Structure of Burkeite and a New Crystalline Species Obtained from Solutions of Sodium Carbonate and Sodium Sulfate

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It has long been recognized that crystallization from solutions of sodium carbonate and sodium sulfate can produce anhydrous or hydrated forms of the pure species or, in certain composition ranges, burkeite—a crystalline double salt of sodium carbonate and sodium sulfate having the nominal stoichiometry $Na_2CO_3 \cdot 2Na_2SO_4$. The present work examines and explains the observed variation of burkeite composition and identifies a new double-salt species whose composition has been determined to contain approximately 2 moles of sodium carbonate per mole of sodium sulfate. The new species was formed at 115 °C from solutions whose compositions range from approximately 5 moles of sodium carbonate per mole of sodium sulfate to 7 moles of sodium carbonate per mole of sodium sulfate.

Introduction

Aqueous solutions of sodium carbonate and sodium sulfate are commonly encountered, and the nature of salts recovered by crystallization from those solutions is of great importance. The solutions, which are found in many industrial processes and in natural brines, are often evaporated for the express purpose of recovering the solutes. An example is in the recovery of chemicals and energy from process streams, known as black liquor, in the pulp and paper industry. Formation of crystals from such streams is important, not only from the perspective of chemical recovery, but also with regard to the critical problem of evaporator fouling. Obviously, the composition of the crystalline solid impacts its properties and could influence its tendency to foul heat-transfer surfaces.

It is well-known that crystallization from aqueous solutions containing sodium carbonate and sodium sulfate can produce crystals of a double salt commonly known as burkeite. Burkeite crystals are of orthorhombic form and nominally have a carbonate-to-sulfate molar ratio (C:S) of 1:2. Attempts to determine the exact crystal stoichiometry have found C:S molar ratios that actually vary around 1:2 (for example, 1:1.9,[1] 1:1 to 1:3,[2] 1:1.4 to 1:2.2[3]), with the precise value being a function of the composition of the solution from which the crystals are formed. Indeed, burkeite occupies a large area on the phase diagram of $Na_2CO_3 - Na_2SO_4 - H_2O$ mixtures,[3] making it the most important species in the system. Other solid species that can form from this system at temperatures above 100 °C include sodium carbonate, sodium carbonate monohydrate, and sodium sulfate.[2,3]

It is interesting to note that the experimental procedures followed by the researchers cited above achieved apparent equilibrium by adding excess amounts of sodium carbonate and sodium sulfate crystals to solutions of these solutes. The primary concern with this approach is that it might have extended the domains of sodium carbonate and sodium sulfate if the system

had not reached equilibrium. That is, in a system whose equilibrium solid is a double salt, equilibrium between solid and liquid phases can be achieved only through complete dissolution of the excess solute. As the liquid approaches equilibrium, the necessary liquid-phase mediated transformation could be extremely slow. In addition to this difficulty, the experimental procedure used by earlier researchers may have made it impossible to produce some species that could have been generated by crystallization. Moreover, researchers might have overlooked other solid phases due to limitations of the technology they used; namely, the solid phases were detected by the immersion method using a petrographic microscope.

There was early speculation on the formation of double salts other than burkeite in the $Na_2CO_3 - Na_2SO_4 - H_2O$ system when several investigators reported compounds with various ratios of sodium carbonate and sodium sulfate.[2] Later Helvenston et al.[4] prepared a new double salt of sodium carbonate and sodium sulfate from an aqueous solution of sodium hydroxide, sodium carbonate, sodium chloride, and sodium sulfate. They found the X-ray powder diffraction (XRD) pattern of this double salt to be quite different from that of burkeite, and suggested the formula $(Na_2CO_3)_9 \cdot (Na_2SO_4)_4$ on the basis of chemical analysis. Novak[5] also found crystals from the $Na_2CO_3 - Na_2SO_4 - H_2O$ system that had abnormal peaks in the XRD pattern and attributed them to unidentified compounds, suggesting they might be $3Na_2CO_3 \cdot Na_2SO_4$ or $Na_2CO_3 \cdot Na_2SO_4$.

