Hydrogen Bonding Adsorption Principle in Caustic Solution of Aluminium Hydroxide

Meng Ling-li[1] and Zhang Li[2]
1,2. Process Engineers
Zhengzhou Non-ferrous Metals Research Institute of Chalco (ZRI), Zhengzhou, China
Corresponding author: qintian4666@163.com
https://doi.org/10.71659/icsoba2025-aa007

Abstract

In this paper, the concept of hydrogen bonding adsorption was investigated for $Al(OH)_3$-NaOH-H_2O-S (solid) system. Aluminium hydroxide transfer between solid and liquid phase by hydrogen bonding adsorption and desorption, only with hydrogen bond breaking or formation of aluminium hydroxide crystal. When the $Al(OH)_3$-NaOH-H_2O-S (solid) system achieves equilibrium, this is due to hydrogen bonding adsorption. Equilibrium equation of the system was obtained, $CE = 90\ S^{-0.1}N^{1.5}\cdot\exp(-18522.9/(R\cdot T))$. No chemical reaction occurs when aluminium hydroxide dissolves in caustic solution process or crystallises in a seeded precipitation process. In the liquid phase, alumina is in the form of $Al(OH)_3$, rather than $Al(OH)_4^-$. In this concept, supersaturation does not exist in sodium aluminate solution.

Keywords: Bayer process, Solubility, Hydrogen bonding, Phase equilibrium, Seed precipitation.

1. Introduction

Bayer process was born more than one hundred years, The basic principle of Bayer process is established on the Na_2O-Al_2O_3-H_2O system, according to the generally accepted theory, alumina exists in form of $Al(OH)_4^-$ or two poly-aluminate ions in caustic solution. Alumina concentration in caustic solution depends on the solubility, where seeded precipitation process is a chemical reaction, which eventually stops when alumina solubility is reached. However, according to this theory, the super saturation phenomenon is difficult to explain, even it is thought that spent liquid is supersaturated. Researchers have attributed this to the complex structure of $Al(OH)_4^-$ in caustic solution, still there is no reasonable results supporting this up to now.

Researching on the basic principles of the Bayer process is important to the alumina industry, also it is of great significance to improve the quality of the products. In this paper, the principle of hydrogen bonding adsorption was adopted on Al $(OH)_3$-NaOH-H_2O-S (solid) system.

2. Experiment

A series of experiments were conducted to study various aspects of the crystallisation phenomena, such as the effect of temperature, solid concentration and caustic concentration.

2.1 Experimental Materials

Aluminium hydroxide: grade AH-1 GB/T 4294-2010, specific surface area: 0.104 m^2/g. Caustic: chemical pure.

Table 1. Size distribution of aluminium hydroxide.

Size, µm	10	15	20	30	40	50	60	80	120	150	200
%	0.91	3.53	5.80	8.29	11.16	16.69	24.83	44.57	77.91	91.18	99.22

2.2 Experimental Instrument and Analysis

A 5 L stainless steel container was used, with stirring, automatic temperature control of ± 0.1 °C. Laser particle size was analyzed using a Mastersizer 2000 instrument.

2.3 Experimental Operation

2.3.1 The Relationship Between the End Alumina Concentration and Temperature

Sodium aluminate solution 5 L, caustic concentration Na_2O 100 g/L, alumina concentration Al_2O_3 80 g/L, heated to 60 °C. Dried aluminium hydroxide 3 kg was added to the sodium aluminate solution, stirring. After 50 hours, the slurry was separated, analysis alumina concentration, sampling once every 5 hours. Three of difference of alumina concentration is less than 0.5 g/L, that reach the end, three results mean as the end of alumina concentration. Then cooling to 55, 50 and 45 °C, repeated sampling.

2.3.2 Relationship Between the End Alumina Concentration and the Amount of Solid Aluminium Hydroxide

Sodium aluminate solution 5 L, caustic concentration Na_2O 100 g/L, alumina concentration, Al_2O_3 80g/L, temperature 50 °C. Respectively, adding dried aluminium hydroxide 2, 3, 4 and 5 kg. Sampling was the same as described in 2.3.1.

