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Angaben zur Veröffentlichung / Publication details:

Aldrian, Alexia, Johann G. Raith, Daniel Höllen, and Roland Pomberger. 2015. “Influence of chromium containing spinels in an electric arc furnace slag on the leaching behaviour.” *The Journal of Solid Waste Technology and Management* 41 (4): 357–65. https://doi.org/10.5276/jswtm.2015.357.

INFLUENCE OF CHROMIUM CONTAINING SPINELS IN AN ELECTRIC ARC FURNACE SLAG ON THE LEACHING BEHAVIOUR

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ABSTRACT

Electric arc furnace slags are suitable construction and paving materials for roads due to their physical properties (e.g. volume stability). However, concerns are being raised in regard to the leaching behaviour of slags, especially in terms of the element chromium and its toxicity in the hexavalent state. The leaching behaviour is significantly controlled by the mineral phases and their solubility whose formations depend mainly on the process conditions (i.e. additives, temperature, cooling rate). In this contribution, the content, the element distribution and the mobility of chromium for an electric arc furnace slag were investigated and assessed. The extensively analysed material was a slag from a steel production plant in Austria using unalloyed scrap as raw material. XRF and electron microprobe analyses were carried out as well as leaching tests with initial acid/base addition to influence the pH value. XRF results gave a total chromium content of 1.7 mass% Cr. The mineralogical investigation by electron microprobe analyses showed that chromium ions are bound within stable spinel phases. Two different types of spinels occur in the slag: aluminium-chromium-magnesium- and chromium containing aluminium-magnesium-spinels (type I) as well as chromium-manganese-iron-spinels (type II). The chromium content in the accompanying phases (e.g. gehlenite) is insignificant. The natural occurrence of the mentioned type I spinel is quite common and they are found in mafic and ultramafic rocks and soils produced by weathering of these rocks. The leaching tests showed that the extraction of spinel bound chromium of the investigated electric furnace slag is unlikely, even at low pH values.

Keywords: Electric arc furnace slag; Chromium; Spinel; Leaching behavior

INTRODUCTION

Each year, the iron and steel industry generates large quantities of ashes, dusts, mill scales, sludges and slags. The amounts of these residues may be influenced by the steel production process and used aggregates as well as recycling

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rates of wastes, but eventually they are inevitable (Winter et al., 2005). Applying the policy of waste hierarchy laid down in the EU Directive 2008/98/EC (European Union, 2008) on waste, the re-use of these residues takes precedence over recycling, other recovery (e.g. thermal) and disposal.

However, the application of the residues, e.g. slags, should not pose a threat to human beings or the environment in any way (Motz & Geiseler, 2001). In this context, the water solubility of all slag phases and especially hazardous substances (e.g. Cr^{6+}) is of great importance. Therefore, the leaching behaviour is a fundamental part of a full material characterisation and essentially more important than the total content (Tossavainen & Forssberg, 2000). A potential utilisation of slags also strongly depends on the chemical composition and physical properties and therefore mainly on the production process, resulting in the following four different slag types: blast furnace slag, basic oxygen furnace slag, electric arc furnace slag and secondary metallurgical slag (Euroslag, 2012).

In the European Union, approximately 45.3 million tonnes of ferrous slag were generated in 2010, around 3.8 mass% were electric arc furnace slags (EAF slags) from high alloy steel production. Some of the different slag types are even considered non-waste products or by-products in several countries whilst having waste status in others (Euroslag, 2012). In Austria, the steel industry produces more than 2 million tonnes of slag each year, whereof 5 mass% are produced by three electric furnace steel plants. Whereas blast furnace and basic oxygen furnace slag have been utilised as road building materials and in fertiliser or cement production for years, the application of electric arc furnace slag is still controversial in Austria. (Winter et al., 2005) The present national legislation does not consider EAF slags as products or by-products. Therefore, the utilisation as e.g. road building material is not possible, even if suitability in regard to physical and chemical properties is proven.

