MOLTEN SALT ELECTROLYSIS FOR THE RECYCLING OF PULPING CHEMICALS

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ABSTRACT

Molten salt mixtures containing sodium carbonate, sodium sulfide and sodium sulfate have been electrolyzed to generate sodium oxide and sodium sulfide while removing carbon from the system in the form of gas and maintaining a sulfur balance in the melt. This investigation leads towards the development of an electrolytic recycle process for molten pulping chemicals. The molten salts are presently found in the chemical recovery process of kraft pulping. Electrolysis was performed in a divided melt/undivided atmosphere and divided melt/divided atmosphere to avoid consumption of the oxide and sulfide products. The anodic reaction was carbonate oxidation to carbon dioxide and oxygen while sulfide oxidation to polysulfides occurred to a lesser extent at less positive potentials; sulfate oxidation was not observed to occur. The cathodic reaction was sulfate reduction to sulfide and oxide, the desired molten precursors for recycled pulping liquors.

INTRODUCTION

The Kraft Pulping Process and Chemical Recycle

In the United States more than 50 million tons of kraft pulp are produced every year [2]. Regeneration of active pulping chemicals, sodium hydroxide and sodium sulfide, from mainly sodium carbonate and sodium sulfate is one of the largest inorganic chemical processes in the world; in the U.S. alone 25 million tons of the molten pulping salts, also known as kraft melt, are recovered. The development of an electrochemical process is motivated by the ability to supply incremental capacity to pulp mills (both through reduced deadload and incremental capacity increases for chemical recovery), improved energy efficiency, reduced introduction of contaminants into the process, and simplified operation (shortened holdup time, elimination of multiple equilibrium-limited chemical reaction/separation steps, and elimination of the cumbersome lime cycle involving a kiln). The purpose of this work has been to verify the electrochemical reactions occurring in molten kraft melt (mixtures of Na₂CO₃, Na₂S, Na₂SO₄) to develop an alternative process to the traditional equilibrium-limited wet chemical method [1] for recovery of pulping chemicals.

The traditional chemical recovery process (Figure 1, A) after the molten salts (kraft melt) are dissolved in water and proceeds with a chemical equilibrium-limited ion
transfer involving calcium hydroxide (from lime). In the causticizing reaction the hydroxide replaces the carbonate and forms sodium hydroxide and a precipitate of calcium carbonate,

\[
\text{Ca(OH)}_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2\text{NaOH(}aq) + \text{CaCO}_3(\text{s}) \quad (1)
\]

The precipitated calcium carbonate is separated from the solution and re-burned to calcium oxide in a lime kiln

\[
\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \quad (2)
\]

The needed calcium hydroxide (Eq. 1) is formed by slaking, thereby closing the lime cycle,

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (3)
\]

The requirements in kraft chemical recovery cycle for recausticizing are:

1. Remove the carbon from the pulping chemicals
2. Produce sodium hydroxide (or a precursor to sodium hydroxide)
3. Maintain a sulfur balance on the melt, preferably in the form of sulfide

In an attempt to alleviate the lime cycle induced bottleneck in many pulp mills and to reduce their energy consumption by circumventing the necessity of the lime kiln and associated equipment, we have developed a concept for a process using molten salt electrochemistry.

The Proposed Electrochemical Recycle Process

The method is a single-step electrolysis process, eliminating the addition of inorganic chemicals (Figure 1, B). The proposed process produces reduction products of \(\text{C}^+\) and \(\text{S}^-\) while oxidizing \(\text{CO}_3^{2-}\) to \(\text{CO}_2\) and \(\text{O}_2\), thereby generating the molten precursors to white liquor and removing carbon from the system in the form of carbon-containing gas. This paper provides evidence of the desired electrochemical reactions occurring in the molten phase of used kraft pulping chemicals. The off-gas from the electrochemical cell has been analyzed for comparison with the coulometrically anticipated generation of the hypothesized oxidation. Secondly, the post-electrolysis inorganics are dissolved into water after being cooled to room temperature and analyzed for compositional change. The sodium oxide produced during electrolysis reacts with water to form sodium hydroxide,

\[
\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \quad (4)
\]

