MINIMISING THE LEACHING OF V AND Cr FROM ELECTRIC ARC FURNACE SLAGS BY DECREASING THE FeO/SiO₂ RATIO

Simone NEUHOLD¹, Daniel VOLLPRECHT¹, Peter PRESOLY², Burkart ADAMCZYK³, Peter DRISSEN⁴, André VAN ZOMEREN⁵, Susanne SCHÜLER⁶, Dirk MUDERSBACH⁶

¹ Montanuniversitaet Leoben, Chair of Waste Processing Technology and Waste Management, 8700 Leoben, Austria
² Montanuniversitaet Leoben, Chair of Ferrous Metallurgy, 8700 Leoben, Austria
³ Federal Institute for Materials Research and Testing, Division Thermochemical Residues Treatment and Resource Recovery, 12489 Berlin, Germany
⁴ FEhS Building Materials Institute, Department Secondary Raw Materials and Slag Metallurgy, 47229 Duisburg, Germany
⁵ ECN part of TNO, Bio-Energy, 1755 ZG Petten, The Netherlands
⁶ Max Aicher Umwelt GmbH, 86405 Meitingen, Germany

simone.neuhold@unileoben.ac.at, daniel.vollprecht@unileoben.ac.at, peter.presoly@unileoben.ac.at, burkart.adamczyk@bam.de, p.drissen@fehs.de, andre.vanzomeren@tno.nl, s.schueler@max-aicher.de, d.mudersbach@max-aicher.de

Introduction

It is known from literature that the leaching behaviour of heavy metals such as Cr and V from steel slags is influenced by the mineralogy.¹⁻⁶ However, the exact mechanisms are not yet understood for all slag types and all heavy metals. This is because various different mechanisms can influence the leaching behaviour; the stability of the primary mineral phases in which these elements are incorporated, secondary mineral phases, which form during leaching or weathering and/or adsorption onto these newly formed surfaces. The mineralogical composition itself is influenced by metallurgical parameters and the chemical composition.⁷,⁸

In this study, a multi-methodological approach with special emphasis on surface investigations was used to understand these complex interactions between metallurgy, mineralogy and leaching behaviour of electric arc furnace (EAF) slags. Additionally, experimental results were combined with hydrogeochemical and metallurgical models. Hence, it was possible to identify leaching controlling mechanisms for Cr and V and develop conditioning procedures to minimise the leaching of Cr and V from EAF slags. The conducted lab experiments and first results of the upscaling experiments in an EAF (pilot plant scale) are presented in this paper.
Materials and Methods

Based on previous experiments\(^9\) the EAF slag sample with the highest amount of leached V and Cr was chosen for the conditioning experiments with quartz sand. Additionally, pure remelting experiments of the slag were conducted as reference. All experiments were performed using a Tammann furnace and MgO crucibles, in which the slag respectively the slag-quartz-mixture was heated up to 1600°C. The amount of quartz sand needed to adjust the mineral phase distribution was calculated by using FactSage\textsuperscript{TM}. To avoid an oxidation of iron in the melt, the furnace was flushed with nitrogen and iron filings were put into the crucibles. Three different cooling rates: 1) rapid cooling on a steel plate, 2) moderate cooling in air and 3) slow cooling in the furnace were investigated, yielding in total six modified slag samples. The chemical composition of the investigated samples was determined after digestion (ÖNORM EN 13656) by using ICP-MS (ÖNORM EN ISO 17294-2). The pH dependent leaching tests were conducted according to EN 14429. The leachates were analysed analogously to the digested slag samples. Electron microprobe (EMP) analyses were performed with the Superprobe JEOL JXA 8200 system.

Results and discussion

Previous studies\(^9\) revealed that EAF slags with increased V and Cr leaching consist of the same main mineral phases as EAF slags with lower leached amounts, namely, a wuestite solid solution, a spinel solid solution, an olivine solid solution and a melilite group member. None of the phases dissolve after leaching for 48 h with distilled water (Figure 1) according to visual inspection via EMP.