Environmental concerns regarding the utilisation of EAF focus generally on the heavy metal content with special attention to chromium (Fällmann, 2000; Tossavainen & Engström 2000). The chromium oxide content in EAF slags may be almost 15 mass% (Vidacak et al., 2002). Chromium is primarily present in the slag as Cr^{2+} and Cr^{3+}, but Cr^{6+} will form over time if free lime and oxygen are available during or after cooling (Morita et al., 2005). Both Cr^{3+} and Cr^{6+} can be leached from the solid slag when it comes in contact with water (van der Sloot et al., 1997). Cr^{3+} is an essential trace element for mammals and 10 to 100 times less toxic than Cr^{6+} (Fendorf, 1995), but higher concentrations may cause also negative effects (e.g. skin irritation), whereas Cr^{6+} is carcinogenic (H 7 criterion according to the EU Directive 2008/98/EC) (European Union, 2008). Therefore, the release of Cr^{3+} and Cr^{6+} into the environment has to be prevented.

Several possibilities to immobilise chromium in slags have already been presented (Durinck et al., 2008). The incorporation of chromium into stable mineral phases during the production process might be one of the most promising solutions. Particularly spinel phases with the general formula AB_2O_4 with A being bivalent (Mg, Fe^{2+}, Zn, Mn) and B being trivalent cations (Al, Fe^{3+}, Cr^{3+}) gained special attention (Tossavainen & Forssberg, 2000; Kühn & Mudersbach, 2004).

In this contribution, the chromium content as well as the mineral phases and elemental distribution of a quality assured electric arc furnace slag of an Austrian producer are studied using X-ray fluorescence spectroscopy (XRF) and electron microprobe techniques. Special emphasis is placed on the thorough characterisation and description of chromium containing spinels. Although previous works (Mostaghel et al., 2010; Tossavainen et al., 2007; Tossavainen & Forssberg, 2000) mention spinel phases, they have never been studied mineralogically and described in such detail before. The composition of the identified types of spinel phases is also compared to spinels occurring in rocks and minerals of natural settings. This approach allows a new perspective on the assessment of the EAF slag's environmental impact. Additionally, these findings are set in relation to the leaching behaviour of the EAF slag in regard to chromium and several other elements to complete an overall evaluation of the investigated material.

MATERIALS AND METHODOLOGY

Material and sample preparation

The material used in this study was supplied by an Austrian producer of low alloyed steel from scrap in an electric arc furnace process. The complete production process is quality controlled in terms of requirements specified by Gütegemeinschaft Eisenhüttenschlacken e.V. (Motz & Geiseler, 2001). The liquid slag was cooled with water leading to the formation of a granulated (0/500 mm) solid. A sample of 25 kg was immediately taken after granulation. Then, the slag was crushed with a jaw crusher (BB 200, Retsch) to < 30-40 mm before splitting into 0.5 kg sub-samples. The laboratory samples were stored in bottles made of PE until further use.

Chemical composition

For the determination of the total main composition, the slag was oven-dried at 105 ± 2 °C to constant weight. The dried sample was then ground using a ball mill (S1000, Retsch), compressed into a tablet and analysed using X-ray fluorescence spectroscopy (Axios, PANalytical) by an external laboratory. The dried sample was also used for the determination of minor components using inductively coupled plasma mass spectrometry (ICP-MS, 7500ce, Agilent) after a microwave digestion with HF, HCl and HNO_3 according to ÖNORM EN 13656 (ASI, 2002). The analyses were done in triplicate and the results are presented as a mean value.

Mineralogical characterisation

The mineralogy of slag phases was studied on a polished microsection, which was prepared using diamond slurries with different grain sizes and water. Mineral chemical analyses and SEM (scanning electron microscopy) imaging of the material were done using an electron microprobe (Jeol JXA 8200 Superprobe at Universitätszentrum Angewandte Geowissenschaften Steiermark (UZAG) electron microprobe laboratory). Qualitative elemental analyses were performed with an energy dispersive spectrometer (EDS) and quantitative results were obtained with a wavelength dispersive system (WDS). Analytical conditions for WDS analyses were: accelerating voltage 15 kV; sample current 10 nA; counting time 30 s on the peak; 15 s on the backgrounds; K alpha lines were used for all elements; ZAF correction; calibration with natural mineral standards. The detection limits were: Si 90 ppm, Al 110 ppm, Cr 300 ppm, Fe 190 ppm, Mn 200 ppm, Mg 130 ppm, Ca 160 ppm.

