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Cost Effective Technology of Alunite Ore Processing

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Abstract

Soda-alkaline method of alunite ore processing includes crushing, grinding and enrichment (flotation) of the alunite ore. Enriched alunite ore, containing 50 - 60% of alunite, is roasted at temperatures between 520^o – 620^o C for 1 – 3 hours. Roasted alunite is further leached with sodium carbonate solution (5–20 %). Proportion of sodium carbonate for binding of SO_3 aluminum sulfate in alunite accounts for 100 – 110 % of stoichiometric quantities. Leaching takes place at temperatures around 70 – 100^o C for 0.5 – 2.0 hours. Solution of the resulting pulp contains all the potassium sulfate from alunite and sodium sulfate from soda. Solution of sulfates is separated from the insoluble residue and is fed for conversion with potassium chloride. As result of this conversion we obtain quantities of potassium sulfate (fertilizer) and table (common) salt. The remaining insoluble residue contains all the aluminum oxide from alunite and waste rock. Further processing of the insoluble residue based on the Bayer out-of-autoclave process produces alumina and quartz sand. Besides alumina, this method makes it possible to get four times more the amount of potassium sulfate and certain volumes of table salt.

Taking into account the processing capacity of Ganja Alumina Plant (150,000 tons of alumina per year), this method allows the production of fertilizer, potassium sulfate (370,000 tons per year), coagulant for purification of water from mechanical impurities (49,000 tons per year), table salt (NaCl) (126,000 tons per year), and quartz sand for non-ferrous casting and production of construction materials (300,000 tons per year). Approximate yearly financial efficiency of the soda-alkaline technology for processing of 150,000 tons of alumina per year will be around 171,46 million USD.

Keywords: alumina, alunite, aluminum, alkaline, sodium, ore, sulfate, potassium, technology

1. Introduction

Nowadays more than 90% of primary aluminum is produced from bauxite, however the amount of aluminum in the explored bauxite ore deposits accounts for less that 10% of world reserves. The huge demand for alumina has led to a switch of definitions of raw aluminum materials in the world economy. Currently, primary raw materials for aluminum production include bauxite, alunite, nepheline and nepheline syenite, certain types of clay and shale, as well as ashes from thermal power plants that use coal. The deposits of alunite ores are widespread in the Earth’s crust. According to the map of alunite deposits and occurrences, compiled by academician M.A. Kashkai (Kashkai, 1970), industrial deposits of alunite ores are mainly located in the alpine zone, which starts in the Eastern China, then continues through Middle Asia, Caucasus and Transcarpathia to the Mediterranean basin (i.e. within Southern Europe and Northern Africa). Further on, the alunite zone passes across the Atlantic Ocean into North America and the southern part of the United States.

Alunite ore is a raw material for the chemical and aluminum industries. Industrial deposits of alunite ores are widespread in the USA, China, Azerbaijan, Mexico, Iran, Kazakhstan, Uzbekistan, Ukraine, Russia, and other countries.

This article is devoted to a technology of integrated processing of alunite ores, resulting in production of chlorine-free potassium fertilizer – potassium sulfate (SOP), metallurgical alumina, coagulant for purification of drinking and wastewater from mechanical impurities, table salt - sodium chloride (NaCl) and quartz sand for non-ferrous casting and production of construction materials.

2. There exists an alkaline recovery method of alunite ores processing (Agranovskiy, 1970), in which ore after crushing, grinding and roasting is subject to a recovery roasting at temperatures of ≤560 -580^{o}C by the reaction:

$K_2SO_4 . Al_2 (SO_4)_3 . 2AL_2 O_3 + 0,5\ C_2H_4 = 3AL_2 O_3 + K_2SO_4 + 3SO_2 + CO_2 + H_2O$

Main reducing agents for the reaction are diesel fuel or sulfur in gaseous form. SO_2, resulting from the reaction, is used for production of sulfuric acid. The complete process of recovery takes place at temperatures over 580^{o}C. This method was applied at Ganja Alumina Plant (GAP) (Azerbaijan). Due to serious technological drawbacks (low yield of alumina in the product – less 70%; damage to the environment due to dust and gas pollution; the need for expensive auxiliary raw materials; large amounts of solid waste – 5 tons per 1 ton of alumina; low demand for the by-product – sulfuric acid) the plant was shut down in 1992 and is still not working.

