THE EFFECT OF WATER COOLING ON THE LEACHING BEHAVIOUR OF EAF SLAG FROM STAINLESS STEEL PRODUCTION

VPLIV VODNEGA HLAJENJA NA IZLUŽEVALNE KARAKTERISTIKE BELE EOP-ŽLINDRE

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The object of this study was the investigation of the influence of cooling methods of 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 confirmed 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.

Key words: EAF slag, leaching, metals, stainless steel, water cooling

INTRODUCTION

Steel slag is a by-product from the elaboration of steel. According to Proctor et al.1, slags represent about 10–15 % by weight of the steel output. Slag is necessary in all metallurgical processing steps of liquid metal treatment. Steel slags include slags that are produced in the oxygen steel converter process, in electric arc furnace (EAF) steel elaboration and slags from secondary metallurgy2.

Various alloy steel slags are generated in the alloy steel making processes. They usually contain high amounts of alloying elements, such as Cr, Ni, Mn, V, Ti and Mo. Since stainless steel slags contain a high amount of potentially toxic elements, it is necessary to treat them prior to their application or use as landfill1.

Historically, slags have been used for the construction of roads and as fill material. However, more recently, the use of slags has been expanded as cement additives, landfill cover material and for a number of agricultural applications1. In spite of the fact that many of the above mentioned applications are nowadays common practice, significant quantities of slag are still being dumped in landfills or stockpiled for long periods at steel plants.

The environmental impact must be taken into account when slags are disposed in a landfill. Steel slags are often enriched in toxic elements, in particular metals (Cu, Pb and Zn) and metalloids (As and Sb) which can be released into the environment through ageing processes and leaching3. The release of metals and toxic elements from slags can cause environmental problems such as water and soil pollution and a toxicological risk to humans through inhalation of small slag particles (<10 µm)3.

Quick cooling of EAF slags is recommended as steel slag treatment before disposal or use in other applications5. Quick cooling is a common practice for carbon steel EAF slag, but it can also be used for stainless steel EAF slags. It is used to avoid or to minimise the disintegration of slag. Disintegration in slags is probably the result of conversion of unstable polymorphous Ca2SiO4 to the low (γ) temperature form of Ca2SiO4, which is accompanied by an increase of 10 % in volume and leads to disintegration of slags5. Disintegration also occurs in some slags investigated in this work.

It has been reported that if slags are quenched in water thereby producing an amorphous structure, the resulting metal extraction is substantially lower4. The glassy amorphous structure possesses better chemical resistance to decomposition by acid than the crystalline structure6. In some reported studies, the effect of the cooling mode of the molten slag on its leaching charac-
teristics was investigated through re-melting slag and cooling tests\(^6,7,8\).

In our study the leaching characteristics of steel slags in relation to different modes of cooling of hot EAF slag were investigated in order to estimate the effect of water interactions on possible waste disposal.

2 EXPERIMENTAL PROCEDURES

The materials used in our study were slags from stainless steel production. Four electric arc furnace slags from four different stainless steel grades were selected in order to represent different types of EAF slag:

A. Electric arc furnace slag from stainless steel X2 CrNi 18–9; symbol: EX
B. Electric arc furnace slag from stainless steel AISI 304 H; symbol: E304
C. Electric arc furnace slag from stainless steel AISI 316 L; symbol: E3
D. Electric arc furnace slag from stainless steel MKM CrAl 4; symbol: EM

The chemical composition of stainless steel after the EAF procedure was determined during the process of production of stainless steel by optical emission spectrometry (OES ARL MA-310) and by IR adsorption spectroscopy (CS 344, LECO, Michigan, USA) for C and S determination.

