

The effects of cooling rate on leaching behavior of some ferrous and non-ferrous slag systems

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Abstract: Numerous investigations have been carried out over the last several decades to clarify the influence of cooling rate on microstructure and properties of the slag systems; however, there is controversy in the literature as to the effect of rapid cooling, e.g. water granulation, on release of potentially toxic elements. In the current work, a ladle slag, a basic oxygen furnace (BOF) slag, two different electric arc furnace (EAF) slags, from low-alloyed and high-alloyed steel production, and three different “fayalite-type” slags, from zinc-copper smelting processes with different Fe/SiO₂ ratios, are investigated. Semi-rapidly solidified (in crucible system) and water granulated samples for each composition were prepared. The solidified materials were characterized using commonly applied characterization techniques. The experimental work is compared with thermodynamic calculations using the FactSage™ thermodynamic package. Standard European leaching tests were carried out for all samples to investigate the slag leaching behaviors. Results show that rapid solidification and generated amorphous structure do not necessarily immobilize environmentally concerned elements in the glassy network. Instead, due to several factors, a higher reactivity is observed and trace elements dissolve more readily in the aqueous solution. The main reasons behind such a behavior including higher contents of metastable phases, different surface structures, oxidation and increased amount of grain boundaries are thoroughly discussed.

Key words: Leaching behavior, Pyrometallurgical slags, Water granulation, Semi-rapid solidification

1. Introduction

Since the population density in Sweden is quite low, while the country is relatively rich in natural material resources, the demand for using waste and by-product materials in construction has not been very strong. However, public policy calls for a reduction of the total amount of waste to be landfilled. New regulations, including higher landfill tax and stricter laws for environmentally safe landfilling, prompt industries to adopt alternative applications for their generated waste materials; therefore, assessment of leaching behavior of the pyrometallurgical slags is of much interest to metal producers.

The solubility of elements from the metallurgical slags is dependent on major phases' solubility, whereas presence of different phases in the material depends on the chemical composition and cooling condition. In other words, these parameters indirectly govern the material leaching behavior. It is generally accepted that rapid cooling or water quenching results in a glassy or amorphous structure, while slow cooling provides a crystalline material. Earlier work has shown that besides the cooling condition, basicity also plays an important role in the crystalline fraction of the material [1, 2]. It is generally known that formation of an amorphous structure is easier in an acidic slag. However, the question as to how rapid cooling influences leaching behaviors is still a controversial issue.

Vitrification has been proven to be a successful pretreatment technique for encapsulation of the hazardous elements and reduction of their leachabilities in different types of waste materials including bottom ash from the municipal solid waste incineration (MSWI) [1, 3, 4], hospital waste [5], electroplating sludge [2] and copper flotation waste [6]. Some investigations have shown that water quenching and thereby producing an amorphous structure from EAF slags [7] and base metal smelter slags [8], would also reduce the leachability of most of the elements. However, Gislason and Arnorsson [9] have investigated dissolution of primary basaltic minerals in natural water and shown that, since glass thermodynamically has a higher internal energy, basaltic glasses dissolve more readily than basaltic minerals in water. Kierczak et al. [10] have experimentally studied the mineralogy and weathering of slags from treatment of Ni-containing ores in Poland and shown that crystalline minerals are more stable than the glassy materials. This statement has been supported by some other researchers [11-13].

The aim of this work, therefore, is to compare the leaching behaviors of semi-rapidly and rapidly cooled samples from some ferrous and non-ferrous metal production slags to clarify the influence of water granulation on leachabilities of different elements.

