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SYNTHESIS OF SELECTED MINERAL COMPOUNDS FOR IN-DEPTH ANALYSIS OF STEEL SLAGS DURING CARBONATION

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Abstract

Steel slags could be used in the future in mineral carbonation processes at an industrial scale, if an economic method will be found. For this purpose to be achieved, one important aspect of the process should be well understood first, namely susceptibility of steel slags mineral compounds towards carbonation. This paper presents the preparation of seven of the most abundant minerals found in the composition of AOD, CC and BOF slags (akermanite ($Ca_2MgSi_2O_7$), bredigite ($Ca_7MgSi_4O_{16}$), cuspidine ($Ca_4Si_2O_7F_2$), β– and γ–C_2S (Ca_2SiO_4), merwinite ($Ca_3MgSi_2O_8$), and srebrodolskite ($Ca_2Fe_2O_5$)). The resulting synthetic minerals were then characterised in terms of purity.

Introduction

Reusability of steel slags (BOF, AOD and CC slags) in different domains is for the moment difficult to be realised due to susceptibility of the containing heavy metals to leaching and the substantial amounts of free lime and magnesia.[1,2] Reducing the stockpiling of these kind of residues to a minimum is the main purpose of reusing them[3,4], while a second purpose can be the sequestration of carbon dioxide through mineral carbonation.[5]

The process of mineral carbonation applied on steel slags encounters various difficulties that make it economically inefficient. One of these drawbacks is represented by the uncertainties regarding the susceptibility of alkaline minerals that are found in steel slags composition towards reacting with CO_2 and forming stable carbonate compounds.

The work presented in this paper is preliminary to a broader study regarding the behaviour of seven alkaline metals containing minerals (akermanite ($Ca_2MgSi_2O_7$), bredigite ($Ca_7MgSi_4O_{16}$), cuspidine ($Ca_4Si_2O_7F_2$), β– and γ–C_2S (Ca_2SiO_4), merwinite ($Ca_3MgSi_2O_8$) and srebrodolskite ($Ca_2Fe_2O_5$)) that represent the major components of the above mentioned steel slags, during three different mineral carbonation experiments, and comparison with results of the same experiments using steel slags.

Materials and methods

To conduct the proposed study the needed alkaline minerals had to be obtained through synthesis, due to their absence in the market and also because they are rarely found in nature. Solid state sintering was used for the synthesis and for that, temperatures, duration and cooling methods were selected based on literature presenting the synthesis of the desired mineral phases.[6-11] Based on available instruments and characteristics aimed for the synthetic minerals, each synthesis process required different adaptations. The synthesis conditions for the seven minerals are presented in Table 1. All minerals were synthesised using analytical grade stoichiometric quantities of their constituent oxides (CaO, MgO, SiO_2, Fe_2O_3) and CaF_2 in the case of cuspidine. Calcium oxide was produced prior to mineral synthesis from the thermal decomposition of pure $CaCO_3$ at 900°C. The same procedure was used in case of MgO with the purpose of removing possible pre-existing hydroxides and carbonates. To stabilise the β–polymorph of C_2S, 0.4 wt% B_2O_3 was added to its mixture. Synthesised minerals were produced in batches of 50 g; to obtain sufficient material for the experiments in the present study, two batches of each mineral were produced.

After weighing the necessary quantities of chemicals for each mineral, the mixtures were then mixed using a ball mill (Retsch PM 400 MA-type) with ZrO_2 vial and balls (ø 10 mm). A 10:1 ball to powder ratio was used, milling speed was 250 rpm for two hours duration, and 2 ml of ethanol was added to prevent powder adhesion on the milling balls. For the synthesis of bredigite, five rounds of milling were performed with vial wall cleaning and ethanol addition before each round. As in Mirhadi *et al*. (2012)[11], it was found that prolonged milling was required to obtain sufficient bredigite purity, possibly due to the high Ca:Mg ratio of this mineral. Milled mixtures were pelletised into 10 mm pellets at 15 kN/cm^2 pressure to promote better solid state sintering interaction between the mixture components. Pellets were placed in a platinum crucible and heat-treated in a high temperature bottom loading furnace (AGNI ELT 160-02). Slow cooling was performed within the furnace, while rapid cooling was performed by dropping the hot crucible on a pan and cooling under air flow. After heat treatment, the mineral samples were milled to < 80 μm in a centrifugal mill (Retsch ZM100), and the purity of the samples was assessed by Quantitative X-Ray Diffraction (QXRD) on a Philips PW1830. Mineral identification was done in Diffrac-Plus EVA (Bruker) and mineral quantification was performed by Rietveld refinement technique using Topas Academic v4.1. It was desired to obtain at least 70 wt% purity of the target mineral and < 10 wt% free oxides

content. If these targets were not met, the mineral samples were sintered again until the targets were reached.

Results and discussion

Table 1 presents the final mineral purity and free oxide content of each 100 g mixed mineral sample. All samples meet the desired targets, the purity of every synthetic mineral exceeding 70 wt% and the free oxide content being lower than 10 wt%.

Table 1: Mineral synthesis conditions and target mineral purity, determined by QXRD

Mineral name	Milling time (h)	Temp. (°C) / Time (h)	Cooling method	Number of runs	Target mineral (wt%)	Free oxides (wt%)
Akermanite	2	1300 / 24 (air)	5°C/min	4	74.6	0.0
Bredigite	10	1200 / 1 (air)	5°C/min	1	81.7	0.5
Cuspidine	2	1100 / 20 (Ar atmosphere)	5°C/min	1	83.6	0.2
β–C_2S	2	1450 / 3 (air)	Rapid cooling in air flow	2	73.8	5.5
γ–C_2S	2	1400 / 48 (air)	5°C/min	1	73.0	9.5
Merwinite	2	1500 / 20 (air)	1°C/min	1	74.2	0.2
Srebrodolskite	2	800 / 1 1100 / 36 (air)	5°C/min	2	70.5	0.0

These results were obtained, for some minerals, after repeating the sintering step (4 times for akermanite, 2 times for β–C_2S and srebrodolskite). Beside the target mineral and free oxides, the synthetic materials also had in their composition intermediate mineral phases of the targeted minerals (*e.g.* minerals of different Ca:Si or Ca:Fe ratios).

Conclusions

This paper presented the methodology used to synthesise seven alkaline minerals that make the majority of BOF, AOD and CC slags composition. The different methods for mineral synthesis were based on literature and were adapted for the instruments and needs of the study that followed.

The 70 wt% purity and less than 10 wt% free oxide conditions were met for all materials. This made possible a number of carbonation experiments to be performed, with results that will be presented in a future study.

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