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Valuable waste

Recovery of chromite values from ferrochrome industry flue dust

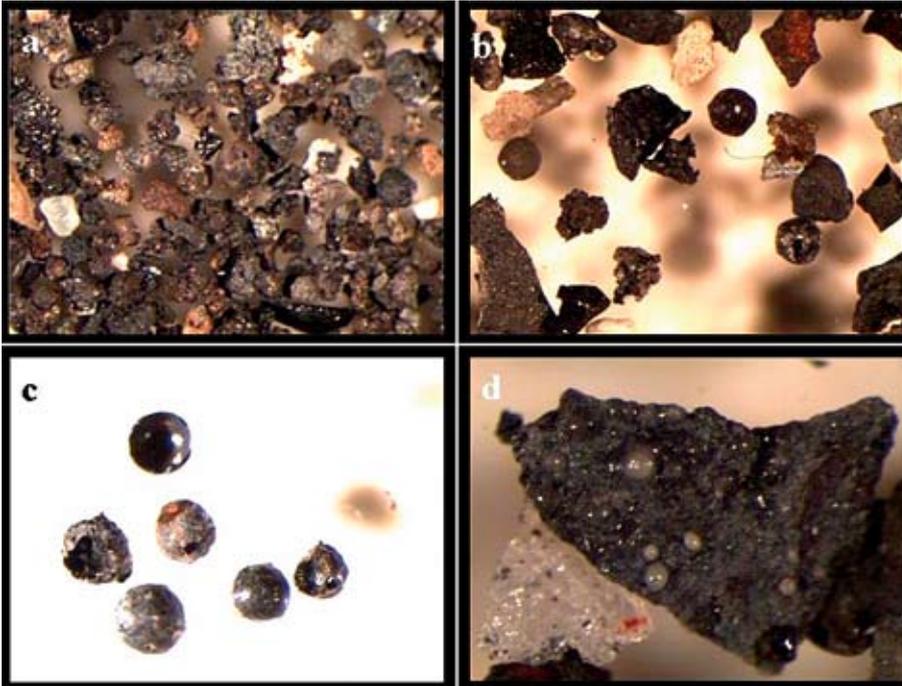
Summary: Ferrochrome industry waste, such as flue dust, contains chromite minerals that are considered to be hazardous materials if left untreated, stockpiled or landfilled. Recovery of chromite values, by physical beneficiation techniques, can be applied to support recycling, the remaining waste being transformed into non-toxic materials for safe disposal. It is beneficial both with regard to saving raw material resources as well as reducing chromium pollution. To understand the nature of this waste and to develop a process for recovery of the chromium values, studies were conducted, with closer examination of the methods and equipment used, e.g. optical microscopy, XRD, Mozley mineral separator and magnetic separation.

1 Introduction

Waste is a source of secondary raw materials, but at the same time can negatively impact the natural environment and public health. The flue dust generated from the ferrochrome industry is one such waste containing chromite minerals. The toxic nature of trivalent and hexavalent chromium makes the flue dust from the ferrochrome industry hazardous. About 400–500 kg residue is generated per tonne of ferrochrome metal produced – this residue includes slag, flue dust and sludge [6]. Flue dust generation is increasing enormously as the production of ferrochrome increases, creating the environmental problem of the disposal of this hazardous solid waste. Hence, the focus of this research is to examine the composition of one such flue dust waste from the ferrochrome industry and to develop processing technologies to recover the chromite mineral values, leaving a less hazardous

residue. The key strategy is to minimize as well as reuse the volume of such hazardous waste.

