

TOWARDS RED MUD VALORISATION: EAF SMELTING PROCESS FOR IRON RECOVERY AND SLAG DESIGN FOR USE AS PRECURSOR IN THE CONSTRUCTION INDUSTRY

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Introduction

Red mud, the main residue of the Bayer process, is produced at a rate in excess of 150 million tonnes per annum.¹ Red mud contains significant amounts of valuable metals such as Fe, Al, Ti and REEs including Sc. A fair share of the produced red mud is stockpiled. Application of red mud in the construction industry is promising for zero-waste valorisation and bulk utilisation of this resource.^{2,3} Direct utilisation of red mud is sometimes met with challenges and pre-treatment of red mud can be a necessary value adding step towards its valorisation.^{4,5} Fe removal from red mud through high temperature processing for downstream recovery of REEs is one such example.⁶ The disadvantage of such a selective processing is the generation of residual waste.

In this study, red mud was smelted in an electric arc furnace (EAF) as a pre-treatment step to design suitable slags for favourable utilisation of this material. The smelting tests were undertaken at 1500°C using lignite as the reductant under fluxing with silica sand and lime, where the reduced Fe was recovered as a pig iron product. The produced slags were evaluated in terms of chemical and mineralogical composition, as well as crystallinity. Crystalline and vitreous slags were produced during the testwork and they were evaluated for use as precursor materials for the production of construction materials.

Materials and Experimental Methods

The red mud used in this study was supplied by MYTILINEOS S.A. Aluminium of Greece. The material was dried for 24 hours and subsequently analysed. The dried red mud was mixed with lignite coke (containing 87 wt% fixed carbon) and flux. The fluxing agents were lime and silica containing 95 wt% CaO and 98 wt% SiO₂, respectively. The additions of the reductant to red mud were 1:10 and for flux to red mud were 1:5 and 1:2.5 for silica and lime, respectively. The blends were based on thermodynamic calculations (FactSage 7.0) targeting low melting slags and vitreous

(for silica fluxing) as well as crystalline calcium aluminate phase rich (for lime fluxing). For each experiment only one of the two fluxes was used. Batch masses of 1.95 kg for silica fluxing and 2.2 kg for lime fluxing of the recipes provided above were fed into a 100 kVA DC EAF. The material was contained in a graphite crucible to minimise slag contamination and the smelting was carried out at temperatures around 1500 – 1550°C, for a holding time of 1 hour. At the end of each experiment the molten material was poured into a refractory lined mould where the material cooled down under ambient conditions (at a cooling rate of about 20 - 30°C/min). The cooled material was separated into metal and slag, and weighed. The slag was crushed and milled to -90 microns. Magnetic separation to remove the entrained metal in the slag was carried out. The metal sample was polished for chemical analysis using a spark spectrometer. Chemical and mineralogical analyses of the red mud and slags were performed using an XRF PANanalytical Axios and XRD Bruker D8 Advanced diffractometer, respectively.

Results and Discussion

Table 1 shows the chemical analysis of the red mud used and the produced slags under the different fluxing conditions. From the low iron oxide content in the slags, it is evident that Fe removal was achieved. A CaO rich slag was achieved under lime fluxing as expected. This was accompanied by a low Na₂O content in the slag. This could be attributed to the high Na activity in this slag, where Na is reduced and volatilised. The silica fluxed slag was enriched in SiO₂ and Na₂O. The Na₂O enrichment in this slag could be attributed to the low Na activity where Na is locked in NaAlO₂ and is not readily available for reduction.⁷

Table 1: Composition of the red mud and the produced slags

	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	Na ₂ O	TiO ₂	LOI
Red mud - Greek	43.5	24.0	10.2	5.5	1.8	6.6	9.4
Slag – silica fluxing	1.2	36.8	15.3	38	2.4	7.3	-
Slag - lime flux	0.6	31.5	53.9	8.9	0.5	6.2	-

Figure 1 shows the XRD patterns of the two produced slags. The SiO₂ rich slag was found to be vitreous with minimal phase formation while the CaO rich slag exhibited crystallinity. The glassy nature of the SiO₂ rich slag can be credited to the high SiO₂ content in the slag which promotes network formation in the slag system. The phases present in the CaO rich slag include calcium aluminate phases, calcium silicate and calcium titanate phases. The added CaO content during fluxing was sufficient to avoid predominance of the gehlenite phase.

