

Thermal behaviour of basic oxygen furnace waste slag

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Abstract

The traditional use of basic oxygen furnace (BOF) slag as an aggregate in road construction has been restricted due to the slag's expansive nature, attributed to the hydration of the calcium and magnesium oxides content. Consequently, a significant proportion of the slag is now being stock-piled. In the present work, the thermal behaviours of an industrial steelmaking BOF slag and of calcium and magnesium oxides, were examined in order to explore means of thermally stabilizing the slag and minimizing its susceptibility to hydration. Thermal analysis techniques, supplemented by Fourier transform infrared spectroscopy and X-ray diffraction, were used to study the materials in dry air, moist air and CO₂. An optimum method for thermally treating the slag is proposed and the susceptibility of the treated slag to form hydroxides on hydration was found minimal.

Keywords: Basic oxygen furnace slag; Stabilization; Hydration; Carbonation

1. Introduction

Basic oxygen furnace (BOF) slag is a major by-product in integrated iron and steel-making operations, with an estimated 1.2 million tons generated annually in Canada. In steelmaking, the slag is normally air-cooled, crushed and processed to recover the metallic content. Some of the slag is then recycled to the blast furnace while a significant portion is used in road construction due to its very high stability and superior skid and wear resistance [1]. In the last few years, however, the latter use of the slag has been restricted in many regions due to an undesirable expansion of the slag aggregate leading to rapid deterioration of the roads. The volume expansion (up to 10% [1]) is attributed to the short and long term hydration of the calcium and magnesium oxides content. Consequently, a

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significant proportion of the slag is now being stockpiled while attempts are being made to resolve the problem and reinstate the slag as a viable road construction material or find other high volume applications.

In the present work, thermal characterization of an industrial BOF slag was carried out as part of a large project on the recycling of steelmaking waste by-products. The thermal behaviour of calcium and magnesium hydroxides (or oxides) in different atmospheres was also examined in an attempt to gain more knowledge on the potential conversion of these materials to carbonates and on the susceptibility of the carbonates, and ultimately the BOF slag, to hydration.

2. Materials and experimental procedure

An industrial sample of basic oxygen furnace slag (about 200 kg) was ground, homogenized and sampled using universal and carousel sample splitters. Chemical analysis of the slag indicated the presence of 18.2% Fe, 25.7% Ca, 6.6% Mg, 4.9% Mn, 0.21% Na, 10.7% SiO₂, 2.3% Al₂O₃, 0.36% TiO₂ and other trace elements. Reagent grade calcium and magnesium hydroxides were also used.

The thermal analysis (TA) measurements were carried out using a Seiko SSC5200H/TG/DTA 320 instrument. The acquired data were transferred to an external computer for plotting using Sigma Plot or Spectra Calc. For the identification of the evolved gaseous species, a BOMEM-MB100 Fourier transform infrared (FTIR) spectrometer was interfaced and used simultaneously with the thermal analyzer. In the TA experiments, 20–40 mg samples were subjected to a preselected heating profile in a stream of dry air, moist air, CO₂ or moist CO₂.

3. Results and discussion

Besides the chemical analysis, physical and mineralogical characterization of the slag was carried out and the results were reported in detail earlier [2]. The density of the slag was found to be 3.45 g cm⁻³. The mineralogical characterization indicated that the major phases in the slag are calcium silicates, iron oxides and complex ferrites. Calcium hydroxide is present in the slag as an intermediate constituent and calcium oxide as a minor constituent. Most of the uncombined calcium oxide and hydroxide particles in the sample (not in the form of silicates or ferrites) were found to be exposed, which explains the hydration of the oxide to hydroxide. Most of the magnesium in the slag is present in the form of simple or complex ferrites with a minor amount in the form of oxide.

