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# Review: Hot stage engineering to improve slag valorisation options

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## Abstract

*A number of studies are briefly reviewed dealing with hot stage processing of slags, i.e. additions during the molten state and variations of the cooling path, and the influence on the microstructure and properties of solidified slags. Emphasis is placed on research and developments in the last five years, although other works that created the thinking framework for several of the current practices are also mentioned. The additions include: a) quartz sand with concurrent oxygen injection for the minimisation of free CaO and MgO, b) various materials for the modification of the composition of liquid blast furnace slag after tapping, c) borates and boron wastes and their distribution in both synthetic and industrial stainless steel slags, d) phosphates in stainless steel slags and their distribution in BOF slags e) waste glass and fly ash for the stabilisation of stainless steel slags, f)  $K_2CO_3$  for the production of potassium silicate fertiliser from steelmaking slag and g) bauxite,  $Al_2O_3$  containing residues and aluminium metal that enhance the Cr recovery and minimise leaching in EAF slags. In terms of cooling, the effect of cooling rate on the final mineralogy, as a way to stabilise stainless steel slags and to control free lime formation in BOF slags, is presented. A more in-depth discussion regarding leaching performance, which has been identified as a key issue in slag valorisation, is also taking place. Although it is acknowledged that many research questions are still open and that both technical and economical barriers exist, it is strongly believed that a conscious hot stage processing step can both increase slag utilisation rates and make higher value applications achievable.*

## Introduction

The iron and steelmaking industry is a major producer of slag, contributing by about 390 million tonnes in 2009.<sup>1</sup> About two thirds of this slag originates from blast furnace processes, while the remaining third comes from steelmaking operations. Considerably less slag is formed during speciality steel and ferrous alloy production. However, the amount of stainless steel slag, for example, still added up to 8.2 million tonnes in 2009.<sup>2,3</sup> In the same year, the copper industry was responsible for approximately 35 million tonnes of slag,<sup>4,5</sup> making it the main non-ferrous slag producer.

In (stainless) steel production, conventionally, the molten slag is disposed with minimal considerations regarding energy recuperation or quality of the cold product. However, this is not the case for blast furnace slags, where granulation has enabled the delivery of a higher added value product that finds application as supplementary cementitious material. It is therefore suggested that there is a considerable potential to influence the functional properties of the cold slag without making compromises towards metal or process quality. This can be done by hot-stage engineering that reflects changes occurring in a liquid state in order to steer the properties of the cold, solidified product, to a desirable direction.

In more detail, hot-stage engineering can involve: a) additions during the molten state of the slag for reduction and separation of a metallic phase or stabilisation of minerals (and complementary additions to secure the dissolution of the materials added); this can be done before, during or after tapping and b) selection of appropriate cooling paths to deliver the desirable product. Energy recuperation during cooling is also a topic of great interest. The drive behind hot-stage engineering is the need for slag products that comply with environmental legislation and possibly, receive higher value in the market. In the majority of the plants nowadays, after the hot (stainless) steel slag is separated from the metal, it is typically cooled slowly to ambient temperatures in the slag yards. Minimal additions take place and granulation is not widely practised although there are indications it is receiving more consideration,<sup>6</sup> possibly also combined with energy recuperation (see also contribution by Guangqiang Li and Hongwei Li in this Symposium Book).<sup>7,8</sup>

This work aims to present laboratory experiments and industrial trials/practices, relevant to hot stage processing that induce better slag properties. As leaching performance has been identified as a key issue in slag valorisation, a more in-depth discussion is presented. This work is building upon a review paper recently published by Durinck *et al.*<sup>9</sup> and aims to establish a tradition linked with the Slag Valorisation Symposia.

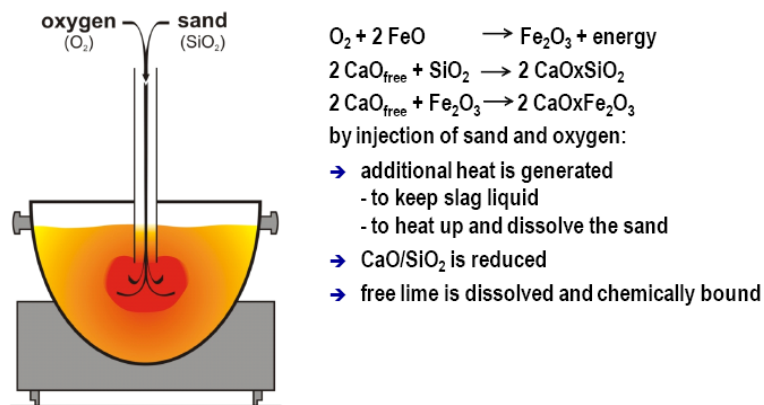
## Additions during the molten state of slag

### Effect on stability due to free CaO or MgO

The presence of free CaO or MgO in the slag leads to a longer term volume instability due to the expansive hydration to  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . However, a process has been devised and implemented to address this.<sup>10-12</sup> The principle of this process lies in the introduction of additives in order for free CaO and MgO to react towards a stable matrix of calcium silicates and ferrites. This can be achieved by the addition of  $\text{SiO}_2$ -containing materials, such as quartz sand, glass cullet and spent foundry sands. The treatment with quartz sand offers the advantage of higher  $\text{SiO}_2$  content per mass of additives and is not introducing other components that can cause side reactions. In Figure 1 a schematic drawing of the process is presented (see also contribution by Mudersbach *et al.* in this Symposium Book). The quartz sand is injected pneumatically into the slag pot. The sand is transported by  $\text{N}_2$ . The necessary oxygen is added in the cone of the dispenser. Oxygen is required for the treatment process in order to supply additional heat by means of FeO oxidation, dissolve the added sand, and keep the slag liquid. The process is currently operational at ThyssenKrupp Duisburg and ArcelorMittal Gent.

