Egyptian Aluminum-containing Raw Materials and the Prospects for its Integrated Processing to Produce Alumina and By-products

Viktor M. Sizyakov[1], Brichkin N. Vyacheslav [2], Amr Basuony Saad ElDeeb[3], Roman V. Kurtenkov[4]
1. Professor at the Metallurgy Department
2. Head of the Metallurgy Department
3. PhD student at the metallurgy department
4. Assistant at the Metallurgy Department
St. Petersburg Mining University, St. Petersburg, Russia.
Responsible author: brichkin52@mail.ru

Abstract

One of the leading alternative raw materials for the production of aluminum in the first place is consider kaolin ore and clay rocks, the world reserves of which are estimated at 20 - 25 billion tons, and their location is confined to various non bauxitic regions. A typical example of the non bauxitic region in the world that needs to be exploited its own raw material base for aluminum production is the Arab Republic of Egypt, which has capacities for aluminum production, but does not have alumina production and has to import it in significant amounts. At the same time, Egypt has significant reserves of kaolin that makes it one of the largest exporters of the upgraded and non upgraded kaolin in the Middle East and Africa. To date, a significant number of methods for the processing of kaolin and clay are known and continue to be improved, among these historical methods, the acidic technologies is in first place. Their advantages and disadvantages are well known, which gives more attentions for solving their existing problems and their industrial implementation in the near future. One of the considerable interest methods for the processing of alkali-free aluminosilicates is the technology of autoclave leaching in an environment of high modulus aluminate solutions with the precipitation of silica in the form of ferrous hydrate or sodium-calcium hydrosilicate. A high degree of development includes number of technologies based on sintering of 2 and 3 component charges, with a well-developed scheme of utilization of calcium-silicate sludge in the production of Portland cement. At the same time, the final choice is required to focus on regional conditions for the organization of a specific production, consumers of main and by-products, the possibility of further improving of the technological process with the optimization of its modes and indicators.

Keywords: Kaolin, deposits, complex processing, alumina and by-products.

1. Introduction

It is well known that aluminum production is the basis of leading industrial sectors and ensures stable growth of any national economy. Russia occupies one of the leading positions in this field, and United Company RUSAL is one of the world leaders in the production of primary aluminum. At the same time, the problem of the domestic raw material base, associated with the insufficient amount of high-quality bauxite reserves, led to the need to use alternative types of low-grade raw materials, which are used by most of the domestic companies. According to leading experts, the role of this resource will invariably increase due to the growth in global aluminum consumption and the exhaustion of high-quality bauxite reserves. In Russian such materials include the tailings of apatite-nepheline ores, the accumulated volume of which in sludge dumps of different times is more than 2 billion tons. Significant amounts of low-grade aluminum raw materials are associated with natural aluminosilicates in the composition of urtitic, rischorritic and other alkaline rocks, as well as slags, sludge and ashes of the existing industrial complex [1-4]. Alkaline aluminosilicate rocks are widely distributed not only in Russia, but also in other regions of the world. They often occur due to the geological conditions where bauxite is absent. Such regions include the USA, Canada, Mexico, Argentina, Iran, Egypt, Spain, Bulgaria and other countries. Practically all the massifs of these rocks are characterized by their large reserves, as well as favorable mining and technical conditions that allow the use of open mining method. One of the most interesting alternative in these regions is the possibility of using alkali-free aluminosilicates, the most common types of which include kaolin ores and various clay rocks. In the historical aspect, this became the basis for the development of numerous methods for the production of alumina - acidic, alkaline, and electrothermal, some of which were implemented on an industrial scale. Recently, such raw materials have regained considerable interest from the standpoint of its regional use, which is associated with the steady demand for aluminum, alumina and by-products in the context of a significant increase in transport costs [5-8].

2. The World Reserves of Kaolin Ores and their Development

The world reserves of clay and all types of kaolin ore are estimated at 20 - 25 billion tons. The reserves of kaolin ore from this amount approximately 16 billion tons, and their consumption is quite stable and is currently at least of 60 million tons per year as shown in Figure 1.