Despite the fact that the slag had been subjected to high temperatures in the basic oxygen furnace, some changes in weight, thermal activities and gas evolution were observed during the TA experiments. Fig. 1 represents a TG/DTA/FTIR diagram obtained by heating a slag sample (<355 μm particle size), placed in an alumina container loosely covered with a platinum lid, in dry air. The sample was predried by heating to 300°C in dry air. The TG curve in Fig. 1 shows three distinct stages of mass loss at 300–440, 440–570 and 660–785°C, accompanied by endothermic peaks on the DTA curve. A

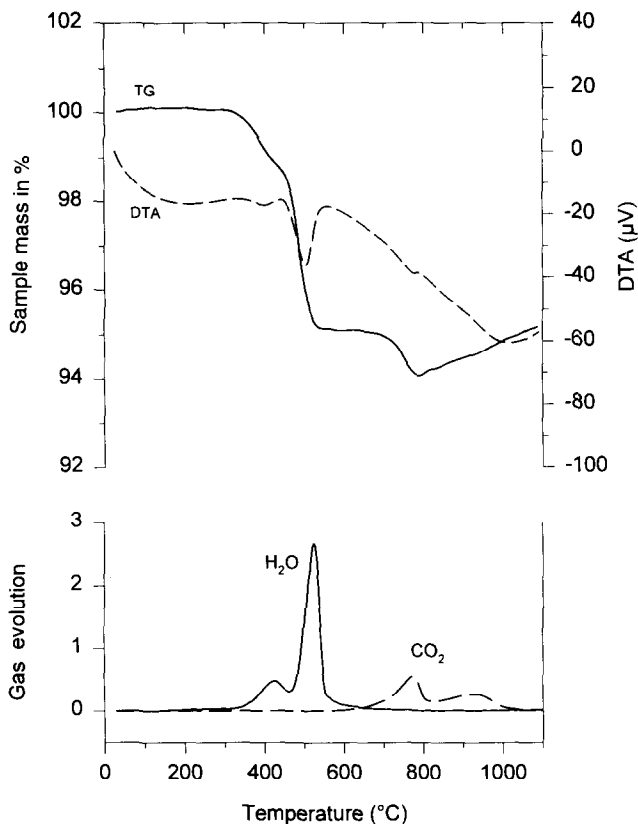


Fig. 1. TG/DTA/FTIR curves for a slag sample in dry air.

gradual mass gain above 785°C was also detected. The first and second changes are typical of the dehydroxylation of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, respectively, and the third is typical of the decomposition of CaCO_3 , according to the following reactions:



The mass gain above 780°C is most likely due to the oxidation of iron or iron oxide in the sample (the mass gain did not occur when a slag sample was heated in an inert atmosphere in a separate experiment). The three stages of mass loss measured 1.3%, 3.6% and 1%, indicating the presence of 4.2% $\text{Mg}(\text{OH})_2$, 14.8% $\text{Ca}(\text{OH})_2$ and 2.3% CaCO_3 , respectively. The theoretical mass losses of reactions (1)–(3) on completion are 30.88%, 24.3% and 44.0%, respectively. The reactions were further verified by the appearance of corresponding H_2O and CO_2 bands on the FTIR gas evolution profiles in Fig. 1. Both

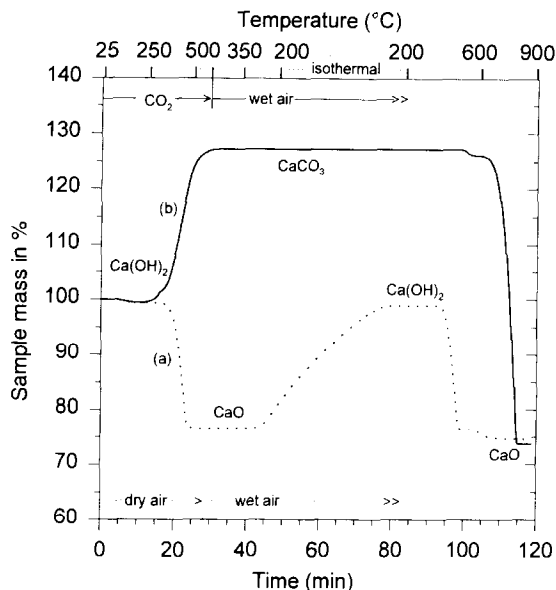


Fig. 2. TG curves for $\text{Ca}(\text{OH})_2$ in dry air then moist air (a) and in CO_2 then moist air (b).

