

OPPORTUNITIES WITHIN THE ALUMINA REFINERIES TO MAKE BAUXITE RESIDUE EASY TO DOWNSTREAM USE

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Abstract

The soda content of the bauxite residue (BR) hinders its uses for various purposes (e.g. iron metallurgy, additive in raw meal for making cement clinker or concrete), or at least makes it difficult and is associated with extra costs. The Na₂O content of BR varies between the extremes of 0.1 and 12.3. The soda content should be less than about 3 %, the less the better. The paper reviews the forms and sources of the chemically combined soda content of BR in connection with the major silica constituents of bauxite and the digestion conditions of the Bayer process.

The paper focuses on the options to make the BR leaving the refinery with such a chemical composition so that it be at least relatively easy to downstream use. The options which are discussed for the reduction of the chemically combined soda content, possibly recovery of some alumina:

- *lime addition to the digestion*
- *hydrothermal treatment of BR in presence of lime (causticisation included)*
- *pyrometallurgical processing of BR*
- *Improved Low Temperature Digestion (ILTD) and related processes*

An estimate of the soluble caustic soda content for various dewatering options is also given, which is to be accounted for on the top of the chemically combined Na₂O.

Keywords: bauxite residue, red mud, combined and soluble soda content

Introduction

The intention of utilisation of the bauxite residue is practically as old as the Bayer process. Huge intellectual efforts have been made and large amount of research and development funds have been spent on the issue. The Na₂O content of BR varies¹ between the extremes of 0.1 and 12.3, the average is 4.5. A recent overview of the BR management estimated the extent of the industrial use of BR to be 1.6 % of the annual amount produced all over the world.² The question is therefore justified: is there any real chance to significantly increase the industrial use of BR?

The two major obstacles of the use of BR are: its caustic soda content and the physical appearance (consistency).

Principal Digestion Variants, their Connection with the Chemically Combined Caustic Soda in Bauxite Residue

The main silica minerals that can be found in bauxites are clay minerals (first of all kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and quartz (SiO_2)). The amount of these minerals is highly variable in bauxites of different locations and origin.

The low temperature digestion and high temperature digestion are the two variants which are important in the view of the chemically combined soda content of BR.

In the low temperature (LT) digestion the gibbsite content of bauxite is solubilised at about 140-150 °C. The gibbsite itself dissolves in minutes. In the course of LT digestion the clay minerals also dissolve, at slower rate. The LT digestion reactors are designed to allow sufficient retention time so that sodium silicate content be decreased close to its equilibrium concentration by the crystallisation of the sodium-aluminium-hydrosilicate desilication product (DSP). The chemical composition of the sodalite³ that is formed in the course of LT digestion is $3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (1-2)\text{H}_2\text{O}) \cdot \text{Na}_2\text{X}$, where $\text{X} = \text{CO}_3^{2-}, 2\text{AlO}_2^-, 2\text{OH}^-, 2\text{Cl}^-, \text{SO}_4^{2-}$. There are other formulae in the technical literature as well.

Most, usually all clay minerals react during the conventional LT digestion, meanwhile the quartz remains un-attacked. The clay minerals cause chemical losses of caustic soda. The alumina in kaolinite is on the top of the soluble hydrated alumina minerals.

The high temperature (HT) digestion is designed to solubilise boehmite and diasporite content of bauxite, at a temperature of about 240-250 °C in case of boehmite.

At temperatures higher than about 180 °C, quartz starts reacting, clay minerals obviously react. At temperatures higher than about 180 °C, cancrinite starts to be the preferred sodium-aluminium-hydrosilicate. At a digestion temperature of 240 °C, 55-60 % was found to be cancrinite in BR, the rest was sodalite.⁴

Solubilisation of diasporite requires more severe conditions, i.e. higher digestion temperature (e.g. 250-280 °C) and/or higher caustic concentration, and/or lower digestion A/C ratio than applied for the digestion of boehmite. CaO addition highly facilitates the dissolution of diasporite.

In several alumina refineries the so-called pre-desilication is incorporated into the low or high temperature digestion systems. Prior to digestion considerable amount of clay minerals is converted to DSP, thereby the residence time in the digestion reactors can be reduced and/or lower dissolved silica content can be attained in the digester effluent. The composition of the sodalite that formed⁵ at about 100 °C was found to be $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (2+k)\text{H}_2\text{O}$ ($k=0-2$). At temperatures of about 70-90 °C, Linde zeolite 5A type DSP is formed⁶ its formula is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$.

