

Correlation between Iron and Sodium Oxide Contents of Aluminum Hydroxide Samples

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Summary: It is necessary to consider carefully the economy of alumina production due to different chemical and mineralogical properties of aluminum hydroxide. A significant amount of cost can be saved by reducing the number of aluminum hydroxide sample analysis.

For this purpose, a linear relationship has been developed between the contents of sodium and iron oxide in the aluminum hydroxide. The main benefit from such a relationship is to predict the aluminum hydroxide content from rather cheaply obtainable sodium contents.

The application of this relationship has been demonstrated for alumina production at Seydisehir Alumina Plant in Turkey.

Introduction

Aluminum is the third most abundant element in the earth's crust after oxygen and silicon. It is a constituent of many common and relatively rare minerals and ores including feldspars, micas, kaolin, bauxite, corundum, spinel and turquoise. Furthermore, it is an amphoteric element, forming aluminum salts and aluminates. Aluminum finds important applications in the metallurgy of iron and steel [1].

Since each bauxite reserve has different chemical and mineralogical composition, the economical investigation of alumina production must be made according to the characteristics of individual reserve. It is the Bayer-technology that is used worldwide in the industrial processing of the bauxites [2].

The main objective of this paper is to obtain a relationship between sodium and iron oxide

contents in aluminum hydroxide by a conveniently developed statistical model based on the classical least squares technique.

Results and Discussion

The results of chemical analyses concerning aluminum hydroxide samples from Seydisehir plant are given in Table-1. In order to search for a relationship between the two variables i.e., Na_2O and Fe_2O_3 contents, primarily a scatter diagram from the data was prepared. Then the correlation between the two parameters was investigated. The best relationship, if available, is then sought from linear, exponential, power, and logarithmic functions for various combinations of (D_1/D_2) and (M_1/M_2) ratios, where D_1 and M_1 are iron and sodium contents, D_2 and M_2 are iron and sodium mean percentage contents, respectively.

Table 1: Chemical analyses of aluminum hydroxide (%)

Sample No.	Fe ₂ O ₃	Na ₂ O
1	0.023	0.330
2	0.022	0.400
3	0.026	0.370
4	0.021	0.370
5	0.024	0.430
6	0.024	0.330
7	0.021	0.370
8	0.021	0.390
9	0.022	0.330
10	0.030	0.495
11	0.021	0.330
12	0.021	0.330
13	0.021	0.340
14	0.022	0.330
15	0.021	0.324
16	0.021	0.321
17	0.021	0.327
18	0.021	0.317
19	0.021	0.321
20	0.027	0.432
21	0.022	0.390
22	0.021	0.327
23	0.021	0.330
24	0.021	0.327
25	0.021	0.320
26	0.021	0.321
27	0.021	0.327
28	0.021	0.321

The methodology employed for finding the convenient relationship is the classical least squares technique which is based on the minimization of sum of squared errors, (deviations of data points from the model).

Fe₂O₃ and Na₂O values in Table 1 are plotted on different papers such as ordinary, semi logarithmic and double logarithmic scales. The best linear relationship emerged on a double logarithmic scale as shown in Figure 1. It is to be remained therein that rather than using a double logarithmic paper the logarithms of both variables are plotted on an ordinary paper which is equivalent to using a double logarithmic paper in case of its absence.

The data obtained for each of the aluminum hydroxide samples are grouped around a straight line and remained in a narrow area. The equation representing the straight line can be expressed by the general equation.

$$\ln y = \ln a + b \ln x \quad (1)$$

where $x = M_1/M_2$ and $y = D_1/D_2$. It should be stated herein that D_1 and D_2 indicate actual and mean Fe₂O₃ contents whereas M_1 and M_2 are the contents of sodium oxide and its average value. If the linear equation is represented by

$$Y = c + bx \quad (2)$$

in which $X = \ln x$, $Y = \ln y$ ve $c = \ln a$ the coefficients c and b can then be determined by the following set of simultaneous linear equations. These equations can be found in any statistics textbook [9].