2. Experimental

A ladle slag, a basic oxygen furnace (BOF) slag, two different electric arc furnace (EAF) slags from high-alloyed and low-alloyed steel production, and three different “fayalite-type” slags were investigated. The fayalite-type slags were mixtures of an industrial zinc-copper production slag with different additives to obtain Fe/SiO₂ ratios equal to 1.35, 1.10, and 0.65. These samples are named slags 1-7, respectively. The chemical compositions of the steel slags were analyzed using inductively coupled plasma emission spectroscopy, (ICP), and X-ray fluorescence spectroscopy, (XRF). The Fe and FeO concentrations were determined using titration, while that of carbon and sulfur were determined by using infrared adsorption spectroscopy, (IR). The chemical composition of the fayalite-type slags were analyzed by using inductively coupled plasma methods (ICP-AES and ICP-SFMS). All chemical compositions are shown in table 1. Slag samples were re-melted by an induction furnace. To avoid excessive reaction between refractory materials and the slags with various chemical compositions, different types of crucibles were used; a graphite crucible for slag 1, magnesium oxide crucibles for slags 2-4, and alumina crucibles for slags 5-7. All slag samples were treated by semi-rapid cooling (in crucible system) and rapid quenching by water granulation. For semi-rapid cooling, after the final isothermal step at the chosen maximum temperature for each slag, the samples were left in the furnace to be cooled down to room temperature; the approximate time to obtain a completely solidified material was about 3 hours. For rapid quenching, two sets of granulation units were designed (figure 1). After obtaining the liquid phase, the furnace was tilted to pour the molten slag into a granulation box. High pressure water jets (25 °C) were used to break the stream of the molten slag into small droplets (particle size of 2-4 mm), which resulted in rapidly quenched granules. The required time for granulation was less than a minute. The glass content of the granulated steel slags was analyzed according to the ER-9103 method (Scancem Research AB, Sweden) using an optical microscope.

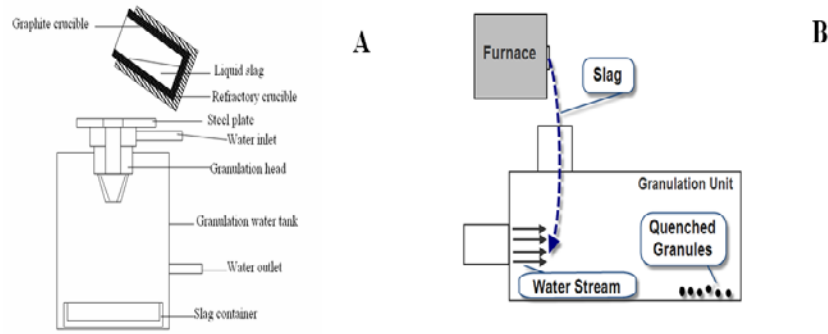


Fig. 1: Water granulation units used for: A) steel slags B) fayalite-type slags

X-ray diffraction (XRD, Siemens D5000 diffractometer with Cu-K α radiation) and scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS, Philips XL 30) were applied for characterization of the materials. The experimental characterizations were compared with stable phases at equilibrium condition by using the FactSageTM thermodynamic package [14]. For leaching tests, all samples were crushed to a particle size of <4 mm and specific surface areas were determined according to BET-method with a micrometric flowsorb 2300. The samples were then leached according to a standard one-stage batch leaching test EN 12457-2 [15] with liquid to solid ratio of 10, except for two samples, ladle slag (slag 1) and granulated EAF slag (slag 3), which were leached according to the two-stage batch test EN 12457-3.

Table 1: Chemical composition of the investigated slags

Steel slags	%							ppm							
	Fe ₂ O ₃	FeO	Al ₂ O ₃	CaO	MgO	MnO	SiO ₂	Cr	Mo	Zn	Ni	Cu	V	K	Na
Slag 1	1.1	0.5	22.9	42.5	12.6	0.2	14.2	2700	280	370	70	20	280	80	<20
Slag 2	10.9	10.7	1.9	45	9.6	3.1	11.1	506	39	37	25	8	14800	220	<10
Slag 3	1	3.3	3.7	45.5	5.2	2	32.2	32700	500	130	3180	140	310	590	150
Slag 4	20.3	5.6	6.7	38.8	3.9	5	14.1	26800	70	260	90	160	1700	<20	<20
Fayalite-type slags	"Fe ₂ O ₃ "*	Na ₂ O	Al ₂ O ₃	CaO	MgO	MnO	SiO ₂	Cr	Mo	Zn	Ni	Cu	V	As	Pb
Slag 5	56.7	0.4	11.7	4.7	1.6	0.6	29.4	2940	1130	13800	294	6480	57	88	313
Slag 6	53.9	1.1	5.8	5.0	1.6	0.6	34.4	1800	1190	15400	285	6500	41	147	7050
Slag 7	40.1	3.0	5.0	4.2	1.4	0.5	42.9	793	854	10500	192	3710	29	148	12300

