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## SEPARATION OF IONIC SPECIES UNDER SUPERCRITICAL WATER CONDITIONS

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and  
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### **ABSTRACT**

The unique characteristics of supercritical water (SCW) offer potentially attractive processing options that can be explored for reaction and separation purposes. While supercritical water oxidation (SCWO) can achieve high organic conversion efficiencies, low and relative solubilities of inorganic species in SCW may be further utilized for *in situ* separation of potential by-products from the SCWO process effluent.

This paper describes a novel method for separating ionic species under SCW conditions. The concept is based on relative solubilities of different ionic species in SCW. Laboratory-scale demonstration tests were conducted with a Nylon monomer manufacturing process wastewater containing sodium hydroxide, sodium borate, carboxylic acids, and water. The process achieved (1) effective destruction (>99%) of organic components in the wastewater; (2) selective precipitation of sodium (>99.5%) as carbonates produced from oxidation of the organic components; and (3) efficient recovery of boron (>90%) as boric acid in the reactor effluent. The sodium removal efficiency is governed by the solubilities of sodium carbonates in SCW and, therefore, can be directly improved by increasing process temperature. As a result of the temperature increase, both organic destruction and boron recovery efficiencies may be enhanced.

This method of selective separation of ionic species in SCW has potential for a wide range of processing applications.

## INTRODUCTION

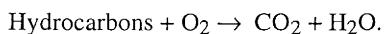
Many industrial wastewaters contain both organic and inorganic (electrolyte) components. A method is needed for recovering certain components while treating the wastewaters. Toward this end, a new concept involving waste conversion and product recovery under hydrothermal conditions has been developed. Specifically, the concept relates to hydrothermal oxidation for the conversion of chemical wastes into useful products and *in situ* separation of these products. This process is based on relative solubilities of the product species in water at elevated temperatures and pressures.

The new processing concept relies on the unique properties of water at elevated temperatures and pressures. The properties of water undergo marked changes near its vapor-liquid critical point (374.2°C and 22.1 MPa). In particular, both the static dielectric constant<sup>1</sup> and the density of water decrease significantly as water is heated from subcritical (below the critical point) to supercritical (above the critical point) conditions. As a result, the solvent polarity and solubility characteristics of supercritical water (SCW) are reversed, as compared with those features of water at ambient conditions. Organic compounds become soluble in SCW,<sup>2,3</sup> while inorganic compounds become insoluble. As shown in Table 1, solubilities of the selected inorganic salts in SCW range from a few mg/kg to a few hundreds of mg/kg. In addition, oxygen becomes completely miscible with SCW.<sup>4,5</sup> Because organic compounds, oxygen, and SCW form a homogeneous reaction medium, the oxidation process, also known as supercritical water oxidation (SCWO), is rapid and efficient. Typically, organic destruction efficiencies of greater than 99.99% can be achieved by SCWO at a temperature of 500°C and a reactor residence time of 5 min.<sup>6</sup>

Phase equilibria and solubilities of aqueous electrolyte mixtures have been studied extensively.<sup>7</sup> For separation purposes, aqueous electrolyte mixtures can be divided into single-solute and multiple-solute systems. A binary aqueous electrolyte system may contain a salt, an acid, or a base as the second component. Because of the drastic decrease in solubilities of salts in water, changing the process from subcritical to supercritical conditions for water can achieve desalination. However, for multicomponent aqueous electrolyte mixtures, solubilities of different ionic species may vary significantly in response to process

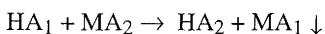
condition changes from subcritical to supercritical conditions for water. As shown in Table 1, solubilities of acids and bases in SCW are generally higher than those of salts. The relative change in solubilities of inorganic compounds in SCW makes selective separation of ionic species possible. This relative solubility concept is similar to the distribution coefficient defined in the liquid-liquid extraction process. The ionic species, which form less-soluble compounds in SCW, are selectively separated by precipitation from those that are more soluble in SCW.