Sodium carbonate and sodium sulfide both dissolve in water where the sulfide maintains equilibrium with the \(\text{HS}^-\) and \(\text{OH}^-\) ions, accounted for in the analysis. The solutions are analyzed by standard techniques used within the pulp and paper industry. The results of the analysis are calculated and compared to the expected composition based upon the hypothesized electrochemistry and charge passed during the experiment.
Thermodynamic predictions and the literature both point to the possibility of converting a molten mixture of sodium carbonate, sodium sulfide and sodium sulfate into a mixture of sodium oxide and sodium sulfide while simultaneously discharging carbon-containing gases with electrochemistry. Prior investigations with cyclic voltammetry have supported the hypothesis that used pulping chemicals, in the molten phase, can be recycled (or "recausticized", meaning to re-make caustic) into molten precursors of pulping solutions of sodium hydroxide and sodium sulfide [4, 5]. At the limit of the potential window for the positive branch of the cyclic voltammograms (Figs. 2 and 3), sodium carbonate oxidizes to carbon dioxide and oxygen. In pure sodium carbonate melts, sodium ions preferentially reduce to sodium metal yet the limit of the potential window for the negative branch has been determined to be carbonate reduction to carbon monoxide and oxide (Figure 2) [4].

\[
\begin{align*}
\text{CO}_3^- & \rightarrow \text{CO}_2 + \frac{1}{2} \text{O}_2 + 2e^- & E_{900\text{°C}}^0 &= 0 \text{V} \\
\text{Na}^+ + \text{e}^- & \rightarrow \text{Na}^0 & E_{900\text{°C}}^0 &= -2.19 \text{V} \\
\text{CO}_3^{2-} + 4e^- & \rightarrow 3\text{O}^+ + \text{C} & E_{900\text{°C}}^0 &= -2.28 \text{V} \\
\text{CO}_3^{2-} + 2e^- & \rightarrow 2\text{O}^+ + \text{CO} & E_{900\text{°C}}^0 &= -2.625 \text{V}
\end{align*}
\]

Lorenz and Janz [6] report that the reduction of carbonate to carbon monoxide and oxide becomes thermodynamically favored around 870°C in a (Li/Na/K)_2CO_3 melt. Our prior investigation of pure sodium carbonate melts by cyclic voltammetry confirmed the occurrence of these reactions in addition to oxide oxidation [4].

Cyclic voltammetry has also been conducted on mixtures similar to the kraft melt [5]. Figure 3 shows a cyclic voltammogram for a mixture of sodium carbonate, sodium sulfide, sodium sulfate and sodium oxide. The oxidation is similar to the pure sodium carbonate system where the discharge of carbonate occurs according to Eq. 5. The reduction differs from the pure carbonate system (Figure 2) as determined by the smaller potential span between the limits of the potential window. The span between the limits of the potential window indicates sulfate was the main reduction reactant (Figure 3). The reduction of sulfate occurs in many steps as suggested by Rapp and Goto [7],

\[
\begin{align*}
\text{SO}_4^{2-} + 2e^- & \rightarrow \text{SO}_3^- + \text{O}^+ & E_{900\text{°C}}^0 &= -1.822 \text{V} \\
\text{SO}_3^- + 2e^- & \rightarrow \text{SO}_2^- + \text{O}^+ \\
\text{SO}_2^- + 2e^- & \rightarrow \frac{1}{2} \text{S}^0 + 2\text{O}^+ \\
\frac{1}{2} \text{S}^0 + 2e^- & \rightarrow \text{S}^+ & E_{900\text{°C}}^0 &= -0.701 \text{V}
\end{align*}
\]

The cyclic voltammogram in Figure 3 has a span comparable to the first step of the reduction series, which is significantly less, by ca. 0.8V, than the span in the pure sodium
carbonate melt. Since the oxidations in the two systems are similar, the difference in span supports sulfate as the limiting reduction over sodium or carbonate reduction.

