr(VI) by the formation of an insoluble, stable $(Cr,Fe)(OH)_3$ precipitate. However, this treatment increases the salt content in the water which introduces an additional threat of contamination. In view of the continual leaching of chromate from BFD, a once-off treatment thereof with ferrous ions is not sufficient and slimes dams continue to pose a threat to health and the environment, particularly to the natural water resources. For this reason two alternative treatment options for BFD were investigated.

It was demonstrated that the incorporation of up to 15 % BFD into cement blocks made with ferrochrome and EAF slag was an effective treatment to immobilize soluble chromate as judged by water, TCLP and Acid Rain leaching tests. The addition of $FeCl_2$ during the manufacture of the cement blocks proved to be very effective to ensure up to 99.7 % chromate immobilization as judged by water leaching tests on crushed cement blocks. In the same tests it was found that about half the salt, contained in the BFD, could also be immobilized in this manner. Partial immersion of whole cement blocks in water indicated that all the Cr(VI) and >98 % of

the salt was retained therein. The results of leaching tests were used to calculate, according to the DWAF Guidelines, the EEC values for chromate leaching from cement blocks. It was found that whole blocks produced leachates that were within the prescribed values but the leachates of crushed blocks exceeded these values. Disposal of whole cement blocks containing BFD would therefore pose no threat to the environment. The cost of producing cement blocks in this manner was estimated to be R235/t of BFD.

More effective chromate immobilization was observed in fired clay bricks containing 50 per cent BFD. A minimum firing temperature of 1200 °C is required to effectively immobilize the Cr(VI) and salt in the clay bricks. Leaching tests on the crushed, fired clay bricks were used to calculate the EEC values in accordance with the DWAF Guidelines. These results indicate that the chromate and salt are effectively immobilized in a glassy phase and do not pose a threat to the environment. The cost of production of the coal fired clay bricks treated in this manner was estimated to be *R190/t of BFD.*

The authors are not aware of local ferrochrome producers that uses any of the above options to dispose of BFD for building or other materials of construction. The current tendency in the local ferrochrome industry is to recycle the BFD by mixing it with fine chromite ore. This is achieved either via agglomeration of these fines with bentonite and calcining at 1300 °C (Otokumpu Process), or related technologies developed in-house, or via producing blocks using cement as a binder. Excess energy available from closed ferrochrome furnaces in the form of CO gas can also be used for the calcination option. Whatever the treatment option preferred, the local ferrochrome industry has minimized the environmental threat posed by BFD. These recycle options have only been installed recently and the long-term build-up of salt and metal ions in the furnace and the corrosion and production problems posed by this option have as yet not been fully evaluated.

If recycle of BFD is a successful option for utilizing and disposing BFD in the local ferrochrome industry then it is only necessary to monitor the ground water in the vicinity of these operations to ensure that there is no evidence of further Cr(VI) contamination. For this purpose a more reliable and accurate analytical method for measurement of very dilute chromate concentrations in aqueous media would have to be developed using a preconcentration step.

It is recommended that efforts be made to implement the technologies developed in this report in other Cr(VI) containing metallurgical wastes and related operations where it is not possible to recycle, i.e., waste paint producers, leather tanning and electroplating sludges, etc. Opportunities to further optimize the developed technologies should be explored. Particularly for the production of cement blocks, the addition of more $FeCl_2$ could allow for further Cr(VI) immobilization. Further it is also suggested that the approach developed in this study, to produce cement blocks and clay bricks from metallurgical wastes, be applied to other wastes originating from the local metallurgical industry that have been identified as toxic (Kornelius, 1995). Hopefully these efforts, and any future endeavours in this regard, indicate that implementation of waste recycling and minimization technologies would help to preserve the environment and valuable natural water resources and allow for sustainable growth of these industries in the future.

8. REFERENCES

Allan, ML and Kukacka, LE (1995). Blast furnace slag-modified grouts for *in situ* stabilization of chromium-contaminated soil. *Waste Manage.*, vol. 15, pp. 193-202.

Anderson, RA (1999). Chromium as an essential nutrient. The Chromium File, No. 6, ICDA, Paris, September, p. 8.

Auer, S (1992). Bindung umweltrelevanter Ionen in Ettringit und Schichtstrukturen vom Typus TCAH. *Doctorate Thesis*, University of Erlangen-Nurnberg, p. 242. (German Text).

Balzamo, S and Marchetti, A (1996). A new standard leaching test on stabilized wastes. *Mikrochim. Acta*, vol. 123, pp. 145-150.