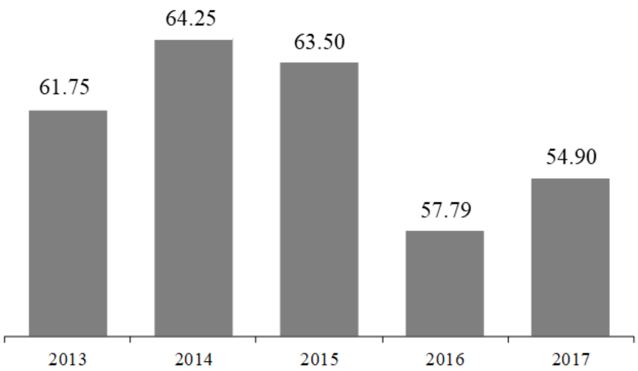

Figure 1. World production of kaolin ore, million tons per year [9].

Like other mineral resources, kaolin ore are distributed in the earth's crust and between countries unevenly enough, which puts some in a leading position and others in a disadvantageous position. Paradoxical is the fact that the share of Russia, the largest in the world, accounts for only 3 % of the world reserves of kaolin ore as shown in Figure 2 [9].

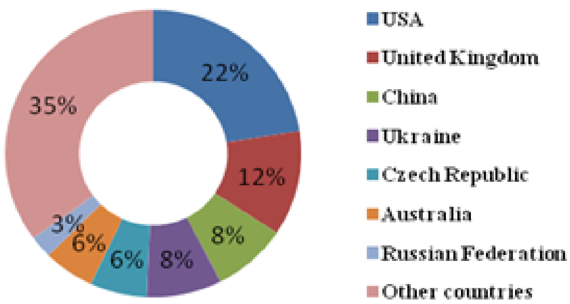

Figure 2. Distribution of kaolin reserves in the world [9].

Currently, in the countries of Soviet Union kaolin is mined in 51 fields in Russia, Ukraine, Georgia, Kazakhstan, Uzbekistan and Turkmenistan. At the same time, the total reserves of kaolin ore in this area are estimated at 1.4 billion tons, of which about 25 % are found in the Russian Federation [10]. Table. 1 shows the distribution of the proven reserves of kaolin ore and clays in the Russian Federation, which suggests the potential importance of this type of raw material for industrial use. It is clear that in a few Federal districts this raw material has sufficient reserves for organizing large-scale production and can be considered as a regional-value resource for aluminum production.

Table 1. The distribution of the kaolin and clay reserves in the Russian Federation [10].

Federal District	Number of deposits	Reserves, million tons	Share, %
Central	7	114,4	17,7
North western	1	2,4	0,3
Southern	1	10,2	1,6
Volga	3	48,6	7,7
Ural	6	312,3	48,4
Siberian	15	149,2	23,3
Far Eastern	2	6,6	1,0
Total for the Russian Federation	35	643,7	100,0

A typical example of non-bauxitic region of the world, which needs to exploited its own raw material base for aluminum production, is the Arab Republic of Egypt, which has capacities for aluminum production, but does not have its own alumina production and has to import it in a significant amounts. At the same time, Egypt has significant reserves of kaolin and considered as one of the largest suppliers of upgraded and non upgraded kaolin ore in the Middle East and Africa. Its deposits and production are confined to three regions of Egypt, including the Sinai Peninsula, the Red Sea coast and Aswan, as shown in Figure 3 [11].

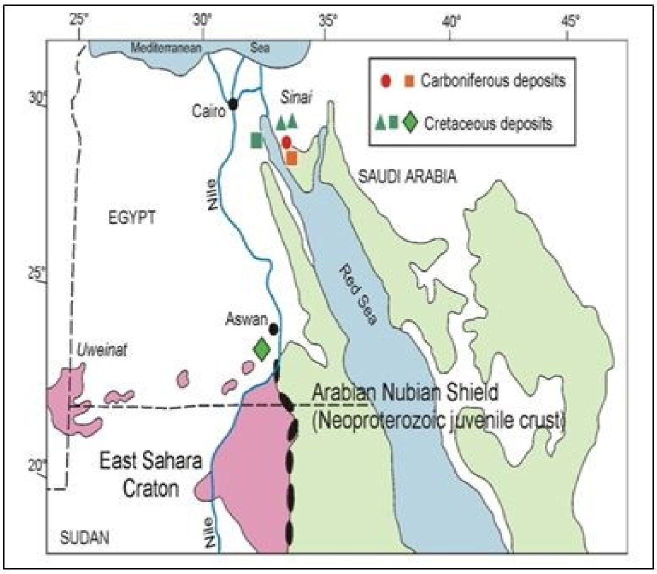

Figure 3. The occurrences of kaolin and clay deposits in Egypt [11].

