Cr (VI)-CONTAINING ELECTRIC FURNACE DUST AND FILTER CAKE: CHARACTERISTICS, FORMATION, LEACHABILITY AND STABILISATION

by

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To my lovely wife Yinhua,

my son, Junteng and

my parents

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Abstract

In South Africa, the ferrochromium industry produces approximately 100,000 t bag house filter dust and slurry, while the stainless steel industry produces 24,000 t of dust annually [17,39]. The toxic substances in these wastes potentially pose a threat to the environment and human health, especially Cr (VI) due to its toxic, carcinogenic, highly soluble and strongly oxidizing properties. Therefore, the existence and treatment of wastes from stainless steel and ferrochrome production remain a challenge and an issue of concern. The increase of environmental legislation globally and the trend towards sustainable development are drives for alternatives to landfill.

In the present thesis, the characteristics, formation mechanisms, leachability and stabilisation of the Cr (VI)-containing electric furnace dust and filter cake were investigated using various techniques such as XRD, XRF, TG/DTA, XPS, SEM-EDS, FT-IR, Raman spectrometer and UV/Vis spectrometer.

The study on the characteristics of these wastes showed that the electric furnace dust and filter cake are very fine particles. The electric furnace dust has bulk densities that vary between 0.49 and 2.42gcm^{-3}, and has low moisture contents. The main phases that are present in the stainless steel plant dust are the $(Mg,Fe,Mn,Cr)_3O_4$ spinel phase, quartz, $Ca(OH)_2$ and nickel. The dominant phases of the coarse fraction of ferrochrome plant dust are chromite, partly altered chromite, quartz and carbon, while the main components of the fine fractions include chromite, SiO_2, ZnO, NaCl and Mg_2SiO_4. The major phase present in the filter cake is CaF_2. It is assumed that Cr (VI)-containing species in ferrochrome dust are generated at the top of the SAF or in the off-gas duct, as Cr (VI) is found on the surface of the dust.

Stainless steel dust forms by the entrainment of charge materials, evaporation or volatilisation of elements and ejection of slag and metal by spitting or the bursting of gas bubbles. It was found that ferrochrome dust is formed by the ejection of slag and metals droplets from the electrode hole, the entrainment of charge materials, vaporisation as well as the formation and precipitation of compounds from vaporised species in the off-gas duct. Filter cake contains crystal phases (CaF_2 and $CaSO_4$) and metal rich amorphous phases. It is formed due to super saturation and precipitation.

Leaching experiments on the wastes showed that Cr (VI) rapidly leaches out by distilled water. The aging experiment of the stainless steel plant dust and filter cake shows that the Cr (III) species in these wastes can be oxidised into Cr (VI) in the presence of lime at room temperature. Increasing the molar ratio of CaO to Cr_2O_3 and increasing temperature promotes the oxidation of Cr (III) into Cr (VI). Cr (VI) in the wastes can also be reduced into Cr (III) possibly by Fe (II).

Bricks were produced by mixing wastes (stainless steel plant dust, ferrochrome dust and filter cake) and clay. The optimum sinter parameter was found to be 1100^{o}C and 5 hours for a 50wt% SPD-50wt% AS mixture in the brick. Decreasing sinter temperature, increasing waste content in the brick and reducing sinter time increase the Cr (VI) leachability. The leachability of Cr(VI) is strongly influenced by the mass%CaO/mass%SiO_2 ratio and alkali metal oxides content in the wastes. Ferrochrome dust and filter cake that were sintered with 50% AS clay at 1000^{o}C for 5 hours could not be stabilised as the concentrations of zinc and/or Cr (VI) from the stabilised wastes in the modified TCLP and ASTM D 3987-85-tests exceed the regulation limits. The emission factors from the stabilised wastes (SPD, FCD1, FCD2 and FC) are similar to those reported for the cement industry.

Semi-dynamic leaching tests indicated that the predominant leaching mechanisms of chromium species are initial surface wash-off followed by matrix diffusion. The cumulative release fractions of chromium from the solidified wastes are lower than 2% over a period of approximately 5 months. More than 80% of the leachable chromium from the stabilised products is Cr (VI) species.

Keywords: Cr (VI), dust, filter cake, waste management, leachability, stabilisation, sintering, stainless steel, ferrochrome, electric furnace

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