Bartlett, RJ (1991). Chromium cycling in soils and water: Links, gaps and methods. *Environ. Health Perspect.*, vol. 92, pp. 19-24.

Beukes, JP, Pienaar, JJ, Lachmann, G and Giesekke, EW (1999). The reduction of hexavalent chromium by sulphite in wastewater. *Water SA*, vol. 25, pp. 363-370

Blowes, DW, Ptacek, CJ and Jambor, JL (1997). *In-situ* remediation of Cr(VI) contaminated groundwater using permeable reactive walls: laboratory studies. *Environ. Sci. Technol.*, vol. 31, pp. 3348-3357.

Boucher, PSRJ, van Eeden, JJ and van den Heever, SJ (1997). Brickmaking with Ferrosilicon bag filter dust. *SA Patent*, 96/7693. 12 September.

Boucher, PSRJ and van Eeden, JJ (1995). Brickmaking with an acid slag. *SA Patent* 95/4974. 15 June.

Coetzer, G (1996). The generation of Cr(VI) from metallurgical waste. *Mintek Technical Memorandum*, No. 14631, pp.32, April.

Coetzer, G, Giesekke, EW and Guest, RN (1997). Hexavalent chromium in the recovery of ferrochrome from slag. *Can. Metall. Quart.*, vol. 36, pp.261-268.

Cox, XB, Linton, RW and Butler, FE (1985). Determination of chromium speciation in environmental particles. Multi-technique study of ferrochrome smelter dust. *Environ. Sci. Technol.*, vol. 19, pp. 345-352.

Crosbie, J, Brown, R, Ramage, T and O'Niel, S (1993). In situ treatment of chromium (VI) with an iron reduction process. *Proc-Water Environ. Fed. Annu. Conf. Expo.* 66th, vol. 5, pp. 71-83.

Cross, HJ, Faux, SP, Sadhra, S, Sorahan, T, Levy, LS, Aw, TC, Braithwaite, R, McRoy, C, Hamilton, L and Calvert, I (1997). *Criteria document for hexavalent chromium*. International Chromium Development Association (ICDA), Paris.

Csetenyi, LJ and Tritthart, J (1997). Stabilization of chromium-containing electroplating sludge by cementation. *World Cem. Res. Dev.*, pp. 114-116.

Department of Water Affairs and Forestry (1998). Waste Management Series. Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. CTP Book Printers, Second Edition.

DIN 38414 (1984). German Standard Procedure for Water, Wastewater and Sediment testing-Group S (Sludge and Sediment); Determination of Leachability (S4). Institut fur Normung, Berlin.

Eary, LE and Rai, D (1988). Chromate removal from aqueous waste by reduction with ferrous ion. *Environ. Sci Technol.*, vol. 22, pp. 972-977.

Fairhurst, S and Minty CA (1989). *The toxicity of chromium and inorganic chromium compounds*. London, Her Majesty's Stationary Office.

Gericke, WA, Pollard, MS, Astrup, EG, Aw, C, Barnhart, J, Cunat, PJ, Darrie, G, Defrance, A, Huvinen, M, Lacoude, M, Ossko, A and Smythe, GR (1998). *Chromium Industry Guidelines*. ICDA, Paris, Revision 2, October.

Gericke, WA (1998). *Personal Communication*, September.

Gericke, WA (1995). Environmental aspects of ferrochrome production. *INFACON 7*, Tuset, Tveit, Page (editors), FFF, Trondheim, Norway. pp. 131-140.

Gilbert, GW (1999) Personal Communication

Goske, J (1997). Personal Communication.

Kersten, M, Schulz-Dobrick, B, Lichtensteiger, T and Johnson, AC (1998). *Speciation of Cr in leachates of a MSWI bottom ash landfill. Environ. Sci. Technol.*, vol.32, pp. 1398-1403.

Kilau, HW and Shah, ID (1984). Preventing chromium leaching from waste slag exposed to simulated acid precipitation: A laboratory study. *US Bur. Mines, RI* 8878, p. 21.

Kindness, A, Macias, A and Glasser, FP (1994). Immobilization of chromium in cement matrices. *Waste Manage.*, vol. 14, pp. 3-11.

Kornelius, G (1995). Dust from air pollution control operations in the ferro-alloy industry: Problems and opportunities. *SA J Chem. Engn.*, vol. 7, pp. 28-38.

Langard, S (1982). *Biological and environmental aspects of chromium.* Amsterdam, Elsevier Biological Press.

Lin, CK, Chen, JN and Lin, CC (1996). An NMR and XRD study of solidification/stabilization of chromium with Portland cement and □-C_2S. *J Hazard. Mater.*, vol. 48, pp. 137-147.

