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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

Namen raziskave je bil ugotoviti, kako različni načini hlajenja bele EOP–žlindre, ki nastane pri proizvodnji nerjavnih jekel, vpliva na izluževalne karakteristike kovin in drugih pretežno anorganskih parametrov. Preučili smo žlindre, nastale pri izdelavi štirih različnih kvalitetah nerjavnih jekel. Izluževalne preizkuse smo izvedli po standardu SIST EN 12457–4:2004. Ugotovili smo, da različni načini hlajenja vplivajo na delež izluževanja kovin in drugih pretežno anorganskih parametrov. Izluževanje Ca, Al, Ba in Se je bilo pri vodno hlajenih belih EOP-žlindrah nižje kot pri hlajenju belih EOP–žlinder na zraku, obenem pa se je pri hlajenju z vodo koncentracija Si in Mg v izlužkih belih EOP-žlinder povečala.

Ključne besede: bela EOP-žlindra, izluževanje, kovine, nerjavna jekla, vodno hlajenje

1 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 metallurgy[2].

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 landfill[3].

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 aplications[1]. 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 leaching[4]. 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 applications[5]. 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 Ca_2SiO_4 to the low (γ) temperature form of Ca_2SiO_4, which is accompanied by an increase of 10 % in volume and leads to disintegration of slags[5]. 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 lower[6]. The glassy amorphous structure possesses better chemical resistance to decomposition by acid than the crystalline structure[6]. In some reported studies, the effect of the cooling mode of the molten slag on its leaching characteristics 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^-, F^- and SO_4^{2-}, by FAAS for Mg and Ca and by UV–VIS spectrophotometry (Cary 1E (UV VIS), Varian) to determine Si and Cr(VI).

To determine the total composition of slag, XRF spectroscopy (MAGI´X FAST, PANALYTICAL) was used for major components, IR adsorption spectroscopy for C and S (CS 244 W, LECO, Michigan, USA), thermal decomposition in tube furnace and measuring F^- with electrochemical method, ICP–AES (OPTIMA 2000 DV, Perkin Elmer) and ICP-MS (4500, Agilent) for trace elements in acid digested slag samples.

To determine their leaching characteristics, slag samples were crushed to a particle size of <10 mm and leached according to the SIST EN 12457–4 one-stage batch test (24 h water extraction of slag samples at an L/S ratio of 10). The leaching tests were done in triplicate. The leachate samples were centrifuged and filtered through a 0.45 μm filter. pH, EC, redox potential and the concentration of elements were determined in the leachates. ICP–MS (Agilent 4500) was used for determination of Be, Mg, Ti, V, Cr_{tot}, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Ba and Pb concentrations, ICP–AES (OPTIMA 2000 DV, Perkin Elmer) for Al and Ca, spectrophotometry (Cary 1E (UV VIS), Varian) for Si and Cr(VI), IC (761 COMPACT IC, Metrohm) for Cl^-, SO_4^{2-} and F^- 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

Table 1: Elemental composition of stainless steel after EAF process in mass fractions *w*/%.

Preglednica 1: Elementna sestava nerjavnih kvalitet jekel po EOP-postopku v masnih deležih *w*/%.

	quality of steel, *w*/%			
element	X	304	3	M
C	1,037	0,593	0,816	0,067
Si	0,38	0,01	0,17	0,01
Mn	0,97	0,89	0,98	0,04
P	0,033	0,039	0,043	0,003
S	0,011	0,013	0,011	0,005
Cr	19,67	18,89	17,15	0,02
Cu	0,42	0,38	0,32	0,03
Ni	6,38	7,38	7,27	0,04
Al	0,01	0,004	0,008	0,275
Sn	0,015	0,013	0,011	0,005
Mo	0,36	0,38	1,54	0,01
V	0,097	0,053	0,064	0,005
Ti	0,016	0,005	0,006	0,005
Nb	0,014	0,006	0,005	0,005
W	0,031	0,054	0,05	/
Co	0,107	0,117	0,154	0,01
Zr	/	/	/	0,003
B	0,001	0,001	0,001	0,001
Pb	0,001	0,002	0,002	0,004
Sb	/	/	/	0,005
Ca	0,0005	0,0008	0,0009	0,0013

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[9]. 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 %), SiO_2 (10.78–22.95 %), Al_2O_3 (6.59–15.55 %), MgO (8.69–13.81 %), Fe_{tot} (4.40–10.60 %), MnO (1.45–3.63 wt %) and Cr_2O_3 (1.54–12.70 wt %). The amount of Cr_2O_3 was higher than that reported [1,8,9,10]. 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_2 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 Cr^{III}, Sb^{III} and V^{III}. Spinels are oxides of the form $(M^{2+})(Fe^{3+})_2O_4$ where M^{2+} and Fe^{3+} are the divalent and trivalent cations, respectively, occupying tetrahedral and octahedral interstitial positions in the lattice formed by O^{2-}. The elements are thus also leached as more reduced species compared to other waste[11].

