Soda Recovery from Carbonate Sodium in Alumina Complex

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ABSTRACT

Iran Alumina Company supplies alumina powder from bauxite by Bayer method. Alumina production process from bauxite through Bayer method includes dissolution, red rose separation, sedimentation, filtration and calcinations processes. To dissolve bauxite, caustic (Na_2O) is used. Soda and vapor unit have been installed to provide caustic required for process. Thin caustic is changed to dense after vaporization and de-salting. Dense caustic production is together with carbonate sodium salt production. Carbonate sodium produced in this unit can recover soda. Higher requirements of caustic and its high price require a part of needed caustic be processed by carbonate sodium. In this research and in order to achieve maximum rate of soda recovery from carbonate sodium, many different methods were examined including reaction of carbonate sodium with lime, reaction of carbonate sodium with hydrated lime, increasing lime successively, lime more than stoichiometric ratio, and lime milk produced in complex. Finally we can reach yield of 87% and caustic of 136.4 g/liter using successive lime method, yield of 88%, caustic of 111 g/liter using lime more than reaction stoichiometry, yield of 85% and caustic of 142.6 g/liter using clear lime.
KEY WORDS: Soda; Carbonate sodium; Alumina.

1. INTRODUCTION

Alumina complex produces Alumina powder from Bauxite stone using Bayer process. The process can be most simply described by the following steps [1]. 1: Dissolution of extractable aluminium bearing minerals from bauxite in sodium hydroxide at elevated temperatures (and pressures). 2: Removal of insoluble impurities and clarification of the remaining solution. 3: Precipitation of pure diaspore from the clarified solution by cooling to highly supersaturated levels and seeding with previously precipitated diaspore crystals [2]. 4: Calcination of the crystallised diaspore at 1100°C to remove chemically bound water to produce alumina [3]. Iran Alumina Complex, located at Jajorm city, Iran, is only producer of Alumina powder by Bayer method in Iran. Due to available carbonate magnesium and carbonate sodium in initial bauxite, carbonate sodium is produced in this complex after process. Many studies have been carried out to produce soda from carbonate sodium salt [4]. In a report considering chemical and physical variables, some variables such as rate of water of reaction, ratio of reactors, carbonate sodium method, type of mixture, and temperature were studied[5]. Another study uses the carbonate sodium crystals (as a secondary process of main reaction) as a reaction bed. Main goal of this study is lower rate of penetration layer of reacting materials. In another study, the main goal is producing carbonate calcium, but caustic soda is also produced. In this study, temperature of reaction, numbers of increasing carbonate sodium, reactor volume, and speed of mixing are studied. Shape and size of particles of produced carbonate calcium are the main goals of this study. Another study uses carbonate sodium salt in recovery of soda from red rose [6]. As already observed, almost studies have been carried out according to the type of application of products in some industries such as paper. Rate of density of soda produced in these studies is lower than soda consumed in factories producing alumina. Therefore, produced carbonate sodium salt is transferred to the sub-industries in almost all factories producing alumina. Our main goal in this study is raising yield of reaction. The less rate of carbonate in liquor recovered the more rate of recovery yield.

2. EXPERIMENTAL PROCEDURE

2.1. Analysis of Carbonate Sodium Salt

Sampling was first performed from different sections of salt stored in complex. Different densities of carbonate sodium salt were solved in water. Then, we took 10cc of each sample and transferred to a 20-cc balloon. Of provided sample, 10cc of any density were transferred to two dry & clean Orlon Mayers. cc25 $BaCl_2$ 10% was added to one of orlons. After 15 minutes, we added 10cc sodium gloconate (according to the alumina). At the presence of phenol, we titrate arisen solution with normal 2% acid choleric. Rate of caustic is calculated according to the extracted volumes and volume of used acid. We added cc EDTA 05/05 molar to the other orlon. Then, we did titration before phenol by normal acid 2% (V $_{HCl}$). 5cc of normal acid chloride 2% was added.

