Solubility of Sodium Aluminosilicates in Synthetic Bayer Liquor

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The solubility of two major sodium aluminosilicate Bayer refinery scale phases, sodalite and cancrinite, has been measured in sodium aluminate liquor as a function of time, sodium carbonate concentration, initial seeding phase, and temperature. Solubility is assessed by the measurement of SiO_2 concentration in solution for at least 13 days. At both 90 °C and 160 °C, sodalite seed partially transforms to cancrinite over 13 days. As this transformation is partial, the use of the term "equilibrium solubility" is not justified. The kinetics of this process are faster at the higher temperature; hence, the proportion of cancrinite in the final crystalline products is greater at 160 °C. As expected, the more thermodynamically stable product, cancrinite, was found to be less soluble. Hence, SiO_2 solubility in sodalite-seeded solutions was not greater at 160 °C than at 90 °C. In cancrinite seeded solutions, where no further phase transformation occurs, the equilibrium SiO_2 concentration in solution increases with increasing temperature. Increasing Na_2CO_3 concentration does not appear to affect the sodalite-to-cancrinite transformation kinetics. In all sodalite or cancrinite-seeded solutions, SiO_2 solubility decreases with increasing Na_2CO_3 concentration.

Introduction

During the Bayer process, bauxite is digested in hot caustic liquor; on filtration, cooling, and then seeding of the clarified liquor, gibbsite is precipitated. SiO_2-containing minerals such as quartz and kaolin, present in bauxite, also dissolve in the caustic liquor. In pregnant liquors (i.e., liquors from which gibbsite, $Al(OH)_3$, has not yet precipitated) the initial supersaturated and final equilibrium concentrations of SiO_2 are approximately 0.60 g dm^{-3} and 0.30 g dm^{-3} (Ostap, 1986), respectively. The precipitation process required to obtain an approximate equilibrium concentration of SiO_2 takes up to five times as long as the time required to digest bauxite. This renders such a SiO_2 reduction process cost prohibitive. Therefore, SiO_2 equilibrium is not reached, and the caustic aluminate solutions remain supersaturated with respect to both $Al(OH)_3$ and SiO_2. After the precipitation of gibbsite, the solubility of SiO_2 is reduced (Ostap, 1986) owing to the decreased $Al(OH)_3$ content in the spent liquor. This results in the formation of sodium aluminosilicate scale in the downstream section of the Bayer cycle.

In designing processing conditions to minimize formation of this scale, it is necessary to know and understand the factors controlling the solubility of the precipitating aluminosilicate phases. This paper reports on three factors influencing the solubility of SiO_2 in synthetic sodium aluminate solutions (i.e., synthetic Bayer liquors undersaturated with respect to gibbsite), namely; temperature, crystalline phase, and the effect of Na_2CO_3 concentration.

Temperature. In the study carried out by Breuer et al. (1963), the solubility of SiO_2 in unseeded sodium aluminate solutions, supersaturated with respect to SiO_2, was observed to increase from 150 °C to 250 °C. The solutions were allowed to equilibrate for variable times from 69 to 117 h. Kraus et al. (1968) also reported that the solubility of sodium hydroaluminosilicates increases with increasing temperature from 120 °C to 280 °C. These solutions were allowed to equilibrate for 12 h and were not

seeded. The final crystallization products were not reported.

Eremin et al. (1968) carried out a series of SiO_2 solubility measurements in solutions containing between 76.5 and 137.6 g dm^{-3} $Al(OH)_3$ and 70 and 209 g dm^{-3} NaOH. These solution were seeded "corresponding to a content of 0.6 g/L SiO_2 in the pulp". The phase of the seed is not given. At "equilibrium" a decrease in SiO_2 concentration between 90 °C and 125 °C, followed by an increase between 125 °C and 175 °C, is reported. This observation was explained as being due to the presence of an equilibrium between ionic, colloidal, and deposited SiO_2 that was influenced by temperature. (In light of results reported in this paper, it is likely that this observation is due to transformation occurring within the solution precipitation products.) It is unclear whether all these solutions were allowed to equilibrate for the same length of time. Also, no indication of the phase of the final crystallization product is given. Lack of information makes these results difficult to interpret; however, clear patterns of decreasing SiO_2 solubility with increasing caustic concentration and increasing SiO_2 solubility with increasing $Al(OH)_3$ content were observed.