### Chemistry of blast furnace slag

It is known that granulated blast furnace slag has latent hydraulic properties and is used as supplementary cementitious material and as addition in concrete. Experiences in recent past however indicate a drop-down of both, slag basicity ( $\text{CaO}/\text{SiO}_2$ ) and  $\text{Al}_2\text{O}_3$ -content, in blast furnace slag.<sup>13</sup> This change has as a result lower compressive strength of mortar or concrete and an influence on the early stage of strength development. A thorough presentation on the way FEhS-Institute



**Figure 1:** Kühn *et al.*<sup>11</sup> developed a process for dissolving a large quantity of  $\text{SiO}_2$  (~10 wt%) in carbon steelmaking slags. By co-injecting oxygen, the slag is stirred and FeO in the slag is oxidised to  $\text{Fe}_2\text{O}_3$ , generating the required heat to dissolve the  $\text{SiO}_2$ . Adapted from Ref.<sup>13</sup>

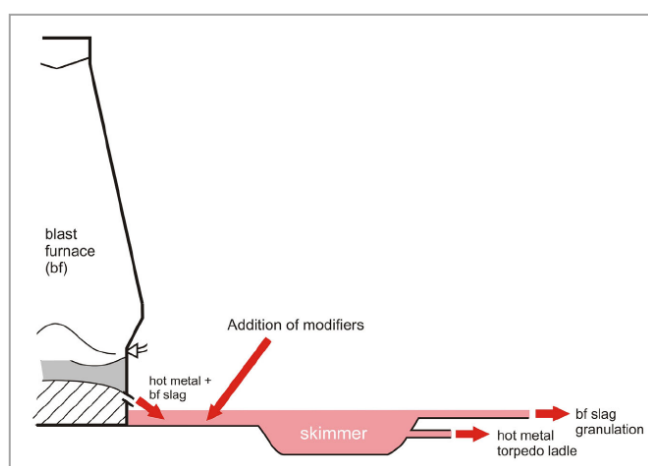
attempted to tackle this challenge was given by P. Drissen and D. Mudersbach;<sup>13</sup> a summary is presented herein.

As described, the envisaged solution involved modification of the composition of the liquid blast furnace slag after tapping, prior to granulation.<sup>14</sup> Tests were done with lime, calcium carbide, synthetic fluxes of lime and aluminium oxide, BOF-slag and slag from secondary metallurgy. During operational trials the injection of modifiers has been tested in the main runner (slag and hot metal), in the skimmer and in the slag runner (slag only). A schematic drawing of the process is shown in Figure 2.

Addition into the slag runner was not successful because the heat capacity of the slag limited the amount of modifiers. Experiments with exothermic modifiers, like calcium carbide, were stopped for safety reasons. Trials on the pneumatic injection in the skimmer had to be stopped because too much hot metal was spilled over to the slag runner and might have caused trouble in granulation. The addition of lime by pneumatic injection into the main runner was successfully tested. The lime was totally dissolved in the slag and the slag ratio was increased from 1.1 to 1.4. This increase was the reason for roughly 25% gain in compressive strength of mortar prisms. Unfortunately the injection process had to be operated batch wise. Continuous operation throughout the entire tapping time was not possible due to the limited capacity of the available bunker system and the required injection rates of up to 100 kg lime per minute.

### Effect on stability due to beta to gamma transformation of dicalcium silicate

The option of inhibiting the  $\beta$  to  $\gamma$  transformation of  $C_2S$  was first elaborated in 1986 by Seki and co-workers,<sup>15</sup> who developed a borate based stabiliser for stainless steel decarburisation slag. Typical boron minerals are kernite ( $Na_2B_4O_6(OH)_2 \cdot 3H_2O$ ),



**Figure 2:** Modification of blast furnace slag composition, schematic drawing. Adapted from Ref.<sup>13</sup>

colemanite ( $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$ ) and borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) whereas lately, boron-containing glazing powders<sup>16</sup> with promising results were also used.

In terms of boron distribution in the slag, D. Durinck *et al.*<sup>17</sup> performed experiments on a 52% CaO – 39% SiO<sub>2</sub> – 9% MgO synthetic stainless steel slag. Sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) was added to the slag, and after heating at 1640°C, slow cooling and quenching experiments were performed. The overall borate level in the synthetic slags of this study varies from 0 to 1.83 wt% B<sub>2</sub>O<sub>3</sub>. Six phases were identified and analysed using EPMA-WDS for their borate content: C<sub>2</sub>S (C = CaO, S = SiO<sub>2</sub>), bredigite (C<sub>7</sub>MS<sub>4</sub>, M = MgO), merwinite (C<sub>3</sub>MS<sub>2</sub>), akermanite (C<sub>2</sub>MS<sub>2</sub>), pseudo-wollastonite and a C<sub>x</sub>S<sub>y</sub>B<sub>z</sub> phase. Results show that B<sub>2</sub>O<sub>3</sub> is found in solid solution with C<sub>2</sub>S. This is the boron which is responsible for the stabilisation of β-C<sub>2</sub>S. The substitution occurs as  $(\text{Ca})_{2-0.5x}(\text{SiO}_4)_{1-x}(\text{BO}_3)_x$ .<sup>18</sup> Dissolved B<sub>2</sub>O<sub>3</sub> is also found in the other phases, such as bredigite and pseudo-wollastonite. The highest concentration, however, is found in a C<sub>x</sub>S<sub>y</sub>B<sub>z</sub> phase. This phase is a ternary compound between CaO, SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> with composition: 18-23 at% Ca, 3-4 at% Si, 15-19 at% B and 55-60 at% O. The authors conclude that the only way to significantly increase the borate level in C<sub>2</sub>S is to add more borates. Changing the slag composition has little effect. Moreover, it is suggested that slag stabilisation with borates not only depends on the chemical stabilisation but also on the cooling rate and the matrix constraint. The latter is believed to be influenced by the amount of C<sub>2</sub>S in the slag and, therefore, the slag composition. A low basicity slag contains a low amount of C<sub>2</sub>S grains, which are better constrained by the surrounding phases.

