Evaluation of Alternative Raw Materials and Processes for Alumina Production

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Abstract

Inclusion of bauxite in EU's latest version of the Critical Raw Materials list is indicative of the importance of primary aluminium as a technological commodity, but also of the inelastic nature of its supply chain, from mine to metal. Central to this supply chain is the dominance of the Bayer Process for alumina production from high quality bauxite. Although there is no doubt of the inherent benefits of the Bayer Process, its complete dependence on the availability of bauxite, along with the persistent challenge of Bauxite Residue handling and reuse, are increasingly becoming obstacles to the transition of the industry in circular, near zero waste modus operandi. Consequently, a diversification of the primary aluminium supply chain with the inclusion of aluminate raw materials besides bauxite is becoming increasingly important. Especially for the case of EU who is a major importer of both bauxite and aluminium. The Laboratory of Metallurgy of NTUA, investing in its decades long experience of in the field of alumina and aluminium metallurgy, has been actively engaged in research projects that evaluate alternative alumina production processes. In the course of these studies several alternative, primary and secondary, raw materials have been investigated in both acid and alkaline process routes. This paper summarizes the most significant results and findings produced in the course of our investigations with aluminosilicate raw materials, aluminate rich tailings from different sources, Ca-rich and Si-rich aluminate slags. Different process routes are investigated for each raw material with ultimate goal of producing several process alternatives for each material and evaluating the best alternatives for further upscaling.

Keywords: Alumina Production, Aluminosilicate raw materials, Aluminate Slags, HCl Process, Alternative Alkaline Process

1. Introduction

Aluminium is a metal of high technological significance. Its unique combination of properties (light weight, electrical conductivity, resistance to corrosion, malleability, excellent thermal properties etc.) and recyclability, elevate it to a superior status among other technological metals, making it virtually indispensable to modern societies. This dependence is reflected on the current global production of primary aluminium which, for 2020, was estimated at just over 65 million tonnes, with China accounting for more than half of this production [1] [2]. Moreover, the projected demand of aluminium is expected to continue its upward trend. In a recent critical review on the demand of major metals [3], based on the median of the 197 data points, obtained by 70 studies, the largest growth rate in demand in 2050, relative to 2010, was estimated for aluminum, with a projected median increase of 215%. Consequently, the production of primary aluminium will remain an issue of immense technological significance for decades to come.

For more than 120 years primary aluminium has been produced by the combination of two industrial processes: (i) the Hall-Héroult electrolytic process for the production of metallic aluminium from alumina dissolved in cryolite bath and (ii) the Bayer Process, for refining bauxite ore to obtain Al_2O_3 of quality suitable for electrolysis (metallurgical grade or MG Al_2O_3) [4]. In other words, the world's primary aluminium is produced almost exclusively by the Hall-Héroult, with the Bayer Process serving as its dominant supplier of metallurgical grade alumina for the Hall-Héroult cells. These extraordinary conditions give rise to a one-of-a-kind value chain, from bauxite to alumina and then to aluminium, with each ring in the chain imposing limitations to the others.

First of all, not all bauxite ores are suitable for treatment by the Bayer process but only those with a high concentration of Al_2O_3 (usually ≈35% - 50%) and sufficiently high mass ratio of alumina to silica (A/S), (usually >9). Consequently, the supply of primary aluminium is directly dependent on the uninterrupted availability of high-quality, low in silica, bauxite. On the other hand, bauxite reserves are unevenly distributed, usually found in areas around the tropics and their control is considered, as "a *sine qua non* for business success" [5].

The near absolute dominance of the Bayer Process and the century long process of accumulating engineering optimizations have created a winner-takes-it-all scenario. Without a doubt, alumina production is up to this point synonymous with the Bayer Process and the treatment of high-quality bauxite. Furthermore, with high purity bauxite reserves estimated in magnitudes that could sustain the demand in the future [1], it appears as though there is no real need for changing the *modus operandi* of the industry. That is true, only if one considers the issue solely on grounds of cost effectiveness which, for the greater part of the 20th century, is where the undisputed benefit of the process lied.

In the beginning of the 21st century, an acute awareness of the inelastic character of the primary aluminium production value chain, as previously described, has arisen. For instance EU is dependent on bauxite imports from areas where political conditions tend to be unstable, such as Guinea and Brazil. Such considerations have urged the EU to include bauxite in its most recent list of Critical Raw Materials [6]. Moreover, owing to its inflexibility, the value chain of primary aluminium production could become susceptible to various forms of political, strategic, or economic manipulations. These factors have also been identified in other economic areas as well, e.g., in Russia [7].

On the environmental front, what has been an enduring thorn on the industry's side is the accumulation of the aluminium depleted residue of the bauxite ore after the Bayer leaching process, termed Bauxite Residue (BR). It is estimated that more than 120 years of bauxite ore treatment by the Bayer Process inherited to the world an estimated 2.7 billion tonnes of BR. This vast repository is ever-growing with a rate of approximately 160 million tonnes per annum [8]. The excessive production volumes of this residue, its mineralogical heterogeneity, both within the residues produced by the same plant and among the residues originating from different bauxite locations, and its alkalinity, are some of the defining features of this material that, on one side have driven research on possible utilization routes for more than 50 years, while, at the same time, are considered the main obstacles for the non-application thereof [9].

The term “alternative alumina producing technology” generally applies to any technology that aims at producing alumina from raw materials other than bauxite suitable for the Bayer Process. Aluminium is the most abundant metal in the earth’s crust and there is a long list of rocks and ores that serve as candidate materials. Moreover, owing to the amphoteric character of aluminium, both alkaline and acid extraction processes have been proposed. As a consequence, a long line of researchers, spanning in time from the very beginnings of the aluminium industry to the present day, have tackled this issue.

From a technical standpoint, alumina production is, reportedly, feasible from a number of alternative technologies and a number of them have progressed up to pilot scale research, yet none has achieved industrial operations status, with the exceptions of nepheline syenite processing in Russia and of the Pedersen Process until the mid-20th century. It is on the cost-effectiveness side, compared to the costs of the Bayer Process, that these technologies are outperformed by the latter, as shown by a relevant study by the U.S. Bureau of Mines in the mid-1970s [10]. Yet, there are other, more subtle reasons, that have prohibited advancements and technological maturity to be reached for the alternative processes.