Chromium ore, or chromite, occurs exclusively in ultramafic igneous rocks. The chromium occurs as a chromium spinel, a complex mineral-containing magnesium, iron, aluminium and chromium in varying proportions depending upon the deposit. Chromite has varying proportions of trivalent chromium and iron and can be represented as $(\text{Fe Mg})\text{O}(\text{Cr Fe Al})_2\text{O}_3$. Large variations in the total and relative amounts of chromium and iron in the lattice occur depending on the different geological and geographical distribution of chromite deposits. These not only affect the Cr_2O_3 content but also the Cr : Fe ratio, which determines the chromium content of the ferrochrome metal product. The variation also affects the reducibility of the ore. Increasing amounts of



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- a) +500 μm sieve fraction sample showing presence of fused carbon particles (black), metallic particles (shining) and silicates (light/white coloured) (20 x)
- b) +210 μm sieve fraction sample showing presence of different types of globules with or without metallic particles (30 x)
- c) +210 μm sieve fraction sample showing presence of broken hollow globules (top), porous globules (bottom right extreme), solid globules and fractured globules (30 x)
- d) Some of the silicate globules are entrapped within the fused carbon mass in the +210 μm sieve fraction (30 x)

magnesium compared with iron in the divalent site will make the chromite more difficult to reduce whereas increasing amounts of iron in the trivalent site replacing aluminium will increase the reducibility of the chromite.

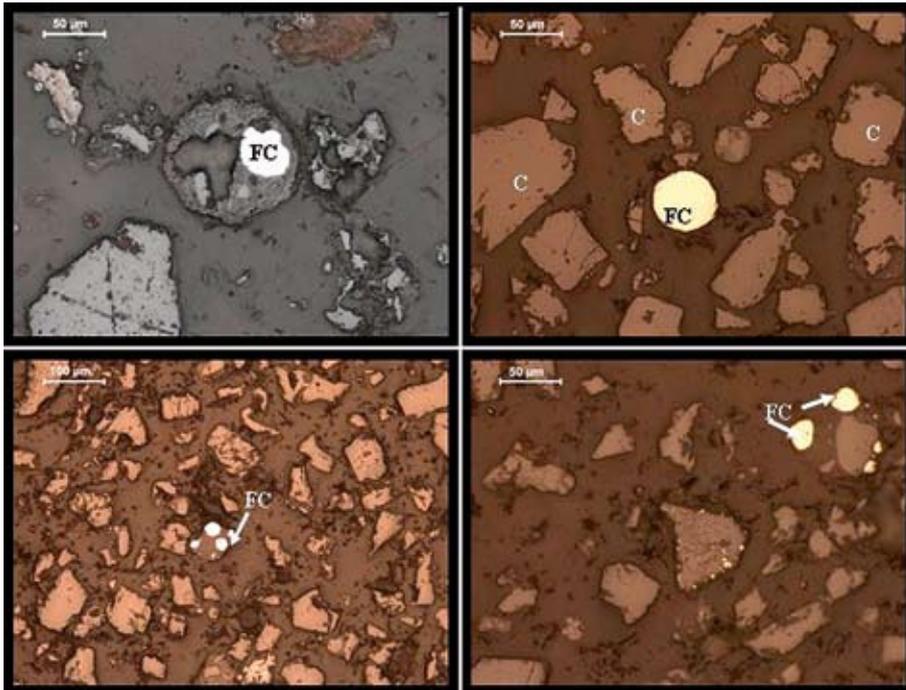
Most of the world's production of chromite (95 %) is used in the metallurgical industry in the form of ferrochromium alloys. The alloys are produced by high-temperature reduction (smelting) of chromite. They are essentially alloys of iron and chromium with much lower amounts of carbon and silicon, the amounts depending upon the grade or type of alloy, and impurities such as sulphur, phosphorous and titanium. The conversion of chromite to ferrochromium alloys is dominated by electric submerged arc furnace smelting with carbonaceous reductants, predominantly coke, and fluxes to form the correct slag composition. Slag and furnace dusts (flue dust) are generated as waste in enormous quantities during ferrochrome production. These flue dust particles released into the environment, during the ferrochrome production process, are the sources of high levels of toxic elements [1, 3, 4, 8] that pose ecological problems.

