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Experimental Study of Pollutant Removal Chemical Techniques in the Bayer Process

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1. Introduction

In the Bayer process, bauxite is mixed with lime and concentrated caustic soda solution at high temperature to dissolve alumina in caustic liquor. The produced sodium aluminate solution is sent to the precipitation stage. The bauxite is the main source of organics in the Bayer process. In addition to organic compounds, there are inorganic materials such as sodium carbonate and sulfate. Carbonate and oxalate pollutants enter into the Bayer process through bauxite, lime and sodium hydroxide solution and cause a number of problems in the alumina production cycle. Therefore, development of new techniques for removing these impurities from Bayer liquor is of great interest to the alumina refining industry. Several methods have been presented to remove carbonate and oxalate pollutions. Selecting an appropriate method depends on various parameters including operational and economic conditions. The method of chemical elimination by the use of additive compounds to remove carbonate and oxalate impurities from the Bayer process solution has more efficiency and flexibility due to the conditions governing the alumina refining process. The aim of this work was to indicate the role of different materials in formation of carbonate and oxalate and increase the removal efficiency of the pollutants for the Bayer process using chemicals. The removing method has been applied using phosphate–lime, calcium aluminate with the structure of $Ca_3Al_2(OH)_{12}$ and barium aluminate with the structures of $BaAl_2O_4$, $Ba_2Al_2O_5$ and $Ba_2Al_4(OH)_{16}$. In addition, experimental data were obtained from Iran Alumina Company under different operational conditions. The experiments were carried out on sodium aluminate solution in different units of this company. We tried to find a workable, effortless, versatile and accessible method with minimal adverse side effects and good efficiency in accordance with the terms governing the Bayer process.

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2-Experimental

For investigating the bauxite's effect on the carbonate and oxalate concentration in the Bayer process's liquor, 736 ml of sodium hydroxide solution was separately mixed with 271.8 g of two Jajarm bauxite samples at 70 ^oC for 1 hour. Lime is another raw material in the Bayer process which can react with sodium hydroxide solution. This reaction can increase the carbonate content in the Bayer process. In this study 32.2 g of lime with different amounts of CaOact was mixed with 740 ml of sodium hydroxide solution at 70 ^oC for 1 hour. Investigating the effect of temperature on removing carbonate from sodium aluminate liquor was carried out by mixing 51 g of calcium aluminate with sodium carbonate solution at various temperatures for 1 hour.

Each operational unit in Jajarm Alumina Complex has especial conditions in terms of temperature, pressure and concentrations of the compounds in sodium aluminate solution. In order to study the removal efficiency of the carbonate, the Bayer process solutions with certain chemical and physical conditions were separately mixed with 14.55, 11.6 and 11.2 g of sodium phosphate–lime and calcium aluminate, respectively.

The effect of sodium phosphate–lime and calcium aluminate with structure of $Ca_3Al_2(OH)_{12}$ and barium aluminate with structures of $Ba_2Al_2O_5$, $Ba_2Al_4(OH)_{16}$ and $BaAl_2O_4$ was investigated to remove the carbonate and oxalate. These substances were individually added to the spent liquor at 75 °C.

3-Results and Discussion

The XRD diffraction pattern of bauxite shows that there is calcite ore in the Jajarm's bauxite. The results of the bauxite effect on concentration of carbonate and oxalate in Bayer process liquor are shown in Table 1. These results indicate an increase in Al_2O_3, Na_2O_u, SiO_2 and oxalate and a decrease in Na_2O_c and Na_2O_t. The reaction of bauxite's organic materials with sodium hydroxide solution can produce oxalate in the Bayer process.

Table 1 Chemical analyses of the solution before and after using bauxite

	Na_2O_C	Al_2O_3	Na_2O_t	Na_2O_u	SiO_2	oxalate
					g	٪
Initial solution	72.12	0.0	73.5	1.55	0.0	0.0
Sample 1	63.9	3.19	67.03	3.13	2.32	0.21
Sample 2	62.95	3.75	66.95	4.0	2.19	0.26

Investigation of the effect of the CaOact content in the lime shows that the amount of carbonate in the Bayer process decreases with increasing in lime activity (Table 2).

Table 2 Chemical analyses of the solution before and after using lime with various CaO_{act} content

CaO_{act}%	Na_2O_c	Na_2O_t	Na_2O_u
	g		
Initial solution	72.12	63.5	1.38
86	69.57	73.5	3.93
75.9	67.8	73.5	5.7
63.4	66.55	73.5	6.95
$CaCO_3$ (0)	66.06	73.5	7.44

To study the effect of temperature on the removal efficiency of carbonate, calcium aluminate was separately used to remove 25 g of carbonate (in terms of Na_2O) at various temperature (20, 70 and 90 ^oC).

The results indicate that the sodium phosphate–lime method has higher efficiency than the calcium aluminate method. In addition, better removal efficiency of carbonate was obtained from the experiment with the output solution of stages of wet grinding and alumina hydrate precipitation and filtration. Investigation of alumina concentration in both methods shows that in addition to removing carbonate, the sodium phosphate–lime method leads to removal of alumina and the rate of alumina removal increases in proportion to the alumina concentration in the initial solution. However, using calcium aluminate causes to release alumina and increase its concentration in the solution phase.

These results also imply even though the reaction of purifying carbonate has higher efficiency, lower amounts of Al_2O_3 are removed from the sodium aluminate solution. The results indicate that the concentration of Na2Oc in the initial solution is also effective on removing of carbonate solution and the efficiency of the operation declines by increasing its content. According to the reaction formula of carbonate removing, that is associated with producing sodium hydroxide, the presence of the caustic soda in the solution phase can be an interruptive factor in performing this operation.

To study the effect of additives on the removal efficiency of carbonate and oxalate, sodium phosphate-lime, calcium aluminate and barium aluminate were used with different structures. Based on the stoichiometry of the reaction, these additives were added to the spent liquor for removing 5.5 g of sodium carbonate (in terms of Na_2O).

The reactions show that, the carbonate removing process is associated with caustic soda recovering. The relation of the reaction for removing oxalate was similar to the reaction of carbonate except that instead of carbonate; there were oxalate ions ($C_2O_4^{-2}$).

The results indicate that barium aluminate with the structure of $Ba_2Al_4(OH)_{16}$ has the highest efficiency compared to other additives in removing carbonate. The use of sodium phosphate - lime and barium aluminate with the structure of $Ba_2Al_2O_5$ has a good yield in the operation. Barium aluminate with the structure of $BaAl_2O_4$ and calcium aluminate have the lowest removal efficiency of carbonate. In terms of oxalate removal, the highest and lowest efficiency have been related to phosphate and lime and calcium aluminate, respectively. The results also show that alumina in the liquid phase is reduced only by using sodium phosphate-lime, while its value is increased in other methods.

4- Conclusions

In this study, several methods were applied to remove carbonates and oxalate from Bayer process. Results show 66.9% of carbonate pollutant and 99.9% of oxalate are coming from lime and bauxite, respectively. To remove impurities from the sodium aluminate solution, several chemical methods were applied using additives of sodium phosphate-lime, calcium aluminate and barium aluminate. In addition to carbonate and oxalate removal, these methods led to recovery of soda from these materials which is a major advantage for this method because it does not require an additional stage for causticization. The results showed that using barium aluminate with the structure of $Ba_2Al_4(OH)_{16}$ with the removal efficiency of carbonate equal to 80.2 % and oxalate removing by the heating method with the separation of 72.2% have the highest efficiency compared to other methods. Results also indicate increasing of temperature enhanced the removal efficiency.