Intermediate reactions oxide and sulfide oxidation are also indicated by the cyclic voltammogram in Figure 3 [5].

\[
\begin{align*}
O^\text{-} & \rightarrow \frac{1}{2}O_2 + 2e^- & E^0_{900^\circ C} = -0.888 \text{ V} \\
S^\text{-} & \rightarrow \frac{1}{2}S_2 + 2e^- & E^0_{900^\circ C} = -0.701 \text{ V} \\
xS^0 + S^\text{-} & \leftrightarrow S_{2+x} & (15) \\
\frac{1}{2}S_2 + Na_2S & \leftrightarrow Na_2S_2 & K_{900^\circ C} = 1.27 \cdot 10^2 \\
S_{2+x} + 2e^- & \leftrightarrow 2S^- & E^0_{900^\circ C} = -0.988 \text{ V} \\
\end{align*}
\]

In order to minimize these reactions, which act to decrease the current efficiency of the desired recausticizing reactions (Eq. 9 through 12), physical separation of the cathodic products must be made from the anode. Additionally, oxygen generated by Eqs. 5 and 13 serve to oxidize sulfide to sulfate, which is an undesirable process,

\[
Na_2S + 2O_2 \leftrightarrow Na_2SO_4 & \quad K_{900^\circ C} = 1.29 \cdot 10^{38} \quad (17)
\]

Therefore, gas phase separation of the individual electrode compartments must also be investigated. It is also important to verify that sulfate oxidation does not occur anodically as it does in pure sodium sulfate melts [8],

\[
SO_4^\text{-} \rightarrow SO_3 + \frac{1}{2}O_2 + 2e^- & \quad E^0_{900^\circ C} = +1.203 \text{ V} \quad (18)
\]

which can be verified by off-gas analysis and by a sulfur balance of the melt.

The gas and chemical analyses will be evaluated for current efficiency with respect to the reactions occurring at the limits of the voltage window. Specifically, sulfate reduction, where the full reduction from Eqs. 9 to 12 is assumed to occur, along with carbonate oxidation,

\[
\begin{align*}
\text{Cathode:} & \quad SO_4^\text{-} + 8e^- \rightarrow S^- + 4O^\text{-} & E^0_{900^\circ C} = -1.663 \text{ V} \\
\text{Anode:} & \quad (CO_2 \rightarrow CO_2 + \frac{1}{2}O_2 + 2e^-) \times 4 & E^0_{900^\circ C} = 0 \text{ V} \quad (5)
\end{align*}
\]

leads to the overall reaction:

\[
Na_2SO_4 + 4Na_2CO_3 \rightarrow Na_2S + 4Na_2O + 4CO_2 + 2O_2 & \quad E^0_{900^\circ C} = -1.663 \text{ V} \quad (20)
\]

These reactions need to be experimentally verified, as will now be discussed.
EXPERIMENTAL

Electrochemical Cell

A flanged Inconel reactor (20 cm inner diameter, 76 cm height) was inserted into a top loading electric furnace (model 56822, Lindberg, Watertown, WI). The temperature of the bulk molten salts in an alumina crucible was controlled to ±5°C as monitored by a K-type thermocouple (Omega Engineering, Inc., Stamford, CT) in a one-fourth inch round-bottom alumina well (Omega Engineering). Multiple ports on top of the reactor were equipped with plastic compression fittings (Swagelok, Solon, OH) facilitating height adjustment of electrodes, purge port (Omega Engineering) and thermocouple. The fittings also provided electrical isolation of the electrodes from the reactor vessel. The cell was operated in a two- or three-electrode configuration. Two arrangements of the electrochemical cell were used. The first provided division between the anolyte and catholyte, but did not separate their atmospheres (Figure 4, A). This was accomplished by drilling a hole (0.051 cm dia.) on the sidewall near the bottom (Figure 4, A, a) of an alumina crucible (Figure 4, A, b; 3 cm outside dia., 4.1 cm outside height, 0.2 cm wall thickness, CoorsTek, Golden, CO). This alumina crucible served as the anolyte chamber and fit into another alumina crucible of larger diameter (8.3 cm dia, 16 cm tall, 99.8% Al2O3, CoorsTek) serving as the other electrode chamber. The hole in the side of the smaller crucible allowed for communication between the two electrode compartments. The second configuration was developed to provide a division between both the melts and associated atmospheres (Figure 4, B). A closed end alumina tube (Figure 4, B, a; 61 cm in length and 2.54 cm diameter) had a hole drilled in the end with a diameter of 0.051 cm (Figure 4, B, b) and served as the anolyte chamber. This tube allowed division not only of the molten salts, but also of the gases evolved from each compartment. Individual argon purges were passed over each compartment to facilitate removal of gaseous products, as shown by the curved arrows in Figure 4. The electrode materials were all platinum wires (0.5 cm diameter) (Alfa Aesar, Ward Hill, MA) attached to the potentiostat through insulated fittings in the reactor.