The ferrochrome market demand is increasing day by day, as a result the world production of ferrochrome has increased

to 7.3 mill. t/a. South Africa is the leading producer [7] of ferrochrome accounting of about 41 % (3.0 mill. t) of the world production followed by Kazakhstan 16.2 % (1.2 mill. t), China 13.5 % (1.0 mill. t) and India 8.6 % (0.6 mill. t). In view of this, the ferrochrome industry is directing its efforts to the utilization of this flue dust waste as products to reuse and recycle in order to meet their environmental responsibility. So far, only sporadic attempts have been to characterize and beneficiate such waste and the data are still inadequate.

2 Material and methods

The flue dust sample was collected from one of the operating plants of the ferroalloy industry situated in the eastern part of India. The flue dust sample was analysed with an optical stereomicroscope as well as with a polarized light microscope to determine its phases. The C800 mineral separator supplied by Richard Mozley Ltd/UK, which has V-type tray profile, was used in the gravity separation experiments. A laboratory wet high-intensity magnetic separator (WHIMS) Box Mag supplied by Eriez Magnetics Europe Ltd/UK was used in the magnetic separation tests.



- 1 a) Remnants of ferrochrome metal trapped within the slag
 b) Remnants of ferrochrome metal along with the flue dust
 c) Remnants of ferrochrome metal trapped within the silicates
 d) Remnants of ferrochrome metal along the outlines of the chromite grains
 C = chromite and FC = ferrochrome metal

3 Results and discussion

3.1 Characterization studies

The flue dust microparticles were analyzed with the optical microscope. This flue dust sample consists of a variety of particles that differ in size, morphology, internal microstructures, mineralogy and chemical composition. Optical microscopic analysis revealed that the flue dust sample consists of

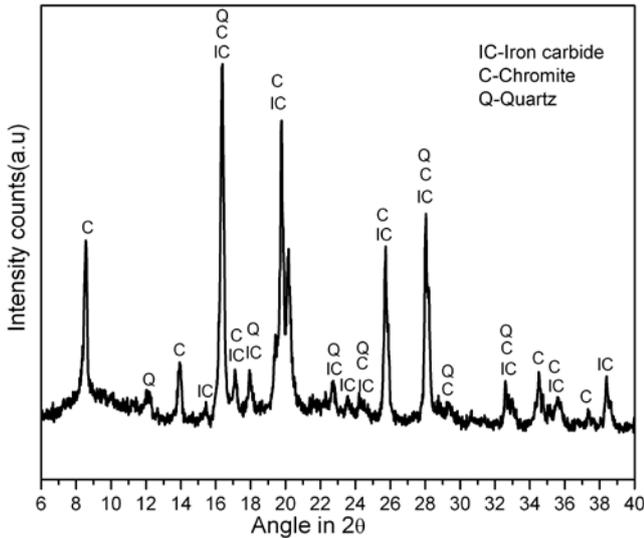
three different mineral phases, i.e. silicate phase quartz, chromite phase and a metallic phase that is ferrochrome. Unlike these three phases, the carbon also occurs as unburnt carbon/fused carbon (Lead picture). The metallic phase stands for the ferrochrome mostly found along the grain boundaries of chromite as well as along the fracture planes. At times this ferrochrome metal rims the chromite grains, which may be due to the partial reduction commencing from the grain boundaries and proceeding further into the core. But before complete reduction occurs, these grains might have been carried away to produce the flue dust (Fig. 1). Most of the metallic phases are rounded/globular in shape. Similar characterization results were reported by Geldenhuis, [2] for flue dust fines generated by a stainless steel plant. XRD pattern studies indicated that the sample consists of iron carbide, chromite and quartz (Fig. 2). Some of the carbon might have reacted with the iron of the chromite phase and formed the iron carbide phase.

