Phase Equilibria in the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ System

Yang Zhang,[†,‡] Shili Zheng,*[,†] Hao Du,[†] Hongbin Xu,[†] and Yi Zhang[†]

Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China, and Graduate University of the Chinese Academy of Sciences, Beijing, 100049, China

Equilibria data for the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system at (40, 60, and 80) °C were measured, and the phase diagrams at (80 and 40) °C were constructed. Furthermore, the crystallization areas in the phase diagrams are discussed in detail. In addition, the solubility of Na_2CrO_4 in NaOH solutions was compared with that in Na_2CO_3 saturated NaOH solutions, and the solubility of Na_2CO_3 in NaOH solutions was also compared with that in Na_2CrO_4 saturated NaOH solutions. On the basis of the phase diagrams, a strategy for effective separation of Na_2CO_3 from the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system has been proposed.

Introduction

A novel chromite ore treatment process using molten sodium hydroxide as reaction media has been proposed by the Institute of Process Engineering, Chinese Academy of Sciences, and the main reaction involved in the process is the oxidation of chromite ore with oxygen in molten sodium hydroxide. Because of the presence of carbon dioxide in the air (to provide oxygen) and the carbonate impurities in the sodium hydroxide reagent, sodium carbonate usually coexists with sodium hydroxide and sodium chromate. To produce high-purity sodium chromate, it is very important to effectively separate sodium hydroxide, sodium chromate, and sodium carbonate on the basis of their salting-out effect. In this regard, it is necessary to study the phase diagram of the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system to get a separation method.

Some research has been done regarding the phase diagrams of the ternary subsystems of the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system,[1−4] but a study of the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system itself has not been reported so far.

Experimental Section

Apparatus and Reagents. A HZQ-type thermostatic vibrator with temperature control (precision of 0.1 °C) was used to prepare the samples to an equilibrium state. The content of sodium and chromium in all samples was determined by inductively coupled plasma/optical emission spectrometry (ICP-OES, PE Optima 5300DV, Perkin-Elmer). The solid-phase analysis was done by X-ray diffraction (XRD, Phillips PW223/30).

The chemicals used in the experiments were all of analytical grade, and deionized water was used in all of the experiments.

Experimental Method. The solubility was determined employing an isothermal solution saturation method.[5] Predetermined amounts of sodium hydroxide, tetrahydrate sodium chromate, and sodium carbonate were mixed homogenously in a given amount of water before putting into sealed polyethylene bottles, and then the bottles were placed in the thermostatic vibrator. The experiments were performed at ambient pressure, and the temperature was fixed at three specific values: (40, 60, and 80) °C. The liquid phase of each sample was examined

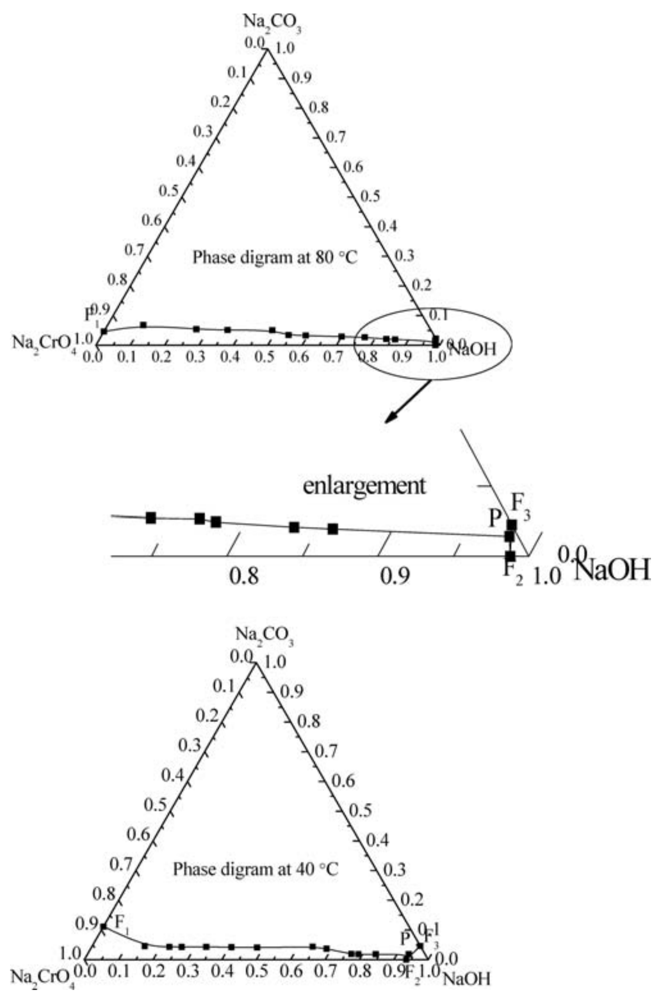

Figure 1. Phase diagram of the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ system at (80 and 40) °C. Point P is the invariant point, and points F_1, F_2, and F_3 represent the equilibrium composition of the solid phases at the two extremes of the corresponding side, respectively.

