

THE INFLUENCE OF THE MINERAL COMPOSITION OF LOW-GRADE ALUMINUM ORES ON ALUMINIUM EXTRACTION BY ACID LEACHING

Alexander G. Suss, Alexander A. Damaskin, Alexander S. Senyuta, Andrey V. Panov, Andrey A. Smirnov

UC RUSAL Engineering and Technology Centre (VAMI), Saint Petersburg, 199106, Russian Federation

Keywords: low grade ores; processing technologies; alumina; hydrochloric acid method.

Abstract

As part of the hydrochloric acid technology elaboration for processing of non-Bayer raw materials to alumina the conditions of acid leaching of Siberian non-bauxite aluminous ores were studied. Based on the minerals' structure the mechanism of aluminum transition to acidic solutions was suggested. The conditions of the acid leaching process which required for different kinds of aluminum raw materials were determined.

The phenomenon of silica and titanium partial dissolution with subsequent transformation to colloidal form as a result of aging is found. The methods of artificial ageing of such liquors and slurries are suggested to produce sufficiently filterable residues.

1. Introduction

Now, at a new turn of aluminium industry development the interest to effective alumina production from non-bauxite natural and man-made sources by new acid process is growing again. The deposits of non-bauxite ores with relatively high alumina content are explored and reserves are estimated in dozen billion tons with convenient logistics for Al_2O_3 users like Siberian (Russia) Canadian, Chinese and other smelters. Significant work is done in China, Russia, Canada and Australia to industrially master new technologies, including those based on hydrochloric acid [1, 2].

In recent decade in the chemical and metallurgical industries new processes are commercialized that can be used for alumina production by acid methods. Previously, such processes were unrealizable in large scale alumina production because of several reasons. One of them was absence of available acid-proof materials withstanding high temperatures, high pressures, abrasion and other negative impacts and, respectively, inability to manufacture reliable equipment.

Hydrochloric acid has significant advantages over wide range of organic and mineral acids suitable for alumina production:

- relatively simple conversion of alumina from ore into acid solution. The reactions of hydrochloric leaching of Al-silicates are exothermic that minimizes heat consumption for autoclave processes. Low partial pressure of vapors over the surface of slurry in the course of leaching allows to carry out the process with slight overpressure;
- low solubility in HCl of main ballast (silica), diffusion process of Al_2O_3 recovery, and relatively simple removal of Si-residue from acid liquors without chemical losses of acid. For removal the solid phase of SiO_2 the additions, like calcium oxide (like in alkaline processes) are not required. It reduces the production cost and the tonnage of waste;
- possibility of selective crystallization of $AlCl_3 \times 6H_2O$ from acid liquors by evaporation or HCl sparging as result of increasing of HCl concentration;

- commercially proved processes for iron removal from acid liquor and obtaining of high quality hematite concentrate;
- possibility of $AlCl_3 \times 6H_2O$ thermal decomposition producing Al_2O_3 and gaseous HCl allowing to organise a closed acid circuit;
- commercially proven process of hydrogen chloride rectification with recovery of strong hydrochloric acid that can be recycled to the head of the process for ore leaching.

For large scale commercial implementation of acid process some significant technical issues should be addressed, namely:

- reduction of specific energy consumption and other operation costs through heat recuperation in the process circuit;
- production of smelter grade alumina (SGA) corresponding to the modern requirement of smelters both by chemical and phase analysis and physical-mechanical properties;
- establish material balance of the process cycle in view of ballast and harmful impurities including iron, phosphorous, calcium, magnesium, alkalis, etc with acid regeneration from above salts;
- find effective solutions for utilization of Si-residue and process for other by-products (including hematite concentrate, rare earth elements, gallium, scandium, etc), and making environmentally safe production.

2. Raw materials

In 2011-2013 the research divisions of UC RUSAL carried our technology ranking of different raw material sources available in Siberia considering the type of the main aluminous mineral [3]. Among the Russian Siberian ores the most predominant are nephelines, sillimanite, kaoline clays.