The so-called double digestion and the sweetening processes are combinations of the LT and HT digestions, the details are beyond the scope of this paper.

Lime Addition to Digestion

Lime is added to the digestion for different purposes, such as to

- convert the caustic soluble P-compounds to insoluble Ca-phosphates
- convert sodium titanates to Ca-titanates
- convert sodium-aluminium-hydrosilicates to Ca-aluminium-hydrosilicates
- enhance the conversion of the (alumo)-goethite into hematite
- enhance the digestion (solubilisation) of diaspore

Lime is added to the digestion either as quicklime (burnt lime, CaO), or in slaked form $\text{Ca}(\text{OH})_2$. If CaO is added, it reacts with water and $\text{Ca}(\text{OH})_2$ forms.

Phosphorus control

Usually 0.5-1 % CaO for the bauxite weight is added to the LT digestion to convert P-content to insoluble compounds.

Reaction of sodium titanates with lime

Wefers synthesised crystalline sodium titanate in pure caustic soda solution.⁷ At concentrations of higher than about 100 g/l Na_2O (171 g/l caustic soda as Na_2CO_3), and temperatures higher than 150 °C the product was $\text{Na}_2\text{Ti}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$. At temperatures of higher than about 260 °C, $\text{Na}_2\text{Ti}_3\text{O}_7$ product was formed.

Studying scalings on the walls of the preheaters operating at 145-155 °C in the course of preheating of bauxite slurry, anatase and rutile were not found, and CaTiO_3 and $\text{Ca}(\text{Mg})$ -titanate were observed instead.⁸ It is deemed that rutile (TiO_2) reacts similarly to anatase, though at higher temperatures and/or higher liquor concentrations and/or lower A/C ratios and/or longer retention times. When sodium-hydro-titanates, which are part of the residue of the bauxite digestion are submitted to multistage washing, they slowly hydrolyse and some 80(-90) % of the

caustic is recovered.⁹ When Na-titanate reacts with Ca(OH)₂ in the course of digestion, mostly perovskite (CaTiO₃) is formed.

Reaction of sodium-aluminium-aluminium-hydrosilicates with lime, conversion of (alumo)-goethite into hematite

Zöldi et al.¹⁰ claimed that 3CaO.(Fe_xAl_{1-x})₂O₃.kSiO₂.(6-2k)H₂O is the composition of the hydrogarnet type silicates which are formed from a considerable proportion of silica by the conversion of iron minerals. During the LT digestion, where the liquid phase is nearly saturated for dissolved alumina k ≤ 0.5. In the course of causticisation of bauxite residue, the liquid phase is weak in dissolved alumina, k = 1.0-1.2. During HT digestion of karst bauxites, when the calcite (CaCO₃) and possibly dolomite (CaCO₃.MgCO₃) react with the caustic liquor and lime may also be added to bauxite, k=0.5-0.8, only a few percent of alumina is substituted with iron. When goethite is converted into hematite in presence of catalytic additive, the SiO₂ content increases, and may attain 1 mole (k=1), and the iron substitution of Al³⁺ may exceed 10 %. The overall formula of hydrogarnet is



where A denotes divalent cation, such as Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺, Co²⁺
 B denotes trivalent cation, such as Al³⁺, Fe³⁺, Cr³⁺.

Fe²⁺, Mn²⁺, Fe³⁺ in the hydrogarnet structure, and presence of some anions as SO₄²⁻ facilitate the conversion of (alumo)-goethite into hematite. During the high temperature digestion, some 20 % savings in the chemically combined soda can be attained¹¹ due to partial replacement of Na₂O of DSP to CaO.

