Evolutional Development of Alkaline Aluminosilicates Processing Technology

Andrey Panov, Sergey Vinogradov, and Svyatoslav Engalychev

Abstract

Alkaline aluminosilicates are of significant interest for metallurgical and chemical industries. They are widespread in countries like Russia, USA, China, Canada, Venezuela, Mexico, Iran, etc. and can present a viable alternative to bauxites. Complex and waste-free alkaline aluminoslilcates processing technology into alumina, soda ash and cement was developed in VAMI institute in 20th century from idea till successful realization at several industrial facilities in Russia, operating till now with competitive production cost of alumina. Russian Alumina refineries are using feedstock with unique high alumina content (Al_2O_3 26–28%) whereas there are other nepheline sources in Russia and in other counties of lower quality ($Al_2O_3$19–22%) and their processing results in more cement produced per tonne of alumina. An economical beneficiation technology has been developed that opens the possibility for more efficient industrial processing of comparatively poor aluminosilicate raw materials in Russia and the rest of the world.

Keywords

Alkaline aluminosilicates • Processing properties • Quality • Beneficiation

Introduction

Alkaline aluminosilicates (nepheline syenites, leucites, anorthosites, dawsonites) being widespread in the world are a promising but underestimated raw material source for aluminium production. Nepheline ores are the second most significant raw material for alumina production after bauxites. To date, alumina is produced from nepheline ores at industrial scale only in Russia using two major sources (Kiya-Shaltyr in the Kemerovo Region in Siberia; Kukisvumchor, Yukspor, Rasvumchor in the Murmansk Region). The industrial value of alkaline aluminosilicates is defined by the possibility to produce multiple products (soda ash, potash, cement, Ga, Cs, Rb), assuring the profitability of processing the raw material where the silica content is 1.5–2.5 times higher than that of alumina. Russia has pioneered the processing of this raw material into alumina. Continuous improvement of the technology by RUSAL is creating the possibility to widen the existing raw material base by including aluminosilicate raw materials with lower alumina content of which there are huge resources globally.

Nepheline Syenite Raw Material Base Review

Igneous Nepheline rocks vary greatly in structural features, the presence of secondary elements, and quantitative interrelation between coloured and colourless components (theralites, nepheline syenite, miaskites, mariupolites etc.). The most industrially important are the nepheline syenite, ijolite and urtite ores.

Nepheline syenites are the most common type of nepheline rocks, and form a quite abundant group of igneous alkali minerals comprising 20–45% of nepheline $Na_3K[Al_2Si_4O_{16}]$, 20–60% of alkali feldspar (K, Na)[$AlSi_3O_8$] (these two minerals generally making 80–90% of the rock),

A. Panov (✉) · S. Vinogradov · S. Engalychev
UC Rusal Engineering and Technology Centre (VAMI),
Saint Petersburg, 199106, Russian Federation
e-mail: Andrey.Panov@rusal.com

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orthoclase or microcline $K[AlSi_3O_8]$, and auxiliary minerals of biotite, alkali pyroxene, amphibole, apatite, augite and others. The chemical composition of the rock is typically: 50–56% SiO_2, 19–24% Al_2O_3, 12–17% K and Na, some Ca and Mg.

Igneous rocks of this group form often large, isometric, intrusive deposits that stretch over dozens of kilometers. Due to their formation, such deposits often have pillar like structures and penetrate up to hundreds of meters deep. This ensures their potential for long life open cast mining. The majority of such masses develop within crystalline shields (such as Canadian, Baltic, Ukrainian, Zimbabwe, Malagasy etc.), and in folded mountain regions (Kuznetsk Alatau, Andes, Urals etc.).

Nepheline syenites are widely distributed in Russia (Kola peninsula and Siberia), Canada (Ontario, British Columbia), USA (Arkansas, New Jersey/Beemerville, Massachusetts, Texas), South Greenland, Mexico, Norway (Northern Norway, Oslo district), Sweden, Finland, Italy, Germany (Dresden district), Czech Republic, the Ukraine, Kazakhstan (Priishimye), China, Iran (Razgah deposit), Pakistan, India, South Africa (Kenya, Uganda etc.), Madagascar, Chile, Bulgaria, Brazil, etc. [1, 2] The mines and deposits of nepheline ores are shown at Fig. 1.

