

SODA SINTERING PROCESS FOR THE MOBILISATION OF ALUMINIUM AND GALLIUM IN RED MUD

Frank KAUSSEN, Prof. Bernd FRIEDRICH

Department of Process Metallurgy and Metal Recycling (IME), RWTH Aachen University, 52056 Aachen, Germany

fkaussen@ime-aachen.de, bfriedrich@ime-aachen.de

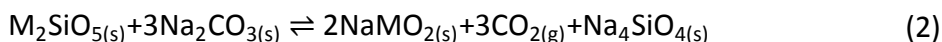
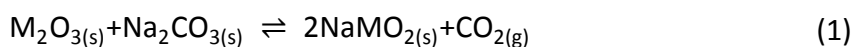
Abstract

This study examines the occurring phases in red mud sinter mixtures testing different amounts of soda addition, lime addition (varying CaO/SiO_2 from 0.4 to 1.5) and coke addition (double stoichiometric $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$) in dependence on different calcination temperatures varying from 480 °C to 1070 °C. The occurring phases are analysed by DTA/TG and XRD and compared to the alumina and gallium recoveries in a subsequent leaching step of the sinter mixtures with water. The experiments reveal alumina recoveries of up to 90 % and gallium recoveries up to 95 %. Thus the content of alumina and gallium in the leaching residue is reduced to 5 wt% and 2 ppm respectively.

Introduction

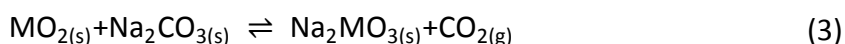
Common process for the extraction of aluminium from bauxite ores is the Bayer-process which employs the caustic pressure leaching with subsequent crystallisation of aluminium hydroxide after the separation of the undissolved bauxite residue, the so-called red mud, from the suspension. About 95 % of the worldwide processed bauxite passes through this process.¹ But the average amount of Al_2O_3 from bauxite residues produced by the Bayer-process is still 12-15 wt%, in some cases up to 20 wt%.² The main reason for these aluminium losses are the formation of insoluble aluminium silicates and sodium aluminium silicates like sodalite or cancrinite, commonly known as desilication products (DSP).³ These compounds occur in presence of dissolved silica. Beside this wet digestion, sintering of red mud with soda even transfers the aluminium bearing compounds into sodium aluminates which can be easily washed out and dissolved by water. This sinter process needs temperatures of 800-1200 °C, in most cases 1000-1200 °C and is therefore called “dry digestion”. Several authors carried out many experimental works in order to find the optimum process parameters.⁴⁻⁷

The basic idea is the soda-pot-ash digestion well known for chemical analysis. But applied for the alumina extraction, the process works in absence of pot-ash and follows the reactions (1) and (2).⁸



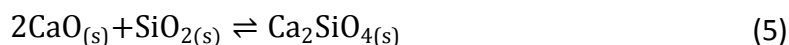
In this case M represents trivalent metal ions like Al^{3+} and Fe^{3+} which are solved from the silica by soda and under the release of carbon dioxide and transferred to sodium compounds. The advantage is that even metal silicates get cracked according to reaction (2).

The tetravalent metal oxides like Si^{4+} or Ti^{4+} are “digested” according to reaction (3).⁹



It becomes obvious by these chemical equations, that the released carbon dioxide can be used to optimise the soda consumption. The addition of carbon at high temperatures of about 1000 °C allows the Boudouard reaction to reduce the formed carbon dioxide to carbon monoxide (4). Thereby the partial pressure and thus the activity of carbon dioxide is reduced, forcing the equilibrium of equations (1-3) towards the formation of products and thus the formation of sodium metal oxides.^{5,7} Moreover the formation of $NaFeO_2$ and thus the loss of soda due to the hematite can be avoided since hematite is reduced to FeO or metallic iron.¹⁰

Nevertheless, the formation of sodium silicate is not appreciated because it is soluble in water, contaminates the sodium aluminate solution and leads to the formation of insoluble DSP's like sodalite and cancrinite. Therefore the reactive silica must be captured in stable phases. This can be achieved by the addition of lime. The chemical equation (5) shows the mechanism of lime addition and the formation of calcium silicates.



