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Thermoanalytical study of EAF dust and its vitrification product

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Abstract

Thermogravimetry, differential thermal analysis and Fourier transform infrared spectroscopy were used to determine the thermal behaviour of the electric arc furnace dust from stainless steel and carbon steel operations. The dust is classified as environmentally hazardous waste in most regions of North America and Europe because of its relatively high levels of lead, cadmium and chromium. The results indicated that, thermally, the two types of dust are still somewhat active and that there are apparent differences in their thermal behaviour. A thermal process for the stabilization of the dust by vitrifying with clay has been developed at the Environment Laboratory of the Canada Centre for Mineral and Energy Technology in Canada. The vitrification product (clinkers) of both types of dust were also examined and were found to be thermally stable at least up to 1000°C.

Keywords: EAF dust; Vitrification; Thermal analysis

1. Introduction

Electric arc furnace (EAF) dust is a major by-product waste generated by the secondary steelmaking industry (mini-mills). It is a complex, fine-grained, high-density material, containing significant amounts of zinc and iron together with variable amounts of calcium, lead, nickel, cobalt, cadmium, etc., depending on the type of steel produced. The dust, which is generated at the rate of over 700,000 t/a in the USA and Canada, is classified as hazardous waste in most regions of North America and Europe. It cannot be disposed of in regular landfill sites because of the susceptibility of the heavy

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metals, particularly lead, chromium and cadmium, to leach into the environment. The chemical, physical and mineralogical characterization of the dust was reported earlier [1]. A pyrometallurgical process was developed to stabilize the contained heavy metals by mixing the dust with clay or other sources of silica and alumina and heating it to 1100–1200°C in a rotary kiln [2]. The produced clinkers are dense, chemically stable materials that comply with the current EPA leachability protocol for hazardous waste. This process was examined earlier and was explained on the basis of the formation of an aluminosilicate polymeric matrix that incorporates and stabilizes the heavy metals [3,4].

In the present work, the determination of the thermal behaviour of stainless steel and carbon steel EAF dusts and their mixtures with clays was carried out using thermal analysis and Fourier transform infrared spectroscopy. The thermal stability of the clinkers produced by the vitrification process was also examined.

2. Materials and experimental procedures

Samples of EAF dust were acquired from stainless steel and carbon steel industries. Two types of clay, namely, Laprairie clay and kaolinite (ball clay) were used in the mixtures. The thermal analysis (TA) measurements were carried out using a TA Instruments SDT-2960 (TG/DTA) or a Seiko SSC5200H instrument with a simultaneous TG/DTA module. The identification of the evolved gaseous species was done using a BOMEM-MB100 Fourier transform infrared (FTIR) spectrometer interfaced with the thermal analysers. The thermal analysis and FTIR measurements were carried out simultaneously, with a time lag between the gas evolution in the thermal analyser and the gas detection in the spectrometer of about 10 s. The samples were 20–30 mg in weight and were subjected to a programmed heating of 20°C min^{-1} in a stream of dry air (50 ml min^{-1}). Some experiments were interrupted at different temperatures and the products were analysed using X-ray diffraction.

3. Results and discussions

3.1. Stainless steel dust

Two types of stainless steel dust, namely, current-production dust and stockpile dust, were examined individually and in mixtures with Laprairie clay. Fig. 1 shows a TG/DTA/FTIR diagram of the current-production dust, examined in air. A small and gradual weight loss, observed on the TG curve up to 400°C, indicates the evolution of H_2O from the sample as verified by the H_2O evolution curve of the FTIR. A slight weight gain in the temperature range 500–700°C signifies the oxidation of contained iron oxide to a higher oxidation state (X-ray diffraction before and after heating indicated partial conversion of Fe_3O_4 to Fe_2O_3). Above 700°C, two stages of weight loss occurred. The first may be due to the decomposition of a small amount of carbonates in the sample as verified by the CO_2 curve of the FTIR. The second may be