Despite the work cited above, we have been unable to find conclusive published evidence demonstrating the existence of a double salt, other than burkeite, present in the $Na_2CO_3 - Na_2SO_4 - H_2O$ system. In the present research, we explored the phase behavior of this system over a wide range of solution compositions and found that the salt composition varied according to the solution composition. Here we document that variation and clarify the conditions leading to various salt species. Moreover, we use modern analytical procedures to identify a new salt that is crystallized from solutions having a C:S ratio between about 5:1 and 7:1. This new substance is thought to be of great importance in processes involving evaporation of solutions that contain sodium carbonate and

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Burkeite and a New Species from Na₂CO₃/Na₂SO₄ Solutions

J. Phys. Chem. B, Vol. 107, No. 29, 2003 **6933**

sodium sulfate, and it may hold the key to developments that will minimize fouling of heat-transfer surfaces in such systems.

Experimental Section

Crystallizations were carried out in a 1-L Parr reactor. A stainless steel impeller driven by a motor with variable rotating speeds, which were kept high enough to ensure turbulent mixing throughout, was used for mixing. A thermocouple and a pressure transducer were used to measure the system temperature and pressure, respectively, and a PID controller adjusted the heater to provide the desired system temperature (generally, 115 °C) and evaporation rate (3 to 5 g/min). The evaporated water was condensed and weighed so that the composition of the residual mixture in the reactor could be estimated by mass balance. The mole ratio of sodium carbonate to sodium sulfate in the solutions was varied to determine the impact of this variable on the crystals formed.

The progress of crystallization was followed using a Lasentec FBRM (Focused Beam Reflectance Measurement) D600L system. Details of the FBRM operation and its use to follow the progress of crystal nucleation are given elsewhere.[6] After crystallization, the resulting suspension was cooled to about 90 °C and vacuum-filtered to collect the crystalline product.

Special care was taken to minimize additional crystallization from residual liquid contained in the collected samples. Such post-sampling crystallization could interfere with the XRD analysis of crystals generated in the well-characterized part of the process. A procedure was developed in which several organic solvents were used to wash away residual liquid from the sample crystals. Ethylene glycol was found to be the best of those solvents tested. The salts of interest have very limited solubility in pure ethylene glycol, but they are quite soluble in ethylene glycol−water mixtures.[7,8] Moreover, experiments showed that mixing the solutions of sodium carbonate and sodium sulfate with a proper mixture of ethylene glycol and water could avoid the precipitation of these salts. As ethylene glycol has a high boiling point and can absorb moisture from the air, it subsequently was washed from the crystal samples with ethanol. The final selected protocol for crystal washing involved using the following five wash liquids in sequential washing steps: (1) 1:1 mixture by volume of water and ethylene glycol, (2) 1:2 mixture by volume of water and ethylene glycol, (3) ethylene glycol, (4) 1:1 mixture by volume of ethylene glycol and ethanol, and (5) ethanol. Finally, the crystals were spread evenly on a filter paper and dried in the air for about 30 min at room temperature.

The crystals were identified by X-ray powder diffraction (XRD) analysis using a Philips PW1800 automatic powder diffractometer with APD 3720 analysis software. A sample of about 1 to 2 g of crystals was required. The sample was ground into fine powder and placed into the sample holder. Copper Kα radiation was used, and the Kα2 contribution was stripped from the powder patterns using a built-in function in the APD software to increase accuracy. The powder XRD patterns were made over a diffraction-angle (2θ) range of 5 to 70°, with a step size of 0.02° and a counting time of 1 s per step. The inorganic substances were determined by comparing the powder patterns obtained with those in the JCPDS powder diffraction files (PDF).[9] The instrument used in this research generally overestimated the diffraction angles by about 0.15 to 0.20°, which was not a serious problem for qualitative analysis. If more accurate data are required, an internal standard can be used.

A scanning electron microscope (SEM) was used to examine the crystal structures. It was a high resolution (2 nm) Hitachi
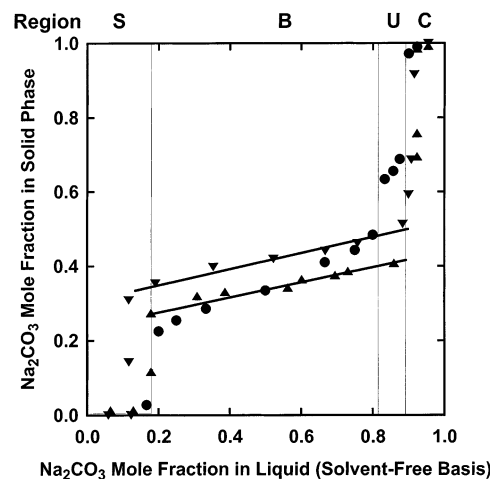

Figure 1. Compositions of the crystals formed (excluding residual or structural water) in the sulfate (S), burkeite (B), unknown (U), and carbonate (C) regions as a function of solution composition. ● experimental data at 115 °C from the present study, ▲ data at 100 °C from Green and Frattali,[3] and ▼ data at 150 °C from Schroeder.[2]

S4100 field emission scanning electron microscope equipped with a Noran thin-window light element X-ray detector. This microscope had accelerating voltages ranging from 0.5 kV to 30 kV.