Materials

Sodium carbonate (anhydrous, granular, 99.5% assay, major impurity is sodium sulfate, VWR) and sodium sulfate (anhydrous, granular, 99.5% assay, VWR) were dried for 24 hours in an oven at 115°C. Sodium sulfide (89.8% purity determined by titration) was obtained from Alfa Aesar where the impurities included sodium sulfate, sulfur and sodium polysulfides as indicated by the slight yellow color of some of the reactants received. Sodium oxide was also obtained from Alfa Aesar (Manufacturer’s assay 85 wt.% Na2O, 15 wt.% Na2O2). Industrial grade argon (Air Products) served as the purge gas. The molten salt mixture was contained in a flat-bottomed cylindrical alumina crucible (99.8 % Al2O3, 8.3 cm dia., 16 cm tall, Coors Technical Ceramics, Golden, CO). A larger diameter crucible (99.8% Al2O3, 10.5 cm dia., 19.4 cm tall, Coors Technical Ceramics) was used to contain the melt in the event of crucible failure.

Electrolysis Experiments

During the electrolysis experiments the following quantities were measured: time (±60 sec.), temperature of the molten salt at a distance approximately 3 cm away from the
electrodes, the current and voltage applied to the cell, and the relevant volume percentages of product gas. The number of coulombs transferred during the experiment was determined by integrating the current data (±0.003 A) with time. The IR-compensation of the voltage was determined by current interrupt.

Gas Analysis

Carbon monoxide (±0.005%) and carbon dioxide (±0.01%) were measured in percent volume by an infrared analyzer (IR-702 Gas Analyzer, Infrared Industries Inc., Santa Barbara, CA). Oxygen (±0.01%) was measured in percent volume by an electrochemical cell analyzer (Model 8000, Illinois Instruments, Johnsburg, IL). The oxygen analyzer was prone to deviations at flowrates below 0.5 L min⁻¹. The analyzers were calibrated with gases of known concentrations (Holox, Atlanta, GA) of the range being measured. The outlet flowrate was measured with a bubble flowmeter (±1 mL) and a stopwatch (±0.01 seconds).

The stoichiometric rate of carbon dioxide and oxygen evolution at any current was calculated according to equation 5 and Faraday’s law. Both actual and stoichiometric rates of gas evolution are presented on the same graph (Figures 3 and 5), allowing a comparison of the actual gas evolution to the theoretical rates based upon coulometry.

Post-electrolysis Chemical Analysis

After the electrolysis experiments the reactor was cooled and the inorganic chemicals were dissolved in a known mass of deionized water. Standard analytical techniques used in the pulp and paper industry were applied to determine the chemical composition. A three-step acid titration based upon the standard TAPPI Method T-586 [9] (ABC titration [1], Mettler DL70ES Titrator, Schwerzenbach, Switzerland) determined the concentrations of sodium hydroxide, sodium sulfide and sodium sulfate. Sodium hydroxide was formed from reaction of sodium oxide with water (eq. 1); this assumption was used when reporting sodium oxide values from aqueous analysis. Capillary ion electrophoresis (CIE, Waters Capillary Ion Analyzer, Milford, MA) [10] determined the concentration of carbonate and sulfate in solution. Inductively coupled plasma analysis (ICP, Perkin Elmer Optima 3000DV, Wellesley, MA) [10] determined the metal contents of the solution and provided verification for the sulfur balance in the melt, as well as a check on the ABC titration (ABC) and CIE. The analysis is reported in moles for comparison to the initial moles loaded into the cell. All analyses have an uncertainty of ±10%.