Table 1: Chemical composition of the ferrochrome flue dust sample

Elemente / Elements	Gewicht % / Weight %
Cr ₂ O ₃	25,69
Fe ₂ O ₃	15,10
SiO ₂	16,30
Al ₂ O ₃	11,44
MgO	14,12
K ₂ O	1,98
Na ₂ O	1,26

Table 2: Size analysis and respective chemical analysis of the flue dust material

Size in µm	Wt. % (Retained)	Cum. Wt % Passing	Cr ₂ O ₃ %	Percentage distribution of Cr ₂ O ₃	Fe ₂ O ₃ %	SiO ₂ %	Al ₂ O ₃ %	MgO %
+1000	1.80	98.20	0.78	0.05	80.02	2.89	1.80	3.29
-1000+500	22.40	75.70	20.67	18.02	20.74	20.18	16.68	11.82
-500+210	0.70	75.00	7.32	0.20	36.24	21.66	12.76	8.93
-210+100	8.50	66.50	29.96	9.91	21.07	15.44	16.11	10.26
-100+75	50.40	16.20	29.99	58.84	18.37	15.03	15.50	11.17
-75+45	5.50	10.70	28.57	6.12	22.04	16.29	15.96	9.97
-45	10.70	0.00	16.46	6.86	20.18	21.41	14.28	18.19



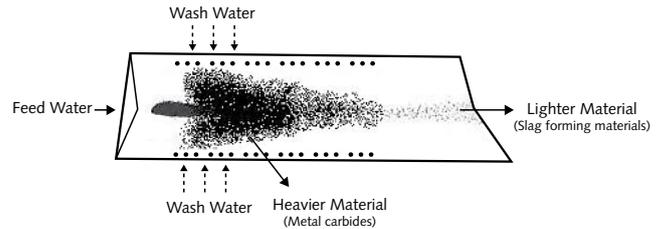
2 XRD pattern of the flue dust sample showing the iron carbide, chromite and quartz phases in the sample

3.2 Composition of the flue dust

Table 1 shows the complete chemical analysis of the as-received ferrochrome flue dust sample. Chromite, an important chromium ore, has as a general formula of the spinel group (spinel, magnetite, chromite, magnesiochromite, gahnite, franklinite) AB_2O_4 . The A represents a divalent metal ion such as magnesium, iron, nickel, manganese and/or zinc. The B represents trivalent metal ions such as aluminium, iron, chromium and/or manganese. Titanium may also occupy this site with a +4 charge. Solid solution is common in this group of minerals. Usually magnesium is present in chromite, substituting the iron, and in fact a solid solution series exists between chromite and the much rarer mineral magnesiochromite. Hence, the chromite structure always contains certain amounts of magnesium and aluminium in it along with chromium and iron. From the analysis (Table 1), it is clear that the sample contains considerable amount of chromite.

3.3 Size classification of the flue dust

Table 2 shows the size and size-wise chemical analysis of the flue dust material. It can be observed from the table that 75 % of the feed material is finer than 210 μm in size. Chemical analysis of the size fractions shows that the



3 Schematic representation of the mineral separator operation

-500+210 μm fraction, accounting for 0.7 % of the total sample, contains the least amount of Cr_2O_3 value while the -100+75 fraction contains the highest chromium value. The highest amount of iron content was observed in the +1000 μm fraction, which is due to flakes of iron scaling.

3.4 Beneficiation studies

Laboratory beneficiation experiments were designed and conducted with the intention of upgrading the metal (ferrochrome) values from the flue dust sample. Gravity separators like the mineral separator were used to perform this task. The C800 mineral separator supplied by Richard Mozley Ltd/UK, which has V-type tray profile, was used in the experiments. About 100 g of flue dust sample was mixed thoroughly with 200 ml of water and fed to the separator. The wash water rate was maintained at about 1000 ml/min. The experiment was continued for 5 min, later the tailing and concentrate samples were dried and analysed to determine their chemical constituents. Fig. 3 shows the schematic representation of the mineral separator operation. The feed material is fed to the equipment wherein the particles experience the cyclic motion (imparted by the tray) and cross-current water flow. The cyclic motion of the tray and cross-current of water enables stratification of the particles. The heavy material settles and is thrown upstream by the end-knock action and the lighter material is thrown to the rear end by the cross-current water to discharge via tailing launder.