Total world nepheline resources are estimated to be in the range of 12-15 billion tonnes. Russia possesses the biggest nepheline resources: apatite-nepheline deposits in the Kola Peninsula are up to 4 billion tonnes of nepheline, and resources of up to 3 billion tonnes in Siberia—Kuznetsk Alatau, Northern Baikal region, Eastern Sayan Mountains, the Sengilen mountain range (South-Eastern Tuva), the Urals (Ilmen and Vishnev Mountains). In Canada about 10 large nepheline deposits are located in the south of Ontario and Quebec provinces [2]. The reserves of each deposit amount to approximately 100 Mt. Third in commercial importance is the Stjernøy deposit located in Norway, which has resources of about 300 Mt. There is the possibility for other big deposits to be explored provided the consumption of nepheline increases.

Nepheline ores are used for 2 main purposes:

(a) as raw material for alumina and by-products at Achinsk Alumina Refinery (AGK) (Kiya-Shaltyr) and in Pikalevo (Khibin concentrate);
(b) for glass and ceramic uses in Canada, China, Norway, Turkey, Russia, South Africa.

For many years two large nepheline syenite deposits have been mined in Canada (Blue Mountain) and Norway (Stjernøy) producing high-purity potassium nepheline-enriched feldspathic concentrates. The composition of the Blue Mountain nepheline ore is 23% $A1_2O_3$, 60% SiO_2, and 4% K_2O. Due to presence of alumina and alkali, nepheline concentrates are used as raw material for production of: (1) Glass (flux to reduce fusion temperature, ensures resistance to scratches and cracks, improved heat resistance, chemical recovery); (2) Ceramics (flux to reduce fusion temperature); (3) Filler in adhesives, paint, plastics, and sealants; (4) Mineral wool (thermal insulation); (5) Building stone, etc.

Fig. 1 Nepheline mines and deposits of the world. Adapted from [1]

Table 1 Typical quality of major nepheline ores

Country	Region	$A1_2O_3$	SiO_2	Na_2O	K_2O	Fe_2O_3	CaO
Russia	Kiya-Shaltyr	26.5	40.0	7.2	4.8	4.5	7.0
	Kolsky concentrate	28.5	44.5	10.7	7.1	2.5	1.7
China	Guangzhou	22.5	55.2	0.4	0.3	2.9	–
	Heilongjiang	23.1	55	5.2	3.5	2.5	–
Iran	Razgah	20.0	54.9	6.0	3.9	3.7	2.0
Pakistan	Kota	22–24	48–48	6.5–8.7	4.3–5.7	2–3	–
North Korea	Sackshu ore concentrate	18.0–22.8	42.0–49.9	6.6–7.8	4.4–5.1	9.9–4.3	7.7–3.8
Mexico	Arroy Grande	19.81	47.33	8.27	5.16	4.03	4.71

The typical quality of major nepheline ores studied by VAMI for alumina extraction in Russia of China, Iran, Pakistan, North Korea and Mexico is shown in Table 1. The data shows that the quality of the Russian Raw material is better with respect to alumina and alkali content compared with other ores.

Besides ore quality, the commercial value of any deposit for alumina production depends on a number of other factors: remoteness, availability of infrastructure, size of resource, demand for such raw material, etc. Based on the analysis of current interest in nepheline ores we can draw the conclusion that only large deposits with high-quality ores and developed infrastructure have commercial significance.

Results of the geological investigation of many large alkaline magmatic provinces having deposits with variable quality, type and structure, give grounds to expect the discovery of new large and high quality deposits suitable for alumina production. Provided that enough investment in new geological exploration will be available, such deposits can be found in the areas like: 1. Kuznetsk Alatau (Russia), 2. South—Eastern Ukraine; 3. Iran, Razgah deposit etc.; 4. Southern part of the Canadian shield—Ontario and Quebec provinces; 5. Pakistan, 6. China; 7. Mexico. It is arguable that there has generally not been enough systematic geological investigations of such raw materials for alumina extraction in the world.

