A Mathematical Relationship between the Sodium and Aluminium Oxide Concentrations of Aluminate Solution Samples

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Summary: The objective of the present study was to investigate the correlation between the sodium and aluminium oxide concentrations of aluminate solution samples from Seydişehir, Turkey. The ultimate purpose of this paper is to find a mathematical relationship between the dimensionless concentration ratios of aluminium and sodium oxides. For this purpose, the observed aluminium oxide concentrations were used to generate an empirical relationship:

$A_1 = 1.013 \,.\, A_2 \,.\, N_1^{-0.284} \,.\, N_2^{0.284}$

where, A_1 is the aluminium oxide concentrations (g/l), A_2 is the mean aluminium oxide concentrations, N_1 is the sodium oxide concentration (g/l) and N_2 is the mean sodium oxide concentration. A plot of Ln (A_1/A_2) versus Ln (N_1/N_2) as nondimensional variables gave a straight line for the present system. Such an empirical relationship facilitates the estimation of aluminium oxide concentrations from the sodium oxide concentrations measurements.

Introduction

Sodium aluminate is a white crystalline solid having the formula $NaAlO_2$ or $Na_2O.Al_2O_3$. It is soluble in water to the extent of 44.3 g/100 g and insoluble in ethanol. Commercial products vary in colour from white to pale green to brown. Colours other than white are generally due to iron oxide impurity. Solutions of pure sodium aluminate product are not stable but hydrolyze readily with the precipitation of alumina trihydrate. Solutions can be stabilized by use of excess sodium hydroxide [1, 2].

In the preparation of sodium aluminate, bauxite ore or alumina trihydrate is dissolved in a hot caustic soda liquor. Solution of alumina trihydrate is effected at 120°C. The viscous liquor is then drum-dried at temperatures not exceeding 200°C to give a white crystalline sodium aluminate containing about 20 % moisture. The final product contains about 0.6 % moisture [3, 4].

In spite of the great significance as regards the complete Bayer technology, the structure of sodium aluminate solutions has not been clear up definited yet. There is in fact, no definite explanation for why the reaction can not be reversed by efficiency higher than 50 to 55 percent, achieved in the industrial practice.

According to the supporters of the colloid structure, sodium aluminate solution is built up from aluminium hydroxide particles in the sodium hydroxide, and there is no sodium aluminate compound in the solution. Precipitation of aluminium hydroxide is considered as the coagulation of a sol out of the colloid solution.

According to the theory of composite structure, both colloid aluminium hydroxide and sodium aluminate dissociated to ions are present in the aluminate solutions. Their proportion is a function of the concentration, temperature and molar ratio of the solution.

Ionic theory regards aluminate solutions to be real solutions, in which aluminium is present in the form of sodium aluminate. Analysis of physical characteristics of different sodium aluminate solutions proved with absolute certainly the ionic character [5-7].

The aim of this study was the evaluation of the aluminate solution reserve of Konya (Seydişehir region of Turkey) with respect to alumina production and the determination of technological parameters defining the quality of the aluminate solution.

Results and Discussion

The results of the chemical analysis of aluminate solution samples are given in Table 1. In order to determine the equation that represents the relation between the two variables, first a scatter diagram was produced on a cartesian coordinate system. Subsequently, the possibilities of any correlation existence between the two variables were investigated through a linear regression technique.

Such a scatter diagram is shown in Fig. 1 for the variables at hand and it is almost obvious that there is a significant relationship between the two variables visually. However, it is necessary to document such a relationship through the objective least squares technique as is done in the following way.

Table 1:Chemical analysis of aluminate solution (g/l)

Samples No	Na_2O	Al_2O_3
1	154.33	134.22
2	152.41	131.33
3	152.21	132.11
4	153.10	131.04
5	151.05	130.84
6	154.80	131.56
7	153.15	138.06
8	151.20	131.92
9	151.35	130.78
10	156.00	132.60
11	151.50	131.17
12	152.11	131.04
13	154.56	131.66
14	151.38	131.14
15	151.58	130.98
16	155.11	131.17
17	153.14	130.89
18	154.82	131.12
19	151.22	130.65
20	153.18	136.51
21	151.24	130.71
22	151.52	130.78
23	156.10	131.30
24	151.56	130.61
25	156.90	131.19
26	151.18	130.54