In industry however, the borates are added to a molten slag and the time scale is much shorter than laboratory scale experiments like above, where the thermodynamic equilibrium was of interest. Consequently, diffusion of the B<sub>2</sub>O<sub>3</sub> into the existing C<sub>2</sub>S is required for the formation of a solid solution. Results reported elsewhere<sup>19</sup> indicate that the borate level in the C<sub>2</sub>S phase of a quenched slag is similar to that in the C<sub>2</sub>S phase of the slowly cooled industrial samples. This corroborates that at high temperatures the diffusion of boron in the C<sub>2</sub>S phase present in the slag does indeed occur.<sup>19</sup>

To validate the experimental borate distribution for a typical industrial practice, the borate distribution in treated industrial stainless steel AOD slag was also determined for two distinct melt shops. In both cases Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> was added to the slag by injection in the slag stream during slag/steel separation. The results were recently reported elsewhere.<sup>20</sup>

In Meltshop 1<sup>19,20</sup> one boron stabilised slag sample was studied in detail. The addition amounted to about 1.5 wt% of the slag weight as B<sub>2</sub>O<sub>3</sub>. The phase

constitution of the industrial slag includes  $C_2S$ , bredigite and merwinite. The boron rich phase  $C_xS_yB_z$  was once more detected. As fluorine is added to the slag to increase its fluidity, cuspidine ( $C_4S_2O_7F_2$ ) formed in the later stages of solidification instead of akermanite and pseudo-wollastonite. Furthermore, the inevitable presence of chromium oxide in the industrial slag leads to  $(Mg)[Cr,Al]_2O_4$  spinel formation. Despite these small differences in phase constitution, the (qualitative) boron distribution is not significantly different from that in the synthetic slags.  $C_2S$  and bredigite show small but clear boron peaks in WDS spectra. The net peak heights are just below those of the same phases in the synthetic sample. Merwinite contains a boron level close to the detection limit. Cuspidine holds some boron as well.

In Meltshop 2<sup>20</sup> five industrial samples (A-E) were studied to quantitatively analyse the boron distribution over the different phases. Boron was measured in each separate mineralogical phase of the different AOD slag yard samples with EPMA-WDS, Table 1, using a Cameca SX52 microprobe.

**Table 1:** Overview of  $B_2O_3$  concentration (in wt%) in the different phases of industrial AOD slag stabilised with boron (5 samples : A, B, C, D, E named)<sup>20</sup>

Phase	$B_2O_3$ , wt% A	$B_2O_3$ , wt% B	$B_2O_3$ , wt% C	$B_2O_3$ , wt% D	$B_2O_3$ , wt% E
Free MgO	0.57	0.43	0.37-0.73	0.37	0.57
$C_2S$	-	0-0.16	0.53-0.60	-	-
Bredigite	0.25-0.39	0.21	-	-	0-0.13
Merwinite	0 – 0.23	-	-	-	-
Cuspidine	1.40 – 1.66	-	-	0.1	0.72
Metal	0.68	0.49-0.52	0.52-0.84	0.52	0.67
$CaF_2$	-	0.55	0.48-0.90	-	-

Q-XRD based on Rietveld analysis was used to determine the amount of the different phases in the sample, Table 2. Metal particles (clearly determined with BSI) and the  $C_xS_yB_z$  phase were not detected by XRD. The overall ' $B_2O_3$ ' level in the oxidic slag phases (excluding both the metal particles and the  $C_xS_yB_z$ ) were determined by combining EPMA-WDS and Q-XRD data. The total B level in the slag was also determined by wet chemical analysis. Finally, results are compared to process data from 52 heats.

The same authors<sup>20</sup> also performed elemental mapping to determine the B distribution, by using a FEG-EPMA JXA-8530F of JEOL. Figure 3 shows the elemental mapping of boron (top right), silicon (bottom left) and iron (bottom right) for two industrial samples. In general, the matrix is poor in B. Distinct phases with high boron



and low silica content are present. The identified phases and the corresponding  $B_2O_3$  content are indicated in Table 3. The phase containing the highest amount of boron  $Ca_xS_yB_zMg_5O_t$  is not identified yet. The phase with the second highest boron content is most probably calcium silicate borate ( $Ca_{11}Si_4B_2O_{22}$ ).

**Table 2:** Q-XRD data (in wt%) for 5 different industrial AOD slags from Meltshop 2 (stabilised with boron) and distinct  $B_2O_3$  levels. b.d.l. = below detection limit for this Q-XRD setup<sup>20</sup>

Slag Phase	Slag A	Slag B	Slag C	Slag D	Slag E
Free MgO (in wt%)	4.6	11.1	12.1	2.2	1.1
Beta- $C_2S$ (in wt%)	b.d.l.	62.2	59.7	b.d.l.	b.d.l..
Bredigite (in wt%)	34.7	9.9	10.2	25.4	13.6
Merwinite (in wt%)	32.8	b.d.l.	b.d.l.	48.1	59.8
Cuspidine (in wt%)	27.9	16.8	18.0	24.3	25.5
$CaF_2$ (in wt%)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Overall ' $B_2O_3$ ' level in the oxidic phases excluding $C_xS_yB_z$ , based on EPMA	0.70	0.44	0.77	0.03	0.21
Overall ' $B_2O_3$ ' level in the slag, based on wet chemical analysis	2.25	0.75	0.46	0.65	1.57
Average theoretical ' $B_2O_3$ ' level assuming all added boron ends up in the slag ( <i>i.e.</i> 100% yield)	1.11 ± 0.32 (based on process data from 52 heats)				

**Table 3:** Phase identification and  $B_2O_3$  content of an industrial slag sample<sup>20</sup>

Number	Phase	Total $B_2O_3$ wt%	Sample	Phase	Total $B_2O_3$ wt%
1	Merwinite	0.37	6	Spinel	< 0.1
2	$Ca_{11}Si_4B_2O_{22}$	5.2	7	Cuspidine	1.83
3	$Ca_xS_yB_zMg_5O_t$	17.0	8	Cuspidine	1.45
4	MgO	0.35	9	$Ca_xTi_ySi_zMg_5O_t$	0.44
5	Merwinite	0.31			

Recently, the use of boron wastes originating from the dressing of boron ores was also studied.<sup>21</sup> Results demonstrated that 1 wt% addition resulted in the stabilisation of a synthetic slag with basicity ( $CaO/SiO_2$ ) = 2. More information is presented in this Symposium Book in a dedicated paper by Pontikes *et al.*