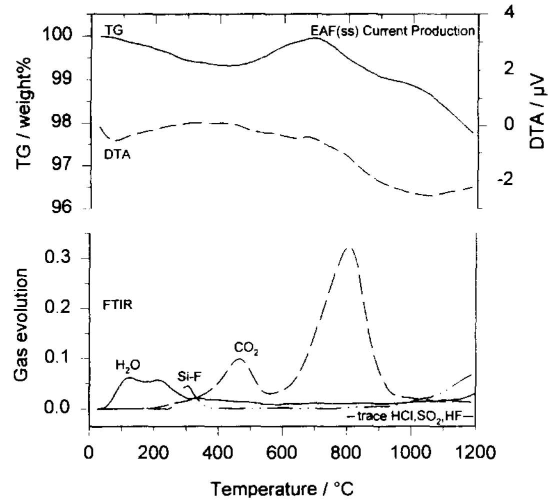

Fig. 1. TG/DTA/FTIR diagram of the current-production stainless steel EAF dust, in air.

due to the volatilization of condensable material from the sample (no gaseous species were detected by FTIR). Si–F species, most likely SiF_4, was detected by FTIR in the temperature range 240–370°C, indicating the presence of HF gas. The formation of SiF_4 can be attributed to the reaction between HF and contained silica. Trace amounts of HF, HCl SO_2 were also detected by FTIR. The total weight loss up to 1200°C was about 2%. No significant thermal activities were registered by DTA.

The results for the stockpile dust, Fig. 2, indicated that the only significant differences from those of the current-production dust are the disappearance of the weight gain

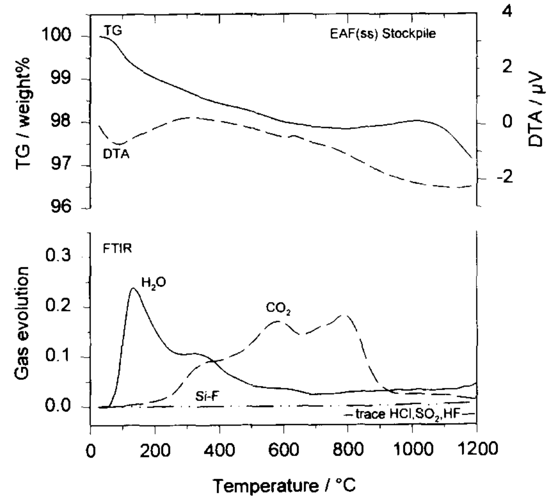

Fig. 2. TG/DTA/FTIR diagram of the stockpile stainless steel EAF dust, in air.

at 500–700°C, signifying that the contained iron may be present in the oxidized form, Fe_2O_3, in this material, and the absence of the low-temperature (240–370°C) evolution of HF. A higher amount of moisture was also detected in this material. Fig. 3 shows the TG/DTA/FTIR diagram of the Laprairie clay. This diagram is typical for the carbonate-containing clays with two characteristic steps of weight loss [5]. The first (500–600°C) is due to the dehydroxylation and the second (600–800°C) to the decomposition of the carbonate, as verified by the FTIR gas evolution curves and the endothermic peaks on the DTA curve.

Fig. 4 shows the TG/DTA/FTIR diagram of a green mixture of the current-production dust with the clay. The gas evolution profiles indicate that the major components are H_2O and CO_2 in the temperature range from ambient to 1000°C. Si–F species appeared above 950°C indicating the presence of HF gas. Traces of HCl, SO_2 and HF were also detected above 550°C. The TG curve indicated a total weight loss of about 5% up to 1200°C and no significant thermal effects appeared on the DTA curve. Very similar results were obtained with the green mixture of the stockpile dust and clay, Fig. 5. The total weight loss in the latter case was somewhat less (4.5%).

After the vitrification processing of 1/1 green mixtures of each of the two types of dust with the clay [2], the vitrified products (clinkers) were examined by thermal techniques. Figs. 6 and 7 show the TG/DTA/FTIR diagrams of the clinkers made from the current-production dust and the stockpile dust with the clay, respectively. The diagrams indicate a high level of thermal stability of the clinker products of the two mixtures, with less than 0.3% change in weight at 1000°C. No significant activities appeared on the DTA curves and only traces of H_2O and CO_2 were detected by FTIR.