In Oku and Yamada's (1971) work examining the effect of temperature, the solubility of SiO_2 (from quartz or bauxite) was found to be independent of temperature between 110 °C and 240 °C. Hence there is disagreement in the literature on the effect of temperature on silica solubility.

Crystalline Phase. The two main aluminosilicate scale phases found in Bayer refineries after gibbsite precipitation are sodalite and cancrinite (Zheng and Gerson, 1997). While these two phases have, ideally, the same framework stoichiometry, $[AlSiO_4]_6$, and are both composed of 12-atom and 8-atom rings made up of $-O-Al-O-Si-$ units, they differ substantially in structure. Cancrinite, of space group $P6_3$, is composed of a series of channels, while sodalite, space group $P\bar{4}3n$, is comprised of an array of cages. X-ray powder diffraction can be used to easily differentiate between sodalite and cancrinite. Cancrinite has a clear 101 diffraction peak for which there are no sodalite

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diffraction peaks of similar *d* spacing. Many of the sodalite diffraction peaks do occur at very similar *d* spacings to those of cancrinite, and therefore it is not easy to identify and quantify the presence of sodalite in a sample where cancrinite is also presnent.

Breuer et al. (1963) measured the solubility of SiO_2 at 70 °C in unseeded solutions. It was found that the initially crystallized Linde zeolite A transformed in situ to sodalite on aging. This transformation was accompanied by a slow reduction in SiO_2 solubility up to 600 h when the experiment was terminated. Further experiments were carried out at 70 °C and 100 °C (for 16 h and 4 h, respectively) in solutions seeded with Linde zeolite A or sodalite. They demonstrated that Linde zeolite A is more soluble than sodalite; i.e., there is a greater concentration of SiO_2 present in solutions where zeolite was present. Ni et al. (1964) carried out similar experiments at 90 °C and also reported that zeolite seed was more soluble than sodalite seed over a 5-day period.

A partial transformation of sodalite to cancrinite (in a caustic aluminate solution supersaturated with respect to SiO_2, seeded with sodalite) was observed after 15 h at 160 °C by Zheng et al. (1997). Avdeeva and Novolodskaya (1969) reported a transformation from carbonate sodalite to carbonate cancrinite above 175 °C. Breuer et al. (1963) also reported that a slight conversion to cancrinite was apparent after 72 h at 150 °C, and at 200 °C this transformation was complete before 44 h.

Kirsch (1959) observed a transformation from basic noselite to cancrinite. Both noselite and sodalite are reported to be cubic with the noselite unit cell being approximately 9.1 Å as compared to 8.9 Å for sodalite. As the distinction between noselite and sodalite is not clearly defined, the term noselite is not used in this text. Instead sodalite refers to all cubic desilication products, and all unit cells are quoted.

Although some solubility experiments have been carried out in sodalite-seeded solutions, the transformation from sodalite to cancrinite has not been recognized and accounted for in the interpretation of the resulting SiO_2 concentrations. Breuer et al. (1963) reported SiO_2 solubilities over a range of temperatures from 70 to 250 °C. These experimental systems were allowed to equilibrate for variable lengths of time from 4 h to 117 h. The crystalline phase in all cases was reported as basic sodalite, in apparent contradiction to the observation of a sodalite-to-cancrinite transformation reported in the same paper. The combination of varying equilibration temperatures and times make their (Breuer et al., 1963) SiO_2 concentrations difficult to interpret in terms of a given crystal/solution equilibrium.

Effect of Na₂CO₃ Concentration. Breuer et al. (1963) reported that increasing solution Na_2CO_3 concentration from 7 to 60 g dm^{-3} resulted in a decrease in SiO_2 solubility of approximately 75 to 90%. Volkova et al. (1971) found that the solubility of SiO_2 was reduced significantly by the presence of CO_3^{2-} and SO_4^{2-} over 20 h. The addition of SO_4^{2-} appeared to enhance the transformation kinetics of sodalite to cancrinite more than the addition of CO_3^{2-}. Hence, for the same reaction time, the SiO_2-solution concentration after addition of SO_4^{2-} was lower than that after the addition of CO_3^{2-}. Avdeeva and Novolodskaya (1969) investigated the effects of CO_3^{2-}, SO_4^{2-}, and Cl^- addition and again found that the addition of SO_4^{2-} resulted in a lower SiO_2 concentration than did the addition of the same concentration of CO_3^{2-}. Solubility experiments were carried out at 175 °C. Again, it was reported that

SO_4^{2-} was the most effective additive in promoting the sodalite-to-cancrinite transformation.