The produced slags with an enrichment in valuable elements and conditioning offer flexibility for use downstream for the recovery of the elements of interest. In view of zero-waste valorisation, utilisation of these slags as precursors in the construction industry is attractive. The vitreous high SiO₂ and high Al₂O₃ slag is a feasible precursor material for inorganic polymer production, while the high CaO crystalline slag low in Na₂O shows phases that could be attractive for an application as a cement clinker.

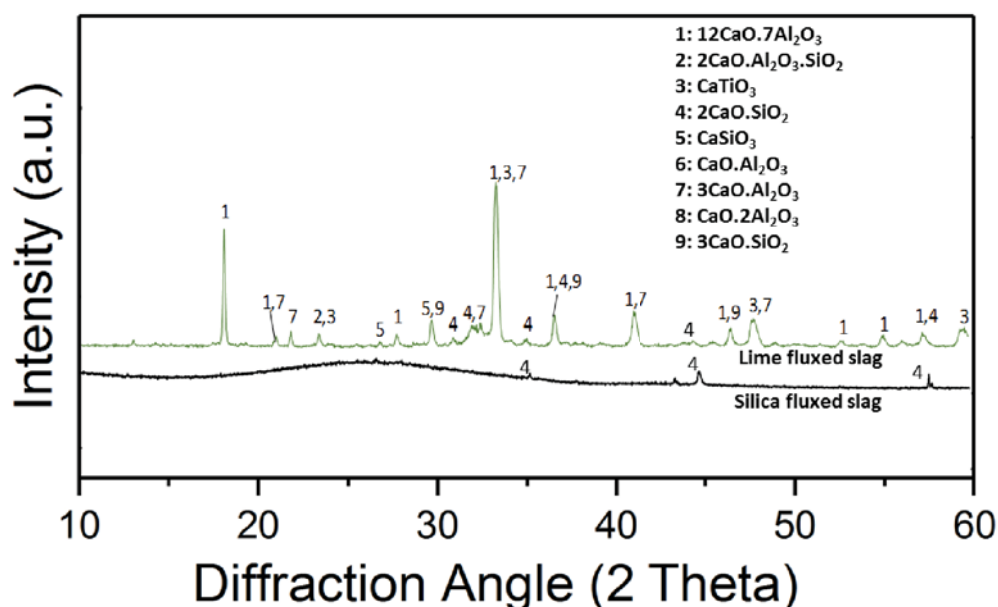


Figure 1: XRD profiles of the produced slags

The chemical composition of the produced metal is shown in Table 2. The Fe recovery to the metal was in excess of 95%. Despite the favourable reducing conditions in the smelting step, low Si and Ti are reported to the metal. This could be due to good control of the smelting process *i.e.* consistent operating temperature at 1500°C and under a reducing potential for selective recovery of Fe under favourable slags. Furthermore, high recoveries of the trace elements including Cr, V and Ni were observed. Low S values in the metal were achieved. Acceptable P content in the metal was reported. The metal is suitable as a feed material in secondary steel making for low Si contents and in the foundry for grey cast iron for higher Si contents.

Table 2: Composition of the produced metal

	Fe	C	Si	Ti	Cr	V	Ni	P	S
Metal - silica flux	91.8	5.0	1.7	0.3	0.5	0.2	0.3	0.1	0.03
Recovery (metal)	Very high	-	low	Very low	Very high	Very high	Very high	-	-
Metal - lime flux	93.0	5.1	0.1	0.3	0.5	0.2	0.3	0.2	0.01
Recovery (metal)	Very high	-	Very low	Very low	Very high	Very high	Very high	-	-

Conclusions

A smelting process for iron recovery and slag conditioning was investigated. Two slags were produced in an EAF under different fluxing conditions using lime and silica as fluxing agents. Iron was mainly recovered to the metal. Low S and acceptable P contents were achieved in the metal product. A vitreous SiO₂ rich slag and a crystalline CaO rich slag were produced. The produced slags were cleaned from Cr, V and Ni as a result of co-reduction of these elements to the metal. The pig iron product is suitable for use in secondary steel making. The produced slags are candidate feed materials for downstream recovery of valuable elements. In view of achieving near zero-waste valorisation of red mud, the produced slags could find application in the construction industry as follows: cement clinker for the crystalline CaO rich slag, and inorganic polymer precursor for the vitreous SiO₂ rich slag.

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