6th International Conference

QUO V♻DIS RECYCLING

June 6th – 9th 2017

High Tatras
Slovak Republic

Edited by: Dušan Oráč
Reviewers: prof. Ing. Tomáš Havlik, DrSc.
doc. Dr. – Ing. Milan Škrobian, CSc.
Published: May 2017
Number of pages: 406
Printed by: Polygrafia Gutenberg, s.r.o.
Issue: first
ISBN 978-80-553-3170-6

HYDROMETALLURGICAL RECOVERY OF CHROMIUM FROM SLAGS

HYDROMETALURGICKÉ ZÍSKAVANIE CHRÓMU Z TROSIEK

Patrik Kuruc[1)*]*, Andrea Miškufová*[1)]*, Olívia Kačalová*[1)]*, Tomáš Havlik*[1)]

[1)] Technical University of Košice, Faculty of Metallurgy, Institute of Recycling Technologies, Letná 9, Kosice, Slovak Republic

[*]Corresponding author: e-mail: patrik.kuruc@tuke.sk, Tel.: +421 055 602 2426

Abstract

At production and refining of steel, more than 600 mil. tons of slags are produced annually. The important group represents slags from stainless steel and FeCr production, the important source of critical and valuable metals (Cr, Mo etc.). The aim of hydrometallurgical processes is to selectively leach out Cr and other valuable metals leaving Fe and other base metals non-leached. Cr in steel slag could occurs mostly as a complex (spinel type) oxides (Fe, Mn, Mg, Zn)O.Cr_2O_3. In this work the thermodynamic and kinetic aspects of Cr leaching from EAF (electric arc furnace) steel slag sample in H_2SO_4 solution and in alkaline (NaOH) solutions without/with the presence of oxidants (H_2O_2, $O_{3(g)}$) were studied. The pilot experiments showed the better leachability of Cr from slag sample in acid solution. By using of oxidants during alkaline leaching only slightly higher extractions of Cr under studied conditions have been achieved. Preliminary experimental results evoke necessity to use more aggressive leaching conditions for the recovery of Cr from steel slag (higher concentration of oxidants, pretreatment by fusion etc.). The present work is a part of project funded by HORIZON 2020 Research and Innovation program under Grant Agreement No.730 471 (CHROMIC).

Keywords: recycling, hydrometallurgy, EAF steel slag, leaching, chromium

Abstrakt

Pri pyrometalurgickej výrobe kovov sa ročne vyprodukuje viac ako 600 miliónov ton trosiek. Významnou skupinou sú trosky z výroby ušľachtilej ocele a FeCr trosky. Tie môžu byť zaujímavý zdroj kritických a cenných kovov (Cr, Mo atď.). Cieľom hydrometalurgických procesov je selektívne oddeliť Cr a ostatné cenné kovy z matrice, pričom Fe a iné matricové kovy ostávajú nedotknuté. Cr sa v predmetných troskách nachádza prevažne vo forme komplexných oxidov – spinelov (Fe, Mn, Mg, Zn)O.Cr_2O_3. V tejto práci sa študovali termodynamické a kinetické aspekty lúhovania chrómu z výroby ocelev v EOP (elektrická oblúková pec) v H_2SO_4 a v zásaditom (NaOH) prostredí s alebo bez prítomnosti oxidantov (H_2O_2, $O_{3(g)}$). Pilotné experimenty ukázali lepšiu vylúhovateľnosť Cr z trosky v kyslom prostredí. Použitím oxidantov v zásaditom prostredí sa iba slabo zvýšili výťažnosti Cr. Výsledky pilotných experimentov evokujú, že pre získavanie Cr z trosky z výroby ocele bude potrebné použiť agresívnejšie lúhovacie podmienky (vyššie koncentrácie oxidantov, predúprava tavením atď.). Predložená práca je súčasťou projektu financovaného z Výskumného a inovačného programu HORIZON 2020, číslo 730 471 (CHROMIC).