Breuer et al. (1963) also investigated the relative desilication effectiveness of a number of additives including CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, and PO_4^-. SO_4^{2-} was again found to be the most effective additive for the reduction of SiO_2 in Bayer-type liquors increasing both the rate of desilication and decreasing the final SiO_2-solution equilibrium concentration. In digestions varying in length from 46 to 96 h where CO_3^{2-} or SO_4^{2-} had been added, the crystallization products were cancrinite.

Rozen et al. (1978) reported similar results where the addition of SO_4^{2-} to a caustic aluminate solution gives rise to a lower SiO_2 solubility than the addition of MoO_4^{2-}, CO_3^{2-}, or CrO_4^{2-}. This effect was ascribed to the lower degree of hydration of SO_4^{2-} than the other bivalent ions examined. A previous study, also by these authors (Pevzner et al., 1974), had shown that SO_4^{2-} was a less effective SiO_2 removal reagent than either ClO_4^- or NO_3^{2-}.

While the relative desilication effectiveness of a number of additives has been studied in reasonable detail, no systematic study has been carried out examining the desilication behavior of one additive over a range of temperatures and concentrations including those used in Bayer plants. Na_2CO_3 is the most concentrated impurity within Bayer liquors, with up to 40 g dm^{-3}. In this text, a systematic study of the effect of CO_3^{2-} addition at 90 °C and 160 °C is reported. Both SiO_2 solution concentrations and resulting crystalline phases are reported as a function of concentration of CO_3^{2-} addition.

It is apparent that the true SiO_2 solubilities in Bayer liquors undersaturated with respect to gibbsite have rarely, if ever, been measured under equilibrium conditions owing to the slow nature of the phase transformations undergone by the crystallization products. SiO_2 solubilities reported are therefore likely to be a function of solution conditions: initial seeding type (size and mass), temperature, solution concentrations, length of time of equilibration, and stirring rates. For SiO_2 solubilities to be meaningful they must be correlated to a phase analysis of the resulting crystalline products.

In light of the difficulty in interpreting much of the SiO_2 solubility measurements carried out previously, it is the aim of this text to cross-correlate solution conditions, crystalline phase, and SiO_2 solubility.

Experimental Method

Synthetic Bayer liquors were prepared from (1) gibbsite (C-31 Alcoa, Arkansas, X-ray fluorescence analyses: 0.01% SiO_2, 0.04% Fe_2O_3, 15% Na_2O by mass, 34.5% loss of mass on heating at 1200 °C), (2) laboratory-grade NaOH (Ajax Chemicals, Australia 97.5% pure, 2.5% Na_2CO_3), (3) Na_2CO_3 anhydrous (BDH, Analar 99%), (4) technical-grade $Na_2SiO_3 \cdot 5H_2O$ (Ajax Chemicals, Australia, SiO_2 27.8–29.2%, Na_2O 28.1–29.5%, H_2O 42–43% by mass), and (5) Milli-Q water (surface tension of 72.8 mN m^{-1} at 20 °C and specific conductivity <0.5 μS).

The minimum concentration of Na_2CO_3 in any of the synthetic spent liquors (i.e., Bayer liquors after precipitation of $Al(OH)_3$) was 4.6 g dm^{-3}. This was due to contamination of NaOH by Na_2CO_3.

Solubility experiments were carried out in synthetic spent liquors as a function of Na_2CO_3 concentration at 90 °C and 160 °C for over 13 days in six stainless steel Parr bombs. Each of these bombs contained a Teflon liner and had an operating volume of 0.027 dm^3. The initial supersaturated SiO_2 concentration was 0.6 g dm^{-3}. All liquors

contained NaOH = 181 g dm^{-3} and Al(OH)$_3$ = 126.7 g dm^{-3}. The Na$_2$CO$_3$ concentration was varied systematically from 4.6 to 40.0 g dm^{-3}.

Pure, synthetic sodalite and cancrinite seed as well as plant-grown cancrinite seed (all characterized by X-ray powder diffraction; unit cells are given in Tables 1, 2 and 3 respectively) were used during this investigation. Sodalite crystals previously precipitated over a 3-day period from solutions with the same NaOH and Al(OH)$_3$ concentrations at 95 °C were used as synthetic sodalite seeds. Synthetic cancrinite was prepared from solution as for the sodalite preparation with the addition of 28.6 g dm^{-3} Na$_2$SO$_4$. Plant cancrinite grown at 180 °C was used as the source of Bayer plant-grown cancrinite seed.