3. These drawbacks can be avoided by applying the potash-alkaline method (Lajner– Taghiyev) (Lajner, 1974), (Taghiyev, 1981, 2001, 2003, 2006). Alunite, roasted at T = 550^{o}C without recovery is leached by potassium carbonate solution by the reaction:

$K_2SO_4.AL_2\ (SO_4\ )_3.\ 2AL_2O_3 + wr +3K_2CO_3 = 4K_2SO_4 + 3AL_2\ O_3 + wr + 3CO_2$ (wr – waste rock)

Solution contains 4 times more potassium sulfate (SOP), and the insoluble residue contains active alumina (¥-AL_2O_3). Insoluble residue is then processed, using the Bayer out-of-autoclave process, and produces alumina and quartz sand. The yield of alumina in the product is-90%. White slurry of process desiliconization goes to production of coagulant for water purification. The major drawback of this method is related to use of high volumes of potassium carbonate, a scarce and expensive auxiliary raw material.

4. Potash Ridge Corporation (PRC) from Utah, USA has developed another processing method (PRC, 2017) for production of sulfuric acid, potassium sulfate (SOP), alumina, quartz sand from alunite ore. After crushing and roasting the alunite ore is subject to a floatation treatment. As a result, the ore contains not less than 60% of alunite. Then the ore is dried and roasted at 600^{o}C or below with a simultaneous alunite recovery by adding of excess diesel fuel. The emitted SO_2 is supplied to the production of sulfuric acid, which is further used by PRC for processing of KCl at the deposit in Quebec (Canada) and obtaining additional quantities of fertilizer K_2SO_4 and hydrochloric acid (HCl). Roasted alunite is leached by the hot water for extraction of potassium sulfate in the solution (SOP). Roasting temperatures less than 600^o C result in incomplete recovery of alunite, however allows the maintenance of an active form of alumina in alunite. Still, leaching of alunite, roasted at 600^{o}C by hot water leads to SOP losses due to formation of basic salt, insoluble in water. Share of SOP in the solution does not exceed 65 – 70 %. Roasting at 800 – 900^{o}C improves the alunite recovery proportion up to 100% with extraction of SO_3 by aluminum sulfate. At the same time, the share of SOP is close to 100%, however ¥- AL_2O_3 changes into an insoluble form α – AL_2O_3. Consequently, Bayer method of alumina extraction from the concentrate cannot be applied. There are no known methods of separation of α – AL_2O_3 and quartz in an insoluble residue, resulting in production of metallurgical alumina.

5. In order to eliminate these drawbacks and improve economic and ecological performance, we offer to perform leaching of the roasted alunite in two stages, as described in (Lajner, 1974) and replace potassium carbonate solution by the sodium carbonate solution at the first stage of leaching (1). After the first leaching the solution– mixture of sodium and potassium sulfates - is fed for conversion with KCl, resulting in the production of potassium sulfate (fertilizer) and table salt -NaCl (2).

