A STUDY ON THE LEACHABILITY OF METALS FROM MODIFIED COPPER SLAG FOR ADDED VALUE APPLICATIONS

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Introduction

Pyrometallurgical copper extraction generates by-products such as slags. The copper slag is a material suitable for a variety of applications, *e.g.*, in abrasives, asphalt, aggregates, concrete, tiles, and glass production.[1,2] Generally, granulated iron silicate copper slag shows low leachability.[3] However, a varied amount of CaO can be added to the slag which can enhance settling of slag inclusions and broaden the range of possible application areas. The CaO-modified slag has to be examined regarding the leachability assuring that the leaching behaviour is not negatively affected. Investigations regarding the leaching behaviour of modified iron-silicate copper slag remelted with various CaO amounts have not been found in the literature.

This study aimed to characterise and investigate the leaching behaviour of crushed crystalline CaO-modified copper slag. The copper slag was remelted with different amounts of CaO, up to 25 wt%, and analysed by scanning electron microscopy, SEM; energy dispersive spectroscopy, EDS; X-ray diffraction, XRD; Inductively coupled plasma optical emission spectroscopy, ICP-OES, and one-stage batch leaching test. These analytical methods are well established for studying slag materials.[2,3]

Experimental

Boliden Mineral AB, Sweden provided the iron silicate slag material used in this investigation. The slag contains as main elements Fe, Si, and Al in amounts of (in wt%) 32.0, 17.8, and 2.5. It also contains Ca, Cu and Zn in 2.7 wt%, 0.96 wt% and 1.0 wt%. Lime addition (CaO) to slag were adjusted to a total CaO content of 3.8, 5, 10, 15, 20, and 25 (in wt%) called C0, C5, C10, C15, C20, and C25, respectively. The slag remelting with CaO was done in a graphite resistance furnace in alumina crucibles (99.7 wt% Al_2O_3) at 1250°C for 120 minutes at an argon atmosphere maintained by a flow rate

of 2 L/min. The samples were cooled inside the furnace exponentially down to 50°C in about 4 h and 24 min. About 25 g of each sample was crushed in a ring mill for 3 s with the identical setup. The crushed samples were split into 5 grams subsamples which were used for leaching studies.

One stage batch leaching tests were performed in duplicates in milli-Q water according to the standard EN 12457-2[4]. The compliance test is suitable for investigation of the leachability of materials such as a copper slag, with a particle size below 4 mm. A Thermo Scientific iCap^{TM} 7200 duo ICP-OES was used for analysing the contents of Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, S, Si, P, Pb, Zn, and Ti in the eluates. The pH and conductivity were measured with calibrated electrodes. The limit of detection, LOD, and limit of quantification, LOQ were calculated by linear regression from the calibration curves for each element. The chemical composition analysis of the samples was carried out by the accredited laboratory ALS Global Luleå, Sweden. All of the other analytical methods were executed at the Division of Minerals and Metallurgical Engineering at Luleå University of Technology, Sweden.

Results & Discussion

Modified slag compositions

Table 1: Chemical compositions of the slags

Compound	Original	C0	C5	C10	C15	C20	C25
Fe_{tot}*, wt%	32.0	30.4	29.5	29.9	27.0	25.5	25.5
SiO_2, wt%	38.1	33.7	33.3	32.9	31.5	27.9	26.6
CaO, wt%	3.77	3.89	4.85	10.6	13.9	19.3	23.0
MgO, wt%	1.52	1.55	1.56	1.73	1.37	1.41	1.26
Al_2O_3, wt%	4.65	6.21	6.06	5.74	5.57	5.03	5.78
MnO, wt%	0.40	0.39	0.40	0.45	0.33	0.34	0.30
Cu, wt%	0.96	1.9	0.82	0.59	0.81	0.56	0.71
Ni, wt%	0.07	0.16	0.06	0.05	0.06	0.04	0.05
Zn, wt%	1.03	0.87	0.83	0.82	0.86	0.77	0.64
Mo, wt%	0.20	0.22	0.23	0.22	0.23	0.19	0.17
As, mg/kg	290	312	164	110	247	117	183
Pb, mg/kg	59.1	145	43.2	42.1	41.6	33.7	25.1

* The oxidation state of Fe was not taken into consideration

Table 1 shows the slag compositions of the original, remelted original slag and the slags with CaO additions. The main slag components Fe and SiO_2 decrease with CaO addition. Al_2O_3 dissolution occurs upon remelting; the amount was higher for all remelted samples *C0-C25* compared with the original slag. The distribution of MgO and inclusion elements showed a higher compositional variance than the main components. However, Cu, Zn, and Pb showed decreasing trends with increasing CaO

contents. Sample *C0* shows a deviation regarding inclusion elements which can be caused by a heterogeneous slag composition.

