



Phase characterization and thermochemical simulation of (landfilled) bauxite residue (“red mud”) in different alkaline processes optimized for aluminum recovery



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ABSTRACT

In coherent studies three different processes of hydrometallurgical, alkaline extraction of aluminum from bauxite residue (BR) are examined and benchmarked regarding their efficiency on aluminum recovery. The employed processes include a direct second caustic pressure leaching, a caustic pressure leaching of the slag produced by reductive smelting of BR with simultaneous pig iron recovery (adapted “Pedersen-process”) and leaching of BR after a sintering stage with sodium carbonate and further additives including lime and coke. In order to ensure a direct comparability, all experiments are conducted using the same homogenized BR from an old industrial landfill. After detailed characterization of the used BR using XRF chemical analysis, XRD phase analysis, SEM optical analysis and Qemscan[®] phase analysis/distribution, occurring phase formations during the employed processes are also calculated and predicted by FactSage[®] simulation software. The actual phase formation and leachability of the formed aluminum phases are verified during experiments and a special focus is set on the dissolution of silicon as major impurity in all processes. It can be shown that aluminum extraction efficiencies of 90% are still possible but interlinked with massive silicon dissolution due to the almost complete dissolution of aluminum silicates.

1. Introduction

Based on published literature this study examines the effects of different (pre-) treatments of BR on the recovery yield of aluminum with special focus on phase formation and phase transitions occurring along the treatment. It is the first time in literature that different processes are compared based on one and the same homogenized industrial BR, in this case taken from the old “red mud” landfill in Lünen, Germany. The benchmark is set on the extraction efficiency of Bayer-process under common industrial conditions of high temperature digestion as best available technology (BAT) without special pre-treatment. The first step of improving is pushing the classical Bayer-process towards its limits by raising process temperature and concentration of sodium hydroxide solution up to 280 °C and 40% NaOH (= 562 g/l) with and without the addition of lime, leading to the “concentrated caustic pressure leaching process”. The second step allows pre-treatment and is based on the “Pedersen-process” by smelting BR with lime including a simultaneous pig iron recovery via carbothermic reduction in an electric arc furnace followed by alkaline pressure leaching of the alumina enriched slag as shown in the flowchart in Fig. 1. But differing from classical “Pedersen-process”, the experiments are conducted with

lower and even completely without lime addition. The produced slag is subsequently ground and treated with pressure leaching at standard Bayer-process parameters as well as higher process temperature and concentrated caustic solution, instead of classical atmospheric leaching usually employed in “Pedersen-process”. The third step applies the soda sintering process and, in combination with lime addition, the lime soda sintering process (“Déville-Pechiney-process”). These sintering processes are further improved regarding the aluminum extraction by the addition of coke. The produced sinter is simply washed out with warm water. So all these processes are checked with and without the addition of lime as additive to immobilize silicon from cracked aluminum silicates and control the silicon concentration in the liquor.

In advance of all experiments, however, thermochemical modelling is done using the software FactSage[®], version 6.4 and 7.0. Especially the smelting process is simulated regarding the process temperature and viscosity. The occurring phases in thermodynamic equilibrium of soda sintering process with addition of CaO and cooled slag from Pedersen-process are also calculated.

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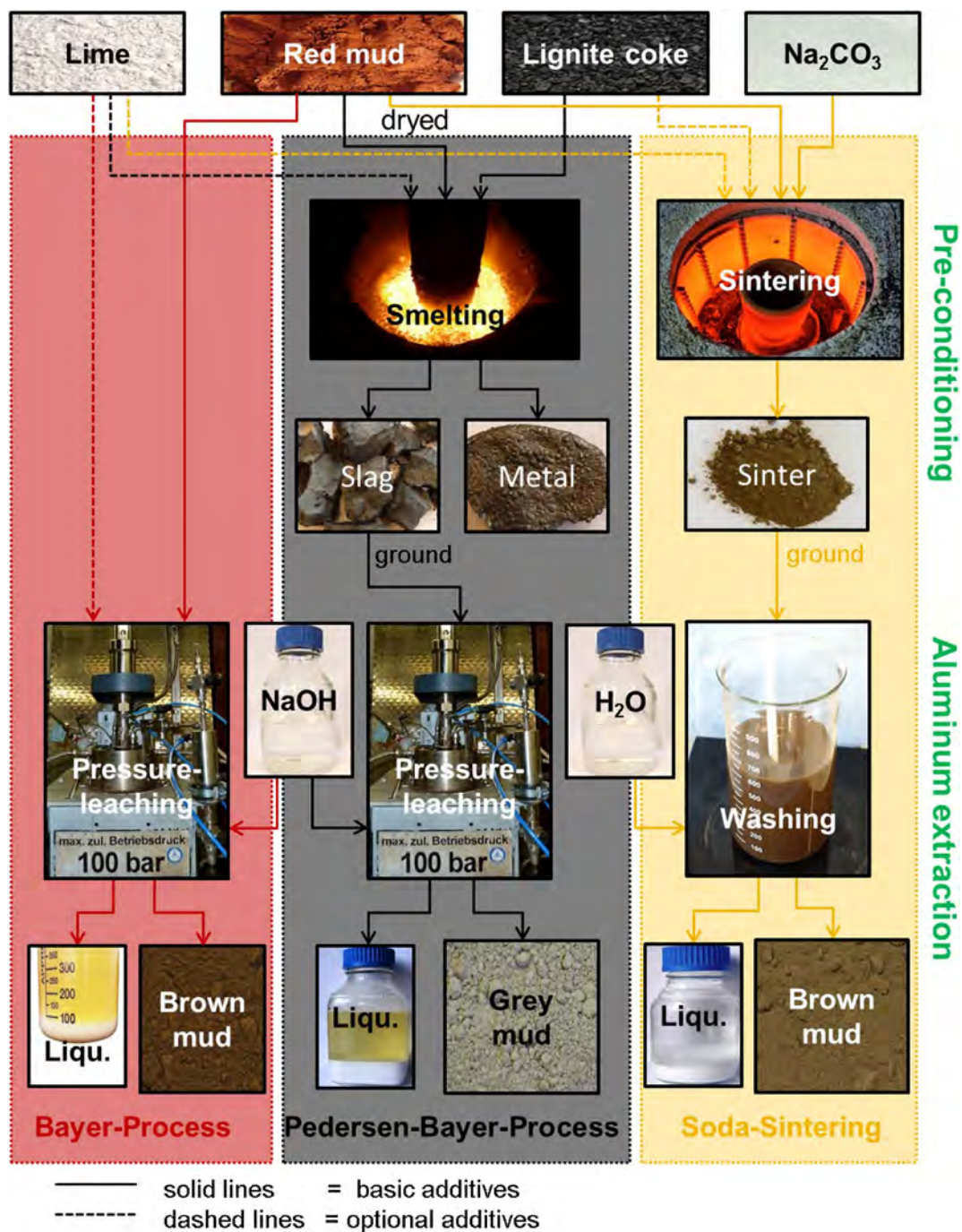


Fig. 1. Simplified flow chart of the examined processes (research strategy).

2. Theoretical background

2.1. Formation mechanism of present phases in bauxite residue

“Red mud” is the residue from the alkaline leaching of bauxite ore, which is the weathering product of aluminum silicates and clay minerals. In order to extract aluminum from bauxite Bayer-process employs the alkaline (pressure) leaching at temperatures of 100–260 °C (up to 300 °C (Aluminium Pechiney, 1996)) with caustic concentrations in the range from 120 g/l and 220 g/l NaOH. The reaction mechanism is shown in Eq. (1), (Authier-Martin et al., 2001; Ostap, 1986; Barnes et al., 1999b; Antrekowitsch, 2010).

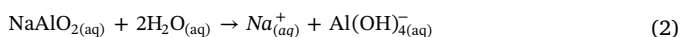


The process parameters in the leaching step are determined by the mineralogy of the processed bauxite. Gibbsite can be dissolved under mild conditions of 120–150 °C and concentrations of 105–250 g/l NaOH (Antrekowitsch, 2010). The mono-hydrates boehmite and diaspor require higher digestion temperatures of 205–245 °C and > 250 °C, respectively, in combination with generally higher caustic concentrations of about 150–250 g/l NaOH (Antrekowitsch, 2010) (up to 400 g/l (Adamson et al., 1963)). Eq. (1) reveals the dependency of soda concentration on the equilibrium. Higher concentrations push the equilibrium to higher sodium aluminate concentrations, and thus to an increased aluminum dissolution. Sodium aluminate dissociates in Bayer-liquor following Eq. (2) and forms $Al(OH)_4^-$ -ions (Paramguru et al., 2005; Verdes et al., 1992; Sakamoto, 2012).

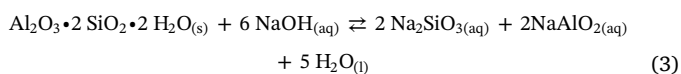
Table 1
Survey of introduced and examined processes for aluminum extraction from bauxite residue and other hardly digestible aluminum sources.

Process	Bayer-process	Concentrated pressure leaching	Pedersen-process	Soda sintering process	Lime soda sintering process ^a
Principle	Wet caustic soda digestion (< 300 g/l NaOH)	Wet caustic soda digestion (> 300 g/l NaOH)	Liquid state lime digestion and washing in alkaline solution	Dry soda digestion and washing with water	Dry soda digestion with lime and washing with water
Possible additives and effects	Lime → better aluminum recovery	Lime → better aluminum recovery	Coke → pig iron recovery	Lime → Silicon immobilization and higher Al-recoveries	Coke → low soda addition, iron reduction
Max. process-temperature	150–300 °C	150–300 °C	> 1500 °C	1000–1100 °C	1000–1100 °C

^a Déville-Pechiney-process.