Thus, the processing concept utilizing this unusual behavior of organic and inorganic compounds in SCW consists of two basic steps to achieve organic conversion and product recovery. The first step involves the oxidation of organic compounds in the wastewater to produce carbon dioxide and water. The second step involves selective precipitation of inorganic salts (such as metal carbonates) from the reaction mixture under SCW conditions. The first reaction step can be represented as the following nonstoichiometric equation:



In this case, since carbon dioxide is the only carbon-containing product, the solubilities of carbonate salts with cation species present in the reaction system are of primary importance. However, if the starting organic compounds contain heteroatoms, such as chlorine, nitrogen, sulfur, and phosphorus, the corresponding mineral acids will be formed upon oxidation and there will be competition for available cations among various anions.

The basic scheme for the second reaction step can be shown as follows:



where H is the hydrogen ion, M is the metal cation, and A<sub>1</sub> and A<sub>2</sub> are the first and second anions, respectively. The distribution of available cations is determined by the relative solubilities of salts that are formed with different anions, similar to the solubility product concept. In many cases, the ionization (or dissociation) constants and solubilities of the given species may not be available. Such data may be experimentally determined, as was the case in the present study.

Traditionally, separation or partial separation of electrolytes in an aqueous solution relies mainly on membrane-based separation processes, such as reverse osmosis and electrodialysis.<sup>18</sup> Specifically, boric acid can be recovered from aqueous organic mixtures via (1) evaporation and crystallization,<sup>19-21</sup> (2) liquid-liquid extraction,<sup>22</sup> (3) incineration,<sup>23</sup> and (4) low-temperature ion-

TABLE 1. SOLUBILITIES OF INORGANIC ELECTROLYTES IN SUPERCRITICAL WATER

| Compound                        | Pressure (MPa) | Temperature (°C) | Solubility (mg/kg) | Reference |
|---------------------------------|----------------|------------------|--------------------|-----------|
| CaCO <sub>3</sub>               | 24.0           | 440              | 0.02               | 8         |
| H <sub>3</sub> BO <sub>3</sub>  | 24.1           | 425              | 24,300             | This work |
|                                 | 24.1           | 450              | 30,100             | This work |
| K <sub>2</sub> HPO <sub>4</sub> | 26.8           | 450              | <7                 | 9         |
|                                 | 29.5           | 450              | 17                 | 9         |
| KNO <sub>3</sub>                | 24.8           | 475              | 275                | 10        |
|                                 | 27.6           | 475              | 402                | 10        |
| KOH                             | 27.7           | 450              | 331                | 9         |
|                                 | 25.3           | 475              | 154                | 9         |
|                                 | 22.1           | 525              | 60                 | 9         |
| LiNO <sub>3</sub>               | 24.7           | 475              | 433                | 10        |
|                                 | 27.7           | 475              | 1175               | 10        |
| Mg(OH) <sub>2</sub>             | 24.0           | 440              | 0.02               | 8         |
|                                 | 27.0           | 450              | 500                | 11        |
| NaCl                            | 27.6           | 500              | 304                | 12        |
|                                 | 30.0           | 500              | 200                | 13        |
|                                 | 25.0           | 450              | 250                | 14        |
|                                 | 20.0           | 450              | 63                 | 15        |
|                                 | 29.8           | 509              | 299                | 16        |
|                                 | 24.1           | 450              | 26                 | This work |
| Na <sub>2</sub> CO <sub>3</sub> | 27.6           | 450              | 66                 | This work |
|                                 | 29.8           | 509              | 86                 | 16        |
| NaHCO <sub>3</sub>              | 27.6           | 450              | 991                | 10        |
|                                 | 27.6           | 500              | 540                | 10        |
| NaOH                            | 28.3           | 400              | 25,000             | 17        |
| Na <sub>2</sub> SO <sub>4</sub> | 30.0           | 450              | 0.02               | 13        |
|                                 | 29.8           | 407              | 136                | 16        |

exchange reaction.<sup>24</sup> Many of these processes require costly concentration, reaction, and purification steps. The new concept may have a unique role in recovering boric acid in the concentration range of a few weight percent.

To demonstrate this concept, a Nylon monomer manufacturing process wastewater was tested using a laboratory-scale, continuous-flow reactor system. This wastewater contained about 0.6 wt % sodium hydroxide, 2 wt % sodium borate, and 3.6 wt % organic (C-9 and C-10 monodicarboxylic and dicarboxylic acids) sodium salts. This paper presents results from these proof-of-the-concept experiments, describes the SCWO reactor system with which the results were generated, and discusses engineering implications and potential applications of this unique separation process.