Lime addition to enhance digestion of diaspor

Addition of lime to solubilise diaspor is practically a precondition of the digestion of diasporic bauxites. A minimum amount of 2 % CaO was needed in the fundamental tests of Mercier and Magrone.¹² As long as the lime addition increased, extraction yield of diasporic alumina sharply increased and at CaO dosages higher than 3-4 % it slowly decreased. When lime was added to digestion, a partial replacement of Na₂O of the DSP to CaO took place, the Na₂O/SiO₂ ratio continuously decreased from 0.65 to 0.3, the latter was reached at 2 mol CaO/SiO₂ ratio. Maltz¹³ explains the catalytic effect of CaO in such a way that Ca-titanates and hydrogarnets are formed instead of sodium-titanates and DSP which impede the dissolution of diaspor.

Gu Songqing¹⁴ reported a Lime-Bayer process. Here DSP is converted to hydrogarnet by extra lime addition in the course of digestion of diaspor. The

hydrogarnet, therefore the BR does not contain chemically combined soda. However, this process route is associated with lower alumina extraction yield, compared with the conventional Bayer process.

Hydrothermal Treatment of BR in Presence of Lime

The Bayer process *per se* is a hydrothermal processing of bauxites in caustic liquor. The presence of lime or $\text{Ca}(\text{OH})_2$ makes the reactions more complex. Causticisation of BR is used for recovering caustic soda from sodium-aluminium-hydrosilicates usually at temperatures lower than the atmospheric boiling point.

Causticisation of bauxite residue

The idea of causticisation has been known for several decades and it was applied in the Hungarian alumina refineries from mid 1950 years for about 25 years.

Nemecz et al.⁶ treated hydroxy-sodalite with $\text{Ca}(\text{OH})_2$ at 90 °C, the product had the composition of $3.1\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 1.65\text{SiO}_2$. Juhász et al.¹⁵ reacted sodium-aluminium-hydrosilicates with $\text{Ca}(\text{OH})_2$ and CaCl_2 and the product had the composition of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot k\text{SiO}_2\cdot\text{H}_2\text{O}$, where k might be even 3 and it had a cubic structure similar to $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$.

Vörös et al. studied the causticisation of sodalites, cancrinites and sodium titanates as model substances and those of in the bauxite residue.¹⁶ It was confirmed that the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio in the product was approximately 3, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio varied between 0.8 and 2.2. The causticisation of cancrinite proceeded rapidly. The hydrogarnet type Ca-aluminium-silicate product had the composition of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot k\text{SiO}_2\cdot(6-2k)\text{H}_2\text{O}$, no matter if the starting material was sodalite or cancrinite. Solymár et al.⁴ claimed k value to be of about 1.5.

Causticisation theoretically requires a lime consumption of 2 kg CaO per kg recovered NaOH. In practice 3-4 kg CaO/kg NaOH is needed.¹⁷ This is probably due to the side reaction of formation of tri-calcium-aluminate-hexahydrate. Causticisation works fairly well at low caustic concentrations and the spike in the concentration of the liquid phase is to be balanced with the washing/filtration of BR.

A novel process route has been proposed by Zhao Qiuyie et al.¹⁸ The DSP content of bauxite residue is causticised, washed and separated. The $3.1\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 1.7\text{SiO}_2\cdot 2.6\text{H}_2\text{O}$ product is converted to $\text{Al}(\text{OH})_3$ and insoluble CaSiO_3 and CaCO_3 by carbonisation. The $\text{Al}(\text{OH})_3$ formed is recovered by caustic leaching, CaSiO_3 and CaCO_3 can comprise feedstocks for manufacturing of cement.

Hydrothermal treatment of bauxite residue at elevated temperatures

The recovery of caustic soda from BR by lime addition significantly increases at elevated temperatures. The results of Solymár et al.⁴ are shown on Figure 1.

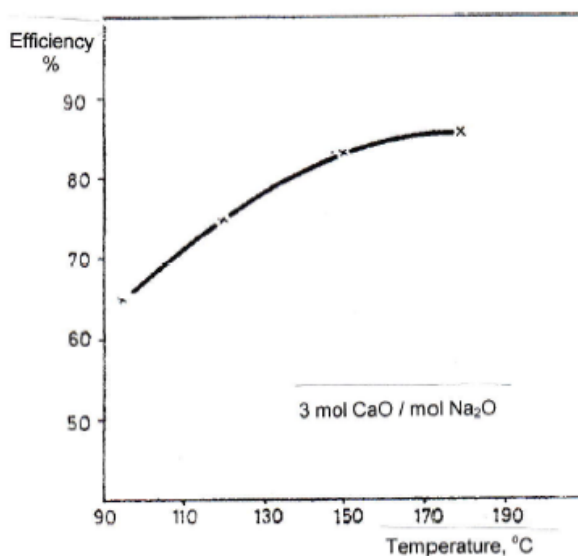


Figure 1: Caustic soda recovery from bauxite residue in the function of temperature