(1): $K_2SO_4.AL_2(SO_4)_3.2AL_2O_3 + WR + 3Na_2CO_3 = K_2SO_4 + 3Na_2SO_4 + (3AL_2O_3 + WR) + 3CO_2$

(2): $K_2SO_4 + 3Na_2SO_4 + 6KCl = 4K_2SO_4 + 6NaCl$,

($3AL_2O_3$ + WR)- Insoluble residue concentrate (32 – 34%% AL_2O_3) from the first leaching is fed for the second leaching, made with the reusable aluminate solution based on the Bayer out-of-autoclave process. Final products of the process are metallurgical alumina and quartz sand. The yield of alumina in the product is - 90%. The alunite roasting process is performed at T^o=520^o-550^o C. Roasted alunite is leached by the sodium carbonate solution (Proportion of sodium carbonate for binding of SO_3 aluminum sulfate in alunite accounts for 100 – 110 % of stoichiometric quantities). Products of the reaction are K_2SO_4- fertilizer, NaCl- table salt, Al_2O_3 –metallurgical alumina, SiO_2 – quartz sand, coagulant for purification of water from mechanical impurities (Taghiyev, 1976). Thus, an ecologically harmful production of sulfuric acid can be excluded from the process. Conversion of the solution of sodium sulfate with KCl from a deposit in Quebec (Canada) leads to production of K_2SO_4 (SOP) and NaCl. Volume of production of a universal and chlorine-free potassium fertilizer (SOP) is increased 4 times– (Appendix A).

The conversion of the Na_2SO_4 with KCl is a well-known process of obtaining K_2SO_4 and NaCl (N. V. Nemets, 1995). From literature (M. E. Posin, 1974) it is known that the process of conversion of natural KCl and Na_2SO_4 with obtaining K_2SO_4 and NaCl was used in Canada. Conversion takes place in two stages: at the first stage as a result of evaporation NaCl is obtained. Glasurit and KCl remain in the solution. When cooled to a temperature below 40 ℃, K_2SO_4 precipitates, and the mother solution returns to the first stage.

The Ganja Alumina Plant (GAP) uses a mixture of potassium and sodium alunite as raw material. Therefore, for the transfer of sodium sulfate to potassium sulphate, the conversion of sodium sulfate with potash alkali was applied. As a result, potassium sulfate and sodium alkali were obtained. The conversion process did not significantly affect the cost of the main products.

In the article (Alizadeh, 2016) the choice of optimal technology of alunite ore with the use of AHP and TOPSIS based on three criteria: technical, economic and environmental is being developed. From the 13 technology options, (Piga L, 1999) technology was chosen. However, to be sure of the correctness of this decision, the experimental confirmation and full disclosure of the technology with the material balance is required.

Note 1. USA is 2nd largest producer of soda ash in the world, and Canada is the world‘s largest producer of potassium chloride (KCl).

Technical and Economic Indicators of SodA-Alkaline Technology of Processing ALunite Ores

Note 2. Economic calculation is made for alunite ores, enriched mechanically up to the 50-51% of alunite in the ore (field Zaglik, Azerbaijan)

The average chemical composition of alunite ore of Zaghlik, weight, %:

$AL_2O_{3\ al}$	AL_2O_{3nonal}	SO_3	Na_2O	K_2O	SiO_2	Fe_2O_3	other
19.2	2.5	20.0	1.5 – 2.0	3.5– 4.0	42-43	4–5	7.3 – 4.3

Calculation of Economic Efficiency of Soda- Alkaline Processing Technology of Alunite Ores for Production Capacity of 150,000 Tons of Alumina Per Year

Calculation of costs is made per each ton of alumina.

Note 3. Prices of manufactured goods and raw materials were calculated as an average between the minimum and maximum wholesale prices, taken from the Internet as of October 09, 2018 (in USD per ton)

Na_2CO_3	Min	311.26	Na_2CO_3 Average price
	Max	328.55	320 USD/ton
KCl	Min	291.3	KCl Average price
	Max	349.3	317.3 USD/ton
K_2SO_4	Min	591.4	K_2SO_4 Average price
	Max	754.0	672.7 USD/ton
NaCl	Min	104.0	NaCl Average price
	Max	126.5	115.25 USD/ton
K_2CO_3	Min	570.6	K_2CO_3 Average price
	Max	726.27	648.4 USD/ton

GAP – Ganja Alumina Plant

Table 1. Costs of raw and basic materials (Section 1)

	Item	Unit	Necessary quantity for production of 1 ton of AL_2O_3	Unit cost in USD	Total in USD
1	Alunite ore (51% of alunite)	ton	5.7	6.3	35.91
2	Sodium carbonate (Na_2CO_3) – 100 %	ton	1.12	320.0	358.4
3	Potassium chloride (KCL -100 %)	ton	1.19	317.3	377.59
4	Sulfuric acid (concentrated, 92 -94 %)	ton	0.3	30.0	9.0
	Total costs Section 1				780.9

