An Environmentally Friendly Method for Removing Sodium in Red Mud

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Iron(III) sulfate or its mixture with aluminium sulfate can be used as a solid phase sulfatizing agent to destroy sodium aluminium silicates in red mud within 2 h at 200–500 °C. These solid phase sulfatizing agents transform sodium aluminium silicates and basic sodium-compounds into water-soluble sodium sulfate without SO_2 or SO_3 evolution. By means of an aqueous leaching of the sulfatized red mud a raw material with high iron and low sodium content is obtained for blast furnace technologies.

Red mud of about one billion of tons have been accumulated so far all over the world and it increases by 3–4% each year.[1] In spite of the efforts directed for the utilization of this material, up till now no economical process has been developed. Utilization in blast furnace[2] is hindered by the high level of sodium present in the mud as water-soluble and non water-leachable constituents. The latter components are the sodium aluminium silicate compounds which form scalings on the wall of the blast furnace. Consequently, decomposition of the sodium aluminium silicates (sodalites, cancrinites), to remove their sodium content, is an essential step preceding utilization. We have studied a solid phase sulfatizing process performed by iron(III) and/or aluminium(III) sulfates. The elemental analysis of the starting red mud and the treated samples, respectively were performed with standard ICP-OES methods (JY Ultima 2C). The material studied was red mud from the MOTIM Alumina refinery, in Mosonmagyaróvár, Hungary. The composition of the starting material (expressed as oxides, wt % for air-dried material) was found to be as follows: Na_2O 9.12, CaO 8.32, SiO_2 15.41, TiO_2 4.26, Al_2O_3 15.62, Fe_2O_3 34.06. XRD study of the starting red-mud was performed by a standard procedure,[3] and showed the presence of hematite (α-Fe_2O_3), hydrogrossular (Ca_3Al_2-$(SiO_4)_3$, and $Ca_3Al_2(SiO_4)_2(OH)_4$), perovskite ($CaTiO_3$), cancrinite ($Na_8Al_6Si_6O_{24}(OH,Cl,(CO_3)_{0.5})_2$) and calcite ($CaCO_3$) phases identified by their ICDD cards. 4×5 g of red mud samples were mixed individually with one of the four sulfatizing agents (5 g of $FeSO_4 \cdot 7H_2O$, 5 g of $Fe_2(SO_4)_3 \cdot 9H_2O$, 5 g of $Al_2(SO_4)_3 \cdot 18H_2O$, and 5 g of 1:4 mixture (in weight) of hydrated aluminium– and iron(III) sulfates, respectively). Four sets of these sample series together with blanks containing no additives were heated at 100, 200, 300, 400, and 500 °C for 2 h. After cooling, each of the samples were leached with 100 mL of water, then the residual sodium contents were measured after acidic digestion of the samples dried at 120 °C for overnight. The residual sodium contents as the function of the treatment conditions are presented in Table 1. The aluminium and the iron sulfate mixture for the sulfatising process was prepared by exhaustive sulfuric acid leaching of the starting red mud.[4] The insoluble residue ($CaSO_4 \cdot 2H_2O$, TiO_2, SiO_2-compounds, etc.) was filtered off,

Table 1. The residual Na_2O content of the treated and leached red mud samples

| Sample[a] Temperature/°C = | Residual sodium content/wt % | | | | |
	100	200	300	400	500
1	9.65	9.51	10.21	10.16	10.02
2	1.67	1.22	0.82	1.72	1.74
3	0.58	0.69	0.47	0.54	0.77
4	2.37	2.48	2.18	4.20	2.89
5	1.11	0.79	1.22	0.84	0.83

[a]1. No additive; 2. $FeSO_4 \cdot 7H_2O$; 3. $Fe_2(SO_4)_3 \cdot 9H_2O$; 4. $Al_2(SO_4)_3 \cdot 18H_2O$; 5. $Al_2(SO_4)_3 \cdot 18H_2O$ + $Fe_2(SO_4)_3 \cdot 9H_2O$, 1:4 mixt. (wt/wt); Each sample was treated in the same manner. The relative error of the measurements is ±1%.

and the aluminium sulfate and iron sulfate mixture was obtained by crystallization. Due to the phase relationships in the Na,Al,Fe//SO_4–H_2O system and their sub-systems,[5] the amount of aluminium and iron sulfates in the mixture was found to be 1:3.98 (wt/wt, re-calculated into the hydrated forms of the metal sulfates). The effect of iron(II) sulfate used for similar purposes[6] has also been compared under analogous conditions.

