SESSION A

Environmental Solutions to Waste Products from Ferrochrome Production

Willem A. Gericke

Samancor Chrome Alloys Division
Private Bag X7228, Witbank, 1035, South Africa

Abstract

The paper describes the methodology adopted by Samancor to classify and characterise waste products from its ferrochrome operations. These wastes were also rated in terms of their impact on the environment.

Efforts were concentrated on finding uses for charge chrome slags, by far the biggest contributor to waste generation.

A novel method of constructing low income housing was developed. This method resulted in 878 houses being built with a 33 % larger floor area than if conventional construction methods were used.

Other uses include the production of fired clay bricks incorporating slag and filter dust. These processes have been patented.

Fine charge chrome slag is also finding applications as a blasting grit.

Low carbon ferrochrome slag and dust are being evaluated as cement extenders where mixtures of up to 70 % slag and dust have been successfully used in mortars.

Finally, LCFeCr slag is also used as a soil conditioner for acid soils.

A number of other applications are in the development stage.

Introduction

The production of ferroalloys is associated with the formation of a variety of waste products. These products mostly have little intrinsic value and have to be disposed of, often at a cost to the producer. Apart from the disposal cost, in recent years these waste products also presented an environmental problem and in some cases, a health risk to humans. Valuable land space is also taken up in the disposal of waste.

It has become necessary in many countries to legislate the disposal of such waste products in order to minimise the effect on the environmental and human life[1,2,3,4,5,6].
Waste disposal has thus become a burden to the producer and costly resources are allocated to disposal to ensure that environmental and health criteria are met.

Samancor, as a major producer of chromium and manganese ferro-alloys is no exception. Through a process of systematic evaluation of options, Samancor has developed novel processes and techniques to dispose of and turn waste products to account. Samancor has recently created corporate management positions for environment, health and safety and has also established departments to manage environment, health, safety and quality at each of its operating centres.

Waste characterisation

Samancor's Chrome Alloys Division produces all commercial grades of ferrochrome alloys as indicated in Table 1. Solid waste from the production units amounts to some 1,5 million tonnes of ChCr slag, 18 000 tonnes of MCFeCr slag and 50 000 tonnes of LCFeCr slag per annum. Additionally, the total dust collected from the semi-closed submerged arc furnaces is in the order of 50 000 tonnes per annum. Disposal of such quantities of waste can thus not be left to chance, but must be managed in a manner which will not cause harm to the environment or to human life. A further objective is to turn such waste to account to offset the costs of waste disposal and to minimise the quantities of waste to be dumped.

Recently promulgated Minimum Requirements for waste management in South Africa are in line with first world standards and even exceed such standards in some instances[4,5,6] The Best Practicable

Environmental Option (BPEO) was adopted in order to provide affordable environmental protection, although it was conceded that such Minimum Requirements would inevitably result in increased costs to the producer. Principles adopted in setting these standards include "polluter pays", "cradle to grave responsibility" and the "precautionary principle". As is evident, the adoption of the Minimum Requirements places an additional burden on the South African ferro-alloys industry.

With this in mind, it was necessary for Samancor Chrome Alloys Division to undertake a systematic classification and characterisation of waste streams from their production processes. The first survey was completed in 1994, followed by an update of the survey in 1997[7,8]. These studies provided valuable information on i.a. the generation of waste, detailed chemical and physical analysis as well as results of Toxicity Characteristic Leach Procedure (TCLP) tests, as per US EPA[9]. A risk assessment as part of the waste classification and characterisation programme of the various waste streams in terms of the US EPA TCLP criteria indicated that charge chrome slag is not a risk, charge chrome scrubber slurry and low carbon ferrochrome slag has a moderate risk whilst charge chrome filter dust, low carbon ferrochrome filter dust and medium carbon ferrochrome slurry are considered to be high risk products in terms of their environmental impact (Table 2).

Typical TCLP values for nine elements in the various waste streams are given in Table 3.
As can be seen from Table 3, in terms of TCLP criteria, only ChCr and LCFeCr dust do not meet the US EPA limits for Cr^{Tot} and Cr^{6+}. All other elements are within US EPA TCLP limits.

