Crystallization from Aqueous Solutions of Na_2CO_3 and Na_2SO_4 as Related to Heat Exchanger Fouling

C. L. Verrill,[1] R. W. Rousseau,[2] and A. P. Wilkinson[3]

[1] Institute of Paper Science and Technology, Georgia Institute of Technology,
Atlanta,GA 30332-0620

[2] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology,
Atlanta, GA 30332-0100

[3] School of Chemistry and Biochemistry, Georgia Institute of Technology,
Atlanta, GA 30332-0400

Abstract

We have obtained new nucleation and crystal property data for sodium carbonate-sulfate salts that crystallize during evaporation of paper industry spent pulping liquors. Earlier lab-scale evaporation experiments at 115°C indicated that a new species, referred to as dicarbonate with approximate composition $2Na_2CO_3{\cdot}Na_2SO_4$, precipitated when the liquid phase was in a narrow range of carbonate-to-sulfate ratio. Our work also suggested that heat exchanger surface fouling was more likely to occur in evaporation equipment when the liquid composition fell in this narrow range. In the present work, we have verified that a dicarbonate-rich crystal phase is formed from supersaturated solutions when the mole fraction $x = (CO_3/(CO_3+SO_4)$ of the liquid phase falls between 0.833 and 0.889 and the temperature is between 125 and 135°C. For temperatures of 110-115°C, there is a sharp transition from burkeite to dicarbonate crystallization at $0.833 < x < 0.840$. At temperatures below 110°C, no evidence of dicarbonate was found in our experiments; the crystal phase was burkeite for $x < 0.834$ or sodium carbonate monohydrate for $x > 0.835$. Dicarbonate solubility decreased slightly (4% of maximum value) from 115 to 145°C. The dicarbonate crystals were found to be hydrothermally stable for temperatures up to 145°C. A relative supersaturation of 5-7% had to be attained before bulk crystallization occurred; this wide metastable zone explains the tendency for dicarbonate to form scale on heat transfer surfaces.

Introduction

Evaporation of spent pulping liquors is typically the first or second highest consumer of steam in pulp and paper mills. Thermal efficiency, processing capacity, and maximum total dry solids contents attainable in evaporators and concentrators are often limited by heat-transfer surface fouling and tube plugging. The fouling problem in about one third of this equipment results from deposition of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) scales [1]. This is often referred to as soluble scaling because the sodium salts can be removed by washing with hot water. A goal of our work is to evaluate options to reduce soluble-scale deposition by manipulation of the crystallization behavior of Na_2CO_3 and Na_2SO_4 during spent pulping liquor evaporation.

The existence of a previously unknown species was identified in early fundamental studies [2]. This species, termed *dicarbonate*, is a double salt of approximate composition $2Na_2CO_3{\cdot}Na_2SO_4$. This work also suggested that dicarbonate crystals cause soluble-scale fouling in spent pulping liquor evaporators operating above 50% total solids content and that calcium ions control the onset of nucleation of both burkeite ($\sim 2Na_2SO_4{\cdot}Na_2CO_3$) and dicarbonate.

For spent pulping liquor, Shi [3] discovered there is an additional composition region, $0.68 < x_{Na_2CO_3} < 0.82$, where $x_{Na_2CO_3}$ is the mole ratio of Na_2CO_3 to $Na_2CO_3 + Na_2SO_4$ in solution, in which both burkeite and dicarbonate coexist (Figure 1). The regions where dicarbonate or both burkeite and dicarbonate are found in the solid products is of importance for industrial spent pulping liquor evaporators. Data collected during a survey of spent pulping liquor evaporator fouling [1] indicate that for about 60% of these evaporators, the weak spent pulping liquor composition falls within the range $0.68 < x_{Na_2CO_3} < 0.89$. The composition of the dissolved sodium salts in the remaining liquors from that survey would move into the dicarbonate composition range when concentrated to more than 70% dry solids content.