* Total analyzed iron is reported as Fe₂O₃

3. Results

Figure 2 shows the XRD patterns of all samples. It is evident that fayalite-type slags became almost completely glassy as a result of water granulation. Among the steel slags, only the ladle slag (slag 1) shows an amorphous structure after water quenching. The glass content of different steel slags after granulation were measured as 98%, 1%, 17% and 1% for slags 1-4, respectively, which confirms the observations made by XRD. In addition to phase identification made by using the XRD patterns (for the sake of simplicity, identified phases are not presented in the figures), the characterization was complemented by using EDS mapping and point analyses. A couple of examples of the results are shown here. Figure 3

and 4 show the EDS mapping of the semi-rapidly cooled EAF slag, from high-alloyed steel production (slag 3), and one of the fayalite-type slags (slag 5), respectively. The experimental results were confirmed and supplemented by thermodynamic calculations. Figure 5 shows the calculations made for the BOF slag (slag 2) and EAF slag (slag 3). The major minerals in the ladle slag (slag 1) are mayenite, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, followed in order by free MgO . $\beta\text{-Ca}_2\text{SiO}_4$, $\gamma\text{-Ca}_2\text{SiO}_4$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ were also identified. The β -form may undergo a phase transformation during cooling at $400\text{-}500^\circ\text{C}$ to γ -form and the volume increase ($>10\%$) causes a pulverization of the slag [16]. The expansive $\gamma\text{-Ca}_2\text{SiO}_4$ is a plausible explanation for the disintegration.

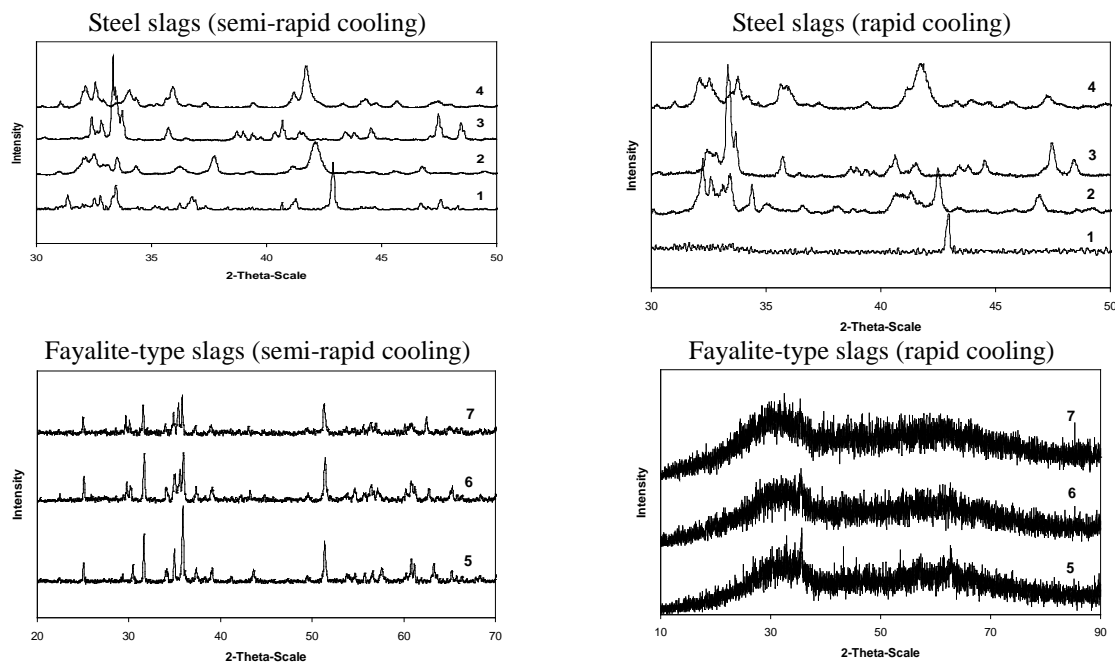


Fig. 2: XRD patterns of the investigated slags, with different cooling conditions

