BR06 - Investigating the Leaching, Desilication and Precipitation of Aluminium Tri-Hydroxides from a Bauxite Residue-Bauxite By-Product Slag

James M. Mwase[1] and Jafar Safarian[2]
1. Postdoctoral Researcher
2. Associate Professor
Institute of Materials Science and Technology, Norwegian University of Science and Technology, Trondheim, Norway
Corresponding author: james.mwase@ntnu.no

Abstract

The ENSURE**AL** initiative is investigating the revival of the long discontinued Pedersen process for use in processing lower grades and different types of bauxite ores. The Pedersen process is a combined pyro and hydro-metallurgical process that has been proposed as an almost waste free alternative to the Bayer process for production of metallurgical grade alumina. This study evaluated the hydrometallurgical processing of slag which was composed of a mixture of bauxite residue (red mud) and a calcite-rich bauxite benefication by-product. The slag contained Al in the form of gehlenite and mayenite. The study investigated the leachability of the slag, the effectivness of a desilication step and the precipitation of aluminium tri-hydroxides. All three processes where investigated at lab-scale using a 1 L jacketed glass reactor. The results from early tests in this ongoing study have been promising.

Samples of the slag (100 g), ground to -75 µm, were leached using a 1 L solution of 60 g/l Na_2CO_3 at 90°C for 90 mins. As much as 65% of the Al was extracted with an indication that perhaps the amount could increase with longer leaching time. The desilication step was carried out by treating the leachate solution with CaO and mixing for 2 hrs at 70°C. This resulted in a small reduction of the Si content by 27%. The desilicated solution was sparged with a mixture of Ar and CO_2 at a gas flowrate of 1.5 slpm and CO_2 partial pressure of 50%. This was done for 30 mins at a temperature of 25 °C. When precipitation commenced the gas flow was stopped. The solution was allowed to age for 3 days at 25°C while agitated at 200 rpm. The resulting precipitate was composed of the aluminium tri-hydroxides bayerite (85%), gibbsite (12%) and nordstrandite (3%).

Keywords: Pedersen process, alumina, leaching, desilication, precipitation.

1. Introduction

A revival of the Pedersen process has been proposed by the ENSURE**AL** initiative in response to the need for more environmentally friendly and sustainable methods to process low grade bauxite ores. Additionally, the Pedersen process may also be used to process red mud resulting from processing high grade bauxite ores through the Bayer process. The Pedersen process was successfully used during the period 1928-1969 to produce alumina in Høyanger, Norway [1]. It was eventually closed due to the economic strain of less efficient smelter technology [2] and it could not compete with the Bayer process in treating high grade bauxite ores. However, improvement in the smelter technology, the need for more sustainable processes in the mining industry and the need to address the red mud product from the Bayer process have renewed interest in this process. The process potentially addresses all these matters while being an almost zero-waste process producing by-products that can be used in other industries.

The process is a combined pyro and hydrometallurgical process that can be described in three stages [3, 4, 5]. The first is the smelting of the bauxite ore to produce calcium aluminate slags and pig iron as a by-product to feed the cast iron industry. In the second stage the slags are leached with sodium carbonate solutions to dissolve the aluminate minerals and leave behind a mostly calcium carbonate product referred to as grey mud. This by-product may be used in the cement or fertilizer industry. The leach liquor is then sparged with CO_2 gas to precipitate alumina trihydroxide which is dried and calcined to produce metallurgical grade alumina.

The precipitation process is very complex and involves the absorption of CO_2 gas by the sodium aluminate solution (equations 1 and 2) which leads to the neutralization of free hydroxyl ions by H^+ ions in solution. During this step several physiochemical sub-processes such as mass transfer through the gas-film occur. This step creates a suitable pH for the hydrolysis (decomposition) of aluminate ions and precipitation of fine aluminum hydroxide particles (equation 3) [6, 7, 8].