$$nc + \left(\sum_1^n X_i\right)b = \sum_1^n Y_i \quad (3)$$

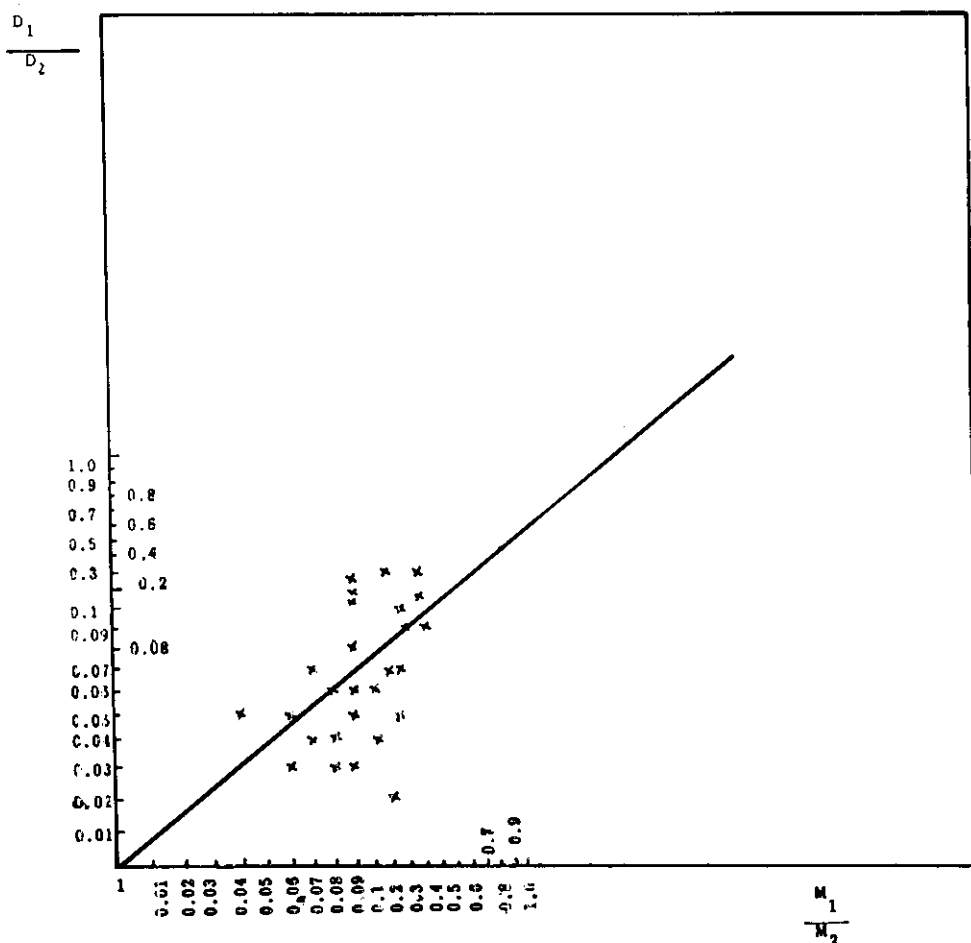
$$\left(\sum_1^n X_i\right)c + \left(\sum_1^n X_i^2\right)b = \sum_1^n X_i Y_i \quad (4)$$

The calculated X_i , Y_i results are given in Table 2.

The numerical values of the terms in the previous equations (3) and (4) are obtained from Table 2 as,

Table 2: The calculated X_i , Y_i results.

Sample No	X_i	Y_i	X_i^2	$X_i Y_i$
1	0.09	0.13	0.008	0.010
2	0.28	0.09	0.078	0.020
3	0.20	0.26	0.040	0.050
4	0.20	0.08	0.040	0.010
5	0.44	0.18	0.190	0.070
6	0.09	0.18	0.008	0.010
7	0.20	0.07	0.040	0.010
8	0.26	0.07	0.060	0.010
9	0.09	0.08	0.008	0.007
10	0.50	0.20	0.250	0.100
11	0.09	0.05	0.008	0.004
12	0.09	0.06	0.008	0.005
13	0.12	0.06	0.010	0.007
14	0.09	0.26	0.008	0.020
15	0.07	0.07	0.004	0.004
16	0.06	0.05	0.003	0.003
17	0.08	0.05	0.006	0.004
18	0.05	0.05	0.002	0.002
19	0.07	0.04	0.004	0.002
20	0.36	0.30	0.120	0.100
21	0.26	0.11	0.060	0.020
22	0.08	0.06	0.006	0.004
23	0.10	0.07	0.010	0.007
24	0.08	0.04	0.006	0.003
25	0.07	0.06	0.004	0.004
26	0.07	0.04	0.004	0.002
27	0.08	0.07	0.006	0.005
28	0.06	0.03	0.003	0.001

Fig. 1: Variations of M_1/M_2 vs D_1/D_2

$$n = 28, \sum_1^{28} X_i = 4.23, \sum_1^{28} Y_i = 2.85$$

$$\sum_1^{28} X_i^2 = 1.004, \sum_1^{28} X_i Y_i = 0.494$$

Coefficient c and b in expression (2) can be solved substituting the sums into Eqs. (3) and (4) which yields $c = 0.07$ and $b = 0.16$. As a consequence of these analyses, the experimental work is accumulated around a straight line as:

$$Y = 0.07 + 0.16 X \quad (5)$$

$$\text{Since, } X = \frac{\ln(M_1)}{M_2}, \quad Y = \frac{\ln(D_1)}{D_2} \quad (5)$$

$$\frac{\ln(D_1)}{D_2} = 0.07 + 0.16 \frac{\ln(M_1)}{M_2} \quad (6)$$

or it can be expressed in exponential form as:

$$D_1 = 1.07 \cdot D_2 (M_1)^{0.16} (M_2)^{-0.16} \quad (7)$$

where the averages are $D_2 = 0.02$ and $M_2 = 0.3$. After having developed the suitable statistical model as in equation (7) it is possible to predict iron oxide or the sodium oxide content of the aluminum hydroxide samples. This work eliminates the actual determination of either of the two components if the percentage of one of the two components is determined experimentally.