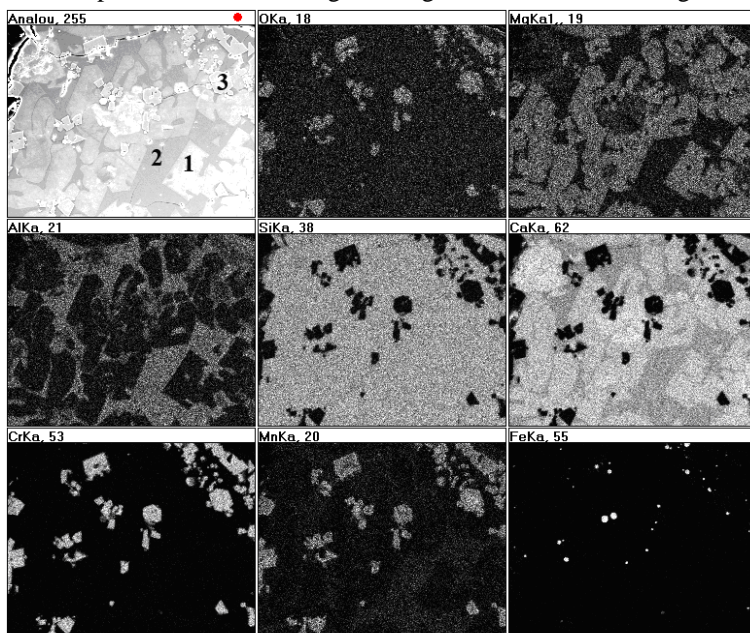


Fig. 3: EDS mapping of the semi-rapidly cooled slag 3 (1) Calcium magnesium silicate, (2) Calcium alumina silicate, (3) Chromium containing spinel

The semi-rapidly cooled BOF slag (slag 2) mainly consists of larnite, β - Ca_2SiO_4 and MgO grains. Parts with high co-existence of iron, manganese and magnesium were distinguished, most probably (Fe,Mn,Mg)O spinel-type solid solution. For slag 3, merwinite, $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, γ - Ca_2SiO_4 , and a spinel solid solution, $(\text{Mg,Mn})(\text{Cr,Al})_2\text{O}_4$ were identified as the main minerals. A small amount of calcium aluminum silicate phase was also detected using EDS maps. Based on the thermodynamic calculations, this phase was identified as gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$). Gehlenite is thermodynamically formed at lower temperatures (below 1270°C) according to the calculations. The late crystallization of gehlenite agrees with the observed texture of this sample i.e. this phase was crystallized between merwinite and spinel phases, characterized by sharp edges.

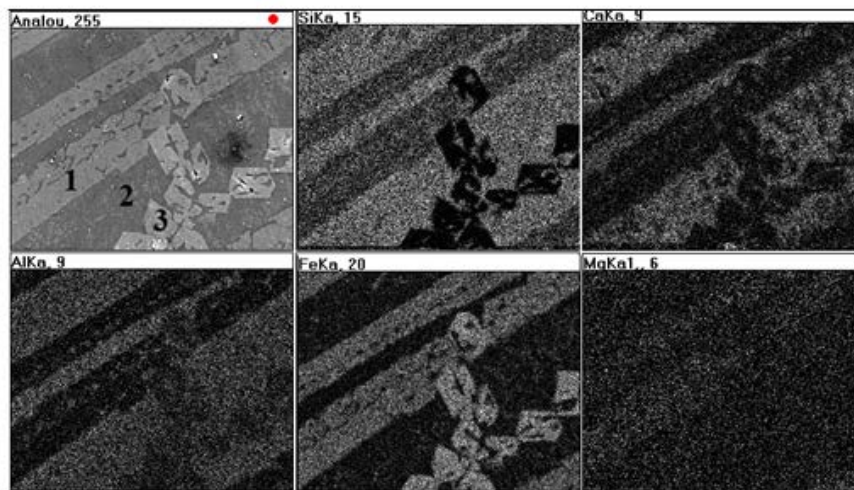


Fig. 4: EDS mapping of the semi-rapidly cooled slag 5 (1) olivine (2) pyroxene (3) spinel