### EXPERIMENTAL

A flow diagram of the laboratory-scale, continuous-flow reactor system is shown in Figure 1. The major components of this SCWO system included (1) an air-driven feed pump, (2) a double-pipe heat exchanger, (3) a preheater, (4) a coiled reactor, (5) a fluidized sand bath, (6) a high-pressure oxygen supply source with flow indication and control capabilities, (7) a trim cooler, (8) a back-pressure regulator, and (9) a gas-liquid separator.

The wastewater was fed into the system by an air-driven pump (Williams Model CP205W300B316TG). The pressurized feed was heated by the heat exchanger (effluent on the tube side and influent on the shell side) and two radiant heaters (Watlow Model 9224C). The temperature of the feed was increased to about 350°C prior to entering the coiled reactor. The reactor tubing was 6 m (20 ft) long. The outside diameter and wall thickness, respectively, were 6.35 mm (0.25 in.) and 1.65 mm (0.065 in.). The entire coil was submersed in the sand bath (Techne, Model SBL-2D), which was maintained at the reaction temperature.

The reactor effluent was cooled by the heat exchanger and a trim cooler. Three in-line filters (50, 15, and 0.5  $\mu\text{m}$ ) were installed upstream from the pressure regulator (Whitney 22-31R4S4). Gaseous and liquid samples were collected from the gas-liquid separator. As indicated in Figure 1, pressure indicators (3D Instruments, Model PN25545-36B1) and thermocouples (Type K, Omega P/N KQIN) were installed at various locations.

The total organic carbon (TOC) analysis (Standard Method 5310C) was performed on all liquid influent and effluent samples, using a TOC Analyzer (Shimatzu Model 5050). To obtain TOC values (TOC = TC – TIC), the total carbon (TC) and total inorganic carbon (TIC) were separately measured. The carbonate concentration was also calculated from TIC values. Concentrations of the elements sodium and boron in these samples were quantified by the inductively coupled plasma emission spectrometry analysis.

### RESULTS AND DISCUSSION

Twelve SCWO tests were conducted on the wastewater from a Nylon monomer manufacturing process. Test conditions and results relative to efficiencies of organic carbon conversion, sodium removal, and boron recovery,

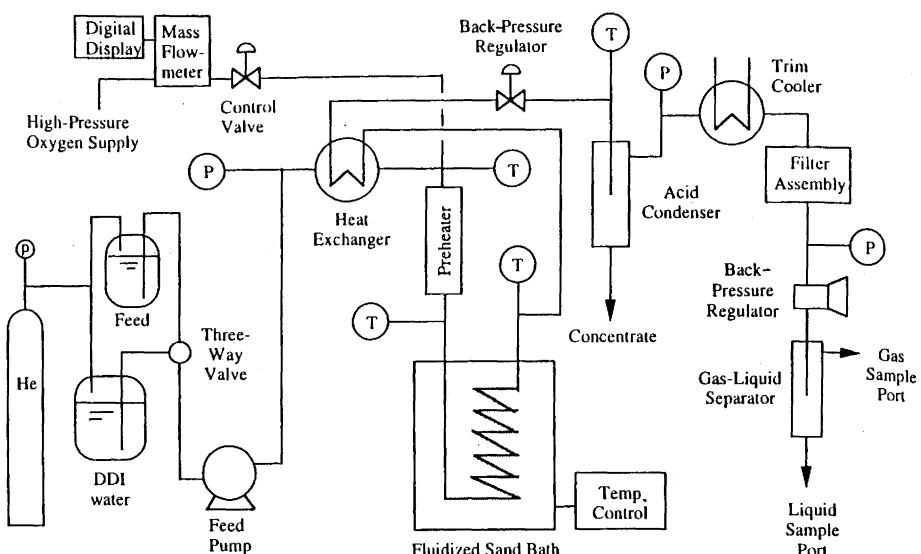


FIGURE 1. Schematic flow diagram of continuous-flow SCWO reactor system.

based on the analyses of the liquid effluent samples, are shown in Table 2. The test conditions covered temperatures from 400 to 500°C, pressures from 24.1 to 27.6 MPa, wastewater concentrations from 10% to 100% (i.e., without dilution), and reactor residence times from about 1 min to about 4 min. Ten of these tests were conducted using pure oxygen, while the remaining two tests were conducted with air. Duplicate samples (ranging from 2 to 5) were collected in most of these tests.