$$CO_{2(aq)} + H_2O_{(l)} \leftrightarrow HCO_3^-{}_{(aq)} + H+_{(aq)} \tag{1}$$

$$HCO_3^-{}_{(aq)} \leftrightarrow CO_3^{2-}{}_{(aq)} + H^+{}_{(aq)} \tag{2}$$

$$Al(OH)^-{}_{4(aq)} \leftrightarrow Al(OH)_{3(s)} + OH^-{}_{(aq)} \tag{3}$$

A part of this study will evaluate the leachability of a slag produced by the smelting-reduction of a mixture of bauxite residue (red mud) and a calcite-rich bauxite benefication by-product. The slag contains some SiO_2 hence the effectivness of a desilication step on the leach solution to reduce Si content in the solution and final product will also be investigated. Finally the precipitation of aluminium tri-hydroxides from the desilicated leach solution will be investigated.

2. Materials and Methods

The procedure for the smelting-reduction process used to prepare the slag is described by Lazou [9]. The starting material for making the slag was 1 kg of a mixture of bauxite residue (red mud) (60%) and a calcite-rich bauxite benefication by-product (40%). To this lime (CaO) in a ratio of 21wt% of the mixture was added. The resulting slag was crushed and screened to produce a bulk sample that was -75 µm. The material was then subject to splitting using 2-way rifle splitters and an 8-way Retsch DR rotary splitter to produce sample sizes of 100 g for leaching test work. Smaller sub-samples were obtained for analysis by XRF (Table 1) while XRD analysis (Figure 1) showed the slag contained Al as gehlenite and mayenite. Perovskite and Larnite were also present.

Table 1. Normalized semi-quantitative analysis of slag wt%.

Al_2O_3	CaO	SiO_2	TiO_2	MgO	Fe	SO_3
39.6	43.9	6.99	5.84	0.17	1.82	0.18
MnO	Na_2O	ZrO_2	SrO	Cr_2O_3	V_2O_5	P_2O_5
0.06	1.19	0.14	0.06	0.03	<0.01	<0.05

2.1 Leaching

A 100 g sample of slag was placed in a jacketed glass reactor and 1 L of solution was added to it. The resulting slurry was heated to 90°C and held at that temperature for 1.5 h. The temperature was controlled by circulating a heated silicon oil through the reactor jacket and a temperature probe was placed in the reactor vessel. The slurry was agitated at a speed of 500 rpm using a stainless-steel overhead stirrer with a paddle impeller. The temperature probe was connected to the agitator which displayed the result in addition to the agitation speed. A glass condenser with cooling water was attached to the top of the reactor to help maintain the reactor volume. During the experiment samples were withdrawn at 15-minute intervals using a syringe and filtered with a 0.2 µm Millipore vacuum filter to produce clear samples suitable for ICP-MS analysis of Al and Si. At the end of the experiment the slurry was cooled and then vacuum filtered using a büchner funnel and general purpose Whatman filter paper to produce a filter cake for further analysis by XRF and XRD. The filtrate was set aside for the desilication and precipitation steps. All experiments were conducted using 1 L solution of 60 g/L Na_2CO_3 prepared from deionized water and analytical grade Na_2CO_3. Higher solution concentrations produce a leachate solution that precipitates dawsonite instead of the desired aluminium hydroxides [10]. In total two experiments were conducted (Table 2); in the first the filter cake was dried and ground with a pestle and mortar. This was done to help remove the passivation layer that has be reported by Azof et al. [11] which limits the extraction of Al in agitated leaching to 50-60%. The sample was then re-leached with the same solution as before. In the second experiment the sample was leached only once with no mechanical treatment but 6 g of NaOH was added. It is reported that this is needed to limit the dissolution of Si [11, 12] which is a critical contaminant in the final alumina product.