The low-alloyed EAF slag (slag 4) is very complex and some phases have varying content of substituted ions. The identified main mineral in this sample is β - Ca_2SiO_4 . A wustite-type solid solution $((\text{Fe,Mg,Mn})\text{O})$, $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$ and Fe_2O_3 were also identified. All the fayalite-type slags (slags 5-7) consist of olivine (mainly fayalite Fe_2SiO_4), pyroxene-group minerals (including augite, $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$, petedunnite, $\text{CaZnSi}_2\text{O}_6$, hedenbergite, $\text{CaFeSi}_2\text{O}_6$, esseneite, CaFeAlSiO_6 , and ferrosilite, $\text{Fe}_2\text{Si}_2\text{O}_6$), and spinel solid solutions. By water granulation, slags 1 and 5-7 became almost completely glassy. The other slags (slags 2-4) were still crystalline after water quenching; however, the mineralogical characteristics of these samples were changed. Such changes in phase distribution and chemical composition of the solid solutions definitely affect these samples' leaching behaviors. For example, the main mineral in the granulated BOF slag (slag 2) was identified as Ca_3SiO_5 . This phase exists at high temperatures, and is liable to transform on cooling to Ca_2SiO_4 and lime [17]. Quick cooling [16, 18] as well as presence of impurity ions [19] prevent formation of γ - Ca_2SiO_4 .

The analyzed concentrations of the elements in the leachates were used to calculate the γ -factor. This factor is defined as the leached amount of an element from the rapidly-cooled sample over that of the semi-rapidly cooled corresponding sample and shown in table 2. It is evident that most of the environmentally hazardous elements have leached in higher quantities due to the rapid cooling as opposed to semi-rapid cooling.

