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Phase Diagram for the $Na_2O-Al_2O_3-H_2O$ System at 130 °C

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A phase diagram for the $Na_2O-Al_2O_3-H_2O$ system at 130 °C is presented in this paper using Schreinemaker's method. The compositions of the clear liquid and the wet solids were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The equilibrium solids are aluminum hydroxide ($Al_2O_3{\cdot}H_2O$), sodium aluminum hydroxide ($Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$), and sodium aluminum oxide ($Na_2O{\cdot}Al_2O_3$) in the different alkali concentration regions.

Introduction

Alkali processing methods, especially the Bayer process, have played a very important role in the production of alumina for more than 100 years.[1,2] It is well-known that the phase diagram is the theoretical foundation of the process.[3,4] The phase diagrams of the $Na_2O-Al_2O_3-H_2O$ system at (30, 60, 95, 150, and 200) °C have been studied by many authors.[5] However, the studies are not complete, especially the equilibrium crystalline phases in the high-alkali region at (150 and 200) °C are not identified.[5] Recently, Zhang et al. studied this system in the high-alkali regions at (95 and 110) °C in order to develop a new digestion process for diasporic bauxite.[6] The identified equilibrium solids are $Al(OH)_3$ and/or AlOOH in the low-alkali concentration region, but sodium aluminates (or hydrate), such as $Na_2[Al_2O_3(OH)_2]{\cdot}1.5H_2O$ and $3Na_2O{\cdot}Al_2O_3{\cdot}6H_2O$, have been identified in the high-alkali concentration region.

Because of the shortage of bauxite with a high ratio of alumina to silica (A/S), the A/S of the bauxite is getting lower for producing alumina, especially in China. For processing low A/S bauxite, a flotation-Bayer process is industrialized in China. The key of the flotation-Bayer process is increasing the A/S of the bauxite by the flotation method, but the efficiency of the bauxite is not high because of the disposal of large gangue.[7,8] In addition, a high-pressure hydrothermal chemical method and a high-alkali atmospheric digestion process were developed to process the low A/S bauxite, which shows great prospect.[9,10] These two processes both include the crystallization operation of sodium aluminate to separate the excess sodium hydroxide, which theoretically is based on the phase diagrams in the high-alkali region for the $Na_2O-Al_2O_3-H_2O$ system. Fricke and Jucaitis first studied the composition of sodium aluminate hydrate appearing in this region and identified an equilibrium crystalline phase (i.e., $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$) by adopting Schreinemaker's method.[11] By employing the XRD technique, Weinberger and other researchers drew the same conclusion and clarified the controversies on the composition of the solid.[12,13]

Recently, by using an iodide ion tracing method, Qiu and Chen found that there is another new equilibrium solid in the high-alkali region (i.e., $4Na_2O{\cdot}Al_2O_3{\cdot}12H_2O$) for the $Na_2O-Al_2O_3-H_2O$ system at 30 °C besides $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$.[14] Zhang et al. reported four equilibrium solid phases, including $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$, $4Na_2O{\cdot}Al_2O_3{\cdot}12H_2O$, $6Na_2O{\cdot}Al_2O_3{\cdot}12H_2O$, and $Na_2O{\cdot}H_2O$ in the high-alkali region of the $Na_2O-Al_2O_3-H_2O$ system at 95 °C. They also found that the equilibrium solid of $4Na_2O{\cdot}Al_2O_3{\cdot}12H_2O$ disappeared when the temperature increased to 110 °C.[6]

As the temperature has significant influence on the composition of equilibrium crystalline and there are no published research results for the $Na_2O-Al_2O_3-H_2O$ system in the high-alkali region at 130 °C, which is the initial crystallization temperature of sodium aluminate in the high-alkali atmospheric digestion process, the phase diagram for the $Na_2O-Al_2O_3-H_2O$ system at 130 °C, especially in high-alkali region, is further investigated in this paper using Schreinemaker's method.

Experimental Methods

To avoid sodium hydroxide contamination of glass or iron components of the reactor, the equilibration experiment in this study was conducted in a polytetrafluoroethylene reactor referencing the method of Meller et al.[4] The supersaturated sodium aluminate solutions were prepared by dissolving aluminum trihydroxide in hot caustic solutions, first prepared by dissolving sodium hydroxide in superpurified water. The total composition of the supersaturated solution was near to its solubility limit. The hot solution was rapidly filtered through a 0.22 μm pore-size membrane and then loaded into a polytetrafluoroethylene cup, 4 cm in diameter by 9 cm in height. The holders were sealed and placed in an oven at 130 ± 1 °C. The rotation speed of the holders in the oven was set at about 130 rpm. In addition, several solutions were obtained by dissolving sodium aluminate in hot caustic solutions in order to identify the equilibration of the process.