Nepheline. The acid processing of nepheline is not rational as far as it is connected with high solvent consumption for formation of sodium and potassium chlorides due to the alkaline nature of nepheline. Moreover there is an effective soda lime sinter process of alumina recovery from such ores allowing complex processing of ore with by-product fabrication like soda, potash and cement, implemented at Achinsk refinery.

Minerals of sillimanite group due to the crystal structure features are very persistent to hydrochloric acid.

This group combines three structurally different substances with similar composition and empiric formula $Al_2O_3 \times SiO_2$ or Al_2SiO_5 named as:

- disthene (synonym: kyanite; kyanos - «dark-blue» in Greek);
- andalusite;

- sillimanite;
- as well as mullite $3\text{Al}_2\text{O}_3 \times 2\text{SiO}_2$ or $\text{Al}_6\text{Si}_2\text{O}_{13}$ structurally similar to the above.

In the technical literature the abbreviation MSG – minerals of sillimanite group is used (andalusite, sillimanite, and kyanite)

The specific feature of the crystal structure of the above components is availability of two Al ion types in each lattice:

- Half of them is always within the lattice with coordination number 6
- The other half can have different coordination numbers:
 - 6 for disthene (kyanite);
 - 5 for andalusite;
 - 4 for other minerals (sillimanite and mullite). In this case Al forms the AlO_4 tetrahedrons which together with SiO_4 form particular strips (chains) in crystal structure (Fig. 1).

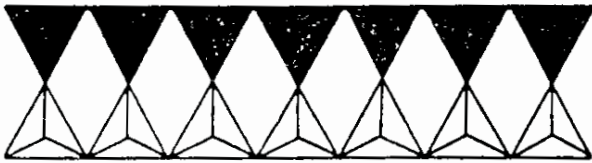


Figure 1. Sillimanite silica oxygen strip $[\text{SiO}_3]$ in which the half of tetrahedrons is occupied by Al [4]

The difference in structure is connected with the conditions of above three minerals genesis. They were formed at significant depth with profound metamorphism of high alumina solids: bauxite or clay. The structure of all three minerals can isomorphically include up to 7 % Fe_2O_3 and some other impurities (MgO , K_2O , etc) [5].

The formation of those three minerals structure under different pressure and temperature influences the structure density and respectively the specific gravity (S_{sp} , g/cm^3):

- andalusite - 3,15;
- sillimanite - 3,24 (it's formed under conditions of regional metamorphism of high degree under high pressure and temperature, therefore the deposits are considerably sparsely);
- kyanite - 3,63;
- mullite - 3,03.

The MSG behavior under atmospheric pressure and high temperature is also different:

- disthene under the heating up to $1300\text{ }^\circ\text{C}$ is decomposed and transformed into mullite ($3\text{Al}_2\text{O}_3 \times 2\text{SiO}_2$) and crystobalite (enriched by silica) glass with considerable volume increase;
- andalusite is transformed into mullite and crystobalite glass under the temperature $1380\text{ }^\circ\text{C}$ with the same volume;
- sillimanite is transformed into mullite and crystobalite glass under temperature $1545\text{ }^\circ\text{C}$ with minor volume increase;
- after further temperature increase up to $1810\text{ }^\circ\text{C}$ mullite is transformed into the mix of corundum and glass SiO_2 ;

- total fusion of the mix occurs under $1880\text{ }^\circ\text{C}$.

The structural differences impact on other properties of this group of minerals; as the diagnostic pattern of disthene is its resistance to the dissolution in HCl but it is more soluble in other mineral acids. Andalusite and sillimanite are resistant to all mineral acids.

The above was confirmed by our digestion experiments of kyanite concentrate (analysis is presented in Table 1) that was grinded to the fraction <100 micron with temperature $200\text{ }^\circ\text{C}$ in 20% hydrochloric acid during 12 hours. The maximum alumina recovery in solution was only 11.5%.

