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Phosphorus speciation in dicalcium silicate polymorphs of basic oxygen furnace (BOF) slag – Preliminary results

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Abstract

This paper gives preliminary results of P speciation in basic oxygen furnace slag, rich in dicalcium silicates and with a phosphorus content that could jeopardize internal recycling within the steel mill.

Introduction

Chemical substitutions of $[\text{SiO}_4]^{2-}$ and $[\text{PO}_4]^{3-}$ occur not only in crystalline minerals but also in glass network formers where the crystal-chemical parameters of both anions are closed. Such is the case, for example, for the large nagelschmidite mineral group $[\text{Ca}_2\text{-}_4(\text{Si},\text{P}_2)\text{O}_8]$ type solid solution. P(V) can also be incorporated in dicalcium silicate Ca_2SiO_4 polymorphs (C_2S) and Ca_3SiO_5 (C_3S) solid solutions (Diouri et al., 1997), providing various compositions that can influence the nature and global stability or reactivity of the material. This kind of substitution is generally complex – coupled with other substitutions or accompanied by vacancies in the crystallographic network to ensure electroneutrality. Here we present and discuss the preliminary results of our investigations into such minerals present in basic oxygen furnace (BOF) slag, with a focus on environmental behaviour and recycling.

Materials

Eight 1.7 t samples of fresh BOF slag, representative of the annual variations in composition produced by a French steel mill, were collected and prepared at the steel mill. Further preparation was performed at BRGM to produce representative samples (homogenised, quartered, milled at 0-20 mm and magnetically separated samples) in the spring of 2008. The samples represent roughly the industrial process (industrial cooling time estimated between 24 and 48h with some skin effect).

Results are detailed specifically for one BOF slag sample (LD7) from the industrial process and from two laboratory cooling experiments performed on the same sample - from 1600°C to ambient- temperature: a very rapid cooling (quenching water) and a slow one of about 72 hours which approaches the thermodynamic equilibrium (details in Gautier et al., this conference).

Methods

The samples were described macroscopically, characterised using standard chemical methods (X-ray fluorescence, ICP-MS) and mineralogical (X-ray diffraction -XRD-,

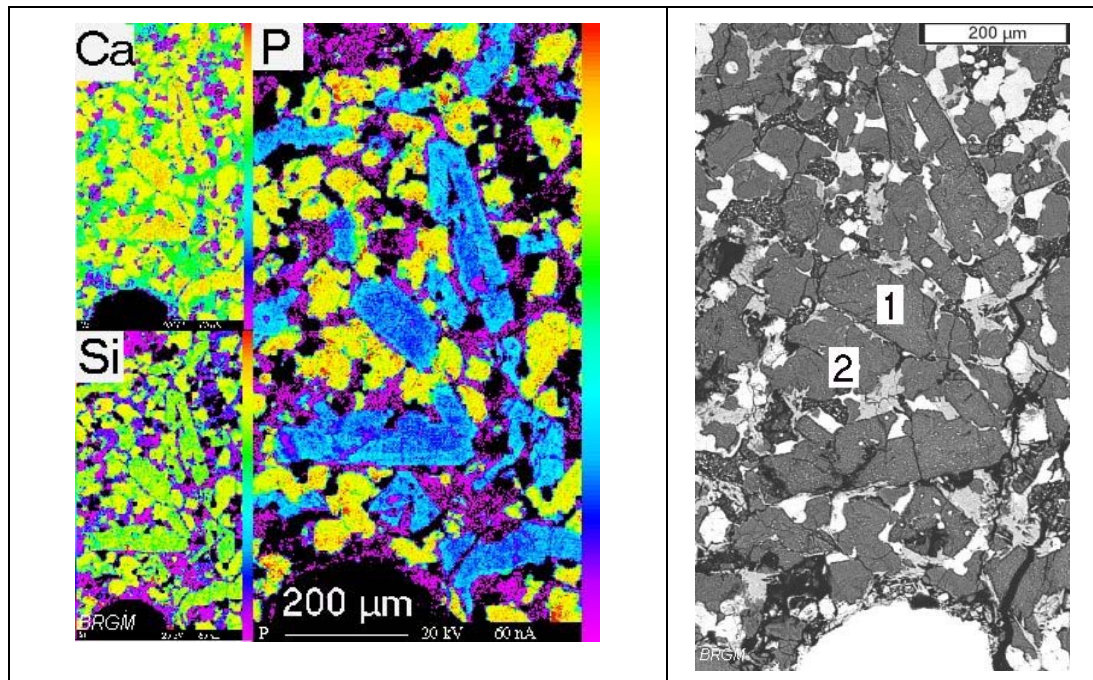
Scanning Electron Microscope – SEM-, Electron MicroProbe – EMP, Reflected light microscope). Non-oriented powder samples were analysed using a diffractometer with a Bragg-Brentano geometry (Siemens D5000), equipped with a monochromator and based on Co K α 1 radiation (λ 1.78897 Å). Polished thin sections of samples were examined under a scanning electron microscope (SEM) and a reflected light microscope and then analyzed using multi-element micromapping with the electron microprobe (Cameca SX 50), along with quantitative wavelength dispersive spectrometry (WDS) spot chemical analyses. Analytical conditions were adapted to the lowest concentrations (namely P here). The counting time, normally 6 sec for the major elements was increased to 20 sec.