Each type of EAF slag was emptied below the furnace, excavated and sampled while still hot. One part of a representative sample of EAF slag was left to cool down in air (1 stands for air cooled samples), whereas another part of the representative hot sample was jetted with water (2 stands for water cooled samples). Sampling of representative EAF slag samples (10–20 kg) was made according to SIST EN 15002:2006. In the case of E304 a different mode of water cooling was used, in which the slag was immersed in a bucket of cold water. A few pieces of hot E304 slag were dropped into a beaker with 500 mL deionised water to evaluate the leaching of slag components during cooling. The solution was filtered and analysed by ICP–AES (OPTIMA 2000 DV, Perkin Elmer) to determine metal concentrations (Al, Mn, Cr, Zn, Cd, Cu, Pb, Sn), by IC (761 COMPACT IC, Metrohm) for Cl–, Si and Cr(VI), IC (761 COMPACT IC, Metrohm) for F–, SO\(_4^{2–}\) and TOC analyzer (Multi N/C 2100S, Analytik Jena) for DOC.

3 RESULTS AND DISCUSSION

The chemical composition of EAF slag depends on the metallurgical process used during steel production and also depends on the steel grade. The elemental composition of the steel types from which the slag samples used in our study originated is presented in Table 1. As can be seen from Table 1, steel M showed the most different composition values comparing to other steel types resulting in different EM slag composition (see Table 2) and furthermore different composition of EM slag leachate (see Figures 1–3).

According to Shen et al.\(^3\) the mineral phases of stainless steel slag are dicalcium and tricalcium silicate, calcium-aluminium silicate, periclase and chromites. The

<p>| Table 1: Elemental composition of stainless steel after EAF process in mass fractions w/%. |</p>
<table>
<thead>
<tr>
<th>element</th>
<th>quality of steel, w/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.037, 0.593, 0.816, 0.067</td>
</tr>
<tr>
<td>Si</td>
<td>0.38, 0.01, 0.17, 0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.97, 0.89, 0.98, 0.04</td>
</tr>
<tr>
<td>P</td>
<td>0.033, 0.039, 0.043, 0.003</td>
</tr>
<tr>
<td>S</td>
<td>0.011, 0.013, 0.011, 0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>19.67, 18.89, 17.15, 0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.42, 0.38, 0.32, 0.03</td>
</tr>
<tr>
<td>Ni</td>
<td>6.38, 7.38, 7.27, 0.04</td>
</tr>
<tr>
<td>Al</td>
<td>0.01, 0.004, 0.008, 0.275</td>
</tr>
<tr>
<td>Mo</td>
<td>0.36, 0.38, 1.54, 0.01</td>
</tr>
<tr>
<td>V</td>
<td>0.097, 0.053, 0.064, 0.005</td>
</tr>
<tr>
<td>Ti</td>
<td>0.016, 0.005, 0.006, 0.005</td>
</tr>
<tr>
<td>Nb</td>
<td>0.014, 0.006, 0.005, 0.005</td>
</tr>
<tr>
<td>W</td>
<td>0.031, 0.054, 0.05, /</td>
</tr>
<tr>
<td>Co</td>
<td>0.107, 0.117, 0.154, 0.01</td>
</tr>
<tr>
<td>Zr</td>
<td>/ / / /</td>
</tr>
<tr>
<td>B</td>
<td>0.001, 0.001, 0.001, 0.001</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001, 0.002, 0.002, 0.004</td>
</tr>
<tr>
<td>Sb</td>
<td>/ / / /</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0005, 0.0008, 0.0009, 0.0013</td>
</tr>
</tbody>
</table>
mineral composition and mineral grain size are variable with chemical composition, mode of cooling and so on. Chemical phase analysis of steel slag indicated that Fe and Cr are mainly (about 70 %) in the form of oxides while Ni and Mo are in the form of metal. The chemical composition of the EAF slag samples used in our study is reported in Table 2. The mass fractions of main components of EAF slag were CaO (35.40–43.62 %), SiO2 (10.78–22.95 %), Al2O3 (6.59–15.55 %), MgO (8.69–13.81 %), Fe tot (4.40–10.60 %), MnO (1.45–3.63 wt %) and Cr2O3 (1.54–12.70 wt %). The amount of Cr2O3 was higher than that reported. The slag samples were also enriched in metals: Mo (158–2100 mg kg–1), Ba (248–560 mg kg–1), Cu (112–450 mg kg–1) and Zn (30–270 mg kg–1).