Table 1. Kyanite concentrate chemical composition, mass %

SiO_2	37,9	MgO	0,03
Al_2O_3	61,0	Na_2O	0,27
Fe_2O_3	0,27	K_2O	<0.15
TiO_2	0,2	V_2O_5	<0.015
P_2O_5	0,25	Cr_2O_3	<0.02
CaO	0,34	MnO	<0.01

Mullite. As it was indicated above mullite conventionally may be considered as the mineral of sillimanite group. The main commercial source of mullite is the ash of Thermal Power Stations, i.e. anthropogenic deposits. However as distinct of mullite formation from andalusite, kyanite and sillimanite by thermal processing in ashes, mullite is formed in the process of silica mineral interaction with gibbsite. Mullite is easily digested by acid. The key challenge of mullite processing is the fact that the tonnage of ash with required composition, accumulated at each individual even large Power Plant can not provide the ore for alumina production during long period of time. On the other hand, the transportation of ash to the long distance is not profitable.

Kaoline. Analysis of numerous literature data and conducted experiments using domestic ore demonstrated that the most promising ore for alumina extraction by acid process is kaoline clay. The kaoline ores has advantage of low inert and harmful impurities, like Fe_2O_3 , TiO_2 , CaO , Na_2O , P_2O_5 , MgO , etc. Given the high solubility of above oxides in HCl the above fact considerably reduces the cost of their removal from the process circuit. Content of Al_2O_3 in kaolinite ($\text{Al}_2\text{O}_3 \times 2\text{SiO}_2 \times 2\text{H}_2\text{O}$) theoretically can not exceed 39.5 % wt., but if 14 mass % H_2O will be excluded, it makes $\sim 46\%$.

Siberia is very rich in the proven reserves of kaoline ore with multi billions tonnage [6]. The above deposits are associated with large surface coal mines and located in the vicinity of main railways Baykal-Amur and Trans-Siberian lines. For some kaoline deposits located in Western and Eastern Siberia the occurrence of gibbsite is a specific feature with positive impact on the valuable component content. In the above deposits the Al_2O_3 content is 32-35% with minimum impurities and inert materials.

The largest Russian smelters are concentrated in Siberian region, but they are mainly using imported SGA as well as alumina from Achinsk refinery processing nepheline ore. Such logistic considerably reduces the advantages of this region as the source of economic power from renewable energy sources. This paper presents some aspects of hydrochloric acid technology for processing of Siberian kaoline ore.

3. Optimization of acid leaching parameters for kaoline ores processing

Kaolinite is poorly soluble in hydrochloric acid under atmospheric pressure (≤ 105 °C), therefore the autoclave digestion is required with temperature ≥ 150 °C. In 30-ies of the last century in Russia due to the lack of acid-proof materials and difficulty of concentrated acid liquor and Si-residue separation the method was developed including the thermal activation of the kaolinite under 650-800 °C with obtaining of metakaoline and its further flow-leaching in vertical reactors [7]. The pre-roasting of kaolinite is comparable with specific power consumption of all Bayer cycle and therefore the method is not competitive for commercial application.

The leaching of raw kaolinite by HCl is exothermic process. The majority of heat for reaction initiation can be supplied with recycled acid and also during the ore milling due to the transition of the mechanical energy into the heat energy.

During the leaching of raw kaolinite considerable chemical dispersion of mineral particles does not occurs and they preserve the initial form. The hardware of thickening and filtration of acid liquor and Si-residue is not a complicated process for new generation of high velocity thickeners, synthetic flocculants and filtering equipment.

The major targets of the acid leaching are:

- high yield of Al_2O_3 with minimum heat consumption for closing water balance while operating in closed loop and maximum efficiency of acid recycling in the process circuit;
- minimum transition of considerable amount of major and minor impurities into acid solutions.

The study was focused on above challenges.

For effective recovery of alumina being the target component of the ore, the leaching process should be carried out by acid with concentration ≈ 20 %, as far as with higher concentration the solubility of aluminum chloride drops sharply that could result in equilibrium concentration before the complete dissolution of aluminous mineral takes place. Moreover with correct optimum stoichiometric ratios the higher concentration of the acid leads to the considerable increase of slurry viscosity. And opposite the reduction of the leaching liquor concentration leads to the higher flow volume and equipment size. Figure 2 shows the impact of the leaching temperature on Al_2O_3 recovery.