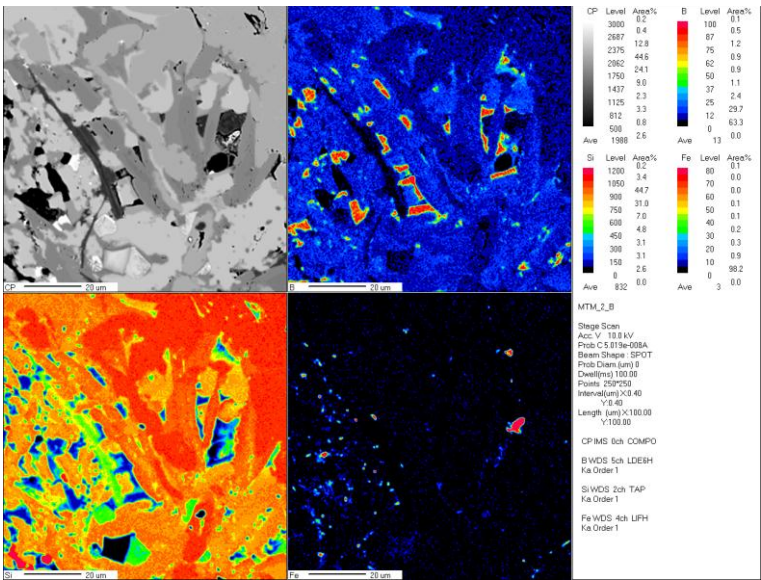
Borate additions are not the only possibility to avoid the expansive transformation of  $C_2S$  and the associated slag disintegration of the slag.<sup>22-25</sup> The crystallographic



coordination number, the ionic radius and the ionic valence of the doping ion all affect the deformation of the C<sub>2</sub>S crystal and, as a consequence, the stabilisation. Recently, a qualitative criterion based on ionic radius, ionic valence and crystallographic structure of the additive was developed,<sup>26</sup> which is capable of predicting whether or not a compound will stabilise the β-polymorph. In practice, different oxides have been reported to stabilise the different polymorphs of dicalcium silicate. The α and α′ polymorphs have been reported to be stabilised by oxides such as MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, BaO, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>O<sub>3</sub>. The β polymorph can be stabilised by the addition of Na<sub>2</sub>O, K<sub>2</sub>O, BaO, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> or their combinations.<sup>22</sup> The difference in the stabilising ability of each oxide provides a certain degree of flexibility if the goal is to avoid the formation of the γ phase.

Based on this knowledge, the effect of phosphate additions to disintegrating stainless steelmaking slags was investigated. Satisfactory stabilisation was obtained,<sup>27</sup> but compared to borate additions a significantly larger amount of phosphates (~ 2 wt%) was required to avoid disintegration. Working on a similar direction, Yang *et al.*<sup>28</sup> studied the effect of a feed grade mono-calcium phosphate (with 47.2 wt% P<sub>2</sub>O<sub>5</sub>) and a by-product from iron ore processing (with 9.0 wt% P<sub>2</sub>O<sub>5</sub>). The formation of γ-C<sub>2</sub>S (and slag disintegration) was prevented for a P addition in the slag higher than 0.3 wt%; only β- and α′-C<sub>2</sub>S were detected.

Even if the mechanism of P stabilisation has not been studied – to the best of our knowledge – on stainless steel slags, some light is shed by a recent work on BOF slags. In this work,<sup>29</sup> the authors study the P speciation in BOF slags, rich in dicalcium silicates and with a phosphorus content that could jeopardise internal recycling

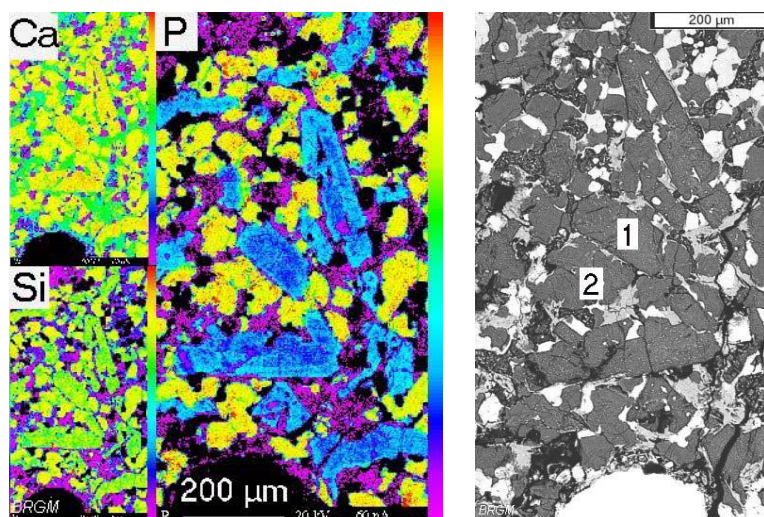


**Figure 3:** Elemental mapping for B, Si and Fe of an industrial slag sample, performed with a FEG-EPMA. Adapted from Ref.<sup>20</sup>

within the steel mill. One industrial sample and two prepared in laboratory conditions (described and studied elsewhere<sup>30</sup>), at different cooling rates, were studied. As indicated, BOF slag recycling in France is limited both in road construction, due to its free lime content, and internally in the steel mill, due to its phosphorus content. Consequently, there is a clear merit in more fundamental studies in order to understand/control both P speciation and free lime formation.

The results indicate that the main phases in the BOF slag are dicalcium silicate (theoretical composition  $\text{Ca}_2\text{SiO}_4$ ), calcium aluminoferrite (theoretical composition  $\text{Ca}_2\text{FeAlO}_5$ ), free lime ( $\text{CaO}$ ) and wustite ( $\text{FeO}$ ), with Fe substituted by Mg and Mn, as well as metallic Fe. Further analysis, performed by means of SEM and EMP mapping, revealed that calcium silicates were found to present two distinct P contents, Figure 4: i) large and porous euhedral laths (grains 1) 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  $\text{Ca}_3\text{SiO}_5$  during cooling.

Results based on around 250 quantitative electron microprobe analyses, yields that the phosphorus contents of these two distinct calcium silicates are 8.1 and 3.0 wt%  $\text{P}_2\text{O}_5$ , respectively. 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  $\text{Ca}_2\text{SiO}_4$ . Laboratory samples with distinct extreme cooling histories have also been analysed by microscopy. Again calcium silicates present two



**Figure 4:** Ca, Si, P mapping (microprobe) and corresponding BSE image (SEM) - Ca silicates with low and high P content (grain 1 and 2 respectively). Adapted from Ref.<sup>29</sup>

distinct P contents. 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  $\text{Ca}_2\text{SiO}_4$  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 4.