Bauxite also contains silica, either as quartz or as a part of aluminum silicates and clay minerals like kaolinite and halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (Gerard and Stroup, 1963). Silica basically behaves inert in Bayer-liquors because of its low solubility and quartz is attacked only at high digestion temperatures. But clay minerals like halloysite, kaolinite or illite dissociate easily. The dissolution of clay minerals according to Eq. (3) liberates aluminum and unfortunately even silicon (Authier-Martin et al., 2001; Ostap, 1986; Adamson et al., 1963; Paramguru et al., 2005; Duncan et al., 1995; Smith, 2009; Xu et al., 2010; Croker et al., 2008; Jamialahmadi and Müller-Steinhagen, 1998; Roach and White, 1987).



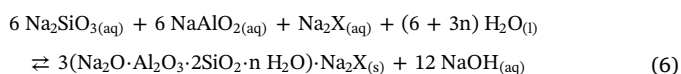
Leiteizen (1936) describes the maximum solubility of silica in Bayer-liquors $c(\text{SiO}_2)_{\text{max}}$ in dependency on the concentrations c of Na_2O and Al_2O_3 according to Formula (4) in g/l.

$$c(\text{SiO}_2)_{\text{max}} = 0,0005 \cdot c(\text{Na}_2\text{O}) \cdot c(\text{Al}_2\text{O}_3) \quad (4)$$

The actual solubility in equilibrium is due to slow precipitation kinetics impossible to measure in experiments and is calculated from the extrapolation of kinetic functions. Moreover, in industrial Bayer-liquors interactions occur in presence of accompanying elements and influence the equilibrium solubility. Adamson (Adamson et al., 1963) developed Eq. (5) in Bayer-liquors with 160 g/l NaOH resulting in a silica solubility of 0.25–0.3 g/l SiO_2 .

$$S_{\infty} = 0,00026 \cdot c(\text{Na}_2\text{O}) \cdot c(\text{Al}_2\text{O}_3) \quad (5)$$

Following Eq. (6), silicon supersaturation in aluminum containing Bayer-liquors inevitably causes the precipitation of sodium aluminum silicate, so-called (Bayer-) sodalite also known as desilication product (DSP) (Power et al., 2011; Evans, 2016; Authier-Martin et al., 2001; Ostap, 1986; Paramguru et al., 2005; Duncan et al., 1995; Smith, 2009; Croker et al., 2008; Cresswell et al., 1984; Barnes et al., 1999a; Barnes et al., 1999c).

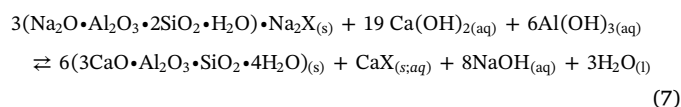


X: anions, like CO_3^{2-} , SO_4^{2-} , 2AlO_2^- , 2OH^- , 2Cl^- , $n \leq 2$.

Sodalite has the composition $n = 2$, but less hydrated compounds may exist as well. (Authier-Martin et al., 2001) Many different species of DSPs exist such as zeolite, sodalite, cancrinite and silicon substituted calcium-aluminate (hydrogarnets). All of these insoluble compounds trap sodium and aluminum and cause sodium losses and reduce the aluminum extraction (Baksa et al., 1986).

Common practice in Bayer-process is the addition of lime in order to lower the concentration of dissolved silicon and precipitate undesired compounds like organic compounds (e.g. oxalates), carbonate ions (caustification), phosphates and fluorides (Chaplin, 2013; Young, 1981). Moreover the addition of lime can reduce sodium losses

resulting from DSPs because calcium is a substituent for sodium in sodalite and cancrinite. The reaction product is (hydro-)grossular, also known as hydrogarnet, with different isomorphous structures of the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot (6-2n)\text{H}_2\text{O}$, $n = 1-3$ (Cresswell et al., 1984; Baksa et al., 1986). The formation of hydrogarnets can lower the sodium content in red mud by almost 90% (Zhao et al., 2002). The basic reaction is given in (7). Unfortunately, liberating each mole sodium by turning cancrinite into calcium cancrinite requires one mole of lime, while the aluminum losses stay the same. The complete transformation of cancrinite into hydrogarnet leads to a much higher lime consumption, which is shown in Reaction (7), (Smith, 2009).



X: anions, e.g. CO_3^{2-} , SO_4^{2-} , 2AlO_2^- , 2OH^- , 2Cl^- .

2.2. Recovery of aluminum from bauxite residue

Various processes have been developed to extract aluminum under alkaline conditions. The most important processes are described and summarized in Table 1 below.

2.2.1. Second leaching via Bayer-process

Since much aluminum in bauxite residue (“BR”) is still entrapped in undissolved aluminum hydroxides (e.g. un-attacked core of particles), the easiest way for a recovery is a second leaching via Bayer-process in combination with an intensified lime treatment, all the while benefiting from the advantageous properties of calcium to replace sodium and bind silicon (see chapter 2.1). The process requires very high temperatures and forms a “brown mud” low in aluminum and sodium (Piga et al., 1993). Cresswell and Milne (1982, 1984) conducted experiments between 250 °C and 300 °C and achieved aluminum recoveries of > 70% and sodium recoveries of > 90% at caustic ratios ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) of 4–6 and an optimum molar ratio CaO/SiO_2 of two. After 1 h at 300 °C the aluminum recovery is 72% and can be increased to approx. 80% at longer leaching times of 2–3 h.

2.2.2. Concentrated caustic pressure leaching

Another idea to push the Bayer-process to higher aluminum extractions is the use of concentrated sodium hydroxide solution. At Bayer-process conditions of < 300 g/l NaOH plant corrosion is reasonable and only aluminum hydroxides and clay minerals are dissolved. More aggressive conditions can dissolve all of the aluminum. By using concentrated NaOH (40% NaOH = 562 g/l) the caustic ratio α (molar ratio $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) is commonly above 10 (Li et al., 2009). At a temperature of 210 °C and through the addition of lime sodalite is decomposed into NaCaHSiO_4 and up to 95% of aluminum can be recovered. The reaction mechanism is assumed as shown in (8).

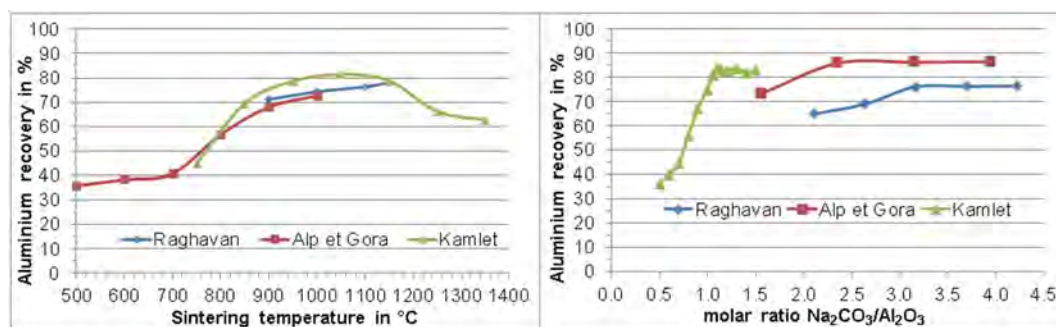
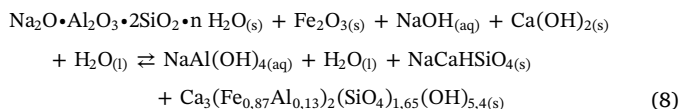


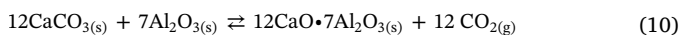
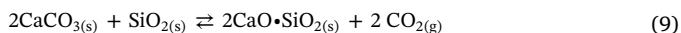
Fig. 2. Left: Influence of sintering temperature on the aluminum recovery by different authors: Raghavan (Raghavan et al., 2011) with 50 wt.-% soda addition ($\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3 = 3.2$), 10 wt.-% lime addition ($\text{CaO}/\text{SiO}_2 = 2.1$); Alp et Gora (Alp and Selim Gora, 2003) with 50 wt.-% soda addition ($\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3 = 3.2$), without lime addition ($\text{CaO}/\text{SiO}_2 = 0.1$) and Kamlet (Kamlet, 1960) at $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3 = 1.1$, $\text{CaO}/\text{SiO}_2 = 2$ plus 1 mol/mol TiO_2 and 15 wt.-% coke addition; Right: Influence of soda addition on the aluminum recovery by different authors: Raghavan (Raghavan et al., 2011) at 1100 °C and $\text{CaO}/\text{SiO}_2 = 1.5$; Alp et Gora (Alp and Selim Gora, 2003) at 900 °C and $\text{CaO}/\text{SiO}_2 = 1.5$ and Kamlet (Kamlet, 1960) at 1000–1100 °C, $\text{CaO}/\text{SiO}_2 = 2$ plus 1 mol/mol TiO_2 and 25 wt.-% coke addition.



Higher concentrations of sodium hydroxide and additions of lime lead to the formation of calcium aluminum silicates and thus to lower extraction efficiencies. These high sodium concentrations increase the solubility of aluminum to values which hinder the crystallization of aluminum hydroxide and require the precipitation of sodium aluminate (Zhongil et al., 2009).

