

INFLUENCE OF WATER ON SLAGS

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Abstract

The search for possibilities of slags utilisation, produced by various metallurgical plants, is relevant mainly due to its connection with circular economy and environmental protection. Using slags in construction or other fields of the industry is closely related to their properties and behaviour in contact with water. In the presented study, slags of different technological origins were studied: blast furnace slags (non-granulated and granulated) and ladle slags. Fresh samples of slags (max. 20 days old) and stored slags in landfills were taken from each type of slag. After sampling, the samples were adjusted to the same grain size ($<0.1 \mu\text{m}$) and their chemical and phase composition were determined. At the same time, aqueous leachates were prepared under defined conditions with different solid to liquid phase ratios. The pH value of water leachates were measured. The concentrations of Ca, Al, and Si were determined using atomic absorption and emission spectrometry. The determined values were analysed in relation to the phase and chemical composition of individual solid slag. The kinetic study performed on the selected slags showed that the contact time of the slag with water may not always lead to the release of a larger amount of cations to the leachate.

Keywords: Blast furnace slag, ladle slag, water leaching, phase changing

1. INTRODUCTION

Iron and steel are still basic engineering materials for industry. Their production is connected with special type of waste, some of which are recyclable and therefore are a fundamental fraction of the circular economy. The 91.5 % of produced 36.3 Mio tons of slag in 2020 were utilised primarily in road and cement industry. But remaining fraction of slags are deposit on landfill and they can negatively affect environment. In the future, the blast furnace and steelmaking slag can be used in others specific industry as adsorbents, basic for wearer of catalytic substances, filler in composites, binder etc. [3-8]. The research importance into the further slag application demonstrated by statistic on European projects dealing with above mentioned topic .

Slags are very often affected by water and therefore change their properties, change phase composition. Authors usually study leaching pollutants from slags as e.g. Cd, Cr, Hg, Ni or Zn [10-12] to describe their effect on environment. The interaction of basic slag compounds with water was in foreground as well [13-16]. The main goal of this study was described influence of water to dissolution major elements contained in slags produced in steelmaking process and were or not were landfilled or modified by granulation. The second goal was identified the dissolved phase and the time dependence of dissolution of the major slag compounds.

2. MATERIALS AND METHODS

Slag samples were collected from iron and steel industrial production by partners from Moravian-Silesian region. The list of used samples of slags shows **Table 1**.

Table 1 Slag samples description

Sample of slag	Slag description
BS1	Ungranulated blast furnace slag, fresh, unsorted, landfilled
BS2	Ungranulated blast furnace slag, one year old, unsorted landfilled
BS3	Granulated blast furnace slag, fresh, unsorted, landfilled
LS1	Ladle slag without magnetic separation, fresh
LS2	Ladle slag after magnetic separation, fresh
LS3	Ladle slag without magnetic separation, , one year old, landfilled
LS4	Ladle slag after magnetic separation, one year old, landfilled

Dried samples of slags were crushed and samples were prepared with a mesh diameter below 10 mm.

Samples were crushed and ground to particles less than 60 µm and the standard tablets were prepared using laboratory hydraulic press (BRIO Hranice s.r.o.). Content of free CaO were determined using ČSN EN 451-1.

The X-ray powder diffraction (XRPD) patterns were recorded under CoK α irradiation ($\lambda = 1.789$ nm) using Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with fast position sensitive detector VANTEC 1. Measurements were carried out in reflection mode, powder samples were pressed in rotational holder. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

Leachates of slags were prepared by methods based on European technical standard EN 12457-2 . Slags leachates were prepared with grain size samples smaller than 10 mm in deionized water (DW, pH 6.8) at different liquid:solid ratio (L:S): A-1:10, B-1:100, C-1:250, D-1:500, E-1:1000. The kinetic study was performed on the selected slags (LS2 and LS3) at ratio L:S=B (1:100).

The suspension was shaken in continuous rotation container by head-heel system for defined time 24 hours. The leachate was separated by vacuum filtration using 0.4 µm pore size filter (Pragopor 6). The pH in leachate were measured by inoLab SenTix 41 immediately after filtration. The fraction of leachate was stabilized with HNO₃ (65 %, p.a.) to pH 2 for metal cations determination. The concentrations of Al, Ca, and Si were determined by inductively coupled plasma emission spectrometry SPECTRO VISION EOP (US EPA method 6010D (SW-846), 2014).

The amount of remove elements during leaching were calculated using determinated concentration of elements in leachate according to the formula:

$$q_i = \frac{V \cdot C_i}{m_i} \cdot 1000 \quad (1)$$

where:

q_i - removed amount of element during leaching test (mg/kg)

V - volume of the deionized water (L)

C_i - concentrations of the metal ions in the leachate (mg/L)

m_i - amount of slag for leaching test (g).