It is well known that the leaching characteristic of metals is strongly related to the structure and chemical composition of the slag. During smelting, reduction conditions are needed to produce metals and metalloids from scrap. The absence of O prevents any oxidation reactions. In the slags themselves, the elements are zerovalent or occur in more reduced valence states, often incorporated in the spinel structure, if the trivalent oxidation state is stable, as in the case of CrIII, SbIII and VIII. Spinels are oxides of the form (M2+)(Fe3+)2O4 where M2+ and Fe3+ are the divalent and trivalent cations, respectively, occupying tetrahedral and octahedral interstitial positions in the lattice formed by O2–. The elements are thus also leached as more reduced species compared to other waste.

The leaching tests showed high and comparable pH values of leachate in the range from 11.67 to 12.75 (see Table 3). Shen et al. reported high and similar pH values in leachate in the range from 10.28 to 10.81. It has been suggested that the release of Ca from slag may be the main reason for the increase in pH according to the chemical composition of the water. Cornelis et al. reported that freshly produced alkaline wastes have a

### Table 2: Total chemical composition of EAF slags. Results are presented as the mean value of duplicate analysis with the standard deviation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>w%</th>
<th>Sample</th>
<th>w%</th>
<th>Sample</th>
<th>c/(mg kg–1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX1</td>
<td>37.4±6.07 20.2±4.06 6.59±0.06 8.690±0.002 12.0±0.1 3.54±0.038 6.7±0.2</td>
<td>EX1</td>
<td>0.64±0.01 0.99±0.01 0.71±0.06 0.283±0.001 0.166±0.003 0.16</td>
<td>P</td>
<td>137±2 114±8 412±30 226±5 7.6±0.5</td>
</tr>
<tr>
<td>EX2</td>
<td>35.4±0.4 19.5±0.2 6.65±0.04 9.10±0.04 12.7±0.3 3.63±0.018 7.3±0.5</td>
<td>EX2</td>
<td>1.03±0.02 1.01±0.01 0.30±0.03 0.243±0.005 0.296±0.003 0.17±0.01</td>
<td>Co</td>
<td>164±2 120±10 450±40 87±4 7.6±0.7</td>
</tr>
<tr>
<td>E3041</td>
<td>41.42±0.002 18.82±0.04 8.865±0.001 9.55±0.04 9.18±0.04 3.03±0.01 4.4±0.1</td>
<td>E3041</td>
<td>0.19±0.02 0.84±0.001 0.43±0.04 0.266±0.006 0.256±0.004 0.18</td>
<td>Cu</td>
<td>137±2 43±2 145±8 150±20 6.2±0.4</td>
</tr>
<tr>
<td>E3042</td>
<td>38.2±0.2 18.52±0.05 8.08±0.03 9.59±0.02 10.61±0.01 3.579±0.004 5.2±0.1</td>
<td>E3042</td>
<td>0.122±0.005 0.78±0.01 0.76±0.09 0.139±0.001 0.095±0.001 0.15</td>
<td>V2O5</td>
<td>120±7 60±4 200±1 58±4 6.0±0.1</td>
</tr>
<tr>
<td>E31</td>
<td>36.4±0.1 22.4±0.2 7.47±0.09 13.8±0.1 5.91±0.06 3.29±0.014 8.0±0.2</td>
<td>E31</td>
<td>0.12±0.01 0.78±0.01 0.76±0.09 0.139±0.001 0.095±0.001 0.15</td>
<td>As</td>
<td>161 140±20 290±40 30±1 9±1</td>
</tr>
<tr>
<td>E32</td>
<td>37.34±0.01 22.95±0.02 7.845±0.004 13.6±0.1 5.24±0.06 3.23±0.006 6.0±0.2</td>
<td>E32</td>
<td>0.129±0.002 0.755±0.003 0.76±0.06 0.137±0.002 0.112±0.003 0.21±0.005</td>
<td>Zn</td>
<td>127±4 150±20 310±60 38±6 9±2</td>
</tr>
<tr>
<td>EM1</td>
<td>43.6±0.1 10.78±0.03 15.55±0.07 10.73±0.04 1.540±0.002 1.45±0.032 10.6±0.2</td>
<td>EM1</td>
<td>0.83±0.01 0.372±0.003 0.11±0.01 0.042±0.001 0.593±0.005 0.13</td>
<td>Se</td>
<td>648±7 23.2±0.2 112.3±0.7 270±40 6.9±0.2</td>
</tr>
<tr>
<td>EM2</td>
<td>35.4±0.2 18.83±0.04 11.13±0.08 8.70±0.03 3.04±0.03 1.76±0.002 10.5±0.1</td>
<td>EM2</td>
<td>0.84±0.02 0.473±0.004 0.18±0.03 0.074±0.001 0.417±0.003 0.37±0.01</td>
<td>Cd</td>
<td>630±20 35±2 150±10 246±5 7.0±0.6</td>
</tr>
</tbody>
</table>