In their review of the history of alumina alternative technologies in the 20th century and their links between the industrial players of the value chain, M. Bertilorenzi and P. Mioche [11] formulate two significant remarks. First, they note that the study of alternative alumina technologies changed significantly in the course of the 20th century. Prior to the 1st World War, when the Bayer Process had not established its dominance, research in several countries aimed at the exploitation of domestic resources that would ensure their respective autarky in aluminium. During the interwar and 2nd World War eras, especially in the U.S., disruptions in the overseas supply of bauxite led to the research. Finally, post-war research was fueled by the formulation of the International Bauxite Association, which was conceived as a raw materials cartel and immediately saw a rise in the price of bauxite [12]. In other words, in the long run, alternative alumina production technologies draw the attention of the industrial players and governments, only in critical moments for the industry’s future and bauxite supply was jeopardized. By following the latter conclusion to its logical end, the authors formulate the interesting hypothesis that R&D programs for alternative alumina technologies served as a form of technological diplomacy, with the sole aim of changing the international conditions within the industry, as soon as it was shocked by disruptive factors. Put simply, the true meaning of the continuous research on these processes is not a genuine desire to switch to another industrial mode of operations, but to provide industrial counterarguments during critical periods.

The present global situation appears once again to be critical for the industry (Ukrainian conflict, inflexibility of the value chain and susceptibility to tempering, BR production and management issues, emerging regulations for sustainable process and a circular economy model, ecological agenda). It comes as no surprise that research has sparked once again on alternative processes. Alongside, emerges anew the danger of turning this research into solely another tool in the briefcase of industrial diplomacy. Yet, the current agenda is not dictated solely on grounds of productivity and surely or of a complete substitution of one process (Bayer) for an alternative one. As one author accurately described: “sustainability is not a singularity, it is plurality*”* [13]. Thus, alternative alumina technologies, should they emerge in the 21st century, must contribute to the plurality of the primary aluminium supply chain by diversifying the raw materials used and the technologies implemented on the basis of regional capabilities. In order to achieve these goals, there is a need to assess technologies that have been studied in the past, establish connections, and address their inherent capabilities and drawbacks in light of the needs of the 21st century.

The Laboratory of Metallurgy of NTUA has been actively investigating several alternative alumina production processes, in the framework of a number of EU funded research projects. In the course of these studies several alternatives, primary and secondary, raw materials have been investigated in both acid and alkaline process routes. In the present paper, our most important findings are presented concerning: (a) alkaline and acid processes for treating calcium aluminate slags, produced from various aluminium sources and (b) HCl processes for the treatment of select secondary and primary aluminosilicate raw materials.

2. Treatment of Calcium Aluminate Slags for Alumina Production

Calcium aluminates are thermodynamically stable phases formed in the binary CaO – Al_2O_3 system. In order of increasing Al_2O_3 content, these are: tricalcium aluminate ($3CaO{\cdot}Al_2O_3$, C_3A), monocalcium aluminate (krotite, $CaO{\cdot}Al_2O_3$, CA), calcium dialuminate (grossite, $CaO{\cdot}2Al_2O_3$, CA_2) and calcium hexaluminate (hibonite, $CaO{\cdot}6Al_2O_3$, CA_6)[1]. In practice and in most technological applications, one more phase is included in the diagram, the so-called dodecacalcium heptaluminate (mayenite, $12CaO{\cdot}7Al_2O_3$, $C_{12}A_7$). $C_{12}A_7$ always appears in the stability regions of C_3A and CA.

The alkaline leaching of the more basic calcium aluminates (C_3A, $C_{12}A_7$ and CA) in an aqueous solution of Na_2CO_3 for the extraction of aluminium is a metallurgical process with a long history. In the 20th century, it has been investigated for the extraction of aluminium from aluminosilicate sources such as anorthosite or clays and submarginal, ferruginous or siliceous bauxites that cannot be treated by the Bayer Process. The only known alternative process for alumina production that reached an industrial status in the 20th century, the Pedersen Process, utilized the leachability of calcium aluminates to produce Fe and Al_2O_3 in an integrated flowsheet.

The Laboratory of Metallurgy of NTUA first revisited the Pedersen Process in the framework of the H2020 ENSUREAL Project, which aimed to investigate the possibility of applying a modified version of the process in the 21st century. The versatility of the process was quickly recognized, and it was also included as core a component in the H2020 RemovAl and SisAl Pilot Projects. In the framework of the RemovAl project, the investigation revolved around its adaptation in integrated flowsheets for the utilization of Bauxite Residue. Correspondingly, in the framework of the SisAl Pilot project, the process is adapted in an innovative process flowsheet that aims to produce Si and MG Al_2O_3 by utilizing secondary raw material feedstocks.

Acid leaching of calcium aluminates in HCl aqueous solutions is a novel concept that is investigated for the first time in the framework of the SisAl Pilot project. The ultimate goal in the case of this process alternative is the production of a precursor (aluminium chloride hexahydrate) for high purity alumina (HPA).

The metallurgical technologies mentioned in the present article are being investigated in close synergy with Mytilinaios S.A. This partnership is mutually beneficial, with NTUA performing the in-depth laboratory scale investigation of the core hydrometallurgical processes and Mytilinaios S.A. screening on a pilot scale of the most promising process alternatives suggested by the laboratory work. This continuous cooperation between laboratory and pilot scale operations decreases the time and costs needed for process optimization and leads to accelerated know-how of the key parameters affecting each process during upscaling.

All process alternatives that are currently being optimized for the treatment of calcium aluminate slags are shown in Figure 1. In the following sections, findings in the alkaline and acid routes presented are summarized.

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[1] Formulas in parentheses follow the convention of nomenclature of the Cement Industry for which: C=CaO, A=Al_2O_3, S=SiO_2, H=H_2O. For this reason, for example, tricalcium aluminate, corresponding to the compound $3CaO{\cdot}Al_2O_3$ is named C_3A. This nomenclature will be followed in text, for the remaining of this document.