Leaching tests

The samples for the leaching tests were further crushed with a jaw crusher (BB 200, Retsch) to < 1 mm. The leaching tests were carried out as batch tests at room temperature for 48 h using an overhead shaker. The slag sample was mixed with the leachant in a liquid to solid ratio 10:1 (100 g slag and 1000 ml leachant). The leaching was accomplished without and with initial acid/base addition to influence the pH according to the standard ÖNORM CEN/TS 14429 (ASI, 2006). Ultra pure water (< 0.2 mS/m) was used as leachant and HNO_3 (1 M) and NaOH (1 M) were added to adjust the pH. The leaching tests were performed under closed conditions, preventing significant atmospheric influence of carbon dioxide and oxygen. The pH of the leachates was measured after 44 and 48 hours using a pH-meter (pH3110, WTW). The subsequent analyses of the leachates were performed by inductively coupled plasma mass spectrometry (ICP-MS, 7500ce, Agilent) after using a filtering device (0.45 µm cellulose nitrate filter) and acidifying with concentrated HNO_3. Bottles of polyethylene (PE) and polypropylene (PP) were used for the leaching tests and for sample storage. The leachate without any initial acid/base addition was also analysed in regard to anions (Cl^-, F^-, PO_4^{3-}, SO_4^{2-}, S^{2-}) according to the standards ISO 10304-1 (ISO, 2007) and DIN 38405-26 (DIN, 1989). Hexavalent chromium was also determined in this leachate in accordance with ISO 18412 (ISO, 2005) as well as the electrical conductivity according to ISO 7888 (ISO, 1985). For the determination of anions and Cr(VI), a filtering device (0.45 µm cellulose nitrate filter) was used before the actual analyses. All leaching tests have been done twice and the results are presented as a mean value.

RESULTS AND DISCUSSION

The chemical composition of the electric arc furnace slag is shown in Table 1. Based on the CaO/SiO_2-ratio (B), the slag can be classified as low basicity with B = 1.6. The results for the main components correspond well to those of other European low basicity EAF slags described in literature (Tossavainen et al., 2007; Mostaghel et al., 2010; Motz & Geiseler, 2001). Noticable is, however, the magnesium content which is merely 2.4 mass% and comparatively low, whereas the aluminium content is more than twice as high in comparison to other EAF slags. In reference to the minor components, the rather low contents of zinc and lead and the

TABLE 1
Chemical composition of the electric arc furnace slag

Element	*mass%*	*Element*	*mg/kg*	*Element*	*mg/kg*
Fe_2O_3*	30.1	Cu	550	Se	4.4
CaO*	25.0	W	460	Hg	2.6
Al_2O_3*	15.4	K	290	Be	0.94
SiO_2*	15.2	Sr	260	Cd	0.80
MgO*	3.9	Ni	100	Pb	0.71
MnO*	3.6	Nb	89	Tl	< 0.13
Cr_2O_3*	2.4	Zn	60		
TiO_2*	0.76	Mo	38		
P_2O_5*	0.29	Sn	20		
BaO*	0.23	Co	21		
Na_2O*	0.20	Li	16		
S*	0.12	As	7.6		
V_2O_5*	0.08	Sb	6.8		

** Analyses with XRF. LOI = 2.0 mass%*

high content of copper are also noticeable in comparison to other EAF slags (Tossavainen et al., 2007; Fällmann, 2000).

The mineralogical study showed that beta-calcium silicate, gehlenite, calcium-aluminium-silicate, calcium-aluminium-iron-silicate and wuestite type solid solutions, (Mn,Fe,Mg)O, are the main phases in the investigated EAF slag. Commonly reported minerals in low basicity EAF slags such as merwinite and akermanite (Engström et al., 2013) could not be detected while wustite type solid solutions, beta-calcium silicate and calcium-aluminium-iron-silicate have been found mainly in high basicity EAF slags (Mostaghel et al., 2010). The present phases might be a consequence of the lower bulk of magnesium and higher amount of aluminium in the EAF slag.

Mineralogical investigations also showed that chromium is primarily bound within spinel compounds. Based on their chemical composition, two different types of spinels could be found:

- Type I: Aluminium-chromium-magnesium-spinels (Mg $(Cr,Al)_2O_4$) and chromium containing aluminium-magnesium-spinels ($MgAl_2O_4$) with small amounts of iron and manganese,
- Type II: Chromium-manganese-iron-spinels ($(Mn,Fe)Cr_2O_4$).