The X-ray analysis of Si-residue shows that the recovery of alumina from kaolinite is mainly terminated at 150 °C. Higher Al_2O_3 yield with temperature increase is mainly connected with recovery of Na-Ca feldspars and micas. Their recovery is connected with transition of alkaline metals into the solution and hence, higher acid losses with alkaline metals chlorides and process complication for their acid recovery. On the other hand, the higher temperature reduces a bit the leaching time and desilication rate allowing to decrease flow in autoclave area and equipment size consequently, but demands effective concepts for heat exchange and recuperation. Therefore actually the majority of the researchers consider more advisable to keep the process temperature of 150 °C.

For leaching process the ore composition (i.e. impurities behavior) should be considered, i.e. the acid dosage for binding of Ca, Na, K, Fe, Ti, Mg into chlorides shall be increased.

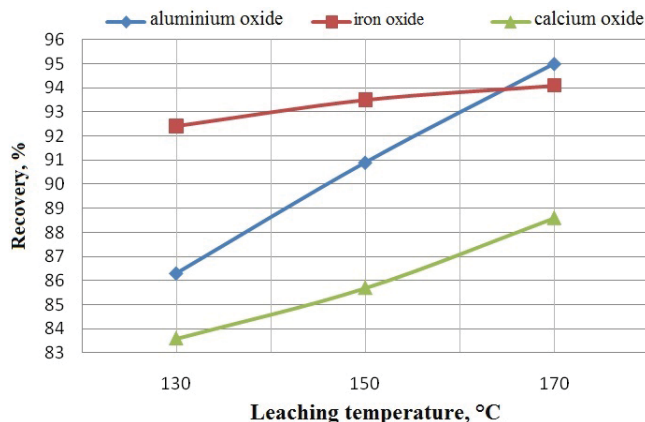


Figure 2. Leaching recovery of kaolinite ore components versus temperature (20 % HCl and acid stoichiometry 1.1)

The majority of above impurities are competitors of Al. The impact of acid dosing on the leaching is shown on fig. 3.

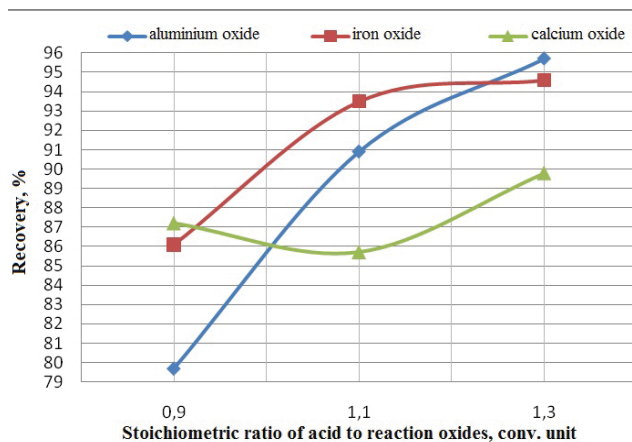


Figure 3. Components recovery versus the acid stoichiometry (20 % HCl, temperature 150 °C, exposure time 3 hours).

Our studies demonstrated that higher acid dosage above stoichiometry 1.1 is not advisable for Siberian kaolinites. Thus, the following conditions of acid leaching process may be recommended:

- milling finesses up to 95 % below 100 microns;
- acid concentration to leaching ~ 20 %;
- leaching temperature ~ 150 °C;
- acid stoichiometry 1.1.

4. Slurries separation after HCl leaching

Using laboratory filtering unit the Si-residue filterability was defined versus the leaching conditions. The filter unit productivity rate was in average $0.325 \text{ t}/(\text{m}^2 \cdot \text{h})$, that is 10 times higher than the similar parameter for red mud. With pressure filtration of hot slurries the production rate of the Si-residue filters area can be enhanced even higher.