The SEM system also included an energy-dispersive X-ray spectroscopy (EDXS) system for chemical analyses and comparison of spatial differences with compositions. The minimum concentration detectable by the EDXS system was about 1000 ppm. The depth of detection was estimated to be several micrometers. This instrument provided semiquantitative analysis because standards were not used.

The composition of the crystals was analyzed using an automatic titrator (Mettler-Toledo DL58). The relative error of the concentration was less than 1%.

Evaporative crystallization from aqueous solutions containing sodium carbonate and sodium sulfate in mole ratios ranging from 1:5 to 12:1 (Na₂CO₃ mole fractions on a solvent-free basis from, $x_{Na_2CO_3}$, 0.17 to 0.92) were conducted. Enough of the sodium salt of ethylenediaminetetraacetic acid (EDTA) was added to give either 400 or 1000 ppm EDTA. This species sequesters calcium ions in the solution and avoids their inhibitive effects on nucleation.[6] Evaporation was stopped once it was clear from the FBRM data that primary nucleation had been completed. Experiments were selectively repeated (a total of 20 experiments were performed) to estimate the average errors.

Results

The crystals recovered from each of the evaporative crystallization experiments were analyzed and the resulting compositions are shown in Figure 1. Also shown are equilibrium data from the literature at 100 °C[3] and at 150 °C.[2] Data in the figure are divided into four regions according to which solid species was determined (by both chemical and XRD analysis) to have crystallized. Boundaries between these regions are given in Table 1.

In the sulfate region (S), sodium sulfate (thenardite) was the dominant solid phase crystallized from solutions having carbonate-to-sulfate mole ratios less than or equal to 1:5 ($x_{Na_2CO_3}$ ≤ 0.167 on a solvent-free basis). The majority of the data in the burkeite region (B) indicate that sodium sulfate was more readily accommodated in the crystal structure than sodium

6934 *J. Phys. Chem. B, Vol. 107, No. 29, 2003*

Shi and Rousseau

TABLE 1: Regions in Figure 1 That Determine the Composition of Crystals Obtained by Evaporation of Solutions of Sodium Carbonate and Sodium Sulfate at 110 °C

region	solution composition[a]	solid composition
sulfate (S)	C:S ≤ 1:5 ($x_{Na_2CO_3}$ ≤ 0.167)	Na_2SO_4 (thenardite)
burkeite (B)	1:5 < C:S < 5:1 (0.833 ≤ x_{Na2CO3} < 0.889)	C:S ≈ 1:2 ($x_{Na_2CO_3}$ ≈ 0.33)
dicarbonate (D)	5:1 < C:S < 8:1 (0.833 ≤ $x_{Na_2CO_3}$ < 0.889)	C:S ≈ 2:1 ($x_{Na_2CO_3}$ ≈ 0.67)
carbonate (C)	C:S ≥ 9:1 ($x_{Na_2CO_3}$ ≥ 0.9)	$Na_2CO_3 \cdot H_2O$ (thermonatrite)

[a] $x_{Na_2CO_3}$ on a solvent-free basis.

carbonate, and the carbonate-to-sulfate mole ratios in the crystals were all less than 1:1. We will explain later this upper limit in the mole ratio.

It is also noteworthy that the crystals in the burkeite region were obtained at 115 °C and that they had a composition different from what would be expected by interpolating the available equilibrium data at 100 °C and 150 °C. This could be explained by the nature of the experiments in the present study; i.e., they and the compositions of the resulting crystals were controlled by kinetics rather than equilibrium.

In the dicarbonate (D) region, solutions with carbonate-to-sulfate mole ratios ranging from 5:1 to about 8:1 (0.833 ≤ $x_{Na_2CO_3}$ < 0.889, on a solvent-free basis) produced crystals of significantly different composition from burkeite, creating a discontinuity in the plot of crystal composition versus solution composition at $x_{Na_2CO_3}$ ≈ 0.833.