$\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ may have been present originally in the slag as free lime and magnesia, but hydrated on exposure to ambient moisture for extended periods of time.

The susceptibility of CaO and that of CaCO_3 to hydration was examined and compared (Fig. 2). Reagent grade $\text{Ca}(\text{OH})_2$ was the starting material in both cases. In the first experiment (Fig. 2(a)), the hydroxide was heated in dry air to 500°C where complete dehydroxylation took place as indicated by the mass loss on the TG curve. The sample was then held isothermally for 5 min while dry air was replaced by moist air (by bubbling the air through water at ambient temperature). It was then cooled to 200°C , an optimum temperature for the hydration of CaO as determined earlier in preliminary experiments. The mass gain indicated that almost complete hydration ($\approx 98\%$) has taken place. On further heating, dehydroxylation of the sample took place again quantitatively. In the second experiment (Fig. 2(b)), the same temperature profile was used but $\text{Ca}(\text{OH})_2$ was subjected to a CO_2 atmosphere during the first heating step (ambient to 500°C). It can be seen that extensive carbonation ($\approx 82\%$) occurred as indicated by the mass gain. It can also be seen that, in the following stages (isothermal at 500°C –cooling–isothermal at 200°C), no hydration took place when moist air was introduced. At higher temperatures, the carbonate decomposed quantitatively to CaO as shown in Fig. 2(b).

Various conditions for the carbonation of CaO and $\text{Ca}(\text{OH})_2$ were explored. The carbonation of CaO , prepared by dehydroxylation of reagent-grade calcium hydroxide, in CO_2 was found to start rapidly then decelerates substantially, probably due to the formation of a carbonate product layer on the surface of the CaO particle. Any further carbonation would take place by diffusion of the CO_2 through the product layer. Significant carbonation took place only when the sample was heated to $>750^\circ\text{C}$. The carbonation of $\text{Ca}(\text{OH})_2$, however, was found to be more successful. Optimum carbonation was found to

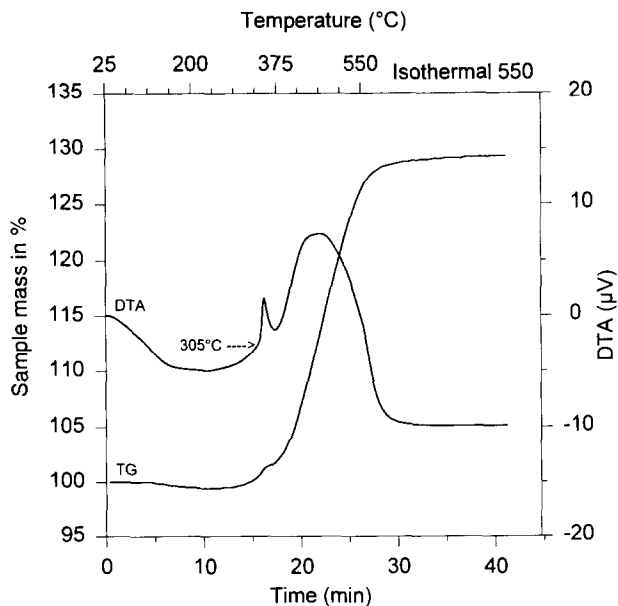


Fig. 3. TG/DTA curves for $\text{Ca}(\text{OH})_2$ in CO_2 .