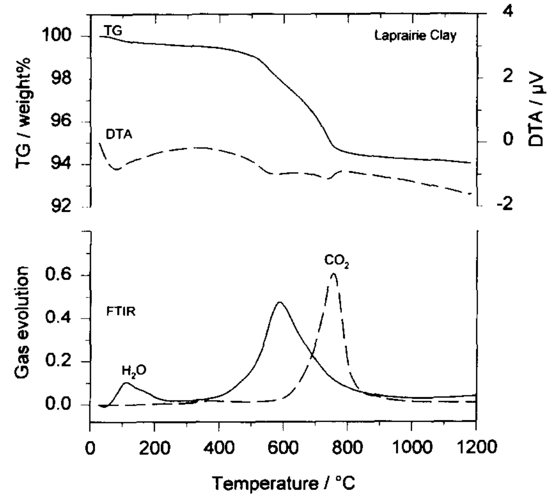

Fig. 3. TG/DTA/FTIR diagram of the Laprairie clay, in air.

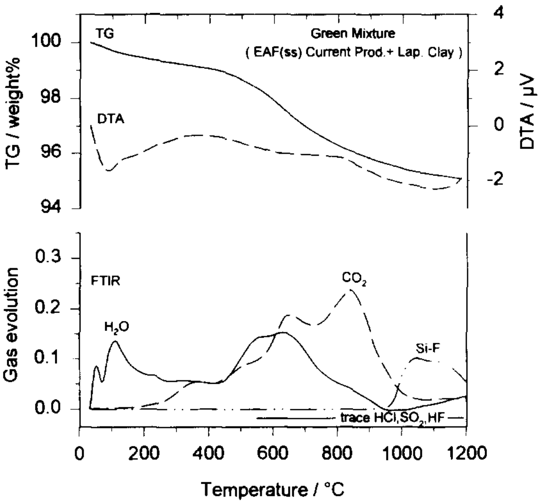

Fig. 4. TG/DTA/FTIR diagram of the green mixture of the current-production stainless steel EAF dust with Laprairie clay, in air.

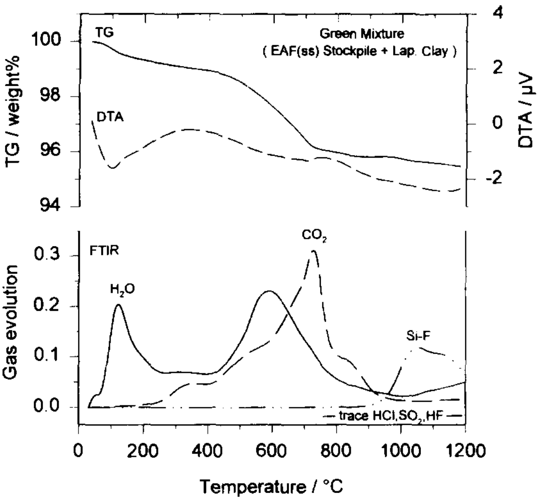

Fig. 5. TG/DTA/FTIR diagram of the green mixture of the stockpile stainless steel EAF dust with Laprairie clay, in air.

3.2. Carbon steel dust

The current-production carbon-steel dust was examined alone and mixed with the ball-clay kaolinite. The TG/DTA/FTIR results of the dust alone (in air), shown in Fig. 8, indicated a thermal behaviour significantly different from that of the stainless

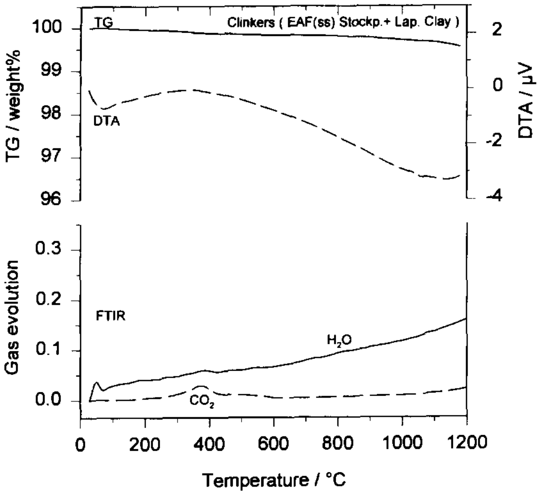

Fig. 6. TG/DTA/FTIR diagram of the clinkers made of the current-production stainless steel EAF dust with Laprairie clay, in air.

