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CAN DYNAMIC MINERAL CARBONATION BE USED TO MAKE LOW CARBON BINDERS FROM BOF SLAGS?

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Introduction

An effective means to reduce CO_2 emissions from cement production is partial substitution of Portland clinker by so-called supplementary cementitious materials (SCMs). Conventional SCMs such as iron blast furnace slags and coal combustion ashes are fully used and will reduce in the mid-term due to the decarbonisation of the power and steel sectors (*e.g.* DRI steel production). To maintain and further increase substitution rates of Portland clinker the cement industry is therefore in search of alternative SCMs. A new approach is to use CO_2-treatment or carbonation as beneficiation step to process residues into SCMs. At present, BOF steel slags are not used as SCM due to their low reactivity and the presence of components that are not compatible with cement such as free lime (CaO) and periclase (MgO). CO_2 treatment neutralises the free CaO and MgO and resolves the incompatibility issues. Reaction of CO_2 with the Ca-silicates (*e.g.* Ca_2SiO_4) in the steel slag results in the formation of $CaCO_3$ and amorphous silica, which will react in combination with Portland cement. As an added benefit, stable carbonates are formed by the CO_2 beneficiation treatment resulting in a CO_2 uptake of 100-150 kg CO_2/tonne SCM.

In the ongoing ERA-MIN3 CO2TREAT and HEU Carbon4Minerals VITO has developed a dynamic mineral carbonation method for the production of SCMs from BOF steel slags.

Materials & methods

Two size fractions (0-3 mm and 3-8 mm) of BOF slags from steel production were sampled at the site of Arcelor Mittal in Ghent, Belgium, as produced by an on-site sieving and magnetic separation plant. The materials were dried (at 105°C) and homogenised by quartering. For powder characterisation, the materials were milled to <63 µm.

Chemical composition was determined by a high-performance energy dispersive X-ray Fluorescence spectrometer (EDXRF) with polarised X-ray excitation geometry (HE XEPOS, Spectro Analytical Systems, Kleve, Germany) on fused beads. Mineralogical composition of the slags was analysed with an X’Pert PRO XRD Philips diffractometer equipped with a Co tube (CoKα1 source with λ=1.7890100 nm). Quantitative mineralogical analysis was carried out using Rietveld analysis, adopting the method of Snellings[1].

For the carbonation experiments, the materials were disc milled (Retsch DM 200 disc mill) to < 2 mm followed by ball milling (Retsch Planetary ball mill pm 400) to a particle size of d99=150 microns. Prior to carbonation, the milled slags were brought to the desired moisture content by mixing with appropriate amounts of deionised water. The moistened mixture was stored for 48 hours in a sealed plastic container to convert calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$).

After hydration, the slags (85 g per run) were placed in an in-house designed stainless-steel rotating drum with 37 stainless steel balls of 8 mm in diameter having a total mass of 506 g. The rotation speed of the drum was 44 revolutions per minute (RPM). The rotating drum was placed in a 105 l Premex autoclave at a temperature of 40°C and 100% relative humidity. Carbonation settings (CO_2 pressure and concentration, duration) were regulated by the autoclave settings.

Degree of carbonation was determined by analysis of total carbon content (TC) with a total carbon element analyser from Analytik Jena (Multi EA 4000). Fourier-transform infrared (FT-IR) spectroscopy was used to follow the degree of polymerisation of the silica gel in selected experiments. FT-IR spectroscopy measurements of the powder samples were acquired in Attenuated total reflectance (ATR) mode on a Thermo Nicolet Nexus FT-IR spectrometer. Mortar samples were prepared according to EN196-1, using 30% replacement of CEM I by the carbonated BOF.

Results

The chemical and mineralogical composition are shown in Table 1 and Table 2, respectively.

Table 1: Chemical composition of BOF slags (Main oxides, in %)

Main oxides	BOF slag 0-3 mm	BOF slag 3-8 mm
CaO	43.9	43.0
MgO	3.3	3.4
Al_2O_3	1.8	2.0
SiO_2	11.7	11.8
Fe_2O_3	22.1	24.7
P_2O_5	1.1	1.2
MnO	1.9	2.1
Cr_2O_3	0.2	0.2
V_2O_5	0.5	0.6
SO_3	0.2	0.2

Table 2: Mineralogy of BOF slags (in %). Carbonatable minerals are indicated in bold