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.[9] 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[9]. Cornelis et al.[11] 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.
Preglednica 2: Kemijska sestava EOP–žlinder. Rezultati so podani kot povprečje dveh paralelk ± standardni odmik.

Sample	*w*/%						
	CaO	SiO_2	Al_2O_3	MgO	Cr_2O_3	MnO	Fe
EX1	37,46 ± 0,07	20,24 ± 0,06	6,59 ± 0,06	8,690 ± 0,002	12,0 ± 0,1	3,54 ± 0,038	6,7 ± 0,2
EX2	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
E3041	41,425 ± 0,002	18,82 ± 0,04	8,856 ± 0,001	9,55 ± 0,04	9,18 ± 0,04	3,03 ± 0,01	4,4 ± 0,1
E3042	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
E31	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
E32	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
EM1	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
EM2	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

Sample	*w*/%					
	F^-	TiO_2	Ni	V_2O_5	S	C
EX1	0,64 ± 0,01	0,99 ± 0,01	0,71 ± 0,06	0,283 ± 0,001	0,166 ± 0,003	0,16
EX2	0,50	1,03 ± 0,02	0,65 ± 0,09	0,285 ± 0,003	0,150 ± 0,001	0,23
E3041	1,19 ± 0,02	1,01 ± 0,01	0,30 ± 0,03	0,243 ± 0,005	0,296 ± 0,003	0,17 ± 0,01
E3042	0,81 ± 0,01	0,842 ± 0,001	0,43 ± 0,04	0,266 ± 0,006	0,256 ± 0,004	0,18
E31	0,122 ± 0,005	0,78 ± 0,01	0,76 ± 0,09	0,139 ± 0,001	0,095 ± 0,001	0,15
E32	0,129 ± 0,002	0,755 ± 0,003	0,76 ± 0,06	0,137 ± 0,002	0,112 ± 0,003	0,21 ± 0,005
EM1	0,83 ± 0,01	0,327 ± 0,003	0,11 ± 0,01	0,042 ± 0,001	0,593 ± 0,005	0,13
EM2	0,84 ± 0,02	0,473 ± 0,004	0,18 ± 0,03	0,074 ± 0,001	0,417 ± 0,003	0,37 ± 0,01

Sample	*c*/(mg kg^{-1})				
	P	Co	Cu	Zn	As
EX1	137 ± 2	114 ± 8	412 ± 30	226 ± 5	7,6 ± 0,5
EX2	164 ± 2	120 ± 10	450 ± 40	87 ± 4	7,6 ± 0,7
E3041	137 ± 2	43 ± 2	145 ± 8	150 ± 20	6,2 ± 0,4
E3042	120 ± 7	60 ± 4	200 ± 1	58 ± 4	6,0 ± 0,1
E31	161	140 ± 20	290 ± 40	30 ± 1	9 ± 1
E32	127 ± 4	150 ± 20	310 ± 60	38 ± 6	9 ± 2
EM1	648 ± 7	23,2 ± 0,2	112,3 ± 0,7	270 ± 40	6,9 ± 0,2
EM2	630 ± 20	35 ± 2	150 ± 10	246 ± 5	7,0 ± 0,6

Sample	*c*/(mg kg^{-1})				
	Se	Mo	Cd	Ba	Pb
EX1	6,4 ± 0,9	470 ± 20	1,27 ± 0,03	251 ± 5	42 ± 1
EX2	10,9 ± 0,6	440 ± 40	0,93 ± 0,08	270 ± 2	8,1 ± 0,1
E3041	11,5 ± 0,4	250 ± 30	0,42 ± 0,03	259 ± 1	5,5 ± 0,1
E3042	6,800 ± 0,003	320 ± 10	0,50 ± 0,01	248 ± 1	6,4 ± 0,2
E31	<4	2100 ± 200	0,83 ± 0,07	560 ± 10	<1
E32	<4	2100 ± 100	0,7 ± 0,2	548 ± 1	2,11 ± 0,04
EM1	7 ± 2	158 ± 7	0,41 ± 0,02	309 ± 1	17 ± 3
EM2	<4	290 ± 60	0,69 ± 0,01	314 ± 6	30,2 ± 0,7