2.3.3 The Relationship between the End Alumina Concentration and Caustic Concentration

Sodium aluminate solution 5 L, caustic concentration Na2O 120, 110, 100, 90 g/L, alumina concentration Al_2O_3 90 g/L, temperature: 50 °C. 3 kg dried aluminium hydroxide was added to the sodium aluminate solution, stirring. Sampling was the same as described in 2.3.1.

3. Results and Discussion

Alumina concentration at the end under the different conditions are shown in Table 2.

Table 2. Alumina concentration at the end under different conditions.

No.	N, g/L	W, g/L	T, °C	C, g/L
1	100	600	60	74.2
2	100	600	55	67.5
3	100	600	50	60.6
4	100	600	45	54.5
5	100	1000	50	57.3
6	100	800	50	58.6
7	100	400	50	62.2
8	120	600	50	79.1
9	110	600	50	69.3
10	90	600	50	51.2

N: caustic (Na_2O) concentration; W: solid content; T: temperature; C: end alumina (Al_2O_3 concentration,

3.1 Relationship between the End Alumina Concentration and Temperature

The end alumina concentration C of the experiment1, 2, 3, 4 were taken logarithm ln(C), temperature 1/T (Kelvin temperature), mapping, Figure 1.

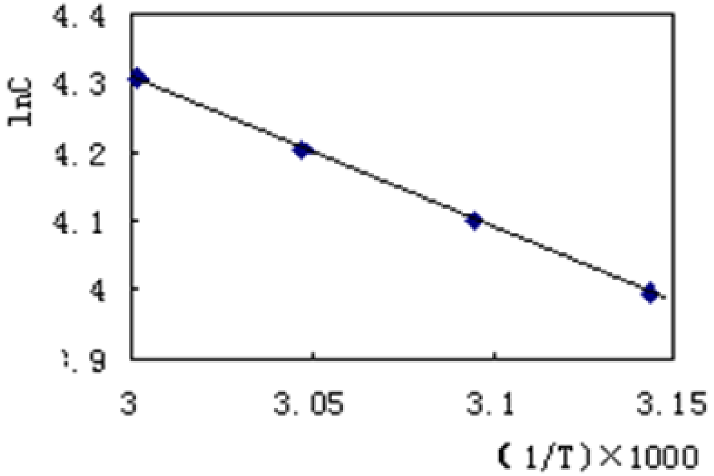

Figure 1. Logarithmic relationship between Temperature (1/T, Kelvin) and the end alumina concentration ln(C).

The linear relationship of the end alumina concentration, ln(C) and temperature 1/T (Kelvin temperature) was good, the slope was of 2227.8. The relationship between the end alumina concentration and temperature was expressed in the form (1):

$$\ln(C) = -2227.8 / T + 10.99 \tag{1}$$

or:

$$C = 59528.8 \exp(-18522.9 / (R \cdot T)) \tag{2}$$

Equation (1) can be rewritten as:

$$\ln(C) = -18522.9 / (R \cdot T) + 10.99 \tag{3}$$

After a long time, the alumina concentration in solution does not change, the system can be thought as being in equilibrium. According Clausius-Clapeyron Equation (4)

$$\ln(C) = \triangle H_m / (R \cdot T) + K \tag{4}$$

In the representation $Al(OH)_3$-NaOH-H_2O-S (solid) system, solid aluminium hydroxide is adsorbent, adsorbate is the aluminium hydroxide. The molecule on solid surface of aluminium hydroxide crystal can be considered as adsorption layer. With alumina in liquid phase continuously precipitating to the solid surface, adsorption layer is continuously changing, but the outer molecular number of aluminium hydroxide on solid remains unchanged, so the surface adsorption amount is a fixed value. Equation (3) completely satisfies the Equation (4), so Equation (3) can be thought as a Clausius-Clapeyron equation. Thus, it can be concluded that the system reaches equilibrium, the system constitutes a two-phase equilibrium system. Differential adsorption enthalpy $\triangle H_m = -18522.9$ J/mol, and the H-O···H hydrogen bond energy of 18850 J/mol are basically consistent, which indicates that the $Al(OH)_3$ transfer between solid and liquid phase through hydrogen bonding adsorption, excluding the formation of ionic bond, covalent and coordination bond. And, in aluminium hydroxide crystal, layers are bonded through hydrogen bonding, that is consistent with the breakage and formation of hydrogen bond when aluminium hydroxide dissolve and precipitate, each 1 mol aluminium hydroxide dissolved or precipitated with 1 mol hydrogen bond breaking or formation, no other bond formation or rupture. The adsorption process is an exothermic process and is consistent that seeded precipitation is exothermic process. So, it can be concluded, aluminium hydroxide molecule in the crystalline state and in solution only has the difference of one hydrogen bond, which is formed in the crystallization of aluminium hydroxide, no other difference. Further inference, in the liquid phase, alumina is in form of $Al(OH)_3$, rather than $Al(OH)_4^-$.