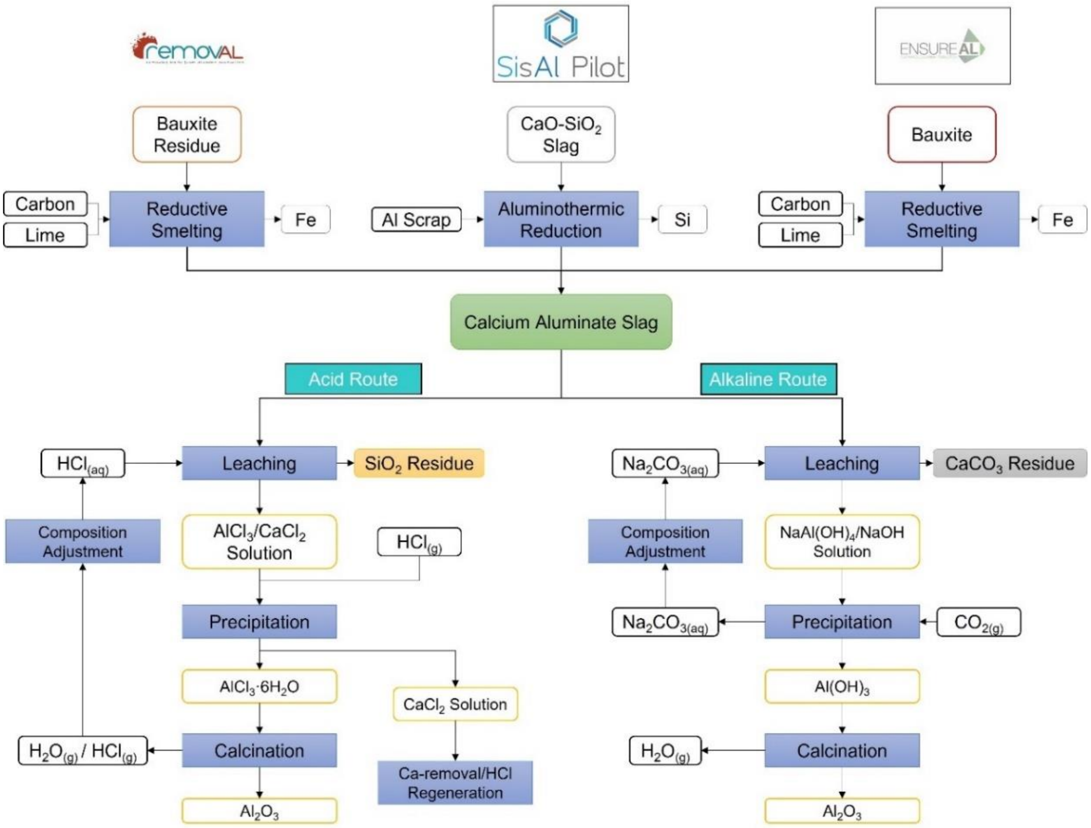

Figure 1. Alternative raw materials and process alternatives for the production of Al_2O_3 by a calcium aluminate treatment route

2.1 Alkaline Leaching of Calcium Aluminate Slags

In Table 1 chemical analyses of calcium aluminate slags that have been investigated by NTUA in the framework of the aforementioned projects (only the principal metal oxides are mentioned).

Table 1. Chemical analyses of calcium aluminate slags investigated by the Laboratory of Metallurgy of NTUA for alkaline extraction of Aluminium.

Project	Raw Material for Slag Production	CaO	Al_2O_3	SiO_2	TiO_2	Fe_2O_3
ENSUREAL	Bauxite	50.4%	45.0%	1.6%	1.3%	0.97%
RemovAl	Bauxite Residue	36.3%	32.0%	13.10%	4.28%	0.89%
SisAl	CaO-SiO_2 slag	39.9%	54.3%	10.1%	-	0.08%

As shown in the right-hand side branch of the flowsheet of Figure 1, the alkaline treatment route consists of two core hydrometallurgical processes: (a) leaching of calcium aluminate slags with a Na_2CO_3 aqueous solution for the production of sodium aluminate solution (pregnant leach solution or PLS) and (b) precipitation of $Al(OH)_3$ from the PLS by carbonation. Both processes have been investigated and key process parameters have been identified.

The extraction of aluminium from calcium aluminate slags is a complex chemical process. The main contribution of NTUA is the proposition of leaching mechanism based on the hydraulic character of calcium aluminate compounds and their tendency to form Ca-Al hydrates whose formation is thermodynamically favored. The effects of the formation of these hydrates in the leaching process are diverse and they can act as (a) inhibitors for the extraction of aluminium, (b) intermediates for a successful leaching process, (c) secondary phases that remove aluminium from the pregnant solution and (d) desilicating agents. a typical example to demonstrate these effects will be shown.

Early in the investigation of the leaching process, it was observed that slags containing C_3A reached an aluminium extraction plateau. For example, a typical $C_3A/C_{12}A_7$ slag containing 14% wt. C_3A never exceeded 70% extraction for Al. By Rietveld XRD analysis it was observed that C_3A remained virtually unaffected by the leaching process. Mechanochemical leaching was studied as a remedy to increase the leaching rates. In figure 2 the results of aluminium and silicon extraction from the same $C_3A/C_{12}A_7$ slag are shown. The pulp after the activation was either left to cool prior to filtration (cooling) or filtered at high temperatures (no cooling). Again, the 70% plateau was never exceeded, leading to the conclusion that C_3A is practically unleachable and should be avoided.