Creswell and Milne carried out laboratory scale hydrothermal treatment experiments in a high temperature reactor of continuous operation.¹⁹ The feedstock material was washed BR probably from high temperature digestion of Weipa bauxite in presence of negligible CaO addition. 2 moles CaO/mol SiO₂ was found to be the optimum lime dosage. Soda recovery of about 90 % and an alumina recovery of about 70 % could be achieved at temperature of at least 260 °C and residence times of 10-15 minutes. The A/C ratio of about 0.12 proved to be a strict limit, above that both the soda and alumina recoveries fell. The alumina recoveries reduced above 270 °C. The main reaction product was 3CaO.Fe₂O₃.2SiO₂, i.e. no chemically combined soda or alumina losses connected with SiO₂ occurred.

The results of pilot scale hydrothermal treatment of BR with CaO of Solymár et al.²⁰ are presented in Table 1. The feedstock material was washed BR of the Almásfüzitő Alumina Plant, Hungary. The bauxite was submitted to high temperature digestion (240 °C) in presence of lime in order to recover some caustic soda and facilitate the conversion of goethite into hematite. The Na₂O recovery reached 90-94 % at 265-270 °C treatment, at CaO dosage of 2.7-3.1 mol CaO/mol SiO₂. The Al₂O₃ recovery was only 7-13 %, probably due to the liquor A/C ratio, and a relative CaO overdosage. The feedstock material of different character from that of Creswell and Milne might have been the reason of the lower alumina recovery.

The low A/C ratio of the hydrothermal treatment effluent could not be harmonised with the use of all the bauxite residue for neither development. This was probably the reason why none of these processes were implemented in commercial scale.

Table 1: Pilot test results of hydrothermal treatment of bauxite residue with CaO

Item	Initial mud	After CaO add.	Hydrothermally treated muds					
			1	2	3	4	5	6
Test conditions:								
Temperature, °C	-	-	268	272	268	268	267	269
Pressure at the end of the holding tube, bar	-	-	82	83	78	78	76	74
Slurry flow, m ³ /h	-	-	2.6	2.7	2.8	2.8	2.8	2.7
Retention time, min	-	-	10	10	9	9	9	10
Liquor analysis:								
Na ₂ O _{caust} , g/l	10.1	140.9	141.2	140.3	145.1	143.8	141.7	144.7
Al ₂ O ₃ , g/l	6.7	49.2	54.6	56.9	56.2	58.3	54.1	55.0
MR, -	2.50	4.71	4.25	4.06	4.25	4.06	4.31	4.33
A/C, -	0.385	0.204	0.226	0.237	0.227	0.237	0.223	0.222
Solids content, g/l	-	-	135	147	130	129	125	130
Red mud analysis:								
Al ₂ O ₃ , %	17.0		13.1	13.5	12.1	11.9	11.8	11.9
Fe ₂ O ₃ , %	34.0		29.1	28.4	28.1	27.2	26.8	26.1
SiO ₂ , %	15.0		12.7	12.0	12.6	12.2	11.8	11.3
TiO ₂ , %	5.0		4.5	4.2	4.3	4.2	4.1	3.6
CaO, %	10.0		25.7	25.0	28.6	30.6	31.6	33.0
Na ₂ O, %	8.6		2.9	2.6	1.4	0.8	0.5	0.4
L.O.I., %	7.9		11.1	12.2	11.5	12.0	12.4	12.5
Al ₂ O ₃ /SiO ₂	1.13		1.03	1.13	0.96	0.98	1.00	1.05
Na ₂ O/SiO ₂	0.57		0.23	0.22	0.11	0.07	0.04	0.04
Calculated data:								
Al ₂ O ₃ recovery, %	-	-	14.0	14.2	15.0	13.0	13.0	7.1
Na ₂ O yield, %	-	-	70.9	80.0	84.3	90.0	94.3	94.3
mol CaO/mol SiO ₂	-	-	2.09	2.29	2.42	2.68	2.86	3.12
kg CaO/kg NaOH reg	-	-	2.99	2.98	2.99	3.06	3.16	3.40