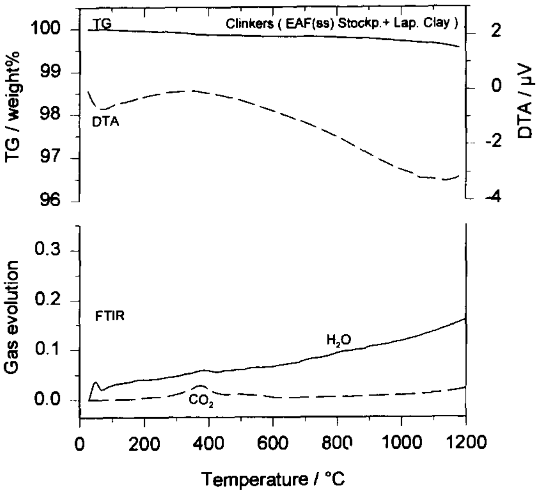

Fig. 7. TG/DTA/FTIR diagram of the clinkers made of the stockpile stainless steel EAF dust with Laprairie clay, in air.

steel dust. The TG curve shows three distinct stages of weight loss at 370–420, 550–700 and 800–1050°C, accompanied by variable-intensity endothermic peaks on the DTA curve. The first two activities are typical of the dehydroxylation of calcium hydroxide and the decomposition of calcium carbonate, respectively, according to the following

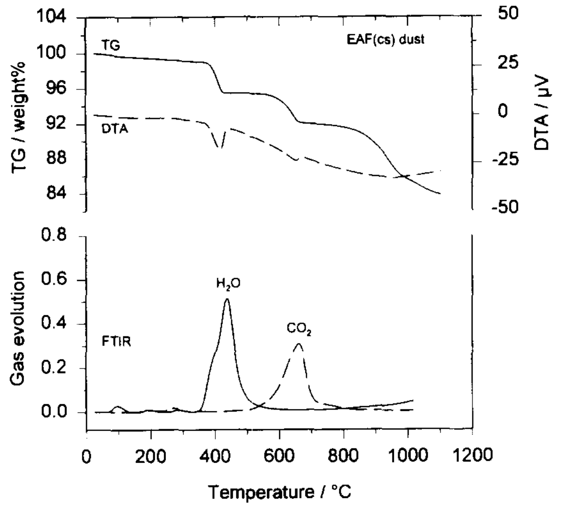

Fig. 8. TG/DTA/FTIR diagram of the current-production carbon steel EAF dust in air.

reactions

$$Ca(OH)_2 = CaO + H_2O \quad (1)$$

$$CaCO_3 = CaO + CO_2 \quad (2)$$

The first weight loss is 3.6%, indicating the presence of 14.8 wt% $Ca(OH)_2$ and the second is 3.4% indicating the presence of 7.7% $CaCO_3$. The third weight loss (7% to the end of the experiment) was accompanied by deposition of a white precipitate on the reaction tube. The precipitate was identified by SEM and XRD as NaCl with traces of KCl and $PbCl_2$. XRD results also indicated that the major components of the sample after heating to 1000°C are ZnO, $ZnFe_2O_4$, Fe_3O_4, CaO, and calcium ferrites. Further verification of reactions (1) and (2) was provided by the appearance and location of the H_2O and CO_2 bands on the FTIR gas evolution profiles. As expected, no gas evolution corresponded to the third weight loss, which indicated that NaCl has deposited entirely on the reaction tube before reaching the FTIR cell. Both $Ca(OH)_2$ and at least some of the $CaCO_3$ may have been present originally in the EAF as free lime which, in turn, may have hydrated and carbonated on exposure to ambient moisture and CO_2 for extended periods of time.