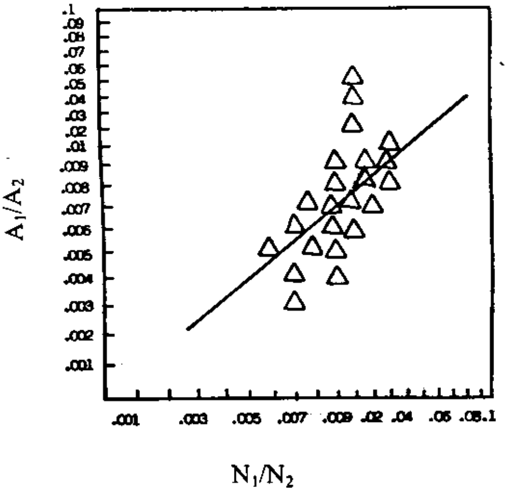

Fig. 1: Log-Log plot showing relation between N_1/N_2 and A_1/A_2

The second stage after the observance of visual correlation is to find the form of the relationship between the two variables leading to a meaningful equation. For this purpose, it is necessary to develop notation for each variable in the study. Hence, A_1, A_2, N_1 and N_2 are adapted for representation of aluminium oxide concentration, the mean percentage aluminium oxide concentration, sodium oxide concentration, respectively. In the presence of correlation, the equation which best fits (linear, exponential, power, logarithmic) the data was approximately determined.

Hence, various combinations of (A_1/A_2) and (N_1), (N_1/N_2) were established, and the values obtained by means of these combinations were plotted on logarithmic and semi-logarithmic scales.

Experimental results were plotted in different scales and it was seen that, the results could be generalized on double logarithmic plots. The data obtained for each of the aluminate solution samples were grouped around a straight line (Fig. 1). The equations representing a straight line can be expressed by the general equation $Lny = Lna+b.Lnx$. If the linear equation is represented by $y= a+bx$ where, $x= Lnx$, $y= Lny$ and $a= Lna$, the coefficients a and b can than be determined, by a set of simultaneous linear equations. Treatment of the data in Table 1 by standard regression leads to [11,12,13]:

$$y = 0.013 - 0.284\, x \qquad (1)$$

However, by considering reverse transformations from $x = \mathrm{Ln}\,(N_1/N_2)$ and $y= \mathrm{Ln}\,(A_1/A_2)$ equation (1) can be rewritten as,

$$\mathrm{Ln}\,(A_1/A_2) = 0.013 - 0.284\,\mathrm{Ln}\,(N_1/N_2)$$

or it can be shown in power form as

$$A_1/A_2 = 1.013\,.\,(N_1/N_2)^{-0.284} \qquad (2)$$

Thus aluminium oxide concentration in aluminate solution can be calculated by the following equation.

$$A_1/\,A_2 = 1.013\,.\,A_2\,.\,(N_1/N_2)^{-0.284} \qquad (3)$$

where, A_1 is the aluminium oxide concentration (g/l), A_2 is the mean aluminium oxide concentration (A_2 =130); N_1 is the sodium oxide concentration and N_2 is the mean sodium oxide concentration (N_2 = 150). Equation (3) is an empirical solution of aluminium oxide concentration for this study. The calculated concentrations from this equation and the results of experimental study are represented in Table 2. Relative errors are also included in Table 2. Inspection of this table shows that relative errors remain between 0.16 and 2.36 for most of the values. The average relative error is 0.85 %, which is less than the 5 % which is within the practically acceptable limits.

Experimental

Aluminate solution was provided from the alumina plant at Seydişehir, Turkey. 25 ml of aluminate solution was transferred to a 250-ml graduated flask and diluted to about 250 ml with distilled water. Analytical grade reagents were used for chemical analysis of the prepared sample.

Procedure for total Na_2O determination

10 ml of the diluted aluminate solution are transferred with a pipette to a 500-ml Erlenmeyer flask. Subsequently, 3 drops of phenolphtalein indicator solution are added and the solution was titrated with standard 0.5 N HCl solution. On the other hand, 10 ml of standard HCl solution was added to the mixture and diluted with about 200 ml distilled water. This mixture was boiled for 5 min and then titrated with standard 0.5 N NaOH solution using phenolphtalein indicator [8-10].

Table 2: Measured and calculated aluminium oxide concentration (g/l)

Sample No	Measured	Calculated	Relative error, percent
1	134.22	131.03	2.37
2	131.33	131.44	0.08
3	132.11	131.44	0.50
4	131.04	131.17	0.09
5	130.84	130.78	0.04
6	131.56	131.17	0.29
7	138.06	131.17	4.99
8	131.92	131.44	0.36
9	130.78	131.17	0.29
10	132.60	130.52	1.56
11	131.17	129.12	1.56
12	131.04	131.44	0.30
13	131.66	131.91	0.18
14	131.14	131.57	0.32
15	130.98	131.41	0.32
16	131.17	130.78	0.29
17	130.89	131.17	0.21
18	131.12	130.91	0.16
19	130.65	131.57	0.70
20	136.51	131.17	3.91
21	130.71	131.57	0.65
22	130.78	131.57	0.60
23	131.30	130.52	0.59
24	130.61	131.44	0.63
25	131.19	130.52	0.51
26	130.54	131.57	0.78

The total Na_2O concentration can be calculated from:

$$Na_2O\ (g/l) = (N_1V_1\text{-}N_2V_2)\,.\,(62/2)\,.\,100$$

where, N_1 = normality of HCl solution; V_1 = volume of HCl solution (l); N_2 = normality of NaOH solution; V_2 = volume of NaOH solution (l).

