

AUTOCLAVE DESILICATION OF DIGESTED BAUXITE SLURRY IN THE FLASHING CIRCUIT

A. Damaskin, A. Suss, A. Panov, I. Paromova, N. Kuznetzova, N. Kutkova, O. Shipova, A. Kuvyrkina

RUSAL VAMI, Sredny pr., 86, St. Petersburg, 199106, Russia

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Abstract

Bauxite digestion conditions should provide not only the maximum alumina recovery from raw material into liquor, but also the required desilication to produce further alumina of high quality. Several desilication circuits are common for alumina industry, namely low temperature pre-desilication of crude and digested slurry, Sumitomo process. These processes usually involve extensive process equipment. The proposed option of autoclave desilication in the flashing circuit of the bauxite slurry allows implementation of the process at higher temperature enhancing chemical reactions of green liquor desilication. This improvement gives an opportunity to sharply reduce the retention time, facilitates reduction in the balanced silica content in the liquor. The mud produced after digestion and high temperature desilication has better sedimentation properties as compared to that obtained as a result of low temperature desilication.

1. Introduction

The bauxite processing conditions should provide not only high alumina recovery, but also the required level of green liquor desilication to produce specified product quality.

The conventional industrial process and equipment schemes of Bayer liquor desilication include:

- low temperature pre-desilication of thick raw slurry and
- desilication of digested diluted slurry under 95-105°C;
- Sumitomo process based on four key operations (1- double stream heating and tube digestion. Alumina is completely recovered from bauxite and half of reactive silica is transferred to the liquor; 2- high rate thickener: the digested slurry is separated within several minutes under pressure in order to stop further dissolution of silica from bauxite; 3- high rate washers: the bauxite residue is rapidly washed by countercurrent decantation; 4- desilication of green liquor in pressure vessels) [1]. For some specific quality bauxites above arrangements are not effective enough.
- at some refineries to achieve required silica concentration the digested diluted slurry / green liquor is treated with lime milk.

At sintering and nepheline processing refineries 4 methods of green liquors desilication are applied [2]:

1. autoclave desilication at 150-170 °C with recycling DSP seed;
2. autoclave desilication with addition of lime or white mud;
3. atmospheric pressure desilication free of any additives;
4. atmospheric pressure desilication with lime or other additive.

The last two methods even with 100 °C required long retention time and this option is not often applied at the plants.

The action of lime under desilication process is based on the cationic exchange with precipitated aluminosilicate where the sodium ions are replaced by calcium ions forming the calcium cancrinite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1,7 \cdot \text{SiO}_2 \cdot n \cdot \text{H}_2\text{O}$ and hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2 \cdot (6-2\text{X}) \cdot \text{H}_2\text{O}$) depending on process conditions [3]. Lower hydrogarnet dissolution ability in alkaline liquors provides the better desilication level when lime is used. Another effect - Na_2O losses in the mud reduce and Al_2O_3 losses increase.

It is known that the more low quality (high silica) bauxites are used to produce alumina by Bayer method, the higher are the losses of alumina and sodium oxides with red mud. Formation of DSP in course of autoclave digestion results in the scaling of heating surfaces in heat exchangers and autoclaves, therefore while processing high silica bauxites, to ensure that maximum silica will be bound into DSP before digestion, one tends to complete most of the process at pre-desilication stage, thus applying longer retention time and temperature about 100 °C. Another benefit of accomplishing most or full of desilication process before digestion is obtaining a possibility to avoid conventional atmospheric pressure post-desilication stage, which limits pushing up the A/C ratio due to increased reversion losses. Pre-desilication stage conditions generally allow to dissolve and bound into DSP the silica which is represented by kaolinite.

However, some of monohydrate bauxites have substantial amount of silica in other minerals, i.e. chamosite (chlorite group) that is the case for bauxites of North Urals and Timan (Russia) and North Viet Nam. For these bauxites requiring high-temperature digestion conditions, carrying out most of desilication before digestion is not possible. Similarly, bauxites with high quartz content (some Guinean or Venezuelan) processing leads to quartz being dissolved at high temperature digestion and/or clarification conditions. It is also known that DSP's depending on their formation conditions are subject to solubilisation / restructuring at desilication and digestions stages, sometimes increasing silica level in green liquors [4].

This paper studies the autoclave desilication of digested slurry in the digestion flashing circuit at temperature ~ 150 °C. This technology allows to process the above complicated bauxites with maximum alumina supersaturation (A/C) in green liquor by excluding atmospheric pressure post-desilication.

