INFACON 7, Trondheim, Norway, June 1995
Eds.: Tuset, Tveit and Page
Publishers: FFF, Trondheim, Norway

ENVIRONMENTAL ASPECTS OF FERROCHROME PRODUCTION

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ABSTRACT

The exploitation of the vast mineral resources of the southern tip of the African continent places a great responsibility on the miners and smelters in terms of awareness and management of the environment. In particular, the ferrochrome industry of South Africa, one of the largest in the world, faces a great responsibility in addressing the environmental impact of ferrochrome smelting.

The paper deals with a brief outline of the production process and how this affects the environment in terms of raw material preparation, smelting and waste disposal. Reference is made to the effect of hexavalent chromium on water and soil quality. Different methods of remediation are discussed.

The steps in establishing an environmental programme are outlined and various techniques are evaluated. The paper also touches on health related aspects of ferrochrome production. A case study is presented, which provides practical guidelines for a holistic environmental approach to ferrochrome production.

INTRODUCTION

Mankind is becoming increasingly concerned about the impact of his actions on the environment. Ferrochrome producers are no exception - particularly in view of the effect of hexavalent chromium release into the atmosphere, water and soil. Apart from the risk to the environment, Cr (VI) also poses a risk to human and animal life. However, the production of ferrochrome, if properly managed, has no adverse effects on either man or the environment. It is nevertheless necessary to be aware of the risks and hazards inherent in any industrial process and the production of ferrochrome is no exception.

As adequate and well established techniques are available to combat noise pollution and to prevent pollution of the ambient air and atmosphere by fume and dust, this paper deals mainly with the effects of Cr (VI) resulting from the production of ferrochromium.

Cr (VI) is a suspected carcinogen. In 1991 an OECD Report entitled "The State of the Environment", chromium is associated with lung cancer, gastro-intestinal cancer and dermatitis [1]. However, chromium is also an essential trace element for man - the difference lies in the oxidation state and intake. According to the US Department of Health & Human Services, a daily intake of 50 to 200 μg Cr (III) is recommended for adults to assist in the metabolism of sugars, proteins and fat [2]. On the other hand, exposure to high concentrations of Cr (VI) can be lethal - a lethal ingestion of Cr (VI) has been stated as 7,5 mg/kg body mass [3].

PRODUCTION PROCESS

The production of high carbon ferrochromium (HCFeCr) and charge chrome (ChCr) in an electric submerged arc furnace has the following environmental impact:

Raw Material Preparation

The handling, crushing, screening and proportioning of raw materials including chrome ore as feed to the furnace do not present a health or environmental risk, apart from manageable risks from noise and dust associated with these activities.

However, in order to determine the potentially hazardous effect of hexavalent chromium, a representative sample of chrome ore concentrate, typically -0,5 mm with a Cr_20_3 content of 45 %, was analysed according to the Toxicity Characteristic Leaching Procedure (TCLP) as specified by the United States Environmental Protection Agency (US EPA), in accordance with requirements stipulated in the Federal Register (Vol 51, November 1986).

The TCLP extract from this sample contained 0,12 ppm total chromium and <0,1 ppm Cr (VI). These levels are below the limit of 5 ppm Cr imposed by the US EPA which implies that chrome ores and concentrates are not classified as a hazardous substance with respect to chromium [4].

Smelting

The solid products obtained from the smelting of ferrochrome are metal, slag and dust. In open top furnaces the dust is collected as such in a bag filter plant, whereas in a closed top furnace, the dust is scrubbed in a venturi system and is produced as a slurry.

Chromium in its metallic state (zero valency) as ferrochrome is generally considered harmless - this is borne out by the International Agency for Research on Cancer (IARC) monograph titled "Evaluation of Carcinogenic Risks for Humans" (Volume 49) where both metallic chromium and Cr (III) are classified as Group 3 Compounds i.e. these compounds are not classifiable as to their carcinogenicity to humans [5]. No special precautions regarding toxicity are thus necessary when storing, transporting or using the alloy.