Mineral	Formula	BOF slag 0-3 mm	BOF slag 3-8 mm
Hatrurite	Ca_3SiO_5	1.7	4.1
Larnite	**β-Ca_2SiO_4**	**7.7**	**13.9**
Calcio-olivine	**γ-Ca_2SiO_4**	**4.1**	**7.7**
Lime	**CaO**	**3.3**	**6.7**
Portlandite	**$Ca(OH)_2$**	**13.3**	**0.5**
Calcite	$CaCO_3$	1.3	0.9
Aragonite	$CaCO_3$	1.1	0
Dolomite	$Ca(Mg(CO_3)_2)$		1.5
Katoite	$Ca_3Al_2(SiO_{12})_{3-x}(OH)_{4x}$	0.4	0
Srebrodolskite	**$Ca_2Fe_2O_5$**	**17.4**	**21.9**
Wustite	FeO	6.3	8.2
Fe (metal)	Fe	0.4	0.1
$MgFe_2O_4$	$MgFe_2O_4$	3.6	3.1
Pyroaurite	$Mg_6Fe_2CO_3(OH)_{16}.4H_2O$	0.4	0.3
Quartz	SiO_2	0.3	0.3
Amorphous		38.7	30.8

The results show a clear difference in mineralogy between both fractions, most probably related to the enrichment of weaker minerals in the fine fraction.

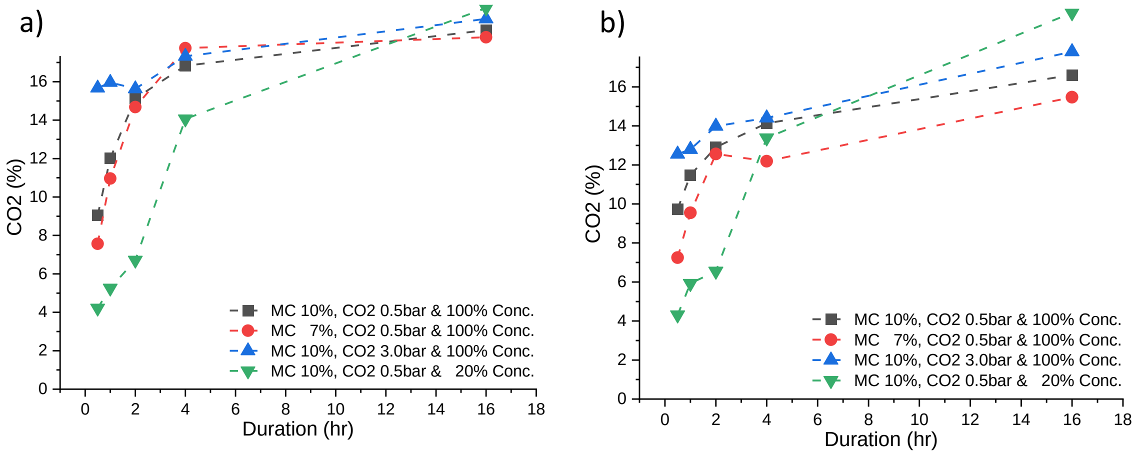

Figure 1: Results of the carbonation experiments of a) BOF 0-3 mm and b) BOF 3-7 mm. MC = moisture content

The results of the parametric study (Figure 1) show that reducing the moisture content of the initial material has limited effect on the carbonation. Increasing the CO_2 pressure leads to a higher initial carbonation, but without an effect on the final carbonation degree. Reducing the CO_2-concentration leads to a slower initial reaction, but a higher final CO_2 content. For the 0-3 mm BOF, final CO_2 uptake is similar for all conditions and close to the theoretical maximum based on the mineralogical composition. For the 3-8 mm BOF, the results vary more strongly between 15-20% CO_2 content. FT-IR measurements confirmed the formation of silica gel.

Strength measurements on mortar samples with 30% replacement of CEM I by carbonated BOF slag (0-3 mm) showed a strength activity index of 0.76 – 0.80 after 7 and 90 days, respectively. This performance is close to traditional SCMs such as limestone.

Conclusion

The results show that mineral carbonation can be used to make SCMs out of BOF slag, with a performance similar to conventional SCMs such as limestone. Further investigations are ongoing to gain a deeper insight into the silica gel formation, and to further increase the reactivity of the SCM.

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References

1. R. Snellings, K. Scrivener, B. Lothenbach (Eds.) A Practical Guide to microstructural Analysis of Cementitious Materials, Crc Press, 2016.