ALKALINE PRESSURE LEACHING OF NEPHELINE SYENITE IN PRESENCE OF LIMESTONE

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INTRODUCTION

Alumina can be extracted from Egyptian nepheline syenity by the sintering process (1, 2); it is only partially leached out by mineral acids (3). Alkaline pressure leaching process (4-9) is based on leaching nephepline syenity with concentrated solutions of NaOH in presence of CaO. Alumina is brought into solution as soluble alkali aluminates.whereas SiO_2 reacts with CaO forming calcium hydrosilicates which are left in the residue. High grade limestone is advantageous over CaO (10, 11). The present investigation aims to find out the optimum conditions of the alkaline pressure leaching process of Egyptian nepheline syenite rock of "Abu-khruq" deposit (12) using high grade limestone of "Sidi-Saleh" locality of the Nile Valley (13). The residue was investigated by X-ray and the mechanism of leaching was studied using the equations developed by Sharp (14) and Satava (15).

EXPERIMENTAL

Materials

The chemical analyses of the samples used are given in the following table:

Component %	Nepheline Syenite	Limestone	
		Soft	Hard
SiO_2	55.17	0.236	0.470
Al_2O_3	21.55		
R_2O_3		0.100	0.064
Fe_2O_3	5.09		
K_2O	5.01		
Na_2O	10.01		
CaO	0.17	55.58	55.74
CO_2	0.16	43.86	43.59

Apparatus and Procedure

Powered nepheline syenity and limestone were placed in a titanium container of a 3.8 l capacity standing autoclave made of acid resistant stainless stell (SA-182-F-316, USA). After the elapse of the leaching time, the slurry was filtered and washed. Al, Si, Fe were determined in the filtrate by atomic absorption.

RESULTS AND DISCUSSION

Effect of Leaching Temperature and Pressure

Experiments were carried out at 140,180,220, 260, 300°C (equivelant to 3.5, 10.0, 22.8, 46.2, 84.7 atmosphere) using mixture of nepheline syenite and limestone at CaO: SiO_2 mole ratio of 1.1 and 232 g/l Na_2O at solid/liquid ratios (S/L, g/100 ml) of 10% and 5% for 30 min. The results illustrated in Fig. 1 show that on using S/L 10% the recoveries are markedly increased reaching 89% at 260°C. The same trend is obtained using S/L 5%, but with S/L 5% higher recoveries were achieved at lower temperatures so that at 220°C 83%, Al_2O_3 was recovered at S/L 5% compared to 39% at S/L 10%.

Effect of Leaching Time

Experiments were carried out at 250°C using 232 g/l Na_2O (Na_2O: Al_2O_3 35.6) and CaO: SiO_2 1.1 at S/L 10%, leaching duration was varied from 5 min up to 120 min. The results in Fig. 2 show that the reaction rate is very fast during the first 5 min and is nearly completed after 30 min where 83% Al_2O_3 was recovered.

Effect of Alkali Concentration

Experiments were conducted at 250°C for 30 min using CaO: SiO_2 1.1 and S/L 5% and 10%. NaOH was added in

different amounts from 77.5 up to 38.7 g/l Na_2O equivalent to 12 up to 95 S (S = stoichiometric Na_2O: Al_2O_3 mole ratio). The results illustrated in Fig. 3 show that maximum Al_2O_3 recoveries of 82% and 92% were achieved using 230 g/l Na_2O (35.6 S and 71.2 S for S/L 10% and 5%, respectively). The same recovery value of 82% was reached with S/L 5% when the Na_2O: Al_2O amounts 53 S. Higher alkali concentration are not recommended due to difficulties in handing and filtration.

Effect of Limestone Additions

Experiments were conducted at 250°C for 30 min using 232 g/l Na_2O (24 S) and limestone: nepheline ratios corresponding to CaO: SiO_2 mole ratios ranging from 0.43 to 1.95 X where X is the stoichiometric amount of CaO forms dicalcium silicate. The results illustrated in Fig. 4 show that in absence of limestone very low Al_2O_3 recovery (13%) was achieved. Increasing limestone to 40 wt% of the charge (CaO: SiO_2 = 0.43X) was accompanied by a considerable increase in Al_2O_3 recovery showing a maximum of 82% at CaO: SiO_2 1.1X. Fig. 5 shows that the SiO_2 and Fe contents of the aluminate solution decrease by increasing CaO: SiO_2 mole ratio. Under optimum conditions (CaO: SiO_2 1.1X) solution nearly free from SiO_2 and Fe (0.73 g/l Si and 0.007 g/l Fe) was obtained whereas solutions produced from the traditional Bayer process applied to bauxite contain in the average 2 g/l Si and 0.025 g/l Fe (16).

Effect of Solid: Liquid Ratio

Experiments were performed at 250°C for 30 min using 232 g/l Na_2O and CaO: SiO_2 1.1X at S/L of 5, 10, 15, 20, 30% (Na_2O: Al_2O_3 70.8, 35.4, 23.6, 17.7, 11.8 S). The results illustrated in Fig. 6 show that high Al_2O_3

recoveries are achieved at S/L < 10% as sufficient Na_2O molecules are present to combine with Al_2O_3 forming sodium aluminate. At S/L > 10% sharp decrease in recovery was achieved due to consumption of alkali for the formation of $Ca(OH)_2$ in addition to bad mixing conditions. Although at S/L 5% better results are achieved but the productivity of the process is lowered which negatively affects its economy.