Slag is also regarded as harmless in terms of the IARC classification, as the chromium is predominantly present in ferrochrome slags as Cr (III). As such, in South Africa it can safely be consigned to a Class II landfill for non-hazardous substances with less onerous conditions than for a class I landfill. However, there exists a great deal of controversy regarding the possibility of oxidation of Cr (III) to Cr (VI). Numerous papers have been published on this topic; none of these relate specifically to ferrochrome slags in landfills. Rather, the papers under review addressed the issue of Cr (III) oxidation under laboratory conditions using Cr (III) solutions in the presence of strong oxidants e.g. $Mn0_2$. In order to allay any fears that may exist regarding the possibility of Cr (III) in ferrochrome slags oxidising to Cr (VI) in a landfill and thus slowly releasing Cr (VI) to the environment, carefully controlled experiments were set up to simulate conditions existing in a typical ferrochrome slag dump in South Africa. These experiments are scheduled to run over a number of months, but results to date indicate that there are no hazards associated with ferrochrome slag dumps in terms of the potential to leach hexavalent chromium.

The greatest risk to health and the environment in the smelting of ferrochrome lies in the dust from the bag filter or sludge from the gas cleaning system. This is particularly the case for open top furnaces where chromium is readily oxidised to Cr (VI) in the off-gas dust. Hexavalent chromium also occurs in the sludge and circulating water from the gas scrubbers of closed-top furnaces, albeit to a much lesser extent. Another factor which influences the occurrence of Cr (VI) in the off-gas dust stream, is the chemical composition of the slag. Furnaces operating under acidic slag regimes have significantly lower water-soluble Cr (VI) content of the dust than furnaces associated with basic slag practice.

The following table illustrates this trend.

TABLE 1. Water soluble Cr (VI) content of furnace dust.

Process		ppm Cr (VI)
Closed furnace:	acid slag practice	5
	basic slag practice	100
Open furnace :	acid slag practice	1 000
	basic slag practice	7 000

It is clear from the table that uncontrolled dumping of bag filter dust or sludge from a scrubber system will result in severe contamination of both surface and ground water by Cr (VI).

ENVIRONMENTAL MANAGEMENT PROGRAMME

Numerous options are available to counteract and prevent water and soil pollution. As with most problems, it is preferable to treat the cause and not the symptoms. Furthermore, a piecemeal approach to any pollution problem will in the long run not be cost effective. A holistic approach is required which should culminate in the formulation and implementation of an environmental management programme (EMP).

Various techniques can be used. The methodology adopted by Samancor has been found to be successful. At the outset, it was realised that specialist knowledge and skills would be required to produce the most cost effective EMP. The services of a consulting engineering firm were thus retained to work in close collaboration with plant personnel.

Geohydrological Survey

The first step in a remediation programme is to determine the extent of the problem, if any. For Samancor's Ferrometals chrome smelting works in Witbank, in the Eastern Transvaal, this involved a geohydrological study to determine soil and rock conditions in order to assess whether groundwater contamination was occurring; if so, to determine the flux, and lastly to model the hydrogeology of the site in the vicinity of potential sources of contamination.

The production facilities at Ferrometals consist of two closed top charge chrome furnaces, an open ferrosilicon furnace, a bottom blown convertor for the production of either medium carbon ferrochromium or ferromanganese and three open top furnaces currently producing ferromanganese.

The investigation included a study of aerial photographs to identify geological faults and topography, auger and core drilling to study ground formation as well as abstraction of groundwater from these boreholes to determine water quality. Another important reason for the geohydrological survey was to identify suitable areas for future landfills. A specific methodology was followed, in accordance with "Guidelines for Geohydrological Investigations as Pertaining to Industrial Ground Water Pollution", July 1992, of the Department of Water Affairs and Forestry (DWAF).

A conceptual geohydrological model was proposed which identified both a confined aquifer as well as a perched aquifer (figure 1) [6]. Analysis of groundwater and slurries revealed that water quality was acceptable both in terms of total chromium as well as Cr (VI). High sulphate levels could be attributed to former coal mining activities in the area.

Evaluation of possible future waste disposal sites was also conducted in accordance with guidelines relating to "Minimum Requirements for Waste Disposal Facilities" (DWAF, 1993). This involved a 6-step plan whereby sites were evaluated and ranked based on criteria such as logistics, topography, geohydrological properties and environmental factors.

Environmental Management Programme

The South African Department of Mineral and Energy Affairs has produced an Aide Memoire for the Preparation of an Environmental Management Programme Report (EMPR). EMPR's are only required for activities falling under the former Mines and Works Act. This act did not apply to Ferrometals; nevertheless the document provides valuable guidelines firstly to undertake an Environmental Impact Assessment (EIA) and secondly to formulate an Environmental Management Programme (EMP). The latter comprises five distinct phases viz a construction phase, an operational phase and a decommissioning and closure phase. A timetable identifying the duration and sequence of each activity as well as the financial implications of the EMP form the last two phases.