2.2.3. Pedersen-process

Pure lime as reactant for the digestion of aluminates is used in the “Pedersen-process”. The chemical mechanism is similar to the reactions of lime in addition to the Bayer-process and should lead to the formation of inert calcium silicates and calcium aluminates which can be easily washed out with diluted sodium solutions. A variety of compounds are formed and only two desired reactions are exemplarily shown in (9) and (10) with either lime or calcium carbonate as reactant. (Smith, 2009) Beside these compounds, even $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (good soluble) and hardly soluble species like $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 are formed.

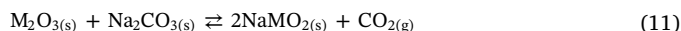


The “Pedersen-process” takes place in completely liquid state at temperatures $> > 1500$ °C. This easily allows for the simultaneous recovery of iron via carbothermic reduction (Ginsberg and Wrigge, 1964). Ziegenbalg et al. (1985) employed this process of smelting BR, recovering a pig iron phase and creating a self-disintegrating slag. The auto decomposition will take place if the lime addition is sufficient for a complete reaction of SiO_2 to Ca_2SiO_4 , Al_2O_3 to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and TiO_2 to CaTiO_3 . Moreover the concentration of alkaline metals must be below 1 wt.-% in total. In this case 75–80% of the aluminum content can be extracted by a soda solution with 60–80 g/l Na_2CO_3 .

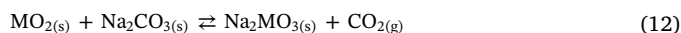
2.2.4. Soda sintering process

The soda sintering process can even decompose minerals which are hardly digestible by Bayer-process at temperatures of 800–1200 °C, mostly > 1000 °C, and the addition of sodium carbonate (Li et al., 2009; Kamlet, 1960; Alp and Selim Gora, 2003; Hrishikesan, 1975; Raghavan et al., 2011). The reaction product is water-soluble sodium aluminate, which can be easily recovered by washing out the ground sinter. This process allows recoveries of 70–80% of the remaining aluminum in BR, which was obviously not extractable by Bayer-process (Kamlet, 1960; Hrishikesan, 1975). The reaction mechanism of soda digestion in case of trivalent metal ions like aluminum and iron is shown in Reaction (11), (Meher and Padhi, 2014; Raghavan et al.,

2011; Tathavadkar et al., 2002), and the mechanism for tetravalent ions like silicon or titanium is given in Reaction (12), (Smith, 2009; Meher and Padhi, 2014; Raghavan et al., 2011; Tathavadkar et al., 2002).



M: trivalent metal (Al, Fe, etc.)



M: tetravalent metal (Si, Ti, etc.)

The formed sodium compounds are in general water-soluble. This property is desired in case of NaAlO_2 . But also sodium ferrite is dissolved in a first step and subsequently iron precipitates immediately as hematite (Smith, 2009; Raghavan et al., 2011; Meher and Padhi, 2014) or goethite (Rich, 2007), while the dissolved sodium stabilizes the aluminate ions in solution. Also Na_2TiO_3 precipitates after its dissolution as TiO_2 (Rich, 2007; Raghavan et al., 2011). Therefore the formation of these species causes soda losses in the sintering stage, but the process itself is not influenced negatively. Na_2SiO_3 also dissolves rapidly and leads to a significant silicon concentration in the leachate. The dissolved silicon ions react with aluminate ions of the sodium solution and precipitate as DSPs, following Reaction (6) and causing aluminum losses.

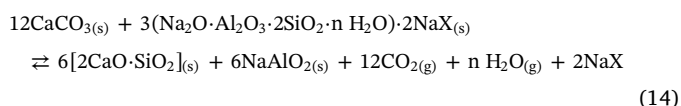
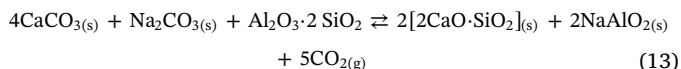
Alp and Selim Gora (2003) conducted experiments with 50–150% soda addition regarding the mass of BR at sintering temperatures between 500 °C and 1000 °C. The sinter was leached out with boiling sodium hydroxide solution (120 g/l) for 2 h. Even the addition of 50 wt.-% soda was sufficient to extract $> 70\%$ of the aluminum at 1000 °C sintering temperature. The influence of the sintering temperature is compared to different studies on the left side of Fig. 2. (Tathavadkar et al., 2002) examined the stoichiometric addition of soda to BR at 775 °C sintering temperature and successfully extracted up to 98% of the containing aluminum by a washing step with hot water.

The chemical equilibrium is dependent on the activities of educts and products. Reactions (11) and (12) contain soda as educt and carbon dioxide as product and can be influenced into direction of the products by an excess of soda or the reduction of the carbon dioxide partial pressure. While the variation of soda is already described, the carbon dioxide partial pressure can be lowered by the addition of reductants like coke or an increased exchange of atmosphere, which is difficult inside the filling (Li et al., 2009; Hrishikesan, 1975). The advantages of the reductive sinter process are a possible simple magnetic separation of the iron fraction and the formation of the inert iron phases magnetite and metallic iron, which do not interact with soda, as shown in Reaction (11). As a consequence, the addition of coke lowers soda consumption and increases the extraction of aluminum. This effect is possibly responsible for Hrishikesan's (1975) and (Kamlet's (1960) observations that just a small excess of 5–15% wt% soda, regarding the stoichiometric sodium aluminate reaction, is sufficient for highest

extraction yields. But the presence of reductants at high sintering temperatures leads to the reduction and a vaporization of sodium and again lowers the efficiency of the soda addition (Kamlet, 1960). Fig. 2 shows the effect of soda additions on the extraction of aluminum on the right side.

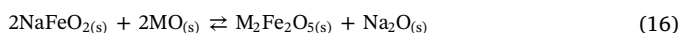
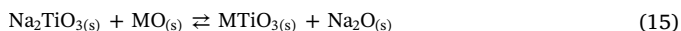
2.2.5. Lime soda sintering process/Déville-Pechiney-process

Even in the soda sintering process the aluminum extraction can be improved by the addition of lime. This procedure is known as “lime-soda-sintering-process” or “Déville-Pechiney-process”. The desired chemical reactions can be summarized in Reaction (13), while sodalite and cancrinite can be decomposed following Reaction (14)



X: Anions, like $\frac{1}{2}\text{CO}_3^{2-}$, $\frac{1}{2}\text{SO}_4^{2-}$, $\frac{1}{2}\text{AlO}_2^-$, OH^- , Cl^- , $n \leq 2$.

The addition of sodium carbonate and lime is again based on the formation of sodium-aluminate and di-calcium-silicate (Smith, 2009). The dry digestion is more aggressive than Bayer-process and even cracks DSPs because it takes place at higher temperatures and in direct contact with sodium. Unfortunately, during the washing step the same undesired reactions of DSP formation occur following Reaction (6). Therefore it is intended to precipitate the dissolved silicon which can be achieved by adding alkaline earth metals like lime or magnesia. Furthermore, even trials with barium oxide have been undertaken. The mechanism follows Reaction (14) by replacing calcium carbonate with barium oxide (then without the release of carbon dioxide). The alkaline earth metals “M” can also liberate sodium from formed sodium titanite or sodium ferrite compounds, shown in Reactions (15) and (16). The recovered sodium is then available for further reactions with e.g. aluminum oxides (Meher and Padhi, 2014).



The results of different authors with respect to the effect of the lime addition on the recovery of aluminum are displayed in comparison in Fig. 3.

Meher and Padhi (2014) investigated the addition of different alkaline earth oxides at 25 wt.-% soda addition (regarding the mass of BR) between 900 and 1100 °C. The best aluminum recoveries of 99.5% were gained with 15 wt.-% barium oxide addition at 1000 °C. 10 wt.-%

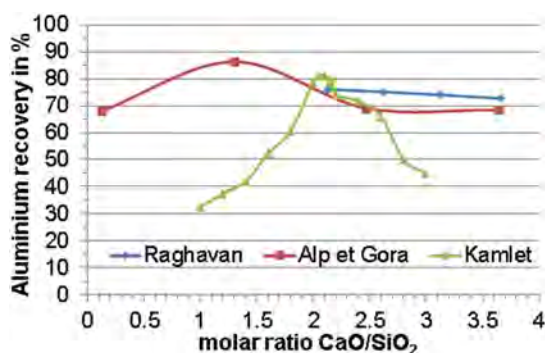


Fig. 3. Influence of lime addition (calculated as molar ratio CaO/SiO₂) on the recovery of aluminum by different authors: Raghavan (Raghavan et al., 2011) at 1100 °C and 50 wt.-% soda addition (Na₂CO₃/Al₂O₃ = 3.2); Alp et Gora (Alp and Selim Gora, 2003) at 900 °C and 50 wt.-% soda addition (Na₂CO₃/Al₂O₃ = 3.2) and Kamlet (Kamlet, 1960) at 1000–1100 °C and Na₂CO₃/Al₂O₃ = 1, with 15 wt.-% coke addition, plus 1 mol lime per mol TiO₂.

magnesia addition at 900 °C leads to a maximum aluminum recovery of 98.7%, while lime at a molar ratio CaO/SiO₂ of approx. two recovers 97.8% aluminum from BR at 1100 °C.