By comparing the composition of the solution made by different materials (aluminum hydroxide or sodium aluminate) in the holders every other week, the equilibrium state was determined. Once the system was in equilibrium, the holder was removed from the oven and cooled rapidly. After that, the cup was taken out of the holder. The clear liquid and wet solid were sampled for the analysis of their compositions by inductively coupled plasma atomic emission spectrometry (ICP-AES). The

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Table 1. Equilibrium Data of the $Na_2O-Al_2O_3-H_2O$ System at 130 °C[a]

sample no.	composition of initial solution (wt %)		composition of liquid phase(wt %)		composition of wet solid phase (wt %)		equilibrium crystalline phases
	Na_2O	Al_2O_3	Na_2O	Al_2O_3	Na_2O	Al_2O_3	
1	5.86	7.18	6.05	3.40			A
2	11.33	13.36	2.32	9.34			A
3	16.69	22.05	17.68	19.00			A
4	19.57	25.18	20.44	23.90			A
5	23.72	35.37	22.54	29.43 (K)			A + B
6	26.36	24.60	25.78	15.15	26.98	30.63	B
7	28.90	22.01	28.86	14.11	28.55	28.55	B
8	29.40	23.40	29.05	14.91	29.08	25.22	B
9	34.63	19.03	36.71	8.17	32.38	29.74	B
10	36.27	19.02	37.71	7.48 (E)	35.80	29.51	B + C
11	39.27	8.90	39.45	5.78	39.31	16.20	C
12	45.13	6.51	45.43	2.67	44.11	13.14	C
13	46.88	4.66	7.25	1.96	46.71	8.16	C
14	51.36	4.98	52.16	0.94	50.12	10.51	C
15	53.83	10.84	56.74	0.62	54.56	6.83	C
16	59.81	4.98	61.45	0.38 (F)	60.64	7.85	C + D
17			61.42	0.00 (G)	61.42	0.00	D

[a] A, B, C, and D represent the solids of AlOOH, $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$, $Na_2O{\cdot}Al_2O_3$, and NaOH, respectively. A combination of symbols (such as A + B) means that the compounds coexist.

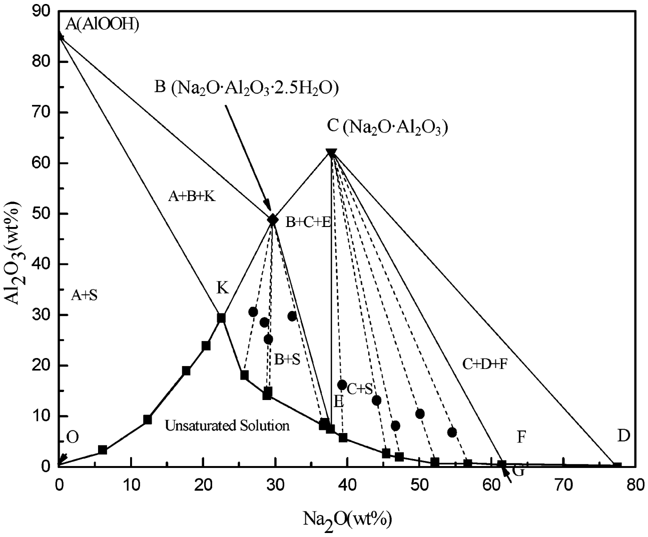

Figure 1. Phase relations for the $Na_2O-Al_2O_3-H_2O$ system at 130 °C. A, $Al_2O_3{\cdot}H_2O$; B, $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$; C, $Na_2O{\cdot}Al_2O_3$; D, NaOH; E, three-phase point; F, three-phase point; G, solubility of Na_2O in pure water at 130 °C; K, three-phase point; S, saturated sodium aluminate solution; O, the solubility of alumina in pure water at 130 °C. A combination of symbols (such as A + S) means that the items coexist. OK, KE, EF, and FG indicate the compositions of saturated ternary solutions that are in equilibrium with the solids $Al_2O_3{\cdot}H_2O$ (A), $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$ (B), $Na_2O{\cdot}Al_2O_3$ (C), and NaOH (D), respectively. Thick solid lines are tie-lines between coexisting phases. The dashed lines connect the compositions of saturated solution with the corresponding wet solid.