For discussion purposes, several terms used in the study require definitions. These terms include TOC destruction and removal efficiency, separation efficiency, sodium removal, boron recovery, and selectivity. Since the wastewater contained several organic components and the treatment goal was to mineralize all of these organic components and reaction intermediates, the TOCs of the influent and effluent samples were monitored to quantify the overall organic conversion. Therefore, the TOC destruction and removal efficiency (DRE) is defined as

$$DRE (\%) = \frac{TOC_{in} - TOC_{out}}{TOC_{in}} \times 100\%.$$

The separation efficiency of a given species is given by

$$\text{Separation efficiency (\%)} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%,$$

where  $C_{in}$  and  $C_{out}$  are the concentration or mass flow rate of the species in the influent and the effluent, respectively. Furthermore, the separation efficiency can be expressed in different ways, such as sodium removal and boron recovery as defined below:

$$\text{Sodium removal (\%)} = \frac{(Na)_{in} - (Na)_{out}}{(Na)_{in}} \times 100\%,$$

$$\text{Boron recovery (\%)} = \frac{(B)_{out}}{(B)_{in}} \times 100\%.$$

The selectivity of species B over species A is given by

$$\text{Selectivity (B/A)} = \frac{(B/A)_{out}}{(B/A)_{in}},$$

where A and B are the masses of species A and B, respectively.

One series of tests was conducted using the waste diluted to 10% of its initial strength. At a pressure of 24.1 MPa, both organic carbon conversion and sodium removal efficiencies at each temperature were comparable, ranging from about 90% at 400°C to 98% at 500°C. At a pressure of 27.6 MPa, similar trends were observed, except that the sodium removal efficiency was only about 64% at 400°C. This decrease in sodium removal efficiency was due to increased sodium solubility of carbonates at this high density level. In all of these tests using the 10% waste, the boron recovery efficiency was only about 50%.

Tests were also conducted using more-concentrated feed solutions (ranging from 50% to full strength). Although efficiencies for both organic carbon conversion and sodium removal were greater than 95% at all three waste feed concentrations and a temperature of 450°C, the efficiency of boron recovery was typically around 85% and reached 90% only when treating the full-strength waste. The remaining boron may have existed as sodium salts. In principle, an increase in process temperature above the highest temperature used in the current study (i.e., 450°C) can further improve organic conversion efficiency as well as sodium removal efficiency as a result of higher reaction rates and lower solubility of sodium carbonate in SCW.

