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Thermal reduction of steel-making secondary materials
I. Basic-oxygen-furnace dust

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Abstract

A study of the thermal reduction of basic oxygen furnace (BOF) dust was carried out using simultaneous thermogravimetry, differential thermal analysis and Fourier transform infrared spectroscopy. X-ray diffraction, chemical and mineralogical analyses were also used. BOF dust, which mainly consists of higher iron oxides (magnetite and hematite), is the largest by-product flue waste released in the integrated steel-making process. Blast furnace (BF) dust, a carbon–iron-rich flue waste released in the iron-making process, was used as a reductant. Both of the starting materials were examined individually using the same techniques. The effect of the reaction atmosphere, the amount of reductant and the temperature were examined. The results indicated that, at 1300°C in inert atmosphere, a partial reduction of the contained iron oxides takes place with 20% reductant in the mixture. With 50% reductant, under the same conditions, a complete metallization of the iron oxides in the dust takes place. The thermal analysis results were verified by identifying the reaction products as well as the gaseous species evolved during the reduction reactions. © 1998 Elsevier Science B.V.

Keywords: BF dust; BOF dust; Reduction; Steel-making; Thermal Analysis

1. Introduction

After ferruginous slags, basic oxygen furnace (BOF) dust is the second largest solid-waste residue generated by the integrated steel mills, with over 2 million t/a in the USA and Canada alone. This by-product, which is collected as flue dust during the steel production in the basic oxygen furnace and largely stockpiled or landfilled, contains over 50% iron in the form of oxides. At the same time, the mills generate over one million t/a of blast furnace (BF) flue dust (excluding filter cake). This material, most of which is also stockpiled, contains an average of 30% carbon and 30% iron in the form of oxide. A process for the recovery and recycle of the iron units from both residues back to the iron-making process may result in a significant energy and raw material savings. Substantial environmental benefits may also be achieved through the replacement of virgin ores by recycled materials, minimizing CO_2, NO_x and SO_x emissions, diverting large amounts of solid residues from landfill sites and, potentially, recovering valuable elements, e.g. zinc.

One of the major difficulties in the recycling of these residues is their fine particle size. With an ultimate objective to recycle BOF dust back to the blast furnace, it is necessary to process the fine powder

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into agglomerates or pellets with certain physical characteristics, e.g. high-temperature strength, similar to those of iron-ore pellets used as blast-furnace feed. Chemically, it is desirable to produce self-reducing agglomerates or pellets to promote metallization which, ultimately, would lead to the production of stronger agglomerates for recycling and to a higher efficiency for metal production in the blast furnace. This objective may be accomplished by utilizing the carbon-rich BF dust as a reductant for the BOF dust, with the potential benefit of utilizing two major by-product residues to generate a value-added recyclable material. In an earlier study on the production of self-reducing pellets from iron and steel-making wastes, Dressel et al. [1] suggested that the reduction roasting of pellets containing BOF and BF dusts and mill scale at 1100°C results in a significant metallization of the iron and a substantial reduction and removal of zinc and lead from the BOF dust. The direct recycle of agglomerated BOF dust/sludge to the electric arc steel-making furnace rather than to the sinter plant, after the removal of zinc, lead and alkali metals was also suggested by Piret and Muller [2].

In the present work, the reduction of BOF dust by BF dust in different atmospheres is explored using thermal analysis and Fourier transform infrared spectroscopy. The high-temperature behaviour of the individual powders was also examined. Earlier investigations of other steel-making by-product residues were carried at the Canada Centre for Mineral and Energy Technology using the same techniques [3,4].

2. Materials and experimental procedure

Industrial samples of fine basic oxygen furnace dust (oxide) and blast furnace flue dust (ca. 10 kg of each) were ground, homogenized and sampled using universal and carousel sample splitters. Chemical analysis of the starting materials indicated that the major components of the BOF dust are 59% Fe, 7.4% Ca, 2.1% Mg, 2.1% Mn, 1.48% Zn, 1.23% SiO_2 and 0.46% C and of the BF flue dust are 30.3% Fe, 28.9% C, 5.91% Ca, 1.92% Mg, 1.26% Mn, 6.1% SiO_2 and 1.77% Al_2O_3.

