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THE 16TH INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT
ICCC 2023
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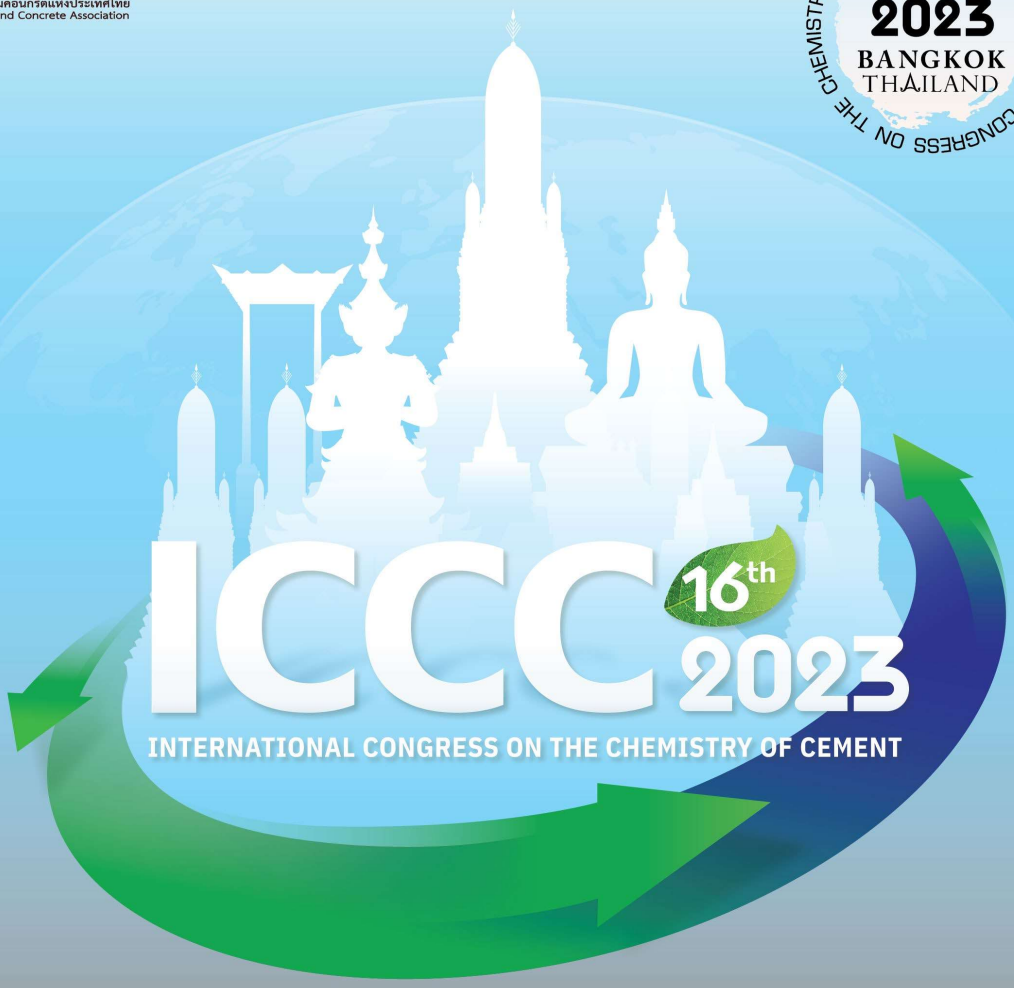

ICCC 16th 2023

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CONGRESS PROCEEDING VOLUMN III

Further reduction of CO_2-emission and circularity in the cement and concrete industry

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The 16th International Congress on the Chemistry of Cement 2023 (ICCC2023)
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Production of a hydraulic material from post treated steelmaking slags

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ABSTRACT

Steelmaking slag is a by-product of steel production, of which 4.5 Mt were produced in 2020 in Germany alone. It is mainly used in road construction, earthwork and hydraulic engineering. A smaller part is returned to the metallurgical cycle, used as fertiliser or landfilled.

With this use, iron oxides still contained in steelmaking slag are lost. In addition, the possibility of producing higher-grade products from steelmaking slag is foregone. In recent decades, many researchers have investigated the production of Portland cement clinker and crude iron from basic oxygen furnace slags (BOFS) via a reductive treatment. Carbothermal treatment of liquid BOFS causes a reduction of iron oxides to metallic iron, which separates from the mineral phase due to its higher density. Simultaneously, the chemical composition of the reduced slag is adapted to that of Portland cement clinker.