**Table 4:** P content in calcium silicates in BOF slag; various cooling conditions<sup>29</sup>

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

Alternatively, slag disintegration can be averted by modifying the slag composition in order to avoid the presence of  $\text{C}_2\text{S}$ . Already in 1942, compositional limits were defined for disintegrating slags,<sup>31</sup> based on the stability field of  $\text{C}_2\text{S}$  in the  $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$  system, with an adjustment for the sulphur content (S) in the slag. However, in many cases, slags that meet these conditions do not have the appropriate high temperature metallurgical functionality. In stainless steelmaking,  $\text{C}_2\text{S}$  free, low basicity slags cause rapid refractory degradation and low chromium yields.<sup>32</sup> To avoid making such compromises towards process and metal quality, the slag composition must be adjusted after slag/metal separation. Adding a relatively large amount of silica seems to be the best way to avoid  $\text{C}_2\text{S}$ . This was proven on a laboratory scale by Sakamoto,<sup>33</sup> who stabilised a stainless steel decarburisation slag with 12 wt% of waste glass, containing 70-75 wt%  $\text{SiO}_2$ . The same authors also demonstrated the potential of this method in trials with waste glass in the slag pot. A similar approach by adding quartz sand was investigated by Yang *et al.*<sup>28</sup> In this case, the formation of  $\gamma\text{-C}_2\text{S}$  (and slag disintegration) was prevented for a sand addition of 5.12 wt%, resulting to a basicity  $\text{CaO/SiO}_2 = 1.34$ . Depending on the amount required for stabilisation, an additional slag treatment process is potentially required for an effective dissolution. The principle of this step can be similar to the method developed by Kühn *et al.*<sup>10,11</sup>, Figure 1.

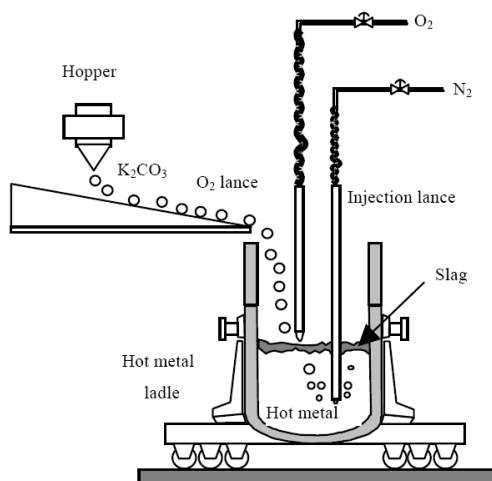
An alternative option, as described by Kitamura *et al.*<sup>34</sup>, is to mix stainless steel slag with cold or preheated non-ferrous fayalite slag. In this way, the basicity of the slag can be substantially reduced, avoiding the formation of  $\text{C}_2\text{S}$ . The  $\text{FeO}$  from the non-ferrous slag is used as an additional energy source (exothermic reaction to  $\text{Fe}_2\text{O}_3$  results in additional heat to dissolve the  $\text{SiO}_2$ ). However, this method has only been shown to work on a lab-scale level. Heat balance calculations<sup>34</sup> have shown that a mixing ratio of maximum 15% (non-ferrous slag to stainless steel slag) can be

achieved. However, this would be insufficient to reduce the C/S ratio to a low enough level. The scale up of this process to the industrial level is probably going to necessitate additional measures.

In a similar direction, fly ash originating from lignite's combustion was investigated for the stabilisation of a synthetic slag with basicity  $(\text{CaO}/\text{SiO}_2) = 2$ . Results indicate that 22 wt% is sufficient. More information is presented in this conference in a dedicated paper by Pontikes *et al.*

In Japan, a new steelmaking process developed by NKK and referred as ZSP (Zero Slag Process)<sup>35,36</sup> claims to lower the amount of generated slag and also stabilises the composition of slag generated through hot metal pre-treatment. The production of a potassium silicate fertiliser is an interesting example. The newly developed fertiliser is difficult to dissolve in water, and slowly dissolves in the weak citric acid released by plant roots. The process is presented in Figure 5. At the desiliconisation station in the hot metal pre-treatment process, hot metal is first subjected to desiliconisation treatment and then, potassium carbonate ( $\text{K}_2\text{CO}_3$ ) is continuously added into the hot metal ladle from the hopper above the ladle while agitating the hot metal using nitrogen gas. Uniformly melted slag is recovered from the hot metal ladle, solidified by cooling, and crushed into a granular form.

The effectiveness as a fertiliser was investigated by the "Japan Fertiliser and Feed Inspection Association". NKK's fertiliser demonstrated an effectiveness equal to other commercial potassium silicate fertilisers and combined potassium chloride-calcium silicate fertilisers.<sup>37</sup> In January 2000, as a result of these tests verifying the effectiveness of a potassium silicate fertiliser made from steelmaking slag, the



**Figure 5:** Production of potassium silicate fertiliser from steelmaking slag. Adapted from Ref.<sup>36</sup>

Ministry of Agriculture, Forestry and Fisheries of Japan issued a new official fertiliser standard “Fused potassium silicate fertiliser” in its Notice No. 91 based on the Fertiliser Control Law. NKK registered its fertiliser as “Mn-containing 20.0 fused potassium silicate fertiliser” with the Ministry in April 2000 and started marketing it in December 2001.

In another work, Mudersbach *et al.*<sup>38</sup> suggest the additions of bauxite,  $\text{Al}_2\text{O}_3$  containing residues and aluminium metal as a method to increase the stability of stainless steel EAF slags and to stabilise chrome. The aim of the additions is to decrease the basicity of the slags and favour the formation of spinel type phases during solidification. In that event, even if the slag contains high chrome contents, the leaching of chrome can be suppressed. Mudersbach *et al.*<sup>38</sup> also developed the so-called “factor sp” to empirically describe the expected chromium content based on the slag composition:

$$\text{factor sp} = a * \text{MgO} + b * \text{Al}_2\text{O}_3 + c * \text{FeO}_n - x * \text{Cr}_2\text{O}_3 \text{ [wt.\%]} \quad (1)$$

Their work shows that there is a correlation between the spinel factor and the actually measured chromium leaching levels (which seem to confirm that spinel behaves, in practice, as a stable phase with respect to chromium leaching). More specifically, the authors propose three types of additions which should mitigate any chromium leaching problems from EAF slags:

- Additions of bauxite (600 kg/transfer ladle), increasing the “factor sp” to 15 wt.%;
- Additions of  $\text{Al}_2\text{O}_3$  containing residues (so-called TE 75, a product containing 75-85 wt.%  $\text{Al}_2\text{O}_3$ );
- Additions of aluminium metal which not only improve the chromium recovery but also enhance the “factor sp”.