For washing and drying of Si-residue it is more advisable to use belt filters for simple simultaneous washing of residue by water. The press filters are less preferred.

5. Impurities' behavior

Together with target component the impurities also pass in the liquor.

Silica. As a rule a Siberian kaoline ore together with kaolinite contains silica in the impurities: quartz, mica and feldspars. Quartz and Na-K feldspars are resistant to the acid leaching and report to tails. During leaching the majority of cage and laminated Al-silicates preserve the form of particles and the silica remains in solid phase. At the initial leaching stage as a rule below 2.5-3 % of SiO₂ is transferred into solution (from the percentage in ore). The behavior of SiO₂ in acid liquor is well described by known procedure. Firstly SiO₂ is transferred into the liquor in form of monomers of metasilicic acid, but further under the temperature above 80 °C the polymerization process occurs with conversion into polysilicic or orthosilicic acid. It allows to remove SiO₂ from the acid eluate [8]. The desilication process may be carried out by the increase of exposure time in autoclaves up to 6 hours with reduction of SiO₂ from 3.5 to less than 1 g/dm³ in the liquor or to arrange the retention of leached slurry under temperature above 90 °C in agitator tanks.

Iron in form of chloride has better solubility than Al chloride. This is the principle of their separation. With increase of acid concentration above 20% the process of "salting out" occurs, i.e. AlCl₃×6H₂O precipitation in solid phase, then this precipitate is washed by strong hydrochloric acid to remove soluble iron from the liquid phase. FeCl₃ remains in the liquor and further is separated in form of hematite.

Titanium. TiO₂ in the Siberian kaoline ore does not exceed 0.5 %. At the initial stages of leaching 6-7 % of TiO₂ are transferred into acid solution. With longer exposure time up to 4.5-6 hours the experiments show the reduction of TiO₂ in 2.5-3.5 times to the acceptable limits. Therefore during post-desilication the titanium will be removed from the liquid phase of digested slurry.

Phosphorous. The P content in kaoline deposit of Siberia does not exceed first fractions of %, but practically all P-bearing materials are well soluble in hydrochloric acid. During acid leaching almost 100% of P transfers into acid solution and is accumulated in form of orthophosphates. As noted by all researchers at the final stages of aluminium chloride precipitation, the phosphorous is co-precipitated with AlCl₃×6H₂O and after calcination is detected in alumina. The removal of P from acid eluate is possible (for example by zirconium chloride) but not economically sound. The methods of P₂O₅ reduction in alumina were repeatedly studied using low temperature of aluminium chloride crystallization (≤ 60 °C) with dissolution of AlCl₃×6H₂O and secondary precipitation at the second stage. This makes the process less economic without radical improvement. The same situation is observed for some other impurities.

6. Technical concepts at downstream areas of SGA production

The crystallization of Al chloride hexahydrate is the key process operation defining the chemical and particle size composition of the alumina product. To provide the purity and required size of the crystals some researchers suggested together with reprecipitation to use other rational technique consisting in initial iron removal using the reactants, including the recycled products of the process.

Calcination of AlCl₃×6H₂O. One of the key problems for AlCl₃×6H₂O calcination is incomplete reaction of its decomposition, providing the mix of alumina and some chloride oxides [from Al(OH)Cl₂ to Al₂(OH)₅Cl]. To avoid this problem previously different methods were proposed, including thermal decomposition of AlCl₃×6H₂O by live steam under ~ 140 °C and recovery of γ-Al₂O₃ and 20 % HCl [9]; two stages thermal decomposition with production at the first stage (200-250 °C) Al oxide-chlorides and further at the second stage ~ 1000 °C of alumina product with high Cl- content considerably above of the admissible for SGA parameter. The further calcination of such alumina allows to reduce the chlorine content, but with high corundum generation (α-Al₂O₃ ≥ 50 %).

To overcome above problem we elaborated the method of low temperature thermal decomposition of AlCl₃×6H₂O in two stages with specified temperature interval at the second stage. This process is patented and allows reducing in ~ 2 times the heat consumption for calcination.