The largest deposit of the Sinai Peninsula has proven kaolin reserves of about 100 million tons with an average Al_2O_3 content of 26 to 35 %. The Abu Darag field is located about 85 km south of Suez, within the western coast of the Gulf of Suez, with total reserves of 32 million tons with an average Al_2O_3 content up to 29.8 %. The Wadi Kalabsha kaolin deposit is located about 105 km south-west of the industrial Aswan region. Its economic potential is provided by a proven geological reserves of about 17 million tons, with an average Al_2O_3 content of 32 - 35 %. Egyptian company GYMCO is already producing and processing kaolin ore in this region [12]. Currently, the Egyptian industry uses kaolin and clay of various grades mainly in the manufacture of ceramic products, porcelain, special cements, paper, alumina and aluminum sulfate. The annual consumption of kaolin for these needs is more than 1 million tons and 75 % are provided by its own mining industry, but for the production of high-quality ceramic and paper products kaolin needs to be enriched using flotation, resulting in a significant amount of unclaimed industrial tailings [13].

Modern mining and processing of kaolin raw materials has a developed infrastructure, is provided with raw materials and in the future can be adapted to the production of alumina and by-products. At the same time, it is necessary to address issues related to the choice of a technological process that meets the regional nature of the raw materials, taking into account the properties of the crystal structure of its mineral components, chemical and physical composition, as well as the consumers of the final products, which can achieve the required efficiency of its production and production process as a whole.

3. Chemical and Physical Characterization of Kaolin Ore from Different Fields

The results of chemical analysis of kaolin ore from three fields belonging to different regions of the world, including the Troshkovsky field in the Irkutsk region, the Borovichsky group of fields in the Novgorod region and the Wadi Kalabsha field in Egypt (Table 2). Table 2 also includes the content of P_2O_5, SO_3, as well as minor impurities V_2O_5, Cr_2O_3, MnO at levels of 0.01 - 0.02 % for the sample of the Troshkovo field. Losses of ignition were determined according to GOST 2642.2-86 and include the total weight loss of the sample at a calcining temperature of 1000 ± 50 °C.

The results of X-Ray Diffraction analysis indicates that all kaolin samples are composed mainly from kaolinite and quartz minerals. The Thermal Gravimetric Analysis of kaolin samples characteristic of the endothermic effects in the temperature range of 519.75 - 535.79 °C, which corresponds to the removal of the chemically bound water with the destruction of the original structure of kaolinite and its transition to metakaolinite. The characteristic of the exothermic peak in the temperature range 938.47 - 981.30°C can be attributed to the phase transformation of metakaolinite into silicon-spinel and mullite.

Table 2. Chemical composition of kaolin ores from differant deposits.

№ Sample	Field, brand of kaolin	The chemical composition of samples in terms of oxides,%									
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	other	L.O.I.
1	Troshkovsky field (Irkutsk region)	52.2	31.90	1.40	0.6	0.6	0.53	0.15	0.15	0.13	13.0
	Borovichsky group (Novgorod region)										
2	BLKP2	55.1	34.7	2.80	4.2	0.3	0.76	0.36	1.20	0.30	12.6
3	BLKPS1	46.7	33.7	1.65	3.2	0.1	0.37	0.44	0.41	0.31	12.9
4	BLKPS2	48.6	33.7	1.61	3.2	0.1	0.34	0.22	0.43	0.51	11.8
5	BLKPS3	50.3	32.8	1.59	3.1	0.1	0.36	0.25	0.39	0.12	10.7
6	BLKPS.3B	53.1	31.9	1.53	3.1	0.1	0.34	0.25	0.40	0.16	9.02
7	Wadi Kalabsha (Egypt)	48.7	31.17	2,21	3.9	0.3	0.13	0.23	0.09	0.86	12.5