![Figure 1: a) BSE image of the original EAF slag sample prior to leaching and b) SE image after leaching; Detail: wuestite (W), spinel (S), olivine (O) and melilite (M)](image)

The significant difference, which determines the leaching behaviour, is the ratio between wuestites and calcium silicates (olivine and/or melilite) as well as the
amount and size of spinels. A lower amount of wuestites and an additional increase in stable calcium silicates (e.g., melilite) and spinels decreases both the V and the Cr leaching. This is because V and Cr leach incongruently from wuestites but are stably bound in spinels.\textsuperscript{9} Additionally, geochemical modelling indicates that adsorption of V onto hydrated melilites impedes the release of V. The ratio of wuestites to calcium silicates itself is influenced by the FeO/SiO\textsubscript{2} ratio in the slags. Therefore, the optimum ratio, at which predominantly calcium silicates are formed and the formation of wuestites is suppressed, was calculated \textit{via} FactSage\textsuperscript{TM} prior to the melting experiments. Figure 2 shows the BSE images of the remelted and conditioned slag samples. As expected and calculated, a lower FeO/SiO\textsubscript{2} ratio led to a lower amount of wuestites and an increased formation of calcium silicates. Additionally, the remelting influenced the spinel formation, leading to more and bigger crystals compared to the original sample (Figure 1). Table 1 shows that the tailored change of the chemical composition and a corresponding change of the mineral phase distribution led to a decrease in V and Cr leaching.

![Figure 2](image-url)

**Figure 2**: BSE images of EAF slag samples cooled on air; a) remelted and b) conditioned; Detail: wuestite (W), spinel (S), calcium silicates (C)

**Table 1**: Leached amount of Cr and V in mg/kg and as percentage of the total content; Original sample (EAFS1), remelted samples (EAFS_R1 to 3) and conditioned samples (EAFS_C1 to 3), with 1: rapid cooling, 2: moderate cooling and 3: slow cooling; Basicity (CaO/SiO\textsubscript{2}) and FeO/SiO\textsubscript{2} ratio

<table>
<thead>
<tr>
<th></th>
<th>EAFS1</th>
<th>EAFS_R1</th>
<th>EAFS_R2</th>
<th>EAFS_R3</th>
<th>EAFS_C1</th>
<th>EAFS_C2</th>
<th>EAFS_C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>11.2</td>
<td>11.0</td>
<td>10.8</td>
<td>10.9</td>
<td>10.1</td>
<td>10.0</td>
<td>10.1</td>
</tr>
<tr>
<td>V (mg/kg)</td>
<td>2.5</td>
<td>1.2</td>
<td>0.37</td>
<td>0.38</td>
<td>0.13</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>V (%)</td>
<td>0.34</td>
<td>0.19</td>
<td>0.06</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
<td>0.13</td>
<td>0.076</td>
<td>0.0024</td>
<td>0.0018</td>
<td>0.046</td>
<td>0.0043</td>
<td>0.0024</td>
</tr>
<tr>
<td>Cr (%)</td>
<td>1E-03</td>
<td>6E-04</td>
<td>3E-05</td>
<td>9E-06</td>
<td>9E-04</td>
<td>6E-05</td>
<td>7E-05</td>
</tr>
<tr>
<td>CaO/SiO\textsubscript{2}</td>
<td>2.03</td>
<td>1.54</td>
<td>1.89</td>
<td>1.59</td>
<td>0.57</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td>FeO/SiO\textsubscript{2}</td>
<td>3.66</td>
<td>3.26</td>
<td>3.35</td>
<td>3.83</td>
<td>1.12</td>
<td>1.21</td>
<td>1.05</td>
</tr>
</tbody>
</table>
The lab experiments were repeated by using a pilot plant EAF. First X-ray diffraction analyses show that the mineral phase distribution has also changed as intended.

Although the described experiments are preliminary tests, they yield promising results for tailoring EAF slags towards a minimisation of V and Cr leaching, demonstrating that a calculated and targeted conditioning is possible if the underlying mechanisms are understood.

Acknowledgment

The authors want to thank the Austrian Research Promotion Agency (FFG) for funding the project MiLeSlag and all participating project partners for the support.

References