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Obtained solution was boiled for 2 minutes. Then, we titrate the solution with normal caustic soda 2% (V_{NaOH}). We added 10cc with frusta ammonium to the obtained solution. The solution is slowly cooled, and then baznik acetate 0.05 molar was titrated at the presence of Zylene (V_{Zinc}). Na_2O_t and Al_2O_3 are obtained from the following relations in g/l:

$$Na_2O_t = 62[(V_{HCL} \times C_{HCL}) - (V_{NaOH} \times C_{NaOH}) + (V_{Zinc} \times C_{Zinc})] \tag{1}$$

$$Al_2O_3 = 102[(V_{EDTA} \times C_{EDTA}) - (V_{Zinc} \times C_{Zinc})] \tag{2}$$

$$C_{Zinc} = C_{EDTA} = 0.05 mol/lit \tag{3}$$

(To determine Na_2O_t, Na_2O_c and Al_2O_3 are used in trial samples in this study under this method). The results of analyzing carbonate sodium salt in densities of 50, g/Lit 100, g/Lit 200, g/Lit 250, g/Lit 300, g/Lit 350, g/Lit are mentioned in Table 1.

Table 1. The results of analyzing carbonate sodium salt in different densities.

Al_2O_3 (g/l)	Na_2Ot (g/l)	Na_2Oc (g/l)	carbonate sodium salt (g/l)
1.02	27.2	2.6	50
2.04	44.57	4.96	100
3.2	93	11.6	200
3.6	114.3	18.6	250
4.3	123.4	19.56	300
5.4	164.61	21.32	350

2.2. Machine Analysis of Carbonate Sodium

XRF available in complex was used to analyze samples. Results of analysis are in the Table 2. According to the obtained analyses and exposure of salt (exposure to the environmental pollutions and CO2), percentage of salt varies in different sections. With accordance that the salt filtered in soda and vapor unit is mixed by soda and we shall consider the process fluctuations, analyses are never similar in case of rate of carbonate sodium and caustic soda. They will be clearly observed in the tests. Note that the reaction temperature is 90° in all tests and moment of reactions is considered 1-2 hour. To study role of lime used in reactions, we first selected a fixed density of carbonate sodium (100 g/l) and carried out the tests by adding lime and providing temperature necessary for reaction and suitable moment. The results of analyzing samples after grout filtration are stipulated in Table 3.

As shown in table 3, reaction yield increases as rate of lime raises according to the reduction of distance of Na_2O_t, Na_2O_c.

Table 2. Results of machine analysis of carbonate sodium.

Sample	Na_2CO_3 %	NaOH %	Al_2O_3 %	SiO_2 %	Fe_2O_3 %
(1)	88.18	6.16	3.2	0.041	0.0031
(2)	75.9	5.72	2.97	0.042	0.0029
(3)	82.86	8.3	4.6	0.059	0.0018
(4)	66.72	6.3	1.18	0.05	0.0025

Table 3. The results of analyzing samples after grout filtration.

Carbonate sodium salt (g/l)	Lime (%)	Na_2Oc (g/l)	Na_2ot (g/l)
100	60	42.5	48.6
100	70	44	49.7
100	80	46.2	49.2

3. Study of different methods to achieve maximum yield of recovery

3.1. Using lime milk produced in complex in this reaction

We first selected 6 fully dry and clean test tubes, and added 1 liter of lime milk to each one. We then added carbonate sodium for rates of 350, 300, 250, 200, 100, 50 g to each one. We observed the mixing problem by increasing of carbonate sodium, filtered the grouts under suitable temperature and time after performing reaction and analyzed solution. The results are shown in Table 4.

According to the results obtained from table 4, the best yield in densities of 50 and 100 g/l was observed.

3.2. Using Lime of Complex

We first supplied solutions of carbonate sodium of 350, 300, 250, 200, 100 and 50 g/l in densities and added lime by 80%. After suitable time and temperature of reactions, grouts were filtered and analysis results are represented in Table 5. (Rates of lime are added according to the stoichiometry of reaction). As shown in Table 5, the best yield is achieved in lower density.

Table 4. The results of analyzed solution with lime milk produced in complex.

Carbonate sodium salt (g/l)	Na_2Oc (g/l)	Na_2Ot (g/l)
50	25.2	26.3
100	46.4	52.4
200	98	123.5
250	110	146.7
300	121	146.5
350	134.2	175.6

Table 5. The results of analyzed solution with lime of complex.