Waste streams from all other products (ChCr slag, ChCr scrubber slurry & LCFeCr slag) have TCLP extracts for all elements within US EPA limits. Thus, in terms of waste disposal and waste utilisation, only dust from ChCr and LCFeCr bag plants require prior treatment to reduce Cr^{6+} to below 5 ppm.

Charge chrome slag

By far the biggest contribution to waste generation arises from charge chrome slag - approximately 1,5 million tonnes are produced each year at Samancor's charge chrome furnaces. It is thus understandable that great efforts were directed towards utilisation of this resource. A number of novel applications have been developed, some of which have made a significant contribution to the communities in the vicinity of the charge chrome plants.

Building Industry

In addition to waste classification and characterisation, charge chrome slags were subjected to tests by the National Building Research Institute (NBRI) of the South African Council for Scientific and Industrial Research (CSIR) as long ago as 1981 with respect to their suitability as concrete aggregate[10]

It was found that in terms of the criteria used by the CSIR, charge chrome slags were within all specified limits. Criteria included water absorption, soluble deleterious impurities, sulphate-, popping- and iron unsoundness, autoclave expansion, dry shrinkage and relative density. Only in terms of relative density, did charge chrome slags exceeded the preferred value of 3,0 (SABS Test Method 844) by 10 %.

More recent tests conducted by the Portland Cement Institute in 1992 again indicated that "this material should prove acceptable for use in the manufacture of concrete masonry units and for concrete"[11].

Apart from evaluating physical properties, leach tests were also undertaken by reputable international laboratories[12,13]. These tests indicated that charge chrome slag used as aggregate in concrete or concrete bricks, was "extremely unlikely to cause any sort of environmental danger or pollution in use".

Having thus established the suitability of charge chrome slags in the building industry, applications were sought where the surrounding communities would derive the most benefit.

Low Cost Housing

As part of the national RDP (reconstruction and development programme), the City Council of Witbank received funds in terms of the National Housing Grant to construct a predetermined number of low cost houses for the previously disadvantaged community in an informal settlement where shacks had been erected (Figure 5), without any services available to the community. The total grant for the project amounted to R15 145 500 ($3 155 300). For this sum of money, the stands had to be surveyed, provided with infrastructure (roads, electricity, potable running water and waterborne sewage) and 878 decent houses had to be built. The provision of services amounted to R8 150 / stand ($1700), leaving an amount of R9 100 ($1 900) for the construction of the house. Conventional building methods would only permit the construction of a 24 m^2 house for the allotted amount. However, creative construction methods, coupled with the availability of washed, sized ChCr slag at no cost from Samancor's Ferrometals plant near Witbank made it possible for houses with an area of 32 m^2 to be constructed for the same amount - an increase of 33 % in area without compromising on the durability of the dwelling or the standard of finish (Figures 3 and 4).

As can be seen in Figure 1, unskilled labour from the informal settlement was recruited by the local contracting firms. The construction method entailed the following : the foundation slab was cast using a mixture of slagment (portland blast furnace cement) and ChCr slag as aggregate to a strength of 15 MPa. Thereafter the walls were cast using steel shutters as formers (Figure 2). Concrete strength for the walls was specified as 10 MPa. A volume of 18 m^3 aggregate was used per house or 15 800 m^3 for the total project.

The houses were designed in such a manner that extensions to the homes could easily be made by the owners themselves at a later stage (Figure 6).

The project has been so successful, that a further 2 400 houses are to be built in the same area to the same standards. These houses are provided at no cost with full ownership to the new owners who qualify for such houses (families with no or little income).

Other uses for ChCr slag as part of the same project include the construction of proper roads using a mixture of 60 % slag, 40 % gravel by volume for the construction of a 150 mm sub base layer. This is topped with a gravel / clay mixture for the base layer followed by a slag chip / tar sprayed top layer.

Paving-blocks and kerb stones will also be made from a mixture of fine slag and slagment.