The thermal analysis measurements were carried out using a TA Instruments SDT-2960 (simultaneous TG/DTA) unit. The identification of the evolved gaseous species was done using a BOMEM-MB100 Fourier transform infrared (FTIR) spectrometer interfaced with the thermal analyser. An infrared gas cell, 10 cm long, with standard KBr windows was used in the spectrometer. 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 ca. 10 s. A quartz-wool filter, placed in the gas-transfer line, allowed the collection of condensables for later examination. The samples, 30 mg in weight, were contained in alumina pans and subjected to a programmed heating of 20°C min^{-1} in a stream of dry air, helium or CO_2 atmosphere (100 ml min^{-1}). Some experiments were interrupted at different temperatures and the products were examined by X-ray diffraction. The latter technique was carried out using a fully automated RIGAKU powder diffractometer with a monochromator, CuK_α radiation at 55 kV and 180 mA with a scan rate of 10°C/min.

3. Results and discussion

The density and surface area measurements for the BOF and BF dusts indicated the values 4.37 and 2.86 g cm^{-3} and 5.39 and 4.96 m^2 g^{-1}, respectively. The particle size analysis indicated that almost all the BOF dust is <100 μm, while only ca. 50% of the BF dust is <100 μm. More details of the physical characteristics of the BOF and BF powders were reported earlier [5]. The mineralogical and X-ray diffraction analyses indicated that the major phases in the BOF dust are iron oxides (Fe_2O_3 and Fe_3O_4) with minor amounts of $Ca(OH)_2$, $CaCO_3$, ZnO and $ZnFe_2O_4$ and trace amounts of various other constituents. In the BF dust, the major constituents were found to be Fe_2O_3 and carbon with minor amounts of FeO, Fe_3O_4, SiO_2 and $CaCO_3$ and trace amounts of other materials. The carbon in the BF dust is present mainly in the elemental form, as discrete, irregularly shaped particles of different sizes and in carbonaceous materials.

In the first series of experiments, the thermal behaviours of the starting materials in air, He and CO_2 were examined. Figs. 1 and 2 show the TG/DTA/FTIR diagrams of the BOF dust in air and CO_2 , respectively. The diagram obtained in helium was identical to that

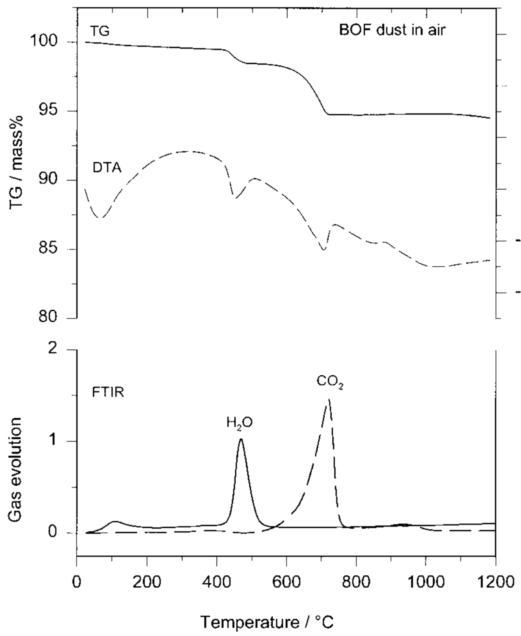

Fig. 1. TG/DTA/FTIR diagram of BOF dust, in air.