Results

Global chemical composition of the 8 BOF slags, expressed in oxide % (Table 1), show that BOF slag are rich in Ca, Fe, Si-bearing phases with additional Mg, Mn, Al, Ti and P traces. The specific BOF slag studied here present high CaO and P₂O₅ contents (52.4 and 2.3 % respectively). Furthermore free lime content is 16.4% and Fe is mainly present as FeII (12.7% in FeO).

Table 1 – Chemical composition of the BOF slag

	Al ₂ O ₃	CaO	FeT as FeO	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	LOI 1000°C
LD7	1.4	52.4	18.4	< 0.05	5.2	2.9	< 0.2	2.3	12.8	0.7	0.3
Min.	1.0	41.1	17.5	< 0.05	4.9	2.3	< 0.2	1.5	7.6	0.4	0.3
Max.	2.7	52.4	30.3	< 0.05	9.6	3.1	< 0.2	2.5	15.3	0.8	5.5



Relative mapping scale for each element (confirmed by spot analyses)

Figure 1 – Ca, Si, P mapping (microprobe) and corresponding BSE image (SEM) - Ca silicates with low and high P content (grain 1 and 2 respectively)

The main phases identified by XRD in the BOF slag are dicalcium silicate (theoretical composition Ca_2SiO_4), calcium aluminoferrite (theoretical composition $\text{Ca}_2\text{FeAlO}_5$), free lime (CaO) and wustite (FeO) with Fe substituted by Mg and Mn. Furthermore Fe° was observed visually and quantified. These phases are typical of BOF slag (Chaurand et al., 2007).

The nature and composition of these phases was further examined by SEM images and EMP mapping. Calcium silicates were found to present two distinct P contents (figure 1): i) large and porous euhedral laths (grains 1) are poorer in phosphorus than ii) smaller and denser anhedral ovoid grains (grains 2) contained in the matrix of the slag. Investigation by reflexion microscopy following specific acid attack, of these two types of grains, reveals the presence of two generations of dicalcium silicates: high P-bearing Ca_2SiO_4 (more probably β than α or α') grains formed from residual liquid after the crystallisation of the instable Ca_3SiO_5 laths and the mixture ($\text{Ca}_2\text{SiO}_4 + \text{CaO}$), with lower P content originating from the decomposition of Ca_3SiO_5 with decreasing temperature (figure 2).