X-Ray Analysis of the Leaching Product

The residue was washed 10 times and then analysed by X-ray. The results illustrated in Fig. 7 show that sodium calcium hydrosilicate is the major component ot the residue. The main lines representing sodium-calcium-, sodium calcium hydroaluminosilicates, both α - and γ - dicalcium hydrosilicates were clearly identified.

Mechanism of Reaction

To investigate the effect to temperature on Al_2O_3 recovery at constant leaching time, the activation energy was calculated applying the three dimentional diffusion reaction using the experimental data for a reduced time scale (17) such as $t/t_{0.5}$ where $t_{0.5}$ corresponds to α = 0.5, thus

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = (k/r^2)\ t = 0.0426\ (t/t_{0.5})$$

where α is the fraction of extracted Al_2O_3 after 30 min, Fig. 1. The $t_{0.5}$ values corresponding to different values at different temperatures were predicted. Plotting log $t_{0.5}$ aganist 1/T straight lines were obtained Fig. 8. The activaltion energy was calculated applying a modified Arrhenius equation

$$E = R.\ \ln \frac{t_{0.5}(T_1)}{t_{0.5}(T_2)} \Big/ \frac{1}{T_1} - \frac{1}{T_2}$$

The activation energies are 21.20 and 11.05 Kcal. $mole^{-1}$ for S/L 10% and 5%, respectively. The difference in values of activation energy is due to high alkalinity of the pulp at S/L 5% leading to higher reactivity of Al_2O_3 to form aluminate solution. The presence of much $Ca(OH)_2$ at S/L 10% favours the formation of calcium hydroaluminosilicate (hydrogarnet) lowering Al_2O_3 recoveries at low temperatures and alkali concentrations. Sharp increase in Al_2O_3 recoveries at temperatures > 220°C using higher alkali concentrations is attributed to the interaction between the formed hydroaluminosicates of calcium and sodium forming sodium calcium hydrosilicate and setting Al_2O_3 to react with NaOH forming sodium aluminate. The incomplete conversion of Al_2O_3 is due to effect of Na_2O, CaO on hydrated nepheline forming sodium calcium hydroaluminosilicate ($4Na_2O.2CaO.3Al_2O_3.6SiO_2.3H_2O$).

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

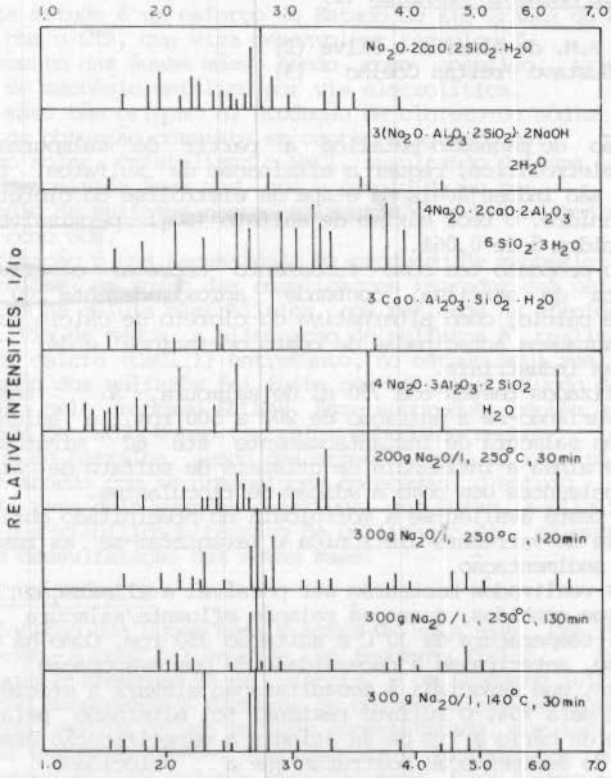
1.0
2.0
3.0
4.0
5.0
6.0
7.0
$Na_2O \cdot 2CaO \cdot 2SiO_2 \cdot H_2O$
$3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot 2NaOH$
$2H_2O$
$4Na_2O \cdot 2CaO \cdot 2Al_2O_3$
$6SiO_2 \cdot 3H_2O$
$3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$
$4Na_2O \cdot 3Al_2O_3 \cdot 2SiO_2$
H_2O
200g Na_2O/l, 250°C, 30min
300g Na_2O/l, 250°C, 120min
300g Na_2O/l, 250°C, 130min
300g Na_2O/l, 140°C, 30min
RELATIVE INTENSITIES, I/Io
d, SPACING, A°

Fig. 7

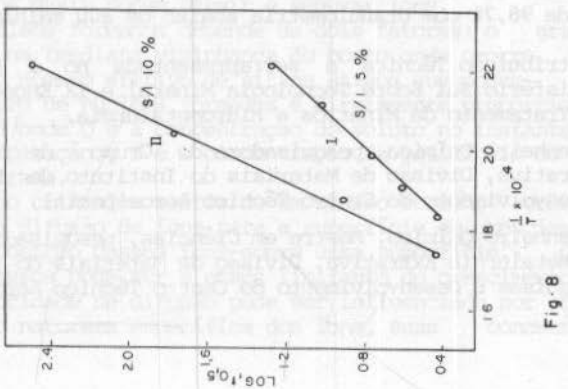
S/V 10 %
S/V 5 %
II
I
$\log r_{0.5}$
$\frac{1}{T} \times 10^{-4}$

Fig. 8