RESULTS AND DISCUSSION

Cell arrangement and design is important in the electrolysis experiments. Initial investigations operated in an undivided cell orientation, but suffered from sulfide oxidation by oxygen to produce sulfate (Eq. 17) and less than 10% current efficiencies for oxide production (Eq. 19). Cyclic voltammetry confirmed that the cathodic products were oxidized at the anode. In the experiments described below, deviations from stoichiometric current for the desired reactions (Eqs. 9 through 12) are explained by the
participation of sulfide and polysulfide in a current shuttle between the electrodes (Eqs. 14 through 16), while oxidation of oxide resulted in oxygen gas (Eq. 13) whose fate was to leave the system or oxidize sulfide to sulfate (Eq. 17). The IR-corrected cell potentials for the experiments were typically 2.5 to 3 Volts.

Sulfur species were not detected in the atmosphere by either gas chromatography analysis of the vapor phase or ICP analysis of hydrogen peroxide solutions, through which the effluent was bubbled. This supports the proposition that sulfate oxidation (Eq. 18) was not an electrochemical reaction occurring at the anodic potential limit.

Electrolysis of molten paper pulping chemicals (850-900°C) was performed in melts where 1) the anolyte and catholyte molten salts were separated, but their atmospheres were not, and 2) both the melt and the atmospheres were separated. Sodium carbonate, sodium sulfide and sodium sulfate comprised the initial mixture for the system without the divided atmosphere (Figure 4, A). To verify sulfate reduction to sulfide and oxide, the second experimental configuration was utilized to divide the melt and the atmosphere while the cell was loaded with carbonate and sulfate of sodium (Figure 4, B).

Divided Melt and Undivided Atmosphere

Figure 5 shows the time variation of the measured carbon dioxide, carbon monoxide and oxygen for the duration of an electrolysis experiment at 820±10°C of a mixture containing sodium carbonate, sodium sulfide and sodium sulfate (1:0.25:0.25 mol ratio). A total of 26,766 ±900 Coulombs were transferred, equating to a 15.4 ±0.5% (extent of conversion) conversion of carbonate loaded into the cell based upon carbonate oxidation.

In Figure 5, gas evolution increased proportionally to the applied current, which is also calculated as the expected rate of production through the stoichiometry of Eq. 5. The gas production dropped off after 23000 sec., when the current was turned off. It began to rise again at 25000 sec., after the current was turned back on. This verifies that gas production is due to the applied current. Although neither the carbon dioxide nor oxygen reached the stoichiometric amount for carbonate oxidation, the oxygen approaches stoichiometry closer than carbon dioxide. This is interpreted as either additional oxygen generation from oxidation of oxide. Although oxide was not initially loaded into the melt, it appears in the anode chamber by thermal decomposition of sodium carbonate,

$$Na_2CO_3 \leftrightarrow Na_2O + CO_2 \quad K_{900°C} = 7.23 \cdot 10^{-8}$$ (21)

or by inefficient separation of oxide produced by reduction (Eq. 19) in the cathode chamber. Carbon monoxide production is also coincident with the passing of charge. This is attributed to the chemical reduction of carbonate by sulfoxylate [4],

$$SO_2^{2+} + 2CO_3^{2-} \rightarrow SO_4^{2-} + 2O^{-} + 2CO$$ (22)

which is an intermediate in the sulfate reduction sequence.
The remaining sodium carbonate after electrolysis was determined by ABC titration and CIE that indicated carbonate was consumed at slightly over stoichiometric conversion. From the carbon dioxide gas analysis data that evolves proportionally to the applied current, it is inferred that carbonate oxidation (Eq. 5) does occur since carbonate is the only source of carbon in the system. Therefore, the carbon dioxide evolved determines the current efficiency for carbonate oxidation, which is 33.8%. When sulfoxylate reduction of carbonate (Eq. 22) is considered by accounting for the carbon monoxide, the carbon removal efficiency is 39.6%. The remaining oxidative current is attributed to a combination of oxide oxidation (Eq. 13) and sulfide/polysulfide shuttling between the anode and cathode (Eqs. 14 through 16). A majority of the sulfide was oxidized to sulfate (Eq. 17) during the experiment by oxygen generated at the anode (Eqs. 5 and 13) and due to atmospheric oxidation during dissolving the chemicals and the delay before analysis. Sodium oxide was produced at 41 to 45.3% current efficiency for sodium sulfate reduction (Eq. 19). Aluminum was found by ICP analysis and is attributed to either sodium carbonate or sodium oxide fluxing with the alumina oxide cell components,