Leaching of modified slags

The leaching from the modified copper slag was generally low, and for most of the elements, it was close to the detection limits of the device for the specific elements. The conductivity was also generally low, below 62 µS/cm, for all of the samples; drinking water has a maximum allowed conductivity of 2500 µS/cm according to the European drinking water directive. The pH was basic for all samples and increased with increased CaO content in the remelted slag, Table 2. Leaching of Ca and Mo was detected for all samples, where Ca showed the most severe leaching for sample *C25,* 6.6 mg/L, Table 2. Most likely Ca was responsible for the increased conductivity in the leachates as the CaO content increased.

Table 2: Eluate data from modified slags, measured according to standard EN 12457-2

Parameters	C0	C5	C10	C15	C20	C25	LOD[a)]
pH	9.6	9.8	9.9	10.0	10.2	10.5	-
Conductivity, µS/cm	39	30	47	47	55	62	-
Elements							
Fe, mg/L	< 0.8[b)]	< 0.8	n.d[c)]	< 0.8	n.d	n.d	0.3
Ca, mg/L	1.1	1.3	2.2	3.4	4.3	6.6	0.2
Mg, mg/L	1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	0.3
Al, mg/L	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	0.8
Cu, mg/L	n.d	n.d	n.d	n.d	n.d	n.d	0.4
Ni, mg/L	0.004	0.003	< 0.003	0.004	< 0.003	< 0.003	0.001
Zn, mg/L	n.d	n.d	n.d	n.d	n.d	n.d	0.3
Mo, mg/L	0.10	0.12	0.39	0.28	0.29	0.19	0.01
As, mg/L	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.01
Pb, mg/L	n.d	n.d	n.d	n.d	n.d	n.d	0.5

[a)] Limit of detection, [b)] below limit of quantification, [c)] not detected

The main slag mineral in the copper slag was changed with CaO addition, from iron silicate to calcium iron silicate based. The phase transformation occurs between sample *C10* and *C15* according to XRD and SEM-EDS results, Figure 1. The SEM micrograph a) with 10 wt% CaO shows the typical mineralogy for the samples with lower CaO content, samples *C0* and *C5*. The SEM micrograph b) shows similar mineralogy and texture as the samples with higher CaO content, except for the shrinkage of phase 2) as phase 1*) grows with increasing CaO content.

The addition of CaO also dilutes the inclusion elements present in the slag, which can affect the leachability of the metals. If these metals are evenly distributed, the concentration of metals at the slag particle surfaces, where the leaching takes place

becomes lower with CaO addition. Unfortunately, the low amounts of leached metals make it not possible to conclude lowered leachability with CaO addition. As CaO-containing slag minerals are formed, the distribution of trace elements might change as well. The trace elements can i) settle or ii) become internally distributed to preferable slag minerals. However, the results showed that leaching of Mo is affected by the addition of CaO, with the highest value of 0.4 mg/L with 10 wt% addition of CaO, *C10*.

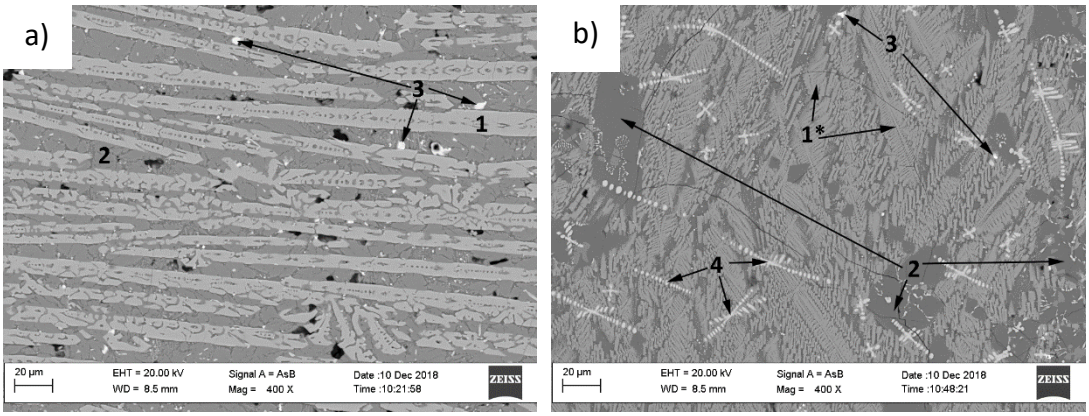

Figure 1: Typical SEM micrographs of modified copper slag with a) 10 wt% CaO, C10, and b) slag with 15 wt% CaO, C15, showing the distribution of 1) iron/calcium silicate,*contain a higher amount of Ca; 2) calcium iron disilicate; 3) copper inclusions; and 4) iron oxide

Conclusions

The leaching of elements was generally low for CaO-modified iron silicate copper slag, maximum 6.6 mg/L of Ca was leached out for the sample with 25 wt% CaO. The addition of CaO to the slag resulted in increased pH and conductivity in the leachates from the samples. The leachability of Mo was affected by the CaO content and was highest at 0.4 mg/L with 10 wt% CaO. However, the leachability of the Cu, Zn, and Pb was all below their detection limits for all of the samples.

References

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