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THEMATIC SECTION: BAUXITE RESIDUE VALORIZATION

Methods for Alkaline Recovery of Aluminum from Bauxite Residue

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Abstract Different ways for alkaline recovery of aluminum from bauxite residue are considered from the literature and examined in experiments. The advantages and disadvantages of a high-temperature digestion via Bayer process and soda-lime sintering process are elaborated and compared. As a hybrid process, bauxite residue undergoes a reductive smelting process with lime addition in an electric arc furnace in order to generate alumina-enriched slag. This slag is subsequently treated with high-pressure caustic leaching at moderated (200–300 g/l) and high (572–762 g/l) sodium hydroxide concentrations. The aluminum extractions are related to phase transitions in mineralogy caused by the process parameter and are analyzed and proofed by x-ray diffraction. The results show moderate aluminum recoveries of 70 % in case of the use of Bayer process, extremely high aluminum extractions of 95 % in case of slag leaching at high NaOH concentrations, and even high recoveries of almost 90 % achieved by an optimized sinter process with subsequent leaching at 50 °C with water. Special focus throughout all experiments is set on the dissolution of silicon as major impurity in the leachate.

Keywords Bauxite residue · Red mud · Aluminum extraction · Aluminum recovery · Sodium carbonate sintering · Bayer process

Introduction

Although aluminum is one of the most abundant metals in earth's crust, its first isolation was succeeded in 1825 by Christian Ørsted who firstly gained anhydrous aluminum chloride [1]. Since aluminum is an ignoble metal with a very low standard potential ($Al^{3+} + 3e^{-} \rightleftharpoons Al$) of −1676 V [2] and a high oxygen affinity (free Gibbs energy $2Al + 2/3O_2 \rightleftharpoons Al_2O_3$ of −1582,207 kJ/mol [3]), an elaborated separation of accompanying elements in raw material (refining step) must be completed prior to the generation of metallic aluminum (reduction step). Therefore, it is a major issue to create to separation as selective as possible. Hereinafter, three processes for the treatment of aluminum-bearing materials like bauxite and bauxite residue are exemplarily shown and experimentally verified by the benchmark of aluminum recovery and selectivity regarding silicon.

Bayer Process

A massive price drop in production of aluminum, which led finally to the breakthrough of this light metal in industrial applications, was achieved with the invention of the so-called Bayer process in 1887 with its first commercial implementation in 1893. Today more than 95 % of the worldwide produced alumina, which is also the intermediate for the production of aluminum metal, is processed by the Bayer process [4]. This process is based on the alkaline leaching of aluminum-bearing ores (mostly bauxite) with sodium hydroxide solution. At this high pH value and elevated temperature and pressure, aluminum hydroxides from bauxite dissolve selectively as following Eq. 1 (in this case gibbsite), while most of the other compounds remain insoluble in the leaching or bauxite residue, the so-called

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red mud. In this step, the entire refining is completed and aluminum is separated from accompanying elements.

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightleftharpoons Al(OH)^{-}_{4(aq)} + Na^{+}_{(aq)} \quad (1)$$

To force reaction 1, elevated or even high temperatures are necessary depending on the mineralogy of the processed bauxite. The main aluminum phases in bauxite are trihydrates like gibbsite (also known as hydrargillite) or monohydrates like boehmite and diaspore. While trihydrates are better soluble at temperatures of about 135–150 °C, boehmite is treated at temperatures of 205–245 °C and diaspore needs the highest digestion temperatures above 250 °C [5]. Due to their mineral composition, bauxites can be divided into two groups: karst bauxites and lateritic bauxites. Lateritic bauxites are weathered minerals containing mostly gibbsite with only small amounts of boehmite and are typical for tropical deposits. Karst bauxites contain boehmite accompanied with small amounts of diaspore [6]. They can be found for instance in Europe. After digestion, the supersaturated liquor is cooled down and the addition of nucleation agents leads to Al $(OH)_3$ crystallization and to an inversion of reaction 1. The released caustic soda can be recycled for the bauxite digestion.

Generally, silica is insoluble in caustic solutions. The exposition to weather turns silicates, e.g., minerals of the feldspar group, partly into clay minerals like kaolinite which dissolves according to Eq. 2. Moreover, at high-digestion temperatures, quartz is also attacked by caustic soda. The dissolved silica is not stable and precipitates immediately due to the reaction with caustic soda and dissolved aluminum as shown in Eq. 3. [5–7]

$$\begin{aligned} &Al_2O_3{\cdot}SiO_2{\cdot}2H_2O_{(s)} + 6NaOH_{(aq)} \rightleftharpoons 2Na_2SiO_{3(aq)} \\ &\quad + 2NaAlO_{2(aq)} + 5H_2O_{(l)} \end{aligned} \quad (2)$$

$$\begin{aligned} &6Na_2SiO_{3(aq)} + 6NaAlO_{2(aq)} + Na_2X_{(aq)} + 12H_2O_{(l)} \rightleftharpoons \\ &3(Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O){\cdot}Na_2X_{(s)} + 12NaOH_{(aq)} \\ &X \ : \ \text{anions like } CO_3^{2-}, SO_4^{2-}, AlO_2^{-}, 2OH^{-}, 2Cl^{-}. \end{aligned} \quad (3)$$

The formed products are sodalite, as shown in reaction 3, as an intermediate product and cancrinite as the thermodynamically stable final product [8]. Especially, Barnes [9–11] examined the kinetics and reaction mechanism of sodalite and cancrinite precipitation and found that firstly sodalite is precipitated as the rate-determining step, and afterward at elevated temperatures, cancrinite with its lower solubility at equilibrium is formed by dissolving and rearranging of sodalite compounds. Nevertheless both compounds leave the process together with the other insoluble compounds as red mud and cause a considerable loss of aluminum.

Overall, the Bayer process is an economic and productive circular process for selective separation of aluminum hydroxide. Nevertheless, the formation of sodium aluminum silicates lowers the aluminum recovery. Commonly used bauxites contain 30–60 wt% Al_2O_3 [4, 6], and afterward the deposited red mud still contains aluminum amounts of 10–25 wt% Al_2O_3 [12].