3.2 Relationship Between the End Alumina Concentration and the Amount of Solid Aluminium Hydroxide

The amount of solid aluminium hydroxide in system is expressed in surface area S, m^2/L. The end alumina concentration, C, of the experiment 5, 6, 3 and 7 were expressed in logarithm ln(C), the amount of solid aluminium hydroxide in the system, versus ln(S) is shown in figure 2.

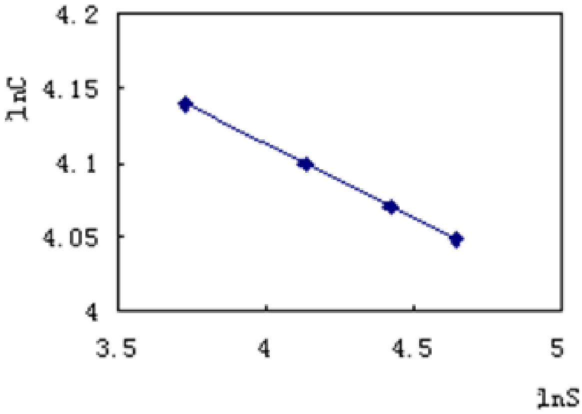

Figure 2. Logarithmic relationship between the end alumina concentration (C) and solids surface area (S).

The end alumina concentration, ln(C), and solid aluminium hydroxide, ln(S), also showed a linear relationship, with a slope of –0.1. So the equation can be rewritten as follows:

$$\ln(C) = -0.1 \ln(S) + 4.513 \quad (5)$$

or:

$$C = 91.24 \cdot S^{-0.1} \quad (6)$$

It can be considered that the alumina concentration is related to the amount of solid aluminium hydroxide. By the discussion in section 3.1, the system achieves equilibrium, the amount of solid phase will affect the system state, a certain amount of the solid phase (seed) coincides with the composition of the liquid phase. Namely, alumina concentration in liquid phase corresponds with the amount of solid content, it does not determine the "solubility". In the actual factory, the larger amount of solid phase (seed) gives a higher seeded precipitation rate, this phenomenon coincides with the liquid-solid adsorption equilibrium, this phenomenon is strong evidence of liquid-solid adsorption equilibrium.

3.3 Relationship Between the End Alumina Concentration and Caustic Concentration

The end alumina concentration C of experiments 8, 9, 3, 10 were expressed in logarithm ln(C), caustic concentration, ln(N), as shown in Figure 3.

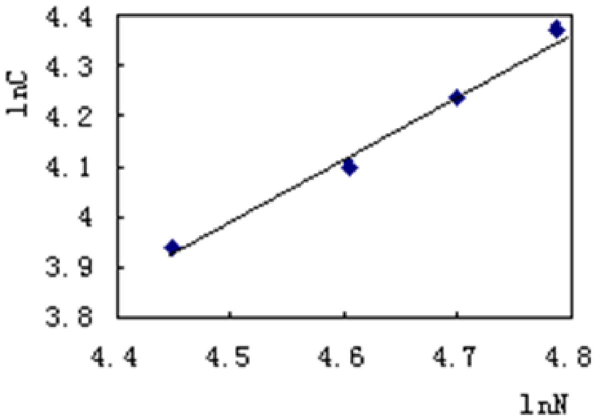

Figure 3. Relationship between the end alumina concentration and caustic concentration.