Alkaline Aluminosilcates Soda-Limestone Sintering Technology

Development of the technology for processing of alkaline aluminosilicate ores started in the USSR early last century to utilize the nepheline rich residues after beneficiation of apatite-nepheline ores from the Kola Peninsula. Development of the basic technology was conducted by the VAMI and GIPCH institutes under the guidance of F. Strokov, P. Vlodavetz, I. Lileev and others. In the middle of the 1930s it was decided to retrofit Volkhov aluminum plant for processing of Kola nepheline concentrates, but the works were interrupted by WWII. Volkhov was converted to the process only in the early 1950s. After mastering at Volkhov, the technology was further improved by VAMI and used for construction of the Pikalevo and Achinsk alumina refineries, which remain in good operating condition today. The principle process flowsheet is presented at Fig. 2.

The complex processing of nephelines involves sintering of the ore or concentrate with limestone in rotary furnaces at temperatures of 1200–1300 ºC. The chemical process of this stage can be summarized by the following reaction:

$$\begin{aligned}&(\mathrm{Na,K})_2\mathrm{O}\cdot\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2} + 4\mathrm{CaCO_3}\\ &\quad = (\mathrm{Na,K})_2\mathrm{O}\cdot\mathrm{Al_2O_3} + 2(2\mathrm{CaO}\cdot\mathrm{SiO_2}) + 4\mathrm{CO_2}\end{aligned} \qquad (1)$$

The sinter is then leached with spent liquor. In this case, sodium aluminate goes into the liquid phase, and solids, i.e. belite mud ($2CaO\cdot SiO_2$) is directed to cement production.

Sodium aluminate is decomposed and alumina trihydrate precipitates with liquor carbonation by the following reaction:

$$\mathrm{NaAlO_2} + \mathrm{CO_2} + 3\mathrm{H_2O} = \mathrm{Al_2O_3}\cdot 3\mathrm{H_2O} + \mathrm{Na_2CO_3} \qquad (2)$$

For aluminate liquor decomposition (precipitation), dust-free flue gases from the sintering kilns containing 10–16% CO_2 are used.

Soda liquors are evaporated for soda ash, and belite mud is further sintered with limestone to produce cement. Other valuable components of the ore (K, Rb, Cs, Ga, etc.) can also be extracted.

Over the more than 70-year period of development and operation of nepheline technology, a variety of problems have been solved and a huge number of improvements and modernizations implemented by our experts, allowing the process to be competitive with the Bayer process. For example, the new method of pregnant liquor deep desilication using a synthesized active ion-exchange additive based on carbo-aluminate developed by VAMI and St. Petersburg State Mining institute, gave the opportunity to achieve the required purity of hydrate and metallurgical alumina, while