While the solution carbonate-to-sulfate mole ratios were 5:1, 6:1, and 7:1 during a set of experiments, the ratios were 1.73, 1.91, and 2.2, respectively, in the recovered crystals. The solid species seemed to be a double salt of sodium carbonate and sodium sulfate that is different from burkeite, and it has a nominal carbonate-to-sulfate mole ratio of 2:1. This is the reason for the reference to this new species as dicarbonate. The dicarbonate region could overlap both burkeite and carbonate regions, and its boundaries might depend on experimental conditions.

In the carbonate (C) region, sodium carbonate monohydrate (thermonatrite) was the first and the dominant solid-phase crystallized from solutions having carbonate-to-sulfate mole ratios greater than about 9:1 ($x_{Na_2CO_3}$ ≥ 0.9 on a solvent-free basis).

It should be noted that Figure 1 was established by analyzing the first solid species that was crystallized in a substantial amount (at least 10 g) from the solutions. As evaporation proceeds, other solid phases may crystallize because of inherent changes in the solution compositions.

Chemical analysis with X-ray powder diffraction is based on two principles:[10] (1) a given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as a constituent of a mixture; (2) under ideal conditions, the intensities of the peaks (lines) given by a mixture depend on the proportion of that substance in the specimen.

The crystals formed from the solutions having carbonate-to-sulfate mole ratios ranging from 1:4 to 4:1 were identified by XRD analysis. Spectra of crystals taken from three such runs are shown in Figure 2 where they are compared with the peak positions and relative intensities of the standard burkeite XRD pattern.[9] All the major peaks of the standard burkeite pattern are found in the three spectra of Figure 2, thereby providing evidence that, indeed, the species obtained by crystallizations from solutions having carbonate-to-sulfate ratios between 1:2
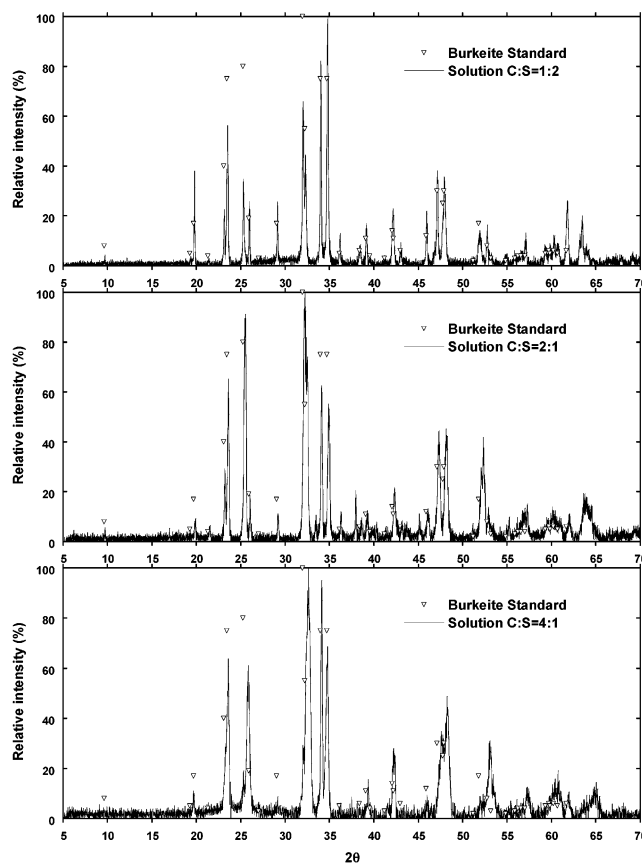

Figure 2. XRD patterns of the crystals obtained from solutions containing various sodium carbonate/sodium sulfate ratios (C:S). The burkeite standard peaks were from JCPDS PDF #24-1134.

and 4:1 were burkeite. Examination of the patterns in Figure 2 show that the lines shift, broaden, and have varying intensity as the carbonate content of the solution (and hence the resulting crystals) is increased. It is asserted that such behavior can only be attributed to carbonate ions partially substituting for sulfate ions in the crystal lattices.

Giuseppetti et al.[11] used a single-crystal diffractometer to examine burkeite crystals that had been prepared by slow evaporation of solutions containing varying ratios of sodium carbonate to sodium sulfate. Figure 3 shows four possible subcells that may be combined to form the unit cell of a burkeite crystal. Figure 3a shows the subcell (a) obtained when carbonate ions partially replace the sulfate ions in the crystal subcells (b), (c), and (d), which differ only in the orientation of the sulfate ion in the middle left of each of these subcells. Among four anionic sites in each subcell, only the two in the middle can be substituted, and they are equivalent positions as determined by lattice symmetry. Carbonate ions can substitute for these sulfate ions because some of the bond lengths and bond angles in the sulfate ions at these two anionic sites are close to those in carbonate ions. It can be concluded that combinations of these subcells to form a burkeite unit cell limit the maximum carbonate-to-sulfate mole ratio to 1:1, which explains the results obtained by chemical analysis and previously cited.