4. Quality Assessment of Kaolin Raw Materials and Selection of the Processing Process

The conducted analytical studies show that, regardless of the region of formation and occurrence of kaolin ores, they have the same chemical and mineralogical composition with high level of consistency as regard to the content of basic chemical elements and minerals. The established amount of the sum of alkaline components at a level of 0.3 – 0.32 % for a sample of kaolin from the Troshkovskoye field and Wadi Kalabsha to a maximum of 1.56 % in one of the samples from the Borovichsky group of fields, suggests a low residual content of the initial alkali silicate of potassium sodium feldspars and a high degree of completion of the geochemical processes of their kaolinitization. The content of free silica and in the first approximation of kaolinite can be estimated taking into account that all Al_2O_3 is in its composition, and the kaolinite itself corresponds to the theoretical stoichiometry of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Its content can be estimated at the level from 78.84 % for the Wadi Kalabsha field to 87.87 % in the sample of kaolin of the BLKP2 brand. The content of free silica varies accordingly from 12.01 % to 14.32 %. The latter value is certainly overestimated due to the fact that it does not take into account the content of alkali aluminosilicates, which reaches a maximum in the BLKP2 sample, and which, taking into account the stoichiometry of $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, can be estimated at 10.14 % at a content of 6.69 % SiO_2 in their composition. These characteristics of the raw materials are of paramount importance for choosing the optimal technological process, since they determine the theoretical yield of alumina, the consumption of reagents in key technological operations and the amount of sludge to be further processed, which should correspond to the capabilities and interests of the corresponding region.

To date, a significant number of methods for the processing of kaolin and clay are known and continue to be improved, among which historically the first place is taken by acid technologies [14, 15]. Their advantages and disadvantages are well known, which allows, hopes to solve existing problems and industrial implementation of these methods in the foreseeable future [5-8]. One of the methods that has considerable interest for the processing of alkali free aluminosilicates is the technology of their autoclave leaching in an environment of high modulus aluminate solutions with silica precipitation in the form of ferruginous hydrogarnet or sodium calcium hydrosilicate ($Na_2O \cdot 2CaO \cdot 2SiO_2 \cdot H_2O$) [15]. The advantage of this method is its versatility and the possibility of using the hydrometallurgical process for processing high-silicon raw materials of various nature. Along with this, it is distinguished by the considerable complexity of the technological scheme and its hardware design, which excluded the industrial implementation of this method to date.

The technology of kaolin processing by sintering differs in clarity and development, which can be considered in three competitive options that have not only significant differences, but also using the same type combination of sintering of the charge and leaching of the sinter for dissolving the raw material. The earliest and industrialized method is the sintering of kaolin raw materials with soda and limestone, which allows, in the first approximation, to describe and evaluate the performance of this technology based on the following stoichiometry [15]:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 4CaCO_3 + Na_2CO_3 = 2NaAlO_2 + 2(2\ CaO \cdot SiO_2) + 2H_2O + 5CO_2 \qquad (1)$$

This stoichiometry makes it possible to determine the mass of the charge, as well as to estimate the consumption of reagents and the output of sludge, which with high accuracy corresponds to the composition of calcium orthosilicate, which is confirmed by industrial processing of nepheline raw materials with similar stoichiometry of the processes as shown in Table 3 [2, 4, 15].

The second technological option is the method proposed by prof. M.N. Smirnov and to which the corresponding nominal name was fixed, with the following stoichiometry of key technological operations [15]:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + 2CaCO_3 + 3Na_2CO_3 = 2NaAlO_2 + 2(Na_2O{\cdot}CaO{\cdot}SiO_2) + 2H_2O + 5CO_2. \quad (2)$$

$$2(Na_2O{\cdot}CaO{\cdot}SiO_2) + 4H_2O = 4NaOH + 2(CaO{\cdot}SiO_2{\cdot}H_2O) \quad (3)$$

In this scheme, equation (2) corresponds to the sintering stoichiometry, and equation (3) the regeneration of the alkaline reagent with the formation of waste sludge of the specified composition. This method has passed pilot tests, and its estimated specific indicators are also given in Table 3.

The third variant of kaolin speculative processing technology was proposed by prof. V.A. Mazel and prof. N.I. Eremin, and the stoichiometry of his key technological operations has the following form, corresponding to the sintering of a two-component charge [15]:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + 5.7CaCO_3 = 1.7CaO{\cdot}Al_2O_3 + 2(2CaO{\cdot}SiO_2) + 2H_2O + 5.7CO_2 \quad (4)$$

$$1.7CaO{\cdot}Al_2O_3 + 1.7Na_2CO_3 + 0,7H_2O = 1.7CaCO_3 + 2NaAlO_2 + 1.4\ NaOH \quad (5)$$

This technology has undergone a comprehensive pilot testing and is characterized by the formation of self-disintegrating sludge, whose composition corresponds to the γ-modification of calcium orthosilicate, which is more resistant to decomposition in aluminate solutions and which is associated with lower losses of Na_2O and Al_2O_3. An additional consequence of this method is the lower content of alkaline components in the sludge, which contributes to the improvement of the quality of Portland cement during its disposal. The calculated indicators of the method are given in Table 3.