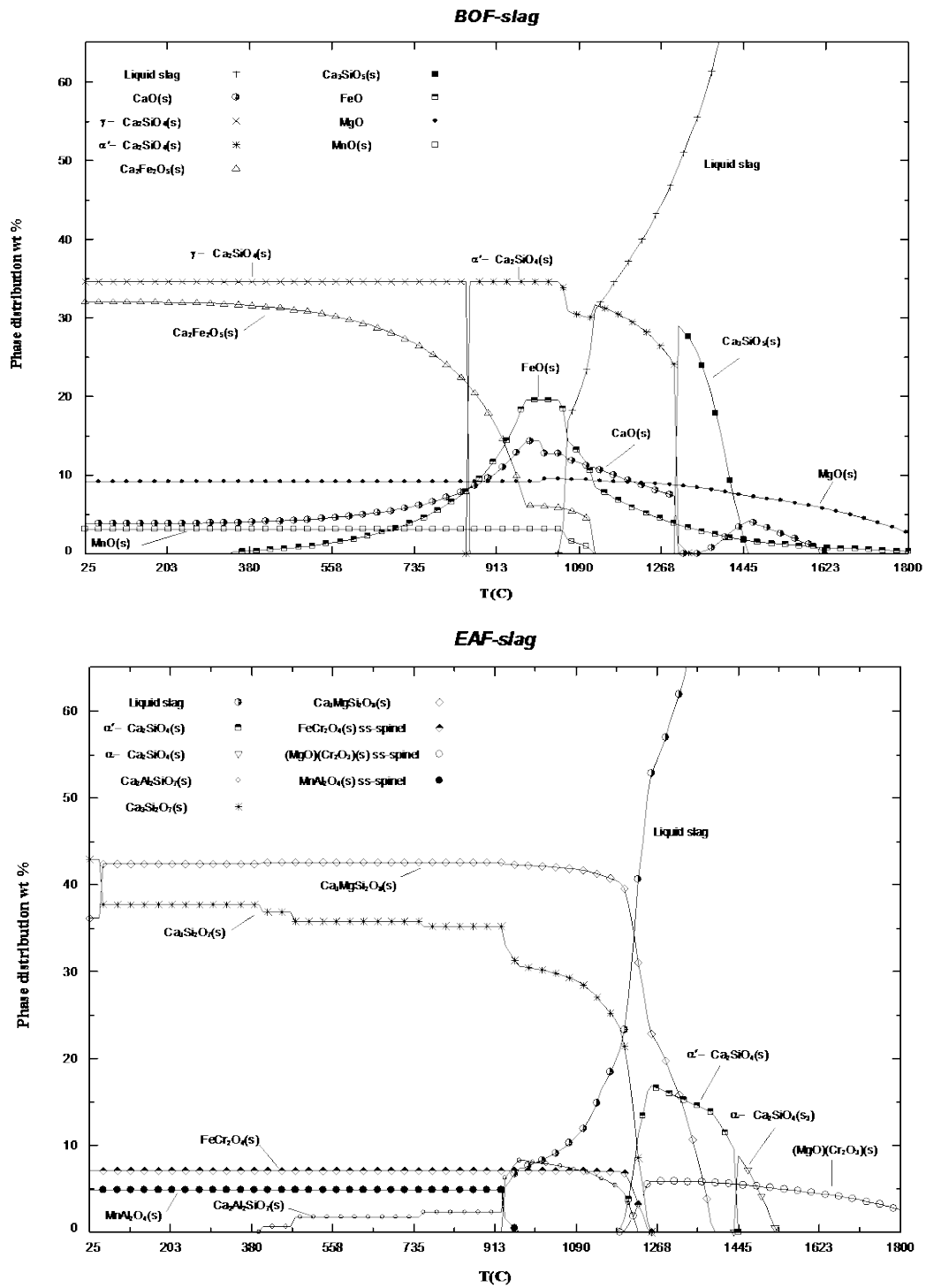


Fig. 5: Thermodynamic calculations for BOF slag (slag 2) and EAF slag (slag 3)

Table 2: The ratio of leached amount from rapidly cooled samples over that of semi-rapidly cooled samples

Steel slags	γ-factors										
	Ca	Mg	Fe	Si	Al	Cr	Mo	V	-	-	-
Slag 2	0.47	Nd	Nd	4.19	0.08	4	1	11	-	-	-
Slag 3	0.71	1.97	Nd	0.94	0.53	1.13	0.64	0.11	-	-	-
Slag 4	0.27	Nd	0.74	46.66	0.11	475	20	125	-	-	-
Fayalite-type slags	Ca	Mg	Fe	Si	Al	Cr	Mn	As	Pb	Cu	Zn
Slag 5	0.52	2	6.79	0.7	0.28	0.18	6.75	0.09	2.89	10.91	10.81
Slag 6	0.25	2.34	7.37	1.11	0.06	Nd	5.6	0.18	8.49	7.16	3.57
Slag 7	0.17	1.58	0.56	0.75	0.02	Nd	8.07	0.07	7.86	4.53	32.04

The leaching solution of semi-rapidly cooled ladle slag (slag 1) was not possible to filter, which might be due to cement-forming properties of the slag. However, the release of elements was not prevented by rapid quenching. Leaching is generally characterized as a surface reaction, followed by a solid-solid diffusion process. Therefore, to gain a better understanding of the leaching behavior of the differently cooled slags, a reactivity factor- α was introduced and calculated according to equation (1).

$$\alpha = \frac{\text{Leached amount}}{\text{Specific surface area}} = \frac{(\text{mg}) \text{ leached from } (\text{kg}) \text{ dry material } (\text{mg}/\text{kg})}{\text{m}^2/\text{kg}} = \text{mg}/\text{m}^2 \quad (1)$$

As an example, the reactivity ratio of the rapidly and semi-rapidly cooled samples from slag 2 is given in table 3. Accordingly, the leachability of almost all elements shows an increase after water quenching.