M. LONCNAR ET AL.: THE EFFECT OF WATER COOLING ON THE LEACHING BEHAVIOUR ...
narrow pH distribution (between 10 and 13), because the
leachate pH is mainly controlled by dissolution of a
limited set of minerals containing Ca, such as portlandite
(Ca(OH)₂), calcium monosulfoaluminate (Ca₄[Al(OH)₆]₂·13H₂O),
hydrocalumite (Ca₄[Al(OH)₆]₂·6H₂O), ettringite (Ca₆[Al(OH)₆](SO₄)₃·32H₂O),
calcium silicate hydrate (CSH) and calcite (CaCO₃). The quantities
of these minerals, however, may vary, as reflected in the
acid neutralization capacity (ANC). According to
Cornelis et al., the minerals containing Ca mentioned
above, exert control over leaching. In our study a narrow
pH distribution and high pH values were also found. The
high pH values in leachates are a consequence of the
high content of Ca in the leachate (see Figure 1),
probably due to Ca minerals in slags such as portlandite
and calcite.

The main elements in slags were Ca, Mg, Si, Al, Mn
and Fe. Although they are not mentioned in Slovenian

Figure 1: Results of the leaching test of major elements in air and
water cooled EAF slags in mg kg⁻¹ (Ca, Al, Si, Mg, Ni, Fe). Results
are presented as the mean value of triplicate analysis with the standard
deviation as error bars. Values that are not presented in the Figure are
under the limit of detection; for Mg (0.05 mg kg⁻¹); for Si (0.1 mg
kg⁻¹); for Ni (0.005 mg kg⁻¹); for Fe (0.025 mg kg⁻¹).

Slika 1: Primerjalno izluševanje glavnih elementov (Ca, Al, Si, Mg,
Ni, Fe) v EOP–žlindrah, hlajenih na zraku in z vodo v mg kg⁻¹.
Rezultati so podani kot povprečje treh paralelk in standardni odmik.
Rezultati, ki v grafih niso podani so pod mejo detekcije, ki je za Mg
(0.05 mg kg⁻¹); za Si (0.1 mg kg⁻¹); za Ni (0.005 mg kg⁻¹); za Fe
(0.025 mg kg⁻¹).

Figure 2: Results of the leaching test of minor elements (Ba, Se, Mo,
Cr) in air and water cooled EAF slags in mg kg⁻¹. Results are
presented as the mean value of triplicate analysis with the standard
deviation as error bars.

Slika 2: Primerjalno izluševanje elementov v sledovih (Ba, Se, Mo,
Cr) v EOP–žlindrah, hlajenih na zraku in z vodo v mg kg⁻¹. Rezultati
so podani kot povprečje treh paralelk in standardni odmik.