Pyrometallurgical Treatment of Bauxite Residue with Lime (Serial Combined Bayer-Sintering Process)

The so-called sintering process is another method in order to substantially reduce the chemically combined soda content of BR. Here the BR is submitted to pyrometallurgical treatment at a temperature of 1100-1400 °C in presence of lime(stone) and possibly some amount of sodium-carbonate. The sodium-aluminium-hydrosilicate content of BR is transformed to beta-dicalcium-silicate (C₂S), meanwhile water-soluble sodium-aluminate and sodium-ferrites are formed. The C₂S could be

used as feedstock for manufacturing cement. The serial combined Bayer-sintering process was used in USA, in China and has been used in Pavlodar (Kazakhstan).

Sintering of BR require fairly high investment cost and high amount of primary energy. The sodium-aluminate leachate contains a high level of dissolved silica of about 4-5 g/l. The silica level is greatly reduced by pressure liquor desilication at about 150 °C, possibly in presence of DSP seed. The silica level can be further reduced with Ca(OH)₂ at atmospheric pressure at the expense of significant dissolved alumina losses.

Chemical compositions of brown muds from serial combined Bayer-sintering process are compared with typical bauxite residues of Bayer process in Table 2.

Table 2: Chemical compositions of typical bauxite residues and brown muds from serial combined Bayer-sintering processes

Origin of bauxite	Weipa	Trombetas	South Manchester	Darling Range	Iszka	Parnasse	Arkansas	Pavlodar
	Australia	Brazil	Jamaica	Australia	Hungary	Greece	USA	Kazakhstan
Digestion temperature	240°C	143°C	245°C	143°C	240°C	260°C	serial combined	serial combined
	red mud	red mud	red mud	red mud	red mud	red mud	brown mud	brown mud
Components, %								
Al ₂ O ₃	17.2	13.0	10.7	14.9	14.4	13.0	5.5	3.7
SiO ₂	15.0	12.9	3.0	42.6	12.5	12.0	23.1	21.6
Fe ₂ O ₃	36.0	52.1	61.9	28.0	38.0	41.0	10.1	21.3
TiO ₂	12.0	4.2	8.1	2.0	5.5	6.2	3.6	n.a.
Na ₂ O	9.0	9.0	2.3	1.2	7.5	7.5	3.6	1.2
CaO	-	1.4	2.8	2.4	7.6	10.9	47.2	43.4
Others	3.5	1.0	2.8	2.4	4.9	2.3	2.5	8.8
LOI	7.3	6.4	8.4	6.5	9.6	7.1	4.4	n.a.

Improved Low Temperature Digestion (ILTD) and Related Processes

The basics of the Improved Low Temperature Digestion (ILTD) Process is discussed in the technical literature.²¹ The dissolution of gibbsite and kaolinite is described as a competition of these reactants for the reactive OH⁻ ions in the liquid phase. Gibbsite in the gibbsitic type bauxites is in a greater amount by at least an order of magnitude and has higher dissolution reaction rate than that of kaolinite. In the course of the short reaction time needed for the dissolution of gibbsite it consumes virtually all the reactive OH⁻ ions and a significant portion of kaolinite stays unreacted. The high

dissolved silica concentration in the ILTD digestion effluent calls for an effective desilication of the liquid phase.

The principal features of an alumina refinery where ILTD Process would be used:

- no pre-desilication is needed
- low reactive OH^- conc., i.e. high A/C ratio, short digestion time
- separation of the bauxite residue just after the digestion of gibbsite preferably at the digestion temperature preferably with Hi-Bar Filtration
- seeded pressure crystallisation of the Desilication Product (DSP) out of the liquid phase. The sodalite type DSP would be a new by-product of the ILTD Process. Its soda and alumina content can be recovered within the refinery.

The chemical composition of the bauxite residue of the ILTD Digestion that would be filtered by HiBar Filtration is expected to be Al_2O_3 : 9.2 %, SiO_2 : 5.8 %, Fe_2O_3 : 70.4 %, TiO_2 : 4.1 %, $\text{Na}_2\text{O}_{\text{combined}}$: 0.6 %, $\text{Na}_2\text{O}/\text{SiO}_2$: 0.1 %. These figures are the average BR of two parallel digestion tests²¹ (taken at 6 minute reaction times).