Therefore, the molar ratio CaO/SiO_2 becomes an important issue. But too much lime leads to the formation of calcium aluminates, which are even hardly soluble or insoluble in water or weak caustic solutions and the aluminium recovery declines.^{4,10}

Materials and Methods

The material used for the experiments is taken from the landfill of the former “Vereinigte Aluminiumwerke” (VAW) near Lünen, Germany. Deposited with 30-32 wt% moisture, the red mud is very sticky and clayey. The chemical composition is shown in Table 1 and offers high amounts of remaining aluminium compounds. This is due to the fact that it is a very old deposit. The plant started its operation in 1939 and processed many different types of bauxite ores from different locations from all over the world like from Hungary, former Yugoslavia, Guinea, Australia, Jamaica, Greece and Canada. The bauxites were partly refractory to dissolve, partly easy to dissolve and even the process technology changed several times employing autoclaves, tube reactor and dry digestion in former times.¹¹ In order to realise high through-puts and cheap but poorly digestible bauxites as raw material these rather high alumina losses were accepted. Therefore X-ray diffraction (XRD) patterns show that the predominant phases beside high amounts of hematite are still aluminium hydroxides (gibbsite and boehmite). Therefore the loss on ignition is about 10 wt% due to the water of crystallisation. But in order to archive a better comparability the elemental values measured by X-ray fluorescence (XRF) are converted into oxides as quite common in literature. Therefore, the sum of all components does not reach 100 % and is about 98.5 % considering the loss on ignition (LOI).

Table 1: Red mud composition of the landfill Lünen, Germany, given in wt%, except for Ga where is in ppm.

Element	Moisture	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	TiO ₂	Na ₂ O	Ga	LOI
Conc.	30.5	27	29.5	13.1	3.8	8	7	67	10

For the experiments red mud was dried at 105 °C and mixed with different amounts of anhydrous soda (Na₂CO₃) powder. Moreover in some cases lignite coke of a grain size < 1 mm and a carbon content of 88.2 wt% was added together with varying amounts of lime powder of 95 wt% purity. The compounds were mixed and homogenised by short grinding step with duration of 10 s in a disc mill. After that the mixture was filled into a 330 ml aluminosilicate crucible and placed into a resistance-heated furnace. During the sintering stage the temperature inside the mixture was measured by two type K thermocouples (one at the crucible wall, one in the middle of the bulk). The duration of the sinter stage was set to at least one hour at desired temperature to ensure a complete adjustment of the equilibrium phases. After the heat treatment, the sinter agglomerates were ground, in some cases of hard agglomerates even by employing the disc mill. Thereafter the sinter powder was leached with water at 50 °C for 30 min. The suspension was separated into liquor and residue by vacuum filtration. For sampling the composition of the liquor was

analysed by Spectro ICP-OES Spectro Flame D. The overview of the entire process is given in Figure 1.

In total three series of experiments have been conducted with a quantity of 100 g red mud in each experiment. In the first series the soda addition was varied from 16 g (which is necessary to convert all aluminium phases into NaAlO_2) to 47 g (which is necessary to convert all aluminium, titanium and iron phases into sodium compounds) up to 80 g to ensure an excess of sodium while the CaO/SiO_2 ratio was adjusted always to 1.3. The sintering was done at 1000 °C for 90 min. The second series was carried out with a fixed amount of 60 g soda on 100 g red mud (60 % soda addition) and lime additions to adjust a molar CaO/SiO_2 ratio varying from 0.4 to 1.5. The sinter was prepared at 910 °C and 1040 °C to observe the temperature dependence on the aluminium and gallium metal extraction. In the third series, the sintering temperatures have been changed. According to the previously conducted differential thermal analysis and thermogravimetry (DTA/TG) measurements, the main loss of mass and the main changes in sample temperature, indicating chemical reactions, take place between 600 °C and 1000 °C. Nevertheless sintering temperatures from 480-1070 °C were used for the experiments.

Results and Discussion

General observations throughout all experiments are the formation of firm agglomerates at sintering temperatures above 800 °C. Below 800 °C the sinter could be ground manually by hand. All sinters gained from experiments above 800 °C had to be ground by the disc mill.

The results from the experiments with varying soda additions are shown in Figure 2. It can be seen that actually about 50 g of soda and thus the necessary amount for the conversion of all components (Al, Fe, Ti) into sodium compounds are necessary for good recoveries of about 80 % in case of aluminium and about 90 % for gallium. Sodium in excess has only little influence on the recovery and rather a negative influence, lowering both, the aluminium and the gallium recovery by 2-4 %.