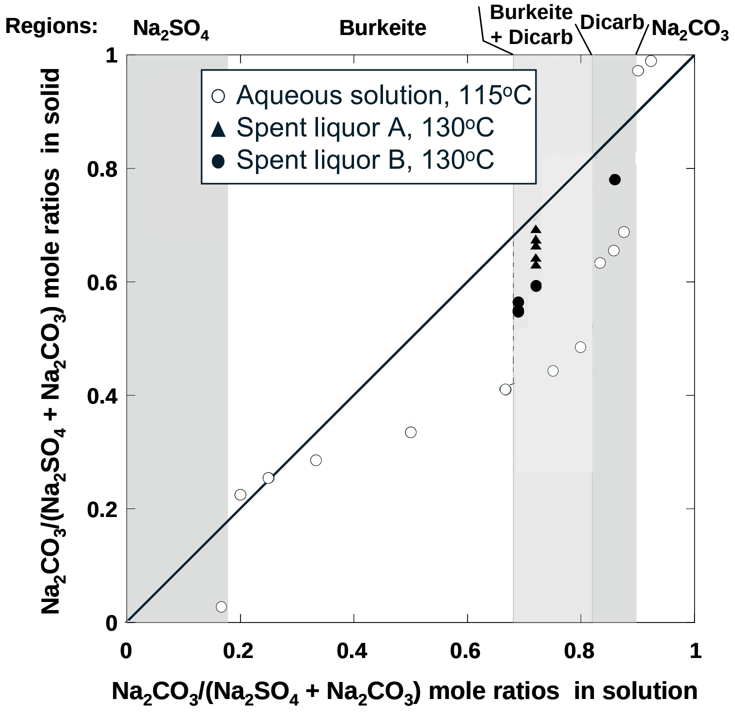

Figure 1. Comparison of the crystal compositions obtained from spent pulping liquors at 130°C and aqueous solutions at 115°C; adapted from Shi [3].

Experimental

For this work, a series of experiments were conducted to better define the temperature and composition boundaries for the formation of dicarbonate and to measure the solubility limit and metastable limit (crystallization point) of dicarbonate. Three batch reactors have been used in this work to study crystallization in spent pulping liquor and salt-water mixtures. Model solutions were made up from ACS grade sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) and deionized water. The molar ratios of Na_2CO_3 to Na_2SO_4 in the initial solution varied from 1:2 to 8:1. 1000 mg EDTA was added per kg of solution to sequester calcium ions. Shi discovered that Ca^{2+} acts as a nucleation inhibitor for burkeite and dicarbonate [4]. Addition of EDTA creates a complex with Ca^{2+} so the burkeite or dicarbonate can crystallize freely without inhibition.

Figure 2 illustrates the apparatus used for metastable limit measurements and for isolating the first crystals produced. During the experiments, suspended crystal particles were detected using a Lasentec® Focused Beam Reflectance Measurement (FBRM) system. Batches of solution were prepared at approximately 30 wt. % total solids content and heated to desired temperature and the solvent evaporated at constant rate (5 g/minute) to reach nucleation as indicated by the FBRM when 9-100 µm particle counts exceeded 2000 per second. Samples were collected through an in-line 2-µm filter element that was preheated to the crystallization temperature. The mother liquor was sampled into a measured portion of dilution water to prevent crystallization as it cooled to room temperature. The crystals trapped by the filter were rinsed using a sequence of hot 1:1 ethylene glycol and water, ethylene glycol, and ethanol. The crystals were removed from the filter and analyzed by x-ray diffraction (XRD) on a Pananalytical X'Pert PRO MPD1 instrument with JADE 6.5 software. Chemical analysis included coulometric titration for CO_3, capillary ion electrophoresis for SO_4, and inductively-couple plasma atomic emission spectrometry for Na, S and trace metals.