Another process route has been proposed by Yang hui-bin and Tu gan-feng.²² This process uses atmospheric digestion, the BR having a Fe_2O_3 content of 55-60 % and a $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of about 0.1-0.13 is separated after the dissolution of gibbsite. The digester effluent has a dissolved silica content of 10-15 g/l, therefore an effective desilication is required. The separated DSP can be converted to $2\text{CaO}\cdot\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ by sintering; the latter can be leached out. The bauxite residue can be submitted to beneficiation to further increase its iron content.

Washing, Dewatering of BR and Soluble Caustic Losses

The various means of washing, de-watering and disposal of BR were summarised in a recent paper.²³ An estimation of the soluble Na_2O content which originates from the liquid phase and remains with the bauxite residue are summarised in Table 3 based on the presentation of Bott.²⁴ 5 g/l Na_2O (8.6 g/l as Na_2CO_3) total soda concentration was used when the soluble Na_2O content of BR was estimated. Low soluble soda content of about 0.2 % Na_2O is expected when leaf filter press filtration and especially when Steam Pressure Filtration is applied.

Table 3: Soluble Na₂O content of BR and moisture contents for dewatering options

	Convention al washer	Deep cone thickener	Vacuum drum filter	Filter press	Steam pressure (HiBar) filter
Solids material, t	1	1	1	1	1
U/F solids, %	30-35	45-50			
moisture content%	65-70	50-55	35-50	32	25
liquid phase	2,079				
liquid phase remaining with BR at disposal, kg	1,220	1,220	540	470	330
BR easy to handle				+	+
Na ₂ O _{soluble} , %	0.61	0.61	0.27	0.24	0.17

Na₂O Content of Bauxite Residue

The Na₂O content of BR consists of chemically combined and soluble soda content. The maximum permitted content was set up 6 % Na₂O for the raw meal of making cement clinker and 4 % for making pig iron in blast furnace.²⁵ For the use of BR in cement clinker, the Na₂O and K₂O content of all constituents and their losses during the process are to be considered. The equivalent Na₂O (total of Na₂O and equivalent of K₂O) content should be less than 0.6 % in case of general purpose cement, the worldwide average of BR in cement raw meal²⁶ is about 3 %. It is deemed that a limit of 3 % Na₂O is acceptable for most potential users of bauxite residue.

Conclusions

The paper reviews different process options in order to reduce the soda content of bauxite residue. The most appropriate option can be selected on individual basis, where the chemical and mineralogical compositions, the value of the residue, disposal options are considered. It is expected that modified and properly dewatered BR will have soda content of well below 3 % Na₂O, moisture content of less than 30 %, easy to handle and possibly will not be ranked as hazardous material. The industrial use of BR with favourable characteristics is expected to greatly increase in 5-10 years.