The substitution of one ion for another usually produces slight changes in lattice parameters, which reflect differences in ionic radii. This leads to line shifting in the XRD patterns. In the present system, for example, replacement of a carbonate ion by a sulfate ion means that the carbon atom will occupy the position previously held by the sulfur atom, and that all of the oxygen atoms in the carbonate ion—this means O(1), O(2), and O(3) in subcell (a)—will occupy the positions of oxygen atoms
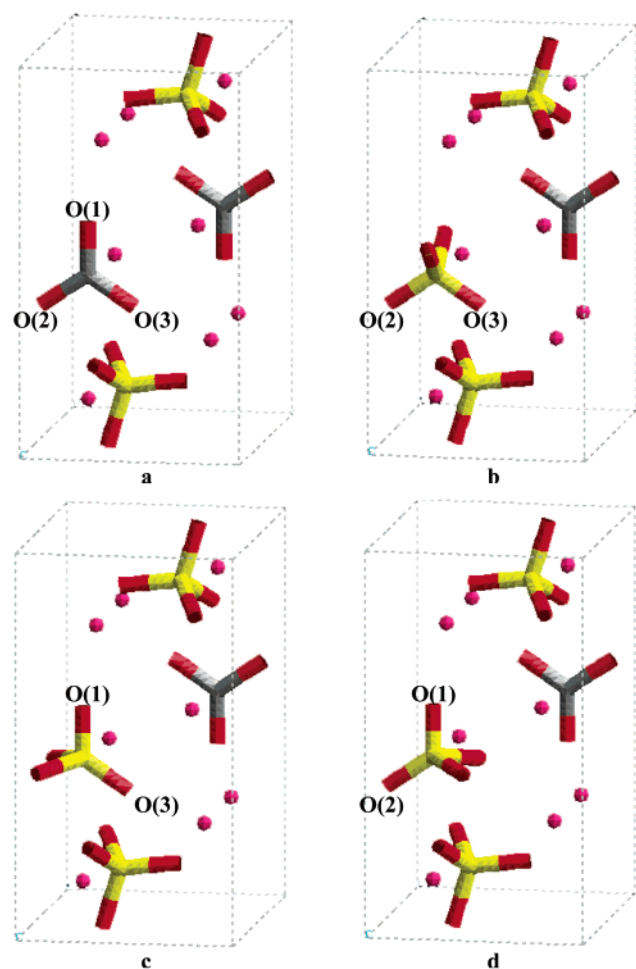
Figure 3. The unit cell of burkeite crystals is a combination of these four kinds of subcells (based on the work by Giuseppetti.[11] (a) $CO_3^=$ partially replaces $SO_4^=$ in two of the anionic sites; (b)−(d) $SO_4^=$ in the middle anionic sites can take three orientations.

O(1), O(2), and O(3) in subcells (b), (c), and (d). Therefore, such substitution produces no new positions in the subcell and no additional lines appear in the XRD pattern. However, the C−O bond length differs from that of S−O and the O−C−O bond angle differs from that of O−S−O, which causes variations in interplanar distances and produces line shifting. Other differences between carbonate and sulfate ions, such as the number of electrons associated with carbon and sulfur and the number of oxygen atoms, can cause changes in the intensities of the lines in the spectra. Ion substitution also results in lattice disorder if the substituting ions are not homogeneously distributed throughout the entire crystal, which again results in line broadening in the XRD powder patterns.

A large spherical particle that was an agglomerate of numerous burkeite crystals was obtained from a solution of sodium carbonate and sodium sulfate that had a C:S mole ratio of 1:2. The particle was examined with a scanning electron microscope. The run from which the particle was obtained had been performed without the addition of EDTA. The particle was severed in the middle to expose the inner structures, and photomicrographs of the SEM images are shown in Figures 4. The crystals are shown to be far from homogeneous and probably result from agglomeration either during crystallization or sample preparation.

Subsequently, EDXS analysis determined that there was significant spatial variation in the composition of the particle. The mole ratios of carbonate and sulfate at different locations

were 1:1.2, 1:1.24, 1:1.85, and 1:2 (±10%). Chemical analysis gave an overall carbonate-to-sulfate ratio in the crystal of 1:2.4. This apparent inconsistency points out that the EDXS was not well-calibrated, but the data show nevertheless that there was significant spatial variation in the composition of the sample.