In a work also related to Al additions, G. Stubbe *et al.*<sup>39</sup> recently reported in a detailed paper their results on aluminium injection to EAF slags. This work has been a co-operation between *VDEh-Betriebsforschungsinstitut* (BFI) and *BGH Edelstahl Siegen* (BGH), Germany. After the successful operational trials, Al injection is industrially applied at the BGH stainless steel plant.

The operational trials have been performed at *BGH Edelstahl Siegen GmbH* in a 40 tonne EBT-EAF furnace. The furnace is equipped with several side wall injectors/burners used for solid material injection (*e.g.* lime and carbon). Preceding the date of the trials, the normal operational included the addition of ferrosilicon (FeSi) for chromium recovery from the slag. For the operational Al injection trials, an

injection device, composed of a rotor injection machine and two dosing units for big-bag charging, was employed. The Al source was mechanically processed Al granules with a maximum grain size of 2 mm. The aluminium was injected via one side wall injector/burner located near the furnace door. The target amount of the injected aluminium was 15 kg Al per tonne of liquid steel. In order to be able to inject the whole amount of aluminium within 10 minutes during the flat bath period at the end of the melting time, the injection rate of the aluminium was adjusted to approximately 60 kg/min.

By injection of the aluminium granules into the EAF slag, the average chromium oxide mass fraction in the final slag was 3.4% for ferritic steels and 1.6% for austenitic steels. In comparison to normal operation, the chromium recovery yield was 67% for ferritic steels and 87% for austenitic steels. Electric energy savings were 9% for ferritic and 6% for austenitic steels. This is attributed to the additional chemical energy input. In both cases, the energy output via slag and cooling water increases significantly.

The authors conclude by reporting that *BGH Edelstahl Siegen* has implemented the aluminium injection into the EAF as new standard operational practice for stainless steel production since mid 2009. For aluminium injection, a new solid material injector has been installed, which is able to inject aluminium or lime alternatively into the EAF slag at an injection rate of maximum 100 kg/min. For a more efficient penetration of the aluminium (or lime alternatively) into the slag, the material is conveyed to the melt supported by a concentric coherent oxygen jet. Due to this supported injection directly into the slag, the solid material losses to the exhaust system are minimal and subsequently an improved material yield is achieved.

The most important benefits of Al injection are summarised as follows: a) high Cr recovery in the steel and low total Cr level in the slag, opening the potential for higher added-value applications, b) electric energy consumption was decreased by 10% approximately and power-on-time by 17%, c) Cr bound most probably in spinel phases, lower leaching expected, d) final slag chemistry close to calcium aluminate cements, potential for production of such hydraulic binders in the plant, high price of calcium aluminate cements in the market. On the other hand, Al is also expensive, with a fluctuating price in the market, and the availability of such streams cannot be taken for granted. Mixed Al sources or lower purity streams could be also seen as options.

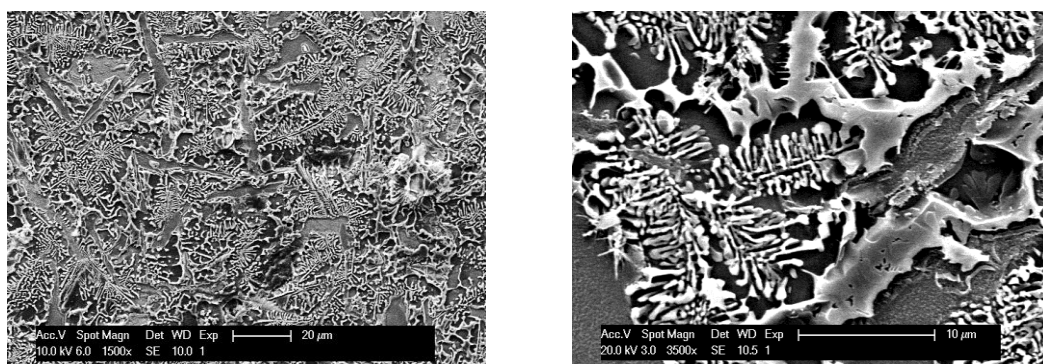
## Variations in cooling rate

### Effect on the stabilisation of tricalcium and dicalcium silicate

Fast cooling in order to prevent the transformation of tricalcium silicate to calcium oxide and dicalcium silicate, as well as, that of  $\beta$ -dicalcium silicate to  $\gamma$ -dicalcium silicate, is standard practice for the cement industry. Dedicated studies have also proved the interconnection between cooling rate, final mineralogy and hydraulic properties.<sup>40</sup> This stabilisation method was further developed by showing on a laboratory scale that a granulation process transforms a disintegrating slag into a slag product suitable for construction applications.<sup>41</sup> Similar results have been reported also elsewhere,<sup>28</sup> where it was demonstrated that air granulation was effective in preventing the formation of  $\gamma$ -C<sub>2</sub>S in a slag with basicity  $\text{CaO}/\text{SiO}_2 = 1.6$ .

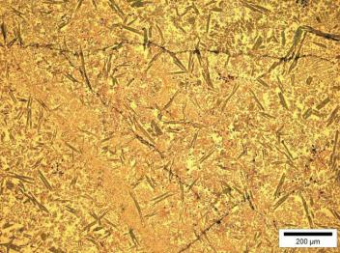
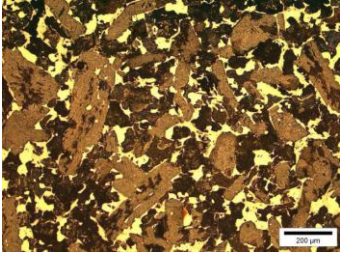
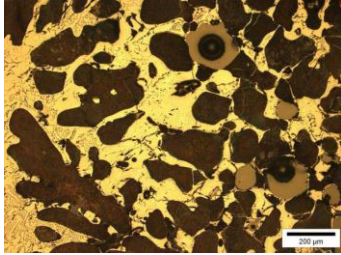
Recent results demonstrate that fast cooling, by means of dry granulation, is effective in suppressing the  $\beta$  to  $\gamma$  transformation of C<sub>2</sub>S, for basicity  $\text{CaO}/\text{SiO}_2$  as high as 2.2. An extensive network of dendritic merwinite is formed on a stabilised  $\beta$ -C<sub>2</sub>S, Figure 6. This work is in progress and results will be presented in the near future.<sup>42</sup>