Table 2. Costs of auxiliary materials (according to GAP)

	Item	Unit	Necessary quantity for production of 1 ton of.AL_2O_3	Unit cost in USD	Total in USD
1	Steel spheres	kg	11.5	Based on information on expenditures, provided by GAP	
2	Filtering cloth	sq. m	0.1		
3	Coagulant (flour)	kg	4.0		
4	Cellulose	kg	6.0		
5	Paper for recycling	kg	6.0		
6	Filters	kg	6.0		
	Total costs Section 2				4.7

Table 3. Costs of electric power and fuel

	Item	Unit	Necessary quantity for production of 1 ton of.AL_2O_3	Unit cost in USD	Total in USD
1	Black oil or gas for roasting alunite	т	0.174	63	10.96
2	Black oil or gas for calcination	т	0.115	63	7.25
3	Electric power x 1000	kwh	1.6	30	48
4	Water x 1000	sq m	0.35	8.9	3.12
5	Steam	Kcal	4.0	2.1	8.4
6	Compressed air x1000	sq m	2.1	5.0	10.5
	Total costs Section 3				88.23

Table 4. Costs of auxiliary materials and amortization

	Item	Unit	Necessary quantity for production of 1 ton of.AL_2O_3	Unit cost in USD	Total in USD
1	Amortization of the equipment, buildings and other constructions				3.4
2	Packing of K_2SO_4 (per 50 kg)	pcs	49	0.22	10.78
3	Packing of AL_2O_3 (per 1 ton)				5.0
	Total costs Section 4				19.18

Table 5. Wages and other expenses

	Item	Unit	Necessary quantity for production of 1 ton of AL_2O_3	Unit cost in USD	Total in USD
1	Wages and social insurance			21.6 + 7.8	29.4
2	Ordinary maintenance and other related expenses				6.7
	Total costs Section 5				36.1

The total amount of expenses on producing of 1 ton of alumina are equal to USD 929.11

Table 6. Income from sales of by-products of production of alumina (per 1 ton)

	Item	Unit	Necessary quantity for production of 1 ton of AL_2O_3	Unit cost in USD	Total in USD
1	Fertilizer (K_2SO_4)	ton	2.47	672.7	1661.6
2	Coagulant for water purification	ton	0.33	146	48.18
3	Quartz sand for nonferrous molding and building materials	ton	2.0	7.5	15.0
4	Table salt (NaCL-100 %)	Ton	0.845	115.25	97.4
		Total income	USD		1822.18

With the average selling price of 1 ton of alumina equaling to USD 250, the total income from sales of the whole will be equal to = 1822.18 + 250 = USD 2072.18.

After subtracting the production costs, the resulting profit will be = 2072.18 – 929.11 = USD 1143.07 per each ton of AL_2O_3.

Considering the whole production capacity of Ganja Alumina Plant (GAP), equal to 150,000 tons of alumina per year, the resulting profit is estimated to be 1143.07 x 150,000 = USD M 171,46 per year.

Note 4. Cost of products for production and raw materials is taken from the Internet, as well as information on production capacities of Ganja Alumina Plant (GAP).

To reduce the capital costs of the implementation of the soda-alkaline technology, the process can be divided into 2 stages.

At the first stage we can implement the part, related to the first leaching of roasted alunite with soda solution (Na_2CO_3) and separation of the insoluble residue (concentrate) for storage. This solution - a mix of potassium and sodium sulfates – is used for conversion with potassium chloride, obtaining sulfate potassium (SOP) and sodium chloride (NaCl) as result. (see Appendix B). Profit from sales of products from the 1st stage will be directed to construction of the alumina processing part of the plant and implementation of the full-scale soda-alkaline technology.

Note 5. The authors have already received a positive decision on awarding of a patent in the Czech Republic with a priority from January 30, 2018.