* Corresponding author. E-mail: slzheng@home.ipe.ac.cn. Fax: +86-10-62520910.
† Institute of Process Engineering, Chinese Academy of Sciences.
‡ Graduate University of the Chinese Academy of Sciences.

10.1021/je900900m
Published on Web 01/20/2010

Table 1. Solubility Data of the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ System

composition of liquid phase, g/100 g of dry salt				
NaOH	Na_2CO_3	Na_2CrO_4	H_2O	equilibrium solid phase
		t = 80 °C		
10.40	6.81	82.79	47.27	$Na_2CO_3 + Na_2CrO_4$
22.63	5.77	71.60	48.18	$Na_2CO_3 + Na_2CrO_4$
26.52	5.36	68.12	48.17	$Na_2CO_3 + Na_2CrO_4$
34.83	5.26	59.91	49.32	$Na_2CO_3 + Na_2CrO_4$
47.78	5.10	47.12	49.70	$Na_2CO_3 + Na_2CrO_4$
54.35	3.43	42.22	51.46	$Na_2CO_3 + Na_2CrO_4$
59.38	3.24	37.38	50.62	$Na_2CO_3 + Na_2CrO_4$
68.79	3.10	28.11	49.13	$Na_2CO_3 + Na_2CrO_4$
73.58	2.75	23.67	48.73	Na_2CO_3+Na_2CrO_4
76.88	2.69	20.43	47.09	$Na_2CO_3 + Na_2CrO_4$
78.04	2.44	19.52	45.74	$Na_2CO_3 + Na_2CrO_4$
83.42	2.07	14.51	41.21	$Na_2CO_3 + Na_2CrO_4$
86.08	1.93	11.99	39.50	$Na_2CO_3 + Na_2CrO_4$
98.02	1.40	0.58	26.64	$Na_2CO_3 + Na_2CrO_4 + NaOH \cdot H_2O$
0	4.62	95.38	97.97	$Na_2CO_3 + Na_2CrO_4$
98.76	0	1.24	47.92	$Na_2CrO_4 + NaOH \cdot H_2O$
97.74	2.26	0	37.84	$Na_2CO_3 + NaOH \cdot H_2O$
		t = 60 °C		
16.21	5.43	78.37	96.93	$Na_2CO_3 + Na_2CrO_4$
25.23	5.03	69.74	99.88	$Na_2CO_3 + Na_2CrO_4$
38.42	4.70	56.88	100.60	$Na_2CO_3 + Na_2CrO_4$
51.85	4.49	43.66	99.55	$Na_2CO_3 + Na_2CrO_4$
58.49	4.25	37.25	101.03	$Na_2CO_3 + Na_2CrO_4$
63.18	3.69	33.14	96.99	$Na_2CO_3 + Na_2CrO_4$
76.90	2.29	20.80	91.90	$Na_2CO_3 + Na_2CrO_4$
79.22	2.00	18.78	89.76	$Na_2CO_3 + Na_2CrO_4$
81.52	1.49	16.99	90.87	$Na_2CO_3 + Na_2CrO_4$
89.59	0.70	9.71	73.89	$Na_2CO_3 + Na_2CrO_4$
91.40	0.62	7.98	65.38	$Na_2CO_3 + Na_2CrO_4$
96.69	0.12	3.19	59.03	$Na_2CO_3 + Na_2CrO_4 + NaOH \cdot H_2O$
0	4.11	95.89	94.05	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
97.56	0	2.44	58.12	$Na_2CrO_4 + NaOH \cdot H_2O$
97.20	2.80	0	75.10	$Na_2CO_3 + NaOH \cdot H_2O$
		t = 40 °C		
15.31	4.56	80.14	102.17	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
22.59	4.33	73.084	104.67	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
26.23	4.29	69.48	100.55	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
33.34	4.31	62.35	103.36	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
40.71	4.22	55.07	104.24	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
48.19	4.09	47.72	108.24	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
64.20	4.41	31.39	122.40	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
68.63	3.66	27.71	110.97	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
76.75	1.88	21.37	115.39	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
78.83	1.86	19.32	116.35	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
83.83	1.83	14.34	111.04	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
93.47	1.82	4.71	67.85	$Na_2CO_3 + Na_2CrO_4 + NaOH \cdot H_2O$
0	11.13	88.87	104.41	$Na_2CO_3 + Na_2CrO_4 \cdot 4H_2O$
93.62	0	6.38	71.10	$Na_2CrO_4 + NaOH \cdot H_2O$
95.39	4.61	0	67.59	$Na_2CO_3 + NaOH \cdot H_2O$