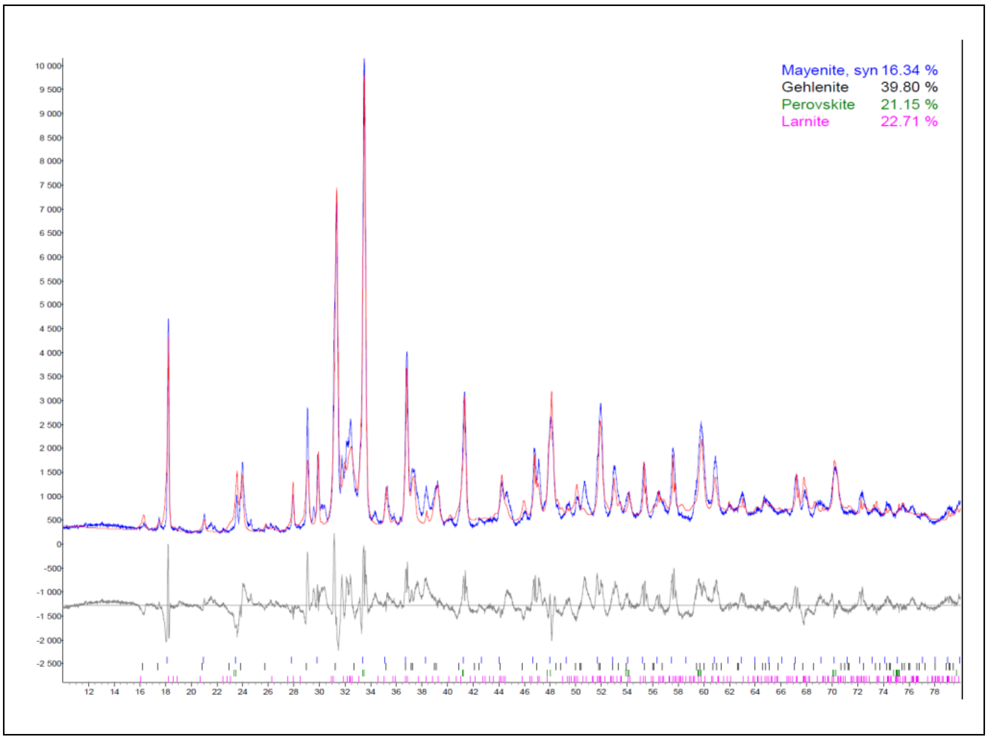

Figure 1. XRD analysis of slag. Minerals were identified using EVA software and quantified using TOPAS software.

Table 2. Leaching tests used 60 g/L Na_2CO_3, 1 L volume of solution and 100 g of slag.

Experiment	**1st Stage Leach**	**Intermediate step**	**2nd Stage Leach**
1	90°C, 1.5 h, 500 rpm	Slag is ground with pestle and mortar	Slag is re-leached with solution from 1st stage leach
2	90°C, 1.5 h, 500 rpm, 6 g NaOH	None	None

2.2 Desilication

The leachate solutions from the leaching tests were allowed to further cool overnight and then the volume measured. To the solution 14 g of CaO was added in the same reactor used for the leaching tests, after it had been cleaned. The mixture was then agitated at 400 rpm and heated up to 70°C and allowed to run for 2 h. The mixture was cooled, filtered, and the filter cake dried for analysis by XRF and XRD. Solution samples were taken before and after the test and filtered using 0.2 µm membrane for ICP-MS analysis of Al and Si.

2.3 Precipitation

The desilicated solutions were allowed to cool overnight and the volumes measured. They were treated by carbonation and aging. The solution was heated up to and maintained at 25°C for carbonation and aging. This was done using the same equipment used for desilication and leaching. Carbonation was done by sparging in a mixture of CO_2 and Ar gases each with a partial pressure of 50% at a gas flow rate of 1.5 slpm while being agitated at 200 rpm. The gases were mixed using digital AlCAT Scientific flow meters. The mixture was delivered into the solution using a fashioned piece of stainless-steel tubing at the end of some silicon tubing. Sparging was done for 30 minutes after which precipitation began and carbonation was ceased. The mixture was allowed to age for 3 days while being agitated. Under these conditions of carbonation boehmite is the expected product and aging is required to convert it to bayerite/gibbsite [13]. On completion of the test the mixture was vacuum filtered, and the filter cake washed with deionized water and oven dried at 60°C for 2 days for analysis via XRF and XRD. Additionally, the precipitates were analysed for particle size distribution (PSD) to determine the median particle size. Samples of solution were also taken before and after the test for ICP analysis of Al.