A solution containing SiO$_2$, NaOH, and Al(OH)$_3$ was prepared. From this, six stock solutions were made by the addition of Na$_2$CO$_3$ so that the final Na$_2$CO$_3$ concentrations were 4.6, 12.0, 19.0, 26.0, 33.0, and 40.0 g dm^{-3}. Approximately 0.3 g of seed was added to each 0.027 dm^3 Teflon insert. The inserts were then filled with the required amount of stock solutions and sealed. They were kept, without any agitation, in the chamber of a thermostatically controlled oven that provided isothermal heating at (90.0 ± 0.3) °C and (160.0 ± 0.3) °C.

Up to five samples were periodically taken from the slurry and centrifuged in order to monitor the change in SiO$_2$ concentration of the liquor. The supernatants were analyzed by the ammonium molybdate method (Wherli, 1990) on a Cary 5 UV−vis NIR spectrophotometer. This procedure was repeated periodically for (1) 10 days for the synthetic-cancrinite-seeded solutions at 160 °C, (2) 13 days for the sodalite-seeded solutions at 90 °C and 160 °C and the plant-cancrinite-seeded solutions at 90 °C, (3) 14 days for the synthesized-cancrinite-seeded solutions at 90 °C, and (4) 16 days for the plant-cancrinite-seeded solutions at 160 °C.

Crystal samples taken from the solutions were washed with water and ethanol and dried in a fume hood overnight. They were analyzed using X-ray powder diffraction (XRD) on a Philips PW 1130/90 using Cu Kα radiation with a step size of 0.2° 2θ and a scan rate of 1° 2θ min^{-1} from 10 to 90° 2θ. Typical XRD patterns of both synthetic sodalite and cancrinite and plant cancrinite have been published previously (Zheng et al., 1997) and, hence, are not included in this text. Fourier transform infrared (FTIR) was carried out in transmission geometry using a KBr disk on a Bio-Rad Digilab Division FTS-65. The disk consisted of less than 2 mass % of the crystalline samples.

Results and Discussion

Sodalite-Seeded Solutions. The SiO$_2$ concentrations measured from the sodalite-seeded liquors are shown in Figure 1. Also shown are some SiO$_2$ solubility concentrations interpolated from the literature. The error in the SiO$_2$ concentration measurements was ±0.02 g dm^{-3}, to the point of 95% confidence. It can be seen from Figure 1 that

(1) The solubility of sodalite (as SiO$_2$) obtained after 13 days decreased from 0.34 to 0.19 g dm^{-3} at 90 °C and from 0.35 to 0.22 g dm^{-3} at 160 °C with the increase of Na$_2$CO$_3$ concentration from 4.6 to 40.0 g dm^{-3}.

(2) The SiO$_2$ solubility data obtained at 90 °C were well-matched with literature values. Ni et al. (1964) reported a SiO$_2$ solubility of 0.34 g dm^{-3} in a solution containing no added Na$_2$CO$_3$. This is very similar to the SiO$_2$ solubility reported here of 0.34 g dm^{-3} for the solution containing 4.6 g dm^{-3} Na$_2$CO$_3$. A SiO$_2$ solubility of 0.20 g dm^{-3} for a
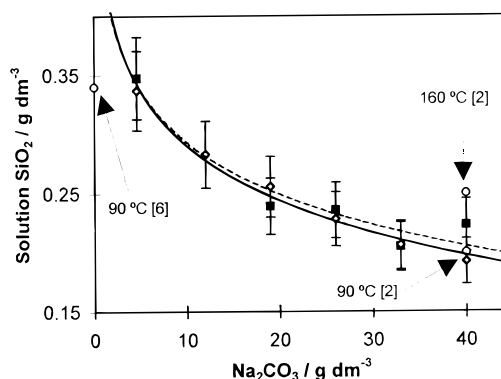

Figure 1. Solution SiO$_2$ concentration in sodalite-seeded solutions as a function of Na$_2$CO$_3$ concentration: $-\diamond-$ 90 °C, --■-- 160 °C.