Procedure for Al_2O_3 determination

10 ml of the diluted aluminate solution was transferred to a 500-ml Erlenmeyer flask. 50 ml of distilled water and 6 drops of methylene blue-methylene yellow mixed indicator were added and the solution was titrated with standard HCl solution, to a colour change from green to purple. Subsequently, this mixture was heated to 80°C then cooled to room temperature. Hence, a uniform mixture was prepared for the following procedures whereby first

of all a certain volume, say, V_2 was diluted according to

$$V_2\,(\text{ml}) = 10\,(V_1 - V_{NaOH})$$

where, V_1 is the volume of 0.5 N HCl solution (in ml) required to titrate 10 ml of diluted solution and V_{NaOH} is the volume of 0.5 N HCl solution and (in ml) equivalent to Na_2O in 10 ml of diluted solution. After the addition of 2 drops of 0.5 N HCl solution to the indicator solution, the color changes from green to purple as already mentioned by various authors [8-10].

The Al_2O_3 concentration can be calculated from:

$$Al_2O_3\,(\text{g/l}) = (V_{HCl}\,.\,N_{HCl} - E_{NaOH})\,(102/6)\,.\,1000$$

where, V_{HCl} = total volume of HCl solution required to titrate 10 ml of diluted solution, N_{HCl} = normality of standard HCl solution; E_{NaOH} = equivalent weight of HCl equal to total sodium oxide in diluted solution.

Conclusions

Aluminium and sodium oxide concentrations play a significant role in different chemical processes. This paper presents a brief formulation between their concentrations and their mean concentrations a dimensionless power relationship. It is an empirical formulation based on the data obtained from alumina plant at Seydiþehir, Turkey. Through this mathematical relationship it is possible to estimate aluminium oxide concentration from other available data.

In this study a linear statistical model on a double logarithmic paper has been sought in order to depict the relationship between the sodium and aluminium oxide concentrations within the aluminate solution.

The following conclusions can be drawn from the explanations in the paper. First of all, the ratio of the aluminium oxide concentration (A_1) in the aluminate solution to the mean aluminium oxide concentration (A_2) was found to fit a linear function represented by plotting (A_1/A_2) versus (N_1/N_2) on double logarithmic paper. The relationship appears in the form of a power function as:

$$A_1 = 1.013\,.\,A_2\,.\,(N_1/N_2)^{-0.284}$$

Comparison of the calculated aluminium oxide concentration with the measured values should a relative error which lies between 0.16 and 2.36 for all but two of the calculations. This is less than the practically acceptable 5 % limit.

References

1. R.E. Kirk and D.E, Othmer, Encyclopedia of Chemical Technology, Vol. 1, Interscience Encyclopedia, New York, (1952).
2. S. Şahin, *J.Tech.Univ.*, **36**, 4, 1978
3. Vami, Report on the Scientific Research Work out of the Equipment Technological Flowsheet of Alumina Production from Turkish Bauxites of Doğankuzu and Mortaş Deposits, Leningrad, (1968).
4. W. Fulda und H.Ginsberg, Tonerde und Aluminium, Walter de Gruyter Co., Berlin, (1964).
5. G. Sigmond, K. Solymar and P. Toth, Chemical Background and Technology of Processing Bauxite to Alumina, Aluterv-fki, Budapest, (1979).
6. Gmelins Handbuch der Anorganischen Chemie, Aluminium, Teil: 1, Verlag Chemie, Veinheim, (1963).
7. S. Şahin, *Hydrometallurgy*, **44**, 1, (1997).
8. K. Solymar, J. Zoldi, A. Toth, I. Feher, and D. Bulkai, Manual for Laboratory, Vol. 8, Aluterv-fki, Budapest, (1979)
9. S. Şahin, *J.Tech.Univ.*, **48**, 2, (1990).
10. F. Snel and S. Hilton Encyclopedia of Industrial Chemical Analysis, Vol: 5, Interscience Publishers, New York, (1967).
11. S. Şahin, *J.Chem.Soc.*, **16**, 3 (1994).
12. R. Caulcutt and R. Boddy, Statistics for Analytical Chemistry, Chapman and Hall, (1983).
13. S. Sahin, *Hydrometallurgy*, **47**, 1, (1998).