The effect of the addition of reductants to the lime soda sintering process was examined by Li et al. (2009). They confirmed the strong dependency of sintering temperature and sintering time on the aluminum recovery. The aluminum recovery increases up to 1050 °C and decreases again at higher temperatures and longer sintering times than 90 min. The explanations are the same as already described in chapter 2.2.4. But at long sintering temperatures the reductant is completely consumed and a reoxidation of the iron species takes place which binds the once liberated sodium (oxides) again. 5 wt.-% carbon addition regarding the mass of BR is insufficient for a complete iron reduction and forms CaFe₅O₇, CaFe₂O₄ and Ca₂Fe₂O₅. 20% carbon addition (approx. three times stoichiometric amount for a complete iron reduction) leads to the formation of metallic iron which can be recovered by magnetic separation. Other compounds are NaAlO₂ and Ca₂SiO₄. Best aluminum recoveries of approx. 90% can be achieved at 1050 °C, 90 min sintering time and 20 wt.-% carbon addition.

3. Materials and methods

3.1. Analysis and characterization of BR

Throughout the experiments the quantitative analysis of solid materials is carried out using the instrument “Axios” made by “PANalytical”(XRF-WDX) or, in case of metal phase analysis, using the spark spectrometer “MAXx” made by “Spectro”. Liquids were analyzed by “Ciros Vision” manufactured by “Spectro” (ICP-OES). For phase analysis the powder diffractometers “STADI P” and “STADI MP” made by “Stoe&Cie” were used, equipped with copper anode (“STADI P” 40 kV, 30 mA) and molybdenum anode (“STADI MP” 55 kV, 35 mA). Germanium monochromators filtered the Kα₁-radiation for analysis (copper: 1.54059 Å; molybdenum: 0.70930 Å). The phase classification was done using the software QualX (version 2.1), based on the “Crystallography Open Database” (COD), and further semi quantitative Rietveld refinements were calculated by the program “Maud” (version 2.33). Advanced phase analysis was done via QEMSCAN®-analysis by the instrument “Quanta650F (FEI)” (REM) equipped with two EDX-detectors “Bruker Dual X-Flash5030 Detector”.

Quantitative chemical and semi-quantitative phase analysis of BR from Lünen landfill are given in Fig. 4. The chemical analyses are carried out by different laboratories and different instruments in parallel, therefore the standard deviation is also shown in the diagram.

Original BR contains 30.5 wt.-% moisture. Qemscan® analysis (Fig. 5) gives an imagination of the particle size and the fine phase distribution. While some larger particles are in the range of 100–400 µm, BR consists mostly of a fine fraction < 20 µm with d₅₀-value of 2–3 µm and an average particle size of 3–6 µm.

It can be seen that the aluminum content with 27 wt.-% is high and worth being recovered. Most of the aluminum is still present as aluminum hydroxide and only a minority is entrapped in DSP-minerals (see chapter 2.1). As the particle size is very small and the BR is weathered through the years of storage, even a mild second leaching using standard Bayer-process should be sufficient to recover high amounts of the remaining aluminum.

3.2. Basic calculations

The achieved aluminum recoveries are calculated on the basis of the chemical (ICP) analysis of the leachate according to Eq. (17), as well as on the XRF analysis from the leaching residue, following Eq. (18).

$$E(\text{Al}) = \frac{c_{\text{L,f}}(\text{Al}) \cdot V}{c_{\text{S,i}}(\text{Al}) \cdot m_{\text{S,i}}} \quad (17)$$

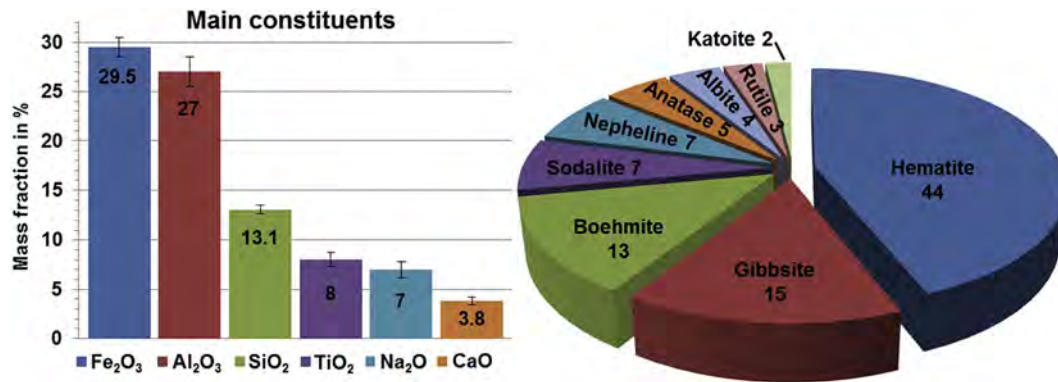


Fig. 4. Quantitative XRF-analysis of main constituents, mean values and standard deviations (left) and semi-quantitative XRD phase analysis (right).

$$E(\text{Al}) = 1 - \frac{c_{s,f}(\text{Al}) \cdot m_{s,f}}{c_{s,i}(\text{Al}) \cdot m_{s,i}} = 1 - C \frac{c_{s,f}(\text{Al})}{c_{s,i}(\text{Al})} \quad (18)$$

E: extraction (= recovery); c_i: concentration in leachate in g/l; c_s: concentration in solids in wt.-%; V: volumen in l (= constant); m: mass in g; index i: initial = source material; index f: final = leaching residue; C: concentration factor.

The calculation of the aluminum recovery via chemical composition of the leaching residue can also be made by a concentration factor “C” without a mass balance, shown in Eq. (18). The concentration factor is then determined by Eq. (19). This simplification assumes that some elements (like Si, Fe, Ti or Ca) remain almost undissolved in relation to their content in red mud and can be considered as “quasi inert”. Actually, the concentrations of these elements in the leachate are in the

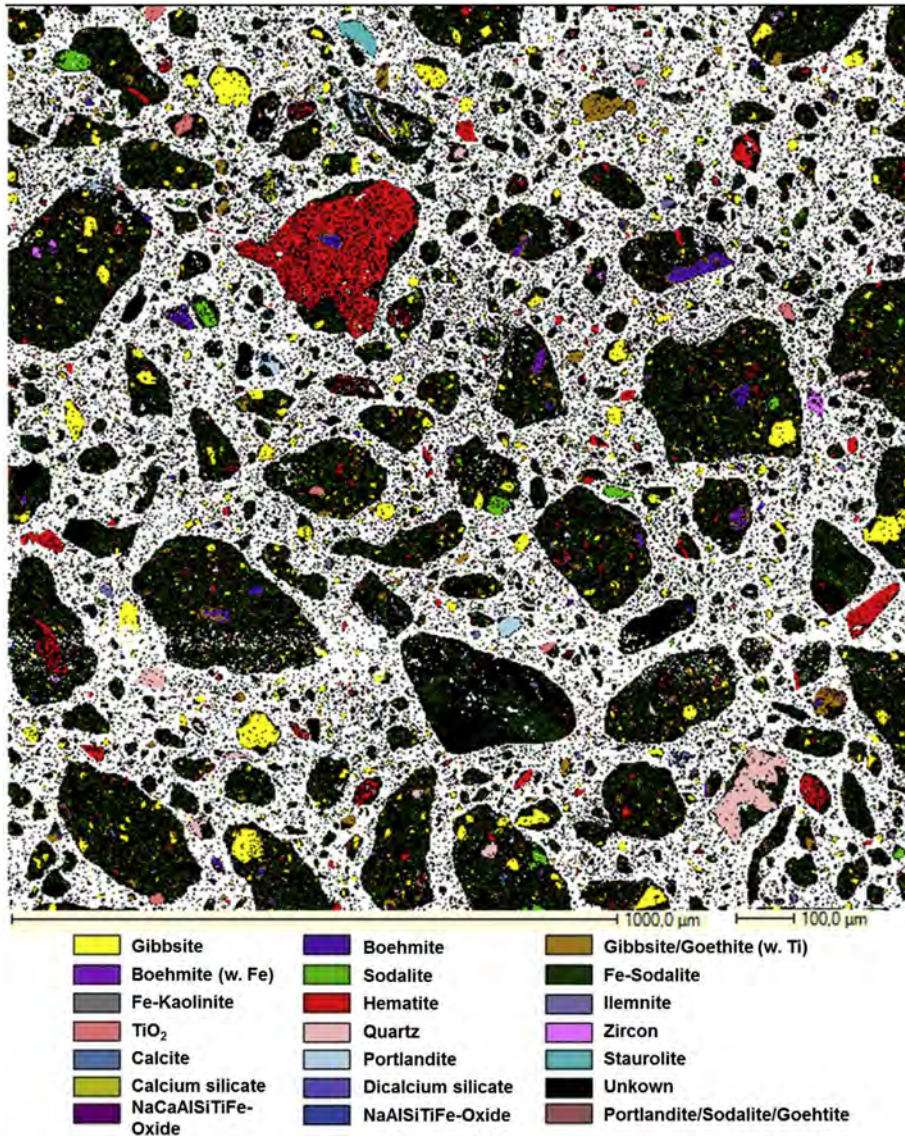


Fig. 5. Qemscan® analysis of BR from landfill Lünen, Germany.