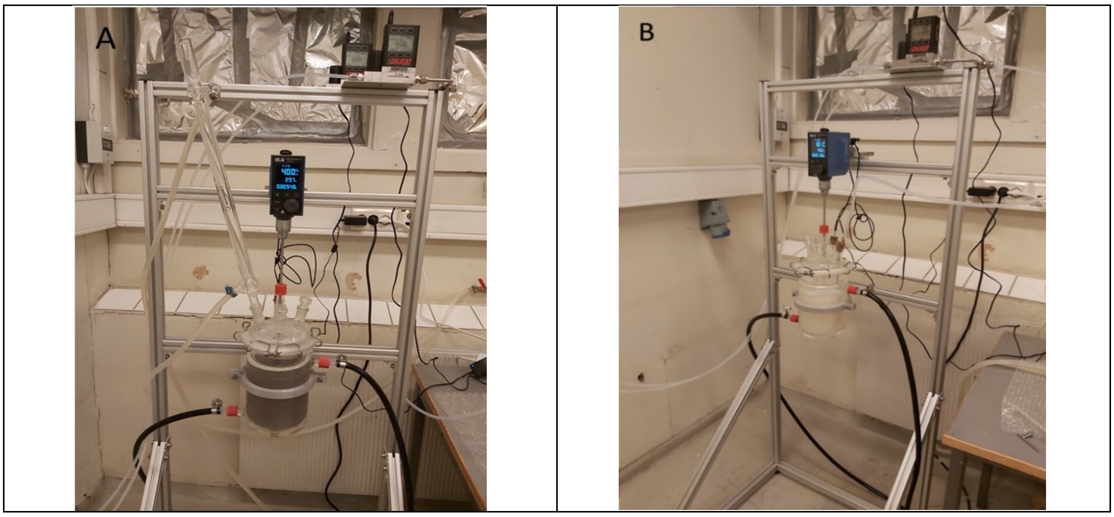

Figure 2. A-Leaching experiment. B-Precipitation experiment.

Figure 2 shows a leaching experiment (A) and a precipitation experiment (B).

3. Results and Discussion

3.1 Leaching

Table 3 shows the percentage extractions of Al and Si as determined by the results of the ICP analysis on samples during leaching and by XRF on the slag before and after leaching. A material balance was not conducted on Si due to the low quantities in the slag and solution samples.

Table 3. Percentage extractions from leach Experiment No 1 and 2.

	Al (ICP)	**Al (XRF)**	**Si (ICP)**
Experiment 1 (leach 1)	65.89	-	5.74
Experiment 1 (leach 2)	63.53	67.12	6.38
Experiment 2	61.20	64.95	6.04

In Experiment 1 66% of Al was extracted in the first leach. This is comparable to what has been achieved in a similar study [11]. This result is also comparable to results from studies conducted within the Ensureal initiative on similar slags where the Al was in the form of mayenite and tri-calcium aluminate [13]. In the latter study up to 56% of the Al was extracted. XRD analysis of the residual slag after leaching (grey mud) shows that while the mayenite was almost completely leached the gehlenite is still present in a significant quantity. Comparing the quantity of gehlenite before (Figure 1) and after (Table 4) it would appear that some of it was leached. Additionally, given that 65% of the Al was leached it is unlikely that this quantity was only from the mayenite. However, it is plausible that this low amount of gehlenite in the grey mud is due to the amount of $CaCO_3$ that was formed and that very little gehlenite was leached. The ICP results were used to draw a leach curve for the Al extraction (Figure 3). The curve has not leveled off at the end of the experiment and appears to be still increasing. This suggests that perhaps a longer leaching time may produce higher extractions of Al. The second leach after physical treatment did not increase Al extraction. At first glance it would seem that the physical treatment was not successful, but it should be noted that in other experiments using similar slag [13] a second leach with fresh solution yield an extra 10% of Al extracted without any physical treatment of the sample. It may be a matter of saturation or another chemical impedance which prevented the recycled solution from extracting more Al. The experiment will be repeated with some tests using fresh solution for the second leach, while other tests that recycle the solution from the first leach will use leach solutions with higher sodium carbonate concentration.