Macias, A, Kindness, A and Glasser, FP (1997). Impact of carbon dioxide on the immobilization potential of cemented wastes: Chromium. *Cem Concr Res.*, vol. 27, pp. 215-225.

Mantel, DG (1992). The manufacture, properties and applications of Portland cements, cement additives and blended cements. Pretoria Portland Cement, pp. 64.

Meegoda, JN, Kamolpornwijit, W, Vaccari, DA, Ezeldin, AS, Walden, L, Ward, WA, Noval, BA and Santora, S (1997). Aggregates for construction from vitrified chromium contaminated soils. *Geotech. Spec. Publ., vol. 59, Engineered Contaminated Soils and Interaction of Soil Geomembranes*, pp. 31-46. Am Soc. Civil Engn.

Nriagu, JO and Nieboer, E (1988). *Chromium in the natural and human environments*. New York, J Wiley.

Omotoso, OE, Ivey, DG and Mikula, R (1998a). Hexavalent chromium in tricalcium silicate. Part I. Quantitative X-ray diffraction analysis of crystalline hydration products. *J. Mater. Sci.*, vol. 33, pp. 507-513.

Omotoso, OE, Ivey, DG and Mikula, R (1998b). Hexavalent chromium in tricalcium silicate. Part II. Effects of Cr(VI) on the hydration of tricalcium silicate. *J. Mater. Sci.*, vol. 33, pp. 515-522.

Omotoso, OE, Ivey, DG and Mikula, R (1996). Quantitative X-ray diffraction analysis of chromium(III) doped tricalcium silicate pastes. *Cem. Concr. Res.*, vol. 26, pp. 1369-1379.

Omotoso, OE, Ivey, DG and Mikula, R (1995). Characterization of chromium doped tricalcium silicate using SEM/EDS, XRD and FTIR. *J Hazard Mater.*, vol. 42, pp. 87-102.

Pannain, MC and Santelli, RE, 1995. On the spectrophotometric flow injection determination of chromium(VI) in natural waters after on-line preconcentration on activated alumina. *Talanta*, vol.42, pp. 1609-1617.

Peterson, ML, White, AF, Brown, GE and Parks, GA (1997). Surface passivation of magnetite by reaction with aqueous Cr(VI): XAFS and TEM results. *Environ. Sci. Technol.*, vol.31, pp. 1573-1576.

Pettine, M, D'Ottone, L, Campanella, L, Millero, FJ and Passino, R (1998). The reduction of chromium (VI) by iron (II) in aqueous solutions. *Geochim. Cosmochim. Acta*, vol. 62, pp. 1509-1519.

Raghu, D and Hsieh, HN (1989). Origin, properties and disposal problems of chromium ore residue. *Intern. J. Environ. Stud.*, vol. 34, pp. 227-235.

Rai, D, Eary, LE and Zachara, JM (1989). Environmental chemistry of chromium. *Sci. Total Environ.*, vol. 86, pp. 15-23.

Richard, FC and Bourg, ACM (1991). Aqueous geochemistry of chromium: a review. *Wat. Res.*, vol. 25, pp. 807-816.

Smit, JP, Giesekke, EW and Mogoai, RJ (1998). Fixation and stabilization of Cr(VI) and soluble salts from the ferrochrome industry in cement bricks. *Waste Processing and Recycling in Mineral and Metallurgical Industries III*. Edited by Rao, SR, Amaratunga, LM, Richards, GG and Kondos, PD. The Metallurgical Society of CIM. pp. 389-401

South African Bureau of Standards (1984). Concrete Masonry Units, *SABS 1215*.

Taylor, HFW (1997). *Cement Chemistry*, Second Edition, Thomas Telford, London. pp. 163.

Thompson, SC and Lawson, F (1984). Alkali roasting of chromite. *Proc. Australas. Inst. Min. Metall.*, No. 289, pp. 247-251.

US EPA (1990). Toxicity Characteristics Leaching Procedure (TCLP). Appendix II, *Federal Register*, vol. 55, No 61, March 29.

Van der Merwe, SW (1996). New WHO recommendations for water quality standards. *Water Supply*, vol. 14, pp. 65-67.

Van der Sloot (1996). Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and field verification. *Waste Manage.*, vol. 16, pp. 65-81.

Weng, CH, Huang, CP, Allen, HE, Cheng, AHD and Sanders, PF (1994). Chromium leaching behavior in soil derived from chromite ore processing waste. *Sci. Total Environ.*, vol., 154, pp. 71-86.