Kľúčové slová: recyklácia, hydrometalurgia, EOP oceliarenská troska, lúhovanie, chróm

Introduction

Annually a large amount of slag is produced (**Tab. 1**) and they can vary in chemical, mineralogical as well as in mechanical properties. In some countries, Indonesia for example, steelmaking slag is categorized as hazardous waste. It is mainly because slag can contain elements that can be harmful in certain form. Composition of produced slag is dependent not only on parameters of individual batch but influenced mainly by desired quality of produced steel and by composition of smelted scrap.

Tab. 1: Published iron and steel production and calculated slag amount [1]

Product	World production [ton]	Slovakia production [ton]
Crude iron	1.15 mld	3.738 mil
Steel	1.6 mld	4.562 mil
Blast furnace slag*	254.1 – 427.3 mil	0.822 – 1.38 mil
Steel slag*	176 – 192 mil	0.502 – 0.547 mil

**calculated on premise that 1 ton of produced crude iron produces 220-370 kg of blast furnace slag and 1 ton of produced steel produce 110-120 kg of steel slag*

However slag can be used as a secondary raw material and should be treated as resources not as a waste. The most commonly, this material is landfill. **Fig. 1** shows other uses of steel slag. It is desirable to find an approach to utilize slag as a source of metals, whereas there are numerous valuable metals contained.

Possibilities of processing of slags are alkaline or acidic leaching, roasting or oxidative leaching [3]. **Tab. 2** shows some examples of steel slags and their typical chemical composition. These studies confirm a variety in composition of different slags. For that reason, it is impossible to invent general process for slag recycling. Origin of the material and its properties and composition must be taken into account before treatment and using it as a resource.

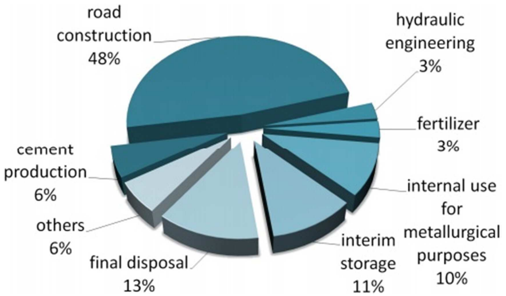

Fig. 1: Use of steel slag in 2010 [2]

Tab.2: Composition of chosen slag published in papers

Type of slag	SiO_2	Cr_2O_3	Al_2O_3	CaO	MgO	FeO	Fe_2O_3	Source
EAF steel slag	31.7	4.7	4.6	47.4	7.0	1.2	-	[4]
Stainless steel slag	29.4	3.7	4.1	36.7	4.6	0	6	[5]
Ferrochrome slag	12	5	12	36	24	-	11	[6]
Stainless steel slag	30	4	4.5	45	10	-	6.5	[6]

1 Experimental

1.1 Termodynamic study of Cr leaching

In this paper, leaching of Cr from electric arc furnace (EAF) steel slag is reported. Prior to experiments, a thermodynamic study was conducted. In **Tab. 3** are given chosen reactions which could proceed in the leaching process and their values of Gibbs energy change at the temperature 293 K. Based on these calculations, it is assumed that leaching of Cr will take place in H_2SO_4 and produce $Cr_2(SO_4)_3$. The use of NaOH as the leaching solution will probably prevent Cr dissolution, but by use of oxidative leaching agents (e.g. $O_{3(g)}$) the reaction creating soluble form of Cr (Na_2CrO_4) could take place (reactions 5 – 8).

1.2 Material and methods

In the leaching experiments the EAF slag sample which is the subject of the solved project Horizon 2020 (CHROMIC) was used. Project CHROMIC aims to develop a process for recovery of metals from slag by use of progressive leaching techniques in collaboration with participants (VITO, MEAM, EWW, ORBIX, FORMICABLU, ARCHE, TUKE, HZDR, BFI, FEhS, BRGM). For the comparision from apperance, chemical and mineralogical point of view the slag from FeCr/FeSiMn production was used, too. **Fig. 2** shows the used slag samples.