In this study, German BOFS was reduced in a small-scale electric arc furnace using petrol coke as a reducing agent. The resulting low-iron mineral product has a similar chemical composition to Portland cement clinker and was rich in the tricalcium silicate solid solution alite (Ca_3SiO_5). Based on its chemical and mineralogical composition, similar to that of Portland cement clinker, the reduced BOFS has the potential to react comparably. In our study, the reduced BOFS produced less hydration heat than OPC, and its hydraulic reaction was delayed. However, adding gypsum has shown to accelerate the hydration rate of the reduced BOFS compared to that known from the calcium silicates of Portland cement clinker.

Further research to improve the hydraulic properties of the reduced slag is essential. If successful, producing a hydraulic binder and crude iron from BOFS has economic and ecological benefits for both the cement and steel industries.

KEYWORDS: *steelmaking slag, alite, hydraulic reactivity, clinker substitute*

1. Introduction

Basic oxygen furnace slags (BOFS) contain 7–50 wt.% Fe_2O_3, 31–56 wt.% CaO, 10–27 wt.% SiO_2, 1–4.5 wt.% Al_2O_3, 0.3–10 wt.% Mn_2O_3, and 0.8–15 wt.% MgO (Menad et al., 2014). Despite their high basicity (CaO/SiO_2 ratio) and a content of up to 20 wt.% alite (Ca_3SiO_5) and up to 60 wt.% belite (β-Ca_2SiO_4) (Das et al., 2007), BOFS are scarcely used for cement production due to their high iron oxides content, low content of hydraulic phases, and content of up to 15 wt.% free CaO and 5 wt.% MgO, which make BOFS a risk for volume instability (Das et al., 2007, Waligora et al., 2010, Menad et al., 2014).

In the past, several different ways to produce a hydraulic or pozzolanic material from BOFS have been investigated, e.g. (Li et al., 2011, Belhadj et al., 2012, Ludwig and Wulfert, 2012, Li et al., 2013, Neto et al., 2017, Liu et al., 2019). A reductive treatment of BOFS as described in (Kubodera et al., 1979, Piret and Dralants, 1984, Dziarmagowski et al., 1992, Reddy et al., 2006, Ludwig and Wulfert, 2012, Wulfert et al., 2013a, Wulfert et al., 2013b, Liu et al., 2017) is advantageous because it allows both the recovery of iron from the BOFS and the simultaneous production of Portland cement clinker. The properties of the final hydraulic product depend on the composition of the original BOFS, the degree of reduction, and the modifications made during the treatment.
However, it was found that the hydraulic reaction of the Portland cement clinker-like material produced from BOFS was significantly delayed compared to ordinary Portland cement (OPC) (Schraut et al., 2021). Since OPC is a product of finely ground cement clinker mixed with a certain amount of calcium sulfates, such as gypsum ($CaSO_4 \cdot 2H_2O$), the next step was to investigate the hydraulic reactivity of the clinker-like material from BOFS with the addition of gypsum. Besides controlling the tricalcium aluminate reaction, calcium sulfates also accelerate the hydration of calcium silicates (Bentur, 1976, Quennoz and Scrivener, 2013) and increase the dissolution of alite (Menetrier et al., 1980).
To keep the complexity of the system low, the addition of calcium sulfates other than gypsum has been refrained from in this study.