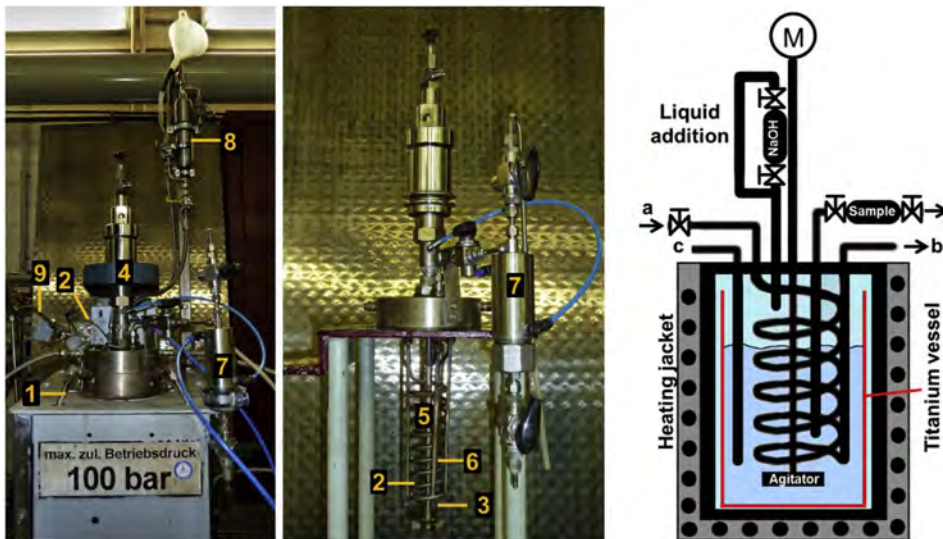


Fig. 6. Autoclave assembled (left) and detail view on the lid including all structures (middle): Tube for pressure measurement (1), temperature measurement (2), disk agitator (3), belt drive of agitator (4), cooling coil (5), immersed tube for sampling (6), water-cooled sample cylinder (7), dosage cylinder (8), excess pressure outlet with bursting disc (9); schematic setup of the autoclave (right): Cooling inlet (a), cooling outlet (b) and thermocouple c (adapted (Kaufßen and Friedrich, 2016)).

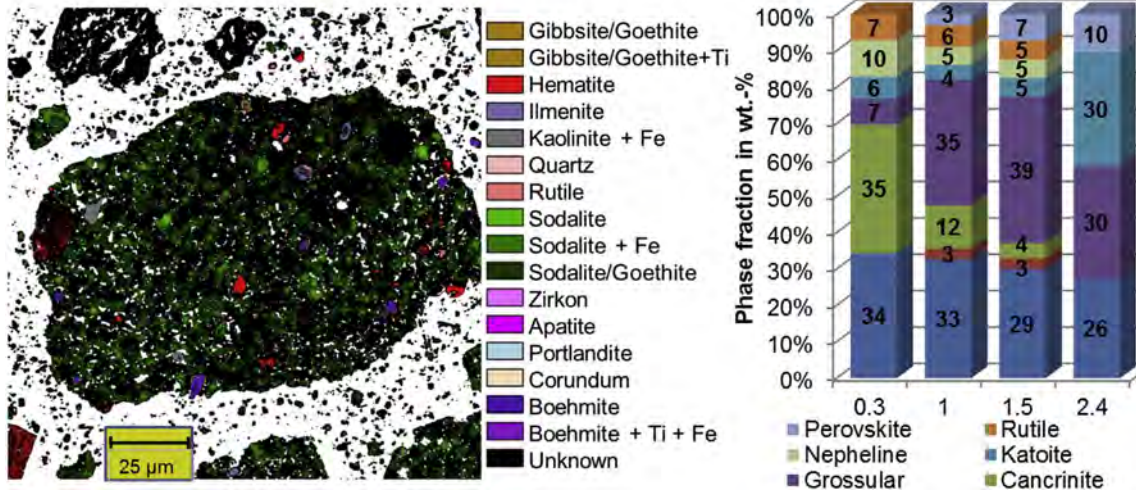


Fig. 7. Qemscan® analysis of leached BR at 250 °C and a molar ratio CaO/SiO₂ of 0.3 (left) and phase distribution in leaching residues at different molar ratios of CaO/SiO₂ (x-axis) at 250 °C and 200 g/l NaOH (right).

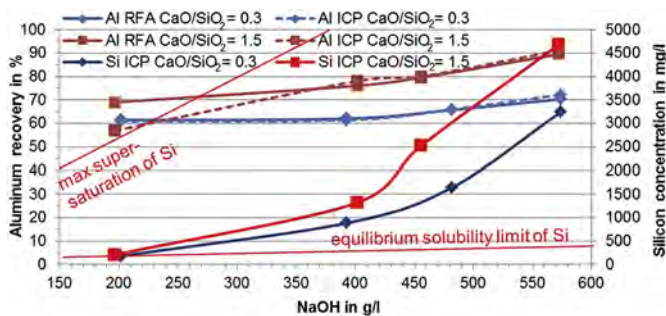


Fig. 8. Aluminum recoveries and silicon concentration in solution at high concentrations of caustic soda after 120 min leaching at 280 °C and S/L = 1:6.

range of 50–200 mg/l in cases of Si, < 30 mg/l and < 10 mg/l for Fe and Ti/Ca, respectively, resulting in a maximum error of 2% (using 140 g BR and 840 ml leachate with a final concentration of 200 mg/l Si). The concentration factor is calculated without consideration of Si in experiments with high dissolution of silicon (especially at higher concentrations of NaOH).

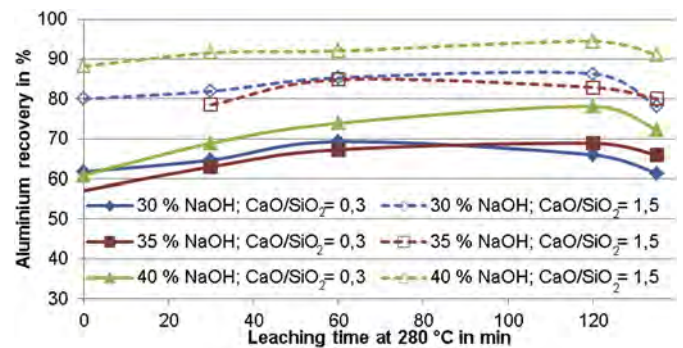


Fig. 9. Aluminum recovery depending on the leaching time after reaching process temperature at different concentrations of NaOH and different molar ratios CaO/SiO₂.

$$C = \frac{1}{n} \cdot \sum_{i=0}^n \frac{c_{S,i}(Me)}{c_{S,f}(Me)} \quad (19)$$

c_s: concentration in solids in wt.-%; i: initial = source material; index f: final = leaching residue; Me: “quasi inert” metals (Si, Fe, Ti, Ca).

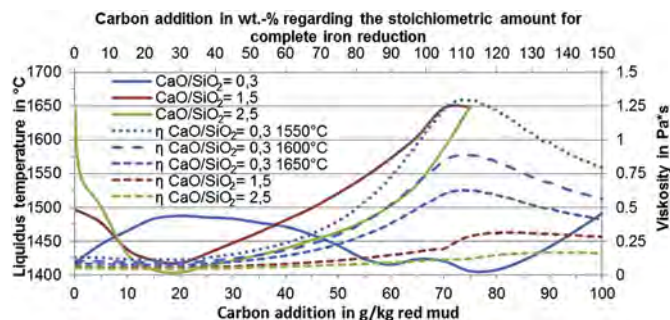


Fig. 10. Course of liquidus temperature and viscosity η during the reduction process dependent on the addition of carbon at different molar ratios CaO/SiO₂ calculated by FactSage® 7 at 1650 °C.

3.3. Direct leaching

The direct leaching experiments are conducted in a stainless steel (316L) autoclave equipped with a titanium vessel for better corrosion resistance and an operating volume of 1 l. The autoclave can handle temperatures of up to 300 °C and pressures of up to 100 atm. The system is shown in detail in Fig. 6. A titanium tube (6) is immersed in the suspension to take samples for kinetic studies even during the experiments. During sampling, the pressure inside the autoclave pushes the sample volume into a water-cooled sample cylinder (7) which cools down the sample rapidly to prevent further reactions. Moreover, an external 300 ml (8) cylinder can store liquid chemicals (e.g. caustic solution) which can be added to the suspension even under pressure during running experiments. A cooling coil (5) prevents the suspension from overheating and enables a rapid cooling at the end of experiments. The autoclave is heated by an outer heating jacket. All parts in contact with the suspension are made of titanium.

For the experiments wet (original) red mud (BR) from landfill Lünen was dispersed in de-ionized water and heated up 25–30 °C above process temperature. Then, concentrated caustic soda solution (50%, technical purity) was added and the leaching time was started. By mixing caustic solution with superheated suspension, the desired process temperature was established. At different times samples were taken to investigate the kinetics. After 120 min of leaching, the suspension was rapidly cooled down and cold filtered by vacuum filtration. All experiments were done at a solid/liquid (S/L) ratio of 1:6, with 140 g BR (dry mass) on 840 ml solution. By using pure chemicals and clean caustic solution the solubility limit of aluminum in leach liquor was never exceeded and thus these trials represent the maximum possible extraction of aluminum. Industrial recoveries will differ and be lower due to aluminum supersaturation. The process parameters for standard Bayer-process leaching were 100–300 g/l NaOH (with steps of 100 g/l) and 150–250 °C (with steps of 50 °C). Due to the use of high concentrated caustic solution the experimental procedure had to be simplified for the leaching experiments with concentrated caustic solutions by dispersing BR in caustic solution with BR prior heating. Heating the suspension to process temperature took 85–105 min, depending on the concentration of caustic soda. All experiments were conducted with and

without the addition of lime powder (94.6 wt.-% CaO, 1.4 wt.-% SiO₂, 1.2 wt.-% MgO, 1.2 wt.-% CO₂).