A linear relationship also was obtained between the end of alumina concentration ln(C) and caustic concentration ln(N)

$$\mathrm{Ln}(C) = 1.5\cdot\ln(N) - 2.8075 \tag{7}$$

or:

$$C = 0.0603\cdot N^{1.5} \tag{8}$$

Combining the Equations (2) (6) (8), gives us an equation of alumina concentration as a function of temperature, solid content and caustic concentration:

$$CE = 90\ S^{-0.1}\cdot N^{1.5}\cdot \exp(-18522.9 / (R\cdot T)) \tag{9}$$

When the system reaches equilibrium, the solid phase (seed) and liquid phase form hydrogen bond adsorption-desorption equilibrium system. Any one of the factors in the system will affect the equilibrium system. When temperature and caustic concentration are constant in the system, alumina concentration in liquid phase is affected by the solid content. Balance is not fixed, which changes with the solid content. This is the reason why alumina "solubility" cannot be measured accurately, ignoring the solid effect, Aluminium hydroxide and the amount researchers used in the determination of "alumina solubility" are not the same, so the numerical value of "solubility" is different.

4. Experimental Verification

Adsorption equilibrium Equation (9) shows, at the same concentration and temperature, a "sodium aluminate solution" with solids, the system state can be in a desorbed state (aluminium hydroxide dissolves) in the case of less solid content, also can be in an adsorbed state (precipitation) in the case of more solid content. For example, the caustic concentration Na_2O 100 g/L, alumina concentration Al_2O_3 110 g/L, temperature 90 °C, the system is in a desorption state, when the solid content expressed in surface area is 20 m^2/L, solid aluminium hydroxide will dissolve. However, the system is in the adsorbed state when the solid content is 70 m^2/L, alumina in liquid will precipitate. As shown in Figure 4, the A-B line with the caustic concentration of Na_2O 100 g/L, temperature 90 °C, it is the balance line of alumina concentration in liquid phase between solid content. The system is in equilibrium along the A-B curve. When the system status is just above the A-B curve, the adsorption rate is greater than desorption rate, alumina solution will precipitate. When the system status is below A-B curve, the desorption rate is greater than the adsorption rate, solid aluminium hydroxide will dissolve.

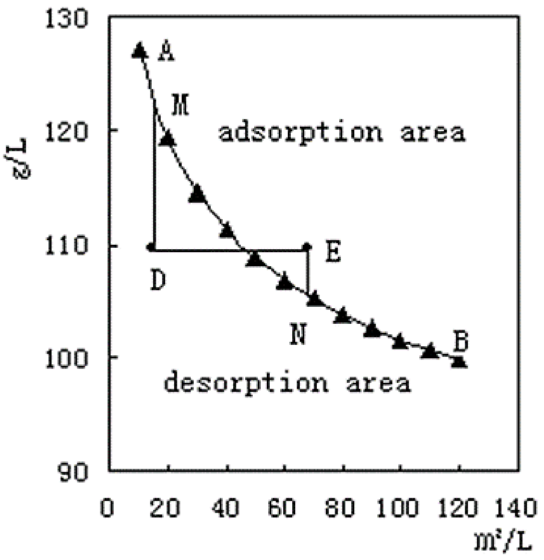

Figure 4. Equilibrium curve and two kinds of status at various solid content.

4.1 Confirmatory Experiment

With the following sodium aluminate solution: caustic concentration Na_2O 100 g/L, alumina concentration Al_2O_3 113 g/L, molar ratio 1.45 (moles Na_2O / moles Al_2O_3). Respectively, two 1 L solution were in sealed containers with agitation, at a temperature 90 °C, adding aluminium hydroxide, experiment D 30 g, experiment E 800 g. Sampling and analysis 8 hours later, the experiment D showed Al_2O_3 118 g/L and molar ratio 1.40, indicating that part of the aluminium hydroxide had dissolve. However, the experiment E showed Al_2O_3 108 g/L and a molar ratio of 1.51, suggesting that alumina precipitated from the solution.

From the above results, although the two solutions have the same initial composition and stays at the same temperature, when the solid content is lower the aluminium hydroxide dissolves. Conversely, at a higher solid content, alumina precipitates from solution. The experimental results prove the inference based on the hydrogen bonding adsorption principle of aluminium hydroxide in caustic solution. This phenomenon cannot be explained according to the solubility theory. Therefore, solubility has nothing to do with the solid content.