Table 1. Unit Cells of Sodalite-Seeded Solutions[a]

			cancrinite	
Na$_2$CO$_3$/g dm^{-3}	t/°C	sodalite a/Å	a/Å	c/Å
initial seed		8.9133(2)		
4.6	90	8.971(8)	12.685(4)	5.187(3)
40.0	90	8.9702(6)	12.684(3)	5.181(2)
4.6	160		12.693(2)	5.490(2)
40.0	160		12.703(1)	5.181(1)

[a] The number in parentheses indicates the standard deviation of the last digit of the unit-cell dimensions.

solution containing 40 g dm^{-3} Na$_2$CO$_3$ was interpolated from Breuer et al.'s (1963) data. This compares favorably with our SiO$_2$ concentration of 0.19 g dm^{-3}. At 160 °C the SiO$_2$ solubilities reported in the literature compared less favorably to our values. A value of 0.25 g dm^{-3} SiO$_2$ was interpolated from Breuer et al.'s, (1963) data for a solution containing 40.0 g dm^{-3} Na$_2$CO$_3$ as compared to 0.22 g dm^{-3} reported here.

(3) The SiO$_2$ solubilities recorded at 160 °C were not significantly higher, as would be expected, than those recorded at 90 °C.

The presence of cancrinite is accurately identified by the 101 diffraction peak (Grundy and Hassan, 1982) for cancrinite. No sodalite diffraction peak is present at this particular d spacing. XRD d data shows that a phase transformation from sodalite to cancrinite was observed in the crystalline product at both 90° and 160 °C. The unit cells of the initial sodalite seed and the crystallization products are given in Table 1. The sodalite 211 and cancrinite 300 diffraction peaks occur at approximately the same 2θ value of 24.5°. By examining the ratio of the intensities of cancrinite 101 with the sum of the intensities of sodalite 211 and cancrinite 300 it is possible to roughly assess the relative concentration of cancrinite in a sample (Zheng et al., 1997). This ratio indicates that the sodalite-to-cancrinite transformation was less complete at the termination of the experiment at 90 °C than at 160 °C. The crystalline products of a sodalite-seeded solution initially containing 0.6 g dm^{-3} SiO$_2$, 181 g dm^{-3} NaOH and 4.6 g dm^{-3} Na$_2$CO^3 held at 90 °C for 13 days had a C(101)/(S(211)+C(300)) diffraction peak intensity ratio of 0.2 as compared to the identical solution held at 160 °C, where this ratio was found to be 0.3. For the same solution but containing 40.0 g dm^{-3} Na$_2$CO$_3$, this ratio after 13 days at 90 °C was found to be 0.1 as compared to the identical solution held at 160 °C where the ratio was 0.4 (Gerson and Zheng, 1997). As there is no proof that this phase transformation has been completed at even the higher
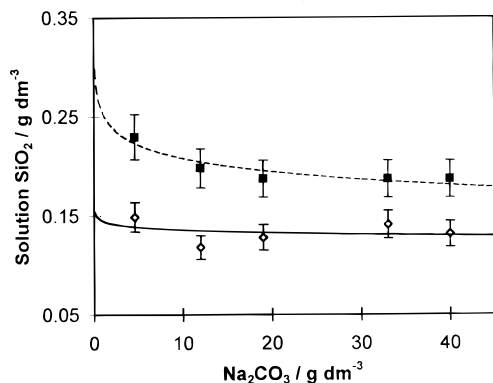
Figure 2. Solution SiO_2 concentration in synthetic-cancrinite-seeded solutions as a function of Na_2CO_3 concentration after 13 days: $-\diamond-$ 90 °C, $--\blacksquare--$ 160 °C.

Table 2. Unit-Cell Dimension and Volumes of the Initial Synthetic Cancrinite Seed and the Crystalline Product from the Solubility Experiments Described in Results Part 2. Synthetic-Cancrinite-Seeded Solutions[a]

Na_2CO_3/g dm^{-3}	t/°C	a/Å	c/Å	volume/Å^3
initial synthetic cancrinite seed		12.789(5)	5.221(3)	740(1)
4.6	90	12.638(7)	5.150(5)	712(1)
40.0	90	12.547(6)	5.104(4)	696(1)
4.6	160	12.645(2)	5.161(2)	714.6(5)
40.0	160	12.645(3)	5.152(2)	713.4(6)

[a] The standard deviation of the last digit is given in parentheses.

temperature, the terminology "equilibrium solubility" has been avoided in this text.

Literature (Hermeler et al., 1991) suggests that the addition of CO_3^{2-} to Bayer-like solutions increases the rate of the sodalite-to-cancrinite transformation, which in turn leads to a reduction in SiO_2 concentration in solution. There is no conclusive evidence in our work to suggest that the addition of a high concentration of Na_2CO_3, i.e., 40.0 g dm^{-3} as compared to 4.6 g dm^{-3}, increases the rate of this transformation. However, the results quoted are after a 13-day experimental period and therefore give no indication of the initial or early sodalite-to-cancrinite transformation rate.