The effect of cooling rate was also studied on BOF slags.<sup>30</sup> A sample with a representative composition of BOF slag was subjected to heating at 1600°C for 5 h, followed by rapid cooling by means of water quenching and slow cooling of 72 h approximately. The cooled sample was compared to a sample from the industrial site, cooled within 24-48 h, which represents an intermediate state. The results demonstrate that cooling conditions strongly affect the microstructure, both qualitatively and quantitatively, Figure 7. Compared to the industrial sample, slow cooling results to very low CaO and Ca<sub>3</sub>SiO<sub>5</sub>, higher Ca<sub>2</sub>SiO<sub>4</sub> and MgO, and formation of Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> instead of FeO. On the other hand, the water quenched slag is composed of mainly Ca<sub>3</sub>SiO<sub>5</sub> and Ca<sub>2</sub>SiO<sub>4</sub>, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, MgO and a small amount of CaO. In addition, the growth of the crystals is different in each cooling process, the silicates



**Figure 6:** SEM images on chemically etched synthetic slag samples of basicity  $\text{CaO}/\text{SiO}_2$ . The dendrites correspond to merwinite.



Rapid cooling	Industrial cooling	Slow cooling
		
Size of silicates : 3-10 $\mu\text{m}$ and 20-80 $\mu\text{m}$ length	Average size of silicates: 50- 150 $\mu\text{m}$	Average size of silicates: 180-250 $\mu\text{m}$

**Figure 7:** Optical microscopy images on the microstructure and comments on the size of the silicates for BOF slag cooled at different rates. Adapted from Ref.<sup>30</sup>

ranging from 20-80  $\mu\text{m}$  in water quenched slag to 180-250  $\mu\text{m}$  in the slow cooled slag. In practical terms, this work demonstrates that cooling rate affects the presence of  $\text{Ca}_3\text{SiO}_5$  and  $\text{Ca}_2\text{SiO}_4$ , which are the two major hydrating phases also in OPC, the amount of free CaO and MgO, where a low amount is a prerequisite both for aggregates and construction applications, as well as the crystal growth, which relates to grinding cost.

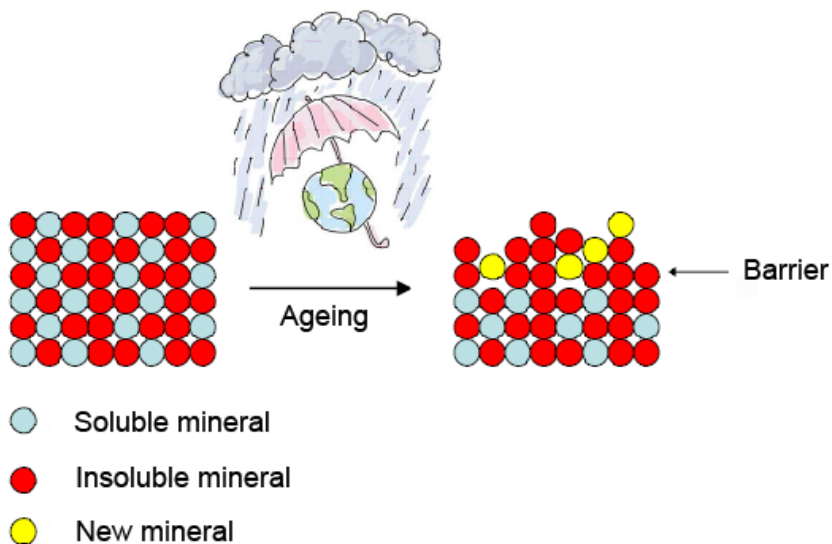
### Leaching

Leaching of potentially hazardous compounds during reuse is a key issue in slag valorisation. The leaching process from slags is generally characterised as a surface reaction, followed by a solid-solid diffusion process, in order to retain equilibrium in the materials.<sup>43</sup> It is therefore reasonable to believe that the rate of leaching decreases with time as the diffusion from the bulk of the solid slag to the surface is slow. Minimisation of the surface area and/or formation of a less reactive surface layer on the slag can therefore be assumed to decrease the leachability. One way of introducing such a layer is by letting the slag react with  $\text{CO}_2$  (g), forming calcium carbonates,  $\text{CaCO}_3$ . Research has shown that carbonation of alkaline solid material can lead to an improvement of their environmental qualities.<sup>44,45</sup> Another way of introducing such a layer is by incorporating insoluble minerals into the microstructure, which after some weathering will result in pacification of the slag surface, Figure 8.

However, when it comes to leaching the exact mechanisms, still remain unclear. The solubility of individual slag minerals as well as the distribution of metal elements in the microstructure is of greatest importance when it comes to be able to fully explain the leaching reaction occurring. Therefore, a lot of effort is being put into a mineralogical interpretation of leaching. On the one hand, high resolution techniques

are used to characterise the slag microstructure in detail, in order to identify all possible sources of release. Chaurand *et al.*<sup>46</sup> used X-ray absorption near-edge structure (XANES) spectroscopy to investigate where Cr and V leaching originates in steelmaking slags. Drissen<sup>47</sup> approached a similar problem using wave length dispersive spectroscopy (WDS). Equilibrium experiments performed on synthetic slag systems, have been conducted both at KTH (Royal Institute of Technology, Sweden) within the steel eco cycle (88035) as well as at the *Katholieke Universiteit Leuven*, Belgium.<sup>19</sup> The distribution of chromium in the microstructure has been the focus for these experiments. On the other hand, the modelling of leaching processes is receiving increasing attention. Thermodynamic and kinetic considerations have been shown to be able to describe the actual leaching behaviour quite well for similar materials, such as cementitious waste<sup>48</sup> and municipal solid waste incinerator fly ash.<sup>49</sup> However, since data regarding solubility of the individual slag minerals are often missing, there is still a lot of fundamental research that needs to be conducted. Regarding slag materials, the leaching behaviour of trace elements from historical Cu slags<sup>50</sup> and Cr ore processing slags<sup>51</sup> have been analysed extensively.