Woods, AI (1996). The South African Ferrochrome Industry. *ICDA News*, No. 69, p3.

Zhang, A, Akhter, H and Cartledge, FK (1997). Solidification/stabilization applied to chromium species. *J. Environ. Sci. Health*, vol. A32, pp. 1731-1742.

9. APPENDICES

9.1 Appendix A

SA installed capacity by 1998 : Cr Ferroalloys

Production Unit	MVA Rating	ChCr Capacity, tpa	Dust Produced, tpa(1)	Production Unit	MVA Rating	ChCr Capacity, tpa	Dust Produced, Tpa(1)
CMI	**204**	**430 000**	**12 960**	**Chromecorp (by 1998)**	**288**	**605 000**	**20 520**
Lydenburg:	*138*	*310 000*	*10 080 (s)*	*Rustenburg (MRP production included):*	*132*	*285 000*	*9 288*
Closed (Tanabe) SAF (A)	33	-	1 800	Semi-closed SAF (1)	30	60 000	2 160
Closed (Tanabe) SAF (B)	33	-	1 800	Semi-closed SAF (2)	30	60 000	2 160
Closed (Tanabe) SAF (C)	33	-	1 800	Semi-closed SAF (3)	33	60 000	2 376
Semi-closed (Pyromet) SAF (D)	39	-	2 808	Semi-closed SAF (4)	39	80 000	2 592
2 x SRC Kilns (>40% Cr Met.)	PC-fired	-	10 080 (s)	1 x Pelletizing Plant		200 000*	
3 x SDK Granulation Units (CMI modified)		300 000#		*Wonderkop (MRP production included–wet jigs):*	*156*	*320 000*	*11 232*
Marketing JV with Mitsui (12.5%)				Semi-closed SAF (1)	39	80 000	2 808
Rustenburg:	*66*	*120 000*	*4 752*	Semi-closed SAF (2)	39	80 000	2 808
Semi-closed (Tanabe) SAF (1)	33	60 000	2 376	Semi-closed SAF (3) (end 1997)	39	80 000	2 808
Semi-closed (Tanabe) SAF (2)	33	60 000	2 376	Semi-closed SAF (4) (end 1997)	39	80 000	2 808
				2 x Pelletizing Plants		400 000*	
Feralloys	**72**	**180 000**	**7 128**	**Hernic Ferrochrome**	**124**	**260 000**	**8 928**
Machadodorp:				*Brits:*			
Open SAF (2)	24	45 000	2 376	Semi-closed SAF (Pyromet)	37	65 000	2 664
Open SAF (3)	24	45 000	2 376	Semi-closed SAF (Pyromet)	37	65 000	2 664
Open SAF (4)	24	40 000	2 376	Semi-closed SAF (Pyromet)	50	130 000	3 600
MRP	Jigs	50 000***					
				Bathlako Ferrochrome (Boshoek)	**12.5**	**25 000**	**720**
				Open SAF (mothballed)	12.5	25 000	720

Notes:
- * Pellets (UG2 + LG6 concentrate + Na_2SiO_4 binder → low temp. sinter?)
- ** RP ChCr product (sustainability dependent on slag dumps)
- *** IC3 product
- # Alloy granulator capacities (not new alloy)
- (1) Assumed 360 working days per annum
- (s) Sludge

9.2 Appendix B

WATER LEACHING OF CRUSHED CEMENT BLOCKS

Mix No	Curing Time Days	Leaching Period	Leachate		
			pH	Concentration, mg/l	
				Cr(VI)	TDS
B	7	24 hours	12.10	0.559	1040
		5 days	12.11	0.437	705
	14	24 hours	12.18	0.714	650
		48 hours	11.75	0.310	330
	28	24 hours	11.86	0.418	900
		48 hours	11.19	0.357	565
	56	24 hours	11.80	0.498	731
		48 hours	11.26	0.247	304
D	7	24 hours	12.06	0.308	920
		5 days	12.03	0.238	540
	14	24 hours	12.46	0.092	1100
		48 hours	11.90	0.072	215
	28	24 hours	11.89	0.074	1000
		48 hours	11.30	0.079	515
	56	24 hours	11.78	0.065	712
		48 hours	11.14	0.050	356
E	7	24 hours	12.01	0.586	1080
		5 days	12.00	0.311	400
	14	24 hours	12.04	0.565	715
		48 hours	11.82	0.205	225
	28	24 hours	11.41	0.372	595
		48 hours	11.08	0.088	320
	56	24 hours	11.60	0.104	713
		48 hours	10.54	0.028	307
F	14	24 hours	12.24	0.621	495
		48 hours	12.03	0.333	370
	28	24 hours	11.66	0.462	900
		48 hours	11.16	0.189	345
	56	24 hours	11.68	0.184	663
		48 hours	10.80	0.071	341
G	14	24 hours	12.29	0.489	905
		48 hours	11.98	0.261	405
	28	24 hours	11.67	0.267	880
		48 hours	11.18	0.113	398
	56	24 hours	11.59	0.529	692
		48 hours	11.08	0.191	357
I	14	24 hours	12.43	0.001	685
		48 hours	12.14	0.000	390
	28	24 hours	11.59	0.000	1157
		48 hours	11.41	0.000	488
	56	24 hours	11.39	0.000	813
		48 hours	10.96	0.000	498