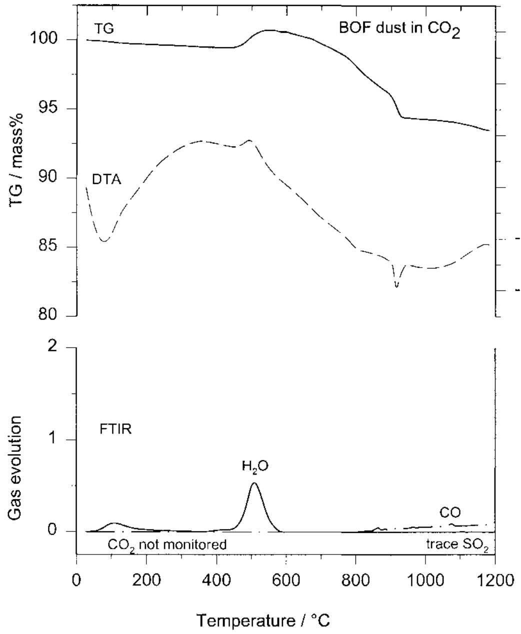

Fig. 2. TG/DTA/FTIR diagram of BOF dust, in CO_2.

in air and, therefore, is not plotted. In air (Fig. 1), besides the release of trace amounts of adsorbed water around 100°C, two main transitions are shown in the diagram. The first transition takes place at 400–500°C with a mass loss of ca. 1% accompanied by an endothermic peak on the DTA curve and the evolution of H_2O as detected by FTIR. This transition corresponds to the dehydroxylation of calcium hydroxide. The second transition occurs at 500–720°C with a mass loss of ca. 4% accompanied by an endothermic peak and the evolution of CO_2, corresponding to the decomposition of calcium carbonate. The dehydroxylation and decomposition reactions can be expressed as follows:

$$Ca(OH)_2 = CaO + H_2O \tag{1}$$

$$CaCO_3 = CaO + CO_2 \tag{2}$$

The mass loss detected in the two transitions indicated that the dust contains 4.3% $Ca(OH)_2$ and 8.4% $CaCO_3$. Despite the fact that Fe_3O_4 is present as a major constituent in the dust and is expected to oxidize to Fe_2O_3 in air, no significant mass increase was detected. This may be due to the presence of Fe_3O_4 as an inclusion inside Fe_2O_3 particles and therefore not exposed to oxidation. Above 1100°C, a gradual mass loss with no corresponding gaseous release was observed. This was found to be due to the volatilization of condensable chlorides of Zn, Pb and K.

In CO_2, Fig. 2, the total mass loss at 1200°C was almost the same as that in the air or helium, but substantially different thermal trends were obtained. A mass gain of ca. 1% in the range 420–550°C, accompanied by a small exothermic peak on the DTA curve and the evolution of H_2O (FTIR curve), appeared on the TG curve. This transition is due to the carbonation of calcium hydroxide according to the following exothermic reaction:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \tag{3}$$

Some CaO, originally present in the sample and available for carbonation may also react at this temperature range to form $CaCO_3$. The decomposition of $CaCO_3$ from both sources occurs above 800°C, as indicated by the mass loss on the TG curve and the corresponding endotherm on the DTA curve. CO_2 evolution was not monitored, since CO_2 was used as the reaction atmosphere in this case. The late decomposition of $CaCO_3$ in CO_2 atmosphere, relative

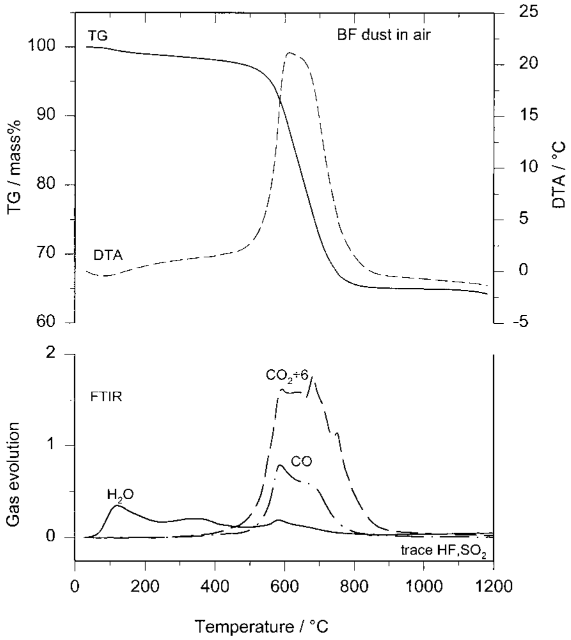

Fig. 3. TG/DTA/FTIR diagram of BF dust, in air.