Soda Sintering Process

The soda sintering process is used for materials which are hardly digestible via the Bayer process and requires high temperatures of 800–1200 °C, usually 1000–1200 °C [13–17]. It is basically a “dry digestion” of aluminum oxides with soda (Na_2CO_3) and employs the principle of the soda-pot-ash digestion, but in this case without the use of K_2CO_3. The reaction mechanisms are shown in Eqs. 4 and 5 for trivalent metals (M) like aluminum or iron [18] and in Eq. 6 for tetravalent metals (M) like silicon or titanium [17]. It becomes obvious that either alumina caused by the calcination of aluminum hydroxides is turned into water-soluble sodium aluminate or alumina strongly bound in aluminosilicates is transferred into water-soluble sodium aluminate as well, while the silica reacts to even water-soluble sodium silicate. Sodium ferrite reacts with water to iron(III)hydroxide and caustic soda [19].

$$\begin{aligned} &M_2O_{3(s)} + Na_2CO_{3(s)} \rightleftharpoons 2NaMO_{2(s)} + CO_{2(g)} \\ &\quad M \ = \ \text{trivalent metal (Al, Fe, etc.)} \end{aligned} \quad (4)$$

$$\begin{aligned} &M_2SiO_{5(s)} + 3Na_2CO_{3(s)} \rightleftharpoons 2NaMO_{2(s)} + 3CO_{2(g)} \\ &\quad + Na_4SiO_{4(s)} \end{aligned} \quad (5)$$

The by-product sodium titanate is insoluble in water and does not influence the subsequent leaching step but causes soda losses.

$$\begin{aligned} &MO_{2(s)} + Na_2CO_{3(s)} \rightleftharpoons Na_2MO_{3(s)} + CO_{2(g)} \\ &\quad M \ = \ \text{tetravalent metal (Si, Ti, etc.)} \end{aligned} \quad (6)$$

Unfortunately, hazardous elements like arsenic or hexavalent chromium are bound in water-soluble species like $NaAsO_2$ and Na_2CrO_4 as well. Moreover, also sodium silicate (Na_2SiO_3) is water-soluble and leads to the contamination of the leachate.

Since the reaction product of all reactions (4–6) is always carbon dioxide, the reactions can be pushed toward the formation of the desired product sodium aluminate by lowering the carbon dioxide partial pressure. This can be either achieved by frequent exchange of atmosphere or by the addition of carbon. At sintering temperatures around 1000 °C, carbon dioxide is split into carbon monoxide, according to the Boudouard reaction, as shown in reaction 7. [14, 16]

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{7}$$

The addition of carbon can also be used for a simultaneous carbothermic reduction of hematite to magnetite or even metallic iron. The reaction takes either place as direct reduction (reactions 8, 10) or by carbon monoxide according to reactions 9 and 11. [16]

$$3Fe_2O_{3(s)} + C_{(s)} \rightleftharpoons 2Fe_3O_{4(s)} + CO_{(g)} \tag{8}$$

$$3Fe_2O_{3(s)} + CO_{(g)} \rightleftharpoons 2Fe_3O_{4(s)} + CO_{2(g)} \tag{9}$$

$$Fe_2O_{3(s)} + 3C_{(s)} \rightleftharpoons 2Fe_{(s)} + 3CO_{(g)} \tag{10}$$

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightleftharpoons 2Fe_{(s)} + 3CO_{2(g)} \tag{11}$$

After sinter crushing, the formed magnetic phases magnetite or iron can be extracted by magnetic separation. This process reduces the mass flow in the subsequent leaching step, minimizes losses of wash-water after filtration, and produces a high iron-containing intermediate product, attractive for the iron industry. Nevertheless the iron recoveries by magnetic separation of magnetite are in the range of 50–60 % [16, 20] and rather improvable. For a complete reduction to metallic iron, the iron recoveries are better and reach values of >80 %, but require higher carbon additions. The idea of iron reduction was predominantly driven by the minimization of the soda additions due to the avoidance of the formation of sodium ferrite. Already in 1975, Hrishikesan [14] found out that the reduction of hematite in combination with magnetic separation does not improve the aluminum yield or further reduce the soda need. Therefore, he comes to the conclusion that the process can waive a magnetic separation in order to save operating and equipment costs. Moreover, it has to be taken into account that aluminum losses also occur due to miss-sorting and entrapments of aluminum-bearing phases in the magnetic fraction. The magnetic separation can be done even after leaching, but in contact with water the formed iron would re-oxidize to magnetite which means that the complete reduction to metallic iron accompanied by higher demand of reduction agents would be futile.

Moreover, the input material must be crushed, dried, and blended with additives. The produced sinter must be crushed and ground again meaning additional effort and preparation for the subsequent leaching step. Therefore, it might be suitable to create a self-disintegrating sinter in order to avoid at least the energy consuming crushing step. The mechanism is based on the phase transformation of dicalcium silicate (see Eq. 12) from its monoclinic into orthorhombic structure during cooling which results in a molar volume expansion of 10 %. Since Ca_2SiO_4 is the preferred phase in order to bind silica, it is theoretically not necessary to add extra amounts of lime just in order to reach the composition for self-disintegrating sinter [21]. Nevertheless, the sintering process is due to the required high temperatures very expensive but for instance in China, the process is still in operation. Furthermore, the simultaneous separation and winning of an iron-rich concentrate for the iron industry may improve the economic efficiency of the sinter process.

Addition of Lime to Avoid Silicon Contamination

Many researchers [22, 23] investigated the possibility of capturing silica even before the dissolution or dissolved silicon in solution by the addition of lime in order to form dicalcium silicates, as shown in Eq. 12.

$$2CaO_{(s)} + SiO_{2(s)} \rightleftharpoons Ca_2SiO_{4(s)} \tag{12}$$

Due to the reaction mechanism, the molar ratio CaO/SiO_2 (C/S) becomes a distinctive parameter to describe this process. Following reaction 12, the optimum ratio C/S should be in the range of 2. Cresswell's [22, 24] high-pressure caustic leaching experiments confirm this assumption and he reports increasing aluminum recoveries with increasing ratio C/S up to 2. But the aluminum recovery declines again at higher lime additions due to the formation of hardly or even insoluble calcium aluminates. Nevertheless, it needs to be emphasized that the actually needed amount of lime may vary due to the composition of the input material and the conditions during the digestion. It is necessary to bond the "reactive" silica. Depending on the mineralogy and process temperature, not the entire silica content is mobilized by the leach liquor and thus lower lime additions may be suitable as well.

Lime is also used to bond titania, which occurs in bauxite mostly as rutile and anatase, in more thermodynamically stable phases like perovskite [25]. This can be an important issue, since Gu et al. [26] found that anatase affects the aluminum recovery from diaspore negatively. The addition of calcium compounds and the transformation of anatase into perovskite reduce the concentration of titanite ions in the liquor and avoid the retardation effect of anatase in bauxite.