9.2 Appendix B (cont.)

WATER LEACHING OF CRUSHED CEMENT BLOCKS (cont.)

Mix No	Curing Time Days	Leaching Period	Leachate		
			pH	Concentration, mg/l	
				Cr(VI)	TDS
J	14	24	12.22	2.314	975
		48	11.89	0.821	350
	28	24	11.32	1.979	957
		48	11.13	0.436	319
	56	24	11.64	1.313	818
		48	10.93	0.26	247
L	14	24	12.10	0.397	855
		48	11.83	0.160	515
	28	24	11.34	0.243	726
		48	11.11	0.071	365
	56	24	11.51	0.743	704
		48		0.204	379
M	14	24	12.18	1.466	1070
		48	11.15	0.553	315
	28	24	11.63	1.782	1055
		48	11.38	0.423	347
	56	24	11.62	0.372	975
		48	11.46	0.135	319
N	14	24	12.20	1.108	1065
		48	11.34	0.672	380
	28	24	11.62	1.448	875
		48	11.48	0.543	413
	56	24	11.60	0.438	694
		48	11.43	0.000	101
O	14	24	12.22	0.795	1000
		48	11.53	0.390	320
	28	24	11.68	1.065	854
		48	11.50	0.398	361
	56	24	11.63	0.371	790
		48	11.44	0.109	462

9.3 Appendix C

WATER LEACHING OF CRUSHED CEMENT BLOCKS AFTER 120 DAYS CURING

Mix No	Leaching Period Hours	Leachate		
		pH	Concentration, mg/l	
			Cr(VI)	TDS
B	24	11.72	0.248	843
	48	10.74	0.000	218
D	24	11.91	0.092	789
	48	11.69	0.000	380
E	24	11.76	0.131	823
	48	11.54	0.000	573
F	24	11.69	0.157	752
	48	11.69	0.000	354
G	24	11.80	0.044	732
	48	11.38	0.029	253
H	24	11.81	0.056	794
	48	11.62	0.024	359
I	24	12.11	0.000	914
	48	11.69	0.000	498
J	24	11.73	0.336	929
	48	11.32	0.092	353
K	24	11.51	0.069	992
	48	11.06	0.000	319
L	24	11.61	0.064	818
	48	11.36	0.000	276
M	24	11.57	0.365	737
	48	11.21	0.090	327
N	24	11.54	0.746	639
	48	11.28	0.245	331
O	24	11.78	0.276	853
	48	11.54	0.065	401
P	24	11.80	0.263	978
	48	11.47	0.069	434

9.4 Appendix D

Mix No	Curing Time Days	Leaching Period Hours	Leachate		
			pH	Concentration, mg/l	
				Cr(VI)	TDS
Q	28	24	11.68	0.060	1212
		48	11.50	0.033	376
	56	24	12.37	0.459	1113
		48	11.90	0.114	368
R	28	24	11.94	0.071	1234
		48	11.75	0.029	457
	56	24	12.32	0.473	1016
		48	11.77	0.110	406
S	28	24	11.89	0.046	1118
		48	11.83	0.025	368
	56	24	12.13	0.362	1057
		48	11.79	0.086	431
T	28	24	11.89	0.111	1244
		48	11.44	0.037	428
	56	24	12.20	0.083	1135
		48	12.01	0.034	374
U	28	24	11.70	0.064	1283
		48	11.50	0.034	370
	56	24	12.26	0.028	1369
		48	12.06	0.014	468
V	28	24	11.63	0.844	1697
		48	11.42	0.221	445
	56	24	12.14	0.615	1374
		48	11.90	0.166	406
W	28	24	11.78	0.422	1529
		48	11.64	0.125	609
	56	24	12.43	0.518	1479
		48	12.18	0.509	515
X	28	24	11.89	0.327	1783
		48	11.60	0.148	560
	56	24	12.48	0.200	1580
		48	12.22	0.150	524
Y	28	24	11.81	0.643	1253
		48	11.46	0.215	425
	56	24	12.39	0.696	1034
		48	12.19	0.214	352
Z	28	24	11.52	2.740	1280
		48	11.31	0.631	365
	56	24	12.17	1.342	1027
		48	11.92	0.541	348

9.5 Appendix E

9.5.1 Distribution of chromium in a clay brick

1 RESULTS

The distribution of chromium was determined in fragments of a fired clay brick and in the raw materials (clay and bag filter dust) from which the brick was manufactured.