The effects of different lime additions can be seen in Figure 3. It becomes obvious that the addition of lime has a strong negative influence on the gallium recovery, which decreases from 72 % at a CaO/SiO_2 ratio of 0.4 down below 60 % at ratios above 1. The aluminium recovery can be increased by the addition of lime from 61 % up to 77 %. However, the recovery maximum is in the range of 1.1-1.2. Higher CaO/SiO_2 ratios again lower the aluminium recovery. Moreover, it can be seen that a higher sintering temperature strongly affects the aluminium recovery from 69 % at

910 °C to 77 % at 1040 °C. The influence of the sintering temperature on the gallium recovery is thereby rather negligible.

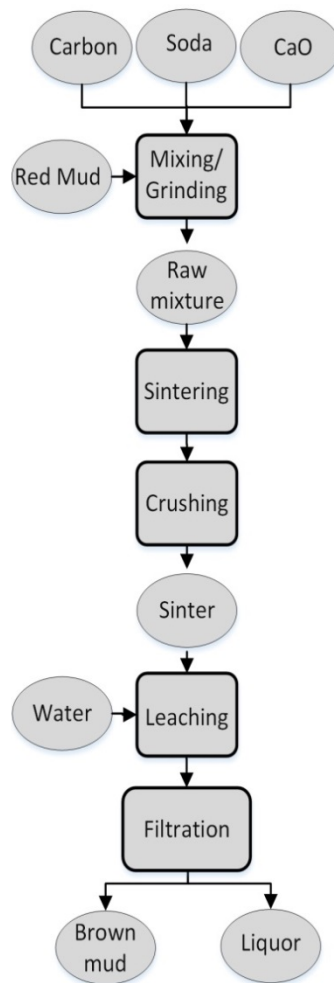


Figure 1: Flowchart of the sintering process

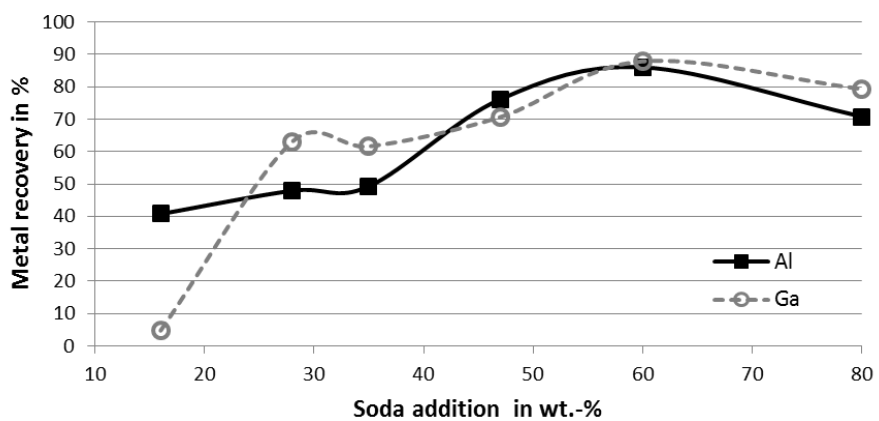


Figure 2: Metal recovery in dependence on soda addition regarding the mass of red mud at $\text{CaO}/\text{SiO}_2 = 1.3$ and 1000 °C sintering temperature