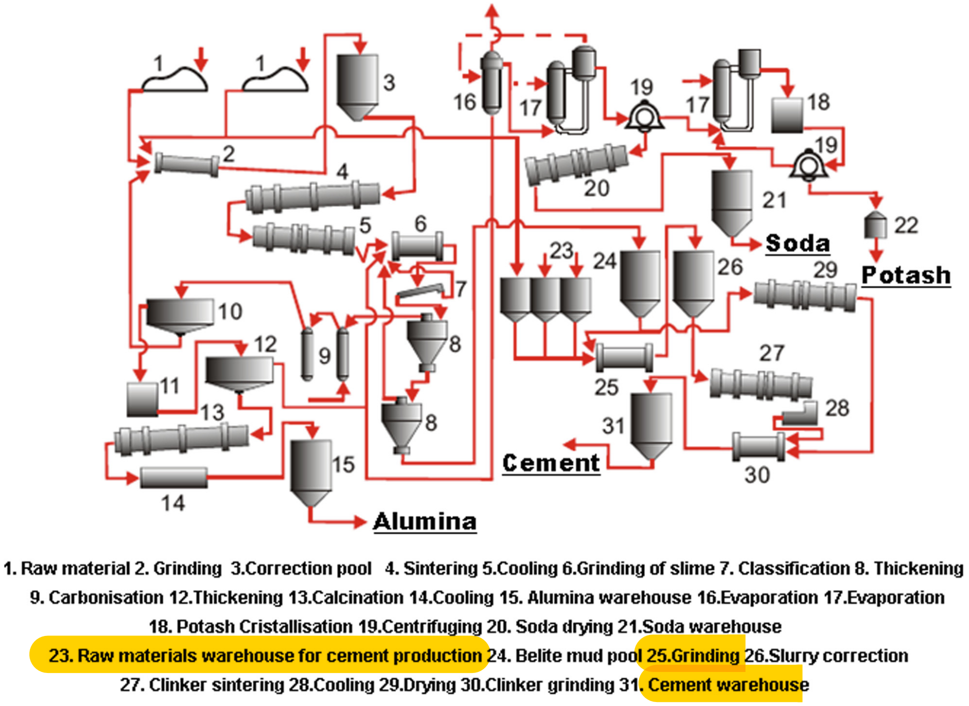

Fig. 2 Principle flowsheet of VAMI sintering technology for processing alkaline aluminosilicates

Table 2 Technical parameters compared to the Bayer process

Parameter	UoM	Process	
		Sintering	Bayer
Content of Al_2O_3 in the ore	mass%	25–28	40–55
Raw material consumption	t/t	4.5 nepheline 6.5 limestone	1.8–2.5
Commercial total Al_2O_3 recovery	%	75–80	87–90
Electricity	Kwh/t	1100	250–400
Fuel	GJ/t	42–47	3–4
Steam	GJ/t	5	4–12
Total energy consumption	GJ/t	50–55	7–16
Typical production cost	US$/t	190	230

reducing lime consumption for this process step. Deep desilication and reduced carbonation temperature have improved the coarseness and strength of alumina hydrate. Physical characteristics of this hydrate and alumina are close to reference sandy alumina.

In spite of relatively high energy consumption (Table 2), the technology of alumina production from nephelines using complex processing can be as commercially attractive as processing high grade bauxites in the Bayer process.

The economic efficiency of sintering alkaline aluminosilicates is achieved due to its complex nature and waste free production. Along with each ton of alumina 0.8 t of soda, 0.3 t of potash (Table 3) and 10 t of cement are produced. These products are highly-profitable and are in demand. The balance of products is determined by the composition of raw materials.

The production efficiency of this technology is mostly dependent on demand for cement products. Often, the cement market in the region can define the volume of alumina production at a specific plant. In case of the inability to sell the full volume of cement produced, other applications of belite mud need to be explored.

Processing of Belite Mud

The efficiency of using nepheline sinter mud for cement production is explained by the following:

Table 3 By-products: characteristics, quality and yield

Product	Quality	Yield, t/t alumina	Application
Soda Ash Na_2CO_3	Superior and 1st grade	0.5–0.8	Chemical, pulp and paper, textile industry, oil treating industries, washing substance and glass production
Potassium sulphate K_2SO_4	1 grade	0.05–0.3	Fertilizers
Potash K_2CO_3	Superior and 1st grade	0.04–0.1	Electronic and radio electronic industry, glass and crystal production
Potassium chloride KCl	Superior and 1st grade	0.003–0.005	Fertilizers
Gallium Ga	Purity 99.99%	0.0000015	Radio electronics, defense

- It is principally prepared for making clinker ($2CaO{\cdot}SiO_2$ content is ~70–80%);
- Clinker yield from a mix containing mud is ~**10–15**% more than from an ordinary mix;
- Cement kiln productivity increases by **25–30**%;
- Reduction of specific fuel consumption for clinker burning by **5–7**% due to the absence of decarbonation.

The process to obtain Portland cement using nepheline sinter mud as part of the raw mix is industrially applied at the Pikalevo and Achinsk cement plants. The composition of belite muds from Achinsk Alumina Plant (AGK) and Pikalevo Alumina Refinery (PGZ) are presented below in Table 4.

Cement production using a two-component mix (limestone and belite mud) without corrective mineral additives can significantly simplify the technology of mix preparation (compared to the classic version of the four-component mix for clinker).

Our industrial experience with nepheline ore processing can be summarised as follows: at Pikalevo alumina refinery (Leningrad region) all the produced belite mud is processed into cement and 100% recovery of waste is achieved. At the Achinsk alumina complex (Krasnoyarsk region, Siberia), the complete utilization of belite is not economically viable due to the high production rate and long distances to potential consumers. Only about 15% of mud is utilized for cement production and a small portion for road construction. The belite is also used in smaller quantities as mine backfill.