Table 2. Comparison of the Solubility of Na_2CrO_4 in NaOH Solution with That in Na_2CO_3 Saturated NaOH Solution at 80 °C

solubility in NaOH aqueous without Na_2CO_3 coexistence		solubility in NaOH aqueous saturated with Na_2CO_3	
c/g·L^{-1}		c/g·L^{-1}	
NaOH	Na_2CrO_4	NaOH	Na_2CrO_4
83	775.73	86.16	685.70
98	760.15	180.43	570.74
166	641.77	192.59	553.61
229	538.97	210.83	541.45
276	479.77	266.58	458.58
290	457.97	277.73	459.52
330	408.12	358.81	353.91
417	314.66	361.86	343.00
464	264.81	398.34	309.39
502	234.59	437.87	275.65
570	196.27	530.11	204.74
604	176.02	564.57	181.60
629	164.18	523.02	213.72
642	162.62	610.19	162.12
678	153.28	625.39	156.39

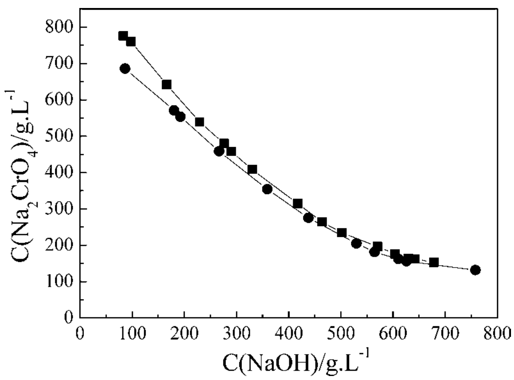

Figure 2. Solubility isotherms of Na_2CrO_4 at 80 °C: ■, in NaOH solution; ●, in Na_2CO_3 saturated NaOH solution.

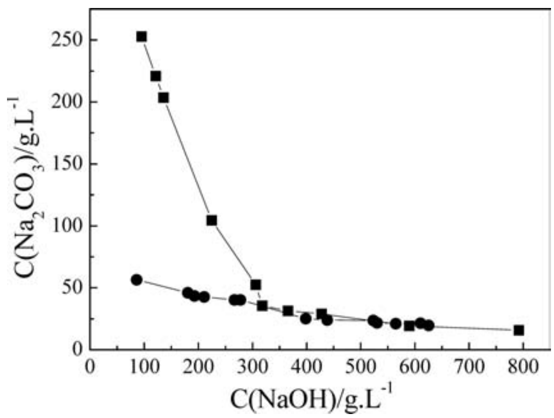

Figure 3. Solubility isotherms of Na_2CO_3 at 80 °C: ■, in NaOH aqueous solution; ●, in Na_2CrO_4 saturated NaOH aqueous solution.

every two days, and an equilibrium state was believed to be achieved when the liquid-phase components became stable. After equilibrium was attained, the shaking was discontinued, and then the samples were allowed to settle for one day before further treatment and analysis. For each sample, about 5 mL of aqueous phase was filtered, weighed, and diluted into a 100 mL volumetric flask. For the determination of sodium chromate content, 5 mL of the previously diluted solution was further diluted 20 times after addition of 2 mL of concentrated hydrochloric acid, and then the solution was analyzed using ICP-OES. Sodium hydroxide and sodium carbonate were determined by titration using hydrochloric acid solution with phenolphthalein solution and methyl orange solution as indicators. The equilibrium solid phase was dried in a desiccator at room temperature and then analyzed by an XRD analyzer.

Results and Discussion

NaOH−Na_2CrO_4−Na_2CO_3−H_2O Quaternary System. The solubility data for the NaOH−Na_2CrO_4−Na_2CO_3−H_2O quaternary system at (40, 60, and 80) °C were measured and are presented in Table 1, and the phase diagrams at (80 and 40) °C are plotted in Figure 1. All of the solubility data in Table 1 are the average values of three measurements, with the relative standard deviation (RSD) values of less than 2 %. The phase diagram at 60 °C is similar to those of (80 and 40) °C and therefore is not shown in this paper.

Figure 1 shows that the NaOH−Na_2CrO_4−Na_2CO_3−H_2O quaternary system has three crystallization zones, which are the Na_2CO_3 crystallization zone, the Na_2CrO_4 crystallization zone (the $Na_2CrO_4 \cdot 4H_2O$ crystallization zone at 40 °C), and the $NaOH \cdot H_2O$ crystallization zone. Among the three zones, the crystallization zone of Na_2CO_3 is far larger than that of the other two. The Na_2CO_3 and $Na_2CrO_4 \cdot 4H_2O$ crystallization zones at 40 °C are similar to those at 80 °C, but the $NaOH \cdot H_2O$ crystallization zone at 40 °C is larger than that at 80 °C. This suggests that Na_2CO_3 could be easily separated from the system at either (80 or 40) °C through crystallization by adjusting the amount of water in the system. Because of the lower energy consumption during the recycling of NaOH through evaporation at high temperatures, the equilibrium data at 80 °C is more useful to the process. The phase diagram provides a theoretical foundation for the separation of Na_2CO_3 and Na_2CrO_4 from the system.