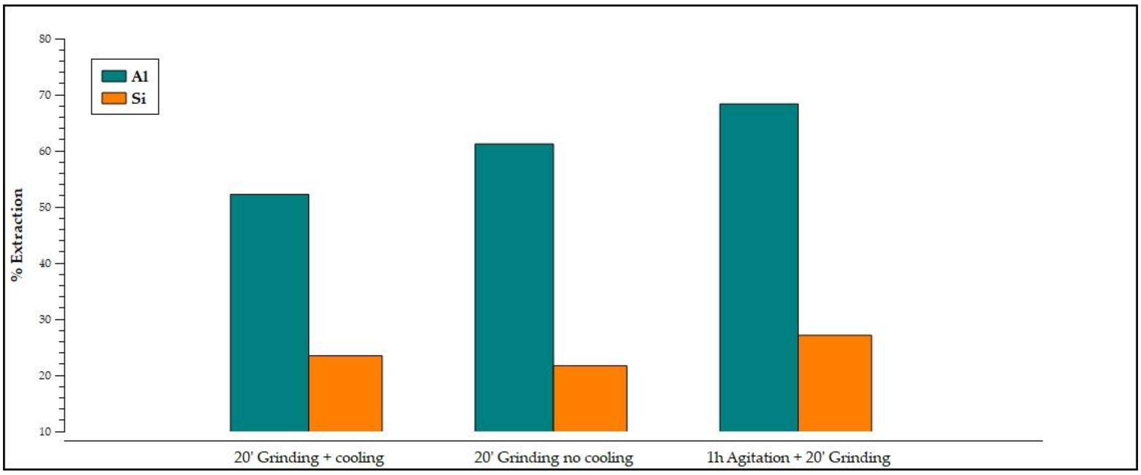

Figure 2. Al and Si % wt. extraction from a $C_3A/C_{12}A_7$ slag under different mechanochemical leaching conditions.

The mechanism can be explained by the hydration properties of C_3A, described in equations (1) and (2).

$$2C_3A + H_2O\,(\text{excess}) \rightarrow C_2AH_8 + C_4AH_{19} \tag{1}$$

$$C_2AH_8 + C_4AH_{19} \rightarrow 2C_3AH_6 + 15H \tag{2}$$

For C_3A it has been observed that the first hydration products form an amorphous gel-like material, which then converts to the metastable phases (Eq.1). The conversion reaction (Eq.2) leads directly to the formation of C_3AH_6. In the case of Na_2CO_3 leaching, the metastable phases appear to transform to vaterite (a polymorph of $CaCO_3$) due to the presence of carbonate ions, which is observed in the residue when cooling is performed immediately after leaching. If the pulp is allowed to cool, instead of vaterite the formation of two hydrates is observed: (a) calcium monocarboaluminate hydrate and (b) the tricalcium aluminate hydrate, which is the stable hydrate of the system. The graphs shown in Figure 3, showing the XRD analysis of the residues of the first two tests shown in Figure 2, are revealing. It should be noted that both these hydrates remove aluminium from the solution.

By closely optimizing the leaching process with a mechanism that incorporates the hydraulic properties and the intermediate hydrates described NTUA has been able to prove that:

- Slags for optimum leachability contain CA-$C_{12}A_7$-C_2S, with increasing amounts of CA being beneficial to the overall leaching process
- % wt. extraction for aluminium even in slags of optimum composition can never exceed 80% unless extremely low S/L ratios are utilized
- Desilication of the aluminate solutions is needed, unless extremely low S/L ratios are utilized, but has the potential to be engineered to take place with the leaching process in a single stage.
- Pregnant solution must contain a minimal concentration of free Na_2CO_3 for a successful precipitation process.

The precipitation of $Al(OH)_3$ from aluminate solutions coming from the previous leaching process is a process affected by numerous parameters such as the composition of the pregnant solution, the concentration of CO_2 in the gas input stream, the flowrate of the gas input, duration of carbonation, temperature, stirring, the presence and the physical, structural and chemical properties of the seed, ageing of the precipitate etc. Nonetheless, there are two major issues that are detrimental to the process: (a) the concentration of free Na_2CO_3 in the pregnant solution and (b) the formation of dawsonite instead of $Al(OH)_3$. The first is detrimental because even the slightest trace of dawsonite affects the purity of the $Al(OH)_3$ and, consequently, of the alumina produced downstream. The second is because it leads to a needle-shaped $Al(OH)_3$ precipitate that is difficult to agglomerate and produces $Al(OH)_3$ of suitable particle size for the calciner.

The work undertaken in the Laboratory of Metallurgy of NTUA was first to identify the distribution of the different phases that can precipitate during the carbonation process as a function of the solution pH and carbonation duration. The results of these studies led to the development of the graph shown in Figure 3.

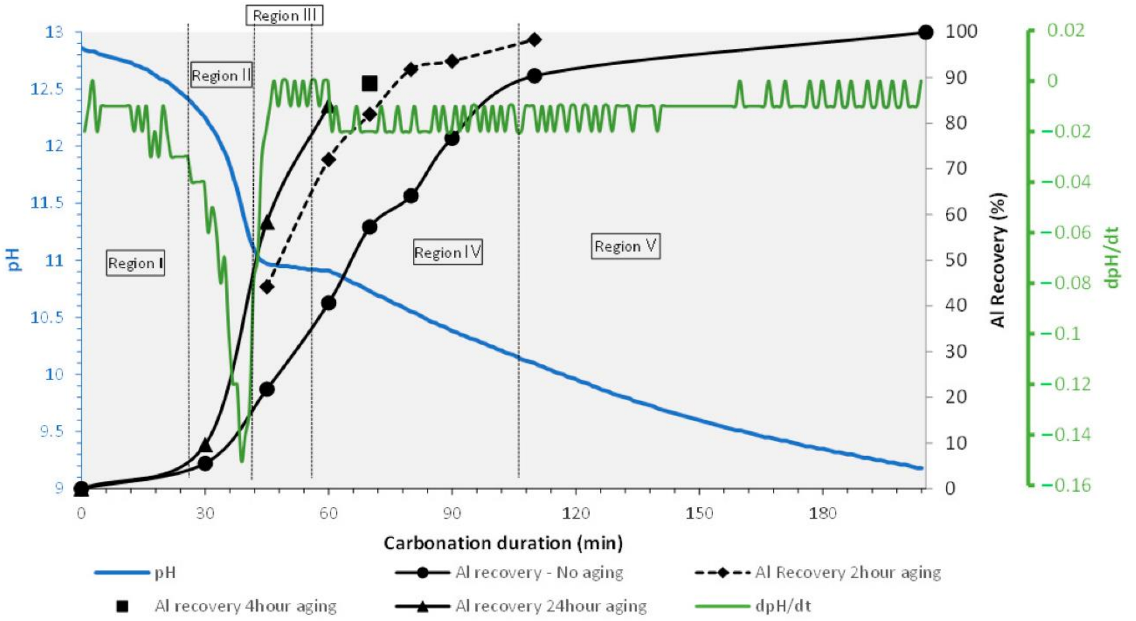

Figure 3. Graph representing the pH during carbonation, the aluminium recovery, and the time derivative of pH (dpH/dt) vs carbonation duration (min). The solution contains 20 g/L free Na_2CO_3, 18.75 g/L NaOH, 8-8.5 g/L of Al and 0.2-0.24 g/L of Si and is carbonated at 40 °C, 160 mLn/min CO_2 flow rate and 200 rpm stirring.