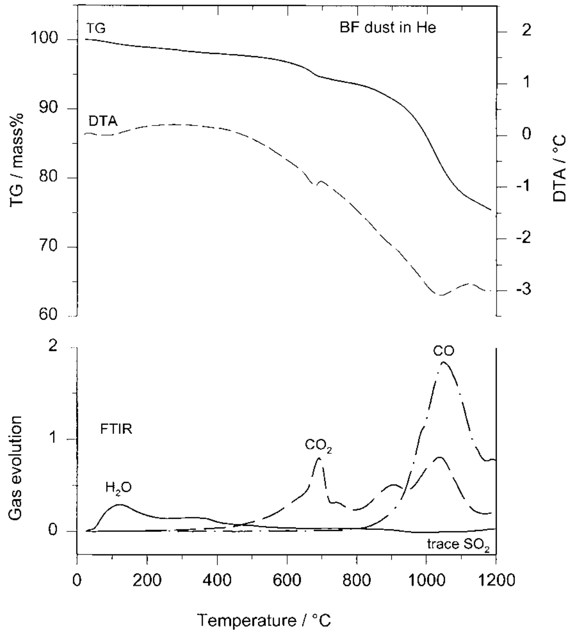

Fig. 4. TG/DTA/FTIR diagram of BF dust, in helium.

to that in air or He is due to an equilibrium shift of reaction 2 to the left as a result of the higher partial pressure of CO_2 [6].

Figs. 3–5 show the TG/DTA/FTIR diagrams of the BF dust in air, He and CO_2 , respectively. In air, Fig. 3, a trace of adsorbed water is evolved around 100°C. At 500–800°C, a major mass loss (ca. 32%), accompanied by a highly exothermic peak and the release of large amounts of CO_2 (highly compressed scale) and some CO indicated the combustion of the contained carbon and other carbonaceous materials. This mass loss also incorporates the decomposition of contained calcium carbonate, which is also expected to take place in this temperature range. No endothermic peak due to the latter reaction appeared on the DTA curve due to the overlap of the large combustion exotherm. No other significant transitions were detected. In oxygen-free helium, Fig. 4, a mass loss accompanied by a small endothermic peak and the release of CO_2 at 650–700°C signified the decomposition of carbonate. Above 800°C, the reduction of contained iron oxides seems to have taken place with a mass loss of ca. 17% accompanied by a broad endotherm and the release of CO and CO_2. In CO_2, Fig. 5, the decomposition of the carbonate occurred above 800°C. Above 900°C, a major mass loss (ca. 30%), accompanied by a broad endotherm and the release of a major amount of CO (highly compressed scale), corresponds to the reaction

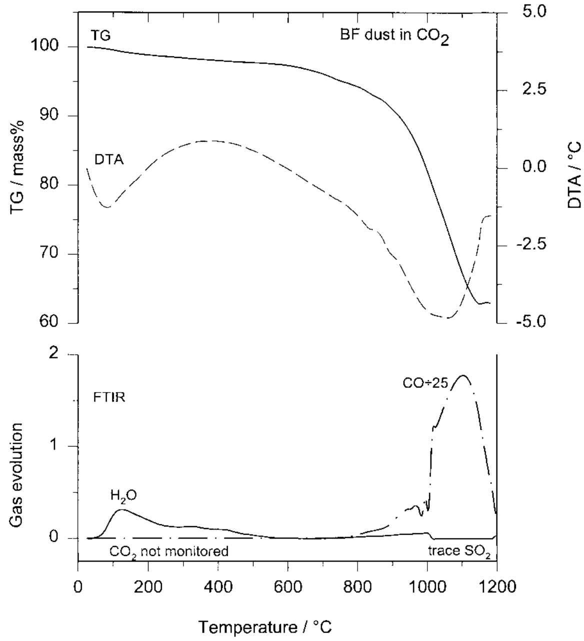

Fig. 5. TG/DTA/FTIR diagram of BF dust, in CO_2.