The relative removed fraction of element - $Re(i)$ - expressed in % was calculated by formula:

$$Re(i) = \frac{q_i}{Q_i} \cdot 100 \quad (2)$$

where:

Q_i - content of element in solid slag before leaching (mg/kg).

3. RESULTS AND DISCUSSION

The content of major elements expressed in oxides and content of the free CaO summarized **Table 2**. Content of K and Na expressed in oxides is low than 0.5 wt. %, TiO₂ (as content Ti) is lower than 0.7 wt. %, P₂O₅ (as content P) is lower than 0.05 wt % in all studied slags. The principal difference in used samples are in content of CaO and SiO₂.

Table 2 The content of major elements in slag samples determined by XRFs expressed in oxides and determined the free CaO

Element	Content of elements in slags (wt%)						
	BS1	BS2	BS3	LS1	LS2	LS3	LS4
Al ₂ O ₃	6.70	5.96	6.21	14.1	8.19	19.1	15.9
CaO	36.1	39.6	38.1	62.4	69.8	51.0	51.6
Fe ₂ O ₃	2.76	1.76	1.63	2.90	3.72	3.72	3.01
MgO	11.1	9.30	11.5	2.57	2.35	3.52	5.51
MnO	0.500	0.559	0.529	2.22	2.68	2.68	2.19
SO ₃	1.26	1.33	1.26	1.17	0.852	0.887	0.82
SiO ₂	36.7	37.8	39.1	5.68	5.14	9.26	11.9
Free CaO	<0.10	<0.10	<0.10	0.96	1.88	1.19	1.52

Determination uncertainty: Al₂O₃ 12 %, CaO 8 %, Fe₂O₃ 6 %, MgO 12 %, MnO 5 %, SiO₂ 9 %, SO₃ 10 %, P₂O₅ 8 %, TiO₂ 10 %, Cr₂O₃ 30 %, Na₂O 25 %, K₂O 6%, and free CaO 10 %.

Calculated values of the relative removed fraction of Al, Ca, and Si during leaching process and resulting pH value of leachate of blast furnace slags show **Figure 1**.

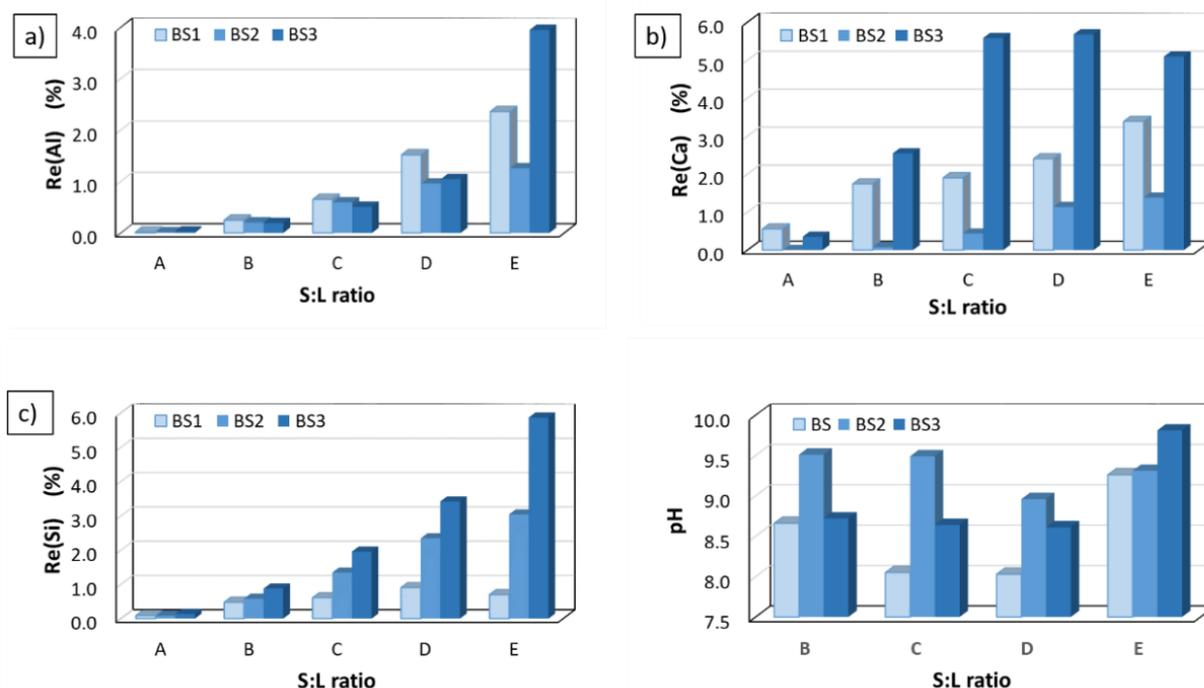


Figure 1 Relative removed fraction of Al (a), Ca (b), and Si (c) during leaching blast furnace slags and pH (d) of leachate

