Phosphorus speciation in dicalcium silicate polymorphs of basic oxygen furnace (BOF) slag - Preliminary results
Françoise Bodénan, Mathieu Gautier, N. Rafai, Jacques Poirier, Patrice Piantone, G. Franceschini, I. Moulin, Perrine Chaurand, Jérôme Rose

To cite this version:
Françoise Bodénan, Mathieu Gautier, N. Rafai, Jacques Poirier, Patrice Piantone, et al.. Phosphorus speciation in dicalcium silicate polymorphs of basic oxygen furnace (BOF) slag - Preliminary results. Environnement, Ingénierie & Développement, 2010, N°57 - Janvier-Février-Mars 2010, pp.13. 10.4267/dechets-sciences-techniques.3142 . hal-00541539

HAL Id: hal-00541539
https://brgm.hal.science/hal-00541539v1
Submitted on 4 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution 4.0 International License
**Phosphorus speciation in dicalcium silicate polymorphs of basic oxygen furnace (BOF) slag – Preliminary results**

F. Bodénan, M. Gautier, N. Rafai, J. Poirier, P. Piantone, G. Franceschini, I. Moulin, P. Chaurand, J. Rose

* Corresponding author
1. BRGM (French Geological Survey), 3 Avenue Claude Guillemin, BP 36009, 45060 Orléans cedex 2, France
2. Université d’Orléans, 45067 Orléans cedex, France
3. CEMHITI CNRS UPR3079, Site Haute Température, 1D avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France
4. LERM, 23 rue de la Madeleine, BP 60136, 13631 Arles Cedex, France
5. ArcelorMittal Maizières, Research and Development, BP 30320, 57283 Maizières-lès-Metz Cedex, France
6. CEREGE, CNRS UMR 6635, Europole de l'Arbois, BP80, 13545 Aix-en-Provence cedex 5, France

**Keywords:** calcium silicates, phosphorus, mineralogy, speciation, BOF slag

**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 [SiO$_4$]$^{2-}$ and [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 nagelschmidtite mineral group [Ca$_2$(Si$_{2-4}$P$_2$)O$_8$ type solid solution]. P(V) can also be incorporated in dicalcium silicate Ca$_2$SiO$_4$ polymorphs (C$_2$S) and Ca$_3$SiO$_5$ (C$_3$S) 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 Kα1 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

|        | Al₂O₃ | CaO | Fe₂O₃ | K₂O | MgO | MnO | Na₂O | P₂O₅ | SiO₂ | TiO₂ | 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 \( \text{Ca}_2\text{SiO}_4 \)), calcium alumino-ferrite (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 \( \text{Ca}_2\text{SiO}_4 \) (more probably \( \beta \) than \( \alpha \) or \( \alpha' \)) grains formed from residual liquid after the crystallisation of the instable \( \text{Ca}_3\text{SiO}_5 \) laths and the mixture (\( \text{Ca}_2\text{SiO}_4 + \text{CaO} \)), with lower P content originating from the decomposition of \( \text{Ca}_3\text{SiO}_5 \) with decreasing temperature (figure 2).

![Figure 2 – Decomposition of \( \text{Ca}_3\text{SiO}_5 \) into \( \text{Ca}_2\text{SiO}_4 \) and \( \text{CaO} \) - Light microscope image after acid attack (see grain 1 figure 1)](image)

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\(_2\)O\(_5\), 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 \( \text{Ca}_3\text{SiO}_5 \) compared to \( \text{Ca}_2\text{SiO}_4 \) 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) |
|---|---|---|---|---|---|---|---|---|
|     | \( \text{Al}_2\text{O}_3 \) | \( \text{CaO} \) | \( \text{FeO} \) | \( \text{MgO} \) | \( \text{MnO} \) | \( \text{P}_2\text{O}_5 \) | \( \text{SiO}_2 \) | \( \text{TiO}_2 \) |
| **Ca}_2\text{SiO}_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 \( \text{Ca}_2\text{SiO}_4 \) | 65.1 | 34.9 | 100 |
| **Decomposed Ca}_3\text{SiO}_5** (\( \text{Ca}_2\text{SiO}_4 + \text{CaO} \)) - 145 analyses | Average | 0.9 | 60.9 | 5.3 | 1.1 | 1.4 | 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 cristallites. Decomposed \( \text{Ca}_3\text{SiO}_5 \) predominates over \( \text{Ca}_2\text{SiO}_4 \) in industrial cooling. On
the contrary slow cooling -closer to equilibrium conditions- favours primary Ca$_2$SiO$_4$ 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).

| % P$_2$O$_5$ | Rapid cooling | ‘Industrial’ cooling (quantity) | Slow cooling (quantity) |
|-------------|--------------|---------------------------------|------------------------|
| Ca$_2$SiO$_4$ (P+) | 4.5 | 8.0 (+) | 5.3 (++) |
| Decomposed Ca$_3$SiO$_5$ (P-) | 2.9 (++) | 2.4 (+) | 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.

**References**

Chaurand P., Rose J., Domas J., Briois V., Olivi L. Bottero J-Y. (2007)’ Environmental impacts of steel slag reused in road construction: a crystallographic approach’, Journal of Hazardous Materials, B139, 537–542

Diouri A., Boukhari A., Aride J., Puertas F., Vazquez T. (1997) Stable Ca3SiO5 solid solution containing manganese and phosphorus. Cement and concrete, 27, 1203-1212

Gautier M., Poirier J., Franceschini G. (2009) - Influence of the cooling conditions on the nature and the size of the mineral phase in a BOF slag. WASCON Proceedings, Lyon, June 2009.

**Acknowledgements**

The authors gratefully acknowledge the financial support of ANR (French Research Agency) under the ORLA project (2008-2010). M. Gamet, M. Beaulieu and M. Menad are thanked for the difficult task of preparing the representative samples. Analyses were performed in BRGM laboratories namely with G. Wille and V. Jean-Prost and in LERM laboratories at Arles.