2. Materials and Methods

A BOFS from a German steel plant was used for the thermochemical experiments. The slag was crushed to a maximum grain size of approx. 20 mm and dried at 200 °C before it was molten and reduced in the small technical scale electric arc furnace of the Bundesanstalt für Materialforschung und -prüfung (BAM). The electric arc furnace has a power of 480 kW and is equipped with three graphite electrodes with a diameter of 60 mm. The experiments were conducted in a graphite-lined furnace vessel with a volume of approx. 0.4 m^3. 58 g of petrol coke per kg of BOFS was added as a reducing agent. The generated metallic iron was sedimented at the bottom of the furnace and was obtained manually after cooling. Cooling took place in the reactor within ~24 h. For more details, see Schraut et al. (2021).
The chemical composition of the samples was determined by CRB Analyse Service GmbH on fused beads by X-ray fluorescence analysis (XRF). The crystalline phase composition was determined by X-ray diffraction (XRD) with a Bruker D8 Advance X-ray diffraction system at 40 kV and 40 mA over an angular range of 5–85 °2θ with a step size of 0.02 °2θ and a velocity of 2 s/step. The instrument was equipped with a Cu-tube, a LynxEye XE-T detector, and a fixed slit (0.3°). To investigate the crystalline hydrates with XRD, the hydration was stopped after 2, 7, 14, 28, 56, and 90 d using the solvent exchange method with isopropanol.
The hydration heat was measured over two weeks in an isothermal calorimeter TAM Air 8-channel from TA instruments at a temperature of 20 °C. 3 g of the ground sample was externally mixed for 1 min with 1.5 g distilled water resulting in a water-to-binder (W/B)-ratio of 0.5.
As a reference, a commercial CEM I 32.5 R from Schwenk Zement KG was prepared and analysed under the same conditions as the experimental samples. Gypsum (EMSURE® p.A. from Merck KGaA) was added to the sample in a concentration corresponding to 1.0 wt.% SO_3.

3. Results and Discussion

The reductive treatment resulted in a transformation of the oxide-bound iron in brownmillerite ($Ca_2(Al,Fe)_2O_5$), wuestite (FeO) and magnetite (Fe_3O_4) to metallic iron, which separated from the mineral slag. Accordingly, the mass fraction of Fe_2O_3 in the mineral slag (reduced BOFS) decreased from about 29 wt.% to about 6 wt.%, while the mass fractions of CaO and SiO_2 increased proportionally (Table 1). The mineralogical composition of the reduced BOFS changed correspondingly. While the Fe-oxides and Fe-Al-oxides disappeared, alite formed the new main mineral phase in the reduced BOFS. Besides alite, belite, mayenite ($Ca_{12}Al_{14}O_{33}$), tricalcium aluminate ($Ca_3Al_2O_6$), portlandite ($Ca(OH)_2$) and periclase (MgO) were identified in the reduced BOFS as crystalline phases. Therefore, it can be stated that the mineralogical and chemical composition of the reduced BOFS is close to the mineralogical and chemical composition of Portland cement clinker.

The formation of alite in reduced BOFS was also reported by Kubodera et al. (1979), Wulfert et al. (2013b) and Dziarmagowski et al. (1992) and is likely to depend on the CaO/SiO_2-ratio of the reduced slag. Alite was identified as the main mineral in reduced BOFS with $CaO/SiO_2 > 2.9$, while belite was the main mineral in reduced BOFS with $CaO/SiO_2 < 2.6$ (Dziarmagowski et al., 1992, Reddy et al., 2006).

Table 1: Chemical composition of the original BOFS, the reduced BOFS (rBOFS), and a commercial OPC CEM I 32.5 R (CEM I) determined by XRF. All mass fractions are given as wt.% oxides, although this may not always represent the actual oxidation state of each element in the samples. Only element oxides whose mass fractions were > 0.1 wt.% in at least one sample are shown.

[wt.%]	CaO	SiO_2	Fe_2O_3	MnO	MgO	Al_2O_3	P_2O_5	Cr_2O_3	TiO_2	V_2O_5	SO_3	SrO	Na_2O	K_2O
BOFS	43.48	12.07	28.59	4.554	3.64	1.79	1.12	0.518	0.524	0.310	0.23	0.025	0.07	<0.03
rBOFS	64.00	19.54	5.64	3.151	3.15	2.53	1.20	0.419	0.730	0.399	0.05	0.035	<0.06	<0.03
CEM I	61.97	19.36	3.06	0.047	3.04	4.96	0.44	0.013	0.322	0.010	3.03	0.148	0.21	0.92

The main hydration reaction of the reduced BOFS was considerably slower than that of OPC and started only after ~9 d of hydration (Figure 1). The hydration heat maximum was reached after about 14 d of hydration. The cumulative heat of hydration after 14.5 d was ~90 J/g. The first hydrates to form were portlandite ($Ca(OH)_2$) and brucite ($Mg(OH)_2$). Additionally, hemicarboaluminate ($[Ca_4Al_2(OH)_{12}][OH(CO_3)_{0.5}\cdot 4H_2O]$) was detected and transformed later to carbonated hemicarboaluminate ($[Ca_4Al_2(OH)_{12}][OH_{0.4}(CO_3)_{0.8}\cdot 4H_2O]$) and monocarboaluminate ($Ca_4Al_2(OH)_{12}(CO_3)\cdot 5H_2O$).
The addition of 1 wt.% SO_3 in the form of gypsum accelerated the reaction of the reduced BOFS significantly. The main hydration reaction started after ~1 d of hydration and the cumulative heat of hydration after 14.5 d increased to ~160 J/g. Furthermore, the heat flow curve showed a sharp peak after ~2 d and 5 h that can be interpreted as the reaction peak of the aluminate reaction. Since the aluminate reaction occurred after the silicate reaction, the sample can be considered properly sulfated (Quennoz and Scrivener, 2013). In rBOFS + 1 wt.% SO_3, ettringite formed besides portlandite and brucite. No carboaluminates formed during hydration of rBOFS + 1 wt.% SO_3.