3.4. Smelting, iron removal and slag leaching

The experiments were conducted in two steps. The smelting was done by using an AC electric arc furnace equipped with a single solid graphite top electrode of 50 mm in diameter and a water-cooled copper bottom electrode. For a fast and complete reduction and enhanced handling graphite crucibles (ash value: 2000 ppm, average grain size: 800 μm) of the size $\varnothing_{\text{outer/inner}} \times \text{height}_{\text{total/inner}}$ of 150/120 mm × 220/170 mm with an operating volume of 2 l were used. During the experiments 3–3.5 kg dried BR, 200–240 g lignite coke (0.1–1.5 mm grain size, 88.2 wt.-% carbon, 10 wt.-% ash) and, in experiments with lime addition, lime powder (94.6 wt.-% CaO, 1.4 wt.-% SiO₂, 1.2 wt.-% MgO, 1.2 wt.-% CO₂) were mixed manually in batches of 600 g and semi-continuously added in small portions by hand into the pre-heated furnace. The feeding time was 60–90 min with an average rate of 2.5–3.5 kg/h at 12 kW (50–60 V at 200–250 A). Due to slag foaming, a dependency between lime addition and feeding rate was observed resulting in a lower feed rate in experiments without lime addition. The holding time to complete the reduction was 1 h at 6 kW (60 V at 100 A). The temperature was discontinuously measured by pyrometer and varied between 1650 and 1700 °C. After reduction, the melt was poured into a steel mold, in which the metal/slag density separation took place and a rapid solidification was achieved within minutes. The slag was then separated and ground/seived to a size < 125 μm and the subsequent leaching was done in the autoclave (see Fig. 6) at temperatures between 170 °C and 280 °C using caustic concentrations of 200–762 g/l NaOH. Leaching times of 120 min and 240 min were selected, and a S/L-ratio of 1:10 ensured that the aluminum concentration did not exceed the solubility limit. Batches of 50 g or 84 g of slag were heated up in 500 ml and 840 ml caustic solution, respectively. Again samples for kinetic investigations were taken during leaching and after the end of the experiment the suspension was rapidly cooled and separated by vacuum filtration.

3.5. (Lime) Soda sintering process

The chemicals used for the experiments were 100 g dried BR, sodium carbonate (anhydrous > 99.5 wt.-%) and, in selected cases, lime powder (94.6 wt.-% CaO, 1.4 wt.-% SiO₂, 1.2 wt.-% MgO, 1.2 wt.-% CO₂) and lignite coke (0.1–1.5 mm grain size, 88.2 wt.-% carbon, 10 wt.-% ash). The materials were mixed and jointly ground in a disk mill for 5–10 s to ensure an intensified blending. Thereafter the mixture was filled into a 280 ml clay crucible and heated up inside the heating coil of a resistance heated furnace to various temperatures under air atmosphere. The holding time varied depending on the process temperature between 90 min at high sintering temperatures and 240 min at low sintering temperatures to enable reaching the equilibrium state. Then the sinter was again ground in the disk mill and immersed into 640 ml de-ionized water at 50 °C for 30 min under intensive agitation, while kinetic samples of the liquor were taken.

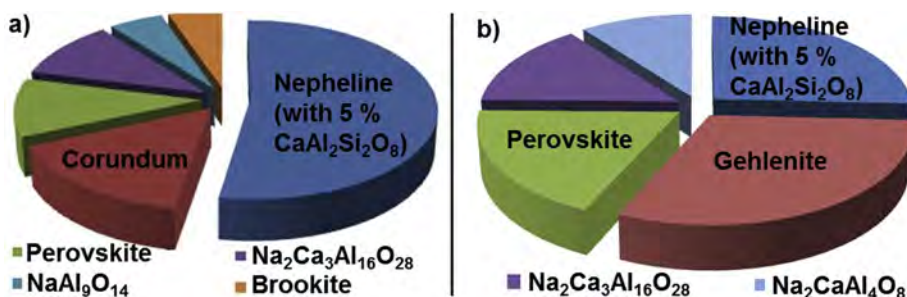


Fig. 11. Phase composition of produced slags after carbothermic reduction process of original BR (CaO/SiO₂ = 0.3) a) and BR with lime addition to CaO/SiO₂ = 1.5 b) calculated by FactSage® 7 at 1000 °C.

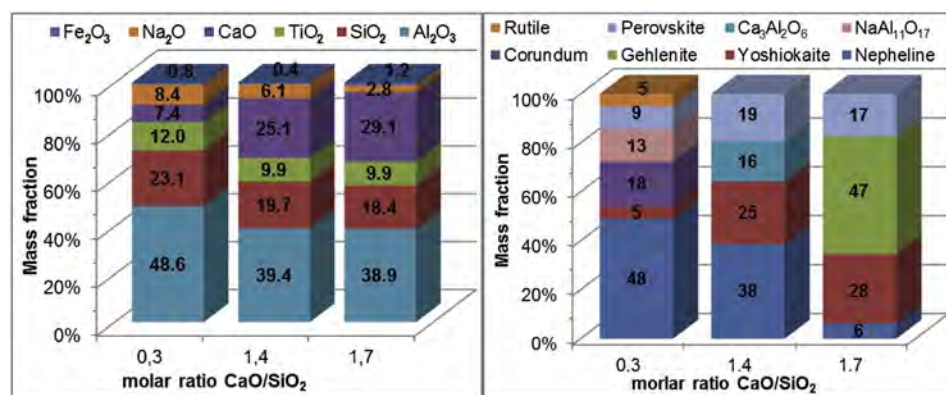


Fig. 12. Chemical composition by XRF (left) and semi-quantitative phase analysis including Rietveld refinement (right) of produced slags after complete iron reduction after 65 min holding time at 1650 °C at different lime additions (molar ratios CaO/SiO₂).

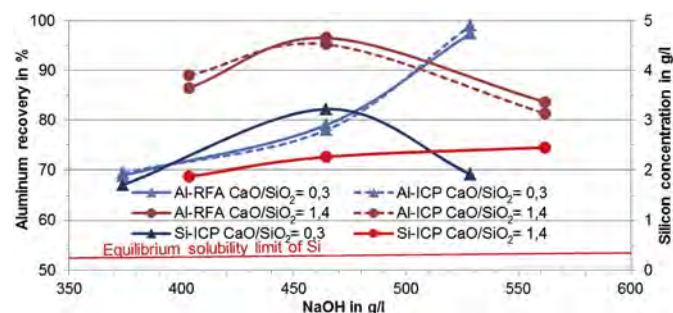


Fig. 13. Aluminum recovery and silicon concentration in leach liquor dependent on the concentration of caustic soda for BR slags after reductive smelting and iron removal with different molar ratios CaO/SiO₂ after 120 min leaching at 280 °C and S/L of 1:10.

4. Results and discussion

4.1. Direct leaching

The results show increasing aluminum recoveries with increasing temperature. While already 47% of the aluminum content can be extracted at 150 °C and 200 g/l NaOH, the recovery is further improved from 55% to 62% especially between 250 °C and 280 °C. The silicon concentration in the received Bayer-solution follows this trend, remaining in the range of 130–140 mg/l between 150 °C and 250 °C, and then increasing rapidly to 180 mg/l at 280 °C. The equilibrium solubility limits of silicon in caustic solution, calculated from Eq. (5), were always exceeded. A variation of the concentration of NaOH at 250 °C did not affect the aluminum recoveries of 52–58% significantly. But the dissolved silicon increased exponentially from 70 mg/l at 100 g/l NaOH to > 300 mg/l at 300 g/l NaOH. XRD patterns and Qemscan® analysis, shown in Fig. 7 (left), reveal that at that point all aluminum hydroxides are either leached out or converted to DSPs, predominantly cancrinite.

The process can be further enhanced by the addition of lime powder. In general, the more lime is added the higher is the aluminum recovery. However, the curve progression is asymptotic. While the increase of aluminum recovery is strong (from 55% to 68%) between molar ratios of CaO/SiO₂ from 0.3 to 1.5, further lime additions to CaO/SiO₂ of 2.4 lead only to 70% recovery. The kinetic investigation reveals that > 90% of the maximum achievable recovery is reached within the first 5–10 min of leaching in any Bayer-leaching experiment. The silicon concentrations in the leachate after lime addition stay in the range of 130–170 mg/l and once again the equilibrium solubility limits of silicon in caustic solution, calculated from Eq. (5), are always exceeded. Due to the addition of lime, the mineralogy of the leaching residue is changed and cancrinite is gradually turned into grossular and, at high lime additions, into katoite, while rutile reacts to perovskite. The semi-quantitative XRD Rietveld refinements of leaching residues are shown in Fig. 7 (right) and verify that especially sodium can be

recovered by turning cancrinite into calcium aluminum silicates. XRF analyses show that the sodium (oxide) fraction in the leaching residue drops from almost 13.7 wt.-% in re-leached BR to 5.5 wt.-% at a molar ratio CaO/SiO₂ of 1.5 and finally to 0.4 wt.-% at CaO/SiO₂ of 2.4.