The Al extracted in Experiment 2 is comparable to Experiment 1. The amount is lower but not significantly as was observed in experiments by Azof [11] where NaOH was observed to notably lower Al extraction. From the leach curve for it (Figure 4) it is seen that the NaOH does seem to impede the leaching at certain times but ultimately almost as much Al is extracted as the test without NaOH. However, the amount of Si extraction in both Experiment 1 and 2 are similar, the presence of NaOH does not seem to influence the amount of Si leached. Going forward the use of NaOH will be discontinued.

Table 4. XRD analysis (wt.%) of Grey muds produced from the leaching Experiments 1 and 2.

Mineral	**Grey Mud (Experiment 1)**	**Grey Mud (Experiment 2)**
Calcite	56	46
Gehlenite	20	24
Perovskite (not $CaTiO_3$)	15	17
Larnite	7	12
Mayenite	1	1
Zeolite A ($NaAlSiO_4$)	0.5	0
Bayerite	0.5	0

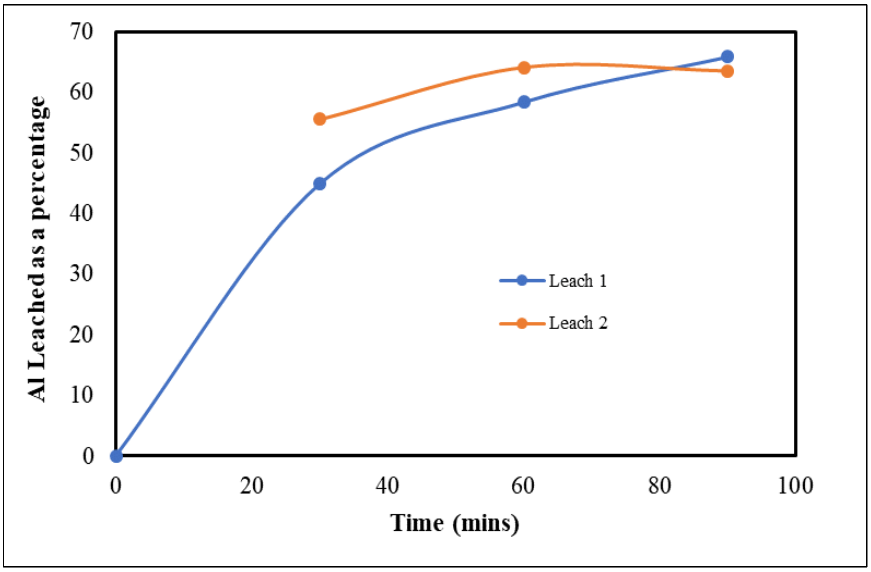

Figure 3. Leach curves from Experiment 1 using 100 g slag with 60 g/L Na_2CO_3 at 90°C for 1.5 h at 500 rpm.