References

1. M. Gräfe et al. "Review of Bauxite Residue Alkalinity and Associated Chemistry", CSIRO Document DMR-3610, Project ATF-06-3: Management of Bauxite Residues" *Department of Resources, Energy and Tourism (DRET)*, 2009.
2. K. Evans, E. Nordheim, K. Tsesmelis, "Bauxite Residue Management", *Light Metals*, pp. 63-66, 2012.
3. R. G. Breuer et al. "Behaviour of Silica in Sodium Aluminate Solutions" *Extractive Metallurgy of Aluminum, Vol 1, Alumina*, Interscience Publishers, 1963.
4. K. Solymár et al. "Methods for Reducing NaOH Losses in the Hungarian Alumina Plants", *5th International Congress of ICSOBA, Zagreb, Yugoslavia, Travaux ICSOBA, (18) 1983*.
5. G. Bánvölgyi, "Reactions of Gibbsite and Kaolinite in the Bayer Liquor: A Comprehensive Kinetic Model and an Improvement of the Low Temperature Digestion", *Proceedings of the 7th ICSOBA Conference, Balatonalmádi, Hungary, Travaux ICSOBA, Vol. 23*, 1996.
6. E. Nemezc et al, "A Bayer-rendszerű Timföldgyártás Során Keletkező Nátrium- És Kalcium-Alumínium-Szilikátokról", *Bányászati és Koh. Lapok – KOHÁSZAT – 101. évf*, 1968.
7. K. Wefers, "Zur Chemischen Technologie des Bauxitaufschlusses IV. Untersuchungen in system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{H}_2\text{O}$ ", *Metall.*, **25** 239-250.
8. G. Bánvölgyi, "Lerakódások Képződése Timföldgyári Feltáró Berendezésekben, A Lerakódások Megelőzése És Csökkentése" (manuscript) Budapest, 1987.
9. J. Zámbo, and Kovács, "Indiai Bauxitok Timföldtechnológiai Vizsgálata", *Fémipari Kutató Intézet Közleményei, VII, Budapest*, 1964.
10. J. Zöldi et al., "Iron Hydrogarnets in the Bayer Process", *Light Metals*, 105-111, 1987.
11. G. Pásztor, P. Siklósi et al. *Könnyűfémek Metallurgiája, Tankönyvkiadó, Budapest*, 1991.
12. H. Mercier and R. Magrone, "Influence de L'addition de Chaux a L'attaque Alcaline en Voie Humide Des Bauxites a Diaspore", *Sommaire de ICSOBA 3e Congres Int., Nice*, 1973.
13. N. S. Maltz, "Efficiency of Lime Use in Bayer Alumina Production", *Light Metals*, 257-262, 1991.
14. G. Songqing, "Key Technology Development of Bayer process in China", in *Proceeding Book of ICSOBA, Zhengzhou, 2014*.
15. Á. Juhász et al. "A Bayer-eljárás Során Keletkező Nátrium-Alumínium-Szilikátok Kémiai Összetételének És Szerkezetének Vizsgálata", *Bányászati és Kohászati Lapok – KOHÁSZAT*, 1965.
16. I. Vörös et al. "Causticisation of red mud. Int. Colloquium on Alumina Production from Low Grade Bauxites, Banska Bystrica", *Ziar nad Hronom (Czechoslovakia), Travaux ICSOBA*, 1974.
17. K. Solymár et al. "Methods for Reducing NaOH losses in the Hungarian Alumina Plants", *Proceedings of the Second International Conference of Aluminium: INCAL-91, The Aluminium Association of India, Bangalore*, 1991.
18. Z. Qiuyue et al. "Economic Analysis of Producing Alumina with Low-grade Bauxite (Red Mud) by Calcification-Carbonisation Method", *Light Metals*, pp. 165-168, 2014.
19. P. J. Cresswell, D. J. and Milne, "Hydrothermal Recovery of Soda and Alumina from Red Mud: Test in a Continuous Flow Reactor", *Light Metals*, pp. 211-221, 1984.
20. K. Solymár et al., "Technical Peculiarities and Viability of Hydrothermal Treatment of Red Mud", *Light Metals*, pp. 49-54, 1997.
21. G. Bánvölgyi, and P. Siklósi, "The Improved Low Temperature Digestion (ILTD) Process: an Economic And Environmentally Sustainable Way Of Processing Gibbsite Bauxites", *Light Metals*, pp. 45-53, 1998.
22. H-B. Yang and G-F. Tu "The Technology of Utilising High Iron Low Silica Gibbsite", *Proceeding Book of ICSOBA, Zhengzhou, China, 2014*.
23. G Bánvölgyi, and T. M. Huan "De-watering, Disposal and Utilisation of Red Mud: State of the Art and Emerging Technologies", *Proceedings of XVIII International Symposium of ICSOBA, Zhengzhou, China, 2010*.

24. R. Bott, et al. "Red Mud Dewatering with Vacuum Drum Filtration and Hi-Bar Filtration" *Int. Seminar on Bauxite Residue (Red Mud), Goa, India, ICSOBA Travaux*, 2011.
25. A. Előterjesztés "Bauxit, ill. a Vörösiszap Vastartalmának Hasznosítására" Manuscript, Aluterv-FKI, 1984.
26. Y. Pontikes and G. N. Angelopoulos, "Bauxite Residue in Cement And Cementitious Applications: Current Status and a Possible Way Forward", *Resour. Conserv. Recy.*, **73** 53-63 (2013).