Figure 3: Leaching of F⁻, Cl⁻ and DOC according to the one–stage
batch leaching test. Results are presented as the mean value of
triplicate analysis with the same standard deviation as error bars. Values
that are not presented in the Figure are under the limit of detection; for Cl⁻
(2.5 mg kg⁻¹); for DOC (10 mg kg⁻¹).

Slika 3: Izluševanje F⁻, Cl⁻ in DOC z enostopenjskim šaržnim
preskusom. Rezultati so podani kot povprečje treh paralelk in
standardni odmik. Rezultati, ki v grafih niso podani, so pod mejo
detekcije, ki je za Cl⁻ (2.5 mg kg⁻¹); za DOC (10 mg kg⁻¹).
waste legislation\textsuperscript{12}, they were also investigated in leaching tests because of the strong dependence between major element concentrations present in slag and the leaching characteristics of trace elements.\textsuperscript{13}

The most leachable element from air cooled slag is Ca, in the range from (1620 ± 80) mg kg\textsuperscript{–1} (E31) to (7000 ± 400) mg kg\textsuperscript{–1} (E3041) which represents 0.62 % and 2.36 % of the total Ca concentration, respectively. The amount of Al leached compared to the total Al concentration is in most cases even higher than for Ca, namely from 1.77 % (E31) to 4.88 % (EX1) of the total concentration, respectively, but in the case slag E3041 leaching of Al is negligible. The leaching of Si, Mg, Ni and Fe from air cooled slags was small (see Figure 1). Mn concentrations in the leachate were under the detection limit of method (0.025 mg kg\textsuperscript{–1}) and are not presented in Figure 1.

The leaching of Ca decreased in rapidly water cooled slag samples, with the exception of slag EM. The leaching of Al also decreased in all samples except E304, when cooled by water. The leaching of Al after rapid water cooling decreased significantly, especially in slag EX by 92.35 % and in slag EM by 78.57 % in comparison with air cooled samples. As can be seen from Table 4 the concentration of Ca and Al in water after several pieces of hot E304 slag were dropped into a beaker containing 500 mL deionized water was quite high (252 mg L\textsuperscript{–1} and 72.1 mg L\textsuperscript{–1}, respectively). However those values could not be directly compared to leaching values due to the different amount of slag samples in both cases. It is impossible to weigh hot slag to determine the S/L ratio. Nevertheless, it can be concluded that leaching of Ca and Al decreased when rapid water cooling was used due to ability of Ca and Al to solubilize in water after jetting hot slag samples. In the case of Si and Mg, water cooling caused an increase in leaching of elements from slags. The leaching of Si increased in all samples cooled with water. Leaching of Mg increased at all samples, too, except for slag E304 and slag EM, compared to air cooled samples. As can be seen from Table 4, the concentration of Si and Mg in water after a several E304 slag were dropped into water were negligible compared to the concentration of Mg and Si in water after dropping several of hot slag into water.

Tossavainen et al.\textsuperscript{8} reported that leaching of Si increased in many cases, while Al leaching decreased when cooled rapidly. Different methods of cooling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>EX1</th>
<th>EX2</th>
<th>E3041</th>
<th>E3042</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>11.85 ± 0.09</td>
<td>11.85 ± 0.10</td>
<td>12.75 ± 0.07</td>
<td>12.43 ± 0.03</td>
</tr>
<tr>
<td>EC</td>
<td>mS cm\textsuperscript{–1}</td>
<td>1.80 ± 0.10</td>
<td>1.02 ± 0.09</td>
<td>6.40 ± 0.30</td>
<td>2.77 ± 0.08</td>
</tr>
<tr>
<td>Redox potential</td>
<td>mV</td>
<td>217.0 ± 0.6</td>
<td>223 ± 7</td>
<td>142 ± 8</td>
<td>186 ± 4</td>
</tr>
<tr>
<td>Parameter</td>
<td>Unit</td>
<td>E31</td>
<td>E32</td>
<td>EM1</td>
<td>EM2</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>12.03 ± 0.03</td>
<td>11.67 ± 0.01</td>
<td>11.89 ± 0.05</td>
<td>12.37 ± 0.01</td>
</tr>
<tr>
<td>EC</td>
<td>mS cm\textsuperscript{–1}</td>
<td>1.41 ± 0.07</td>
<td>0.65 ± 0.07</td>
<td>1.5 ± 0.1</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>Redox potential</td>
<td>mV</td>
<td>148 ± 3</td>
<td>56</td>
<td>101</td>
<td>115 ± 8</td>
</tr>
</tbody>
</table>