5. Conclusion

The main conclusions of this work are that aluminium hydroxide transfers between solid and liquid phase through hydrogen bonding adsorption and desorption, without chemical reaction in the process of aluminium hydroxide dissolved in caustic solution or seeded precipitation, only with hydrogen bond breaking of aluminium hydroxide crystals.

Also, when the system achieves balance, the equilibrium is based on hydrogen bond adsorption.

Furthermore, in the liquid phase, alumina is in form of $Al(OH)_3$, rather than $Al(OH)_4^-$.

And finally, the supersaturation phenomenon of “sodium aluminate solutions” does not exist, according to the findings of this work.

6. Reference

1. Li Xiao-bin et al., Research progress in theory and technology of gibbsite precipitation from sodium aluminate solution, *Chinese Journal of Nonferrous Metals*, 2011, Vol.21, No10
2. Meng Ling-li, Study on dissolution kinetics of the aluminium hydroxide in the caustic soda, *Light Metals*, 2012, Vol.9 (in Chinese).
3. Huang Zhen-qian and Hu Nan-yuan, *Physical Chemistry*. Changsha: Central South University Press, 1991:258-285
4. Bi Shi-wen and Yu Hai-yan, *Alumina production process*, Beijing: *Chemical Industry Press*, 2006, 78-90
5. Zhang Ying et al., Preparation and Characterization of $Al(OH)_3$ Coarse Particles by Decomposition of Caustic Aluminate Solution with Methanol, *The Chinese Journal of Process Engineering*, 2009, Vol.9, 300-305
6. S. Scott Fogler, *Elements of Chemical Reaction Engineering,* Beijing: *Chemical Industry Press*, 2006, 80-141
7. C. Misra and E.T. White, *Chemical Engineering Progress Symposium*, 1970, 67(11):53
8. C. Misra and E.T. White, *Journal of Crystal Growth*, 1971, 8, 172
9. Bi Shi-wen, Xue Hong and Yang Yi-hong, Kinetics of decomposition of Bayer sodium aluminate solution, *The Chinese Journal of Nonferrous Metals*, 1998, 8(1), 131-134
10. Li Xiao-bin et al., Kinetics of carbonation decomposition of sodium aluminate solution. *Chinese Journal of Nonferrous Metals*, 2004, 14(5):850-853
11. Li Xiao-bin et al., Thermodynamics of carbonization of aluminate solution, *Chinese Journal of Nonferrous Metals*, 2003, 13(4):1005-1010
12. Fang Jing-dong,Wu Su-fang and Wang Zhang-mao, The studies of decomposition reaction of sodium aluminate solution, *Journal of Chemical Engineering of Chinese Universities*, 2002, 16(1):33- 37
13. I. V. Davidov et al., Optimization of temperature condition of the liquor decomposition process, *Light Metals*,1976,1:173
14. S. Veesler and R. Boistelle, Growth kinetics of hydrargillite Al(OH)3 from caustic soda solution, *Crystal Growth*, 1994, 142:177
15. Li Jie, Study on the structure character and decomposition mechanisms of supersaturation of sodium aluminate solutions, *Changsha, Central South University*, 2002
16. P. Smith and G. Woods, The measurement of very low growth rates during the induction period in aluminum hydroxide growth from Bayer liquors, *TMS Light Metals,* 1993:113-117
17. C. Misra, Solubility of aluminum hydroxide (hydrargillite) in sodium hydroxide solutions, *Chemistry and Industry*, 1970, (20):157
18. Li Jia-zheng, Sun Jiang-xiao and Shi Zuo-qing, Hydrogen Binding Adsorption and its Prospect, *Ion Exchange and Adsorption*, 2001, 17(6):561-566
19. Huang Jian-gou et al., A thermodynamic study on adsorption of phenols onto D301 resin. *Ion Exchange and Adsorption*, 2003, 19(1):37-42
20. Chen Xiao-hu at al., The mathematic model of the pregnant aluminate precipitation, *Journal of Guizhou University Technology*, 2002, 31(5):22-24