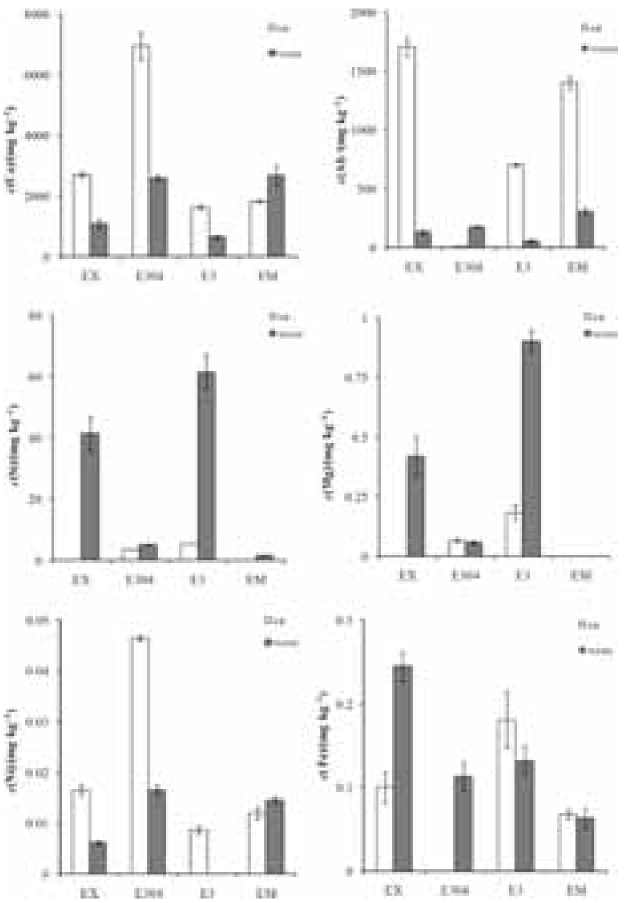

Figure 1: Results of the leaching test of major elements in air and water cooled EAF slags in mg kg^{-1} (Ca, Al, Si, Mg, Ni, Fe). Results are presented as the mean value of triplicate analysis with the standard deviation as error bars. Values that are not presented in the Figure are under the limit 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 izluževanje 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}).

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 ($Ca_4[Al(OH)_6]_2 SO_4 \cdot 13H_2O$), hydrocalumite ($Ca_4[Al(OH)_6]_2 \cdot 6H_2O$), ettringite ($Ca_6[Al(OH)_6](SO_4)_3 \cdot 32H_2O$), calcium silicate hydrate (CSH) and calcite ($CaCO_3$). The quantities of these minerals, however, may vary, as reflected in the acid neutralization capacity (ANC). According to Cornelis et al.[11] 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

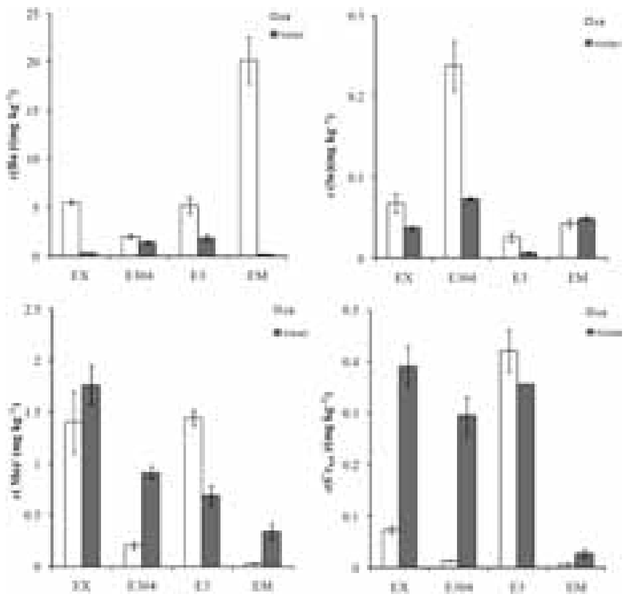

Figure 2: Results of the leaching test of minor elements (Ba, Se, Mo, Cr) in air and water cooled EAF slags in mg kg^{-1}. Results are presented as the mean value of triplicate analysis with the standard deviation as error bars.

Slika 2: Primerjalno izluževanje 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.