Type I spinel is quantitatively the main host of chromium. These spinels can be found rather numerously in the siliceous matrix (mainly calcium-aluminium-silicate). They are 10-20 µm in size and show euhedral crystal shape (Figure 1).

The chemical composition of these spinels varies considerably and the content of Cr_2O_3 ranges from 3 to 45 mass%. This variation is particularly caused by a strong chemical zoning; cores are chromium rich, rims are depleted in chromium but rich in aluminium and iron. Figure 2 shows clearly that within the spinels, higher cromium contents correlate with higher aluminium, magnesium and oxygen signals. The dentritic XO-phase (wuestite) is characterised by higher iron, manganese and oxygen signals whereas calcium, silicon and aluminium are mainly bound to silicate phases.

Table 2 shows part of the performed analyses of type I spinel (analyses no 6-13). A similar phenomenon of chromium rich cores occurring alongside chromium depleted magnesium-aluminium-spinels was also found in spinels in natural soil and soil samples (Oze et al., 2007; Kollegger et al., 2007). The zoning is not based on sub-solidus processes (e.g. metamorphic alteration) but evolves in connection with high-temperature melting processes. The average content of chromium oxide of this type I spinel in the investigated EAF slag is 29 ± 14 mass%.

Type II spinel shows high contents of chromium, manganese and iron with an average content of chromium oxide of 65.0 ± 0.6 mass% (Table 2, analyses no 1-5). As is shown in Figure 1, these spinels are only a few µm in size and occur as euhedral inclusions primarily in metallic iron.

The chromium content in other matrix phases (e.g. gehlenite, beta-calcium-silicate, calcium-aluminium-iron-silicate) is insignificant and at the detection limit (0.08 mass% Cr_2O_3).

The potential formation of chromium-containing spinel phases is significantly influenced by the ratio of MgO to chromium due to the equilibrium between MgO-based and $MgCr_2O_4$ solid solutions (Mostaghel et al., 2010). For the investigated EAF slag, the ratio for total content of magnesium to chromium is 1.4 which seems to be ideal for the formation of chromium containing spinels. Mostaghel et al. (2010) claimed that spinel formation in slags is a kinetically controlled process. But the rapid cooling of the investigated EAF slag had no negative effect on the crystallisation or the crystal size of these spinels. Therefore, it can be concluded that the formation of spinels is no issue as long as the ther-

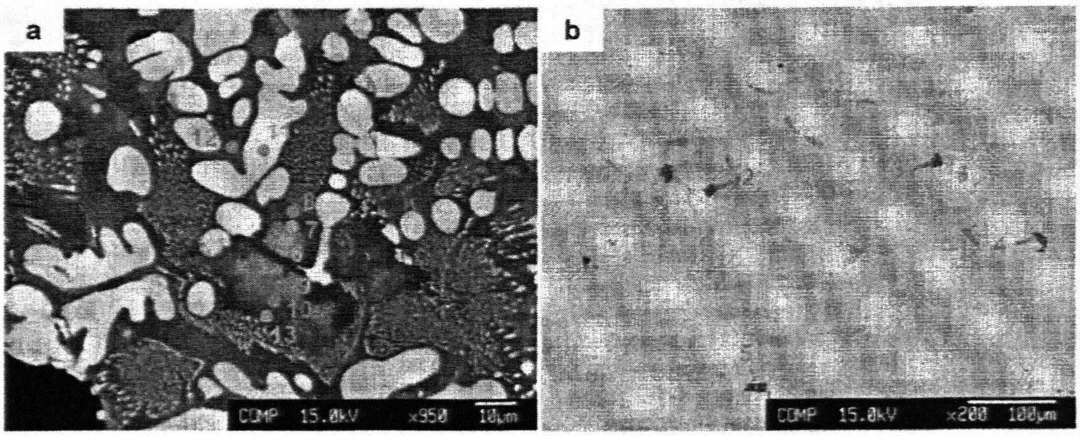

FIGURE 1

Back scattered electron images; a. Type I spinel associated with silicates (12, dark, a gehlenite-type phase) and oxides (11, white grey, a wustite-type phase), another silicate phase contains lots of tiny oxide exsolutions. b. Inclusions of type II spinel (dark grey, euhedral morphology) plus a non-determined phase (medium grey) in metallic iron (bright matrix)

TABLE 2
Electron microprobe analyses of spinels and the matrix (cations calculated based on general spinel form $X_2^{3+}Y^{2+}O_4$), Results in mass%