Discussion

The unit cell of burkeite crystals is formed from a combination of the four kinds of subcells show in Figure 3.[11] (There are more than four when different orientations of sulfate ions on the top and bottom of each subcell are considered.) The proportion of each subcell in the whole crystal lattice is determined by their relative total energies. We determined the following energies for each configuration by Cerius2 molecular simulation calculations: (a) −1538.66; (b) −1360.33; (c) −1264.72; (d) −1258.71 kcal/mol subcell. Since the subcells with lower energy make up a larger fraction of the crystal lattice, the frequency with which a subcell is encountered is of the order (a) > (b) > (c) > (d), although the order may vary somewhat with the temperature and composition of the solution from which a crystal is obtained.

Giuseppetti et al.[11] suggested the formula $Na_4SO_4[(CO_3)_t(SO4)_{1−t}]$ for burkeite rather than the widely accepted carbonate to sulfate mole ratio of 1:2. In other words, they postulate that burkeite has no fixed formula and estimated the value of t to be 1/2 to 2/3, corresponding to carbonate-to-sulfate mole ratios in the range 1:3 to 1:2. We think their estimate is too narrow because the solutions from which they performed crystallizations had sodium carbonate/sodium sulfate ratios ranging from 4:1 to 1:1. That is, the solutions were at the low end of the C:S ratio. The experimental results that were described earlier and shown in Figure 1, illustrate that the carbonate-to-sulfate mole ratios in burkeite crystals approach 1:1 in the present work.

Burkeite consists of a spectrum of compounds having orthorhombic crystal lattices, with sodium carbonate-to-sodium sulfate mole ratios ranging from 1:3 to 1:1. The XRD patterns of crystals obtained in the burkeite region showed continuous variation in composition as the carbonate-to-sulfate mole ratio increased in the solutions from which the crystals were formed. There was a substantial discontinuity in this pattern when the C:S ratio in solution became 5:1, and crystals from solutions in this composition range exhibited crystal-lattice parameters that were significantly different from those in the burkeite region. Figure 5 illustrates this by comparing the XRD patterns of the solid species obtained from solutions of sodium carbonate and sodium sulfate in the mole ratios 4:1 and 5:1. The differences between the two patterns cannot be the result of factors such as shifting, broadening, or intensity variation of the lines in the burkeite pattern, as was found to occur when considering various burkeite compositions. XRD and chemical analysis lead to a conclusion that this new solid crystalline species is a compound other than burkeite. Moreover, crystals from three experiments (C:S = 5:1, 6:1, and 7:1) provided essentially the same XRD pattern. Chemical analysis determined that this new species contained approximately 2 moles of sodium carbonate per mole of sodium sulfate, and we have therefore referred to it as dicarbonate.