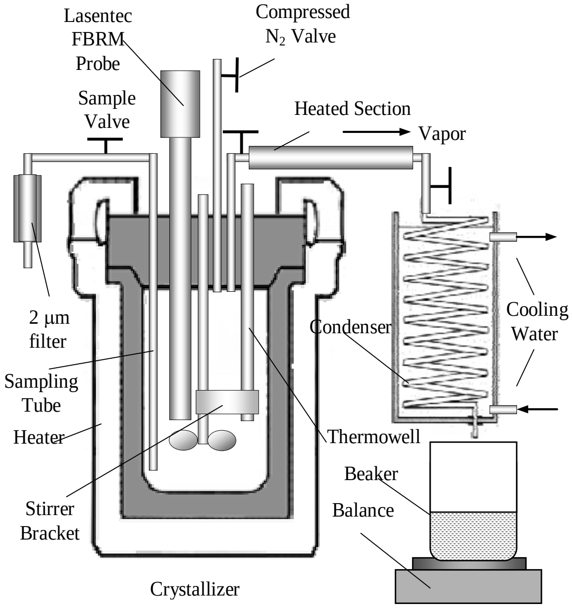

Figure 2. Sketch of 1-L bench-scale batch crystallizer.

Similar equipment was used for separately measuring the solubility limit and collecting crystal samples that had been allowed to equilibrate with the mother liquor. In these experiments, after the correct amount of solvent was evaporated to reach the metastable limit, evaporation was stopped, the reactor sealed and held at conditions of constant pressure and temperature for 22-72 hours prior to sampling.

Results

A significant finding from this work is that the dicarbonate species is the predominant solid phase crystallized from solutions in which the initial carbonate-to-sulfate molar ratio is between 5:1 and 9:1 and the temperature is between 110 and 145°C. Our new data are compared with those of Shi in Figure 3 (Shi's expected crystallization regions are provided for reference). There is a very sharp boundary between burkeite and dicarbonate at 5:1 molar ratio ($x_{Na_2CO_3}$ = 0.833). At a temperature of 105°C the solid phase produced is either burkeite ($x_{Na_2CO_3}$ = 0.833) or $Na_2CO_3 \cdot H_2O$ ($x_{Na_2CO_3}$ > 0.85). Higher temperatures than 145°C were not investigated, because this is near the upper operating temperature of spent pulping liquor evaporation equipment and close to the point where liquor organics will begin to decompose.

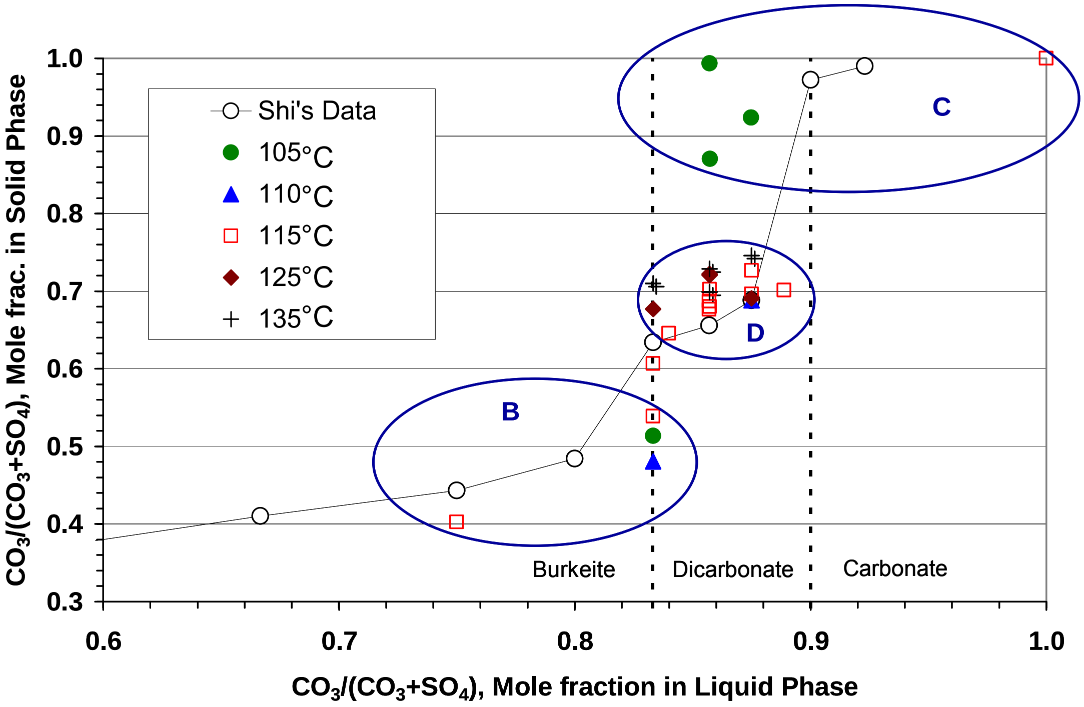

Figure 3. Composition of first crystals produced during batch evaporation of Na_2CO_3-Na_2SO_4 mixtures as a function of initial liquor composition and evaporation temperature; circles group data for solids identified as predominantly burkeite (B), dicarbonate (D), or Na_2CO_3 (C).