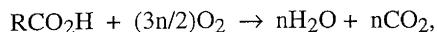
TABLE 2. CONDITIONS AND RESULTS OF SUPERCRITICAL WATER OXIDATION TEST

| Sample ID                 | Temp. (°C) | Pressure (MPa) | H <sub>2</sub> O density (g/mL) | Feed flowrate  |                |                   | Time (s) | Analytical results for liquid effluent |         |            |           |          |
|---------------------------|------------|----------------|---------------------------------|----------------|----------------|-------------------|----------|--|---------|------------|-----------|----------|
|                           |            |                |                                 | Waste (mL/min) | Oxidant (sccm) | Feed strength (%) |          | TOC (mg/L)                             | DRE (%) | TIC (mg/L) | Na (mg/L) | B (mg/L) |
| DP 3-1-3 (feed)           |            |                |                                 |                |                |                   |          | 1017                                   |         | 15.3       | 493.5     | 197.9    |
| DP 3-1-4                  | 500        | 27.6           | 0.1026                          | 8.5            | 138            | 10                | 103      | 14.8                                   | 98.5    | 53.4       | 7         | 75.7     |
| DP 3-1-5                  | 500        | 27.6           | 0.1026                          | 8.5            | 188            | 10                | 103      | 16.4                                   | 98.4    | 43.1       | 4.4       | 73.9     |
| DP 3-1-6                  | 500        | 27.6           | 0.1026                          | 9.0            | 188            | 10                | 97.5     | 23.9                                   | 97.6    | 17.9       | 7.7       | 78.6     |
| DP 3-1-7                  | 500        | 27.6           | 0.1026                          | 9.0            | 187            | 10                | 97.5     | 12.2                                   | 98.8    | 50.3       | 7.7       | 78.3     |
| Averaged Efficiencies (%) |            |                |                                 |                |                |                   |          | 98.3                                   |         | 98.6       |           | 38.7     |
| DP 3-2-1                  | 500        | 24.1           | 0.0858                          | 10.0           | 165            | 10                | 73.5     | 25.3                                   | 97.5    | 46         | 7.9       | 82.3     |
| DP 3-2-2                  | 500        | 24.1           | 0.0858                          | 10.0           | 173            | 10                | 73.5     | 28.3                                   | 97.2    | 48.8       | 7.5       | 79.6     |
| DP 3-2-3                  | 500        | 24.1           | 0.0858                          | 10.0           | 167            | 10                | 73.5     | 27.5                                   | 97.3    | 46.9       | 6.6       | 124.5    |
| DP 3-2-4                  | 500        | 24.1           | 0.0858                          | 10.0           | 161            | 10                | 73.5     | 29.8                                   | 97.1    | 50.3       | 9.9       | 77.7     |
| Averaged Efficiencies (%) |            |                |                                 |                |                |                   |          | 97.3                                   |         | 98.4       |           | 46.0     |
| Oxygen                    |            |                |                                 |                |                |                   |          |  |         |            |           |          |
| DP 3-3-1                  | 450        | 27.6           | 0.128                           | 10.0           | 30             | 10                | 110      | 11.5                                   | 98.9    | 143.9      | 13.3      | 74.2     |
| DP 3-3-2                  | 450        | 27.6           | 0.128                           | 10.0           | 30             | 10                | 110      | 19.5                                   | 98.1    | 149.8      | 16.6      | 70.8     |
| DP 3-3-3                  | 450        | 27.6           | 0.128                           | 10.0           | 30             | 10                | 110      | 41.4                                   | 95.9    | 171.6      | 25.2      | 127.2    |
| Averaged Efficiencies (%) |            |                |                                 |                |                |                   |          | 97.6                                   |         | 96.3       |           | 45.8     |
| DP 3-3-4                  | 450        | 24.1           | 0.1033                          | 10.0           | 31             | 10                | 88.4     | 63                                     | 93.8    | 175.7      | 17.1      | 75.6     |
| DP 3-3-4d                 | 450        | 24.1           | 0.1033                          | 10.0           | 31             | 10                | 88.4     | 35.5                                   | 96.5    | 124.4      | 16.7      | 76.8     |
| DP 3-3-5                  | 450        | 24.1           | 0.1033                          | 10.0           | 31             | 10                | 88.4     | 57.1                                   | 94.4    | 185        | 16        | 76.7     |
| DP 3-3-5d                 | 450        | 24.1           | 0.1033                          | 10.0           | 31             | 10                | 88.4     | 56.2                                   | 94.5    | 192.5      | 14.1      | 70.1     |
| DP 3-3-6d                 | 450        | 24.1           | 0.1033                          | 10.0           | 31             | 10                | 88.4     | 50.7                                   | 95.0    | 172.2      | 11.9      | 69.2     |
| Averaged Efficiencies (%) |            |                |                                 |                |                |                   |          | 94.8                                   |         | 96.9       |           | 37.2     |
| DP 3-3-7                  | 425        | 24.1           | 0.1188                          | 9.5            | 31             | 10                | 107      | 87.8                                   | 91.4    | 144.7      | 56.9      | 80.1     |
| DP 3-3-7d                 | 425        | 24.1           | 0.1188                          | 9.5            | 31             | 10                | 107      | 103.1                                  | 89.9    | 97.1       | 43        | 74.2     |
| DP 3-3-8d                 | 425        | 24.1           | 0.1188                          | 9.5            | 31             | 10                | 107      | 103.6                                  | 89.8    | 85.2       | 40.8      | 85.3     |
| Averaged Efficiencies (%) |            |                |                                 |                |                |                   |          | 90.3                                   |         | 90.5       |           | 40.4     |