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 & \leftrightarrow 2\text{NaAlO}_2 + \text{CO}_2 & K_{900^\circ C} = 2.13 \times 10^4 \\
\text{Na}_2\text{O} + \text{Al}_2\text{O}_3 & \leftrightarrow 2\text{NaAlO}_2 & K_{900^\circ C} = 8.04 \times 10^8
\end{align*}
\]

Three times as much aluminum was found in the catholyte as in the anolyte. With the consideration that 75% of the aluminum found was due to sodium oxide fluxing (Eq. 24), the current efficiency for sodium oxide production is 54±2%. Both sodium and sulfur are maintained in the melt, as shown by ICP analysis and confirmed by combined consideration of the ABC titrations (for sulfide) and CIE analysis (for sulfate). This supports the fact that sulfur-containing gases are not produced during electrolysis.

Figure 7 summarizes the electrochemical reactions, and subsequent chemical reactions, occurring in a melt-separated cell of mixtures containing \( \text{Na}_2\text{CO}_3, \text{Na}_2\text{SO}_4, \) and \( \text{Na}_2\text{S}. \) When the atmospheres of the electrode chambers are not separated, oxygen generated from the anode oxidizes the sulfide to sulfate ions in both electrolytes. Additionally, the sulfide ions undergo electrochemical oxidation to form sulfur that chemically reacts with more sulfide to produce polysulfide ions.

**Divided Melt and Atmosphere**

With a cell configuration where the atmospheres are not separated, it was not possible to decouple the individual electrode contributions to the evolved gas. Additionally, sulfide reduction products will be oxidized by anodic oxygen (Eq. 17). Therefore we separate both the melt and the atmosphere of the electrodes in an electrolysis experiment of sodium carbonate and sodium sulfate to determine individual gas contributions and to minimize sulfide oxidation.

Figure 6 shows the time variation of the measured carbon dioxide and carbon monoxide of the anolyte and carbon monoxide of the catholyte for the duration of an electrolysis experiment 840±10°C of a mixture containing sodium carbonate and sodium sulfate (1:0.33 mol ratio). Carbon dioxide was not detected in the catholyte off-gas. The
total charge transferred was 44,015 ±1,500 coulombs, equating to a 22.8 ±0.8% conversion of carbonate loaded into the cell, based upon carbonate oxidation (Eq. 5). This experiment differs from the experiment described in the previous section by division not only of the melt, but also of the atmosphere.

In Figure 6 carbon dioxide generation in the anolyte was again proportional to the current, verifying electrochemical carbonate oxidation (Eq. 5). As the current density was increased, the rate of carbon dioxide evolution approached the stoichiometric value. Lorenz and Janz [6] have reported this effect at 560°C in pure carbonate melts; as oxide oxidation is the major current consumer at lower current densities while carbonate oxidation dominates at higher current densities. The fluctuation in carbon dioxide is attributed to sulfide shuttling and polysulfide passivation (eqs. 14 through 16) of the electrode surface as well as oxide oxidation (Eq. 13), which consumes current. If carbonate were the electrochemically-reduced species at the cathode, carbon monoxide would be expected to evolve at the rate of carbon dioxide generated by oxidation. More carbon monoxide was detected in the catholyte than the anolyte; this is attributed to sulfoxylate chemical reduction of carbonate (Eq. 22) as opposed to carbonate reduction by direct electrolysis. From the gas analysis it can then be concluded that carbonate was oxidized and sulfate was the major reduction reactant.

The carbonate loss was nearly stoichiometric, yet the carbon dioxide generated is considered to give a more reliable value for the current efficiency of carbonate oxidation (Eq. 5) as 66.2%. This is nearly double the efficiency described in the divided melt/undivided atmosphere experiment and is attributed to operating at higher current densities, where carbonate is oxidized preferentially to oxide. When sulfoxylate reduction of carbonate (Eq. 22) is considered by accounting for the moles of carbon monoxide from the catholyte, the carbon removal efficiency is 74.1%. Again, the remaining oxidative current is attributed to a combination of oxide oxidation (Eq. 13) and sulfide/polytelluride (Eqs. 14 through 16) shuttling between the anode and cathode. No sodium sulfide was added to the initial melt; therefore the sodium sulfide determined by analysis resulted from sulfate reduction (Eq. 19) although its distribution was divided between the catholyte and the anolyte. Considering the combined anolyte and catholyte for sodium sulfide, the current efficiency for sulfate reduction (Eq. 19) is 61.4%. This does not take into account sulfide that was oxidized to sulfate (Eq. 17) which is indicated by the approximately proportional increase in sulfate over the expected value.