Anal. #	*SiO_2*	*Al_2O_3*	*Cr_2O_3*	*Fe_2O_3*	*FeO*	*MnO*	*MgO*	*CaO*	*Sum*
1	0.03	-	64.97	1.10	11.55	20.06	-	0.02	97.72
2	0.04	-	66.01	0.74	10.16	21.68	-	0.04	98.68
3	0.12	-	65.09	0.89	10.17	21.46	-	0.04	97.78
4	0.04	-	64.79	1.23	21.59	10.64	0.02	0.03	98.34
5	0.07	-	64.16	1.71	11.62	19.95	-	0.03	97.54
6	0.10	24.68	39.81	3.84	14.26	3.37	11.64	0.39	98.08
7	0.14	45.63	15.09	6.39	13.87	2.87	14.64	0.31	98.92
8	0.85	57.52	3.27	3.35	15.55	2.87	14.81	1.22	99.43
9	0.11	23.33	41.95	3.87	15.36	3.18	11.22	0.40	99.41
10	0.10	50.34	12.15	5.00	14.07	2.74	15.29	0.27	99.95
13	0.14	52.29	10.62	4.41	14.24	2.71	15.49	0.26	100.2

modynamic requirements are met.

Several earlier studies showed that spinel bound chromium in EAF slags is almost insoluble (Tossavainen & Forssberg, 2000). However, doubts remain due to results presented by Oze et al. (2007) who reported the accelerated dissolution of chromite in the presence of birnessite, a common manganese mineral, and the subsequent oxidation of Cr(III) to aqueous Cr(VI). For this reason, the sole determination of the total content of environmentally relevant elements and their mineral phases was considered insufficient for the assessment of the environmental compatibility of the examined EAF slag. The results of the leaching tests were also included in the assessment of the stability of the found spinels, because it is the relationship between mineral sur-

TABLE 3
Leachable components of the electric arc furnace slag at pH 11.8

Element	*mg/kg*	*Element*	*mg/kg*	*Element*	*mg/kg*
Ca	2010	Cu	0.04	W	< 0.005
Al	1980	V	0.03	Nb	< 0.005
K	120	Cr	0.03	Tl	< 0.005
Ba	41	Se	0.03	Li	< 0.005
Na	38	Ni	0.01	Si	< 0.005
Fe	5.9	As	0.01	Be	< 0.005
Sr	4.5	Hg	0.01	Cl^-	10
P	1.3	Sb	0.01	F^-	7.4
Mg	0.97	Si	< 0.005	SO_4^{2-}	52
Mo	0.66	Ti	< 0.005	PO_4^{3-}	0.08
Mn	0.61	Co	< 0.005	S^{2-}	< 1.0
Zn	0.38	Cd	< 0.005	Cr^{6+}	< 0.1
Pb	0.07	Sn	< 0.005		

faces and mobile species in solution that control the potentially soluble content of cations and anions (Raous et al., 2013).

The leachate without any further acid/base addition was rather alkaline with pH 11.8 due to partial dissolution of the slag lime and the closely-related electrical conductivity (69.7 mS/m). High alkalinity is quite common for EAF slag leachates in terms of batch tests and the applied L/S-ratio, as previous work has shown (Fällmann, 2000). The dissolved concentrations for the matrix elements as well as minor components in the leachate are shown in Table 3, expressed as mg/kg of the element dissolved. Although the total contents of Si, Al, Ca, Mn and Ti as well as Cr are high in the EAF slag, the leachability is very low at pH 11.8. Only for Al, Na and Ba approximately 2 mass% of the total content was dissolved for each of the three elements. The soluble content of minor elements is considered to be insignificant. A correlation between the solubility of the major and minor elements is not obvious. As can be seen from Table 3, the leachability for the anions (Cl$^-$, F$^-$, SO_4^{2-}, PO_4^{3-}, S^{2-}) and hexavalent chromium is very low as well.