Tab. 3: Proposed leaching reactions and their Gibbs energy change at 293 K

No.	Reaction	$\Delta G°_{293}$ [kJ/mol]
(1)	$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O$	-167.229
(2)	$1.5Cr_2O_3 + 4.5H_2SO_4 + O_3(g) = 1.5Cr_2(SO_4)_3 + 4.5H_2O + 1.5O_2(g)$	-275.193
(3)	$Cr_2FeO_4 + 3H_2SO_4 = Cr_2(SO_4)_3 + FeO + 3H_2O$	-110.134
(4)	$6Cr_2FeO_4 + 18H_2SO_4 + O_3(g) = 6Cr_2(SO_4)_3 + 3Fe_2O_3 + 18H_2O$	-262.248
(5)	$2Cr_2FeO_4 + 8NaOH + 2.333O_3(g) = 4Na_2CrO_4 + Fe_2O_3 + 4H_2O$	-630.116
(6)	$Cr_2O_3 + 4NaOH + O_3(g) = 2Na_2CrO_4 + 2H_2O$	-535.109
(7)	$Cr_2O_3 + 4NaOH + 3H_2O_2(a) = 2Na_2CrO4 + 5H_2O$	-682.307
(8)	$2Cr_2FeO_4 + 8NaOH + 7H_2O_2(a) = 4Na_2CrO_4 + Fe_2O_3 + 11H_2O$	-801.859

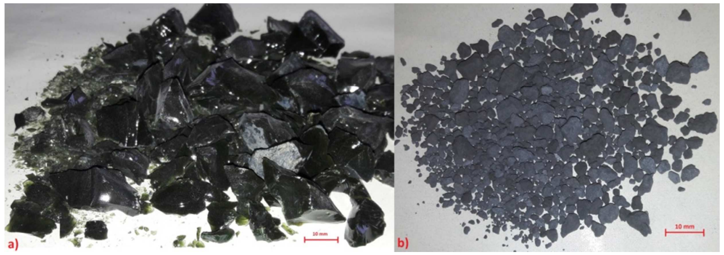

Fig. 2: Samples of slags: a) FeCr/FeSiMn slag; b) EAF slag

The sample of EAF slag was in the form of mat-grey granules on the contrary to FeSiMn/FeCr slag (sample OFZ), which was in sharp shaped vitreous green glassy form. **Tab. 4** shows the semiquantitative analysis of FeSiMn/FeCr slag sample measured by XRF (Niton^{TM} XL3t Goldd). XRD diffraction phase analysis (Panalytical X-Pert Pro) confirms an amorphous character of FeSiMn/FeCr slag sample. It is obvious that Cr is present in FeSiMn/FeCr slags in quite low content and probably in the form of complex oxides [for example $(Fe,Mn,Mg)O.Cr_2O_3$, calcium chromate ($CaCrO_4$), etc]. The chemical and mineralogical composition of the EAF slag sample is not available yet, but it is in the stage of precise chemical and mineralogical analysis. For leaching experiments was used 50g of slag and 400 ml of solution (3M H_2SO_4 or 3M NaOH). The slurry was stirred (300 rpm) for 4 hours. Leaching solutions were heated or oxidants were added, in dependence on experiment set up. Liquid samples were analyzed for Cr concentration by AAS method.