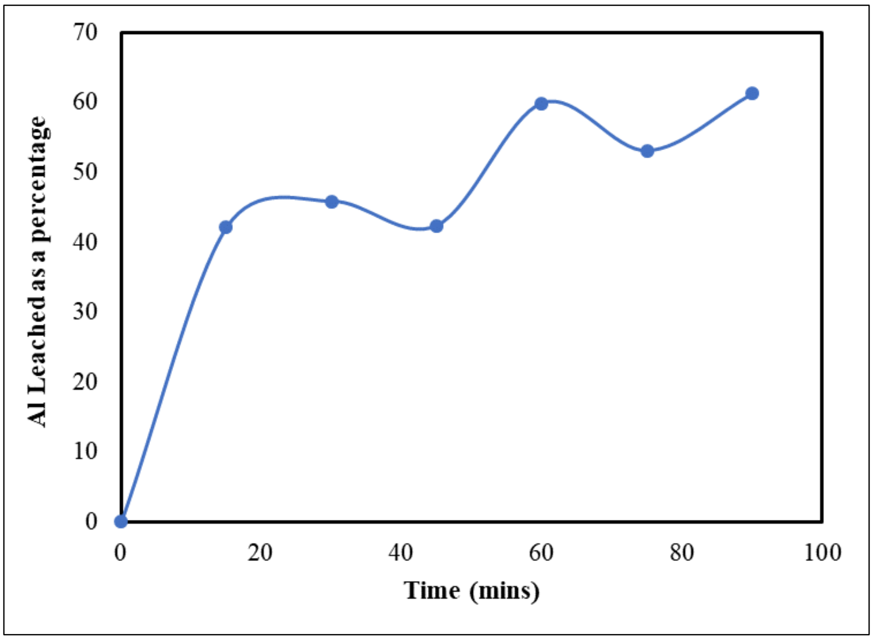

Figure 4. Leach curve from Experiment 2 using 100 g slag with 60 g/L Na_2CO_3 and 6 g/L NaOH at 90°C for 1.5 h at 500 rpm.

3.2 Desilication

The ICP analysis results on the desilicated solution, before and after, show that in both tests the Si content was reduced. However, that the actual amount, calculated using the volumes of solution before and after, is around 27% less Si in both solutions.

Table 5. ICP results before and after desilication of solutions.

		Si (g/L)	Si (g)
Experiment 1	Start	0.2	0.16
	End	0.15	0.11
Experiment 2	Start	0.15	0.13
	End	0.11	0.09

XRD analysis (Table 6) of the material collected after desilication showed no Si in any of the identified compounds. However, XRF analysis determined that 0.88% and 1.09% of the material was SiO_2 from Experiment 1 and 2, respectively.

Table 6. XRD analysis (wt.%) of the product from desilication of solutions.

Minerals	**Experiment 1**	**Experiment 2**
$Ca_4Al_2(OH)12CO_3.11H_2O$	70	58
Calcite	21	33
Portlandite [$Ca(OH)_2$]	9	9

3.3 Precipitation

The combination of carbonation and aging successfully produced products that were mostly composed of bayerite (Table 7). ICP analysis data (Table 8) of the Al before and after precipitation was used to calculate the percentage of Al precipitated in each experiment. In Experiment 1 it was 71.5% and Experiment 2 it was 55.4%. It seems possible to precipitate all the Al with a longer carbonation time. The higher alkalinity in Experiment 2 may account for the lower recovery under identical conditions to Experiment 1. The percentage of Si precipitated was not calculated as it is more useful to relate the ICP data to the quantity of Si in the Al tri-hydroxide products. Table 9 shows the results of the XRF and PSD analyses of the precipitates against typical industrial specifications of metallurgical grade alumina [14]. XRF analysis shows the Si is much higher than the industrially desired quantity of <0.015%. Further, the elements of Ca, Na and Fe are also above the desired specifications. Further focus must be put on the desilication step to not only reduce the Si but also these additional elements in solution prior to precipitation. The precipitates are also finer than the desired median size of 44 µm. However, it is curious that the precipitates in Experiment 2 are considerably coarser than in Experiment 1. This may be due to the presence of NaOH in Experiment 2 as this is the only difference from Experiment 1. The process conditions were identical.

Table 7. XRD analysis (wt.%) of precipitates from Experiments 1 and 2.

Minerals	**Experiment 1**	**Experiment 2**
Bayerite	85	96
Gibbsite	12	0
Nordstrandite	3	3
Natrite (Na_2CO_3)	0	2

Table 8. ICP results of Al and Si in solution before and after precipitation in Experiments 1 and 2.

	Al (g/L)	Si (g/L)	Al/Si Ratio
Experiment 1			
Start	12.04	0.10	120.4
End	3.83	0.05	76.6
Experiment 2			
Start	9.88	0.09	109.8
End	4.57	0.06	76.2

Table 9. XRF and PSD analyses of selected contaminants in precipitates vs industrial specification.