Experimental

Aluminum hydroxide is obtained from Alumina Plant in Seydisehir, Turkey. For this purpose, the Bayer process has been employed by crushing the bauxite. Wet grinding procedure is applied in the presence of the digesting liquid at a pressure of 1 to 40 atmospheres at temperatures

100° to 250° C or even higher. The dilution of slurry has been obtained after digestion. The separation of the non-digested residue has been achieved by settling and washing in counterflow decantation followed by filtration. Finally, purification of the saturated sodium aluminate solution by filtration, cooling and decomposition in the presence of seed alumina has been performed. The subsequent steps are filtration, washing of the product, and calcination at 1100° C, [2,3,4]. The sodium oxide analyses has been performed as explained in the literature [5,6,7].

First of all, 0.5 g of aluminum hydroxide is transferred into a 30 cm³ platinum crucible. Subsequently, 5 cm³ of 1:10 sulfuric acid and 15-20 cm³ hydrofluoric acid are added. This mixture is heated for about 2 hours. The lid is rinsed with water and evaporated to dryness at low heat.

In the mean time, 20-25 cm³ of warm water is added until all soluble salts have dissolved. The solution is transferred to a 100 cm³ flask and latter diluted full volume. A sufficient amount of sodium is filtered for further analyses through dry ashless filter paper.

Sodium contents of the samples are determined by flame photometer readings using the calibration curve which was constructed for photometer responses of standard solutions.

Iron oxide analyses have been carried out according to standard methods explained in the literature [5,6,8].

A stock iron solution is prepared by dissolving 0.1 g of iron wire in 50 cm³ of 1:3 nitric acid. The solution is boiled to extract nitrogen oxides after the completion of dissolving procedure and it is diluted to 1000 cm³ with distilled water. Later, 20 cm³ of this main solution is transferred into a 100 cm³ volumetric flask with 10 cm³ of 1:1 hydrochloric acid.

For calibration six standard iron solutions are prepared by diluting 0, 1, 2, 4, 8 and 12 cm³ volumes of stock solution to 100 cm³ after treating with 1 cm³ of 1:1 hydrochloric acid and 2 cm³ of 1 % hydroxylamine hydrochloride. The pH values have been adjusted between 4 and 6. In the mean time, 1:1 ammonium hydroxide solution and 4 cm³

Table 3: Measured and calculated iron oxide content (%)

Sample No.	measured	calculated	difference	relative error in percent
1	0.023	0.022	0.001	4.34
2	0.022	0.022	0.00	0.00
3	0.021	0.022	-0.001	4.76
4	0.024	0.022	0.002	8.33
5	0.021	0.021	0.00	0.00
6	0.021	0.022	-0.001	4.76
7	0.021	0.021	0.00	0.00
8	0.022	0.022	0.00	0.00
9	0.021	0.021	0.00	0.00
10	0.021	0.021	0.00	0.00
11	0.021	0.021	0.00	0.00
12	0.022	0.022	0.00	0.00
13	0.021	0.021	0.00	0.00
14	0.021	0.021	0.00	0.00
15	0.021	0.021	0.00	0.00
16	0.021	0.021	0.00	0.00
17	0.021	0.021	0.00	0.00
18	0.021	0.021	0.00	0.00
19	0.021	0.021	0.00	0.00
20	0.022	0.022	0.00	0.00
21	0.021	0.021	0.00	0.00
22	0.020	0.021	-0.001	5.00
23	0.021	0.021	0.00	0.00
24	0.021	0.021	0.00	0.00

of 0.25 % *o*-phenanthroline solution are also used. After 5-10 min, the absorbance of each solution is measured at 510 nm wave length versus the blank on a Spectrophotometer leading to the calibration curve.

About 2 g of sample is weighed in a 100 cm³ beaker. For analyses, 50 cm³ of water is added, boiled and filtered through Whatman No: 40 filter paper with washing. The volume of the sample is kept below 90 cm³ after treating with 2 cm³ of 1 % hydroxylamine hydrochloride solution for further dilution. The solution is then treated with 4 cm³ of 0.25% *o*-phenanthroline solution and transferred into a 100 cm³ volumetric flask following dilution and mixing. After 5 to 10 min, the absorbance corresponding to 510 nm is measured. The amount of iron is determined from the calibration curve.

Conclusions

During the Bayer process, not all the impurities precipitate but are partly dissolved in the caustic liquor during the digestion and stay in the aluminum hydroxide to a certain limit concentration [10].

A linear statistical model has been sought in order to depict the relationship between the iron oxide and sodium oxide contents within the aluminum hydroxide. However, in the ordinary scale such a logarithmic relationship becomes an exponential function relating the ratio of the iron oxide content (D_1) in the aluminum hydroxide to the mean percentage iron oxide content (D_2). Consequently, an empirical equation is obtained for the problem studied in this work based on Seydosejor data in Turkey as.

$$D_1 = 1.07 D_2 (M_1)^{0.16} (M_2)^{-0.16}$$

Comparison of the calculated iron oxide contents from this model shows that most of the predicted values are close to analytical results within the 5 % relative error.

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