Brickmaking

In collaboration with the Material Science and Technology Division of the South African Council for Scientific and Industrial Research (CSIR), Samancor Chrome Alloys Division embarked upon a programme to utilise waste products from the ferrochrome industry for the production of fired bricks. This project ran over a period of five years from 1993 to 1997.

The objectives were to investigate the suitability of and to maximise the use of filter dust and charge chrome slag in the production of conventional fired clay bricks.

Clay samples were obtained from local brickworks and subjected to brickmaking tests using 2- and 3 component mixtures of clay, slag and dust. Initially, dust from a 75 % FeSi furnace was used, because of its proven pozzolanic properties. This was later substituted for dust from the charge chrome furnaces. Two types of charge chrome slags were used. Typical analyses of the raw materials are given in Table 4.

Mineralogical investigation of the materials indicated that the clays consisted of predominantly kaolinite with minor amounts of quartz, feldspar and talc. The dusts were amorphous while the slags consisted of $MgAl_2O_4$ spinel and γ-Fe_2SiO_4 as the major phases. For phase I of the project, 16 binary mixtures were used. Tiles were pressed and fired at temperatures ranging from 900° C to 1300° C in 50° C increments. Tiles were evaluated in terms of : green strength, % drying shrinkage, % fired shrinkage, % mass loss as well as water saturation coefficient (ratio of % cold water absorption after 24 hrs : % boiling water absorption after 5 hrs according to SABS method 227-1986) [14] The colour of the fired tiles as well as the propensity for cracking were noted, as these were important criteria in producing acceptable fired bricks.

The same mixtures were also used to extrude and press bricks. Bricks were fired in a clamp kiln at the same temperature range. *Pressed* bricks were evaluated in terms of : pressing behaviour, drying behaviour, green strength, water absorption, firing range, firing shrinkage and appearance after firing.

Extruded bricks were evaluated in terms of : plasticity, dog-earing, green strength, drying shrinkage, air drying and rapid drying, firing shrinkage, mass loss, water absorption, modulus of rupture, compressive strength, colour and appearance after firing. From these thousands of tests, it was concluded that the addition of slag and dust to clay would enhance the quality of both pressed and extruded bricks fired in a clamp kiln where accurate temperature control is not possible. Additions of up to 50 % slag and 30 % dust would still produce acceptable bricks. Higher percentages would impair the extrudability of the bricks. It was found that the slag acts as a filler whilst the dust acts as a flux[15].

Having identified the most promising binary mixtures, phase II of the project focused on 3 component mixtures using only clay W, slag A and FeSi dust. The same procedures were followed for pressing tiles as well as for pressing and extruding bricks, firing and evaluating tiles and bricks. It was concluded that all 17 combinations of clay, slag and dust tested produced acceptable stock bricks while 4 mixtures produced acceptable face bricks in terms of SABS-227-1986[16].

Two South African patents were granted for the production of fired bricks with slag and filter dust.

Finally, in collaboration with a local brick works, it was decided to produce 12 000 bricks of each of the following mixtures :

80 % clay with 20 % FeSi dust
50 % clay with 30 % FeSi dust and 20 % ChCr slag

Full scale trials were hampered by abnormally high seasonal rains, labour problems and difficulties with dust handling, as the brickworks was not equipped to deal with additional raw material components. Nevertheless, bricks were made and were quickly sold out, proving market acceptance. The 50:30:20 clay : dust: slag bricks looked excellent, according to the brickmaker - see Figures 7 and 8[17]. Finally, the FeSi dust was substituted for ChCr dust and bricks were again produced according to the above recipes at the CSIR laboratories. Bricks were crushed and subjected to US EPA TCLP tests to determine whether Cr^{6+} would leach from these bricks. All bricks produced leachates containing less than 0,03 ppm Cr^{6+}, thus well below the limit of 5 ppm. Apart from a potential cost saving to the brickmaker, bricks produced from a clay, slag, dust mixture, had a lower drying and firing shrinkage and most importantly, improved green strength of up to 12,5 %. It now remains for this technology to be marketed on a wider basis.