Fig. 9 shows the TG/DTA/FTIR diagram of the kaolinite with its characteristic dehydroxylation behaviour around 500°C. Traces of CO_2 can be seen on the gas evolution diagrams indicating the presence of minor amounts of carbonates. Fig. 10 shows the diagram of the dust/kaolinite (1/1) green mixture. The diagram resembles that of the kaolinite and indicated that some interaction with the dust may have taken place. Fig. 11 shows the diagram of the dust vitrification product. As in the case of the stainless steel dust clinkers, this product was found to be thermally stable, with a weight

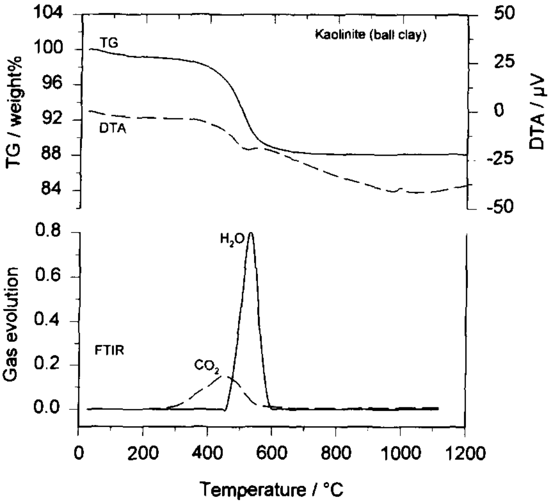

Fig. 9. TG/DTA/FTIR diagram of kaolinite (ball clay), in air.

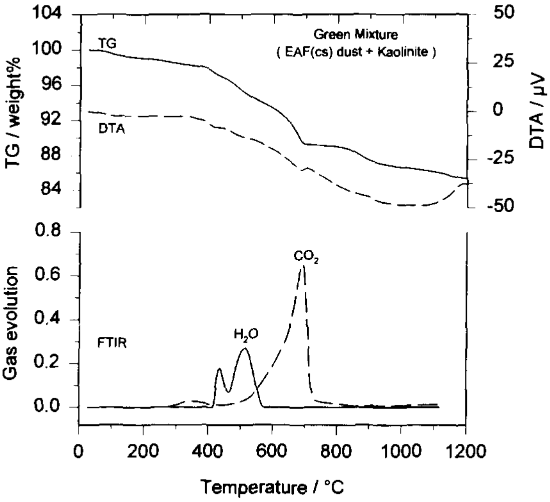

Fig. 10. TG/DTA/FTIR diagram of the green mixture of the current-production carbon steel EAF dust with kaolinite, in air.

loss of 0.3% at 1000°C. No detectable activities appeared on the DTA curve and only traces of CO_2 were detected by FTIR.

4. Conclusions

The thermal behaviour of stainless steel and carbon steel EAF dusts was studied by TG/DTA/FTIR. The results indicated some differences in the behaviour of the two

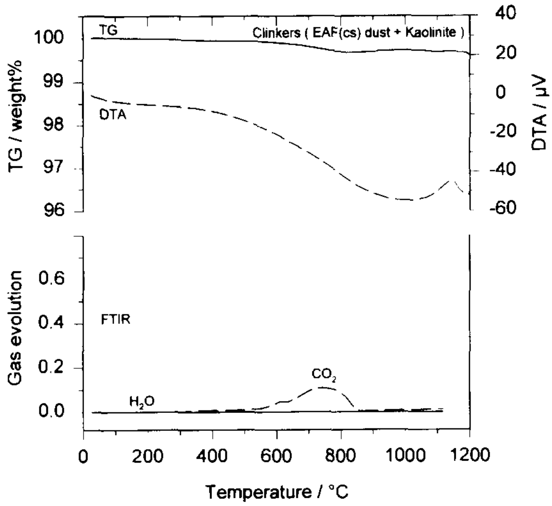

Fig. 11. TG/DTA/FTIR diagram of the clinkers made of the current-production carbon steel EAF dust with kaolinite, in air.

types. The presence of oxidizable components was evident in the stainless steel dust and of calcium hydroxide and calcium carbonate (both of which were identified and quantified) in the carbon steel dust. The results were valuable in evaluating the vitrification process developed to stabilize the dust. The vitrification products of each of the two dusts, mixed with clay, were found to be thermally stable with less than 0.3% weight loss at 1000°C and only traces of gaseous effluents. These results would also be useful in exploring high-temperature applications for vitrification products using significant amounts of these hazardous wastes.

Acknowledgements

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