In the case of Ferrometals, the development of an EMP was relatively simple, as the results of the geohydrological investigation indicated that groundwater was not contaminated by Cr (VI). To control surface water a series of canals and suitably engineered catchment dams was proposed to prevent run-off of storm water from the site. In addition, regular pumping and analysis of borehole water was proposed to monitor ground water quality. A series of boreholes was thus also drilled as part of the investigation to develop an EMP. The location

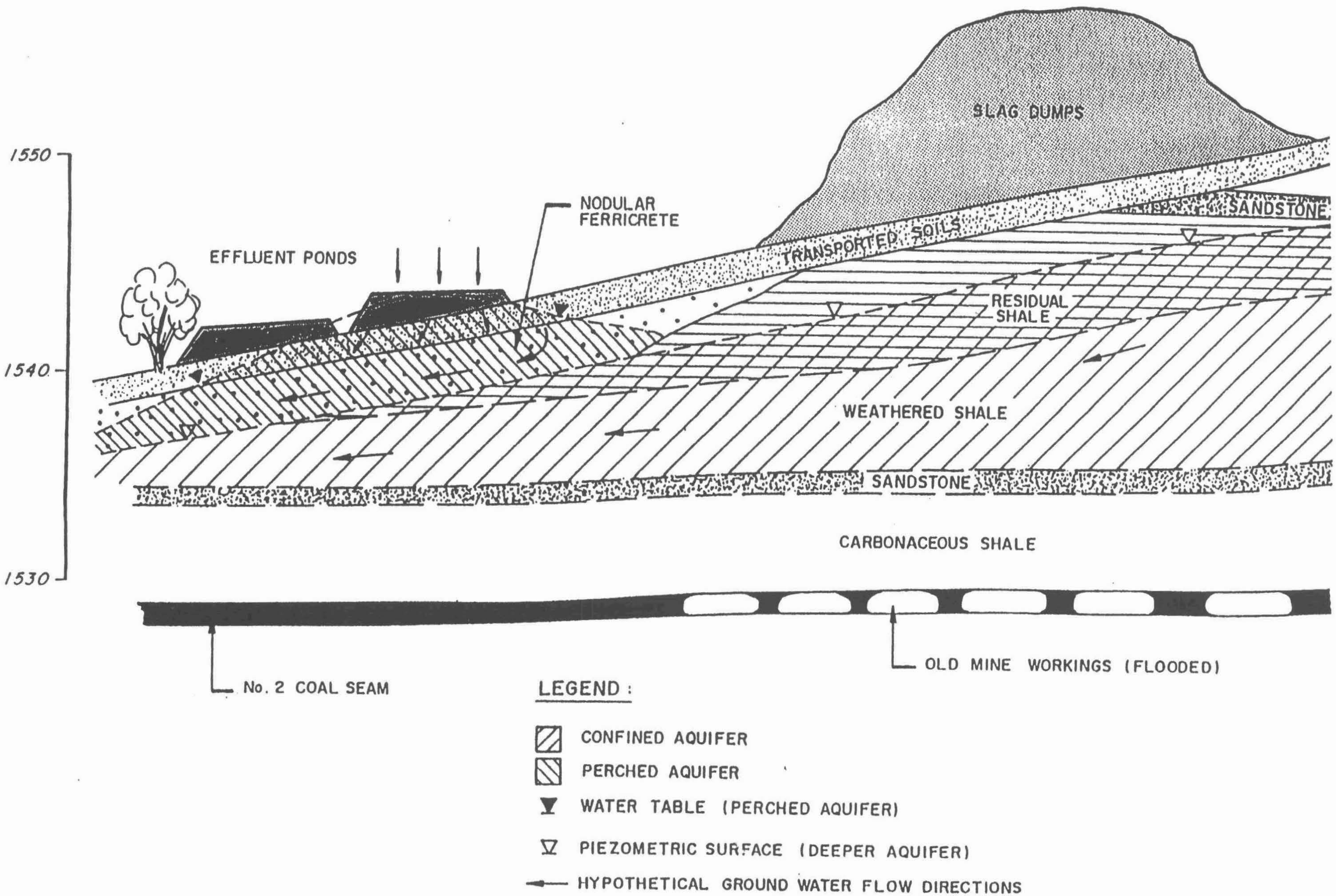

FIG. 1 CONCEPTUAL GEOHYDROLOGICAL MODEL

and depth of these holes were planned to provide maximum information as to the hydrogeology of the site. Water quality from boreholes downgradient from the effluent ponds was found to be within the legal limits (table 2). These effluent ponds contain sludge from the gas cleaning plants of the closed top charge chrome furnaces.