Due to increase of the desilication temperature comparing with conventional atmospheric pressure process, the slurry autoclave desilication process allows to intensify the chemical reactions for

desilication of the slurry liquid part. This process improvement permits to reduce the slurry retention time down to 30 – 60 min and increase the alumina to silica ratio of the liquor (μ_{Si}) up to 300 units. The risk of alumina losses due to reversion normally occurring in the post-desilication tanks at lower temperatures is totally excluded.

The mud after digestion process followed by high temperature desilication is characterised by better sedimentation properties to compare with the mud from low temperature post desilication.

This paper is also dealing with the study of further desilication process improvement through the introduction of the specific sodium hydroalumosilicate (DSP) seed in the reactive zone including noselite and cancrinite. Previously the use of sodalite for this purpose was described [5].

2. Study of desilication process for different quality bauxites

In order to compare atmospheric predesilication and autoclave desilication processes efficiency the studies were conducted using low quality boehmite bauxites from North of Russia, diasporic from North Vietnam and predominantly gibbsitic bauxites from Guinea having high quartz content (tables 1, 2).

Table 1
Chemical composition of bauxite used

Bauxite	Content, mass %					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO
North Russia	6.7	49.4	27.9	3.2	0.26	0.3
North Viet Nam	4.2	57.7	20.5	3.7	0.11	0.08
Guinea	3.1	44.1	23.3	2.0	0.12	0.1

Table 2
Phase composition of bauxite used, %

Bauxite	Gibbsite	Belite	Diaspore	Quartz	Kaolinite	Al-goethite	Al in Algoethite, molar %	Hematite	Anatase	Rutile	Chamosite
North Russia	-	40.8	3.3	0.2	13.9	4.1	10%	20.1	0.9	2.3	13.9
North Vietnam	6.39	-	58.0	0.4	4.22	10.4	20%	9.32	2.11	1.59	6.46
Guinea	62.7	-	3.0	1.4	1.3	10.7	15%	14.7	1.0	1.2	-

2.1. Experimental

Pre-desilication: To study the processes of low temperature predesilication the experiments were conducted using steel cups with agitator, fed with spent liquor and held under 95 °C; further bauxite was charged and in some tests lime was added. The slurry was held from 2 to 8 hours with agitation and then the slurry was digested under specified conditions (table 3). After digestion the slurry was filtered in the Bunsen flask using Buchner funnel, then washed to obtain neutral effluent.

Autoclave desilication: The studies were conducted using large scale autoclave unit Parr 4843 (USA) allowing to introduce different additives in the reaction zone under high temperature and pressure and sample liquid and solid phases from the reaction zone during the experiment.

The appropriate amounts of caustic liquor, bauxite and lime were charged in the reactor, agitated with speed 300 RPM and the produced slurry was heated to the reaction temperature following by the retention period.

After the end of the digestion process in order to reduce the caustic concentration of digested slurry to 145 gNa₂O/dm³ the slow introduction of calculated quantity of wash water into the reaction zone was made with subsequent cooling to 150°C (running water was used as cooling agent).

When the temperature reached 150 °C the time of the beginning of desilication process of diluted slurry was fixed and in pre-set time intervals samples were taken over the period of one and a half – two hours in every 30 minutes to define the process kinetics. Then the samples were filtered on the Buchner funnel. Liquid and solid phases were analyzed. Presented samples of bauxites have different mineral composition (table 2), therefore for their processing it is necessary to maintain different process parameters both of digestion and of desilication (Table 3).

Table 3
Composition of initial liquors and conditions for the bauxite digestion

Bauxite	T, °C	τ , min.	CaO, % mass.	Content, g/dm ³			
				Na ₂ O _c	Al ₂ O ₃	SiO ₂	α_c
North Russia	260	20	-	140.0	82.9	0.130	2.80
North Vietnam	260	90	5	219.7	115.0	0.250	3.15
Guinea	215	30	0,5	197.0	113.0	0.822	2.87

2.2. Results obtained

The study (tables 4 and 5) have shown that for any type of bauxites the autoclave desilication is more effective. It was found that the alumina to silica ratio of the liquor produced after the high temperature desilication is higher than after the preliminary low temperature desilication followed by digestion (fig. 1), the silica content in the liquors after autoclave desilication being 1.5-2.0 times lower than at the low temperature desilication+digestion.