Table 3: Results of standard leaching test SIST EN 12457–4 presented as the mean value of triplicate analysis with the standard deviation.

Table 4: Chemical composition of water after dropping several pieces of hot slag E304 into 500 mL of deionized water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>c/(mg L\textsuperscript{–1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>252</td>
</tr>
<tr>
<td>Al</td>
<td>72.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.26</td>
</tr>
<tr>
<td>Mg</td>
<td>0.005</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>Cr</td>
<td>0.240</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>0.233</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cl\textsuperscript{–}</td>
<td>4.00</td>
</tr>
<tr>
<td>F</td>
<td>5.65</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2–}</td>
<td>1.12</td>
</tr>
</tbody>
</table>

< LOD = less then LOD

Table 5: Results of leaching test for Cr and Cr(VI) in mg kg\textsuperscript{–1}. Results are presented as the mean value of triplicate analysis with the standard deviation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr\textsubscript{tot}</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX1</td>
<td>0.074 ± 0.007</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>EX2</td>
<td>0.39 ± 0.04</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>E3041</td>
<td>0.012 ± 0.0002</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>E3042</td>
<td>0.30 ± 0.04</td>
<td>0.28 ± 0.08</td>
</tr>
<tr>
<td>E31</td>
<td>0.42 ± 0.04</td>
<td>0.36 ± 0.04</td>
</tr>
<tr>
<td>E32</td>
<td>0.3552 ± 0.0004</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>EM1</td>
<td>0.0064 ± 0.0008</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>EM2</td>
<td>0.028 ± 0.008</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

< LOD = less then LOD
Due to the considerable amount of data obtained for leaching of minor elements, only the most significant ones are presented in Figure 2. The leaching from EAF stainless steel slag was generally very low. However some elements in air cooled slags exceeded the legal limit for inert waste material: the leaching concentration of Se from slag E3041 was (0.24 ± 0.03) mg kg⁻¹ (limit value: 0.1 mg kg⁻¹) and of Mo from slag EX1 was (1.4 ± 0.3) mg kg⁻¹ and from slag E31 was (1.44 ± 0.07) mg kg⁻¹ (limit value: 0.5 mg kg⁻¹). Leaching concentrations of Ba from EM1 slag was (20 ± 2) mg kg⁻¹ and is at the limit value (limit value: 20 mg kg⁻¹).

As is shown in Figure 2, in comparison to air cooled slag, water cooling decreased the leaching of Ba and Se, with the exception of slag EM. Water cooling decreased the leaching of Ba in the range from 1.44 to more than 150-fold in comparison to air cooling. The leachable concentration of Ba from air cooled slag was in the range from (2.0 ± 0.3) mg kg⁻¹ (E3041) to (20 ± 2) mg kg⁻¹ (EM1) representing 0.77 % and 6.47 % of the total Ba concentration, respectively. A similar trend was observed in leaching of Mo and Cr on water cooling. Leaching of Mo in the water cooling mode decreased for slag E3, while it increased for slag E304 and slag EM, but in the case of EX it was similar to air cooled samples. A similar result was obtained in the case of Cr leaching where in all three slags (EX, E304 and EM) it increased, while a decrease of leaching in slag E31 was observed in comparison to air cooled slags. Cr(VI) was also analysed in all leachate samples and the results (see Table 5) showed that almost all of the total Cr in leachate was present in form of Cr(VI). Soluble Cr is almost always hexavalent because equilibrium with insoluble Ca–Cr³⁺ minerals causes the Cr(OH)⁶⁺ concentration to be very low.