While aluminum recoveries remain almost constant in the range from 100 g/l to 300 g/l NaOH, higher concentrations to levels > 400 g/l NaOH increase the aluminum recovery significantly and dramatically influence the content of dissolved silicon in the liquor to levels > 3 g/l. The leaching duration at 280 °C was again 120 min. In this series two different molar ratios CaO/SiO₂ of 0.3 and 1.5 were compared. The equilibrium solubility limits of silicon in caustic solution calculated from Eq. (5) and the maximum supersaturation of silicon calculated from (Leiteizen, 1936) (see Eq. (4)) are shown in Fig. 8. While the former solubility limit is always exceeded, the latter is never reached. With CaO/SiO₂ of 1.5 up to 90% of the aluminum can be extracted using 40% NaOH (562 g/l), while the recovery without lime addition increases just a little from 60% at 200 g/l to 70% at 562 g/l NaOH after leaching for 120 min at 280 °C.

Kinetic investigations show that most of the soluble aluminum is extracted even before reaching the process temperature of 280 °C after approx. 90 min heating time. But there is still a slight increase in aluminum recovery during the first 60 min of leaching, obviously indicating that the dissolution of aluminum silicates takes time. The course of aluminum concentration in the leach liquor over the leaching time is shown in Fig. 9. The last sample (at 135 min) was taken after cooling down to room temperature and reveals the precipitation of DSPs indicated by the falling aluminum recovery.

XRD analyses still confirm the presence of sodalite, cancrinite and hematite if original BR is treated and especially katoite, if lime is added to a molar ratio CaO/SiO₂ of 1.5.

4.2. Smelting, iron removal and slag leaching

4.2.1. Thermochemical simulation

As a result of thermochemical calculations, it is basically possible to reduce the iron oxides selectively to a metal phase up to a remaining concentration of 0.5 wt.-% FeO in slag phase, requiring 72 g carbon per kg dry BR, without seriously contaminating the iron phase with carbon or silicon (amounts < 0.5 wt.-% and < 0.1 wt.-% in metal phase, respectively). The stoichiometric amount of carbon for the hematite reduction is only 66.5 g/kg dry BR, but side reactions occur, including a partial reduction of TiO₂ to Ti₂O₃, and some carbon is dissolved in the metal phase, as well. These circumstances require an 8% excess of carbon. The liquidus temperatures and viscosities of the resulting slags during the reduction process are calculated by FactSage® 7, as shown in Fig. 10. It becomes obvious that carbothermic reduction of original BR (CaO/SiO₂ = 0.3) always leads to the lowest liquidus temperatures of 1400–1500 °C, but to highest viscosities due to an acidic slag system with a low basicity and a high silica content, which requires a super-heating up to 1650 °C in order to gain an improved flowability. By

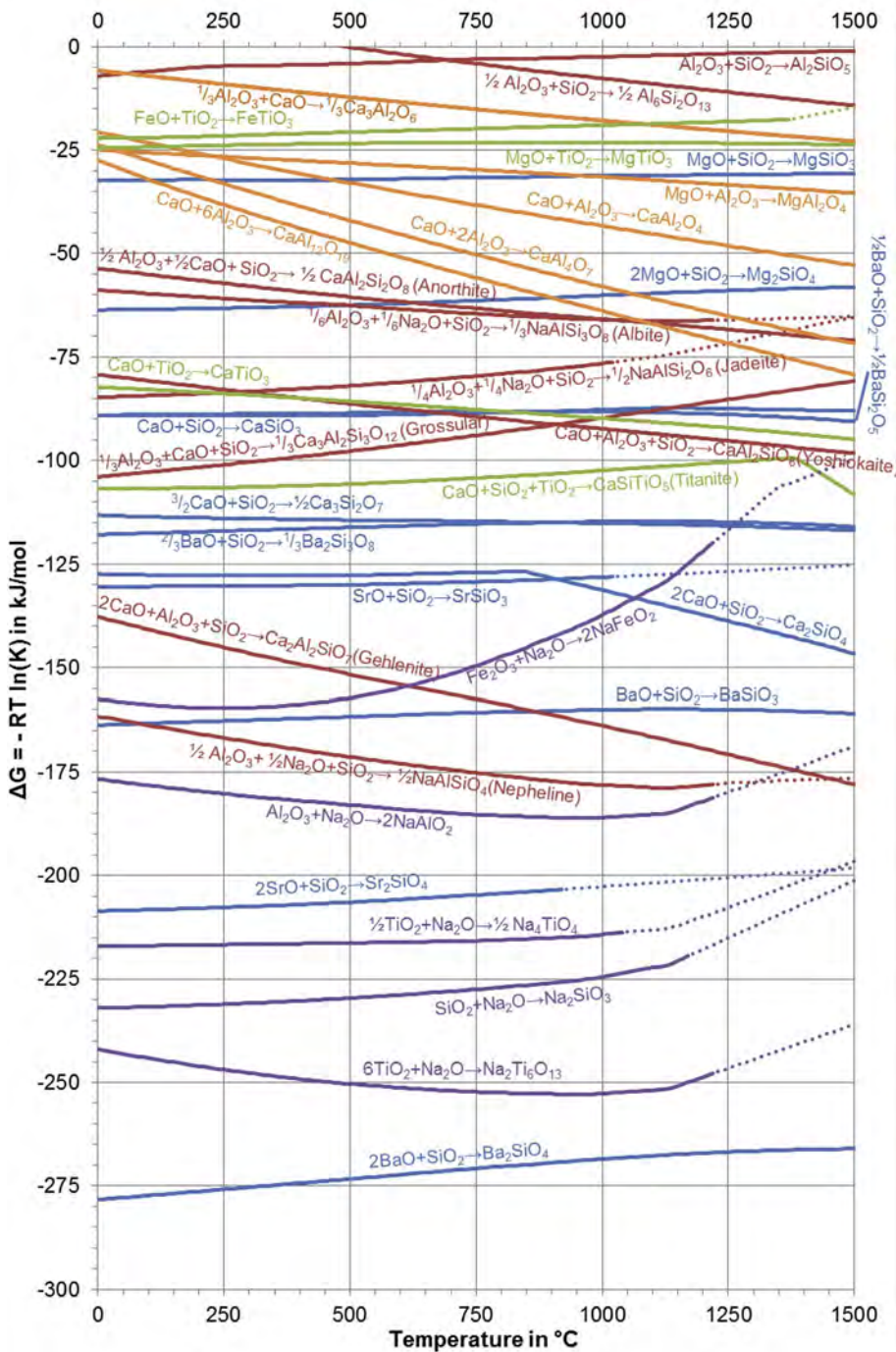


Fig. 14. Gibbs free energy of phase formations during lime soda sintering process and solidification of BR slag, calculated by FactSage® 6.4 and 7. Dashed lines indicate extrapolated data. Red: insoluble aluminum minerals, orange: calcium aluminates, green: titanates (no data for natrisite), blue: desired calcium silicates, purple: soda sinter compounds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adding lime at the beginning of the reduction process the dilution effect of the iron concentration avoids the formation of hercynite and lowers the liquidus temperature. At the end of the reduction process lime keeps the viscosity low, working as a network modifier, but its rising activity causes the formation of perovskite resulting in a sharp increase of the liquidus temperature.

Thus, a process temperature of 1550 °C is basically sufficient for the reduction process of original BR, but the viscosity of 1.3 Pa × s is very high and causes handling problems (tapping, slag foaming, etc.). As a consequence the slag must be superheated to approx. 1650 °C. The addition of lime lowers the viscosity significantly, but also increases the liquidus temperature to 1650 °C due to the formation of perovskite. Therefore 1650 °C is the recommended process temperature in any case.

The occurring phases are calculated with FactSage® 7 and shown in Fig. 11. In both cases (sodium/calcium-)aluminum silicates are the predominant phases, of which nepheline is insoluble in caustic solution, while gehlenite can be transformed by adapted cooling rates into leachable calcium aluminate. Hence, non-dissolvable aluminum compounds remain existent although the mineralogy of the system is changed completely through reductive smelting and iron recovery.

Without lime addition, even corundum phases form. Higher lime additions result in the formation of additional perovskite, yoshiokaite, gehlenite, while brookite and corundum phases disappear. Fig. 14 shows a calculated diagram of Gibbs free energies of several occurring silicates, aluminates and titanates at various temperatures. It becomes obvious that nepheline is the most stable aluminum phase followed by gehlenite, which is the most stable phase in presence of lime. The

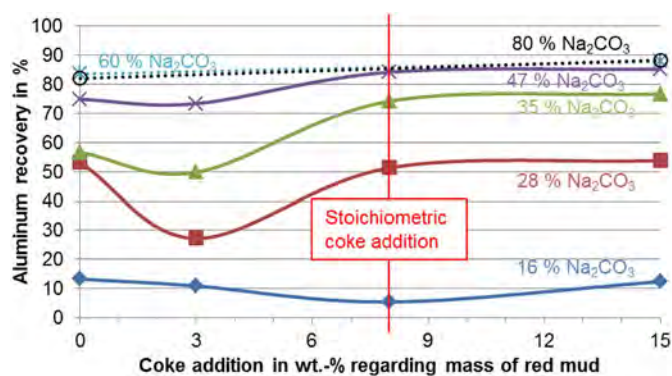


Fig. 15. Effect of coke addition on aluminum recovery at different soda additions at 1000 °C sintering temperature and a molar ratio CaO/SiO₂ of 1.3.

calculations are based on stoichiometric reactions and an activity of all compounds of one. Therefore the coexistence of several aluminum phases is possible and most likely.