Five broad precipitation regions are observed. Region I corresponds to the precipitation of a sodium zeolite phase with Al recovery up to 10%. In region II, alumina hydrates (amorphous boehmite and bayerite) begin to precipitate with Al recovery up to 58%, along with a decrease in pH. In region II most of the free hydroxide ions have been neutralized. Region III is where alumina hydrates are precipitated, with recovery up to 84% after aging. First, boehmite is observed, which, by aging, transforms to bayerite. This region shows an almost steady pH. In this region, the acidity produced by the addition of CO_2 gas is neutralized by the alkalinity produced from the massive precipitation of aluminium. The following region, Region IV, represents a stage of the process where metastable alumina hydrates (since after aging they are transformed to dawsonite) are precipitated with a recovery of Al up to 94%. Finally, in region V, dawsonite is precipitated, initially reaching a recovery of Al up to 100%.

Overall, the work in the Laboratory of Metallurgy of NTUA has established that:

- At concentrations lower than 40 g/L of Na_2CO_3 in the PLS, alumina hydrates (boehmite and bayerite) can be precipitated by carbonation
- At concentrations higher than 60 g/L of Na_2CO_3 in the PLS, dawsonite is co-precipitated, and as the free sodium carbonate concentration increases, it becomes the predominant precipitated phase
- Even at favourable concentrations of free Na_2CO_3, prolonged carbonation will push the system to dawsonite

The continuation of the previous work highlighted another aspect of the process that further illustrates the importance to have a minimal concentration of free Na_2CO_3 in the pregnant solution. In precipitation trials with gibbsite seed, the morphology of the precipitates produced during aging was observed to be needle-like, a feature that is attributed to the presence of carbonate ions. Scanning electron microscope examination of such precipitates is shown in Figure 4.

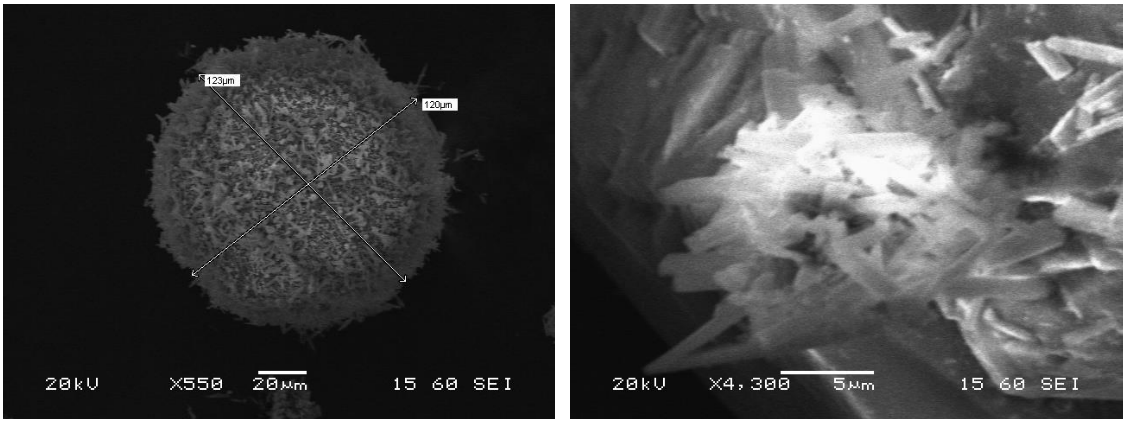

Figure 4. Needle-like morphology of $Al(OH)_3$ precipitated on the surface of gibbsite seed during carbonation.

The above findings have led to important optimization in the leaching process, which has already been mentioned above. Overall, the alkaline route of calcium aluminate slags treatment has reached a level of maturity as a prospective metallurgical technology and the next stage of optimizations is in the direction of pilot scale tests with primary and secondary raw materials.

2.2 Acid Leaching of Calcium Aluminate Slags

Acid leaching of calcium aluminate slags with HCl solutions is a novel process that is being studied in the framework of the SisAl Pilot project. As shown in the left-hand side branch of the flowsheet of Figure 1, the acid treatment route consists of three core hydrometallurgical processes: (a) leaching of calcium aluminate slags with an HCl aqueous solution for the production of metal chloride solution containing mostly Ca and Al, (b) precipitation of

Aluminium Chloride Hexahydrate (ACH) by purging with HCl gas and (c) treatment of the HCl/Calcium chloride solution remaining after the precipitation of ACH. At this stage of research in the Laboratory of Metallurgy of NTUA, key operational parameters for the leaching and the precipitation process have been identified.

The leaching process is a straight-forward dissolution process that takes advantage of the high solubility of metal chlorides in aqueous solutions. A typical chemical analysis of the slags tested in NTUA is shown in the bottom row of Table 1.

Extraction of both Aluminium and Calcium is quick leaving behind a siliceous residue. The main design parameter for the process is the optimization of the properties of the siliceous residue with the goal of obtaining a filterable residue instead of an alumina gel that inhibits S/L separation.