take place when the material was heated to 550°C . Fig. 3 shows a TG/DTA diagram for the carbonation of reagent grade $\text{Ca}(\text{OH})_2$ in pure CO_2 . From the apparent mass gain in the temperature range $250\text{--}550^\circ\text{C}$, it is evident that extensive carbonation has taken place. The sharp characteristic exothermic peak at about 305°C on the DTA curve is due to the crystallization of CaCO_3 , formed initially as an amorphous material on the carbonation of the oxide [3]. The carbonation takes place according to the following scheme:



The easier and more extensive carbonation of $\text{Ca}(\text{OH})_2$, compared to that of CaO , may be explained on the basis of the postulation by Galwey and Laverty [4] that the dehydroxylation of $\text{Ca}(\text{OH})_2$ takes place in two separate stages. The first stage involves the diffusion of water from the hydroxide particle leaving a dehydrated CaO product with the original dimensions of the hydroxide (and therefore with many micropores). The second stage involves the recrystallization of the CaO product. The direct carbonation of the hydroxide, during the dehydroxylation process, may therefore occur by the diffusion of CO_2 into micropores vacated by the evolution of H_2O , before the recrystallization of CaO [4].

The carbonation of $\text{Ca}(\text{OH})_2$ was also examined at different partial pressures of CO_2 in air. The results, as presented in Fig. 4, indicated that nearly maximum carbonation is reached at CO_2 ratios of $\geq 5\%$ in air. The same experimental scheme was used to examine the carbonation of $\text{Mg}(\text{OH})_2$ with little success. Further work for the hydration/carbonation of $\text{MgO}/\text{Mg}(\text{OH})_2$ is planned.

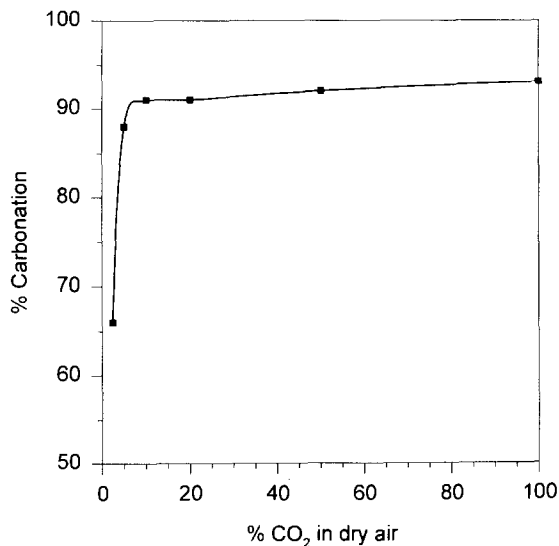


Fig. 4. Extent of carbonation of $\text{Ca}(\text{OH})_2$ in air with different ratios of CO_2 .

Fig. 5 shows a TG diagram for a hydrated slag sample subjected to the same heating profile which was found optimum for the carbonation of $\text{Ca}(\text{OH})_2$ (Fig. 3) in an atmosphere of moist CO_2 . As explained earlier, prehydration seems to be essential for an extensive carbonation. In addition, moist CO_2 was used to ensure the conversion of residual

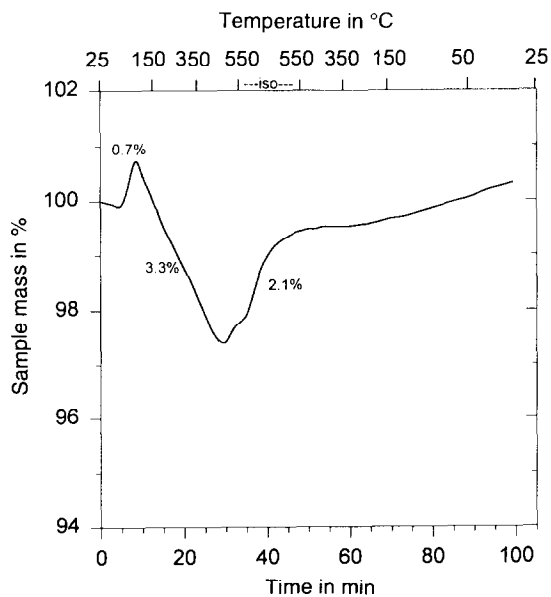


Fig. 5. A TG curve for hydrated slag in moist CO_2 (first 5 min in dry air) under a preselected heating profile.