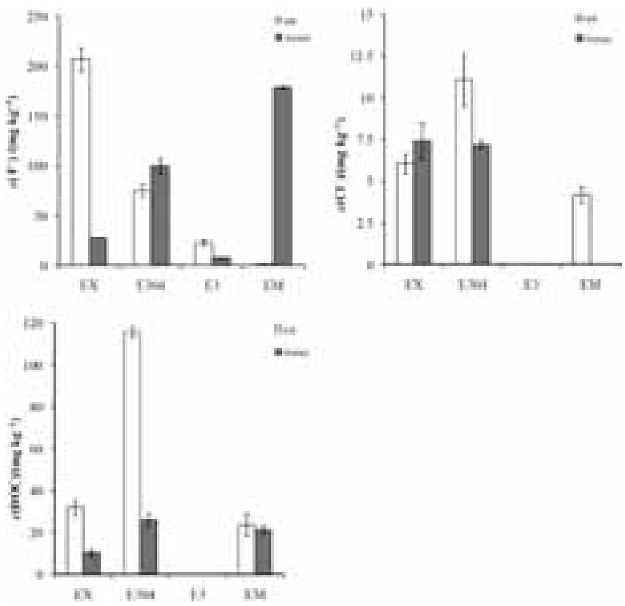

Figure 3: Leaching of F^-, Cl^- and DOC according to the one–stage batch leaching test. Results are presented as the mean value of triplicate analysis with the standard deviation as error bars. Values that are not presented in the Figure are under the limit of detection; for Cl^- (2.5 mg kg^{-1}); for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

Slika 3: Izluževanje 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}).

Table 3: Results of standard leaching test SIST EN 12457–4 presented as the mean value of triplicate analysis with the standard deviation.
Preglednica 3: Rezultati nekaterih parametrov izluževalnega preizkusa SIST EN 12457–4. Rezultati so podani kot povprečje treh paralelk ± standardni odmik.

Parameter	Unit	EX1	EX2	E3041	E3042
pH		11,85 ± 0,09	11,85 ± 0,10	12,75 ± 0,07	12,43 ± 0,03
EC	mS cm^{-1}	1,80 ± 0,10	1,02 ± 0,09	6,40 ± 0,30	2,77 ± 0,08
Redox potential	mV	217,0 ± 0,6	223 ± 7	142 ± 8	186 ± 4
Parameter	Unit	E31	E32	EM1	EM2
pH		12,03 ± 0,03	11,67 ± 0,01	11,89 ± 0,05	12,37 ± 0,01
EC	mS cm^{-1}	1,41 ± 0,07	0,65 ± 0,07	1,5 ± 0,1	2,6 ± 0,1
Redox potential	mV	148 ± 3	56	101	115 ± 8

waste legislation[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.[13]

The most leachable element from air cooled slag is Ca, in the range from (1620 ± 80) mg kg^{-1} (E31) to (7000 ± 400) mg kg^{-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^{-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 deionised water was quite high (252 mg L^{-1} and 72.1 mg L^{-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 Al and Ca 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 Ca and Al. The opposite effect was observed in leaching of Mg and Si in comparison to the concentration of Mg and Si in water after dropping several of hot slag into water.

Tossavainen el at.[8] reported that leaching of Si increased in many cases, while Al leaching decreased when cooled rapidly. Different methods of cooling

Table 4: Chemical composition of water after dropping several pieces of hot slag E304 into 500 mL of deionized water.
Preglednica 4: Rezultati analize vode, potem ko smo v 500 mL deionizirane vode potopili par kosov vroče žlindre E304.

Parameter	c/(mg L^{-1})
Ca	252
Al	72,1
Si	0,26
Mg	0,005
Mn	<0.01
Fe	<0.025
Cr	0,240
Cr(VI)	0,233
Zn	<0.01
Cd	<0.01
Cu	<0.01
Pb	<0.03
Sn	<0.1
Cl^-	4,00
F^-	5,65
SO_{42-}	1,12

< LOD = less then LOD

Table 5: Results of leaching test for Cr and Cr(VI) in mg kg^{-1}. Results are presented as the mean value of triplicate analysis with the standard deviation.
Preglednica 5: Rezultati izlužilnega testa za parameter Cr in Cr(VI). Rezultati so podani kot povprečje treh paralelk ± standardni odmik.

	c/(mg kg^{-1})	
Sample	Cr_{tot}	Cr(VI)
EX1	0,074 ± 0,007	<0.1
EX2	0,39 ± 0,04	0,44 ± 0,02
E3041	0,012 ± 0,002	<0.1
E3042	0,30 ± 0,04	0,28 ± 0,08
E31	0,42 ± 0,04	0,36 ± 0,04
E32	0,3552 ± 0,0004	0,35 ± 0,02
EM1	0,0064 ± 0,0008	<0.1
EM2	0,028 ± 0,008	<0.1

< LOD = less then LOD

(re-melting and water granulation or re-melting and cooling in a crucible) were used by Tossavainen el at.[8], but the results obtained were similar to those in our study.

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[12]: 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–Cr^{III} minerals causes the $Cr(OH)_4^-$ concentration to be very low[9].

The leaching characteristics of F^-, Cl^-, DOC are presented in **Figure 3**. The leaching of SO_4^{2-} 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 leachate 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[12]. 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.

Procter et al.[1] reported that the Sb, As, Ba, Be, Cd, Cr_{tot}, Cr(VI), Pb, Mn, Hg, Ni, Se, Ag, Tl 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 leachtate 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[14], 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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