Sodium oxide was produced at 39.5% current efficiency according to sodium sulfate reduction (Eq. 19). Aluminum was again found in higher quantities in the catholyte than the anolyte. With the consideration that 80% of the aluminum found was due to sodium oxide fluxing (Eq. 24), the current efficiency for sodium oxide production becomes 52%. Both sodium and sulfur are maintained in the melt as indicated by ICP analysis and confirmed by combined consideration of the ABC titrations and CIE analysis. Again, this supports the fact that sulfur-containing gases are not produced during electrolysis.

Figure 8 summarizes the significant electrochemical reactions occurring in a fully separated cell of mixtures containing Na_2CO_3 and Na_2SO_4, as discussed in this section. Carbonate ions are oxidized to carbon monoxide and oxygen while sulfate ions are reduced to sulfide and oxide ions. With a cell setup where both the melt and the
atmosphere are separated, neither oxide nor sulfide will be electrochemically oxidized nor will cathodically produced sulfide react with anodic oxygen.

**CONCLUSIONS**

The electrolysis experiments in a divided melt at 820-840°C confirm the electrochemical reactions suggested by cyclic voltammograms. Sulfate reduction to sulfide and oxide (Eqs. 9-12) occurred with a current efficiency of 50 to 60% and carbonate oxidation (Eq. 5) occurred with a current efficiency of 66%. When sulfoxylate reduction of carbonate (Eq. 22) is considered in the catholyte, the carbon removal efficiency is 74%. Nearly stoichiometric carbon dioxide was generated at current densities at and above 700 mA cm\(^{-2}\). Separating the melt creates an increase in current efficiency for oxide production by a factor of five. Separating the atmosphere of the anolyte and catholyte had the effect of reducing the amount of sulfide oxidation to sulfate by anodic oxygen (Eq. 17). Analysis of the reactor off-gas did not indicate the presence of sulfur species and the melt was determined to maintain a balance of both sodium and sulfur. These experiments show promise for the electrolytic recycling of kraft pulping chemicals in the molten phase since.

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**Figure 1.** A: The conventional kraft chemical recovery cycle B: Kraft chemical recovery via molten salt electrolysis (only main chemicals and reactions shown).

**Figure 2.** Cyclic voltammogram versus carbonate reference electrode scanned at 0.1 V/s of a pure sodium carbonate melt on gold electrodes at 860°C under an argon atmosphere. The carbonate oxidizes at the positive limit of the voltammogram while carbonate reduces at the negative limit. Intermediate reactions of sodium reduction and oxide oxidation also occur [4].
Figure 3. Cyclic voltammogram versus Pt/PtS scanned at 0.1 V/s of a melt containing sodium carbonate, sodium sulfide, sodium sulfate, and sodium oxide on platinum electrodes at 820°C under an argon atmosphere. The carbonate oxidizes at the positive limit of the voltammogram while sulfate reduces at the negative limit. Intermediate reactions of sulfide and oxide oxidations also occur [5].

Figure 4. Configurations of electrochemical cells for divided melt-undivided atmosphere (A) and divided melt-divided atmosphere (B).
Figure 5. Gas evolution data as a function of time for an electrolysis experiment of sodium carbonate, sodium sulfide and sodium sulfate in a divided melt and common atmosphere at 820°C.

Figure 6. Gas evolution data as a function of time for an electrolysis experiment of sodium carbonate and sodium sulfate in a divided melt and atmosphere at 840°C.
Figure 7. Electrochemical reactions occurring at the limits of the potential window in mixtures containing sodium carbonate, sodium sulfide and sodium sulfate at 840±20°C in a cell where the melt of the anolyte and catholyte are separated, but the atmospheres are not.

Figure 8. Electrochemical reactions occurring at the limits of the potential window in mixtures containing sodium carbonate and sodium sulfate at 840±20°C in a cell where both the melt and the atmospheres of the anolyte and catholyte are separated.