of carbon and carbonaceous materials with the CO_2 atmosphere. Again, the CO_2 evolution could not be monitored on the FTIR, since CO_2 was used as the reaction atmosphere. The total mass loss at 1200°C (ca. 37%) was close to that obtained in air.

As mentioned previously, iron is present in the dusts mainly as higher iron oxides. When mixed with carbon at high temperatures, initially, a solid–solid reduction takes place to form lower iron oxides or metallic iron and CO. The main reduction then proceeds as a solid–gas reaction, generating CO_2, which, in turn, reacts with carbon to form CO. The overall reaction may be expressed as:

$$\mathrm{Fe}_x\mathrm{O}_y + C \rightarrow \mathrm{Fe}_x\mathrm{O}_{y-1} + \mathrm{CO} \quad (x = 1, 2\,\mathrm{or}\,3,\ \mathrm{and}\,y = 1, 3\,\mathrm{or}\,4) \tag{4}$$

In preliminary reduction experiments, a mixture of BOF and BF dusts (70% : 30%) was examined in air, helium and CO_2 and the TG results are presented in Fig. 6. In air and in CO_2, the mass loss of the mixture at 1200°C is comparable to the normalized total mass loss of the individual dusts at the same temperature, which indicates that little or no reduction takes place in these atmospheres. These results were confirmed by X-ray diffraction which showed that the product still contained mainly higher iron oxides after heating. In helium, however, a significantly higher mass loss was observed in the mixture indicating extensive reduction. As the mass loss was not completed at 1200°C, another experiment in helium was done up to 1300°C. The results in helium were confirmed by XRD, Table 1.

Table 1
XRD analysis of the reduction products of the 70%BOF : 30%BF mixture in helium at different temperatures

Temperature, °C	Main constituents identified by XRD
1000	FeO, Fe_3O_4, minor $CaFe_2O_4$, C, CaO, $Ca_2Fe_2O_5$
1200	Fe, FeO, minor CaO, $Ca_2Fe_2O_5$
1300	Fe, FeO, minor $Ca_2Fe_2O_5$, Ca_2SiO_4

These results indicate that, in helium, a systematic reduction of BOF dust with BF dust takes place and metallization of the BOF dust progresses with the reduction temperature.

A series of experiments was carried out to optimize the BF addition required for full, or at least extensive, metallization of the BOF dust. Mixtures containing 20–50% BF dust were prepared and heated in helium up to 1300°C. The individual starting materials were also subjected to the same scheme. Fig. 7 shows the