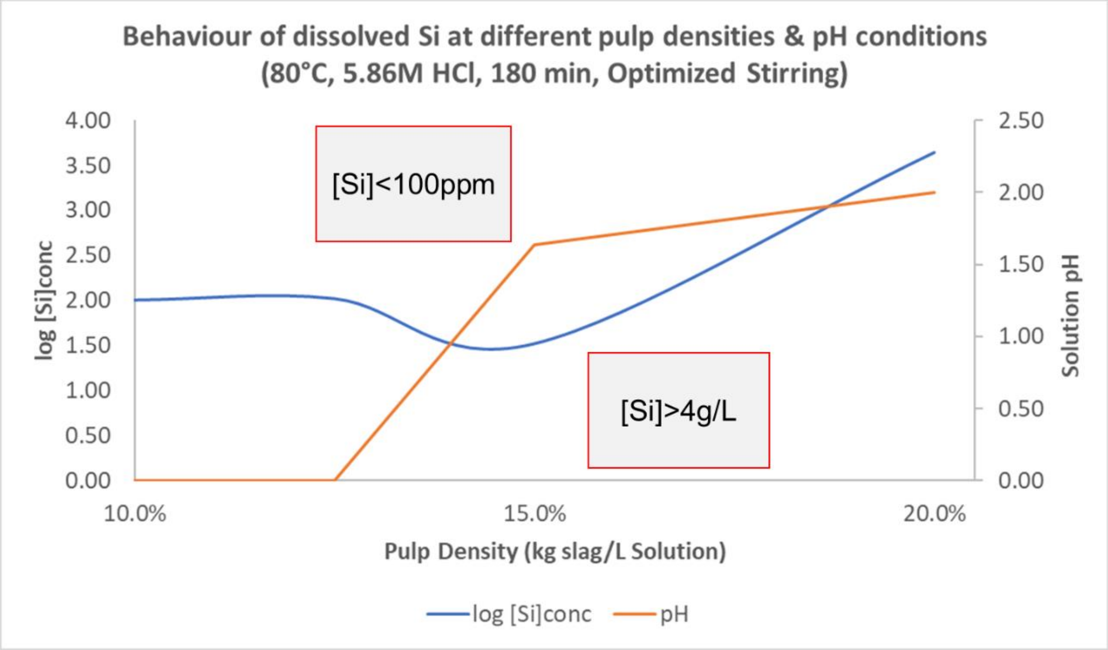

Figure 5. Behavior of Si in the pregnant metal chloride solution as function of pH and S/L ratio.

The behaviour of Si in the solution as a function of the S/L ratio and the solution pH is shown in Figure 5. Two major regions can be observed. The first corresponds to a solution pH<2, which is reached for a 15% S/L ratio for the slags under investigation. In this region concentration of Si is below 100ppm and filterable pulps are obtained. The second region starts abruptly as soon as the solution pH approaches the value 2. Si concentrations in the PLS exceed 4g/L and excessive silica gelation phenomena are observed. Optimizing the leaching process to remain in the first region and tailoring the duration of this stage to achieve a suitable size of silica particles are two parameters that ensure the successful separation of the pregnant solution from the residue.

The course of precipitation of Al by HCl purging from a suitable solution produced by the previous leaching process is shown in Figure 6. It can be observed that almost complete precipitation of aluminium (≈98%) is achieved in a solution that contains 10M of HCl. Along with Al other impurities are also precipitating (Ca, Fe, Si, Mg) in ranges between 2% - 8%. The ACH thus precipitated needs to be further purified to become an effective precursor for HPA.
The next stage of optimization to be performed in NTUA concerns the treatment of the chloride solution after precipitation, from which both Ca and HCl need to be extracted and recycled within the process.

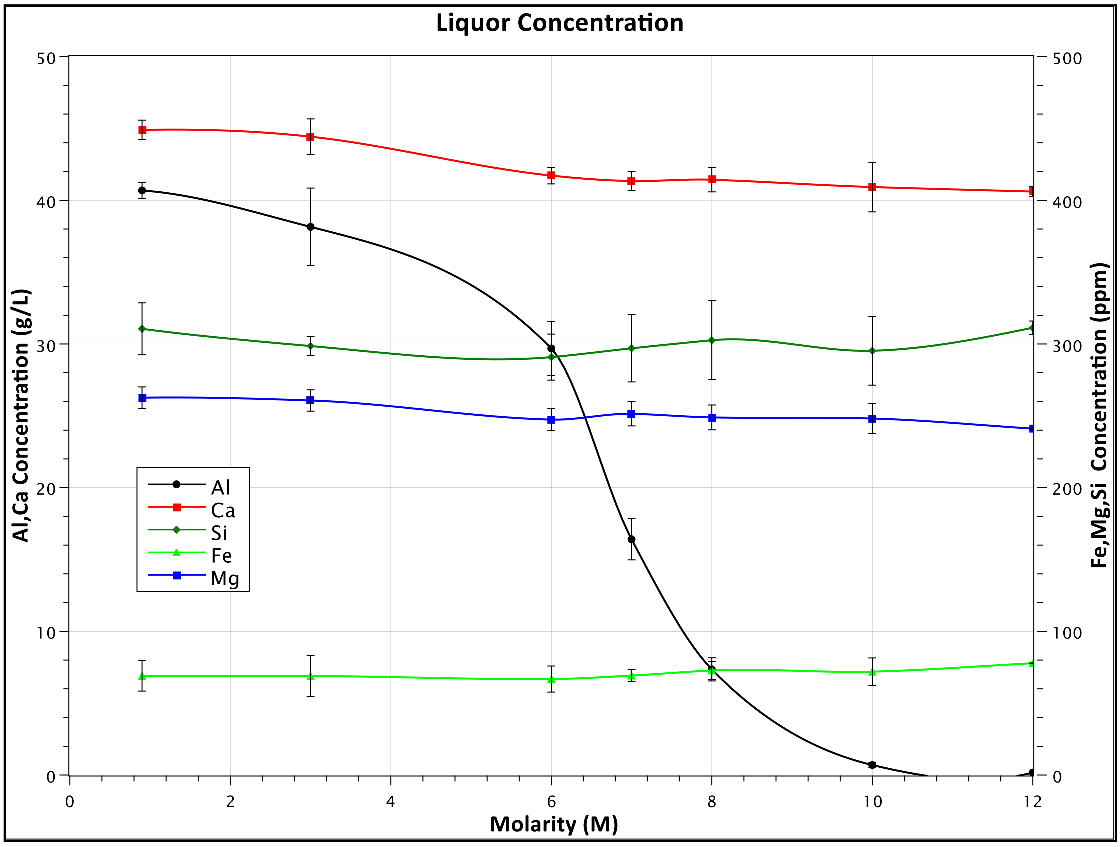

Figure 6. Wt. % precipitation of Al by HCl purging from PLS obtained by the HCl leaching of calcium aluminate slags.