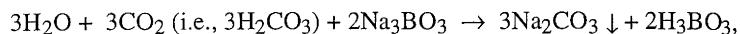
| SEPARATION OF IONIC SPECIES |     |      |        |      |     |     |     |       |      |       |        |
|-----------------------------|-----|------|--------|------|-----|-----|-----|-------|------|-------|--------|
| DP 3-6-0 (feed)             |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-6-2                    | 425 | 24.1 | 0.1188 | 8.3  | 30  | 10  | 123 | 30    | 96.9 | 34.3  | 12.6   |
| DP 3-6-2d                   | 425 | 24.1 | 0.1188 | 8.3  | 30  | 10  | 123 | 27.4  | 97.2 | 20.1  | 12.6   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-7-1                    | 400 | 27.6 | 0.2426 | 9.0  | 32  | 10  | 231 | 18.1  | 98.1 | 138.5 | 180.5  |
| DP 3-7-2                    | 400 | 27.6 | 0.2426 | 9.0  | 32  | 10  | 231 | 16    | 98.3 | 140.7 | 195.6  |
| DP 3-7-3                    | 400 | 27.6 | 0.2426 | 9.0  | 32  | 10  | 231 | 25.3  | 97.4 | 143.9 | 193.3  |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-7-4                    | 400 | 24.1 | 0.1508 | 10.0 | 32  | 10  | 129 | 55.9  | 94.2 | 56.1  | 47.9   |
| DP 3-7-5                    | 400 | 24.1 | 0.1508 | 10.0 | 32  | 10  | 129 | 83.6  | 91.3 | 54.1  | 54.7   |
| DP 3-7-6                    | 400 | 24.1 | 0.1508 | 10.0 | 32  | 10  | 129 | 111.1 | 88.5 | 61.1  | 78.4   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-8 (feed)               |     |      |        |      |     |     |     | 5550  |      | 67.1  | 3587.3 |
| DP 3-8-1                    | 450 | 24.1 | 0.1033 | 8.2  | 151 | 50  | 108 | 196.1 | 96.5 | 90.6  | 24.3   |
| DP 3-8-2                    | 450 | 24.1 | 0.1033 | 8.2  | 150 | 50  | 108 | 233.1 | 95.8 | 73.4  | 28.5   |
| DP 3-8-3                    | 450 | 24.1 | 0.1033 | 8.2  | 153 | 50  | 108 | 254.8 | 95.4 | 86.2  | 27.2   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-8 (feed)               |     |      |        |      |     |     |     | 11100 |      | 134.2 | 7174.6 |
| DP 3-8-4                    | 450 | 24.1 | 0.1033 | 8.8  | 287 | 100 | 100 | 283   | 94.9 | 101.6 | 20.8   |
| DP 3-8-5                    | 450 | 24.1 | 0.1033 | 8.8  | 291 | 100 | 100 | 313   | 94.4 | 98.5  | 17.8   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-28-1                   | 450 | 24.1 | 0.1033 | 8.2  | 270 | 100 | 108 | 95.7  | 99.1 | 172.2 | 26.5   |
| DP 3-28-2                   | 450 | 24.1 | 0.1033 | 8.2  | 270 | 100 | 108 | 88.9  | 99.2 | 182.2 | 28.4   |
| DP 3-28-3                   | 450 | 24.1 | 0.1033 | 8.2  | 270 | 100 | 108 | 31.3  | 99.7 | 31.3  | 32.6   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |
| DP 3-31-1                   | 450 | 24.1 | 0.1033 | 8.8  | 287 | 100 | 100 | 391.3 | 96.5 | 246.2 | 92.6   |
| Averaged Efficiencies (%)   |     |      |        |      |     |     |     |       |      |       |        |

The process may proceed according to the following general reaction scheme:

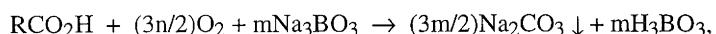
Oxidation



Separation



Overall



where R represents an alkyl group containing  $(n - 1)$  carbon atoms. The precipitation of sodium carbonates releases borate as boric acid, which can be recovered from the reactor effluent. In general, it is important to maintain a greater-than-stoichiometric ratio of carbon to metal ions (i.e.,  $n/3m \geq 1/2$  in the above example) to achieve the highest possible removal of metal ions by metal carbonate precipitation. Since the carbon-to-sodium ratio for the waste used in this study was about 2 to 1, the oxidation process generated sufficient carbon dioxide to form sodium carbonate. Excess carbon (in the form of carbonates) can also act as a buffering agent to control the pH of the solution and therefore reduce the extent of corrosion due to high-pH alkaline hydrothermal conditions.

The solubilities of sodium carbonate, boric acid, and their mixtures were experimentally determined using a magnetically stirred, 300-cm<sup>3</sup> autoclave. The results, shown in Table 3, indicate that separation efficiency and selectivity are limited by the solubilities of associated species in SCW. The solubilities of sodium carbonate and boric acid were individually measured. To evaluate the distribution of sodium between borate and carbonate, a mixture of sodium carbonate and boric acid with an initial feed concentration of  $(BO_3/CO_3)_{in} = 0.973$  was tested using the same procedure as the one used in the single-solute solubility test. The results indicated that the  $BO_3/CO_3$  ratios in the vapor phase were 15.3 and 16.8 at 425°C and 450°C, respectively. Based on these solubility data, the selectivity of borate over carbonate with a common cation, sodium, was about 16 under the given temperature and pressure. Similarly, sodium was preferably precipitated with carbonates, resulting in a boron-to-sodium selectivity of 340 at 450°C and 24.1 MPa.

This separation of ionic species was also verified by analyzing the composition of the precipitates accumulated in the reactor. Two methods were used for this purpose. The first method involved dissolving the salts accumulated

**TABLE 3. SOLUBILITY, SELECTIVITY, AND SEPARATION  
EFFICIENCY OF SODIUM CARBONATE AND BORIC ACID IN  
SUPERCritical WATER**

| Temp.<br>(°C) | Pres.<br>(MPa) | Solubility                                |  |   | Selectivity               |                 | Boron            |      |                 | Sodium           |      |      |
|---------------|----------------|---|--|---|---------------------------|-----------------|------------------|------|-----------------|------------------|------|------|
|               |                | Na <sub>2</sub> CO <sub>3</sub><br>(mg/L) | H <sub>3</sub> BO <sub>3</sub><br>(mg/L) | BO <sub>3</sub> /<br>CO <sub>3</sub> <sup>a</sup> | BO <sub>3</sub> /<br>B/Na | C <sub>in</sub> | C <sub>out</sub> | Rec. | C <sub>in</sub> | C <sub>out</sub> | Rem. |      |
| 425           | 24.1           | 53  | 24,300                                   | 15.3  | 15.7                      | 4.25            | 198              | 79.9 | 40.4            | 494              | 46.9 | 90.5 |
| 450           | 24.1           | 26  | 30,100                                   | 16.8  | 17.3                      | 340             | 916              | 837  | 91.4            | 7175             | 19.3 | 99.7 |

<sup>a</sup> Feed = 752 mg Na<sub>2</sub>CO<sub>3</sub> + 435 mg H<sub>3</sub>BO<sub>3</sub> in 50 mL DDI H<sub>2</sub>O  
[i.e., (BO<sub>3</sub>/CO<sub>3</sub>)<sub>in</sub> = 0.973].

in the reactor. After a given test was completed, the reactor pressure was released, the sand bath heater was turned off, and DDI water was pumped through the reactor. As the reactor cooled below the critical temperature of water, the accumulated salts began dissolving in the rinse water. This rinsing process continued until the reactor temperature was near the ambient condition and the pH of the reactor effluent became neutral. Then, the volume of the rinse water was measured. Detailed analyses indicated that the sodium-to-boron mass ratio was typically 10 to 1 for the tests conducted at temperatures of 450°C or higher.