Table 3. Estimated indicators of complex processing of kaolin ore for the production alumina and Portland cement.

Processing method	Specific indicators of the processing of kaolin ore t/t Al_2O_3						
	Charge consumption	Limestone consumption	Soda consumption	Sinter yield	Sludge yield	Limestone consumption for sludge utilization	Portland cement output
Sintering 3-component kaolinite-soda-limestone charge	7.49	3.92	1.04	4.98	3.37	1.96	4.47
Method of M.N. Smirnov	7.61	1.96	3.11	5.10	2.63	3.92	4.47
Sintering 2-component kaolin-limestone charge	8.12	5.59	-	5.31	5.04	0.29	4.47

An integral feature of the considered methods is the yield of Portland cement of alite composition and the additional consumption of the lime component for its preparation as shown in Table 3, which can be determined according to the stoichiometry of alito formation with the participation of the corresponding sludges formed by reactions (6)-(8):

$$2(2CaO\ SiO_2) + 2\ CaCO_3 = 2(3CaO\ SiO_2) + 2CO_2 \quad (6)$$

$$2(CaO\ SiO_2\ H_2O) + 4CaCO_3 = 2(3CaO\ SiO_2) + 2H_2O + 2CO_2 \quad (7)$$

$$[2(2CaO\ SiO_2) + 1{,}7CaCO_3] + 0{,}3CaCO_3 = 2(3CaO\ SiO_2) + 2H_2O + 2CO_2 \quad (8)$$

According to Table 3, The 3 calculated indices allow indication that, despite the noticeable differences in the sintering technology, the considered methods have similar indicators of flows at this repartition, related to the amount of the charge and the resulting sinter. Significant differences in material flows occur at the leaching stage as a result of noticeable differences in the mechanism of the opening of kaolin raw materials, which subsequently affects the expenditure indicators of sludge utilization in the production of Portland cement. This suggests a significant specificity of each of the considered methods and for an informed choice of technology, it is necessary to take into account the particularities of the chemical and mineralogical composition of the raw materials, which affect both the specific refining indicators and the fundamental possibility of implementing the method, achieving acceptable indicators of alumina yield and obtaining marketable products when disposing of sludge.

The current position of the aluminum and cement industry in Egypt creates sufficiently stable prerequisites for the production of alumina and by-products based on the sintering method of kaolinite ores, which, regardless of its implementation, allows for the production of Portland cement, which is exclusively in demand in the Middle East region. In Egypt, there are significant reserves of kaolin ores and also limestone deposits, which can significantly increase the current production of Portland cement by utilizing silicate-calcium sludge from the processing of kaolin ores for alumina. Given the well-known advantages of this approach, its implementation will have long-term implications for the economic and social development of the regions of Egypt and will ensure the minimal environment influence by associated with the integrated and waste-free production [11]. In this regard, a well-developed method of sintering a two-component limestone-kaolin charge with obtaining self-slaking calcium-aluminate cake has noticeable advantages [15]. One of the tasks of adapting this technology to modern conditions, in our opinion, is to reduce the sintering temperature due to the use of mineralizing and activating additives as part of the charge [16]. Exploratory research allows to give quite encouraging predictions on the effectiveness of the use of activated lime materials of various nature, a limited number of alkaline aluminosilicates and carbon-containing additives.

5. Conclusion

Modern mining and processing methods of kaolin ore have an established infrastructure, are provided with raw materials and in the future can be adapted to the production of alumina and by-product based on the regional nature of this raw material resource and consumers of final products.

Regardless of the region of formation and occurrence of kaolin ores, they have nearly the same chemical and mineralogical composition with a high level of consistency as regard to the content of basic chemical elements and minerals, which indicates a high degree of completion of the geochemical kaolinitization processes of primary feldspathic minerals alumina and associated products.

Until now, the most mastered technology of processing kaolin raw materials are methods based on sintering 3 or 2 component charges with subsequent leaching of sintering, while a reasonable choice of the method of processing a particular source of raw materials is determined by the sum of its chemical and mineralogical characteristics and technical characteristics and economic condition of the region. This suggests that the sintering method of the two component limestone-kaolin mixture in the Arab Republic of Egypt is promising, utilizing the entire amount of lime-silicate sludge in the production of Portland cement.

6. Acknowledgment

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7. References

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