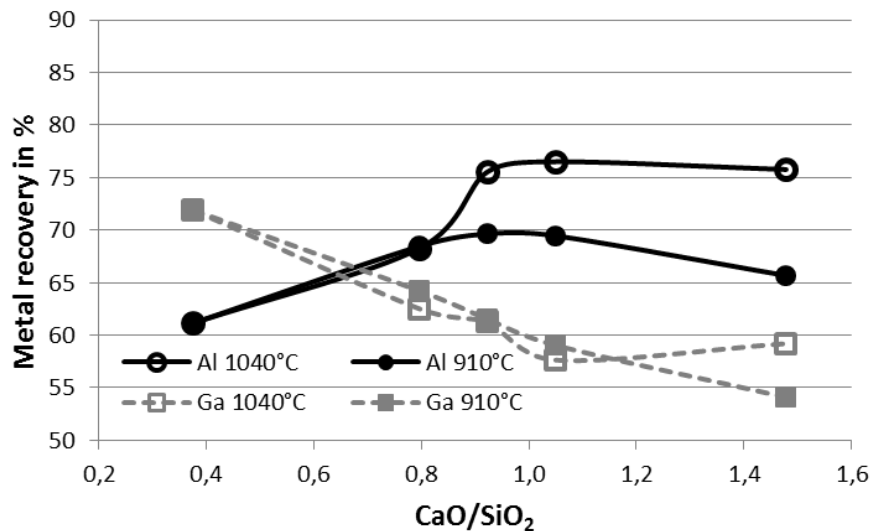


Figure 3: Metal recovery in dependence on the CaO/SiO₂ ratio with 60 % Soda addition

The sintering temperature dependence is examined in detail and the results are shown in Figure 4. Particularly the leaching of aluminium can be significantly increased by using higher temperatures during the sintering step. The addition of carbon increases the recoveries of aluminium and gallium but at sintering temperatures above 1000 °C, the carbon addition loses its beneficial contribution to the leaching efficiency. Even the gallium recovery can be increased with higher sintering temperatures but the recovery stagnates at almost 60 % above 850 °C.

Combining the best parameters, a sinter mixture with CaO/SiO₂ = 1.3, 60 % soda and 15 % coke addition, sintered at 1000 °C, mobilised 89 % of the aluminium but the high lime addition reduces the gallium recovery down to 40 %. However, even the mixture with 60 % soda and CaO/SiO₂ = 1.4 sintered at 1000 °C revealed an aluminium recovery of 86 % accompanied with a gallium recovery of 85 %.

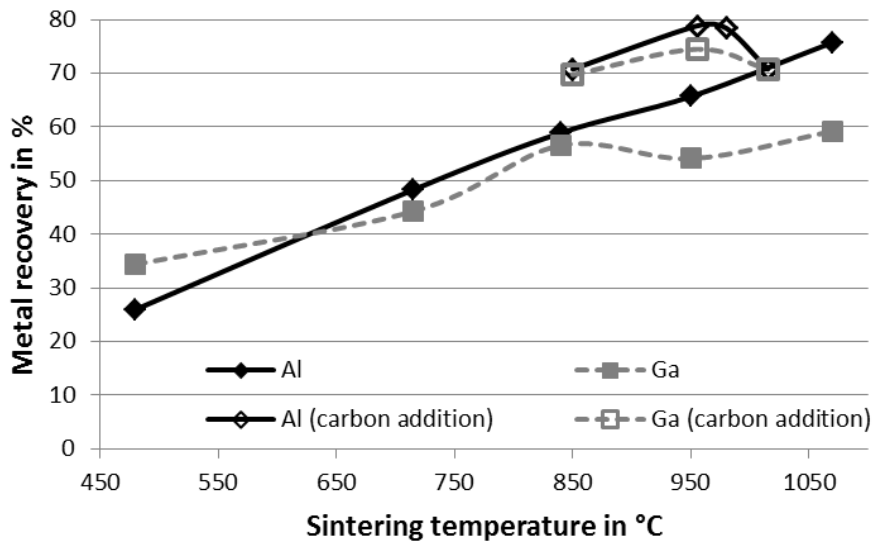


Figure 4: Metal recovery in dependence on the sintering temperature using 100 g red mud, $\text{CaO}/\text{SiO}_2 = 1.4$ and in case of carbon addition with 15 % coke

The obtained results from the experiments support and verify the observations of several researchers.^{2,3,4,7,10} As the DTA/TG reveals and the experiments confirm, the chemical reactions start at about 600 °C and are completed at 1000-1050 °C. XRD patterns show that the chemical conversion of soda into sodium aluminate takes place between 580 °C and 790 °C. Above 790 °C soda is not detectable in the XRD patterns any more. Unfortunately, the created aluminate phases were not detectable by XRD, either because of their grain size or their amorphous state. The final composition of the leaching residue is given in Table 2 and shows that the alumina content could be reduced from initially 27 wt% to 7.5 wt%, considering the average from all experiments with an aluminium recovery > 50 %.

Table 2: Composition of the leaching residue

Element	Al_2O_3	Fe_2O_3	SiO_2	CaO	TiO_2	Na_2O	Ga
Conc. [wt%]	7.5	32.3	14.6	14	8.9	14.1	10 ppm

Acknowledgements

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