During the study the optimum time of high-temperature autoclave desilication was defined for different types of bauxite: for boehmite bauxite from North of Russia – 30 min. ($\mu_{Si} = 275$), for diasporic bauxite from North of Vietnam – 90 min. ($\mu_{Si} = 247$), for gibbsitic bauxite from Guinea – 90 min. ($\mu_{Si} = 214$).

Table 4
Chemical composition of the liquors after 8-hour low temperature desilication and subsequent digestion followed by post desilication at 95 °C for 2 hours

Bauxite	Content, g/dm ³			α_c^*	μ_{Si}^{**}
	Na ₂ O _c	Al ₂ O ₃	SiO ₂		
North Russia	139.9	162.9	0.92	1.41	177
North Vietnam	213.6	244.2	1.59	1.44	154
Guinea	184.8	215.7	1.585	1.41	136

Notes: * α_c - Na₂O_c/Al₂O₃ molar ratio, ** μ_{Si} - Al₂O₃/SiO₂ mass ratio

Table 5
Chemical composition of the liquors after the digestion and autoclave desilication

Bauxite	Time, min.	Content, g/dm ³			α_c	μ_{si}
		Na ₂ O _{est}	Al ₂ O ₃	SiO ₂		
North Russia	30	122.0	145.5	0.53	1.38	274
	60	118.7	144.1	0.55	1.36	262
	120	117.5	139.7	0.53	1.38	265
North Vietnam	30	143.0	161.5	0.71	1.46	227
	60	143.1	161.2	0.69	1.46	234
	90	143.1	160.1	0.65	1.47	247
	120	142.4	159.6	0.62	1.47	256
Guinea	30	149.5	173.1	0.88	1.42	198
	60	152.0	175.6	0.86	1.42	204
	90	148.3	171.5	0.80	1.42	214
	120	139.3	161.9	0.80	1.42	202

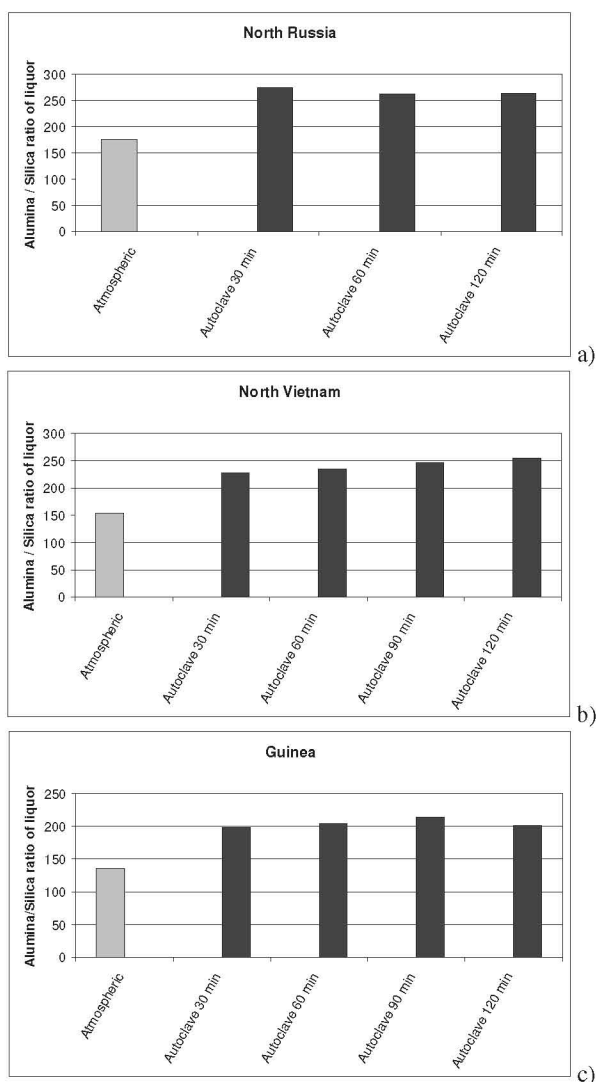


Fig. 1. Alumina / Silica ratio of the liquors produced after atmospheric and autoclave post-desilication for slurries of North Russia (a), North Vietnam (b) and Guinea (c) bauxites.