Another significant result from this work is that the dicarbonate phase exists in equilibrated mixtures of salt and mother liquor. Our XRD investigations have suggested that the dicarbonate phase has characteristic single peaks at 2θ of 12.6°, 27.3°, and a triple-peak cluster between 32 and 35°. In Figure 4, the top XRD plot is from crystals that have been held in contact with the mother liquor for 22 hrs, the lower plot is from crystals that were isolated from the mother liquor immediately after primary nucleation, both plots show nearly-identical features that are characteristic of the dicarbonate phase. Note there is no match with related compounds from the PDF-4 database given in the bottom set of plots.

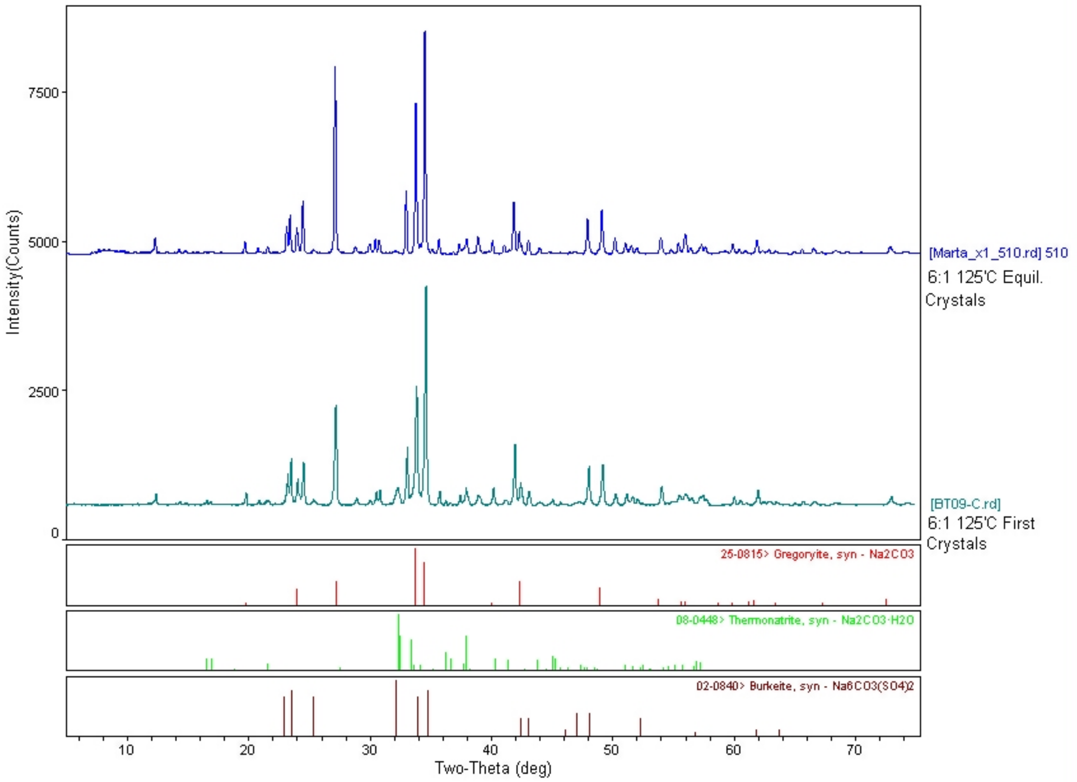

Figure 4. Comparison of XRD spectra of crystals obtained from mixtures of Na_2CO_3 and Na_2SO_4 in the initial molar ratio of 6:1 at 125°C.