As it can be seen from Table 1, each of the sulfatizing agents decrease the sodium content in the temperature range of 100–500 °C. However, the iron(III) sulfate proved to be the most effective. Change in the water content and reactivity of each component during the heat treatment can cause "irregular" changes in the sodium content as the heating temperature increases.

The low value of the relative sodium content in the samples heated even at 100–200 °C is the consequence of the relatively high combined water content due to the presence of hydroxylated compounds of aluminium and iron. Sodium aluminium silicates do not decompose at low temperature as it can be seen in Figure 1, and probably only the sodium aluminate or sodium hydroxide absorbed on high-valence metal hydroxides are transformed. As far as the blast furnace raw material is concerned, the limiting residual sodium content is 1.5%.[6] From an economical and technical point of view, however, the value of the sodium content is supposed to be as low as possible and high iron content is favoured. Considering these requirements, the most economic process seems to be the treatment at 500 °C with the mixture of aluminium– and iron(III) sulfate prepared from the red mud itself. The residual iron(III) oxide content in the end product is higher than 50%, and the concentration of sodium oxide is well below 1%.

The main advantage of the iron(III) sulfate and its mixture with aluminium sulfate is their direct, economical preparation from red mud with exhaustive sulfuric acid treatment. In the last case the recovered sodium content can easily be separated
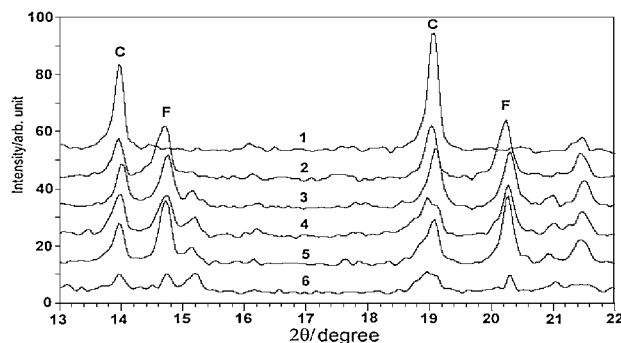
Figure 1. Treatment of red mud with iron(III) sulfate (1; no additive, 2; 100 °C, 3; 200 °C, 4; 300 °C, 5; 400 °C, 6; 500 °C; C-cancrinite; F-residual partially dehydrated iron(III) sulfate (before aq. leaching).

as alum. In addition, their selectivity as a sulfatizing agent is another important factor. Direct sulfuric acid leaching process is difficult to control so that only the sodium component react and destroy the sodium aluminium silicates without the dissolution of other iron and aluminium components. If each metal sulfate reacts with its own oxide species, the product would contain the starting oxide and the sulfate materials, namely no reaction takes place. Cross-sulfatizing reaction (Fe–compounds with aluminium sulfate and aluminium compounds with ironsulfate) of the active compounds, however, gives formation of sulfate of one of the metals and oxide/non-oxide species of the other metal.

$$M^*A_xB_y + M_2(SO_4)_3 \cdot nH_2O = M^*_2(SO_4)_3 + MA_xB_y \quad (1)$$
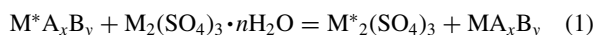
where M^* is Al or Fe (in the reactive compound), M is Al or Fe, A, and B are anionic species (oxide, hydroxide, silicate, aluminosilicate), x and y are stoichiometric coefficients. In this way, even if the reaction of Al- and Fe-content of the red mud takes place with the sulfatizing agent, the sulfatizing activity is kept to be constant. The occurrence of cross-sulfatizing reactions might cause increased crystallinity of the sample heat treated with (Al, Fe)–sulfate compared to the sample heated without sulfatizing agent (Figure 2). The solid-phase reaction ensures the absence of hydrolysis reactions and the formation of amorphous basic sulfates. The hydrolysis reactions could not be avoided in an aqueous-phase interaction.