The XRD pattern of the dicarbonate crystals showed no trace of burkeite or sodium carbonate (including its hydrates), suggesting that the crystals were pure. The XRD pattern matched no other substances (or their mixtures) listed in the JCPDS powder diffraction files, which is the most comprehensive database for XRD powder diffraction analysis. It matched reasonably well with a compound obtained from an aqueous
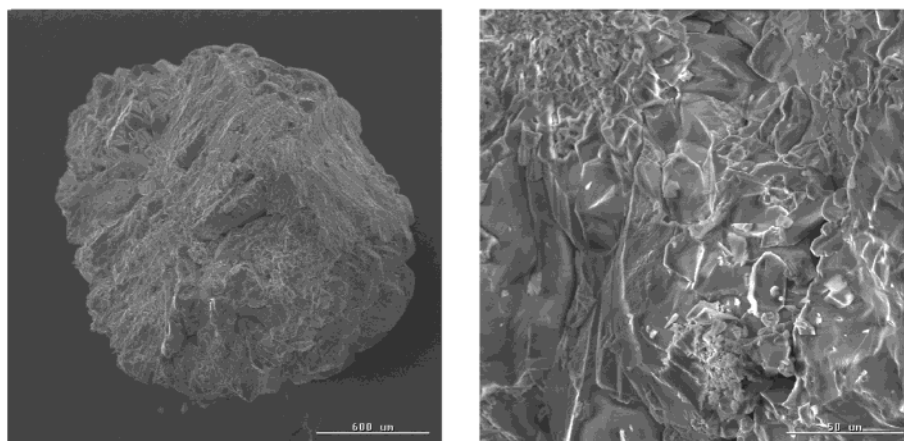
Figure 4. SEM image of a large particle obtained from the solution containing sodium carbonate and sodium sulfate in the mole ratio 1:2. The particle had been cleaved in the middle into halves.
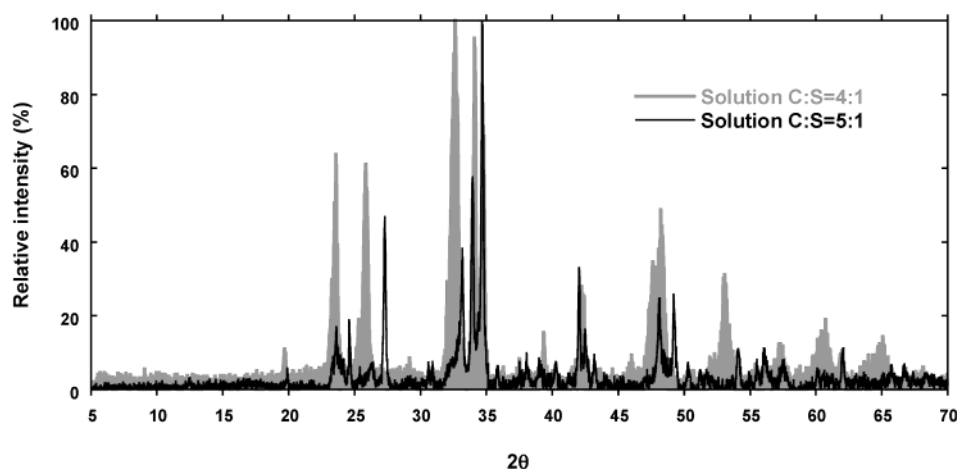

Figure 5. XRD powder diffraction patterns of crystals obtained from solutions have different carbonate-to-sulfate (C:S) ratios. Note that crystals from the unknown region of Figure 1 (C:S = 5.1) are different from those in the burkeite region (C:S = 4:1).
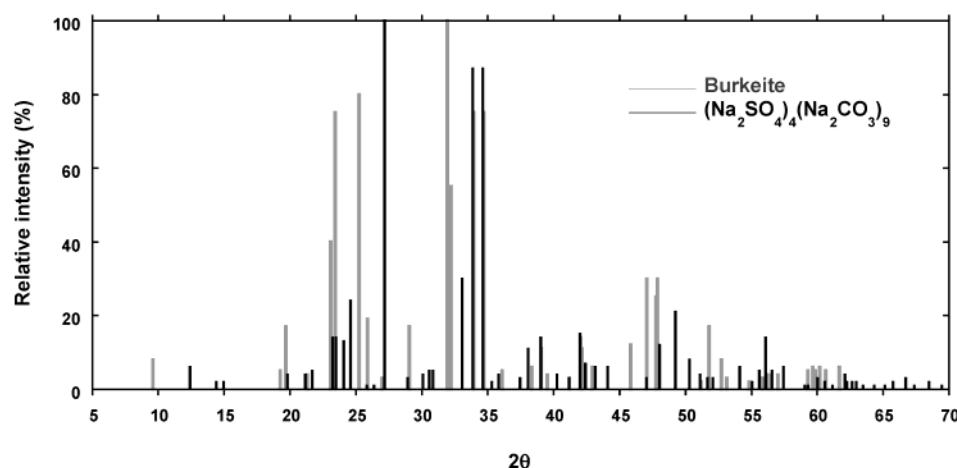

Figure 6. A comparison of the XRD pattern obtained by Helvenston[4] and the standard XRD pattern of burkeite from JCPDS PDF #24-1134.

solution of sodium hydroxide, sodium carbonate, sodium chloride, and sodium sulfate that was described in a patent.[4] That research group used chemical analysis to identify the compound as a double salt of sodium carbonate and sodium sulfate with the stoichiometric composition $(Na_2CO_3)_9 \cdot (Na_2SO_4)_4$. Figure 6 compares the XRD pattern of that species with the standard burkeite pattern. Among the most significant differences are burkeite peaks at 23.42°, 25.24°, and 31.93°, and peaks for the $(Na_2CO_3)_9 \cdot (Na_2SO_4)_4$ at 27.2° and 34.6°.