The addition of acid and base to the conventional leachant (ultra pure water) allowed the preparation of pH-controlled leachates. This way, nine different leachates covering a pH range of 4 to 13 were obtained. Due to a high puffer capacity of the EAF slag, low pH values were only reached using high amounts of concentrated acid (1 M HNO_3) which can hardly ever be reached under realistic conditions. Figure 3 shows the

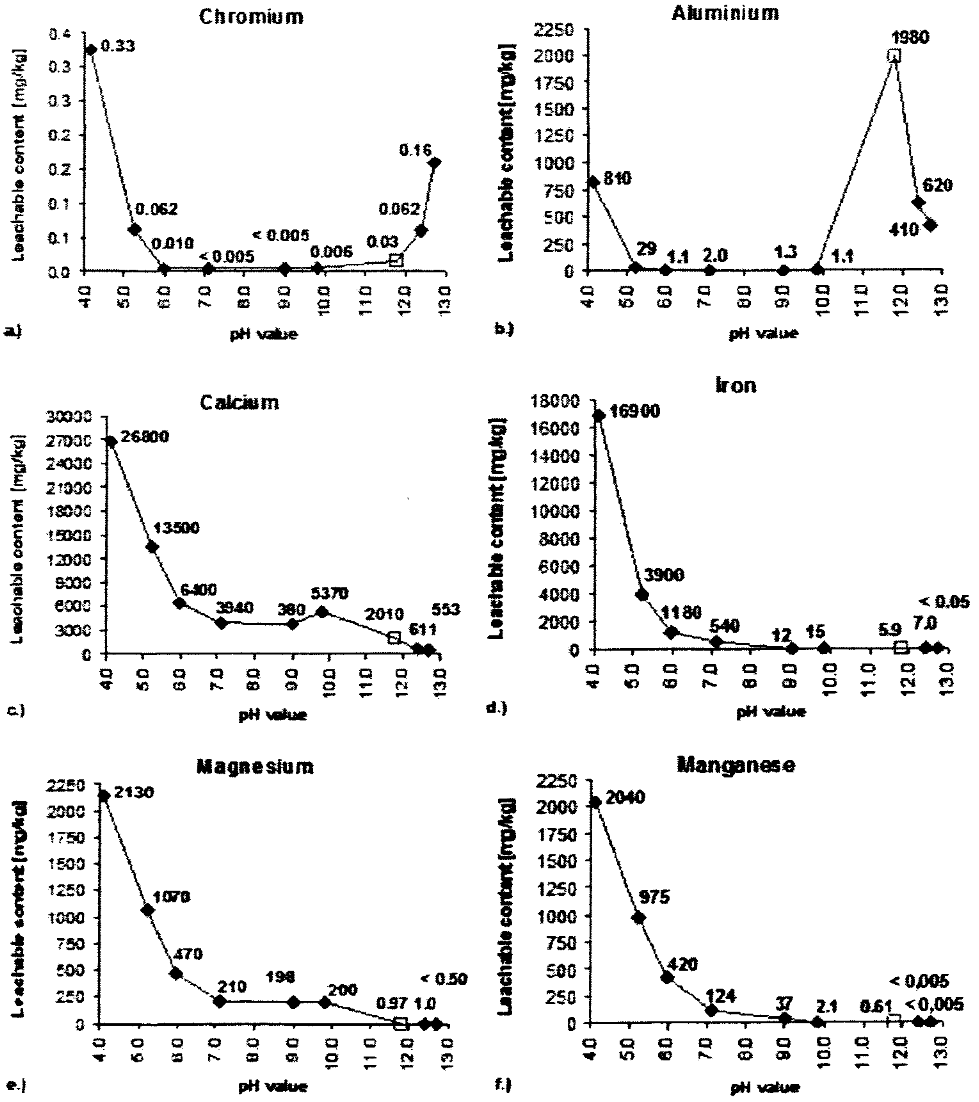

FIGURE 3
pH-dependent leaching behaviour of the main components

soluble content of Al, Ca, Cr, Fe, Mg and Mn, expressed as mg/kg of the element dissolved, as a function of the pH value. The solubility of the major elements (Al, Ca, Fe, Mg, Mn) increases considerably with lower pH values. At pH 4.3 almost 8 mass% of the total content for each of the elements Mg, Fe and Mn are dissolved and 1-3 mass% of the total Al and Ca content. However, the solubility of chromium is very low for the whole pH range and even at pH 4.3 only a percentage of 0.002 mass% of the total chromium content is leachable.

