High temperature smelting reduction of bauxite residue and a CaCO$_3$-rich bauxite for aluminate slag production and pig iron recovery

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Abstract

An alternative way of producing alumina, called the Pedersen process, is suggested in the current study. It is a pyro- and hydrometallurgical process, the main advantage being the valorization of the bauxite residue. In the present research, the smelting reduction of bauxite residue and a CaCO$_3$-rich bauxite beneficiation by-product is studied to produce a calcium-aluminate slag and pig iron. Based on the results, increasing the CaO/Al$_2$O$_3$ ratio in the produced slags, can lead to the formation of phases that are considered leachable for alumina recovery, as 12CaO.7Al$_2$O$_3$, CaO.Al$_2$O$_3$, 3CaO.Al$_2$O$_3$. An optimum wt%CaO/wt%Al$_2$O$_3$ ratio of 1.5 is defined for the formation of a slag with more leachable phases. Proper slag and metal separation occurred, indicating the feasibility of producing two valuable by-products applying the Pedersen process.

Introduction

The Pedersen Process is considered as an alternative method to produce alumina utilizing lower grade bauxite ores, lower Al$_2$O$_3$/Fe$_2$O$_3$ ratios compared to typical ores used for alumina production[1]. The main purpose of investigating this process is to develop an alternative method to avoid the formation of Bauxite Residue[1,2,3]. Bauxite Residue is the main by-product of the Bayer process, which currently is the leading industrial route for producing alumina[1]. The Pedersen process was patented by Harald Pedersen and was operating with an annual production of 17.000 tons yearly within 1929-1969[2]. In this process, bauxite is smelted and reduced using lime as a flux and coke as the reducing agent; this yields a calcium aluminate slag as the main product and pig iron as a by-product. The slag is further used for the extraction of alumina through a hydrometallurgical treatment[2]. Based

on literature sources, the calcium aluminate phases that are classified as leachable are $Ca_{12}Al_{14}O_{33}$, $CaAl_2O_4$, $Ca_3Al_2O_6$[3,4]. The pig iron by-product can be used in ferrous industry. As can be seen in a simplified flowsheet of the Pedersen process, Fig. 1, the CO_2 emissions are recycled through the process and utilized in the precipitation step[1]. While the residue of the leaching step, called grey mud, could be used in making fertilizer, cement, etc.
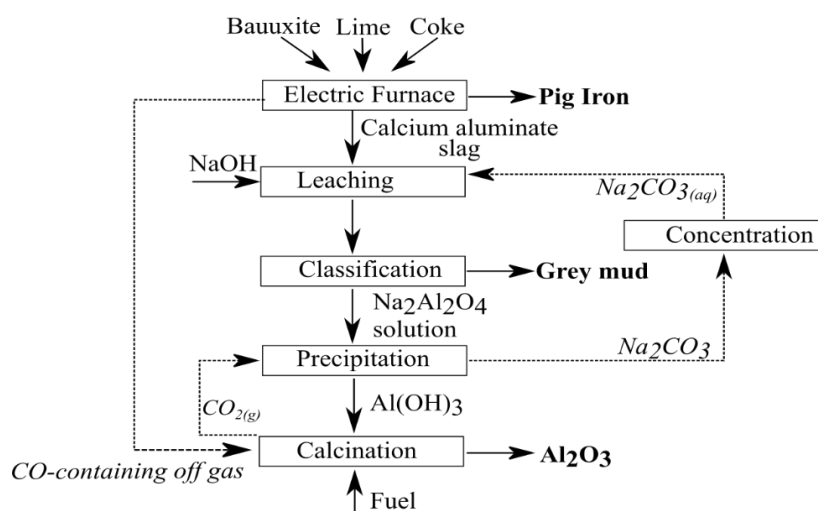

Figure 1. Simplified flowsheet of the Pedersen process

Bauxite Residue contains valuable compounds as Fe, Ti, Al[5], but its utilization is still challenging. In the present study, the application of the Pedersen process using Bauxite Residue instead of bauxite ore is being studied. Bauxite Residue is mixed with $CaCO_3$-rich beneficiation by-product and lime in different analogies. In the current study, $CaCO_3$-rich beneficiation by-product is used as an alternative source of CaO, which can partially replace the flux addition (CaO) and reduce the cost of the lime usage. Additionally, it can increase the Al_2O_3 content of the starting mixtures. The smelting reduction yields calcium aluminate slags and their characteristics are studied in the view of their content of leachable phases, based on the literature[5,6]. The main purpose is to optimize the mixing ratio and flux addition to facilitate bigger scale experiments, and to provide a basis for further experimental trials.