Based on X-ray phase analysis red mud after pre-desilication and digestion followed by autoclave desilication is represented by following phases:

- mud from North Russia bauxite are similar by their phase composition and mostly represented by hematite, DSP and chamosite; with traces of anatase;
- mud from North Vietnam bauxite contain hydrogarnet, chamosite, hematite, DSP; and under low temperature desilication – magnetite and perovskite.
- in mud from Guinea bauxite alumogothite, diaspore and partly boehmite were identified which is the cause of under-extraction of alumina into the liquor. In addition, hematite, DSP, quartz, anatase or rutile are present in mud.

3. Influence of DSP addition to the liquors desilication process

3.1. Method for the conduction of experiments

To study the influence of the DSP seeding on the liquor desilication efficiency, the tests were carried out using bauxite from Guinea that demonstrated the lowest results of desilication under any processing conditions.

For this purpose during the low temperature desilication and subsequent digestion of Guinean bauxite the DSP seed (noselite or cancrinite) was introduced in dry form into the slurry before the pre-desilication. During the digestion and subsequent autoclave desilication the seed was introduced into the slurry before its supply to the digestion. The DSP dosing in all versions made up 2 % mass as SiO₂ from the weight of dry bauxite.

Conditions for the production of DSP-cancrinite and DSP-noselite were as follows: reaction temperature 280 °C, time of the process – 20 minutes. Kaolinite was dosed in amount L:S = 5:1. Aluminium hydroxide – at caustic molar ratio 1.3 (A/C 0.740). RUSAL VAMI tests, carried out earlier [6] shown that DSP of cancrinite type is being formed when carbonates are present in recycling liquor. Ions SO₄²⁻ contribute to the formation of noselite DSP. Therefore the synthesis of cancrinite was carried out using Nikolaev alumina plant spent evaporated liquor and that of noselite – using synthetic liquor with addition of Na₂SO₄. The composition of hydroaluminosilicates being introduced into the slurry is given in table 8.

Table 8
Results of DSP synthesis

DSP type	Chemical composition of precipitate, %					SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃
	SiO ₂	Al ₂ O ₃	Na ₂ O	SO ₄ ²⁻	CO ₂		
Noselite	33.9	33.4	19.8	1.66	-	1.725	0.975
Cancrinite	34.3	30.5	20.5	0.36	3.7	1.912	1.106

3.2. Results obtained

Composition of the liquors obtained after carrying out the processes with DSP additive in form of noselite and cancrinite are given in table 9, figures 2, 3. Investigations carried out earlier show that when digesting bauxite with spent liquor containing carbonate-ions at the temperature exceeding 215 °C, DSP crystallizes in form of cancrinite.

Table 9
Chemical composition of the liquors after desilication followed by digestion

Desilication type	Dosed	Sampling time, h	Content, g/dm ³			α_c	μ_{si}
			Na ₂ O _{est}	Al ₂ O ₃	SiO ₂		
Low temperature	noselite	8+0.5	182.5	215.7	1.428	1.39	151
	cancrinite	8+0.5	184.8	216.7	1.228	1.40	176
High temperature	noselite	0.5	140.3	164.5	0.750	1.40	219
		1	140.3	168.9	0.710	1.37	238
		1.5	138.8	163.8	0.640	1.39	256
	cancrinite	0.5	134.5	160.7	0.580	1.38	277
		1	128.7	156.8	0.550	1.35	285
		1.5	136.9	164.2	0.540	1.37	304

The results of experiments have shown (Table 9) that additives of noselite and cancrinite have a positive influence on the desilication of the liquors at any versions of the process; the seed in form of cancrinite being more preferable as the desilication process proceeds more efficiently. Probably, this relates to the different solubility of structural DSP varieties. It is known that in sodium aluminate liquors the DSP solubility reduces in series of solid phase transformations with following sequence: zeolite – sodalite – noselite – noselite-cancrinite – cancrinite-noselite – cancrinite [7]. Therefore, after the introduction of cancrinite additive into the liquor the desilication is more efficient due to lower solubility of this phase in comparison with other forms of DSP as well as due to that the process is based on ready lattice which is represented by framework consisted of tetrahedrons (Al,Si)O₄ forming four-, six- and twelve-digit rings.

