RECOVERING CHROMIUM FROM STAINLESS STEEL AND FERROCHROME SLAGS

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Introduction

Currently, about 75% of the chromium is being imported into the EU.[1] In the value chain of stainless steel production, significant amounts of chromium (Cr) are lost in ferrochromium (FeCr) slags and stainless steel (SS) slags. FeCr slags are generated during the production of FeCr, an intermediate product for SS production (1.1-1.6 ton slag/ton high carbon (HC) FeCr;[2] 2.4-2.5 ton slag/low carbon (LC) FeCr). In 2014 the global FeCr production amounted to 11.7 Mt.[3] SS slag is a by-product generated during the production of SS, at approximately one ton of slag per 3 tons of produced SS. The global stainless steel production was 38 Mt in 2013.[4] Cr concentrations in FeCr and SS slags are in the range of 2-8% and 1-2%, respectively. Johnson *et al.* has estimated that in 2000 in Europe (including Turkey) 74 900 t/y and 18 700 t/y Cr was lost in FeCr slag and SS slag, respectively.[5] In both materials, Cr is present within entrapped metallic particles (Fe-Cr alloys) and/or as stable spinels. To unlock the potential of these low-grade resources, a radically new approach to metal recovery must be deployed. The aim of the presented work is to develop a process for recovering Cr from SS and FeCr slags based on the smart integration of enhanced pretreatment and selective alkaline leaching or alkaline roasting followed by water leaching.

Experimental

Materials

Four different Cr-containing slags (listed in Table 1) were investigated in this study.

Table 1: Samples investigated in this study

Slag sample	Sample description	Cr [%]	Mineralogical form of Cr in the sample
CS EAF	Carbon steel EAF slag	2.6	Mg-Cr spinel ($MgCr_2O_4$)
LC FeCr	Slag from LC FeCr production	3.2	Mg-Cr spinel ($MgCr_2O_4$); FeCr
HC FeCr	Slag from HC FeCr production	11.5	Mg-Cr spinel ($MgCr_2O_4$); FeCr
SS	Stainless steel slag	2.5	Mg-Cr spinel ($MgCr_2O_4$)

Methods

Physical separation

Magnetic and density separation techniques (listed in Table 2) were applied for selected slag samples. All magnetic separation equipment was produced by Master Magnets Ltd. The wet shaking table used in this test was built by Holman-Wilfley Ltd.

Table 2: Physical separation techniques used in this study

Separation technique	Description (Type)	Basic parameters	Material tested
LIMS	Dry low intensity magnetic separation (Handheld ferrite magnet)	0.15 T magnetic field	HC FeCr
HIMS	Dry high intensity magnetic separation (Handheld RARE magnet)	1 T magnetic field	LC FeCr HC FeCr
WLIMS	Wet low intensity magnetic separation (Wetchute with ferrite magnet)	0.1 T magnetic field	HC FeCr
WHIMS	Wet high intensity magnetic separation (Wetchute with RARE magnet)	1 T magnetic field	SS HC FeCr
WHIMSe	Wet high gradient/intensity magnetic separation (WHIMS 500)	0-2 T magnetic field	SS LC FeCr
WST	Wet shaking table - density separation (Type 800)	stroke speed = 250 rpm washing water = 1000 L/h feed water = 250 L/h	HC FeCr

Microwave (MW) assisted leaching

Microwave assisted leaching and roasting were performed in MW equipment (*Milestone Flexiwave* and *Pyrowave*, respectively) shown in Figure 1.

Figure 1: MW equipment used for MW assisted leaching (left) and MW roasting (right)

During MW assisted leaching 9 g of CS EAF slag was mixed with 15 mL NaOCl (15%) and selected amounts of NaOH (0.2-1.6 g). Conditions of the MW leaching are listed in Table 3. After MW leaching additional 90 mL of distilled water was added and the mixture was shaken for 60 min at 25°C. After filtration, leachates were analysed by ICP-OES (Avio 500, PerkinElmer).

MW roasting followed by water leaching

Samples consisting of a mixture of 3 g of SS slag, an alkali salt (NaOH) and an oxidant ($NaNO_3$) were roasted at conditions listed in Table 3. After MW roasting, the samples were leached in distilled water at 25°C, L/S = 10 for 60 min.

Table 3: Experimental conditions of MW assisted leaching and roasting

Parameter	MW leaching	MW roasting
Max. power used[W]	1000	1000
Time [min]	60 and 120	30
Temperature [°C]	105	400
Material tested	CS EAF slag	SS slag

Results and discussion

Physical separation

Results of physical separation tests (Table 4) show the potential of magnetic and density separation to concentrate Cr from Cr-containing slags.

Table 4: Summary of the results after physical separation

Slag sample	Techniques used	Initial Cr content (wt%)	Cr content after separation (wt%)	Yield (wt%)	Cr recovery (wt%)
LC FeCr	WHIMSe	3.2	7.3	13	25
HC FeCr	LIMS	11.5	27.6	20	50
SS	WHIMS	2.5	8.8	7	31
HC FeCr	WST	10.1	32.8	12	46

*WST was performed only for fraction 1-2 mm

In the case of CS EAF slag, LIMS was performed with the aim to recover steel particles which could be returned directly to the steelmaking process. The yield of the steel particles was 25 wt%.

MW assisted leaching

As seen from Figure 2, 44% of Cr can be extracted from CS EAF slag by applying alkaline MW assisted leaching. It is evident that the amount of NaOH is an important parameter affecting Cr extraction. The dissolution of matrix elements (Fe, Si, Ca, Mg and Al) was below 1%.

MW roasting follow by water leaching

Results of MW roasting followed by water leaching for the SS slag material are shown in Figure 3.

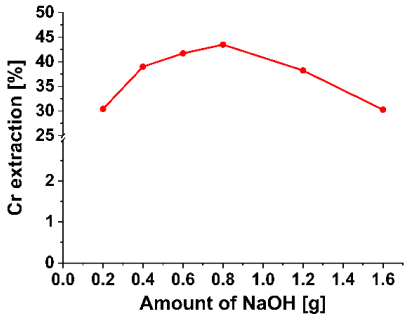

Figure 2: Results of MW assisted leaching (CS EAF slag)

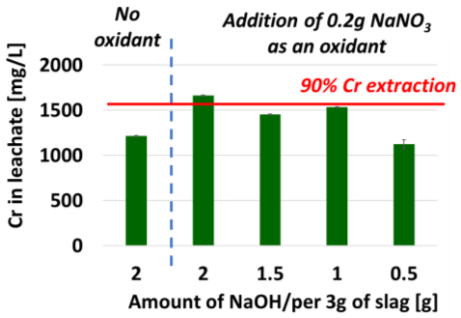

Figure 3: Results of MW roasting followed by water leaching (SS slag)

More than 90% of Cr can be selectively extracted from SS slag by alkali roasting at 400°C at a weight ratio NaOH:slag of 2:3 followed by water leaching in the presence of $NaNO_3$ as oxidant.

Conclusion

Physical separation tests concentrated Cr significantly by using magnetic and density separation, whereby Cr contents can be increased by a factor of 3. More than 90% of Cr can be selectively leached out from SS slag by a combination of alkali microwave roasting and water leaching.

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