Along with the production of high quality cement products, belite mud can be used without additional processing for medium-strength construction materials. The strength of belite cement matches 150 grade concrete, so it can be used for both the bedding of paved roads and for backfilling of mines and drill holes after extraction of raw materials. Tests have shown that belite mud can be used directly for mine backfill, however the pure belite material requires long periods for solidification and cementing (about 3 months for the minimum strength of 20 MPa). The hydraulic activity of nepheline ore and potential for its application as binding material for backfilling depend on the alpha, beta or gamma modification of belite. Selection and dosing of special additives is required to control solidification and cementation. Calcium aluminate and gypsum can be used as such additives are components of cement. By reducing the required strength of the resulting belite stone, it is possible to completely eliminate using thermal processes for transformation of belite ($2CaO{\cdot}SiO_2$) to alite ($3CaO{\cdot}SiO_2$). In this case, materials with the physical and mechanical properties listed in Table 5 can be obtained. The process can be adapted to the specific conditions of the mine to select the backfilling method with the minimum investment cost.

Heat treatment of belite hydration products can increase the strength of the resulting materials (Table 6). It is worth noting that there are other ways of producing binding components using belite slurry, feasibility and cost-effectiveness should be considered in each case for each type of ore.

Based on research, industrial tests and industrial practice, the following are opportunities for belite mud utilization:

- Cement production:
  - Raw material component for clinker formation;
  - Active mineral additive to the ground clinker.
- Road construction:
  - Monolithic carry and frost protected foundations for roads,
  - Road cover;

Table 4 Composition of nepheline ore and belite mud from Russian Alumina Refineries, mass%

Plant	Commodity	Al_2O_3	Fe_2O_3	SiO_2	CaO	MgO	R_2O[a]
Achinsk	Nepheline	25.85	4.46	40.55	9.22	1.78	12.21
	Belite mud	3.70	3.71	29.57	54.25	1.85	2.65
Pikalevo	Nepheline	28.35	2.65	45.09	0.95		17.76
	Belite mud	2.44	2.18	31.14	58.40	1.35	1.60

[a] Sum of Na_2O and K_2O

Table 5 Influence of additives on properties of binder made of belite mud

Composition, %		Normal initial density	Setting time, h-min		Compressive strength (kg/cm^2)/solution of 1:3, storage (day)		
Belite	Additive		Start	End	Wet-air		Water
					7	28	28
Mixed with gypsum							
99	1	18.5	0–42	1–09	34.5	58.5	79.5
98	3	18.5	0–39	1–05	36.0	72.6	85.1
95	5	19.0	0–41	1–13	38.5	80.2	96.6
90	10	22.0	0–57	1–38	53.0	97.0	107.2
85	15	21.0	1–16	3–50	62.1	118.0	114.2
Mixed with lime							
95	5	21.0	0–42	1–28	64.6	119.8	123.2
90	10	22.0	1–17	1–52	64.4	118.4	123.8
85	15	23.0	1–21	1–59	42.8	148.7	78.9
80	20	26.0	1–21	2–11	44.8	61.5	65.3
75	25	30.0	1–20	2–30	35.0	54.7	57.1

Table 6 Influence of temperature on properties of binder made of belite mud

Processing temperature, °C	Associated water	Normal initial density	Setting time, h-min		Compressive strength (kg/cm^2)/solution of 1:3, storage (day)		
			Start	End	Start		End
					7	28	28
–	1.34	Not able to concrete (bind)					
300	0.97	33.5	4–15	6–15	26.1	73.1	51.9
400	0.88	38.0	3–10	5–05	37.5	73.0	61.9
500	0.85	35.0	3–18	5–33	44.0	76.9	74.3
600	0.66	34.6	4–22	6–32	52.3	65.0	36.9
700	0.62	34.6	1–20	4–45	74.9	46.1	33.2

  - Reinforcing poor soils for road construction;
  - Reinforcement of banks;
  - Foundations of ducts for water drainage
  - Road service life increased 1.5 times, decrease of road construction costs by 4–5 USD/m^2.
- Agriculture
  - Normalises acid-alkali balance and assures phosporous retention in the soil;
  - Added for soil amelioration as microelement rich component.
- Manufacturing of construction materials:
  - Binding material
  - Grade M200
    Filling of mined areas in underground mining
    Increasing strength of normal and wet soils
  - Grade M300