In order to improve the aluminum recoveries in the sinter process, besides lime even more expensive divalent alkaline metals like barium oxide or magnesia are used and play an important role in some studies [27]. Here again silica is transformed into insoluble compounds following Eq. 13 by the release of sodium oxide. This reaction can also occur directly in the presence of quartz as described in Eq. 14.

$$Na_2SiO_{3(s)} + 2AO_{(s)} \rightleftharpoons A_2SiO_{4(s)} + Na_2O_{(s)}$$
$$A = \text{divalent alkaline metals} \tag{13}$$

$$SiO_{2(s)} + 2AO_{(s)} \rightleftharpoons A_2SiO_{4(s)} \tag{14}$$

Soda losses due to the reaction with titania can also be avoided by reaction 15 and sodium ferrite will partly react in the presence of alkaline metal oxides with a concurrent release of sodium oxide, as shown in Eq. 16. [15, 25, 27–29]

$$Na_2TiO_{3(s)} + AO_{(s)} \rightleftharpoons ATiO_{3(s)} + Na_2O_{(s)} \tag{15}$$

$$2NaFeO_{2(s)} + 2AO_{(s)} \rightleftharpoons A_2Fe_2O_{5(s)} + Na_2O_{(s)} \tag{16}$$

The sinter process in the presence of sufficient divalent alkaline metals A (according to Meher and Pahdi [27, 28]) forms all the products shown in the reactions 4–6 and 12–16. All chemical reactions in the subsequent leaching process with water are summarized in Eq. 17 and create an aluminum containing caustic solution and an insoluble slurry.

$$\begin{aligned} &NaAlO_{2(s)} + A_2SiO_{4(s)} + 2NaFeO_{2(s)} + A_2Fe_2O_{5(s)} \\ &\quad + ATiO_{3(s)} + 3H_2O_{(l)} \rightleftharpoons \\ &NaAl(OH)_{4(aq)} + 2NaOH_{(aq)} + A_2SiO_{4(s)} + Fe_2O_{3(s)} \\ &\quad + A_2Fe_2O_{5(s)} + ATiO_{3(s)} \end{aligned} \tag{17}$$

Experimental

Red mud from the landfill in Lünen, Germany is used in all experiments. The former VAW (Vereinigte Aluminium Werke) operated an alumina plant from 1939 to 1987. The deposited red mud varies through the decades in its composition due to different bauxite suppliers and bauxite deposits. For test trials, one batch is homogenized and analyzed by x-ray fluorescence (XRF) for chemical composition and by x-ray diffraction (XRD) for phase analysis. The results are shown in Table 1 and indicate that the aluminum extraction in former times was inefficient and therefore the remaining aluminum amount of 27 wt% is comparably high. The x-ray diffractogram in Fig. 1 reveals that the predominant phase is hematite. Only a small amount of iron can be detected as goethite. Aluminum even after the Bayer process is mostly present as gibbsite, to lower extend as boehmite and in traces as diaspore. High amounts of aluminum are bonded in sodalite, and albite is only apparent in traces. Titanium is detectable as anatase and rutile.

In addition to this red mud, the chemicals used for the experiments are concentrated sodium hydroxide solution (technical purity 48–50 %), lime (powder, commercial purity 95 % CaO, 1.4 % SiO_2, 1.2 % MgO), sodium carbonate (anhydrous powder >99.5 %), and lignite coke (88 % C).

The processes employed are described in detail in the following sections. An overview for comparison purposes and better understanding is given in Fig. 2.

Table 1 Chemical composition of used materials and yielded metal phase after reductive smelting

Component in wt%	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	Cr_2O_3	C/S
Red mud, Lünen (dried)[1]	28.5	27	13.1	3.8	7	8	0.35	0.3
Alumina-enriched slag	1.18[2]	39.9	18.4	29.1	2,79	11[2]	0.07	1.7
Component in wt%		Fe	C	Cr	Si	Ti	P	S
Metal phase from red mud smelting		92.4	5	0.95	0.13	0.7	0.33	0.01

[1] Original moisture 31 %

[2] Predominantly metallic (iron), or sub oxides, but calculated as Fe_2O_3, TiO_2, respectively