The results of mineral separator are listed in Table 3. It can be observed from the table that about 38.5 % of the feed material reports to the heavier stream which assays about 40.14 % Cr_2O_3 . About 61.5 % of the feed material reports to the tailing stream assaying 21.78 % Cr_2O_3 . The mineral separator results show that the chromium values could be

Table 3: Results of the mineral separator studies

	Wt. %	Cr_2O_3 %	Percentage distribution of Cr_2O_3	Fe_2O_3 %	SiO_2 %	Al_2O_3 %	MgO %
Concentrate	38.50	40.14	60.14	18.66	9.77	13.88	11.85
Tails	61.50	16.60	39.84	20.52	20.25	15.89	13.26

Table 4: Results of the magnetic separation studies

	Wt. %	Cr_2O_3 %	Percentage distribution of Cr_2O_3	Fe_2O_3 %	SiO_2 %	Al_2O_3 %	MgO %
Magnetic fraction	77.30	26.44	79.20	22.51	16.61	15.29	11.26
Non-magnetic fraction	22.70	23.61	20.80	9.49	23.58	14.43	18.01

enriched to 40.14 % from the feed Cr_2O_3 with 25.69 %. The enrichment of Cr_2O_3 occurs mainly because the light and fine silicate-bearing materials are mostly discarded in the tailings. This is reflected in the chemical analysis of the tailings, which indicates 20.25 % SiO_2 in contrast to 9.77 % in the concentrate.

A laboratory wet high-intensity magnetic separator (WHIMS) Box Mag supplied by Eriez Magnetics Europe Ltd/UK was also used in the investigations. The experiment was conducted with 8000 gauss magnetic strength as it was presumed that some of the iron particles liberated during the reduction process could be separated efficiently. The experimental results are summarized in **Table 4**. It can be observed from the table that the Fe_2O_3 content in the magnetic product increases to 26.4 % from the feed containing 15.1 %. The Cr_2O_3 values are almost distributed equally to the magnetic and non-magnetic product. This indicates that very few particles of Fe_2O_3 formed during the reduction process.

4 Conclusions and recommendations

Increasing costs of waste disposal and strict environmental rules and regulations suggest that priority should first be given to minimizing the flue dust from the ferrochrome industry. Then the possibilities for partial or full recycling and/or metal recovery should be investigated. In this research gravity (C800 mineral separator) and magnetic separation wet methods were applied as the flue dust sample contains quartz, carbon and useful chromite of significant value which have different phase densities and magnetic properties. However, toxic substances such as Cr(VI) can leach out during these wet mineral separation process. This necessitates further treatment of the waste water from these processes. However, wet beneficiation processes have their specific advantages as well as disadvantages over dry beneficiation processes. For example, wet processes can be very effective with regard to sharp separation of the constituent phases and produce a high-grade concentrate whereas dry methods appear to be less sharp with regard to separating the phases.

In the present case better results were achieved, Cr_2O_3 content enhanced from 25.6 to 40.14 % with a weight recovery of 38.5 % with the gravity method than with the magnetic separation method. Further studies are in progress concerning dry beneficiation methods as well as the further enrichment of the chromium values in the concentrate with better weight percentage recovery.

Great potential exists for application of this low-cost gravity separation technique on a commercial scale, although a more extensive pilot-scale test programme should be performed

prior to commercialization. Of course a number of factors, like the composition of the flue dust which varies with respect to changes in composition/grade of feed/raw materials as well as operational parameters, influence the choice of ferrochrome flue dust treatment.

Gericke [3] reported that heavy metals in the ferrochrome flue dust can be immobilized by mixing 20 % ferrochrome dust with 80 % clay or 50 % clay with 30 % ferrochrome dust and 20 % ferrochrome slag. Maine et al. [5] also used 50 % clay and 50 % ferrochrome bag filter dust and sintered it at 1200°C to stabilize the Cr(VI) and salts in the ferrochrome dusts. The results showed that more than 99 % Cr(VI) and 90 % salt in the ferrochrome dusts were stabilized. The Cr(VI) concentration in the leachate also decreased with increasing sintering temperature. These tests can be performed for the tailings of the ferrochrome dust samples after a sufficient chromium values are extracted by physical means for the stabilization of Cr(VI) values if any.

Acknowledgements

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