Experimental Procedure

Bauxite Residue (BR) and a $CaCO_3$-rich bauxite beneficiation by-product (BBBP) were provided by Mytilineos S.A, Metallurgy Business Unit (former Aluminium of Greece). The BBBP is produced from the mineral processing of bauxite ore. The chemical compositions of the raw materials were determined with X-ray

fluorescence (XRF), as shown in Table 1. The mineralogical compositions were determined using X-ray diffraction (XRD), D-8 Focus analyser using CuKα radiation, 10 to 75 deg diffraction angle, 0.01 deg step size, and 2.5 deg for both primary and secondary soller slits, Fig. 2a. The particle size distribution was determined with a Horiba Partica LA-960, and the D_{90} of BR, BBBP, and lime are 1.25 μm, 481 μm, and 178.5 μm, respectively. The raw materials were calcined before their smelting reduction, to ensure a smoother operation during smelting. The experiments were executed in a 75kV open induction furnace using graphite crucibles of 32mm inert diameter and 95mm height, for 30 min at 1650 °C. At the end of the experiment, the material was left in the furnace to cool down to room temperature.

The experiments presented in the current study can be divided into three main categories. The A-series are the preliminary experiments where different mixing analogies are studied to achieve a %wt CaO/%wt Al_2O_3 ratio of 0.86 to 0.88. Charcoal, with 79.4 wt% C-fix is also added as the reducing agent, in the stoichiometric amount to reduce all iron oxides of the mixtures to metallic iron. The B-series were designed after the assessment of the A-series results. The mixing analogies were revised to achieve a higher C/A ratio, 1 to 1.2, without the need for flux addition. The C-series were designed accordingly, and lime was added in excess to achieve an even higher C/A ratio, 1.5 to 1.9. In the B and C series, the reduction completed with the graphite crucible. Selected slags of the C-series (C-3 and C-4) have been presented elsewhere[7]. Details of the mixing analogies can be found in Table 2.

Results and Discussion

Raw materials' characteristics

The chemical analysis of the raw materials is presented in Table 1. BR has a high concentration of Fe_2O_3, while the Al_2O_3 content is significant. The BBBP is rich in CaO, and according to the XRD analysis in Fig. 2a, the detected mineralogical phase is the calcite, $CaCO_3$.

Table 1. Chemical composition of raw materials (wt%)

Raw materials	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	CaO	Na_2O	$CaCO_3$	LoI
Bauxite Residue	22.01	43.52	7.19	5.83	8.72	2.99	-	8.25
Beneficiation by-product	20.48	5.70	1.22	1.02	37.88	-	-	34.17
Lime	0.24	0.08	0.46	0.02	95.5	0.12	1.70	-

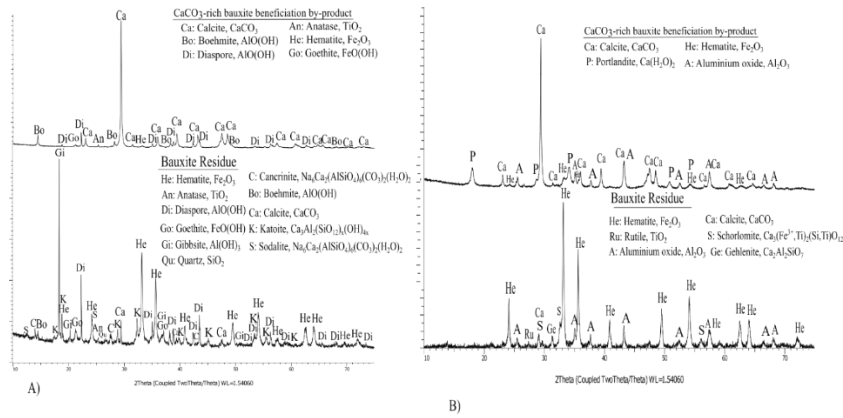**Figure 2**. XRD analysis of a) raw materials, b) calcined raw materials