Since the thermal decomposition of aluminium or iron sulfates start above 500 °C,[7] no SO_2 or SO_3 evolution could be observed in the tests carried out. The sulfatizing process is probably proceeding with the same mechanism as it was observed in the case of the sulfation of zinc ferrite with ammonium sulfate.[8]

In concluding, using this reaction sequence, by means of the dissolution of a part of the red mud, and sulfatizing the other part
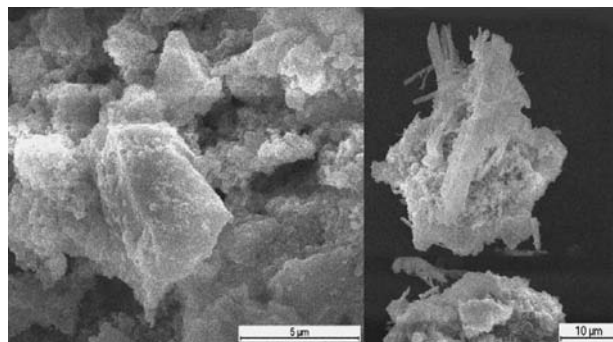

Figure 2. SEM pictures of heat treated red mud samples without (left) and with (right) (Al, Fe) sulfate at 500 °C.

with the formed and crystallized trivalent sulfate mixtures in a solid-phase reaction at 500 °C, which is followed by an aqueous leaching at room temperature, the sodium oxide content of the red mud can be removed by more than 94%. Consequently, the residue (with an Fe_2O_3 content higher than 50% and with an Na_2O content less than 1%) can be used for blast furnace along with other Fe_2O_3-containing feedstock materials.

References
1   *Red mud—Analysis and Utilisation*, ed. by R. S. Thakur, S. N. Das, Wiley Eastern Limited, Daryaganj, New Delhi, **1994**; T. Kasai, T. Mizota, *Shigen to Sozai* **1996**, *1112*, 131; R. Hind, S. K. Bhargava, S. C. Grocott, *Colloids Surf., A* **1999**, *146*, 359.
2   V. A. Utkov, V. V. Meshin, Y. I. Shmigidin, S. I. Petrov, S. A. Nikolaev, *Tsvetn. Met.* **1991**, 71; X.-G. Mei, M.-L. Yuan, J. Chen, *Youse Jinshu, Yelian Bufen* **1996**, 27.
3   J. Sasvári, J. Zöldi, K. Papp, G. Horváth, *Mater. Sci. Forum* **1994**, *166–169*, 695; I. E. Sajó. *Powder Diffraction Phase Analytical System*, Budapest, Hungary, **1994**.
4   B. A. Simanovskii, T. M. Sporysheva, Y. A. Lainer, *Tsvetn. Met.* **1995**, 58; I. V. Nikolaev, V. I. Zakharova, R. T. Khairullina, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.* **2000**, 19.
5   F. Wirth, B. Bakke, *Z. Anorg. Chem.* **1914**, *87*, 48; V. M. Laptev, F. I. Akhmarov, B. A. Dmitrevskii, O. K. Kamalov, *Zh. Prikl. Khim.* **1992**, *65*, 2363; A. S. Mosinskii, *Zh. Obshch. Khim.* **1977**, *47*, 7.
6   H. Takashi, K. Nobuyuki, Jpn. Kokai Tokkyo Koho 56-77309.
7   H. Tagawa, *Thermochim. Acta* **1984**, *80*, 23; R. V. Siriwardane, J. A. Poston, Jr., E. P. Fischer, M.-S. Shen, A. L. Miltz, *Appl. Surf. Sci.* **1999**, *152*, 219; G. P. Coombs, Z. A. Munir, *J. Therm. Anal.* **1989**, *35*, 967.
8   B. S. Boyanov, *Thermochim. Acta* **1994**, *240*, 225.