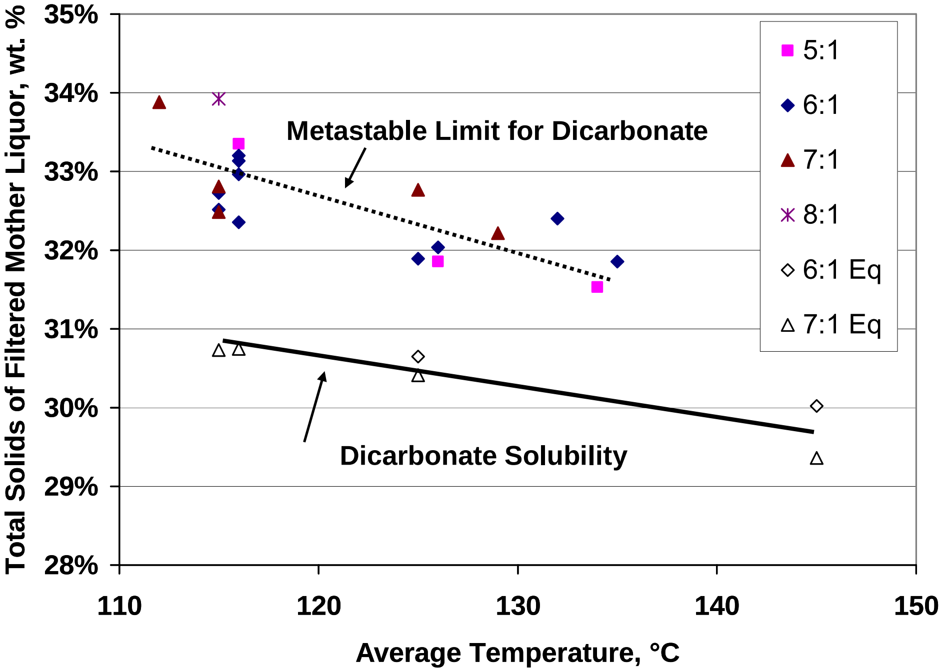

Figure 5. Solubility and metastable limits (point of primary nucleation) for dicarbonate versus temperature; legend indicates initial CO_3:SO_4 molar ratio.

In Figure 5, the measured total solids content of the mother liquor is plotted versus temperature for experiments in which the first crystals were harvested immediately after nucleation was detected and for the cases where the crystals were allowed to equilibrate with the mother liquor for 1-3 days. Only data in which XRD confirmed that dicarbonate was the solid phase are included in this plot. This is the first data clearly showing that significant supersaturation of dicarbonate must be attained before bulk crystallization can occur; this wide metastable zone helps explain why dicarbonate has a tendency to form scale on heat transfer surfaces [5].

Solubility Predictions

A goal of our work is to obtain thermodynamic properties of dicarbonate. These data are needed for accurate modeling of soluble-scale formation. We are pursuing two collaborations to update first-principals models. One model is based on Gibbs free energy minimization involving activity coefficient estimation by the Pitzer method [6] and calculation of the solubility constant, with the empirical fit of a 2-parameter quadratic equation. Testing the model against the literature solubility data has shown a good agreement between the experimental and predicted values of solid phase composition in the burkeite region for the temperatures 100-115ºand 150ºC.

An empirical model was also developed from Shi's data to predict the crystallization (metastable limit) of burkeite and dicarbonate as a function of the relative concentrations of Na_2CO_3 and Na_2SO_4 in solution; this model is described elsewhere [7].

Conclusions

Crystallization of dicarbonate, a double salt of Na_2CO_3 and Na_2SO_4, contributes to soluble scale fouling in pulp and paper industry spent liquor evaporators operating above 50% solids content. The new data presented in this paper supports earlier work and better defines the limits of temperature and composition necessary for the crystallization of dicarbonate.

The new data is being used to develop first-principals models of crystallization in spent liquor evaporators. These predictive tools will enhance our ability to recommend changes to equipment design and operation with expected benefits to energy efficiency resulting from reduced soluble scaling.

Acknowledgements

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