The raw materials calcined in a muffle furnace for 3 hours at 850 $^{\circ}$C and the XRD patterns can be found in Fig. 2b. Upon calcination, the aluminium- and iron-hydroxides in both materials, Fig. 2.a, have been transformed to Al_2O_3 and Fe_2O_3, respectively. Part of the $CaCO_3$ in the BBBP transformed to CaO and subsequently partially to $Ca(H_2O)_2$ due to the absorption of moisture after calcination. However, the temperature and duration were not high enough for the complete decomposition of calcite.

Slag characteristics

The chemical composition of the A-series, B-series and C-series determined with XRF and can be found in Table 2. The iron content of the slags is low, indicating high iron recoveries and proper slag and metal separation. However, this is not the case for the slag C-1 (~50% iron reduction). In Fig. 3, the mineralogical compositions of the produced slags are presented. As can be seen, for the A-series, the produced slags have similar phases, as expected since their C/A ratio kept constant. The main phases are Gehlenite, $Ca_2Al_2SiO_7$, and mono-calcium aluminate, $CaAl_2O_4$. While in the slag A-4 and A-2, $CaAl_2O_7$ is also detected. The Gehlenite phase is considered as a non-leachable phase[8], and this will retard the alumina recovery. Based on the XRF and XRD analysis, the titanium content is lower than expected, and it was observed that it forms complex oxy-carbides on the surface of the metallic phase. Thus, it was found that the graphite crucible is significantly involved in the reduction reactions, along with the reducing agent (charcoal). Therefore, no charcoal was used for the next series.

Table 2. Chemical composition of the produced slags (wt%)

Slags	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	CaO	SO_3
A-1 (75% BR-25% BBBP)	54.1	0.3	9.4	0.5	41.2	0.9
A-2 (85%BR-15%BBBP)	52.2	0.4	12	0.7	40.1	1
A-3 (70%BR-30%BBBP)	54.3	0.8	8.9	0.7	40.1	0.8
A-4 (80%BR-20%BBBP)	54.2	1.3	9.5	0.7	40.2	0.9
B-1 (50%BR-50%BBBP)	44.1	2.1	6.1	3.7	43.1	0.5
B-2 (60%BR-40%BBBP)	44.1	1.8	7.2	4.0	42.1	0.5
C-1 (50%BR-50%BBBP)	24.9	11.7	3.7	3.0	54.6	0.2
C-2 (70%BR-30%BBBP)	33.6	2.9	6.1	5.0	51.9	0.3

C-3 (80%BR-20%BBBP), C-4 (60%BR-40%BBBP) presented elsewhere[7]