4.2.2. Smelting and leaching experiments

The generated slags are shown in their compositions in Fig. 12. Nepheline is again the predominant compound, as predicted by FactSage®. But with increasing lime addition the sodium content in slag decreases due to a favored sodium reduction and evaporation at increasing slag basicities. This effect can be seen well in Fig. 12 (left) as the sodium content decreases strongly, while the content of other compounds is only slightly diluted due to lime addition. This leads to a complete conversion of the titanium content into perovskite and the formation of yoshiokaite and gehlenite.

The detected mineral phases in the generated BR slag are mostly insoluble or require aggressive conditions and longer leaching times of 30–60 min at > 250 °C to recover the aluminum content. Leaching experiments at 250 °C with 200 g/l NaOH verify that only 50% of the aluminum can be extracted and 200 mg/l liberated silicon is found in Bayer-solution, independent of the ratio CaO/SiO₂. Only higher concentrations of caustic soda and higher process temperatures can extract more aluminum. As shown in Fig. 13, the aluminum recovery can be pushed to 95% at CaO/SiO₂ of 1.4 using a much stronger parameter set of 465 g/l NaOH, 120 min leaching time and 280 °C.

By reducing caustic concentrations to 400 g/l NaOH only 88% of the aluminum can be recovered. Without lime addition much higher caustic concentrations of almost 550 g/l NaOH are needed in order to reach similar aluminum extractions of 95%. But in both cases massive silicon dissolution takes place and concentrations of 2–3 g/l silicon are detected in the leach liquor, which require an intensified desilication. The dissolution kinetics are comparable to the slow kinetics of a direct leaching with concentrated caustic solution and increasing aluminum recoveries of up to 30–60 min residence time at 280 °C.

Phase analyses of leaching residues show high amounts of sodalite,

Table 2

Comparison and parameters of tested processes regarding the maximum recovery of aluminum from bauxite residue from landfill Lünen. (Economically recommended parameters and expected recoveries in brackets).

Parameters	Caustic leaching of BR	Pedersen-Bayer-process	(Lime) Soda sintering
Aluminum-recovery	ca. 90% (ca. 70%)	ca. 97% (ca. 87%)	89% (ca. 84%)
Process temperature	280 °C Pressure leaching (280–300 °C)	1650 °C Smelting 280 °C Pressure leaching (280–300 °C)	1050 °C Sintering (1050 °C) 25–50 °C Washing
Chemicals ^a	572 g/l NaOH (200 g/l) 15% Lime (8–15%) CaO/SiO ₂ = 1.5	460 g/l NaOH (375 g/l) 15% Lime (15%) CaO/SiO ₂ = 1.5 8–9% Coke (8–9%) for pig iron recovery	80% Na ₂ CO ₃ (47%) Na ₂ CO ₃ /Al ₂ O ₃ = 3.3 (2.1) 15% Lime (15%) CaO/SiO ₂ = 1.5 15% Coke (10–15%)
Silicon contamination	Very high, 4.6 g/l (Low, 0.2 g/l)	High, 2.2 g/l (Moderate, 1.9 g/l)	Low, 0.2 g/l (Low, 0.2 g/l)

^a In wt.-% regarding the mass of treated bauxite residue.

nepheline and natisite (probably leached titania from titanium vessel) in case of slag with CaO/SiO₂ of 0.3 and perovskite and combeite at CaO/SiO₂ of 1.4.

4.3. (Lime) Soda sintering process

4.3.1. Thermochemical simulation

Thermochemical equilibrium calculations were done to forecast the stable compounds during the lime soda sintering process. The resulting Gibbs free energies are plotted in the diagram shown in Fig. 14 for the relevant system CaO-Al₂O₃-SiO₂-TiO₂-Fe₂O₃. Again all calculations are based on ideal conditions with activities of all compounds equal to one.

It becomes obvious that in case of soda addition all sodium-ferrites, -aluminates, -titanates and -silicates have the lowest Gibbs free energy and are thus most stable and preferred to form. Moreover it is expected that Na₂O will firstly react with TiO₂ and SiO₂ and cause sodium consuming side reactions before sodium aluminates are formed. Only barium oxide forms stronger compounds with silica and avoids side reactions of silica with sodium- and aluminum-oxide, while lime is basically incapable even to bind TiO₂ because sodium titanates are thermochemically more stable than calcium titanites. But sodium losses due to these side reactions with titania are lower than expected in literature (see chapter 2.2) due to the formation of compounds with low Na:Ti ratios like Na₂Ti₂O₅, Na₂Ti₃O₇ or Na₂Ti₆O₁₃ depending on the availability of titania. Moreover it becomes obvious that magnesium silicates are less stable than calcium silicates and thus the use of magnesia is not expected to improve the immobilization of silicon. Only barium oxide forms thermochemically preferred barium silicates and binds silicon successfully.

4.3.2. Sintering experiments

The results generally show an increasing aluminum extraction in the leaching step at higher sintering temperatures, but a complete melting has to be avoided. Temperatures above 600 °C significantly increase the aluminum recovery from 20% at 600 °C to ~ 80% at 1000 °C, while also the silicon concentration in the wash solution rapidly increases from 25 mg/l to > 200 mg/l in the same temperature range. Soda addition reduces the solidus temperature of the mixture, and thus sintering temperatures between 1000 and 1100 °C are recommended. Detailed diagrams and further information regarding basic experiments on sintering process have already been published in (Kaufßen and Friedrich, 2016) and (Kaufßen and Friedrich, 2015). A similar connection can be drawn regarding the addition of soda. The extraction efficiencies of aluminum without any addition of lime and coke increase up to a soda addition of 60 wt.-% regarding the treated mass of BR and is equivalent to a molar ratio Na₂CO₃/Al₂O₃ of 2.56. This indicates that sufficient soda must be supplied for a complete conversion of Fe₂O₃, SiO₂ and Al₂O₃ into their sodium compounds, while TiO₂ likely forms compounds with a low ratio Na:Ti (e.g. Na₂Ti₆O₁₃) and consumes less soda than expected in literature.

Further addition of lime scarcely increases the aluminum recovery, but the effect is especially noticeable at lower sintering temperatures of 800–900 °C. In this temperature range the same extraction efficiencies are reached with lime addition which otherwise require 1000 °C sintering temperature without lime addition. But added lime generally reduces the silicon concentration in the liquor by > 25% from ~200 mg/l to 130–150 mg/l. These effects can already be observed at rather low molar ratios CaO/SiO₂ between 0.8 and 1.1 and show that the formation of Ca₂SiO₄, as commonly assumed (see chapter 2.2.1 and 2.2.5), is not relevant. The aluminum recovery can be significantly improved to almost 90% by the addition of coke at 60 wt.-% soda addition and 1000 °C sintering temperature. Besides the maximization of aluminum recovery, the addition of coke can be used to substantially lower the soda consumption without a decrease in extraction efficiency, in accordance with chapter 2.2.4 and 2.2.5. Fig. 15 shows that the same extraction efficiency of 80%, reached with 60 wt.-% soda addition, can be achieved at even 47 wt.-% soda addition combined with 8 wt.-% coke addition, required for the stoichiometric reduction of hematite to metallic iron. Even at 35 wt.-% soda addition, the aluminum recovery can be increased from 55% to 75% by the addition of 8 wt.-% coke.

The “digestion” takes place during the sintering stage by the formation of water-soluble sodium aluminate, which can be washed out with water within 5–10 min. Therefore kinetic investigations reveal that the washing step is completed within minutes due to the good solubility of the formed sodium aluminates.

5. Benchmarking the process alternatives and conclusion

The maximum achieved aluminum recoveries are shown in comparison with the accompanied process parameters in Table 2. It can be verified that it is basically possible to extract as much as 80–90% of the aluminum content from BR by using selective alkaline processes.

However, the selectivity is strongly decreased due to very aggressive conditions, which cause problems concerning plant corrosion, desilicification, crystallization of aluminum hydroxide and so on. As a consequence it is recommended to trade high recoveries for process simplicity and high selectivity by using the proven Bayer-process a second time expecting aluminum recoveries of about 50% under very mild conditions (100 g/l NaOH at 250 °C for 10 min), winning a very pure aluminum hydroxide. Alternatively, in combination with lime addition and increased process temperature up to 70% aluminum can be recovered. Sintering experiments reveal that the addition of lime improves the aluminum recovery slightly, but the required molar ratio CaO/SiO₂ of ~1 is much lower than recommended in literature. Moreover the soda losses due to side reactions with titania are lower than reported in literature, and FactSage® calculations confirm that sodium-titania compounds with a low ratio Na:Ti (e.g. Na₂Ti₆O₁₃) are more stable than the assumed formation of Na₂TiO₃. The addition of coke in the sintering stage reduces the soda demand and improves the aluminum recovery substantially. In summary, the lime soda sintering process reaches aluminum recoveries of approx. 80%, but can only be commercially successful in combination with iron reduction, magnet separation and winning of an iron by-product due to high efforts recovering the spent soda from the solution. Slag leaching after BR smelting and pig iron recovery achieves high aluminum recoveries as well, but only in combination with high concentrations of caustic soda in case of Bayer-process or high soda additions in case of sinter process. Due to high costs resulting from plant corrosion and other above mentioned problems or high consumption of soda, this process route is not recommended. All experiments and recovery rates were based on the employed bauxite residue from the ancient landfill Lünen, which contains comparably high aluminum amounts. Extraction efficiencies from other BR sources may differ.

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