Table 3: A comparison between reactivity factor- α of slag 2

Element	Semi-rapid cooling	Rapid cooling	(Rapid)/(Semi rapid) %
Ca	1.87E+00	9.86E+00	526%
Si	6.34E-03	2.98E-01	4694%
Al	8.15E-03	7.76E-03	95%
Cr	3.29E-06	1.74E-04	5284%
Mo	2.79E-05	3.11E-04	1117%
V	2.98E-04	3.67E-02	12317%

4. Discussion

As was expected, basicity influences glass formation considerably. According to Daugherty et al. [20], an acid slag with M_b factor $(\text{CaO}+\text{MgO}/\text{SiO}_2+\text{Al}_2\text{O}_3)<1$ produces a glassy material more readily compared to a more basic slag when cooled rapidly. This statement is confirmed by the current investigation. Among the steel slags, the most acidic one is the ladle slag (slag 1), which showed almost a complete amorphous structure (98%) after water granulation. The only observed peak in its XRD pattern, which represents a crystalline phase, corresponds to unassimilated MgO. Presence of these fragments could be confirmed by SEM images (figure 6). According to the thermodynamic calculations, the MgO crystallization from the liquid ladle slag already starts at approximately 1800°C. Only ~38% of the total MgO content is

present in the liquid slag at the experimental re-melting temperature in this study (1400°C). The remaining 60% has already been crystallized as pure MgO. The fayalite-type slags are relatively more acidic and all three of them become amorphous by water granulation. Comparing the leaching behaviors of the rapidly and semi-rapidly cooled samples (tables 2 and 3) most of the elements of environmental concern have leached in higher quantities when slags were cooled faster.

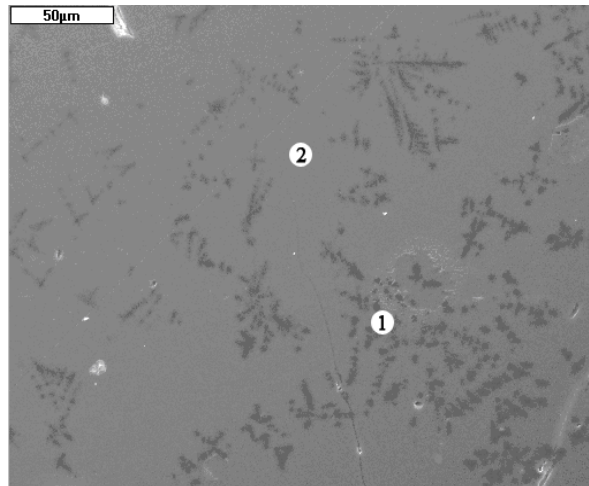


Fig. 6: SEM picture of the water granulated ladle slag. Dark fragments of (1) MgO in a matrix (2) with high content of calcium, silicon and aluminum (glass)

Loncnar et al. [7] reported a decrease in Ca and Al leachability due to the water cooling of the EAF slags; however, they observed that Si and Mg have leached more after modification. Their observation agrees rather well with findings concerning the EAF slags (slags 3 and 4) of the current study. Both these samples show γ -factors < 1 for Ca and Al, but γ -factors for Mg and Si vary oppositely in these two samples. Loncnar et al. [7] reported an increase in Cr and Mo leachability after water cooling in three of their four investigated EAF samples. Similar trends can be seen in the current study. Among the hazardous elements in the fayalite-type slags, water granulation led to a decrease in leachability of As and Cr; whereas, Pb, Cu, and Zn have leached in much higher quantities than the semi-rapidly cooled samples. It is believed that such a behavior originates from a higher reactivity of the rapidly cooled samples, which depends on the following factors.

1. Oxidation: during the rapid cooling with water, oxidation on the surface may occur, which leads to formation of soluble phases.
2. Surface structure: when a phase can be formed thermodynamically, the crystal size depends on the temperature to which the crystals are exposed and the duration of the exposure. For instance, a significant difference could be observed between the crystal sizes of the two modified BOF slags. The size of the crystals present in the semi-rapidly cooled slag varied between 40-200 μm , indicating that these minerals have had more time to grow. In the rapidly cooled BOF slag, the variation in crystal size is more pronounced compared to the semi-rapidly cooled sample. The existing wustite-type solid solution and the tricalcium silicate had a crystal size varying between 20-100 μm . The matrix had a much smaller size than the other two phases mentioned. The reason is simply the lack of time for development of large crystals. Based on the thermodynamic calculations, it can be

concluded that both the wustite-type solid solution and the tricalcium silicate were present in the liquid slag at the time the rapid cooling with water was carried out. However, α - Ca_2SiO_4 is expected to form during rapid cooling with water. Similar changes in grain size due to the different cooling conditions were observed in some other samples as well. Presence of smaller grains results in an abrasive surface, which tends to be more reactive than a plane surface, due to the increased vapor pressure that occurs over a convex surface.