The second method involved sacrificing the reactor. This verification test was performed during the last experiment when the reactor was purposely clogged after running full-strength waste for about 1 h. The salt precipitation condition was monitored by observing the pressure differential across the reactor. When the pressure drop increased to more than 7 MPa, the pump was turned off and the system pressure was released while the reactor was hot. Then the reactor was cooled to ambient temperature and was disconnected from the system. To collect salt precipitation data at various reactor locations, the reactor was cut into small segments starting from the reactor inlet. A given amount of water was used to dissolve the salts accumulated in each segment. The salt solutions were then analyzed for carbonates, borate, and sodium, respectively. The mass distributions of these three species are shown in Figure 2.

It was found that most salt masses had accumulated in the first 1.5-m section, and the mass distribution showed a peak at a distance of about 0.7 m from the reactor inlet. In almost all segments, the concentration of borate was

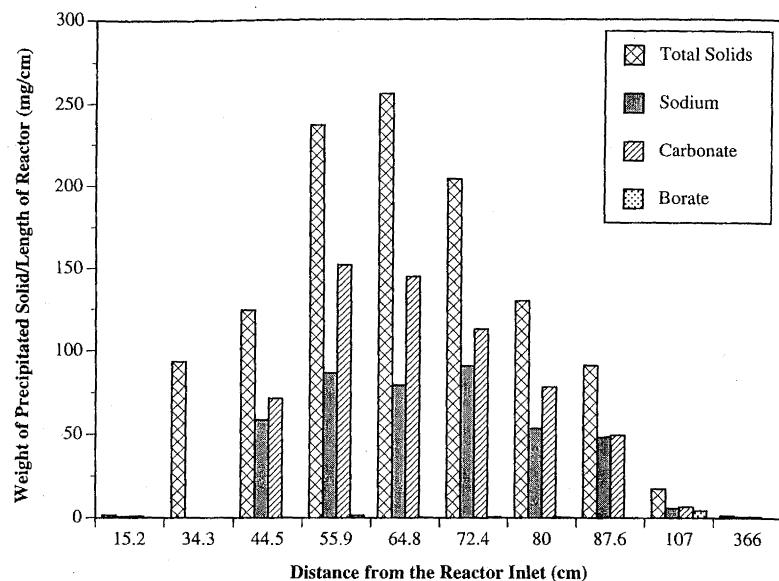


FIGURE 2. Distribution of precipitated solids over the reactor length.  
(Test conditions:  $P = 24.1 \text{ MPa}$ ,  $T = 450^\circ\text{C}$ , waste feed flow =  $10 \text{ cm}^3/\text{min}$ ,  
oxygen flow = 100% excess)

negligible. A relatively high level of borate, corresponding to about 25% of the total mass in the segment, was found in only one segment at about 1.1 m from the reactor inlet. Although the temperatures at these locations were not measured directly, such temperatures were verified using similar reactor systems. The temperature of the feed stream could increase rapidly from  $350^\circ\text{C}$  at the reactor inlet to the preset sand bath temperatures ranging from  $400$  to  $500^\circ\text{C}$  within the first meter of the reactor. These solids distribution results verified that the separation of carbonates from borate via salt precipitation in SCW was effective.

This concept of selective separation of ionic species based on relative solubilities in SCW can be utilized for processing a broad spectrum of electrolyte-containing aqueous mixtures. The key is to identify the compounds with relatively lower solubilities. In the case of SCWO processes involving organic compounds, the solubilities of carbonate salts are of primary importance. In

general, both efficiency and selectivity of the separation process are limited by the relative solubilities of the associated ionic species in SCW.

### CONCLUSION

A novel method for separating ionic species under SCW conditions has been developed. Using a laboratory-scale, continuous-flow reactor system, this method has been successfully demonstrated for treating a Nylon monomer manufacturing process wastewater.

The separation efficiency of ionic species is governed by the salt solubility limits in SCW. Due to the characteristically low salt solubility in SCW (typically a few mg/L), high separation efficiencies can be readily achieved. Furthermore, the salt solubility can be effectively decreased by lowering the water density (i.e., higher temperature and lower pressure). At the same time, increasing the process temperature can enhance organic conversion rates and efficiencies.

This method of separation of ionic species in SCW can be used in conjunction with SCWO processes to recover useful products from wastewaters. Finally, this waste treatment and product recovery concept can be integrated into a wide variety of process applications, including hydrothermal synthesis.

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