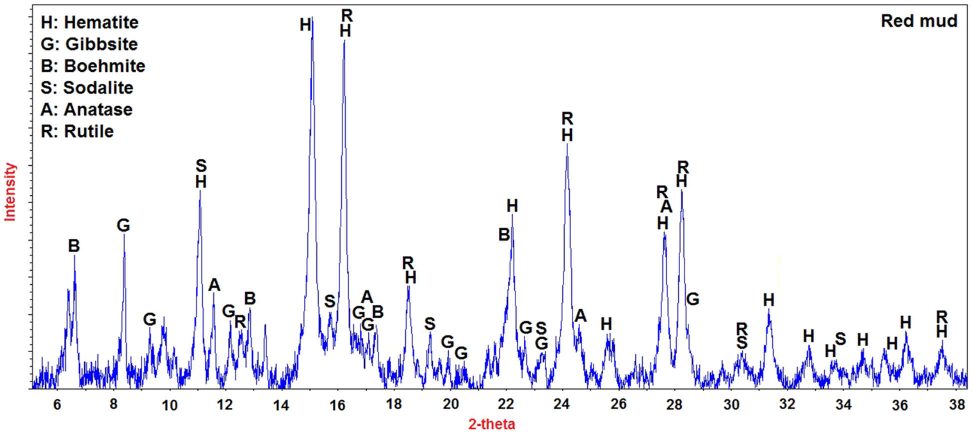

Fig. 1 X-ray diffractogram (Mo-Kα_1-radiation 0.70930Å) of used red mud

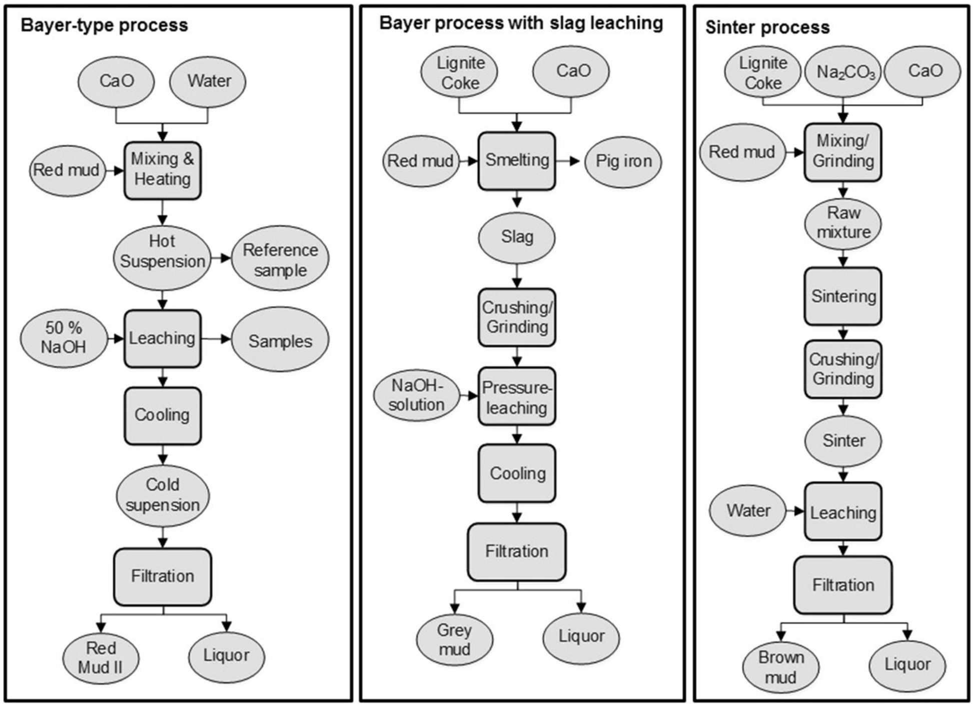

Fig. 2 Flowchart of the experimental compared processes for aluminum recovery from red mud

Bayer Process

All experiments are conducted in a 2 l autoclave. For best corrosion resistance, the leach suspension is kept in a titanium vessel inside the stainless steel pressure cylinder. The titanium vessel limits the operating volume to 1 l. An agitator avoids settling of the suspension and a cooling helix cools the suspension rapidly down after the experiment or in case of exothermic reactions to keep the process temperature on the preset level. An immersion tube enables taking samples during the experiment. The pressure inside the autoclave presses a sample volume inside a water-cooled sample cylinder which quenches the sample within seconds from process temperature down to 50 °C. The temperature is measured by a type K thermocouple which is immersed in the suspension and controls the heating jacket outside the pressure cylinder. Agitator, thermocouple sheath, and immersion tube for sampling and cooling helix are made of titanium. Liquid reagents (weak acids, caustic solutions) can be added during the experiment by an external feeding system made up of stainless steel (Fig. 3).

In every experiment, 147 g dry material consisting of red mud with composition shown in Table 1 and if applicable lime are mixed together with 590–730 ml water (depending on the sodium hydroxide concentration in the experiment) to form a suspension. Under constant agitation, the suspension is heated up for approx. 150 min to 270–280 °C. Thereafter, the first sample (7 g material and 30 ml solution) is taken, and by the subsequent addition of concentrated sodium hydroxide the desired solid-to-liquid ratio of 1:6 (140 g:850 ml) is created. Due to the liquid feed, the temperature drops to 220 °C and reaches 250 °C process temperature within 10–15 min. The process temperature is kept for 120 min, while frequent samples track the course of reaction. At the end, the suspension is cooled for 30 min and the leach residue is separated from the liquor by vacuum filtration.

Bayer Process with Alumina-Enriched Slag

In order to change the mineralogy of the input material and reduce the hematite completely to metallic iron, overall 5000 g red mud is smelted with 1200 g lime and 500 g lignite coke as reduction agents in two batches in an electric arc furnace (direct current setup with water-cooled bottom electrode and graphite top electrode), as shown in Fig. 2. After preheating of the furnace, the material is continuously fed in the graphite crucible. To ensure the complete reduction of the entire hematite content, carbon is supplied in excess by lignite coke and the graphite crucible. Moreover, after the input material was completely smelted, a holding time of 1 h at temperatures in the range of 1650–1700 °C was kept to finish the reduction. Due to the high amount of alumina (see Table 1), the liquidus temperature of the slag phase is increased and requires process temperature of >1600 °C for a stable process with a fluid slag. After smelting, the entire melt is then poured into a steel

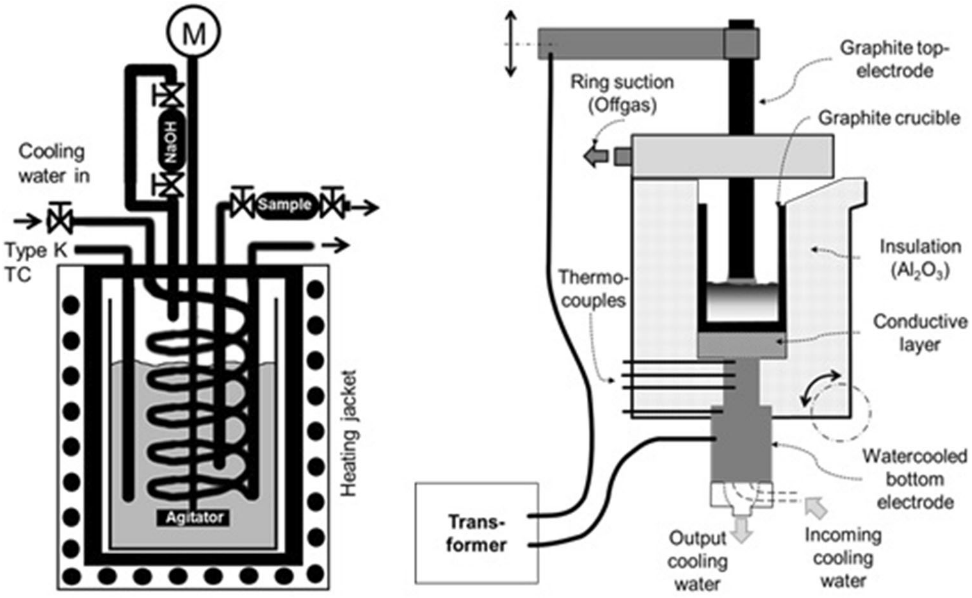

Fig. 3 Sketch of used autoclave and electric arc furnace

mold in which the formed pig iron phase is separated from the slag phase by settling. The chemical composition of used materials and yielded metal phase after reductive smelting are shown in Table 1. Apparently the metal phase can be described as typical pig iron, which is carbon saturated, rich in phosphor and has to be further treated and refined in a converter to produce steel [30]. For further processing, the slag phase is crushed and ground to grain size <125 µm, and entrapped metal droplets are removed by magnetic separation. It can be seen from the composition shown in Table 1 that enough lime is added to transform the entire titania content into calcium titanate (perovskite) and to offer sufficient lime to form calcium silicates. The XRD analysis in Fig. 4 reveals that the transformation of titania to perovskite occurs completely but no stoichiometric calcium silicate phases are detectable. The only silica containing detected phase is dicalcium dialuminum silicate trioxide. Thus, it is liable that calcium silicates are present in the slag phase but as mixed phases with varying C/S stoichiometries or as amorphous phase.