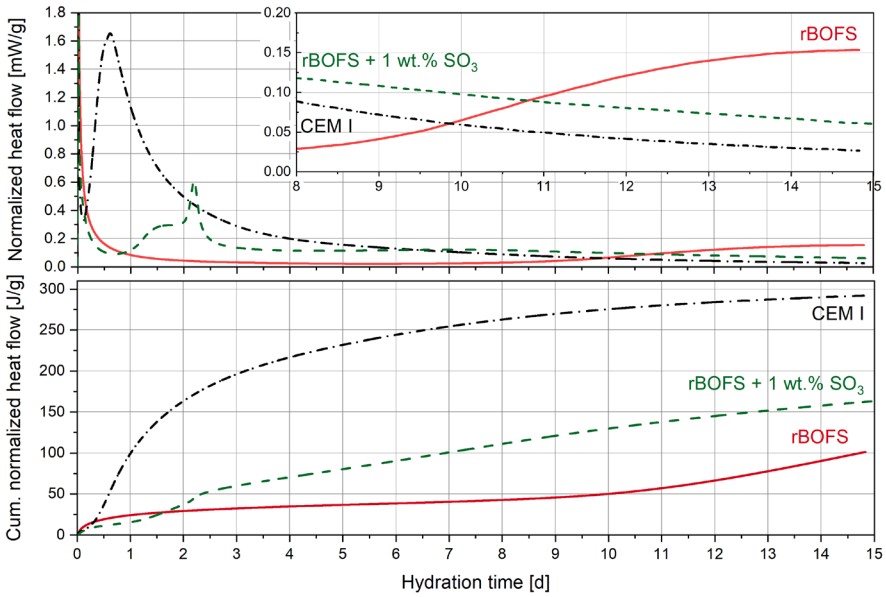

Figure 1: Normalised heat flow and cumulative normalised heat of the reduced BOFS (red, solid line), the reduced BOFS with the addition of an equivalent of 1 wt.% SO_3 as gypsum (green, dashed line) and of a commercial CEM I (black, dash-dotted line) measured for 14.5 d.

Sulfate is known to influence the silicate reaction. An accelerated dissolution of the alite with addition of sulfates was reported by (Bentur, 1976, Menetrier et al., 1980, Zajac et al., 2014, Bergold et al., 2017, Zunino and Scrivener, 2020, Andrade Neto et al., 2022). The reasons for this are still debated. The effect

was proposed to be caused by a promotion of C-S-H growth by ettringite acting as additional nuclei (Bergold et al., 2017, Tan et al., 2019) or by a change in C-S-H morphology (Andrade Neto et al., 2022). Other researchers assumed that a decrease of Ca^{2+} activity due to the formation of $CaSO_4^0$ species or an increased protonation of the C_3S surface by sulfate ions enhances the alite dissolution (Nicoleau et al., 2014). The binding of Al ions as ettringite is most likely not the causative agent, as acceleration by gypsum was observed in C_3S with and without Al (Andrade Neto et al., 2022).

4. Conclusions

The reductive treatment of BOFS can be used to recover iron from BOFS while simultaneously producing a material similar to Portland cement clinker. The majority of iron was reduced to metallic iron and separated from the mineral melt. The reduced BOFS had a chemical and mineralogical composition close to that of Portland cement clinker and contained alite as the main mineral.
The reduced BOFS reacted considerably more slowly with water than OPC. However, the reaction rate was increased with the addition of gypsum. Further investigations are needed, including using different sulfate carriers and SO_3 contents, to determine the actual mechanisms behind this acceleration. Nevertheless, the reduced BOFS shows potential as a cement component or concrete addition contributing to long-term hardening.

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