From a more pragmatic viewpoint, possible slag treatments to reduce leaching are being investigated. Tossavainen *et al.*<sup>52,53</sup> studied the influence of rapid cooling with water (water granulation), in order to investigate the effect on total leachability. The differences between the original cooled and granulated slag samples were low. Further investigation of the material showed that the reactivity at the surfaces increased as rapid cooling with water was preformed. The cause for this increase is believed to be correlated with the oxidation that occurs at the surface, the increased amount of grain boundaries and the presence of metastable phases on the surface.<sup>54</sup>



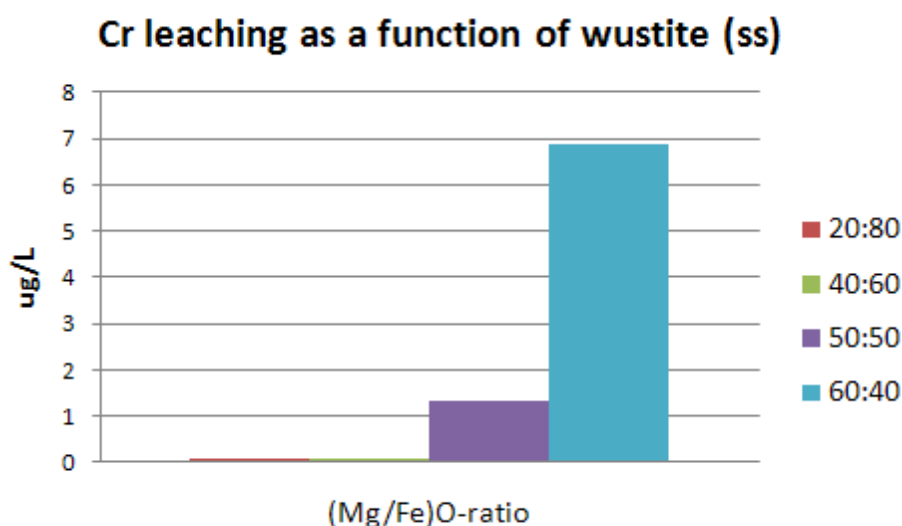
**Figure 8:** Schematic picture of non reactive surface layer

More recently, Mojca Lončnar *et al.*<sup>55</sup> studied the effect of the cooling rate on hot electric arc furnace (EAF) slag from stainless steel production on the leaching behaviour of the slag. EAF slags from four different grades of stainless steel were sampled and water or air cooled. Leaching tests were done according to the SIST EN 12457-4:2004 one-stage batch test. It was concluded that the cooling method has a significant effect on the leaching behaviour of slags. In EAF water cooled slag samples, a decrease of Ca, Al, Ba and Se concentrations in the leachate was observed. On the other hand, water cooling caused an increase in leaching concentrations of Si and Mg.

### **Case study: Cr leaching as a function of microstructure (EAFS)<sup>56</sup>**

As a case study, the leaching of chromium from low-basicity ( $B_2 = 1.4$ ) and high-basicity ( $B_2 = 2.5$ ) EAF slag can be used. In the low-basicity EAF slag the most common minerals found include merwinite, akermanite, gehlenite and solid solution spinel phases. At  $B_2 = 2.5$ , typical minerals found in the EAF slag is (alpha, beta, gamma) dicalcium silicate, wustite type solid solution, dicalcium ferrite and merwinite. For the low-basicity EAF slag, investigation has shown that chromium will be enriched in spinel-type solid solution and in the merwinite phase, while the chromium is primary crystallised in the wustite-type solid solution and secondary in spinel phases for the high-basicity EAF slag.<sup>19</sup> When it comes to the low-basicity EAF slag, studies have shown that the spinel phase is crystallised at high temperature and is considered as being insoluble.<sup>56</sup> However, the merwinite is considered as being soluble throughout the entire pH range, which will make chromium dissolve parallel to merwinite. Since merwinite is considered as a possible matrix mineral, enclosing other elements into its structure, it can be assumed that the leaching of chromium from these types of slags will continue as long as merwinite dissolves. For the high-basicity EAF slag the primary crystallisation of chromium occurs within the MgO solid solution.

In order to save refractory materials and create a foamy slag, these types of EAF slags are often saturated with MgO, meaning that solid particles of MgO will be present in the liquid slag. The crystallisation of chromium will start in these particles and continue until equilibrium conditions are reached, thereafter forming spinel. As the solubility of chromium in the magnesium based solid solution (MgO-ss) is influenced by the temperature, it is reasonable to assume that  $\text{MgCr}_2\text{O}_4$  will further nucleate as the temperature decreases, dissolving the MgO-ss. However, since this transformation is a solid-solid phase transformation, occurring at “low” temperatures, the kinetics of the transformation are believed to be slow. A pure magnesium oxide phase enriched in chromium is not a desired phase when it comes to chromium solubility. Numerous studies have shown that pure magnesium oxide will hydrate and expand but also dissolve. However, there is a solution to this



**Figure 9:** Chromium leaching as a function of (Mg:Fe)O composition

problem. Since these slags often have a high concentration of iron oxide it can be assumed that wustite will enter the MgO-ss as the temperature decreases (liquid-solid reaction) due to their complete solubility in each other. Investigations performed have shown that the composition of the wustite-type solid solution in slag will vary with the rate of cooling. A rapid cooling will result in an MgO-based wustite-type solid solution, while a slower cooling rate will promote the enrichment of iron oxide into the structure. Experiments conducted on the MgO-FeO + 4 wt% Cr<sub>2</sub>O<sub>3</sub> system have shown the importance of the iron oxide on the leaching behaviour of chromium from the wustite-type solid solution, Figure 9.<sup>56</sup> According to Figure 9, the leaching of chromium from the wustite-type solid solution decreases with an increasing amount of FeO. In terms of cooling, this means that a slower cooling rate is preferable when these types of phases are present. However, thermodynamic calculations performed on similar systems, have shown that the cooling should not be too slow. Below 1100°C, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> is recrystallised, meaning that wustite will leave the MgO-based wustite-type solid solution, once again forming the reactive MgO phase.

## Conclusions

A number of studies, dealing with hot stage processing and the influence on the microstructure, were reviewed. Although several aspects have not been investigated yet, the potentially beneficial effects on the valorisation potential have clearly been shown. These may include the delivery of final slags with increased volume stability, hydraulic properties and lower leaching potential. Emphasis was given to leaching in particular. It is demonstrated that despite extensive research efforts on the area, lots

of questions remain. As the leaching behaviour is still the primary cause for valorisation difficulties, additional research work is expected in the field. It is strongly believed that a conscious hot stage processing step can both increase slag utilisation rates and make higher value applications achievable.

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