In B-series the target was to achieve a higher C/A ratio without lime addition; this led to the formation of the phases that are considered more leachable, according to the literature[3,8,9], as $Ca_{12}Al_{14}O_{33}$, $CaAl_2O_4$. The formation of Gehlenite that detected in the slags is a problem as it is not digested in the leaching step. The results of C-series indicate that increasing the lime addition and thus the C/A ratio, the formation of Gehlenite is minimized while $Ca_{12}Al_{14}O_{33}$ and $Ca_3Al_2O_6$ are becoming the dominant phases. For the slags in the B and C series, the formation of $CaTiO_3$ and Ca_2SiO_4 will not retard the alumina recovery based on the literature[9]. However, they may affect the lime addition and consumption. As mentioned, the slag C-1 was self-disintegrated due to the volume expansion caused by the phase transformation of β-C_2S to γ-C_2S[9]. The SEM analysis of the slag C-1, Fig. 4, shows that there are metallic entrapped in the slag matrix.
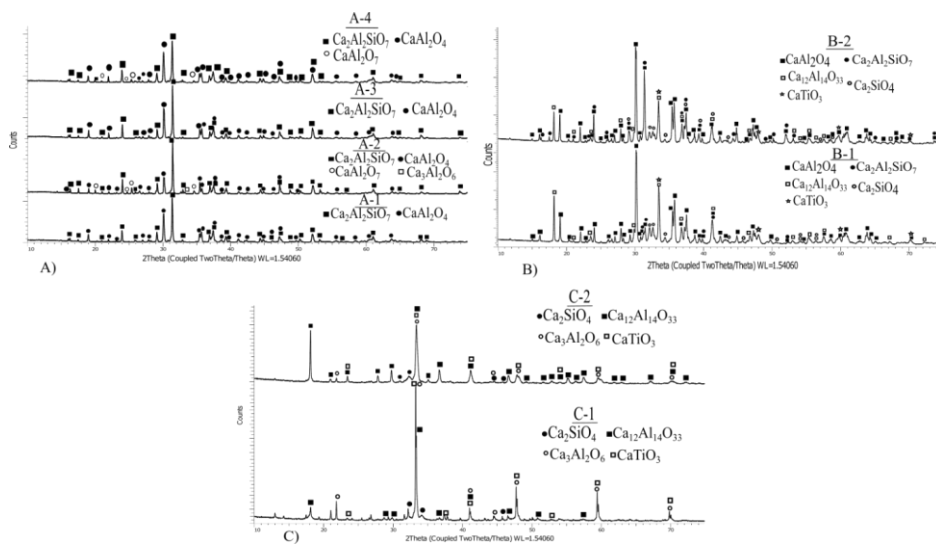
Figure 3. XRD analysis of produced slags a) A-series, b) B-series, c) C-series.

Although tests A-3 and C-2 are not directly comparable (no charcoal addition), we may claim that with increasing the lime addition leachable phases can be more easily formed as proved with the tests B-1 and C-1. The same behavior has been observed in previous work, in comparison with the slag B-2[7]. We observe here that in the slag C-1 there is an excess of lime in comparison with slag C-2, and therefore a C/A ratio of 1.5 can produce a slag with more leachable phases. Additional.ly, based on the discussed results and the optimum analogies, the addition of BBBP can reduce the lime addition by 10%, which is important from an economic point of view.
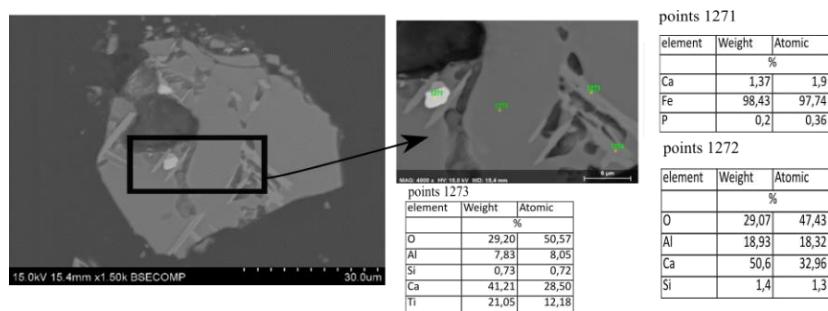

Figure 4. SEM and EDS analysis of test C-1, point 1271 is the bright phase, 1272 the continuous phase, and 1273-1274 the dendritic phase

It is observed that by controlling the mixing ratios of the BR and BBBP, the formation of alumina-containing leachable phases in the slag is feasible. More experimental and thermodynamic work is in progress to understand the mechanism for the formation of the different phases during the smelting and reduction step.

Conclusion

- The charcoal addition in the presence of graphite crucible create an excess of reduction conditions and, as a result, the titanium content in the slags is low.

- Low CaO to Al_2O_3 ratio, resulting in the formation of non-leachable phases in the slags, such as Gehlenite.

- The mixing of the by-products in analogies that yield a $wt\%CaO/wt\%Al_2O_3$ equal to 1 in the slags improves the results, while Gehlenite is still present in the slags. Increasing more the $wt\%CaO/wt\%Al_2O_3$ enhanced the formation of the leachable phases, defining an optimum ratio of 1.5.

Acknowledgements

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