Ni et al.'s (1964) data for 90 °C (as shown in Figure 1) was reported for a solution containing no added CO_3^{2-}. No explanation was given as to how Na_2CO_3 contamination of the NaOH was avoided. This solubility corresponds extremely well to our minimum Na_2CO_3 concentration of 4.6 g dm^{-3}. A possible explanation for the discrepancy between the data obtained at 160 °C is that Breuer et al.'s (1963) solubility experiment was allowed to equilibrate for up to 4 days only, and therefore the sodalite-to-cancrinite transformation is likely to have been less complete than in the solutions reported here (13 days). It is predictable, therefore, that the SiO_2 solubility recorded would have been higher than the SiO_2 solubility reported here for a similar solution.

The FTIR vibrations characteristic of cancrinite were present at 691, 629, and 565 cm^{-1} (Leiteizen et al., 1974) after the solubility experiment at 160 °C for the liquor containing 40.0 g dm^{-3} Na_2CO_3. The FTIR vibrations of sodalite at 737, 711, and 665 cm^{-1} (Leiteizen et al., 1974) are present in the FTIR spectra of the initial sodalite seed but not in the final product.

Synthetic-Cancrinite-Seeded Solutions. The SiO_2 solution concentrations, after 13 days, in caustic aluminate solutions seeded with synthetic cancrinite are shown in Figure 2. It is apparent from Figure 2 that

(1) The SiO_2 concentration of solutions in contact with synthetic cancrinite seed decreased from 0.15 to 0.13 g dm^{-3} at 90 °C and from 0.23 to 0.19 g dm^{-3} at 160 °C as the Na_2CO_3 concentration was increased from 4.6 to 40.0 g dm^{-3}.

(2) In synthetic-cancrinite-seeded solutions the solubility of SiO_2 at 160 °C is always greater than at 90 °C for a given Na_2CO_3 concentration.

Neither XRD or FTIR analyses gave any indication of a phase change from cancrinite to sodalite at either 90 °C or 160 °C. It is apparent, therefore, that cancrinite is the more thermodynamically stable phase. A decrease in the
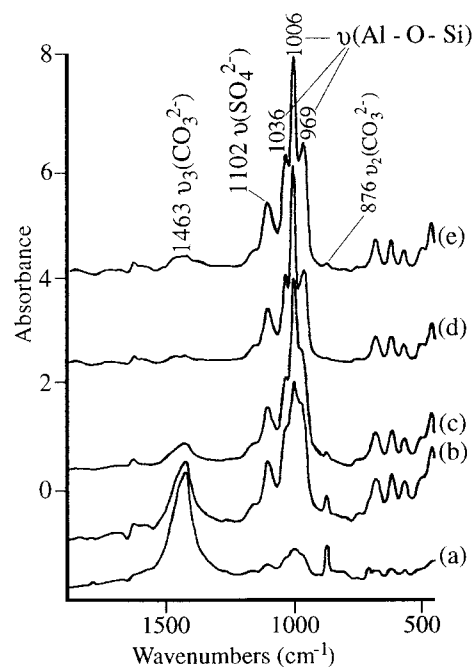

Figure 3. FTIR of synthetic-cancrinite-seeded solutions indicating the reduction in CO_3^{2-} concentrations. (a) synthetic cancrinite seed, (b) cancrinite obtained at 90 °C from a solution containing 4.6 g dm^{-3} Na_2CO_3, (c) cancrinite obtained at 90 °C from a solution containing 40.0 g dm^{-3} Na_2CO_3, (d) cancrinite obtained at 160 °C from a solution containing 4.6 g dm^{-3} Na_2CO_3, and (e) cancrinite obtained at 160 °C from a solution containing 40.0 g dm^{-3} Na_2CO_3.

unit cell volume of the resulting cancrinite phase as compared to the synthetic cancrinite seed was observed (Table 2). FTIR spectra indicate that these unit cell reductions were coupled with a reduction in CO_3^{2-} concentration (seen as v_3 near 1460 cm^{-1}) in the solid phase (Figure 3). This reduction in cancrinite CO_3^{2-} content was most significant at 160 °C.