The leaching characteristics of F⁻, Cl⁻, DOC are presented in Figure 3. The leaching of SO₄²⁻ was negligible and is not shown in Figure 3. The leaching of F⁻ is the highest in slag EX1, (210 ± 10) mg kg⁻¹.

In the cases of slag EX and slag E3 a decrease in leachable F⁻ concentrations was observed when cooled with water. On the other hand, an increase of F⁻ concentrations was observed in water cooled slag E304 and slag EM samples. Water cooling in most cases caused a decrease of Cl⁻ concentrations (an exception was slag EX) and also a decrease of DOC concentrations.

The results of our investigation showed that different modes of cooling affected the leaching behaviour of slags. Mainly it affects the leaching characteristics of major elements such as Ca, Al, Si, Mg and significantly the leaching of Ba and Se. Some similarities in leaching of Mo and Cr were also observed.

The results from the single batch leaching test were compared to limits set by Slovenian legislation for the acceptance of inert waste for landfilling. From the comparison it can be concluded that most potentially hazardous elements did not exceed the established criteria, except for air cooled slag, where Mo (in slag E31 and slag EX1), F⁻ (in slag EX1, slag E3041 and slag E31), Se (in slag E3041) where concentrations in leachate exceeded the limit values. Leaching concentrations of Ba from EM1 slag was at the limit value. Although F⁻ concentrations in leachate from air cooled slag in most cases exceeded the legal regulation (10 mg kg⁻¹), it represents only from 0.63 % (E31) to 3.23 % (EX1) of the total fluoride concentration in slag.

Proctor et al. reported that the Sb, As, Ba, Be, Cd, Cr(III), Cr(VI), Pb, Mn, Hg, Ni, Se, Ag, Ti and Zn concentrations in leachates of steel slag, using the TCLP test for leaching evaluation, were very low. The only metals that were detected at concentrations higher than 1 mg L⁻¹, were Ba and Mn. These metals were also found at much higher concentrations in the slag samples. Also in our study, although using different standard procedure, high values for Ba in leachate were observed (see Figure 2).

4 CONCLUSION

The results of our study showed that leaching of metals from EAF slag is generally very low. These results indicate that metals are very tightly bound and are not released from the matrix. Nevertheless, some exceptions exist. Relatively high leachate concentrations were observed for Ba and Mo. F⁻ is the most problematic anion in leachate. The solubility of metals in slag depends on the solubility of the major phase. Leaching of major elements (for example Ca) is more extensive. Due to the high content of Ca in slags, EAF slags are alkaline solid waste.

Water cooling had an effect on the leaching behaviour of the investigated slags. Water cooling caused a decrease in leaching of Ca, Al, Ba and Se, and on the other hand, increased leaching of Si and Mg. Some similarities in leaching of Mo and Cr after water cooling were observed. Mo and Cr leaching in all three slags (EX2, E3042 and EM2) increased, while for slag E32 a decrease in leachable metal concentrations comparable to air cooled slags were observed.

According to Sloot, the single step extraction test is very limited in its capability to provide answers to complex questions such as: whether a material can be disposed in a particular type of landfill or it the material been sufficiently treated to meet requirements for disposal or beneficial applications. Future research will be focused on more sophisticated testing that will provide insight into the mechanistic aspects of leaching of EAF slag and on the effect of the rate of cooling on slag leaching behaviour.
To investigate the cooling effect on the leachability of slag in detail the mineralogical characteristics of water and air cooled slags will be included in further studies.

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5 REFERENCES

4 V. Ettler, Z. Johan, B. Krňbek, O. Šebek, M. Mihaljević, Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia, Appl. geochem. 24 (2009), 1–15
5 M. P. Luxán, R. Sotolongo, F. Dorrego, E. Herrero, Characteristics of the slags produced in the fusion of scrap steel by electric arc furnace, Cem. concr. res., 30 (2000), 517–519