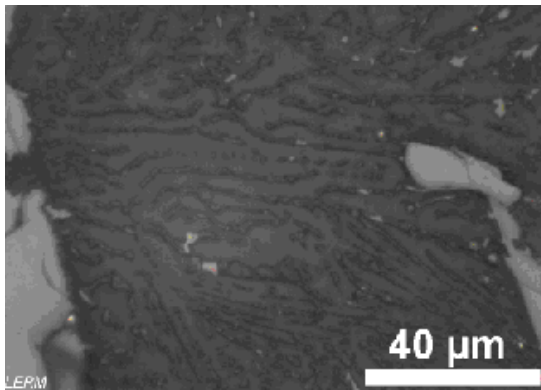


Figure 2 – Decomposition of Ca_3SiO_5 into Ca_2SiO_4 and CaO - Light microscope image after acid attack (see grain1 figure 1)

Detailed treatment of around 250 quantitative electron microprobe analyses of the sample yields the compositions of these two calcium silicates (table 2) with two distinct phosphorus contents (8.1 and 3.0 % P_2O_5 , respectively 3.5 and 1.3 % P). This variation is clearly related to the origin of the calcium silicates. The capacity to incorporate P in their structure appears to be smaller in Ca_3SiO_5 compared to Ca_2SiO_4 as already discussed by several authors (Diouri et al., 1997 and references)

Table 2 – Electron microprobe analyses of two types of calcium silicates in BOF slag (LD7)

	Al_2O_3	CaO	FeO	MgO	MnO	P_2O_5	SiO_2	TiO_2	Total
Ca_2SiO_4 - 117 analyses									
Average	0.8	60.5	1.8	0.5	0.2	8.0	25.2	0.6	97.7
Standard deviation	0.21	2.13	0.87	0.26	0.16	0.59	1.12	0.21	2.32
Theoretical Ca_2SiO_4		65.1					34.9		100
Decomposed Ca_3SiO_5 ($\text{Ca}_2\text{SiO}_4 + \text{CaO}$) - 145 analyses									
Average	0.9	60.9	5.3	1.1	1.4	2.9	23.3	0.2	96.1
Standard deviation	0.30	8.87	8.25	1.82	1.46	0.63	3.62	0.10	4.21

Laboratory samples with distinct extreme cooling histories have also been analysed by microscopy. Again calcium silicates present two distinct P contents - even if analytical distinction was not possible in the case of rapid cooling due to the small size of crystallites. Decomposed Ca_3SiO_5 predominates over Ca_2SiO_4 in industrial cooling. On

the contrary slow cooling -closer to equilibrium conditions- favours primary Ca_2SiO_4 formation that incorporates larger amounts of P in its structure. Phosphorus content is thus ‘diluted’ in a higher proportion of grains, which explains the decreasing values from 8 % to 5.3 % with slower cooling (table 3).

Table 3 – P content in calcium silicates in BOF slag; various cooling conditions

% P_2O_5	Rapid cooling	‘Industrial’ cooling (quantity)	Slow cooling (quantity)
Ca_2SiO_4 (P+)	4.5	8.0 (+)	5.3 (++)
Decomposed Ca_3SiO_5 (P-)		2.9 (++)	2.4 (+)

Prospects

Crystallographic data on phosphorus speciation using spectroscopic methods (IRTF, Raman, NMR, XAS) are underway. Namely the study of the speciation of P using P K-edge micro-XAS will help determine whether P is incorporated in the calcium silicate structure or associated to small calcium phosphate domains incorporated in larger minerals.

The substitution of Si(IV) by P(V) in calcium silicates is relatively unknown in BOF slag. Our study should thus provide new results concerning the stability of the mineral structure in terms of solubility and reactivity variations.

In terms of applications, the recycling of basic oxygen furnace slag is a current challenge to alleviate the pressures on natural resources, to reduce landfilling and to cut down the greenhouse effect emissions of the steel industry. At present BOF slag, with an annual tonnage around 1.2 million tons in France, is poorly recycled; its use is limited both in road construction due to its free lime content, and internally in the steel mill due to its phosphorus content. Improving BOF slag recycling in these two areas requires a better understanding of the free lime formation during cooling (Gautier et al, this conference) and of the phosphorous speciation.

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