TABLE 2 South African Water Quality Standards and Criteria

		mg total Cr/l
Drinking water:	recommended limit	0,1
	negligible risk limit	0,2
	crisis limit	0,4
Effluent discharge:	total chromium	0,5
	hexavalent chromium	0,05

The final stage of the EMP involved quantifying the cost of the EMP both in terms of capital expenditure as well as operating costs. The EMP was structured in phases to result in the greatest reduction in risk of pollution after the implementation of phase 1. Capex was spread evenly over the period of implementation [7].

REMEDIATION

In most cases, remediation of already polluted water and soil will be necessary. For greenfield sites however, the task is much simpler and in this instance, a proper environmental impact assessment (EIA) is required beforehand. Prevention is always better than cure!

Environmental Impact Assessment

The purpose of an EIA is to determine the effect of any future activity on the environment in terms of current and pending legislation as well as to recommend ways to minimize and control the impact. In South Africa, there are currently twelve acts applicable to the environment, of which the most important are the Environment Conservation Act, the Water Act, the Health Act, the Atmospheric Pollution Prevention Act and the Hazardous Substances Act to name but a few. Similar situations will hold for other countries as well. Following on from an EIA, the next logical step is the formulation of an EMP as mentioned previously. However, the most important phase is the implementation of and ongoing commitment to the EMP.

Chemical Reduction of Cr (VI)

One of the remedies available to render bag filter dust or scrubber sludge environmentally acceptable in terms of the hexavalent chromium content, is by reduction of Cr (VI) to Cr (III). Solid state reduction is not feasible and thus the dust must be leached to get the water soluble chromium into solution before reduction. The most commonly used reducing agent is ferrous sulphate ($FeS0_4$). As the price of this commodity has trebled over the last year in South Africa, Samancor launched an investigation to determine the optimum "window" in terms of i.a. pH of leachant, temperature, reaction time and percentage of stoichiometric Fe (II) addition in order to minimise the addition of $FeS0_4$ whilst at the same time ensuring that the resultant water quality conforms to the set standards (table 2) and the precipitate formed, would not continue to leach Cr (VI).

As a prerequisite for the Cr (VI) reduction testwork, it was necessary to investigate the extent to which Cr (VI) leaches from bag filter dust under conditions of varying temperature, time, pH and liquid : solid ratio's. The effect of agitation and aeration was also determined. Results indicated that pH was the most important factor with maximum leaching occurring in the pH range 2-6. Temperature was of less importance whilst aeration had minimal effect. It was also found that leaching of elements other than Cr was extensive. The concentrations in the leach liquor for different liquid : solid ratios are given in table 3 for a leach period of 23 hours.

TABLE 3 Concentration of Elements in Leachate (ppm)

Element	L/S Ratio	
	5 : 1	20 : 1
As	1,13	0,28
B	3,3	0,83
Ba	0,13	0,03
Ca	151	37,8
Cd	0,67	0,17
Cr (VI)	480	120
K	3470	867,5
Mg	1423	355,8
Mn	21	5,3
Na	7424	1856
P	19	4,75
Pb	<0,70	<0,18
S	4155	1039
Si	30	7,5
Zn	4995	1249

The next phase of the testwork involved the reduction of Cr (VI) with $FeSO_4$ at different stoichiometric levels of $FeSO_4$ in order to determine optimal conditions. It was found that over the pH range 2-8, Cr (VI) was reduced from an initial value of 480 ppm to less than 0,05 ppm at 128 % stoichiometric $FeSO_4$ addition. As the natural pH of the charge chrome bag filter dust leachate varies between pH 8-10, the result was important inasmuch as pH conditioning was found to be unnecessary. The reduction of Cr (VI) to Cr (III) by $FeSO_4$ resulted in the formation of $Cr(OH)_3$ precipitates. These precipitates contained $<0,05$ ppm soluble Cr (VI) in the range pH 5-8 [8,9,10].

A further investigation which was necessary, was to develop a standardised procedure for determining the water soluble Cr (VI) content of bag filter dust. It was found that virtually complete leaching of Cr (VI) was obtained at a liquid : solid ratio of 20:1 and with vigorous agitation over a 24 hour period at ambient temperature (20 °C).