Bayer Plant-Cancrinite-Seeded Solutions. The SiO_2 solubilities resulting from caustic aluminate solutions seeded with plant cancrinite are given in Figure 4. These solubilities indicate that:

(1) On increasing Na_2CO_3 concentrations from 4.6 to 40.0 g dm^{-3}, the SiO_2 solubilities reduced from 0.20 to 0.13 g dm^{-3} at 90 °C and from 0.26 g dm^{-3}, to 0.21 g dm^{-3} at 160 °C. At Na_2CO_3 concentrations greater than 10.0 g dm^{-3} the influence of increasing Na_2CO_3 concentration on SiO_2 solubility was not very significant.

(2) As for synthetic cancrinite, the SiO_2 solubility resulting for plant-cancrinite-seeded solutions increased with increasing temperature.

(3) For all three types of seeding examined, the increasing addition of CO_3^{2-} had the largest effect on sodalite-seeded solutions at 90 °C and 160 °C. The decrease in SiO_2
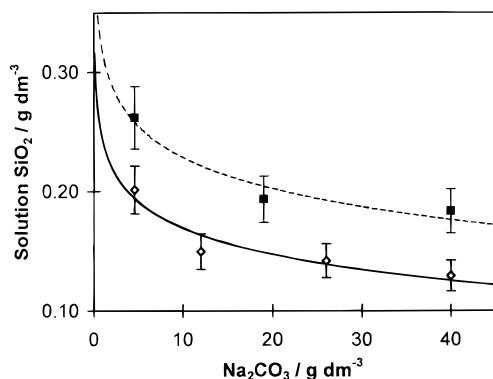
Figure 4. Solution SiO_2 concentration in Bayer plant-cancrinite-seeded solutions as a function of Na_2CO_3 concentration: $-\diamond-$ 90 °C, $--\blacksquare--$ 160 °C.

Table 3. Unit-Cell Dimensions and Volumes of the Initial Bayer Plant Cancrinite and the Crystalline Product from the Solubility Experiments Described in Results Part 3. Bayer Plant-Cancrinite-Seeded Solutions[a]

Na_2CO_3/g dm^{-3}	t/°C	a/Å	c/Å	volume/Å^3
initial plant cancrinite seed		12.712(3)	5.179(2)	724.7(6)
4.6	90	12.654(4)	5.178(6)	718 (1)
40.0	90	12.704(1)	5.189(1)	725.2(3)
4.6	160	12.684(2)	5.184(2)	722.2(5)
40.0	160	12.680(2)	5.182(1)	721.5(4)

[a] The standard deviation of the last digit is given in parentheses.

Table 4. Difference of SiO_2 Solubility in Synthetic Bayer Liquors Containing 40.0 and 4.6 Na_2CO_3 g dm^{-3} [a]

seed	t/°C	ΔSiO_2 solubility[b]
sodalite	90	0.02
synthetic cancrinite	90	0.02
plant cancrinite	90	0.07
sodalite	160	0.13
synthetic cancrinite	160	0.04
plant cancrinite	160	0.08

[a] For the liquors compared the other experimental conditions were identical. [b] From 40.0 to 4.6 Na_2CO_3 g dm^{-3} solution.

concentration, $\Delta[SiO_2]$, from 4.6 to 40.0 g dm^{-3} Na_2CO_3 is shown in Table 4.

No systematic variation in unit cell size was observed in plant-cancrinite-seeded solutions (Table 3). FTIR analysis indicated that initial CO_3^{2-} concentration in the plant cancrinite seed was much lower than in the synthetic cancrinite. No detectable change in CO_3^{2-} concentrations in the plant cancrinite seed were apparent during the experiment.

Sodalite seeded solutions at 90 °C appear to be the most affected by the increasing addition of Na_2CO_3. If increasing CO_3^{2-} content does enhance the rate of sodalite-to-cancrinite transformation (Hermeler et al., 1991), the component of cancrinite in the crystalline product would be expected to increase with increasing Na_2CO_3 concentration. This would, in turn, further depress the SiO_2 concentration in the sodium aluminate liquors.