1.1 Cr in the clay

A sample of the clay was separated into three fractions by means of elutriation and magnetic separation.

- The clay fraction contained mainly the clay mineral illite
- The non-magnetic fraction contained mainly quartz
- The magnetic fraction contained mainly iron oxides, ilmenite and chromite

Only a few chromite particles were present with a composition of approximately:

$A1_2O_3$	14.3% ^{mass}
FeO	29.4% ^{mass}
MgO	7.1% ^{mass}
TiO_2	1.4% ^{mass}
Cr_2O_3	47.9% ^{mass}

1.2 CR in the bag filter dust

The EMP investigation of the BFD shows that the same host of phases as reported on in Technical memorandum 14631[1] were encountered. The presence of chromium in all of them was confirmed. These include two high chromium bearing phases (a spinel and a Cr-glass) olivine - ~ (Fo_{15}-Fa_{85}), a Mg, Al-silicate, an Al silicante and a K, Al-silicate.

The compositions of the two high Cr bearing phases are reported in Table 1. They both have a considerable variation in composition.

The spinel particles are angular in shape with an average size of 10m. The Cr-glass particles seldom exceed 5m in diameter and are usually rounded (globular) in shape.

Table 1. Composition of spinel and a Cr-bearing glass in the BFD

$\%^{mass}$	Spinel	Cr-glass
Al_2O_3	15.91 to 18.62	8.42 to 18.78
FeO	22.92 to 28.19	11.5 to 23.74
MgO	7.61 to 9.80	10.77 to 13.52
TiO_2	0.38 to 1.1	0.14 to 0.78
MnO	0 to 0.72	0.04 to 0.96
Cr_2O_3	43.11 to 49.49	19.14 to 35.31
CaO	0 to 0.26	0.2 to 6.04
ZnO	0.25 to 1.17	5.88 to 8.39
K_2O		0.15 to 1.19
Na_2O		5.90 to 7.70
SiO_2		3.88 to 19.33

1.3 Cr in the clay brick

The brick samples investigated consisted mainly of large quartz and chromite particles in a glass matrix. The BFD components are also included in the glass (Figure 1)

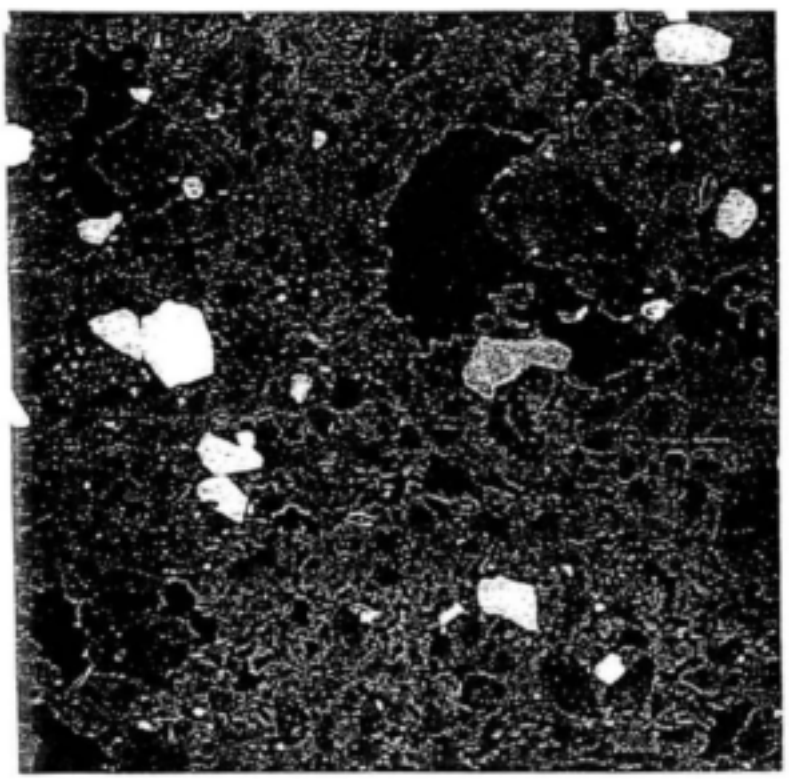


Figure 1 : Backscattered electron image of an area on the fired clay brick showing the presence of chrome spinel (white) and quartz (grey) particles as the major phases present in the glass ground mass (light grey)
Width of the area viewed : 2500 μm

Chromium is present in :

1.3.1 Large spinel particles

The large spinel particles (100m to 300m) exhibit ex-solutions of two spinel phases as displayed in Figure 2.