Blasting Grit

A relatively new use for charge chrome slag is as a blasting grit. Slag based blasting grits are being used in i.a Finland and Japan, but as yet, have found limited application in South Africa.

Extensive tests by independent laboratories have indicated that the material is safe to use and poses no threat to the environment either, provided normal precautionary measures are followed, such as wearing the necessary protective clothing. EPA TCLP extracts for the following elements are all within the threshold levels : arsenic, barium, cadmium, chromium, lead, mercury selenium and silver.

Because of its relatively low cost, hardness and angular shape, it is forecast that the use of charge chrome slag as a blasting grit will find increasingly wider applications.

LOW CARBON FERROCHROME SLAG

CEMENT EXTENDERS

Both LCFeCr slag and bag filter dust are being evaluated in terms of their suitability as cement extenders. It is believed that this is a novel application. Test cubes were made from mixtures containing up to 70 % LCFeCr slag in combination with varying levels of ordinary portland cement (OPC) and LCFeCr dust and allowed to cure for 7 and 28 days respectively.

Compressive strengths were between the specifications for OPC (16 MPa @ 7 days; 32 MPa @ 28 days) and rapid hardening cement (RHC) (33 MPa @ 7 days; 47 MPa @ 28 days)[18].

Cubes were crushed and subjected to the US EPA TCLP. It was found that the leachate contained lower concentrations of the 8 EPA defined elements than the TCLP limits.

However, the long term stability of mortars made from these mixtures must be evaluated before commercialisation of this technology takes place.

AGRICULTURAL SOIL CONDITIONERS

The use of LCFeCr slag as an agricultural soil conditioner is not new[19]. In South Africa, the LCFeCr slags from Samancor have been used as such for many years. However, more recently, the environmental impact of the use of such slags has been questioned and to this end Samancor undertook extensive tests to determine the effect of the water soluble Cr^{6+} on the environment in terms of potential uptake of Cr^{6+} in the food chain. The slag addition rate is normally well below 10 t/ha (1 kg/m^2). In conjunction with the Institute for Soil, Climate and Water, soils from areas where LCFeCr slag had been applied for periods of up to eight years, were sampled and analysed. This was compared to soils where slag had never been applied.

It was found that the level of plant - available chromium was less than 0,4 mg/kg, thus well below the proposed limit of 50 mg/kg soil[20].

The conclusions drawn were that the use of LCFeCr slag from Samancor as an agricultural soil conditioner poses no threat to the environment. In fact, in chrome-deficient soils, LCFeCr as a liming agent may even prove beneficial to provide edible crops (eg maize) with sufficient chromium to satisfy the minimum dietary requirement of chrome in humans. The nutritional role of chromium in man has been well described[21]. It has been shown that small amounts of chromium could lead to an improvement in impaired metabolism of glucose.

Other applications

A number of other applications for waste products from the ferrochrome production process are currently under investigation i.e. the extraction of Zn and other metals from filter dust. Results are encouraging and could form the basis of future papers.

Conclusions

A number of novel applications have been found for products which are typically discarded as having no value. Further work is in the pipeline which could yield positive results.

All potential uses for waste products will increasingly be subjected to an evaluation of their impact on humans and the environment and only applications which meet these criteria will find acceptance.

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Table 1 : Samancor Chrome Alloys Production Capacity