In each trial, 50 g of ground slag are mixed with 500 ml sodium hydroxide solution of varying NaOH concentrations, and the suspension is filled in the titania vessel of the above-mentioned 2 l autoclave. The heating process to test temperatures of 170, 200, and 250 °C takes approximately 90–150 min and the subsequent holding period at process temperature lasts 180 min. Afterward, the suspension is cooled down within 30 min to 50 °C and the residue is separated from the liquor by vacuum filtration.

Sinter Process

For sinter preparation, the mixture of 100 g red mud and various amounts of sodium carbonate, lime, and lignite coke are intensively mixed and ground in a disk mill. The raw mixture is sintered in a 280 ml fire clay crucible at

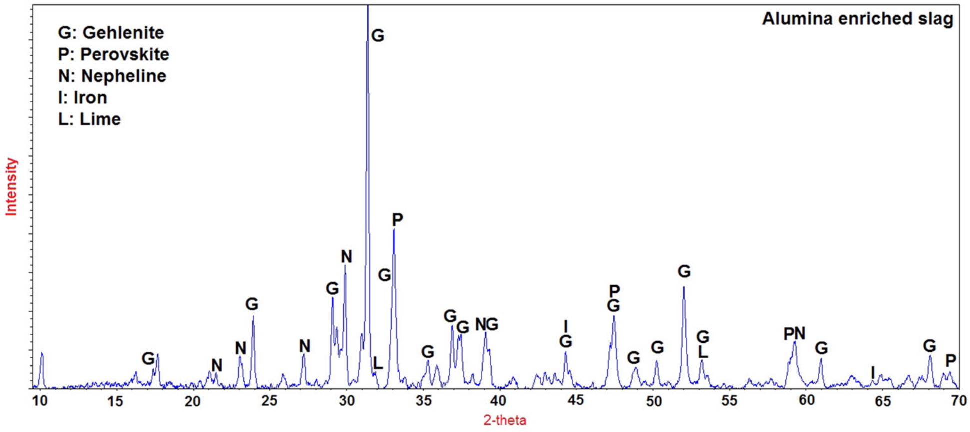

Fig. 4 X-ray diffractogram (Cu-Kα_1-radiation 1.54059 Å) of alumina-enriched slag after carbothermic reduction of red mud (Cu radiation)

different temperatures. A type K thermocouple inside the bulk material monitors the heating process and ensures that the mixture is held at process temperature for least 90 min to establish the chemical equilibrium state. After cooling, the sinter is crushed and milled again for the subsequent leaching step with 640 ml water at 50 °C for 30 min. The leaching residue is afterward separated from the liquor by vacuum filtration.

Analytics

The samples of slag, sinter, and leach residues are analyzed by XRF (model: PANanlytical Axios) and XRD (model: Stoe&Cie STADI P with Cu-Kα1-radiation 1.54059 Å, 40 kV, 30 mA for low iron-containing samples and Stoe&Cie STADI MP with Mo-Kα1-radiation 0.70930 Å, 55 kV, 35 mA for high iron-containing samples). For crosschecking purpose also the leaching solutions are analyzed by inductively coupled plasma optical emission spectrometry (model: Spectro ICP-OES Spectro Flame D). Therefore, the aluminum concentration in the liquor is kept below the solubility limit, which is ensured by the high solid-to-liquid ratios of 1/6 in case of Bayer process with bauxite residue and sintering and 1/10 in case of alumina-enriched slag leaching.

Results and Discussion

The assumption that the treated red mud still contains digestible aluminum phases (gibbsite and boehmite according to XRD) from which aluminum can be mobilized is verified throughout all series of trials. First of all, the influence of leaching temperature is examined by keeping the sodium hydroxide concentration at 200 g/l, without any lime addition. It can be seen from Fig. 5 that the aluminum recovery can be improved from 48 % at 150 °C to 53 % at 250 °C according to the analysis of the residue after the filtration and verified by the ICP analysis from the solution. The highest temperature of 250 °C is then chosen with different sodium hydroxide concentrations varying from 100 up to 300 g/l. The results are shown in Fig. 5 as well. Even a low concentration of 100 g/l, NaOH extracts more than 50 % of the aluminum content. Following the ICP results, the aluminum recovery drops at higher NaOH contents and is contradictory to the XRF analysis of the leaching residue which shows a slightly increasing aluminum yield at higher NaOH concentrations.

The comparably high extraction efficiencies at a low NaOH concentration of 100 g/l and even at a low temperature of 150 °C can be explained by the ongoing weathering and aging process inside the landfill. Although the bauxite residue has been washed and pre-neutralized after Bayer process, the remaining moisture has a pH value of 10–12 and seems to disintegrate the minerals through the period of 20–70 years. It is expected that aluminum recoveries increase with increasing sodium hydroxide content and aggressiveness of the leach liquor. But strong sodium hydroxide solutions even dissolve silica compounds and lead to an increased concentration of dissolved silicon which is shown in the diagrams of Fig. 5 as well. The formation and precipitation of sodium aluminum silicates result and lower the aluminum concentration and thus the aluminum recovery. This effect becomes obvious by comparing the course of aluminum recovery with the silicon concentration in the liquor during the leaching, exemplarily as shown in Fig. 6 for experiments with increasing sodium hydroxide concentration from 100 to 300 g/l. At 100 g/l NaOH, the leaching is completed after 60 min, and the concentrations of aluminum and silicon stay at the same level. At 200 g/l, the leaching is completed after 30 min and aluminum and silicon concentrations decrease simultaneously with ongoing leaching time. At 300 g/l NaOH, the leaching is completed within 10–15 min. With increasing leaching time, mainly silicon dissolves, while aluminum dissolves only very slowly and an equilibrium of newly dissolved ions and firstly precipitated sodium aluminum silicates is reached. After 60 min,