In summary, systematically increasing the Na_2CO_3 concentration from 4.6 to 40.0 g dm^{-3} resulted in the SiO_2 solubilities shown in Table 5. Parts a and b of Figure 5 show the solubilities of the three different seed types at 90 °C and 160 °C, respectively.
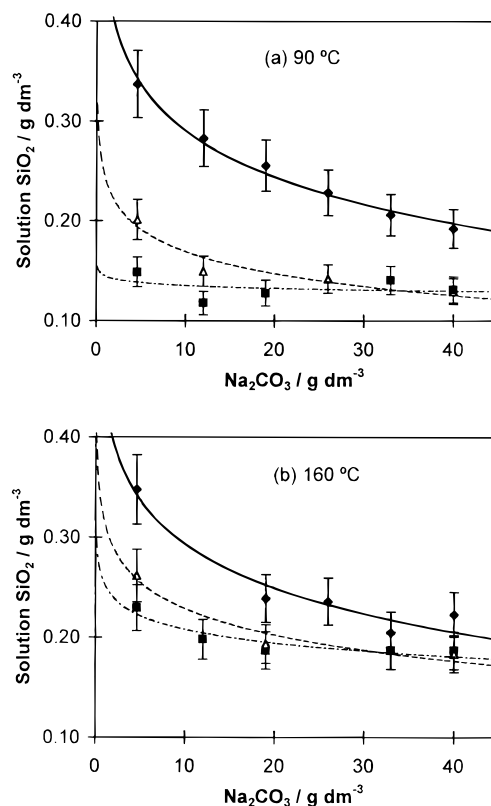

Figure 5. Solution SiO_2 concentration in seeded solutions as a function of Na_2CO_3 concentration: $-\blacklozenge-$ sodalite, $--\triangle--$ Bayer plant-grown cancrinite, $-\cdot\blacksquare-\cdot$ synthetic cancrinite.

Table 5. Experimental SiO_2 Solubility Data

seed	t/°C	Na_2CO_3/ g dm^{-3}	SiO_2 solubility/ g dm^{-3}	duration of expt/days
sodalite	90	4.6	0.34	13
		12.0	0.28	
		19.0	0.26	
		26.0	0.23	
		33.0	0.21	
		40.0	0.19	
sodalite	160	4.6	0.35	13
		19.0	0.24	
		26.0	0.24	
		33.0	0.20	
		40.0	0.22	
synthetic cancrinite	90	4.6	0.15	14
		12.0	0.12	
		19.0	0.13	
		33.0	0.14	
		40.0	0.13	
synthetic cancrinite	160	4.6	0.23	10
		12.0	0.20	
		19.0	0.19	
		33.0	0.19	
		40.0	0.19	
plant cancrinite	90	4.6	0.20	13
		12.0	0.15	
		26.0	0.14	
		40.0	0.13	
plant cancrinite	160	4.6	0.26	16
		19.0	0.19	
		40.0	0.18	

Conclusion

This work is the first study reporting on the solubility of sodium aluminosilicates in synthetic Bayer liquors that takes account the crystalline phase transformations and their effect on the solubility of SiO_2 in sodium aluminate solution of industrial liquor strength proceeding gibbsite

crystallization. The numerical values of the SiO_2 solubilities measured in caustic aluminate solutions of varying Na_2CO_3 concentrations, seeding types, and temperature are given in Table 5.

At both 90 °C and 160 °C over the entire range of Na_2CO_3 concentrations, the sodalite-seeded solutions gave rise to the highest concentration of SiO_2 in solution. At low concentrations of Na_2CO_3 (i.e., between 4.6 and 30.0 g dm^{-3} Na_2CO_3), the Bayer plant-cancrinite-seeded solutions gave rise to a lower SiO_2 solubility than did the synthetic-cancrinite-seeded solutions. Between 30.0 and 40.0 g dm^{-3} Na_2CO_3, the SiO_2 concentration for both the synthetic-cancrinite-seeded solutions and the plant-cancrinite-seeded solutions were the same to within experimental error.

The crystalline product from all of the sodalite-seeded solutions included some cancrinite. The proportion of cancrinite present was greater for the solutions held at 160 °C than for the solutions held at 90 °C. Where no phase change took place, i.e., with cancrinite seeded solutions, the SiO_2 solubility was always greater at 160 °C than at 90 °C. The SiO_2 solubility did not increase significantly between 90 °C and 160 °C for the sodalite-seeded solutions owing to the phase change from sodalite to the more stable, less soluble cancrinite.

Systematically increasing the Na_2CO_3 concentration in all the seeded caustic aluminate liquors caused the SiO_2 concentration to decrease. This drop was most pronounced for the sodalite seeded solutions at 90 °C. A reduction in CO_3^{2-} concentration in the solid phase is observed in both sodalite and synthetic cancrinite on aging of these phases in situ. This trend was not observed in the plant-cancrinite-seeded solutions where the initial concentration of CO_3^{2-} was very low.

Acknowledgment

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