Plant	Location	Furnace Type	MVA Rating	ChCr Capacity (t/a)	Fume Abatement Facility
Ferrometals	Witbank	Semi-closed SAF (F1)	25	40 000	Bag filter
		Semi-closed SAF (F2)	25	40 000	Bag filter
		Semi-closed SAF (F3)	36	45 000	Bag filter
		Closed SAF (F4)	48	90 000	Wet scrubber
		Closed SAF (F5)	48	90 000	Wet scrubber
		Semi-closed SAF (F6)	48	70 000	Bag filter
		CLU converter		60 000[(1)]	Wet scrubber
Palmiet Ferrochrome	Krugersdorp	DC-Arc (P1)	40	50 000	Wet scrubber
		Open SAF (P2)	20	35 000	Bag filter
		Open SAF (P3)	20	35 000	Bag filter
Tubatse Ferrochrome	Steelpoort	Semi-closed SAF (T1)	30	55 000	Bag filter
		Semi-closed SAF (T2)	30	55 000	Bag filter
		Semi-closed SAF (T3)	30	55 000	Bag filter
		Semi-closed SAF (T4)	37	60 000	Bag filter
		Semi-closed SAF (T5)	37	60 000	Bag filter
		Semi-closed SAF (T6)	37	60 000	Bag filter
Middelburg Ferrochrome	Middelburg	Semi-closed SAF (M1)	48	85 000	Bag filter
		Semi-closed SAF (M2)	48	85 000	Bag filter
		DC-arc (M3)	62	100 000	Wet scrubber
		Open SAF (B)	10,5	}	Bag filter
		Open SAF (C)	10,5	} 45 000[(2)]	Bag filter

Note : (1) MCFeCr production

(2) LCFeCr production

Table 2 : Risk Assessment of Chromium-bearing Waste Streams

Risk	Waste Stream
Low	Charge Chrome slag
Moderate	Charge Chrome scrubber slurry LCFeCr slag
High	Charge Chrome filter dust LCFeCr dust MCFeCr scrubber slurry

Table 3 : TCLP Results on Waste Streams

Waste Stream	Concentration in TCLP Extracts (ppm)								
	Ag	As	Ba	Cd	Cr^{Tot}	Cr^{6+}	Pb	Hg	Se
US EPA Limits	5	5	100	1	5	5	5	0,2	1
ChCr slag	-	-	-	-	0,10	-	-	-	-
ChCr dust	0,02	<0,02	0,36	0,08	10,1-13,1	11,6	0,03	<0,02	<0,02
ChCr scrubber slurry	-	<0,25	0,53	<0,03	0,72	<0,02	<0,07	-	-
LCFeCr slag	-	-	-	-	0,9	0,14	-	-	-
LCFeCr dust	-	-	-	-	18-80	60,8	<0,06	-	-

Note : "_" indicates not determined

Table 4 Raw Material Analyses for Brickmaking Trails

	ChCr slag A	ChCr slag B	Clay M	Clay P	Clay W	75 % FeSi dust	ChCr dust
SiO_2	32,0	22,5	51,4	53,7	49,6	89,3	52,9
Al_2O_3	28,3	27,4	31,1	24,9	30,7	2,65	5,40
Cr_2O_3	9,5	8,70	0,03		0,06	0,15	5,00
Fe_2O_3	5,35	8,53	3,20	8,15	4,60	1,33	3,90
MgO	16,3	19,7	0,00	0,62	0,07	1,14	10,0
CaO	1,46	8,01	0,03	0,18	0,00	0,53	0,33
ZnO							12,0
Na_2O	0,35	0,33	0,02	0,33	0,03	0,27	4,00
K_2O	0,29	0,15	0,52	2,99	0,58	1,16	3,70
P_2O_5	0,18	0,15	0,55	0,19	0,18	0,18	0,03
TiO_2	1,01	0,57	1,31	0,72	1,61	0,58	0,08
MnO	0,47	0,39	0,02	0,02	0,04	0,18	0,75
LOI*	-1,26	-1,91	11,00	7,23	11,70	3,32	