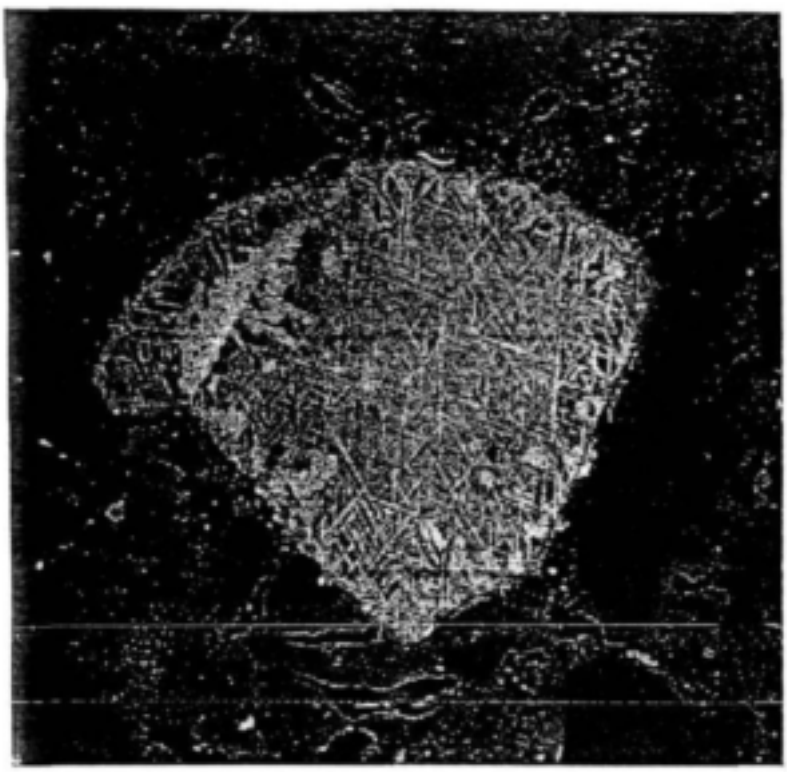


Figure 2 : Backscattered electron image of a chromium spinel with ex-solutions of iron rich spinel lamellae
Width of area viewed : 315μm

The composition of the lamellae and the matrix of this particle are reported in Table 2.

Table 2. Composition of the ex solved phases in Cr-spinel particle

$\%^{mass}$	Lamellae	Matrix
Al_2O_3	9.76	16.92
FeO	33.57	12.58
MgO	1.17	18.62
TiO_2	1.55	0.34
Cr_2O_3	50.31	50.47
ZnO	0.26	0.67

1.3.2 Small CR-spinel and Cr-glass particlues

These angular spinel particles (10m average size) and Cr-glass particles (<3m) are present in the glassy matrix of the brick and are marked by a high Zn content as shown in Table 3.

Table 3 Composition of the small Cr-spi8nel and Cr-glass particles in the brick

$\%^{mass}$	Cr-spinel	Cr-glass
Al_2O_3	13.30 to 14.92	9.83 to 17.83
FeO	8.79 to 10.36	10.92 to 10.36
MgO	12.66 to 12.88	15.74 to 18.49
TiO_2	0.49 to 0.67	0.31 to 0.94
MnO	0.56 to 0.63	0.95 to 1.08
Cr_2O_3	46.09 to 48.42	21.62 to 30.43
CaO		0.24 to 0.26
ZnO	11.95 to 13.15	7.72 to 8.80
K_2O		0.71 to 0.75
Na_20		nd
SiO_2		10/93 to 19.75

Nd – not detected

1.3.3 Cr in solid solution

Chromium is present in solid solution in :

The original BFD constituents still present as such in the clay brick
A glassy matrix (Figure 3) containing varying amounts of Cr_2O_3 The composition of the matrix material is reported in Table 4.

Reaction zones between the matrix and the constituents of the original raw material (BFD) are frequently encountered.