3. Alumina Production from Aluminosilicate Sources

NTUA has been investigating the potential of alumina extraction from various aluminosilicate materials in the framework of the H2020 AlSiCal project [14]. In Figure 7 the different raw materials testing, and their corresponding process alternatives, are shown. A few observations can be made by inspecting the Figure. First of all, the conceptual flowsheet from the leaching process and downstream resembles the Acid Route branch of Figure 1. That is to be expected because the leaching of aluminosilicate raw materials is based on the same principles as the calcium aluminates leaching, i.e., the high solubility of metal chloride salts in aqueous solutions. The main difference lies in the composition of the raw materials, with the calcium aluminate slags being high in Ca and Al and lower in Si and the aluminosilicates high in Al and Si and lower in Ca (or Ca is absent). On the other hand, the different aluminosilicate materials might contain a greater amount of impurities in varying concentrations. Thus, there are two types of chloride solutions represented. Metal Chloride Solution I is meant to describe the aluminium rich solution resulting from the leaching process, which also contains all the possible impurities. Metal Chloride Solution II is meant to describe the aluminium depleted chloride solution after the precipitation of ACH, which contains mostly impurities, the composition of which depends on the original raw material leached. Work in NTUA has mostly been focusing on the leaching optimization for each material.

Table 2 presents the typical chemical analyses of the materials tested (only the principal metal oxides are mentioned).

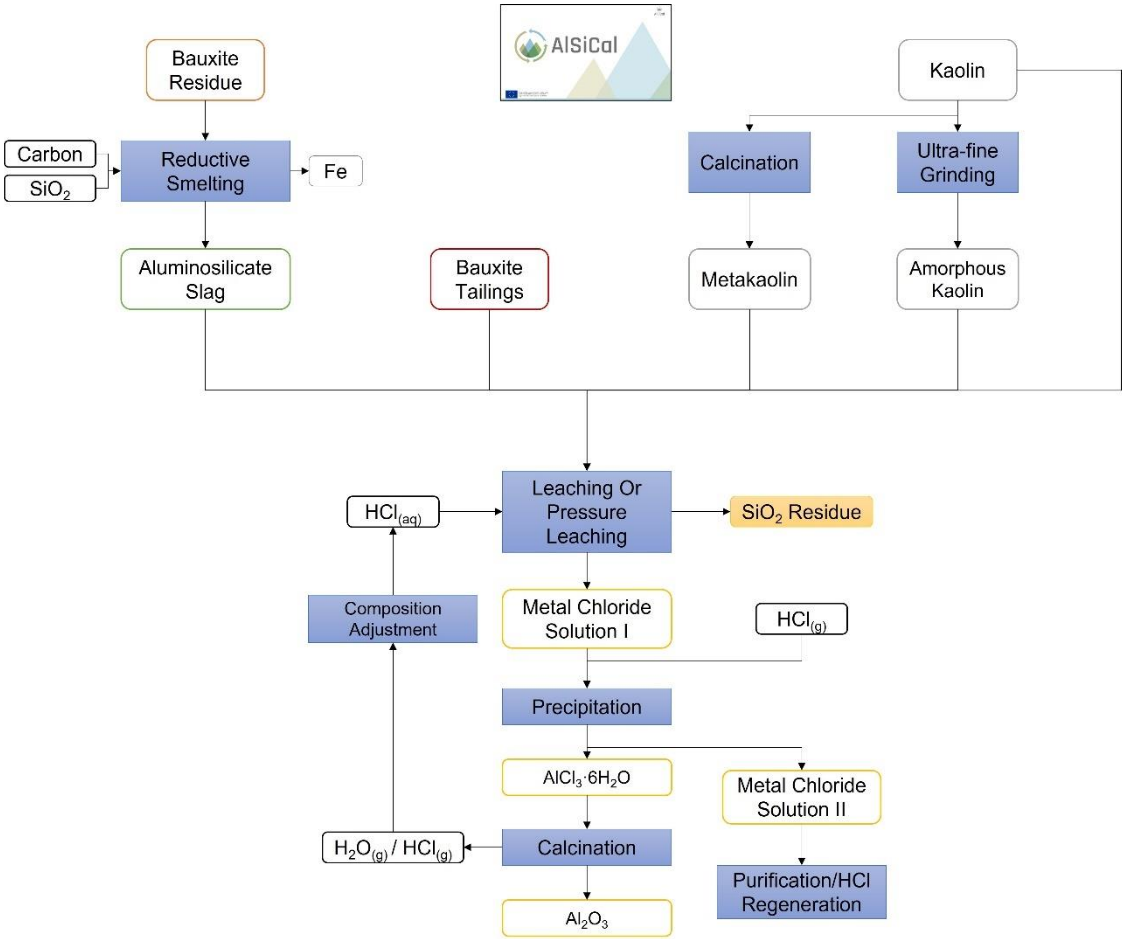

Figure 7. Alternative raw materials and process alternatives for the production of Al_2O_3 from aluminosilicate materials tested in NTUA.

Table 2. Chemical analyses of aluminosilicate raw materials investigated by the Laboratory of Metallurgy of NTUA for acid extraction of aluminium.

Raw Material	**Al_2O_3**	**SiO_2**	**TiO_2**	**Fe_2O_3**	**K_2O**	**CaO**		**Na_2O**
SiO_2 rich slag	25.00	37.44	6.73	7.23	-	15.5		4.39
Bauxite Tailings	38.89	18.76	1.55	20.41				
Kaolin A	20.20	71.18	0.37	0.09	-			-
Kaolin B	33.38	53.16	0.36	0.43	2.93			1.10

The most important results obtained until this point for each material are summarized below.