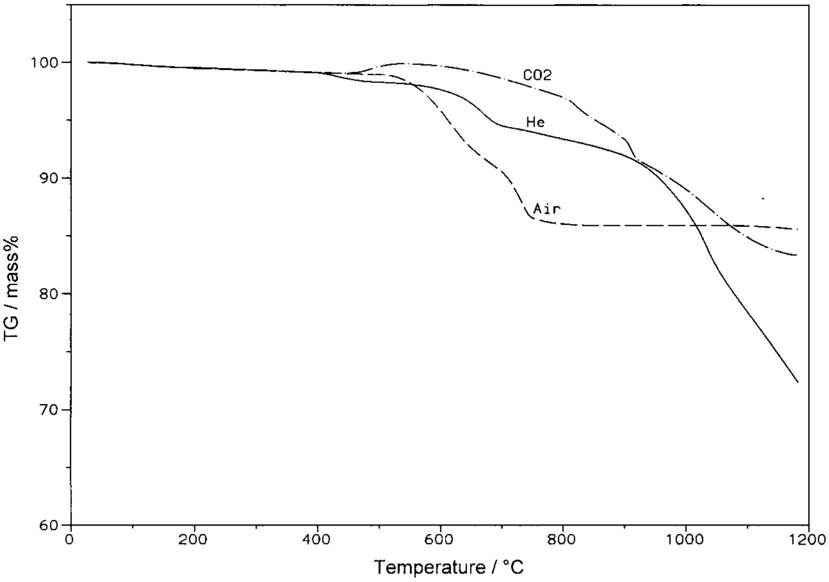

Fig. 6. TG (mass loss) curves of a 70% BOF : 30%BF mixture in air, helium and CO_2.

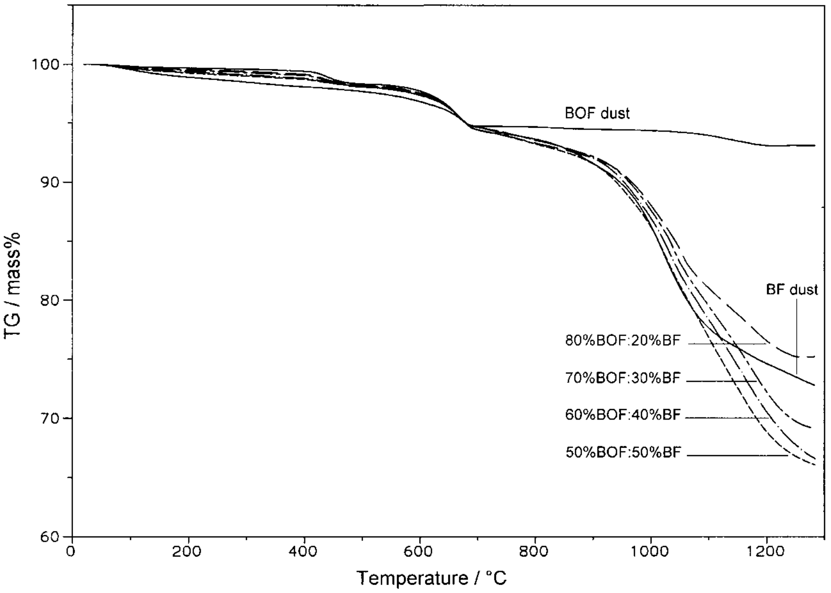

Fig. 7. TG (mass loss) curves of BOF and BF dusts and of BOF/BF mixtures of different ratios in helium.

TG curves for the mixtures as well as for the starting materials. It can be seen that the higher the BF ratio in the mixture the higher the mass loss. This mass loss, however, is not entirely due to the BOF/BF-reduction reaction, but partially due to the mass loss of the individual dusts when heated separately in helium. By subtracting the total contribution of the individual dusts, the maximum mass loss corresponding to the reduction was found to be in the mixture containing 40% BF dust, implying that, for maximum reduction of BOF dust, at least 40% BF dust is required in the mixture. After the thermal treatment, the individual dusts and the reaction products were examined by XRD and the results are summarized in Table 2. These results confirm that almost complete metallization of the iron oxides in the BOF dust occurred when 40% BF dust was used as a reductant and a full metallization occurred at 50%.