In contrast to the blast furnace slags, the ladle slags have strong basic character, which is reflected in the resulting pH of leachate (as show **Figure 2d**). The S:L ratio have not significant effect on pH of individual slag. **Figure 2 a,b,c** show the calculated value of the relative removed fraction of Al, Ca, and Si during leaching process of leachate of ladle slags without or with magnetic separation. It is obvious that Al compounds was dissolved in DW very intensively from fresh slags in comparison with landfilled slags. It means that the Al-containing phase was almost completely dissolved. The value of relative removed fraction of Al, Ca, and Si from fresh ladle slags proved, that fresh slag dissolved more intensively than deposited.

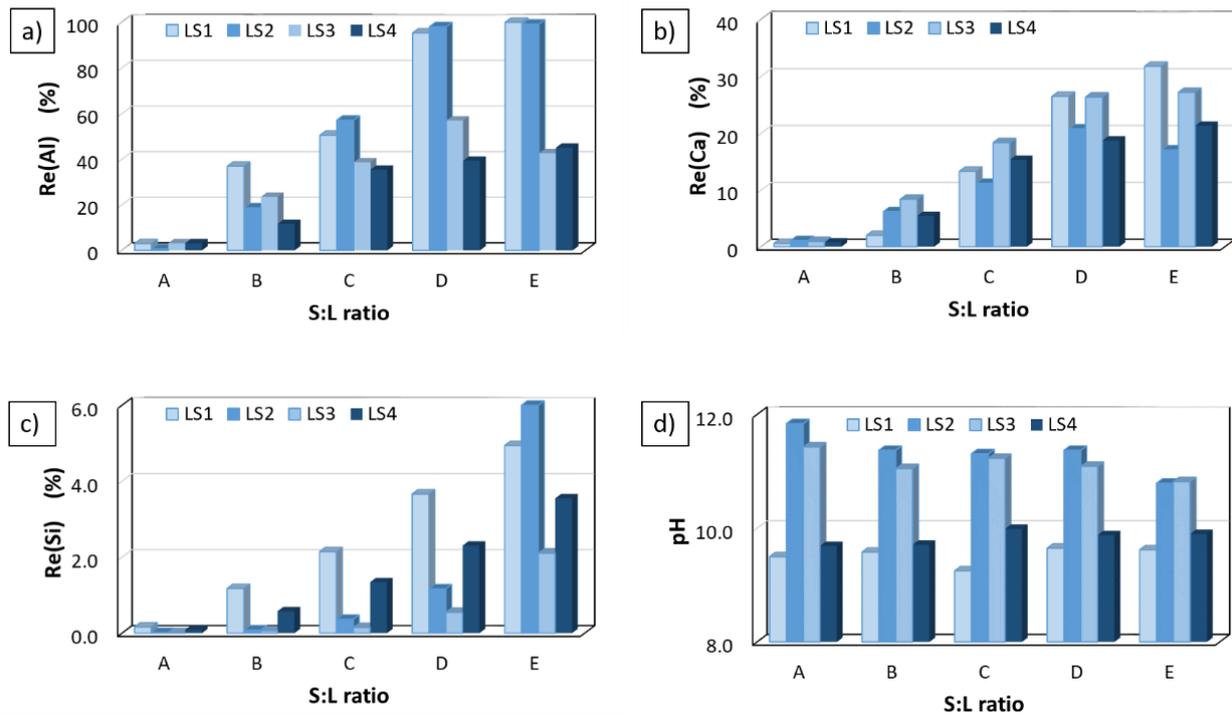


Figure 2 Relative removed fraction of Al (a), Ca (b), and Si (c) during leaching ladle slags and pH (d) of leachate

The kinetic study of relative removed fraction of Al and Ca from LS2 and LS3 slags show **Figure 3**. Results proved that the Ca (especially CaO) and Al compounds of LS2 slag was dissolved immediately after contact with DW. It is probably, that in leachate prepared from fresh slag, interaction between the dissolved ions occur to form insoluble compounds. The relative removed fraction decreased with increasing leaching time.