Comparison of the Solubility of Na_2CrO_4 in NaOH Solution of with That in Na_2CO_3 Saturated NaOH Solution. The solubility data of Na_2CrO_4 in NaOH solutions and in Na_2CO_3 saturated NaOH solutions at 80 °C are presented in Table 2, and the isotherms are plotted in Figure 2. As shown in Table 2 and Figure 2, when compared with NaOH solutions without Na_2CO_3, the concentration of Na_2CrO_4 in Na_2CO_3 saturated NaOH solutions decreases only slightly at 80 °C. On the other hand, the concentration of Na_2CrO_4 decreases significantly with an increase of the NaOH concentration in both the NaOH−Na_2CrO_4−Na_2CO_3−H_2O and the NaOH−Na_2CrO_4−H_2O systems. These results indicate that the salting-out effect of Na_2CO_3 to Na_2CrO_4 is negligible, and Na_2CrO_4 can be separated effectively by evaporation crystallization from the NaOH−Na_2CrO_4−Na_2CO_3−H_2O system. There are similar results at (60 and 40) °C.

Comparison of the Solubility of Na_2CO_3 in NaOH Solution of with That in Na_2CrO_4 Saturated NaOH Solution. Solubility data of Na_2CO_3 in NaOH solutions and in Na_2CrO_4 saturated NaOH solutions at 80 °C are presented in

Table 3. Comparison of the Solubility of Na_2CO_3 in NaOH Solution with That in Na_2CrO_4 Saturated NaOH Solution at 80 °C

solubility in NaOH aqueous without Na_2CrO_4 in coexistence		solubility in NaOH aqueous saturated with Na_2CrO_4	
c/g·L^{-1}		c/g·L^{-1}	
NaOH	Na_2CO_3	NaOH	Na_2CO_3
95.2	252.8	86.16	56.41
121.2	221	180.42	45.98
135.8	203.5	192.58	43.40
224.6	104.5	210.83	42.60
306	52.4	266.58	40.29
318.2	35.5	277.73	40.22
365.6	31.3	398.34	25.13
427.7	28.9	437.88	23.91
589.7	19.3	523.02	23.60
792	15.7	530.11	21.79
		564.58	21.14
		610.19	21.35
		625.39	19.56

Table 3, and the isotherms are plotted in Figure 3. It is concluded from Table 3 and Figure 3 that, when compared with NaOH solution without Na_2CrO_4, the concentration of Na_2CO_3 decreases significantly if the alkali solution is saturated with Na_2CrO_4 at 80 °C, which suggests that the salting-out effect of Na_2CrO_4 to Na_2CO_3 is strong. The results indicate that when Na_2CO_3 coexists with Na_2CrO_4 it can be separated easily from the system by evaporation crystallization before the saturation point of Na_2CrO_4.

Conclusion

Phase equilibria for the $NaOH-Na_2CrO_4-Na_2CO_3-H_2O$ quaternary system at (40, 60, and 80) °C was studied. The phase diagrams of the system and the solubility isotherms of Na_2CrO_4 and Na_2CO_3 were plotted. This study provides a theoretical basis for the separation of Na_2CO_3 and Na_2CrO_4 from the NaOH solutions.

Literature Cited

(1) Xing, Z. Basic chemistry research on phase separation of $Al^{3+}/Na^{+}/CrO_4^{2-}/OH$ (in Chinese). Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 1998.
(2) Hostalek, Z. Ternary system H_2O-Na_2CO_3-NaOH. *Chem. Listy* **1956**, *50*, 716–720.
(3) Linke, W. F. *Solubilities, inorganic and metal-organic compounds: a compilation of solubility data from the periodical literature*, 4th ed.; Van Nostrand: Princeton, NJ, 1958; Vol. 2, p 65.
(4) China Soda Industry Association. *Soda engineering science* (in Chinese); Chemical Industry Press: Beijing, 1990.
(5) Shu, Y. G.; Lü, B. L.; Wang, X. R. *Phase Diagram Analyses of Inorganic Chemical Production: Basic Theory* (in Chinese); Chemical Industry Press: Beijing, 1985.

Received for review October 27, 2009. Accepted January 12, 2010. Financial support from the National Basic Research Development Program of China (973 Program) under Grant No. 2007CB613501 and 2009CB219901 and Key Project in the National Science & Technology Pillar Program under Grant No. 2006BAC02A05 are gratefully acknowledged.

JE900900M