By-products. To compare with conventional alkali methods the HCl process opens the convenient approaches for recovery of rare and rare earth metals from kaoline ore (Sc, Ga, La, Ce, Pr, Nd, Sm, Eu, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), as far as all of them during the leaching together with aluminium are transferred into chloride solution. There are some approved technologies (mainly ion-exchange) for their recovery in form of collective concentrates and individual oxides. The production of by-products allows to reduce the cost of alumina recovery.

Quality of alumina product. The non-solved issues with balance of some impurities (including Na, K, Ca, U, Th, etc.) as well as difficulty of alumina to meet the SGA requirements, as was also shown in CSIRO studies [10] requires to find innovative ways to improve quality of alumina. One of the ways is impurities removal from clarified chloride liquor after acid leaching of kaoline, for example using ion-exchange processes. Other approaches are under investigation also.

7. Conclusions

1. One of the key processes of the acid alumina production is acid leaching of the ore. Based on the experimental data the ranking of the different minerals in terms of amenability to acid leach was done. Large deposits of such minerals are discovered in Siberia being applicable as raw material for acid process. Regarding the leaching ability the studied ores can be classified as following (in ascending order): minerals of sillimanite group – mullite – kaoline.
2. The HCl processing of Siberian kaoline in relatively soft modes allows to achieve Al₂O₃ recovery at the level of at least 90% and obtain the liquor with low soluble SiO₂ and well filtrable Si-residue.
3. For implementation of acid process in commercial scale the following preconditions are available:
 - available and cheap raw material base, represented by kaoline clays, located in the vicinity to UC RUSAL aluminium smelters;
 - recent advances in the development of corrosion-proof materials and equipment;

- the commercial processes of HCl gas utilization are available with production of strong hydrochloric acid that allows to establish a closed cycle with only waste in the form of Si- residue composed mainly by quartz and amorphous silica;
 - potential to reduce the cost of acid technology through improvement of individual production areas and application of the state-of-the-art technologies.
4. The fabrication of by-products on the base of proven methods in form of collective concentrate and individual oxides will allow to improve the competitiveness of acid process for alumina production from such raw material as kaoline.

8. References

1. Alexander Senyuta, Andrey Panov, Alexander Suss, et.al. Innovative technology for alumina production from low-grade raw materials. Proceedings of TMS Annual Meeting and Exhibition, San Antonio, USA, 2013, Light Metals, pp. 203-208.
2. Wangxing Li. Refining Alumina from Fly Ash. Proceedings of the XXXI International Conference of ICSOBA, Krasnoyarsk, Russia, 2013, pp.408-410.
3. A.G. Suss, A.A. Damaskin, A.S. Senyuta et. al. Behavior of Al-Si Minerals in the Process of Acidic Leaching of Siberian non Bauxitic Raw Materials, Proceedings of the XXXI International Conference of ICSOBA, Krasnoyarsk, Russia, 2013, pp.427-432.
4. N.V. Belov «Essays on structural mineralogy», M., Nedra, 1976, 344 p.
5. A.G. Betehtin «Mineralogy», M. Gosizdat of geological literature, 1950, 958 p.
6. «Non-bauxite aluminous ores of Siberia» / Mingeo USSR; Siberian research institute of geology, geophysics and mineral ores. Composed: A.N. Chercasov, A.M. Prusevich, A.N. Sucharina and others. M., Nedra, 1988, 167 p.
7. V.A. Mazel «Development of alumina production from kaoline by hydrochloric acid - alkali method», Leningrad, VAMI, 1950, 32 p.
8. L.V. Myshlyaeva, V.V. Krasnoschekova «Analytical chemistry of silicon», Moscow «Science», 1972.
9. Invention certificate SU № 1258815, C01F 7/22, Publ. 23.09.1986.
10. D. Elsner, D.H. Jenkins and H.N. Sinha “Alumina via hydrochloric acid leaching of high silica bauxites - process development”, Light metals, 1984, pp. 411-426.