Carbonate sodium salt (g/l)	Lime (g)	Na_2Oc (g/lit)	Na_2Ot (g/lit)
50	27	28.2	30.2
100	53	40.2	48.7
200	106	90.4	120.3
250	133	98	135.4
300	159	115	145
350	185	121	166

3.3. Using Hydrated Lime

Adding very low rates of water to lime, lime surface and volume increases as much heat releases. This test aims at increasing reaction surface.

As observed (according to Table 6), distance of Na_2O_t, Na_2O_c has been reduced more than the last conditions and the caustic rate obtained in density of 350 g/l is considerable.

Table 6. The results of analyzed solution with hydrated lime.

Carbonate sodium salt (g/l)	Lime (g)	Na_2Oc	Na_2Ot
50	27	25.4	27
100	53	47.6	50.3
200	106	101	125
250	133	111	135
300	160	125	150
350	185	142.3	170.3

3.4. Using Lime More Than Reaction Stoichiometry

As the yield of reactions is higher in low densities, we used higher densities of carbonate sodium in this method. We selected rate of reacting lime more than stoichiometric ratio. (According to the Lochatilet principle, adding reactors causes higher product). After suitable time and temperature, grouts are filtered and the results are mentioned in Table 7 (mixing is impossible by using more densities). According to the table 7, the best yield was observed in density of 200 g/l in which the distance of Na2Oc, Na2Ot is reduced.

Table 7. The results of analyzed solution with lime more than reaction stoichiometry.

Carbonate sodium salt (g/l)	Lime (g)	Na_2O_c	Na_2O_t
150	220	99.8	123
200	320	111	123.46
266	360	116.08	133.8
280	380	125.24	142.99

3.5. Using Lime in Two Successive Processes

In this method, we used the higher densities of carbonate sodium. After adding lime; we provided suitable temperature and time of reaction. Then we filter the obtained grout and added again lime to the solution obtained. After suitable temperature and time, we filtered again grout. The arisen solution was analyzed. The results are shown in Table 8.

Table 8. The results of analyzed solution with lime in two successive processes.

Carbonate sodium salt (g/l)	Lime in first stage (g)	Lime in second stage (g)	Na₂oc (g/lit)	Na₂ot (g/lit)
200	90	100	105.2	118.7
250	90	100	115.96	128.7
300	120	135	142.6	162.75
310	120	145	136.4	153.14

4. Description

4.1. Study of reactions mechanism

Reactions performed in the mentioned tests include:

$$CaO + H2O \rightarrow Ca(OH)_2 \tag{4}$$

$$Ca(OH)_2 \Leftrightarrow Ca^{+2} + 2OH^- \tag{5}$$

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3{}^{2-} \tag{6}$$

$$2Na^+ + 2OH^- \rightarrow 2NaOH \tag{7}$$

$$CO_3{}^{2-} + Ca^{2+} \Leftrightarrow CaCO_3 \tag{8}$$

According to the mentioned reactions, we shall understand that in the volume of reaction, two types of sediments are being equilibrated with their related ions. Then, we shall observe that as density of reactors (Na_2co_3, Cao) increases, volume of sediments also increases. Therefore, there is no penetration layer and possibility of effective contact of particles. It can be one of the most principal deficiencies of non –development of reaction in higher densities such as 350 g/l. As density of NaOH increases in solution, density of ion –OH increases in the right side of reaction 1, and finally reaction of separation of $Ca(OH)_2$ to the effective ions decreases and returns back to the left side.

5. Conclusion

We shall tell about study of results of tests and theory that: Normally, reactions are relatively complete and yield of method is high in low densities such as 50&100 g/l of carbonate sodium. Under change in conditions including increasing surface of reactors (hydrated lime), increasing a component of reactors (more than stoichiometric rate),adding lime successively (from removing solid materials and increasing penetration layer),we can achieve an appropriate yield in higher densities. We can reach in this study yield of 87% of caustic 136.4g/l by using successive lime method and yield of 88% and caustic 111 g/l by using lime more than reaction stoichiometry and yield of 85% and caustic 142.8 g/l by using hydrated lime.

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