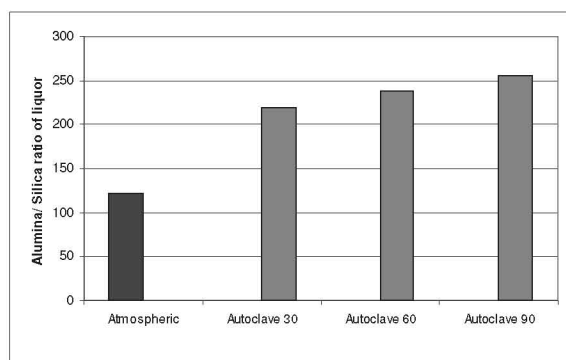


Fig. 2. Alumina / Silica ratio of the liquors, obtained with DSP seed (noselite) depending on way of post-desilication

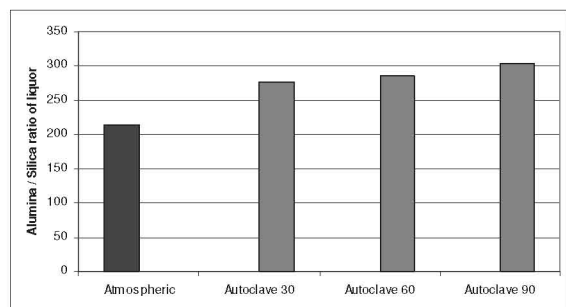


Fig. 3. Alumina / Silica ratio of the liquors, obtained with DSP seed (cancrinite) depending on way of post-desilication

When adding noselite which lattice represents the framework formed by rings from four and six tetrahedrons, the desilication proceeds not so efficiently because of higher solubility of this compound than that of cancrinite. However under these conditions of digestion-desilication process the noselite structure deformation and re-crystallization into the form of noselite-cancrinite (proven by data of X-ray-phase analysis) and with the lapse of time into cancrinite-noselite take place; speeding up desilication process. Therefore, higher solubility of noselite as well as its structural transformations slow down the desilication process when adding noselite as opposite to the cancrinite adding.

It was discovered that the high-temperature desilication and the introduction of the seed in form of DSP into the process contribute to the reduction of equilibrium silica content and to the increase of alumina/silica ratio to 300.

4. Conclusions

1. Improved post-desilication technology is proposed for bauxites of complicated mineralogy, comprising high temperature post-desilication with DSP seeding.
2. It was found that the desilication at high temperature is more efficient than low temperature one as it significantly reduces the duration of post-desilication for all studied bauxites (gibbsitic, boehmitic, diasporic) and leads to 1.5-2 times lower SiO₂ concentration in the liquor. The risk of alumina losses associated with reversion usually taking place in post desilication tanks at atmospheric pressure is completely excluded.
3. At the autoclave desilication it is advisable to introduce at once all wash water for the dilution. If introduce part of water and carry out the autoclave desilication and then introduce the remained part after the separation system, the silica solubility would change and the alumina / silica ratio would be reduced.
4. The study has shown that the use of DSP cancrinite seed for the desilication would have a positive influence on the SiO₂ removal from the liquor and it increases the alumina / silica ratio up to 300.

References

1. T. Harato, T. Ishida, H. Kato, K. Ishibashi “The development of modified Bayer Process that reduces the desilication loss of soda by 50% compared to the conventional process”. 8th International congress of ICSOBA, Milan, Italy, April 16/18 – 1997, 205-213.
2. A.A. Lainer “Production of alumina”, Metallurgizdat, Moscow, 1960, pp. 496-504.
3. M. Loan, B. Loughlin, M. Fennell, et.al. “In situ time-resolved synchrotron diffraction studies of high temperature Bayer digestion”, proceedings of the 7th International Alumina Quality Workshop, Perth, WA, pp. 117-121.
4. E. Tizon, P. Clerin, B. Cristol “Effect of Bayer liquor impurities on DSP stability and silica level during predisilication and digestion operations”. 15th International Symposium of ICSOBA, St. Petersburg, Russia, June 15/18 – 2004, pp. 129-134.
5. P.G. Cousineau and G.D. Fulford “Aspects of the Desilication of Bayer Liquors”, Light Metals (Denver, 1987), R.D. Zabreznik, TMS-AIME, pp. 11-17.

6. A. Kuvyrkina, N. Kuznetsova, et.al. “The Effect of DSP Structure on Removal of Impurities from Refinery Liquor and Efficiency of Alkali Recovery Process”, *Light Metals* (New Orleans, 2008), pp. 127- 132.

7. M.G. Manvelyan, A.A. Khanamirova “Desilication of alkaline aliminate liquors”, Academy of Science, Armenian SSR, 1973, pp. 95.