	Industrial Spec.	**Experiment 1**	**Experiment 2**
CaO	<0.04	0.09	0.20
SiO_2	<0.015	0.55	0.55
TiO_2	<0.004	0.00	0.00
Fe_2O_3	<0.015	0.01	0.03
Na_2O	<0.4	0.57	3.01
PSD / median size (µm)	50 % > 44 µm	15.97	28.91

4. Conclusion

Early test work has shown that the Pedersen process is a potential route to further explore as an alternative to the Bayer process for processing secondary bauxite materials. All processes involved in the hydrometallurgical section of this process have produced promising results that leave room for further investigation. The leaching has produced extractions of 65% Al and can potentially produce more with longer leach times and higher Na_2CO_3 concentrations in the leach solution. The desilication step has shown it can remove Si by using Ca. Use of higher amounts of CaO may help reduce the Si and Ca further in the solution prior precipitation. The combination of carbonation and aging has shown it can produce the desired Al tri-hydroxide precipitates. Longer carbonation times are likely to result in complete precipitation of the Al from solution.

5. Acknowledgements

We would like to thank the European Community's Horizon 2020 Programme for their funding and support of this study and the entire ENSURE**AL** project under Grant agreement 767533. We also thank the partners in the ENSURE**AL** consortium for their continued support.

6. References

1. J. Miller, A. Irgens, Alumina production by the Pedersen process-history and future. From *Light Metals* 1974, Helge Forberg, Editor, 977-982.
2. Kjell Nielsen. 1978. The Pedersen process-an old process in a new light. From Don Donaldson and Benny Raahauge, *Essential Readings in Light Metals, Alumina and Bauxite,* 523-525.
3. M. Vafeias et al., From red to grey: revisiting the Pedersen process to achieve holistic bauxite ore utilization, *2nd International Bauxite Residue Valorisation and Best Practices Conference,* Athens, Greece, 7-10 May 2018.
4. F.I. Azof, L. Kolbeinsen, J. Safarian, Characteristics of calcium-aluminate slags and pig iron produced from smelting-reduction of low-grade bauxites, *Metallurgical and Material Transactions B*, submitted 12 Feb. 2018, published online 25 July 2018, https://doi.org/10.1007/s11663-018-1353-1.
5. J. Safarian, L. Kolbeinsen, Sustainability in alumina production from bauxite, *2016 Sustainable Industrial Processing Summit and Exhibition*, Volume 5: Starkey International Symposium/Mineral Processing, Flogen, 2016.
6. A. Czajkowski, A. Noworyta, M. Krótki, Studies and modelling of the process of decomposition of aluminate solutions by carbonation, *Hydrometallurgy*, 7 (1981) 253-261.
7. Z. Wang, Bi Siwen, Y. Yihong, Y. Zhangfu, Evolution of particle size and strength of hydrargillite from carbonization in seeded sodium aluminate liquors, *Journal of Crystal Growth* 274 (2005) 218-225.

8. S. Shayanfar, V. Aghazadeh, A. Saravari, P. Hasanpour, Aluminium hydroxide crystallization from aluminate solution using carbon dioxide gas: Effect of temperature and time, *Journal of Crystal Growth* 496-497 (2018) 1-9.
9. A. Lazou et al., Smelting reduction of bauxite residue and beneficiation by-product in view of a leachable slag and pig iron production, *Proceedings of EMC Europe 2019,* Dusseldorf, Germany, 2-6 September 2019.
10. D. Marinos et al., Carbonation of sodium aluminate/sodium carbonate solutions for precipitation of alumina hydrates avoiding the dawsonite formation, *Minerals,* in review.
11. F.I. Azof et al., The leachability of a ternary CaO-Al2O3-SiO2 slag produced from smelting-reduction of low-grade bauxite for alumina recovery, *Hydrometallurgy* 191 (2020) 105184.
12. A.M. Hollum et al., Process of producing alumina from slags or sinters prepared from lime and alumna-bearing materials, *US Patent 2,544,231,* filed Jan 18, 1947 granted Mar 6, 1951.
13. J. Mwase, Precipitation of alumina in the Pedersen process, *Ensureal Consortium online meeting,* Trondheim, Norway, Confidential presentation, 16 March 2020.
14. L.K. Hudson et al., Aluminum Oxide, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a01 557, 2005, 33.