Ca or Mg oxides in the slag to hydroxides before carbonation. The minor mass gain (about 0.7%), observed on the TG curve at ambient to 55°C, may be due to hydration/carbonation of residual CaO or MgO in the sample. The hydration and carbonation schemes of CaO were verified in separate experiments. In the temperature range 55–480°C, a mass loss of 3.3% appeared on the TG curve representing the net change in weight of overlapping reactions, namely, the hydration/carbonation of the slag and the evolution of adsorbed water and the dehydroxylation of contained $\text{Ca}(\text{OH})_2$ and, possibly, $\text{Mg}(\text{OH})_2$ [5]. Above 480°C, and isothermally at 550°C, a mass gain of 2.1%, signifying the continuation of the carbonation of CaO, appeared on the curve. On cooling, still in moist CO_2 , a small and gradual mass gain which may be due to the hydration of MgO was observed.

The susceptibility of the carbonated slag to hydration was examined by preparing a sample in moist CO_2 atmosphere according to the above-mentioned method. The sample was then examined by thermogravimetry and the thermal behaviour was compared to that of the original slag. Fig. 6 shows the TG curves for the slag before and after carbonation. The TG curve for the carbonated slag did not reveal any significant mass change in the temperature range corresponding to the dehydroxylation of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, namely, 300–500°C. Only the mass loss step corresponding to the decomposition of CaCO_3 was evident at higher temperatures. The TG curve of the original slag (before carbonation), replotted in Fig. 6 for comparison, clearly shows the dehydroxylation steps of the two hydroxides in the temperature range 300–500°C. The absence of the dehydroxylation steps and the significant increase in the size of the CaCO_3 decomposition step in the carbonated sample indicated that most, if not all, the free calcium oxide/hydroxide in the sample was converted to carbonate. A relatively small mass loss below 200°C on the TG curve for the carbonated slag indicates the presence of adsorbed water in the sam-

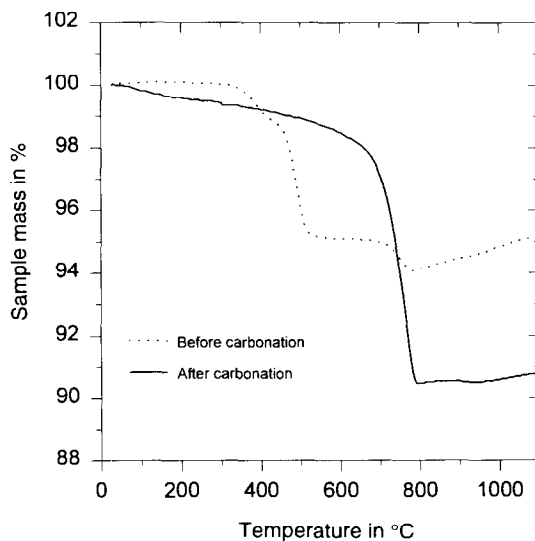


Fig. 6. TG curves for slag samples before and after carbonation in moist CO_2 .

ple. Unlike the original slag, the carbonated slag was not preheated to 300°C before the experiment.

4. Conclusions

The present study indicated that the carbonation of $\text{Ca}(\text{OH})_2$ in CO_2 takes place more extensively and at lower temperatures than that of CaO . The optimum carbonation of the hydroxide was found to take place by heating to 550°C in air with $\geq 5\%$ CO_2 . Carbonation of the slag is accomplished by heating in moist CO_2 to 550°C, holding for 15–20 min then cooling in the same atmosphere. It is concluded that, under the present experimental conditions, carbonated slag does not form hydroxides when exposed to hydration.

Acknowledgements

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