3. Increased amount of grain boundary: fast cooling will result in more grain boundaries due to the increase in the number of small crystals in the material. Diffusion reactions are known to occur easier and faster along the boundaries.
4. Metastable phases: metastable phases that may form as a result of water quenching are prone to react with the aqueous solution, to reach stability. Products of such reactions may be more soluble and cause higher leachability from these samples.
5. Formation of a glassy structure: amorphous structures that may form as a result of quenching show an increased solubility in water due to their relatively higher internal energy.
6. Changes in chemical composition of solid solutions: mineralogical characterization of the samples with different cooling conditions show that, although in some samples rapid cooling did not lead to formation of an amorphous structure, the chemical compositions of the existing solid solutions have been changed. As an example, the composition of the wustite-type solid solution is different when comparing the semi-rapidly and the rapidly cooled BOF slag. As was mentioned, according to the thermodynamic calculations, figure 5, MgO is already present as crystals in the liquid slag at 1600°C. The slight shift in position of the corresponding peak in the XRD diffractogram is explained in terms of having a higher concentration of MgO in the wustite-type solid solution. As the slag is cooled rapidly, neither the FeO nor MnO had the same possibility of crystallizing and forming solid solution with MgO, due to their later crystallization in comparison to MgO, figure 5. The latter was further confirmed by the examinations with the SEM instrument. According to semi-quantitative analyses, the solid solution contains 51% MgO, 42% FeO and 7% MnO, in the semi-rapidly cooled slag, while the solid solutions in the rapidly cooled slag were made up of 78% MgO, 16% FeO and 6% MnO.

The current results show that water granulation, as a tool for leaching minimization of slags, cannot be applied generally for all elements in slags with all chemical compositions. It is necessary to identify the specific hazardous element in each type of slag (for example, Cr in steel production slags or As, Pb, and Zn in base metal production slags) and design a specific treatment technique applicable for the desired process. The first possible alternative to reduce leachability of a metal is to stabilize it into a durable mineral such as spinel. However, there are some limitations with this method that preclude its general application. As an example, in order to save refractory materials and create a foamy slag in the EAF processes, slags are often saturated with MgO, meaning that solid particles of MgO will be present in the liquid slag. The crystallization 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 MgCr_2O_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 is 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 dissolve [16, 21]. Therefore, other measures should be taken to overcome such a limitation. 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 complete solubility in each other. Investigations have shown that the composition of the wustite-type solid solution in slag will vary with the rate of cooling. A rapid cooling rate 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% Cr₂O₃ systems have shown the importance of the iron oxide concentration on the leaching behavior of chromium from the wustite-type solid solution. As shown in figure 7, 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.

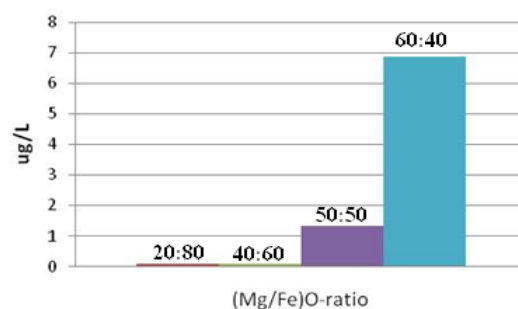


Figure 7: Cr leaching as a function of (Mg:Fe)O composition

5. Conclusions

The final properties of the slag are strongly affected by the temperature at which the cooling starts as well as the cooling conditions. By water granulation of the slags, there would not be sufficient time for crystals to grow, and slags with lower basicity or M_b factor form an amorphous structure more readily than the basic slags. Rapid cooling will also enhance the formation of metastable phases at low temperatures, which are more reactive in the aqueous solution, to reach stability. The leaching of environmentally hazardous elements (Cr from steelmaking slags and Pb and Zn from base metal production slags) are not necessarily prevented by rapid quenching. It is needed to identify the specific element of environmental concern in a certain slag, and design a particular pretreatment technique to immobilize it.

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