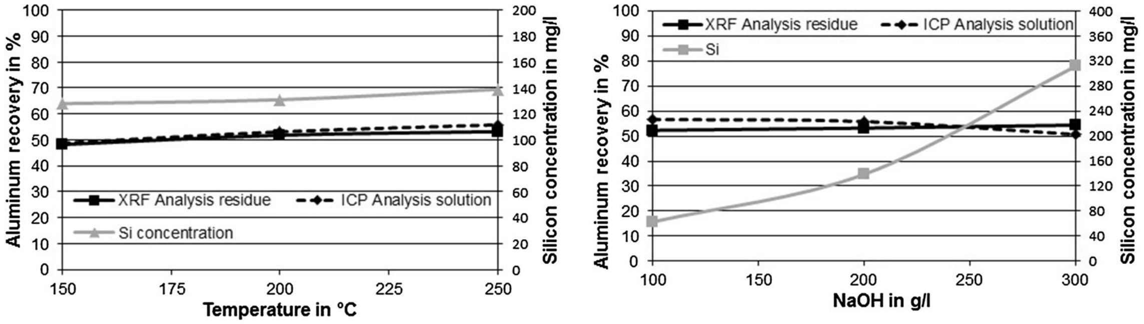

Fig. 5 Effect of temperature and NaOH concentration on aluminum recovery from red mud in Bayer process after 120-min leaching at process temperature

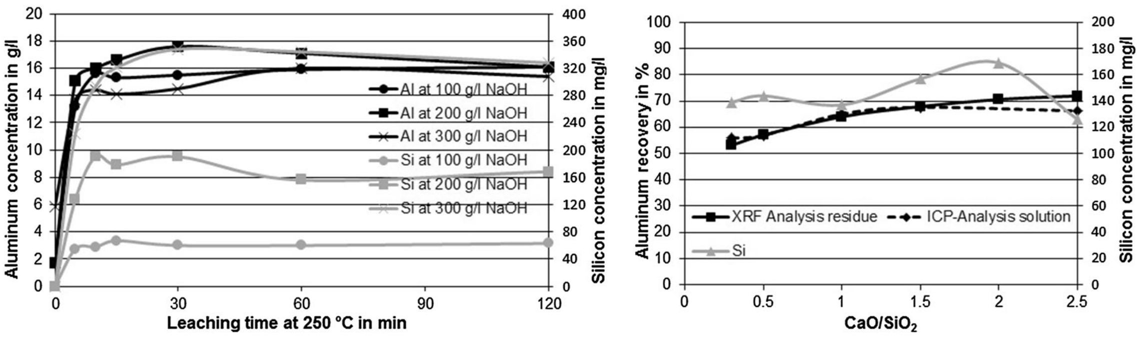

Fig. 6 (Left) Kinetics of aluminum and silicon dissolution at 250 °C, without lime addition (C/S = 0.3), solid/liquid ratio of 1:6 and various NaOH concentrations. (*Right*) Effect of lime addition on aluminum recovery from red mud in Bayer process after 120-min leaching at 250 °C, solid/liquid ratio of 1:6 and 200 g/l NaOH

the precipitation of sodium aluminum silicates becomes dominant and decreases both aluminum and silicon concentrations in the leachate.

The best way to avoid simultaneous dissolution of silica is leaching at low sodium hydroxide concentrations. Increasing the sodium hydroxide concentration from 100 to 300 g/l increases the dissolved silicon concentration by the factor of five from 60 mg/l to more than 300 mg/l. Therefore, the sodium hydroxide concentration is kept at 200 g/l and the addition of lime is examined by varying the C/S from 0.3 (initial red mud) to 2.5, as shown in Fig. 6. By increasing C/S to 1–1.5, the aluminum recovery can be significantly improved from 55 to 68 %. Further addition of lime has only little advantages on the extraction of aluminum, increasing the recovery from 68 to 72 % by raising C/S from 1.5 to 2.5. The silicon concentration in the leach liquor remains at the same level between 120 and 170 mg/l.

XRD patterns of leached red mud confirm that aluminum hydroxides (gibbsite and boehmite) are completely leached out. The remaining aluminum-containing phases are sodium aluminum silicates like albite, sodalite, and especially cancrinite and in traces diaspore. Anatase has turned into rutile, and the characteristic hematite peaks dominate the diffractogram. But the first phase transformations occur even during heating to process temperature with water. At 250 °C, only small amounts of boehmite are detectable and the predominant aluminum hydroxide is diaspore, which can even be proved after 120 min of leaching at 250 °C with 200 g/l NaOH. Lime addition makes the mineralogy more complex and besides hematite and cancrinite, katoite and zoisite are formed. Moreover, several other calcium silicates like alite, wollastonite, and combeite capture silica and allow higher aluminum extractions.

The changed mineralogy of smelted red mud slag affects the leaching behavior, and the aluminum recoveries are shown in Fig. 7. Calcium aluminates are more difficult to dissolve than gibbsite or boehmite and as a consequence the aluminum recoveries at 200 g/l NaOH are below 50 %. At 300 g/l NaOH, the alumina extraction is comparable with the results from the red mud leaching. Cracking the strong calcium aluminate compounds requires higher digestion temperatures. Below 250 °C, even high sodium hydroxide concentrations are not able to mobilize the aluminum and the recoveries are in the range of 60 %. But with increasing temperature, aluminum recoveries >90 % can be achieved at elevated sodium hydroxide concentrations of >500 g/l.

Generally, the silicon concentration during slag leaching is slightly higher than measured in the experiments with red mud even at lower leaching temperatures and low sodium hydroxide concentrations. This indicates that the silica minerals in slag are more reactive than quartz compounds in original red mud. With increasing sodium hydroxide concentration, the silicon content in the leachate increases simultaneously, and especially at sodium hydroxide concentrations >572 g/l, the silicon concentration rises exponentially up to values of 4 g/l and more. But in contrast to the leaching behavior of red mud, the aluminum concentration in the leachate increases continuously during the experiment, while the silicon concentration continuously decreases which allows higher aluminum recoveries with longer leaching durations.

The leaching residue has been analyzed by XRD and reveals the aluminum entrapments as undissolved calcium aluminate, gehlenite, and small amounts of grossular. Well-known minerals from the Bayer process, sodalite, and cancrinite do not appear, but due to the high lime addition the entire titania content is transformed into perovskite. It is noticeable that the alumina content in slag can be reduced from 40 wt% to values in the range of 2–4 wt% meaning an aluminum recovery of up to 95 %.

Comparable to the reductive smelting of red mud, the chemical and phase compositions of bauxite residue are completely changed by the dry digestion with sodium carbonate and the addition of lime and coke, respectively.