Results from laboratory leaching tests can only be applied to some extent to evaluate the mobility of Cr and other elements from slags under natural conditions because of differences in regard to material amounts and grain sizes, aggregation, L/S-ratios and the nature of the leachant. But normally, laboratory tests overestimate the leaching reaction substantially compared to the actual application because varying degrees of abrasion are more liable to occur when applying batch tests (Bialucha et al., 2012). Therefore, the results from the leaching tests for the investigated EAF slag can be seen as a worst-case scenario.

The phenomenon of high total chromium contents that are almost insoluble can also be found in natural geological settings. Although ultramafic rocks show high chromium contents (634 to 125,000 mg/kg), chromium solubility is generally low since chromium-bearing spinels are insoluble and slowly weathered (Quantin et al., 2008). In ultramafic rocks, chromium is mostly bound within spinels of the chromite series, e.g. chromite, $FeCr_2O_4$. Substitution of Al^{3+}, Fe^{3+} and Ti^{4+} in the octahedral sites and Mg^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} in the tetrahedral sites are, however, very common (Garnier et al., 2008). The reported chromium content of these spinels ranges from 15 to 45 mass% (Raous et al., 2013). Chemically and mineralogically, these naturally occurring spinels are very similar to the spinel type I found in the investigated EAF. A comparison of the main components is shown in Figure 4.

Type II spinel shows clearly higher amounts of Fe and Mn in comparison to natural spinels. The insolubility of the spinels in rocks and soils similar to the composition of type I spinel has been reported several times (Raous et al., 2013; Garnier et al., 2008). As an example, in stream sediments in the Kraubath massif in Austria, very high concentrations of chromium bound within spinels were found, but due to their insolubility no negative effect on the water quality was observed so far (Kollegger et al., 2007).

CONCLUSION

The utilisation of EAF slags as e.g. road construction material depends significantly on their pollutant potential which can be best characterised by their mineralogical properties and leaching behaviour, especially with regard to hazardous substances (e.g. Cr^{6+}). In the course of this contribution, a quality assured EAF slag from an Austrian steel producer was characterised chemically and mineralogically in regard to chromium. Although the total chromium content is 1.7 mass%, the mineralogical characterisation with an electron microprobe showed that chromium is bound mainly within two types of spinel phases ($Mg(Cr,Al)_2O_4$ and $(Mn,Fe)Cr_2O_4$). The chromium content in the accompanying silicate phases (i.a. gehlenite) is insignificant. Spinels of the chromite series similar to those occurring in EAF slags are common in natural environments; i.e. mafic and ultramafic rocks and soils formed by weathering processes of such rocks. In these settings chromium is practically insoluble and fixed as Cr^{3+} in the spinel structure. Leaching tests performed on the EAF slag supported the mineralogical findings; it was shown that even at low pH values, almost no chromium could be leached.

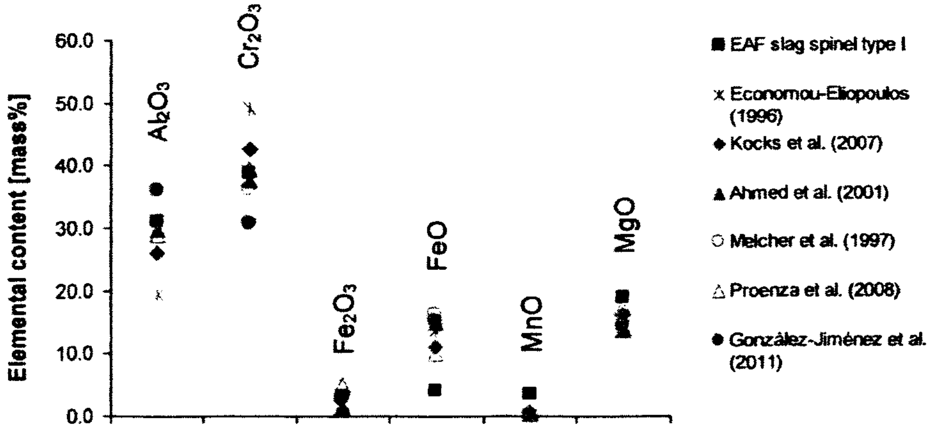

FIGURE 4
Comparison of type I spinel found in the EAF slag with naturally occurring spinels in soils and mafic-ultramafic rocks

ACKNOWLEDGMENTS

The authors would like to thank Marienhütte Stahl- und Walzwerk GmbH for providing the investigated EAF slag. H. Mühlhans is thanked for assistance with the electron microprobe analyses.

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