As mentioned earlier, black liquor evaporation is one of the important technologies concerned with evaporation of solutions of sodium carbonate and sodium sulfate. It is unfortunate that researchers in this field apparently have missed the work of Helvenston et al.[4] For example, one research group obtained an XRD pattern from a sample of scale from a black-liquor evaporator that was very similar to the dicarbonate species.[12] However, it appears that group erroneously concluded that the scale was a mixture of several compounds such as Na_2CO_3,

Na$_2$S·H$_2$O, Na$_2$S$_2$, burkeite, K$_2$Ca(CO$_3$)$_2$, and CaCO$_3$. In another instance,[5] samples of scale formed from solutions of sodium carbonate and sodium sulfate gave XRD peaks at 27.25° and 34.65°; these are the same as the peaks shown in Figures 5 and 6. Some of these samples were described as having a high carbonate content that was attributed to unknown double salts of sodium carbonate and sodium sulfate and to sodium carbonate monohydrate. The unknown double salts were assumed to be 3Na$_2$CO$_3$·Na$_2$SO$_4$ or Na$_2$CO$_3$·Na$_2$SO$_4$ based on chemical compositions. However, in a later and more widely cited work,[13] the same researcher apparently reconsidered the earlier conclusion and described these double salts as belonging to the burkeite phase. This could be the reason that no progress has been made in identifying this new species over the past two decades, despite its frequent appearances in black-liquor evaporation.

The dicarbonate species can belong to the orthorhombic crystal system, but it differs from burkeite because carbonate ions might have started to substitute for the top and bottom sulfate ions in the subcells shown in Figure 3, which is said never to occur in burkeite.[11] Such substitution leads to a carbonate-to-sulfate mole ratio in the crystals over the 1:1 limit of burkeite, and since it substantially changes the dimensions of the subcells, significantly different XRD patterns are produced. Although significant effort was expended in the present work to obtain the parameters of the lattice structure of this new species, no satisfactory results were obtained because low-symmetry crystal systems (such as orthorhombic) require high-quality XRD data with errors less than 0.03° in diffraction angles, which could not be attained using the current instrument.

In the carbonate region, i.e., when the mole ratio of carbonate to sulfate in the solutions reached 9:1 or higher, sodium carbonate monohydrate was always the first species to form despite the use of EDTA. An interesting phenomenon in this region is that both the anhydrous and monohydrate forms of sodium carbonate were crystallized from the pure solutions of sodium carbonate, while the anhydrous form was absent when there was a small amount of sodium sulfate (e.g., at a carbonate-to-sulfate mole ratio of 12:1) in the solution at the operating temperature of 115 °C. According to the phase diagram of sodium carbonate, anhydrous sodium carbonate is the stable form and should be crystallized rather than the monohydrate form at 115 °C (the recognized transition temperature from monohydrate to anhydrous forms is 109 °C). The most probable explanation is that crystallization was controlled by kinetics rather than equilibrium, and the deciding factor was the relative nucleation and crystal growth rates of the stable and metastable phases. This sort of behavior was first generalized by Oswald with "the rule of stages". (According to this rule, an unstable system does not necessarily transform directly into the most stable state, but into one which mostly closely resembles its own, i.e., into another transient state whose formation from the original is accompanied by the smallest loss of free energy.[14])

Conclusions

Evaporative crystallizations were carried out with aqueous solutions of sodium carbonate and sodium sulfate in mole ratios ranging from 1:5 to 12:1. According to the solid species crystallized, the solutions were classified into four regions: sulfate, burkeite, dicarbonate, and carbonate regions.

In the burkeite region, XRD patterns showed shifting, intensity variation, and broadening of the lines as the carbonate content in the crystals increased. This phenomenon was explained by carbonate ions substituting for sulfate ions, changing the lattice parameters, and bringing disorder into the crystal lattice of burkeite. The crystals were found to be inhomogeneous by both scanning electron microscopy and energy-dispersive X-ray spectroscopy. The maximum ratio of carbonate to sulfate in burkeite crystals was shown to be 1:1, and this limitation was explained by examination of the lattice structure of burkeite.

A new crystalline species was the first crystallized from a solution whose composition was determined to fall into a specific range (region). Both the chemical compositions and the XRD patterns in this region showed discontinuity from the adjacent regions. This species could result from carbonate ions substituting for sulfate ions in locations other than those possible with burkeite. Chemical analysis indicated this species had an approximate carbonate-to-sulfate mole ratio of 2:1.

In the carbonate region, sodium carbonate monohydrate (thermonatrite) was the dominant phase crystallized, despite it being less stable at the operating temperature than anhydrous sodium carbonate (natrite).

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