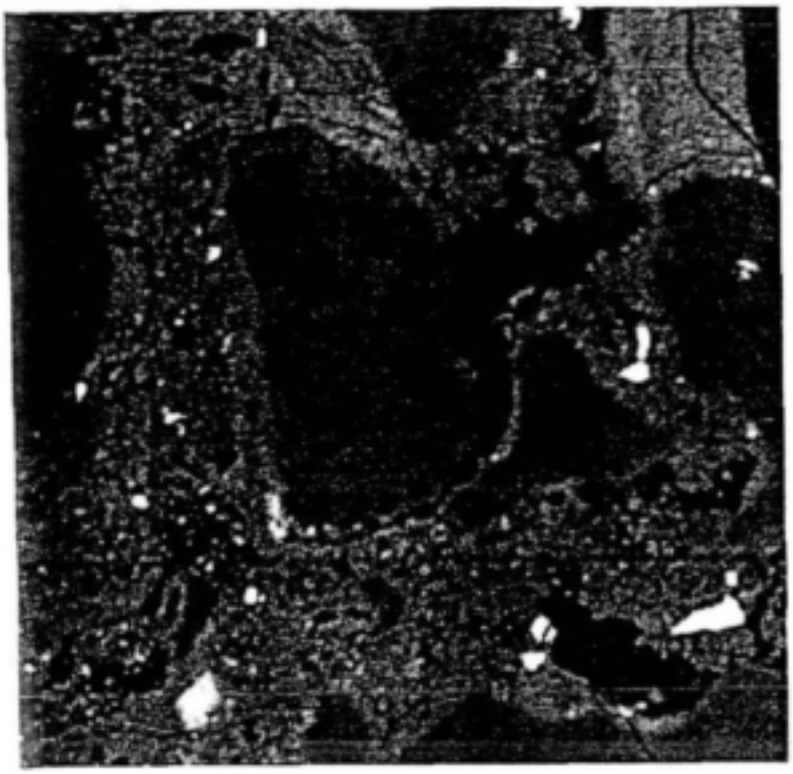


Figure 3 : Backscattered electron image of quartz particles (grey) in a matrix of the glass phase (light grey). Small angular particles of the Zn-bearing Cr-spinel (white) can be seen in the matrix.
Width of area viewed : 100µm

Table 4. Composition of the matrix of the brick

	% mass
MgO	9.97 to 14.07
Al_2O_3	16.62 to 32.52
TiO_2	0.63 to 1.07
Cr_2O_3	0.82 to 2.15
MnO	0.18 to 0.51
FeO	8.16 to 35/33
ZnO	3.63 to 5.02
Na_2O	6.17 to 7.83
SiO_2	20.29 to 38.23
SO_3	0.02 to 2.11
K_2O	1.74 to 2.75
CaO	0.72 to 1.66

2. DISCUSSION AND CONCLUSION

The matrix of the brick is a glass, a melted product of the clay material after being fired at 1180°C. The original constituents of the BFD reacted to a certain extent with the glass phase in the brick.

The Cr_2O_3 content of the matrix varied from 0.8%^{mass} to 2.1%^{mass} and was possibly derived from:

Reaction-melting of the Cr-bearing glass particles (also contributed to the Zn-content of the matrix) and the BFD constituents containing Cr in the solid solution.
Incorporating the Cr^{6+} -bearing glass particles into the glass matrix. The presence of sulphur at levels of p to 2.1 could be an indicator of such a reaction.

From this investigation it can, therefore, be concluded that the soluble Cr^{6+} is most probably incorporated into the glass matrix of the brick and thus immobilized.

The CaO content of the glass is below 1.7%^{mass}, which could be a bit low to generate a glass that effectively incorporates Cr in solid solution and thus immobilize the Cr^{6+}.

Other related WRC reports available:

The extraction of nickel with the use of supported liquid membranes (SLM)

Smit JJ

The main aims of the project were the qualification of supported liquid membrane (SLM) extraction with regard to the concentrations of the feed and strip solutions, their respective acidities, the concentration of the extractant mix, and the effect of temperature variations on these processes.
The technical feasibility of SLM extraction was demonstrated on anions such as HPO_3^{2-} and $H_2PO_2^-$, as well as lactates and acetates. Further positive results were also obtained with Ca, Ni and Cr from a synthetic sulphate medium and extraction of Zn from industrial effluent.
Capsulated membrane extraction (CME), where the extractant is confined in a capsule placed in the feed solution, was shown to achieve extraction rates of an order of magnitude higher than that achieved by SLM extraction.
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