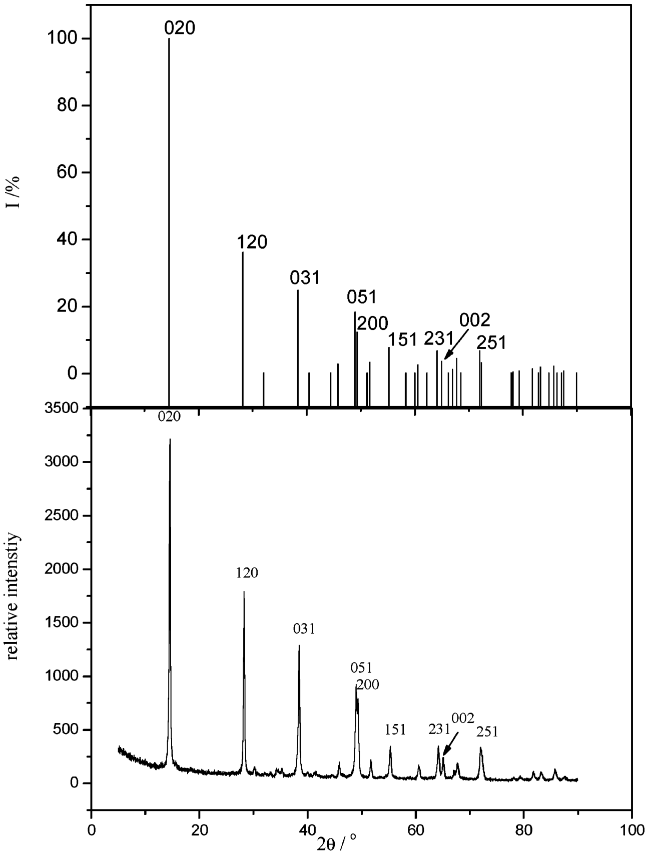

Figure 2. ICDD pattern of boehmite (above) and XRD pattern of crystalline in the low-alkali region (below) showing the presence of boehmite with good crystallinity (tall, narrow peaks).

wet solid was washed by ethanol or pure water and then dried at 100 °C for at least 10 h. The structure of solid was identified by X-ray diffraction (XRD) with a Japan Rigaku D/max-2400 X-ray diffractometer with Cu Kα radiation. All samples were scanned over a (5 to 90)° 2θ range. Some duplicate solutions show that the results are reproducible.

Results and Discussion

The experimental results are summarized in Table 1 and shown graphically in Figure 1. In Figure 1, points A, B, C, and D represent the solids $Al_2O_3{\cdot}H_2O$, $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$, $Na_2O{\cdot}Al_2O_3$, and NaOH, respectively. Points O, K, E, F, and G are all located on the saturated liquid line. Point O on the ordinate of the diagram represents the solubility of alumina in pure water at 130 °C, and point G on the abscissa shows the solubility of Na_2O in pure water at 130 °C, with 61.42 wt % of Na_2O.

Curves OK, KE, EF, and FG indicate the compositions of saturated ternary solutions that are in equilibrium with the solids $Al_2O_3{\cdot}H_2O$ (A), $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$ (B), $Na_2O{\cdot}Al_2O_3$ (C), and NaOH (D), respectively. Area ABKA is a three-phase region of coexisting $Al_2O_3{\cdot}H_2O$ (A), $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$ (B), and saturated solution (K); area BCEB is for $Na_2O{\cdot}Al_2O_3{\cdot}2.5H_2O$ (B), $Na_2O{\cdot}Al_2O_3$ (C), and saturated solution (E); area CDFC is for $Na_2O{\cdot}Al_2O_3$ (C), NaOH (D), and saturated solution (F), respectively. K, E, and F are three invariant points whose compositions are shown in Table 1. The area above line ABCD is the all-crystalline phase region, and below the saturated liquid line OKEFG is the unsaturated sodium aluminate solution region.

Compared with the phase diagram for the $Na_2O-Al_2O_3-H_2O$ system at lower temperature,[6] this diagram at 130 °C shows $Al_2O_3 \cdot H_2O$ (A) but not $Al_2O_3 \cdot 3H_2O$ to be the equilibrium crystalline in the diluted sodium aluminate solution (the weight concentration of Na_2O is less than 22.54 %). The crystalline phase was further identified as boehmite by X-ray diffraction analysis whose pattern is shown in Figure 2. This crystalline phase is the same as the one at (150 and 200) °C in the low-alkali region.[5]

In the high-alkali region (the weight concentration of Na_2O is more than 22.54 %) for the $Na_2O-Al_2O_3-H_2O$ system at 130 °C, one of the equilibrium crystalline phase is still $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$, which can be seen from Figure 1. The phase area of $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ at 130 °C is narrower than that of the Zhang et al. results[6] at 110 °C. Besides, the other sodium aluminate—$Na_2O \cdot Al_2O_3$—is observed when the weight concentration of Na_2O is more than 37.71 %, which implies that the area of CEF involving the equilibrium crystalline $Na_2O \cdot Al_2O_3$ (C) would be broader at higher temperature. Obviously, both straight lines connecting $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B) and $Na_2O \cdot Al_2O_3$ (C) to the original point in the diagram do not cut their corresponding saturation curves, which indicates that the two sodium aluminates decompose in the presence of water at the experimental temperature of 130 °C.

Conclusions

Phase relations for the $Na_2O-Al_2O_3-H_2O$ system at 130 °C were investigated in the present study. In the low-alkali region (the weight concentration of Na_2O is less than 22.54 %), boehmite was shown to be the equilibrium crystalline phase, which is different from that at 95 °C identified as gibbsite by Fricke and Jucaitis[11] and the same as that at (150 and 200) °C. While in the high-alkali region (the weight concentration of Na_2O is more than 22.54 %), $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ and $Na_2O \cdot Al_2O_3$ were found to be equilibrated with the corresponding solutions besides NaOH, which is quite different from that at 110 °C. Three invariant points, with their corresponding pairs of equilibrium solids (AlOOH and $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$; $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ and $Na_2O \cdot Al_2O_3$; $Na_2O \cdot Al_2O_3$ and NaOH) were identified along with their corresponding compositions. This work provides a significant database for the study of the crystallization process of high-alkali sodium aluminate solutions.

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