Tab. 4: Semiquantitative XRF chemical analysis of FeSiMn/FeCr slag sample

Sample	Fe total	CaO	MgO	Al_2O_3	SiO_2	K_2O	Mo	Mn	Cr	V	P	Ti
OFZ	11.30	7.14	0.77	8.38	45.15	0.21	0.08	0.25	0.12	0.02	0.23	0.12

3 Results and discussion

In **Fig. 3** the results of leaching experiments are shown. **Fig. 3a** displays leaching of Cr in H_2SO_4 compared to NaOH leaching. Preliminary experiments confirmed the better leachability of Cr from EAF sample in sulphuric acid than in sodium hydroxide at 60 °C. The concentration of Cr in 3 M H_2SO_4 represented 200 mg/ml. Acid leaching of slag indicated higher extraction of Fe and problematic filtration of leaching residue obtained (Ca-precipitates). Due to fact that Cr was practicaly not leached in the NaOH at 60 °C, the oxidative leaching was applied. **Fig. 3b** shows the dependance of Cr concentration on time during leaching in NaOH with addition of oxidants at 20 °C or 60 °C (gaseous O_3 and liquid H_2O_2). In this case, increase in recovery by adding H_2O_2 or O_3 can be seen. But even with addition of these intensificators, concentration of Cr in leachate did not exceed 4 mg/ml.

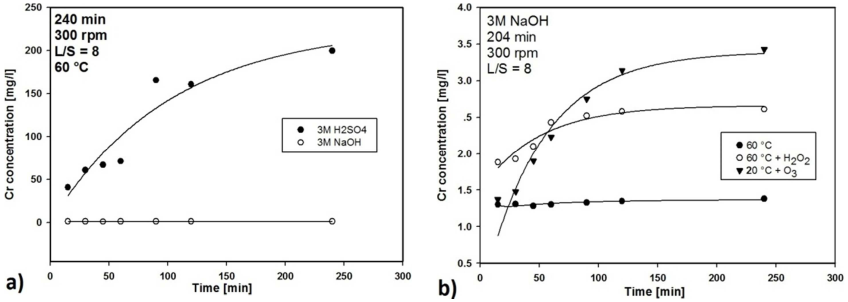

Fig. 3: Leachability of Cr from EAF slag (CHROMIC): a) comparison of acidic and alkaline leaching; b) NaOH leaching with addition of H_2O_2 and $O_{3(g)}$

Conclusions

Recovery of Cr and other metals from slags by hydrometallurgy looks like a possible alternative for effective slag utilization. Experimental results indicated a problematic leachability of Cr from EAF steel slag in NaOH solution even by using of oxidants (H_2O_2 and $O_{3(g)}$). Although, ozone assisted leaching showed the most progressive trend in Cr leaching from the slag. Leaching of slag in acidic solution yield higher Cr concentrations but due to high Fe content, it is desirable to process slag by alkalies. In case the intensification of alkaline leaching does not increase significantly metal extraction neither by increased temperature nor concentration of added oxidants (H_2O_2 and $O_{3(g)}$), material must be probably pre-treated by roasting (with NaOH or Na_2CO_3) or other way of process enhancement must be invented.

Acknowledgement

This project received funding from the European Union’s Horizon 2020 Reasearch and Innovation program under Grant Agreement nº 730471.

References

[1] Takáčová Z., Miškufová A.: Základne informácie o odpadoch, Equilibria, s.r.o., 2011, 236s, ISBN 978-80-89284-78-8

[2] Position Paper on the Status of Ferrous Slag, The European Slag Association, 2012, Available on http://www.euroslag.org/fileadmin/_media/images/Status_of_slag/ Position_Paper_April _2012.pdf

[3] Kim E., et.al: Selective recovery of Cr from stainless steel slag by alkaline roasting followed by water leaching, Hydrometallurgy, Vol. 158, /2015, 139-148.

[4] Saman Mostafaee, A Study of EAF High-Chromium Stainless Steel making Slags Characteristics and Foamability, Doctoral Thesis, Royal Institute of Technology, Stockholm, 2011, ISBN 978-91-7415-968-4

[5] Xingrong Wu, et. al: Crystallization Behaviour of Chromium in Stainless Steel Slag: Effect of FeO and Basicity, Journal of Residuals Science & Technology, Vol. 13, 2016, doi:10.12783/issn.1544-8053/13/S1/10

[6] Kevin M. Fox, et. al: Advances in Materials Science for Environmental and Nuclear Technology, 2010, 300, ISBN 9780470930977