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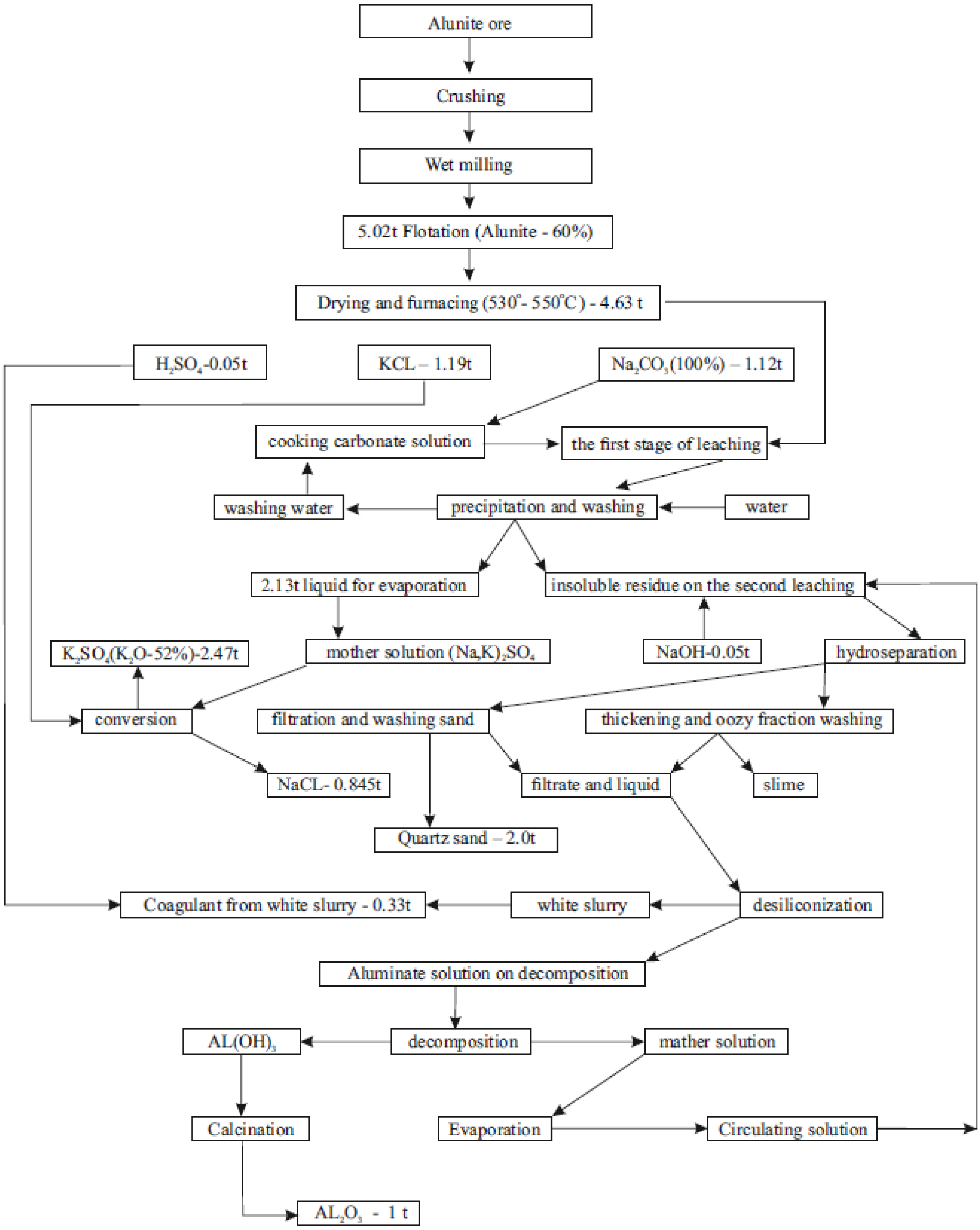
Appendix A. Technological scheme of soda-alkaline method of processing of alunite ores with approximate quantities of materials for alunite ore enriching by flotation (60% alunite)



Appendix B. Technological scheme -1st stage of implementation of soda-alkaline technology of alunite ore processing