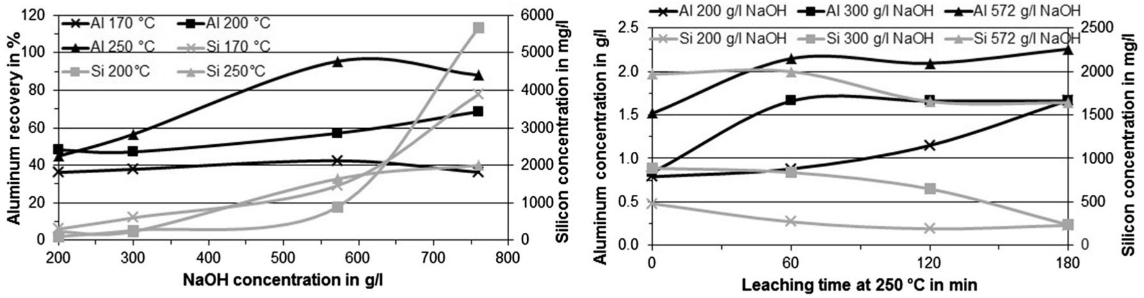

Fig. 7 Bayer process of alumina-enriched slag: Effect of NaOH concentration and temperature (*left*) and leaching time (*right*) on aluminum recovery and silicon concentration in solution after 180-min leaching time and solid/liquid ratio of 1:10 (*left*) and (*right*) kinetics of aluminum and silicon dissolution at 250 °C, solid/liquid ratio of 1:6 and various NaOH concentrations

As a result, many different phases occur which are very difficult to distinguish. Most abundant are disodium calcium silicate (Na_2CaSiO_4), calcio-olivine (Ca_2SiO_4), $CaSi_2O_5$, and perovskite ($CaTiO_3$). It was not possible to detect iron-containing phases clearly. Only in the case of coke addition, strong α-iron peaks prove the presence of iron. Aluminum can be detected as calcium aluminates ($Ca_3Al_2O_6$, $Ca_4Al_6O_{13}$), albite ($NaAlSi_3O_8$), plazolite ($Ca_3Al_2Si_2O_{12}$), and combeite ($Na_{4.5}Ca_{3.5}Si_6O_{18}$).

The first series of trials examined the best process temperature for sintering regarding the highest aluminum recovery in the subsequent leaching with water. It can be seen from Fig. 8 that the alumina recovery generally increases with increasing sintering temperature up to the solidus temperature of the mixture. Two series with sufficient sodium carbonate addition of 60 % regarding the mass of used red mud and different lime additions (without lime and with 15 % lime addition) resulting in a C/S of 0.3 and 1.5, respectively, are conducted. The courses of the recovery graphs show that lime addition positively affects the aluminum yield at lower sintering temperatures below 800 °C. At higher temperatures, red mud/sodium carbonate mixtures without lime show higher aluminum recoveries compared to mixtures with a high C/S of 1.5. The latter reach almost the same alumina extraction of about 80 % but at higher sintering temperatures of almost 1100 °C in contrast to pure red mud/Na_2CO_3 mixtures which show the same recoveries even below 1000 °C.

At elevated temperatures above 800 °C, a third series with reduced sodium carbonate addition of 28 % (regarding red mud mass) slightly reduced C/S of 1.3, and stoichiometric ($Fe_2O_3 \rightarrow Fe$) coke addition of 8 % has been conducted. Up to 900 °C, this mixture allows comparable aluminum recoveries which decline at higher temperatures. A forth series with over stoichiometric coke addition of sufficient sodium carbonate content (60 %) yields generally higher aluminum recoveries at lower sintering temperatures.

The effect of sodium carbonate addition is examined at 1000 °C sintering temperature and C/S of 1.5. According to reactions 4 and 6, the calculated necessary sodium carbonate addition for stoichiometric transformation of Fe_2O_3, Al_2O_3, TiO_2, and SiO_2 into their sodium compounds is 70 % regarding the red mud mass input. As shown in Fig. 8, the sodium carbonate addition was raised from 16 up to 80 % and demonstrates that the highest aluminum

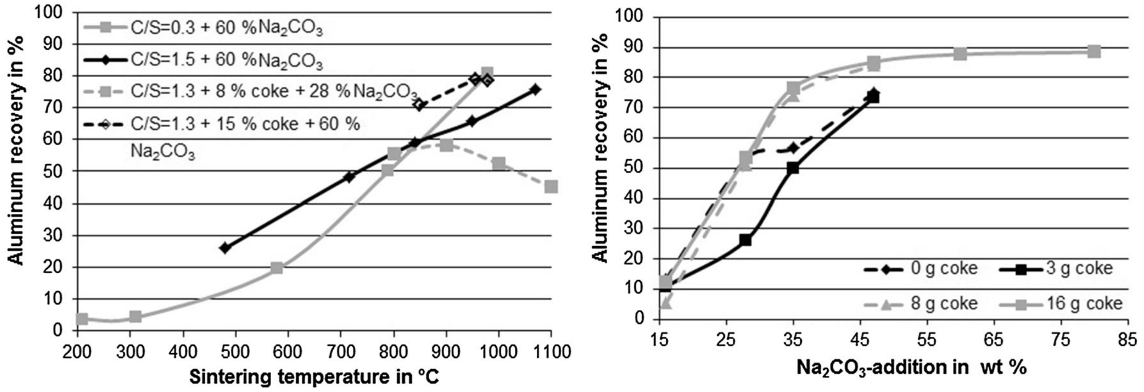

Fig. 8 Red mud sintering: Aluminum recovery depending on the sintering temperature (*left*) and depending on the sodium carbonate addition and lignite coke addition in the sintering stage at 1000 °C and C/S of 1.3

recovery of 88 % cannot be reached below this stoichiometric necessary amount of 70 % sodium carbonate addition. On the contrary, the extraction rate approximates asymptotically to this maximum, so that the aluminum recovery of 80 % at approximately 40 % sodium carbonate addition can only be increased by 10 to 88 % by doubling the sodium carbonate addition.

The effect of coke addition is also shown in Fig. 8. All trials are done at 1000 °C with C/S of 1.3. Coke additions of 3 % (double stoichiometric regarding $Fe_2O_3 \rightarrow Fe_3O_4$), 8 % (stoichiometric $Fe_2O_3 \rightarrow Fe$), and 16 % (twice the stoichiometric $Fe_2O_3 \rightarrow Fe$) are compared with the aluminum recovery of experiments without coke addition. It becomes obvious that the addition of only 3 % coke lowers the aluminum extraction even below the mixtures without coke addition at sodium carbonate additions below 50 %. In addition, the other coke additions of 8 % and 16 % do not improve the aluminum extraction below 30 % Na_2CO_3 addition. An improvement in aluminum yield takes place by adding more than 35 % Na_2CO_3. Then, the addition of 8 % coke increases the recovery by 10–15 % to values of 77 % (35 % Na_2CO_3) and 85 % (48 % Na_2CO_3) compared to 57 and 74 %, respectively, without coke addition. A further increase of coke addition does not improve the aluminum recovery at all.