  Manufacture of iron concrete blocks based on B15 concrete
  Manufacture of commodity concrete B15 for foundations, walls, ceilings etc.
  - Density 400, 500, 600 kg/m^3
    Load carrying wall material in domestic construction (up to 4 stories);
    Internal wall construction;
    Highly efficient thermal insulator (heat transfer coefficient 0,1 W/(m °C))
  - Cost of material reduction by 25–30 USD/m^3
- Other applications
  - Fillers;
  - Sorbents;
  - Glass materials;
  - Slag stone casting;
  - Refractory products;
  - Construction ceramics;
  - Synthetic zeolites, hydrosilicates,
  - White silicate bricks (autoclave process);
  - Asbestos-cement materials for roofs, etc.
  - Specialty concretes (acid and alkali proof, heat proof, water proof, etc.)

Integration of Beneficiation Technology

Under conditions of limited demand for soda ash and cement/belite mud binder products, to allow industrial scale low grade ore processing, the beneficiation of alkaline aluminosilicates can increase alumina and alkali content in the alumina refinery feed while reducing silica and thus reducing the cement produced per tonne of alumina. Russia and other countries have abundant but predominantly low alumina (19–23%) nephelines, consequently our specialists have developed beneficiation processes for these low grade ores.

Depending on the mineral composition and grain structure of ores, the most suitable beneficiation technology can be selected involving steps of gravimetric separation, magnetic separation, floatation, X-ray sorting and chemical beneficiation. This opens the possibility to process ores of any quality. For example, processing of a Russian raw material with alumina content about 22% leads to a concentrate with 27% alumina. A variety of available beneficiation technologies allow regulation of the alumina vs cement production ratio, depending on market scenarios.

The main target of beneficiation is increased aluminium oxide and alkalis in nepheline concentrate, regardless of the mineral form of the initial materials and to regulate output of highly profitable by-products. The possibility to apply different beneficiation processes and the yield of products recovered from the concentrate produced is defined experimentally by laboratory studies of the ore and concentrate properties. A detailed model of production and the local market should be made allowing selection of most profitable way to develop a new plant.

Conclusions

1. Technology for alkaline alumina silicate processing into alumina and by-products using a sintering process was developed and only used industrially in Russia. This technology has enormous application potential for many other deposits globally.
2. The main features of the technology are:
   - Relatively high consumption of raw materials compared to the Bayer process. Processing of 4–4.5 tons of nepheline/concentrate with limestone gives 1 tonne of alumina, up to 0.8 t of soda ash, 0.3 t of potash and 10 t of cement; The main economic and environmental advantage of nepheline technology is the possibility for full utilization of all raw material components for different products, leading to waste-free production;
   - The consumptions of fuel, steam and electricity are significantly higher than for bauxite processing technologies, however those are compensated by absence of soda consumption and the income from by-products or intermediate by-products (alkali liquors for soda ash and belite mud for cement production);
   - Even taking into account higher costs for repair and maintenance of the main equipment, the production cost of alumina from nepheline ores may be comparable (or even lower), to that of high grade bauxite;
   - The location of nepheline syenite deposits close to aluminium smelters in areas without high quality bauxites (like Canada, USA, China, Iran, etc.), has the potential to significantly reduce the aluminium production cost by lowering transportation costs compared with imported alumina.
3. Conditions for successful implementation of a new project are:
   - Availability of local deposits of good quality nepheline ores and limestone which can be mined and furnished to the plant at reasonable prices;
   - Availability of an alumina refinery site with sufficient access to appropriate quality fuel (gas/coal/oil), electricity and water, which may be supplied to the plant at reasonable prices;
   - A market for all the products which may be produced (including alumina, soda ash, potash, aluminum sulfate, cement and belite mud) in the vicinity of the plant.

To develop nepheline technology based on available nepheline deposits, it is necessary to continue research and development and evaluation studies to identify the right conditions to support new industrial operations.

4. Depending on local belite mud/cement market, technology can be optimized by adjusting cement vs alumina production ratio by applying beneficiation technologies.

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