Another complication was the accuracy of analysis of Cr (VI) in the presence of Fe (II) and at low concentrations. Various methods as recommended by the US EPA were evaluated. The two most suitable methods were found to be UV spectroscopy with diphenylcarbazide indicator and ion chromatographic analysis. The latter method is expensive both in terms of cost of the apparatus as well as running costs. However, where accurate analysis of Cr (VI) in the presence of Fe (II) and Cr (III) is required, this is the recommended procedure [11].

Bacterial reduction of Cr (VI)

This topic is comprehensively described in a paper by Apel and Turick entitled "Bioremediation of Hexavalent Chromium by Bacterial Reduction" [12]. It was shown that the bacteria *Pseudomonas aeruginosa* and *Pseudomonas fluorescence* both have the ability to reduce Cr VI to Cr (III). However, Samancor also operates closed top charge chrome furnaces where a significant percentage of the carbon requirements for chromite reduction can be in the form of coal, resulting in a build-up of phenols in the closed circuit scrubbing water of the venturi gas cleaning system. A laboratory experiment is currently underway where Cr (VI) leachate is spiked with 50 ppm phenol and the bacteria introduced into solutions of chrome (VI) - phenol water together with nutrients. It has been found that the bacteria can tolerate the presence of phenols. The next step is to determine whether the bacteria can utilize the phenols as an energy source thereby solving the Cr (VI) and phenol problems simultaneously.

Solidification / Stabilization

This topic has also been researched extensively; however no reference was found with regard to stabilization / solidification (S/S) of ferrochrome bag filter dust and therefore it was necessary to undertake a S/S programme specifically for bag filter dust [13].

The most commonly used S/S agent is Portland cement and a series of laboratory tests was conducted using Portland cement in different concentrations to solidify the dust and stabilize i.a. the hexavalent chromium. Evaluation of the S/S products included leaching tests, permeability measurements and strength tests. The results indicated that cement additions of between 7,5 % and 15 % resulted in solidified masses which leached <5 ppm Cr using the EPA TCLP. Further testwork is underway to determine long term stability and strength of the solidified dust using combinations of Portland cement, fly-ash and lime. However, it has already been demonstrated that S/S techniques have the potential to prevent Cr (VI) contamination of soil and water from bag filter dust.

Other Methods of Remediation

There are numerous other methods available to prevent Cr (VI) in bag filter dust or scrubber sludge from polluting the environment. An obvious procedure is to recycle the dust back to the furnace. Some form of prior agglomeration is necessary, as fine dust cannot be returned to the furnace as such. Well proven methods of agglomeration include briquetting and pelletising. However, these are costly options which require additions of binders as well as curing processes to render the agglomerates strong enough to withstand handling and to prevent thermal spalling.

Samancor is researching the suitability of an agglomeration process which requires neither a binder nor a curing process, but relies on a high intensity mixer. Results to date are promising. The long term effect of recycling heavy metals back to the furnace must still be determined. It is envisaged to bleed off a stream of dust from the bag filter at appropriate intervals to prevent a build-up of such metals.

Another technique is DC plasma arc melting/smelting of bag filter dust to produce an environmentally acceptable slag whilst at the same time recovering residual chromium and iron oxides from the dust as ferrochrome. The plasma furnace is also a useful tool i.a. to remelt unsaleable metal fines and chrome rich scrap.

Finally, it has been shown that selected grasses and other plants have the ability to take up chromium from the soil [14]. Unfortunately, the chromium taken up by plants remain mostly in the roots. Chromium removal by harvesting the stem and leaves of the plants thus does not seem to be feasible; nevertheless it affords a method of polishing Cr (VI) contaminated soils. Suitable plants for South African conditions have been identified and laboratory trials are underway.

CONCLUSIONS

The environmental impact of ferrochrome production can be effectively contained using existing techniques and processes. However, as was demonstrated in the paper, the problems associated with hexavalent chromium require special consideration. Initiatives launched by Samancor will ensure that sources of Cr (VI) contamination are identified and treated in the most cost effective manner whilst ensuring that all applicable environmental standards are met and legislation conformed to.

ACKNOWLEDGEMENTS

The author is indebted to engineering consultants Steffen, Robertson & Kirsten as well as the personnel at Gencor Process Research and Gencor Laboratories for their guidance and input. The author also wishes to thank Samancor for permission to present and publish this paper.

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