- **SiO_2 rich slag from bauxite residue reductive smelting**: Extraction of Al is high and the same holds true for most metals contained in the slag. What is observed is that a solubility limit is observed for Al at approximately 22% S/L ratio, for an azeotropic HCl leaching solution at atmospheric pressure (Figure 8). At higher S/L ratios although the concentration of Al, Fe and Ca is slightly raised, the % wt. extraction is decreasing for all metals.
- **Bauxite tailings from Guinea**: The same phenomena as with the SiO_2 rich slags are obtained. The solubility limit for this material is located at 20% S/L for an azeotropic HCl leaching solution at atmospheric pressure.

- **Kaolin leaching**: Two different Kaolin materials have been tested thus far, one from IMERYS (Sample A) and one from Quartzsandwerke GmbH & Co (Sample B). Kaolin A, which is a purer sample was investigated in the metakaolin process route. In general, the calcination of kaolin to metakaolin leads to an easily leachable material with more than 95% Al extraction.

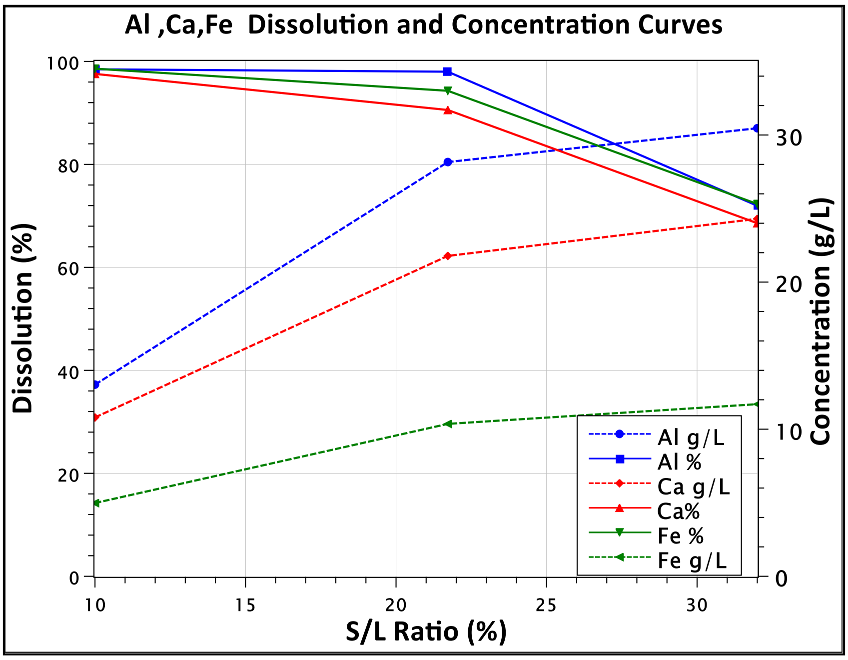

Figure 8. Extraction results from the leaching of SiO_2 rich slag (5.9 M HCl, 1h, 90°C, optimized stirring rate).

Kaolin B was investigated under pressure leaching conditions to assess the potential of the process as an alternative to metakaolin transformation. Leaching with an HCl solution with azeotropic concentration, for 6h, a 20% S/L pulp, at 150°C led to ≈60% wt. Al extraction.

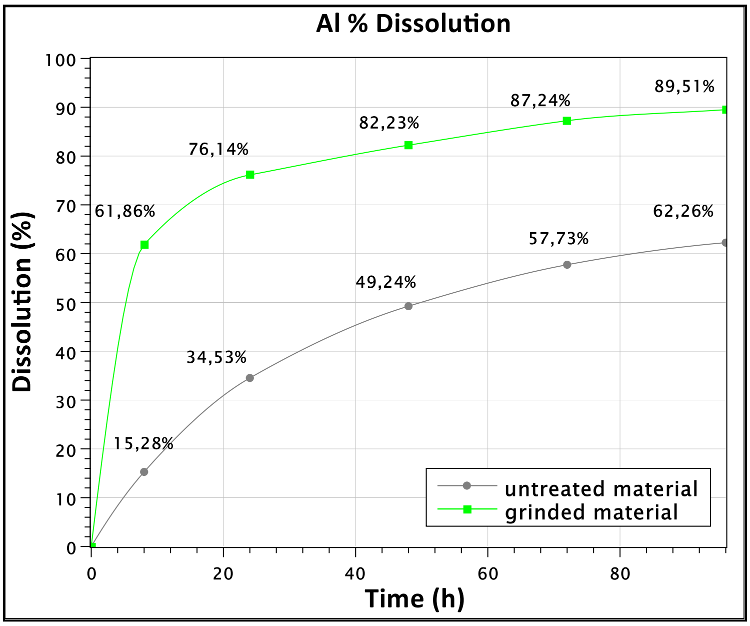

Figure 9. Kinetic leaching study of ultrafine grinded kaolin and comparison to the untreated material (5.9 M HCl, 90°C, optimized stirring rate).

Finally, Kaolin B was intensively ground to induce amorphicity to the structure of kaolin. The activated kaolin was then leached in an HCl solution of azeotropic concentration, at 90°C with an optimized stirring rate. The kinetic study results in comparison with the extraction results of the original sample are shown in Figure 9. The potential of the ultra-grinding process is apparent, and research continues toward further optimizations.

4. Conclusion

In this paper, a comprehensive summary was presented of the most important findings of the work performed in the Laboratory of Metallurgy of NTUA in the field of alternative alumina production technologies. Two major sources of alternative raw materials and their various process alternatives were presented: (a) calcium aluminate slags, which could be treated by an alkaline and an acid process route and (b) aluminosilicate materials that are treated by an acid route. Calcium aluminate slags have proved to be versatile materials and are studied in the context of various integrated flowsheets as raw materials for MG grade alumina and high purity alumina production. Challenges of both routes have been identified and the technological maturity of these processes is accelerating towards pilot scale tests. From the various aluminosilicate materials studied up to this point, the most promising appear to SiO_2 rich slags produced by the reductive smelting of BR and kaolin. In the case of kaolin, several process alternatives are being investigated.

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