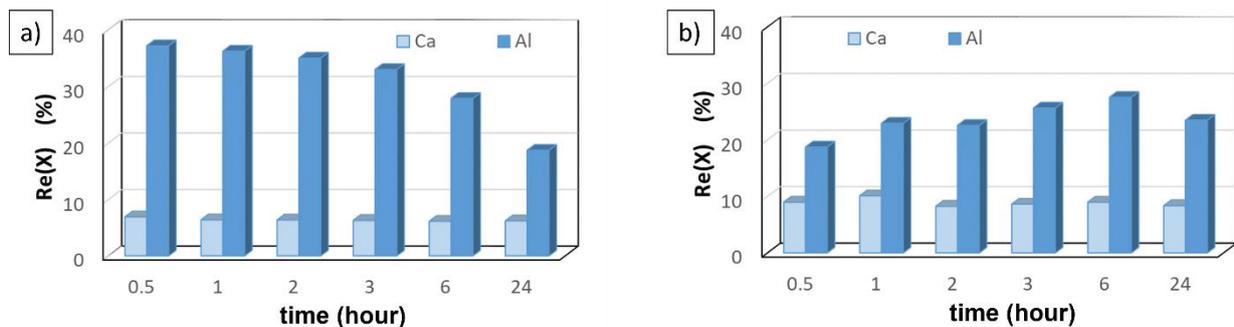


Figure 3 Relative removed fraction of Al and Ca during leaching different leaching time of ladle slags LS2 (a) and LS3 (b) (=Ca or Al)

Changes in the phase composition of LS2 and LS3 slags are shown in **Figure 4**, and the list of major detected compounds summarized **Table 4**. The above mentioned slags contain the Periclase ($Mg_{0.974}Fe_{0.026}O$), Lime (CaO), Periclase (MgO), Quartz (SiO_2), Allite (Ca_3SiO_5), Gehlenite ($Ca_2Al_2SiO_7$), and Tobermorite ($Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})H_2O$) whose diffraction peaks are not marked for clarity of **Figure 4**. It is evident, that during the leaching, all the Mayenite was dissolved. This results are consistent with the results presenting in **Figure 2a**.

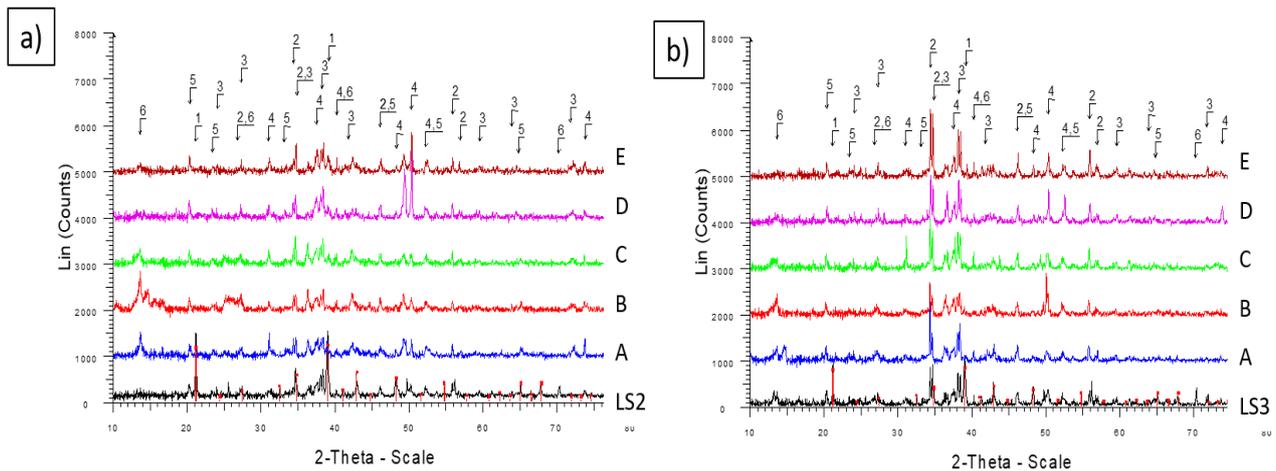


Figure 4 Rtg. diffraction patterns of ladle slag LS2 (a) and LS3 (b) before and after leaching (A, B, C, D, E), the major phases are listed in Table 3, diffraction peaks of Mayenite are highlighted by the red lines

Table 3 The label list of the major phases in slag samples determined by powder diffraction

No.	Chemical formula	Name	No.	Chemical formula	Name
1	$Ca_{12}Al_{14}O_{33}$	Mayenite	4	Ca_2SiO_4	Larnite
2	$CaCO_3, CaMg(CO_3)_2$	Calcite, dolomite	5	$(CaO)_3(Al_2O_3)_{1.425}(H_2O)_{4.8}$	Katoite
3	Ca_2SiO_4	Calcio-olivine	6	$(Fe_2Mg_6(OH)_{16}CO_3(H_2O)_{4.5})_{0.375}$	Pyroaurite

4. CONCLUSION

The presented study proved that fresh slags interacted with water intensively than landfilled slag, which change phase composition under air condition. The dissolution of some Si compounds were caused by the high pH values of the leachate. The main source of Al ions in the leachate is the Mayenite, which is almost all released into the leachate from fresh slags. The kinetic study performed on the selected slags showed that the contact time of the slag with water may not always lead to the release of a larger amount of cations to the leachate. Calcium passed into solution immediately after the first contact of slag with water.

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