Table 2
XRD analysis of the individual dusts and the reduction product of BOF/BF mixtures of different ratios, heated to 1300°C in helium

Sample	Main constituents identified by XRD
BOF dust	Fe_3O_4, trace $Ca_2Fe_2O_5$, MgO
BF dust	Fe, minor MgO, trace Ca_2SiO_4, C
80%BOF:20%BF	FeO, Fe, minor $Ca_2Fe_2O_5$, Ca_2SiO_4
70%BOF:30%BF	Fe, FeO, minor $Ca_2Fe_2O_5$, Ca_2SiO_4
60%BOF:40%BF	Fe, minor FeO, trace Ca_2SiO_4, $CaFeO_2$
50%BOF:50%BF	Fe, trace Ca_2SiO_4

Fig. 8 shows the full TG/DTA/FTIR analysis of the 50% BOF : 50% BF mixture, heated to 1300°C in helium. Two main transitions are evident. The first, at 600–720°C, with a 3.2% mass loss accompanied by an endothermic peak and the evolution of CO_2, is due to the decomposition of calcium carbonate in both dusts; the second, above 850°C, with a major mass loss of 27% accompanied by a broad endothermic peak and the evolution of CO and CO_2, is due to the reduction of BOF dust by the BF dust and the self reduction of the BF dust alone.

4. Conclusions

The thermal reduction of basic oxygen furnace dust by blast furnace dust, both of which are major by-product residues in the steel-making industry, was simultaneously explored using thermal analysis and Fourier transform infrared spectroscopy. The reduction experiments were carried out in air, helium and CO_2. The reduction was found to be most extensive in

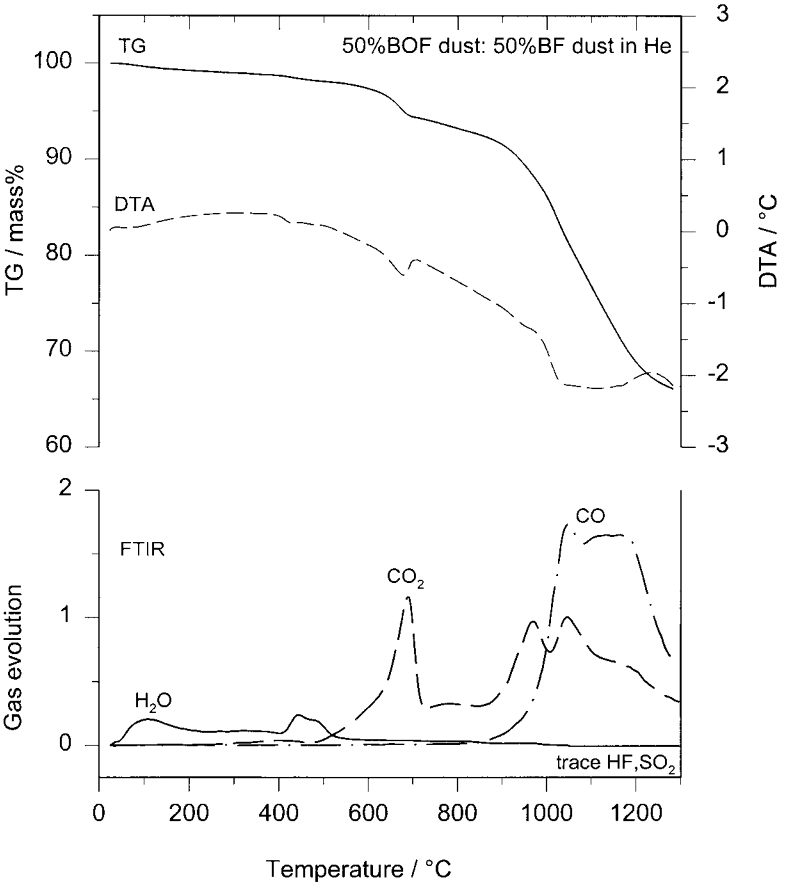

Fig. 8. TG/DTA/FTIR diagram of a 50% BOF : 50%BF mixture in helium.

the inert atmosphere (He). A complete metallization of iron oxides, the main components of the BOF dust, in a mixture with 50% BF dust, takes place when the mixture is heated to 1300°C in an inert atmosphere. Such a mixture, when cold-bonded or pelletized, could represent an iron-rich, self-reducing agglomerate viable for recycling back to the iron or steel-making process.

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