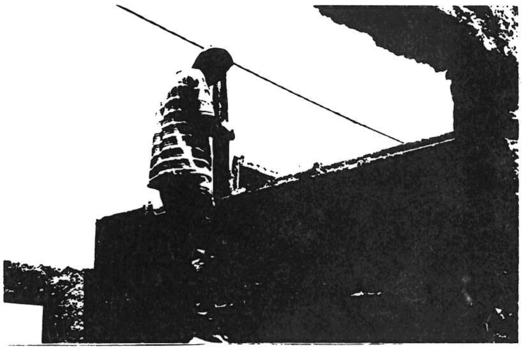

Figure 1 Method of construction

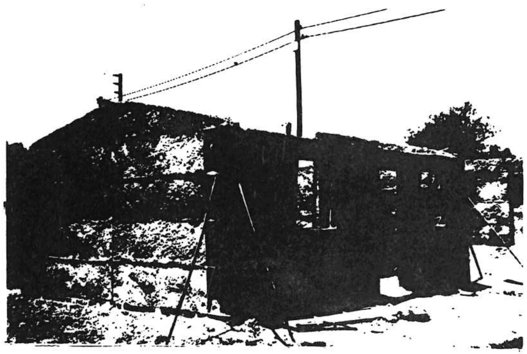

Figure 2 Completed shell

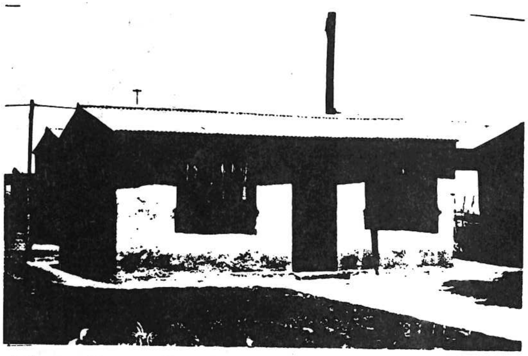

Figure 3 Finished product

Figure 4 Proud new homeowners

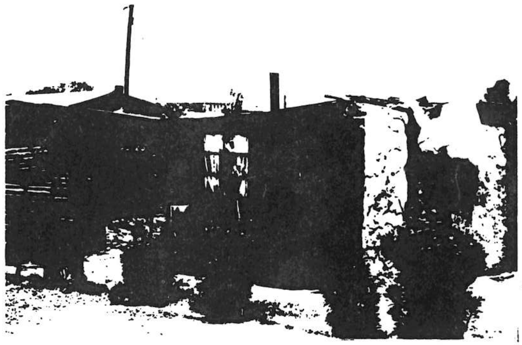

Figure 5 Before ....

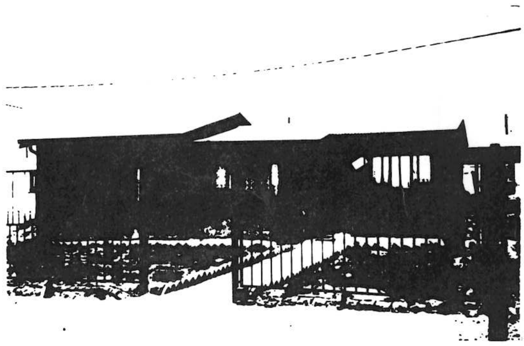

Figure 6 ......and after

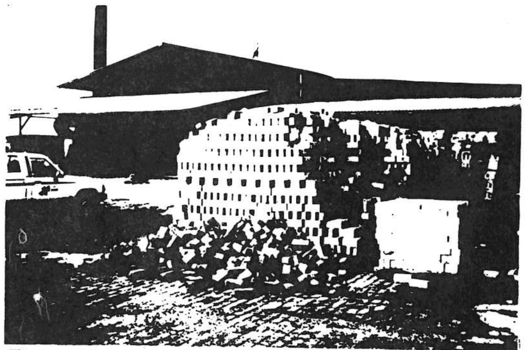

Figure 7 Fired bricks produced from clay ChCr slag / filter dust mixture

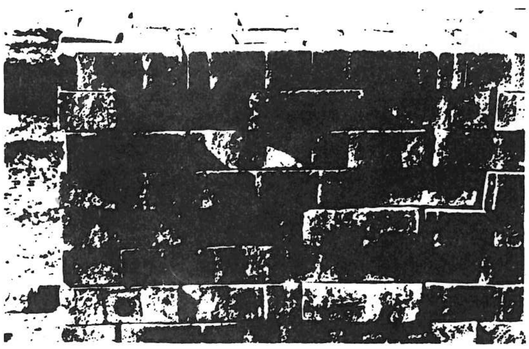

Figure 8 Close-up of fired bricks