A study varying the C/S ratio from 0.3 (native red mud) to 1.5 is examined in two series of experiments at 910 and 1040 °C. It is clearly shown in Fig. 9 that the aluminum recovery increases with increasing C/S up to 1.1. Thereafter, the recovery decreases slightly. The higher sintering temperature further improves the aluminum yield only at C/S above 0.8 and it becomes obvious that the responsible chemical reactions at higher C/S need higher temperatures of >950 °C to take place. Figure 9 also shows the silicon concentration in the leachate. According to reaction 12, the silicon can be successfully bonded by higher lime activities in the system and this thesis is confirmed by the results from the experiments. The ratio C/S of 0.8 seems to be critical due to the used red mud composition. At higher C/S values from 0.8 to 1.1, the concentration of dissolved silicon drops by 25 % at sintering temperature of 1040 °C, by 50 % at 910 °C, respectively. Above C/S of 1.1, the effect of lime becomes negligible.

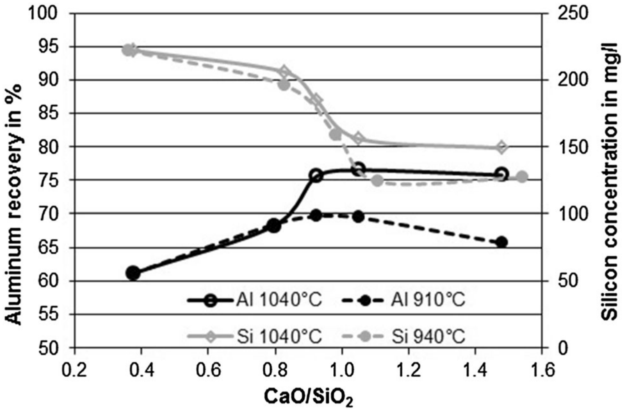

Fig. 9 Effect of lime addition on aluminum recovery at 910 °C and 1040 °C sintering temperature with 60 % Na_2CO_3 addition

The results from leaching experiments of the sintered material can be explained by XRD analysis. At higher lime additions, the calcium activity increases and compounds like albite ($NaAlSi_3O_8$), plazolite ($Ca_3Al_2Si_2O_{12}$), and combeite ($Na_{4.5}Ca_{3.5}Si_6O_{18}$) are formed which reduce the amount of soluble silicon and thus the silicon concentration in the leachate. The liberated aluminum reacts to sodium aluminate which is water-soluble and increases the aluminum recovery. The temperature dependency observed in Fig. 9 is difficult to explain because at lower temperatures the diffractograms show more amorphous phases but especially the formation of calcio-olivine seems to be preferred at higher temperatures and can be an explanation for higher aluminum recoveries at higher sintering temperatures.

Conclusions

Bauxite residues from legacy sites and from former times may still contain leachable amounts of aluminum compounds like gibbsite, boehmite, or diaspore. It has been shown in experiments that these amounts can be easily extracted using the Bayer process once again. Even mild conditions like low temperatures of 150 °C at 200 g/l NaOH or low NaOH concentrations of 100 g/l in combination with 250 °C process temperature can extract almost half of the aluminum content. With the optimized parameters, i.e., higher temperatures than 250 °C, higher concentrations than 200 g/l NaOH and lime addition to a C/S of 1.5 (for better recoveries even C/S up to 2.5 are possible, but it has to be proven if higher lime additions are economical reasonable) up to 70 % of the aluminum content can be recovered without the simultaneous leaching of silica. The remaining aluminum losses are connected with the formation of sodalite and cancrinite. The use of higher concentrations of sodium hydroxide solutions predominantly results in a higher silicon contamination of the liquor without considerable benefits on the extraction of aluminum.

Reductive smelting of bauxite residue with lime addition as flux and silicon binder will create a slag phase with considerably high alumina contents of approximately 40 wt % and completely changed mineralogy compared to the original red mud. The extraction of aluminum from calcium aluminate slags requires especially high-digestion temperatures of 250 °C and more. Moreover, higher sodium hydroxide concentrations of >500 g/l can be used to extract almost the entire aluminum content and afterward the leaching residue contains less than 3 wt% Al_2O_3 bonded in compounds like remaining calcium aluminate and gehlenite. But generally, these drastic conditions of elevated process temperatures and high sodium hydroxide concentrations mean an increased wear of equipment and result in very high concentrations of dissolved silicon in the leachate (2 g/l) with corresponding effects on quality and purity of the crystallized aluminum hydroxide. Furthermore, the solubility limit of aluminum in caustic liquor increased with increasing sodium hydroxide concentrations and it becomes difficult to reach the aluminum saturation necessary for a crystallization of aluminum hydroxide.

The best combination of high aluminum recoveries and low silicon concentrations in the leachate is achieved with the sodium carbonate sinter process. To achieve aluminum recoveries above 70 %, the sintering temperature should be above 900 °C and the sodium carbonate addition should be at least 35 % regarding the mass of treated red mud. The addition of lime up to a C/S of 1.1 improves the aluminum extraction, lowers the silicon concentration in the leachate, and assures later on a crystallized aluminum hydroxide product of comparable purity to the Bayer process. Moreover, the addition of coke in order to reduce the hematite to metallic iron improves the aluminum recovery further. Therefore, with best parameters of 60 % Na_2CO_3 addition, C/S of 1.1, stoichiometric coke addition for a complete hematite reduction (8 % regarding mass of red mud), and 1000–1050 °C sintering temperature, almost 90 % of the aluminum content in red mud can be recovered. Moreover, the sodium hydroxide concentration in the leachate compared to Bayer process is very low and simplifies the winning of aluminum hydroxide in the subsequent crystallization step.

Surely the sintering process is very cost intensive due to its high process temperature and the need of high sodium carbonate additions. The sodium containing spent liquor must be further treated, for instance, by vaporization, in order to recover and recycle sodium. Yet, this process offers exceptional recovery rates within expected short process times and an aluminum hydroxide product of high purity. The use of coke and the solid reduction of hematite to metallic iron which can be separated by magnetic separation create a salable by-product which might improve the financial viability of the process.

Although these processes have yet been proven for high aluminum-containing bauxite residues from legacy sites, after increased efficiency and reduced processing cost, they might be even practical for fresh bauxite residues.

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