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Recycling Kraft Pulping Chemicals with Molten Salt Electrolysis

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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 toward the development of an electrolysis-based recycle process for 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.

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The Kraft Pulping Process and Chemical Recycle

In the United States more than 50 million tons of kraft pulp are produced every year.[1] Regeneration of active pulping chemicals, sodium hydroxide and sodium sulfide, from spent chemicals (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 annually. The development of an electrochemical process is motivated by the ability to supply incremental production 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 a simulated molten kraft melt (mixtures of Na_2CO_3, Na_2S, Na_2SO_4) to develop an alternative process to the traditional equilibrium-limited wet chemical method[2] for recovery of pulping chemicals.

Valuable cellulose fibers are liberated from wood by the kraft process, using an aqueous mixture of sodium hydroxide and sodium sulfide at an elevated temperature and pressure. A liquid to be recycled (called black liquor) is separated from the fibers. Black liquor is an aqueous mixture of sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), sodium sulfide (Na_2S), other inorganics at lower concentrations (chloride, metals, transition metals) and the dissolved organics from the wood. Water is partially evaporated from the black liquor, and the remaining solution is fed into the kraft recovery furnace[3] where it acts as a fuel (combustion of the organics). A molten salt mixture recovered from the bottom of the recovery boiler contains mainly sodium carbonate, sodium sulfide, and some sodium sulfate, the balance being mainly sodium/potassium chloride, metal and transition metal compounds, and carbon. This melt is continuously recovered at 750-900°C by gravity drainage through smelt spouts from the bottom of the recovery boiler where it is immediately dissolved in water. The conversion of sodium sulfate to sodium sulfide in the recovery boiler depends upon the extent of reduction within the char bed at the bottom of the recovery boiler. The molten salt composition of $Na_2CO_3{:}Na_2S + Na_2SO_4$ ranges generally from 1:1 to 4:1 (mole basis).

The recausticizing process (meaning the process to re-make caustic) has the goal of replacing carbonate ion with hydroxide ion (Fig. 1A) after the molten salts (kraft melt) are dissolved in water. This process 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

$$\mathrm{Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow 2NaOH(aq) + CaCO_3(s)} \qquad [1]$$

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

$$\mathrm{CaCO_3 + heat \rightarrow CaO + CO_2} \qquad [2]$$

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

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \qquad [3]$$

The requirements in kraft chemical recovery cycle for recausticizing are then: (*i*) remove the carbon from the pulping chemicals, (*ii*) produce sodium hydroxide (or a precursor to sodium hydroxide), and (*iii*) maintain a sulfur balance on the melt, preferably in the form of sulfide.

In an attempt to alleviate the bottleneck of many pulp mills induced by the lime cycle and reduce the 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 (Fig. 1B). The proposed process produces reduction products of O^{2-} and S^{2-} while oxidizing CO_3^{2-} to CO_2 and 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 recovered kraft pulping chemicals. The off-gas from the electrochemical cell has been analyzed for comparison with the coulometrically anticipated generation of the hypothesized oxidation. Second, the postelectrolysis 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

$$\mathrm{Na_2O + H_2O \rightarrow 2NaOH} \qquad [4]$$

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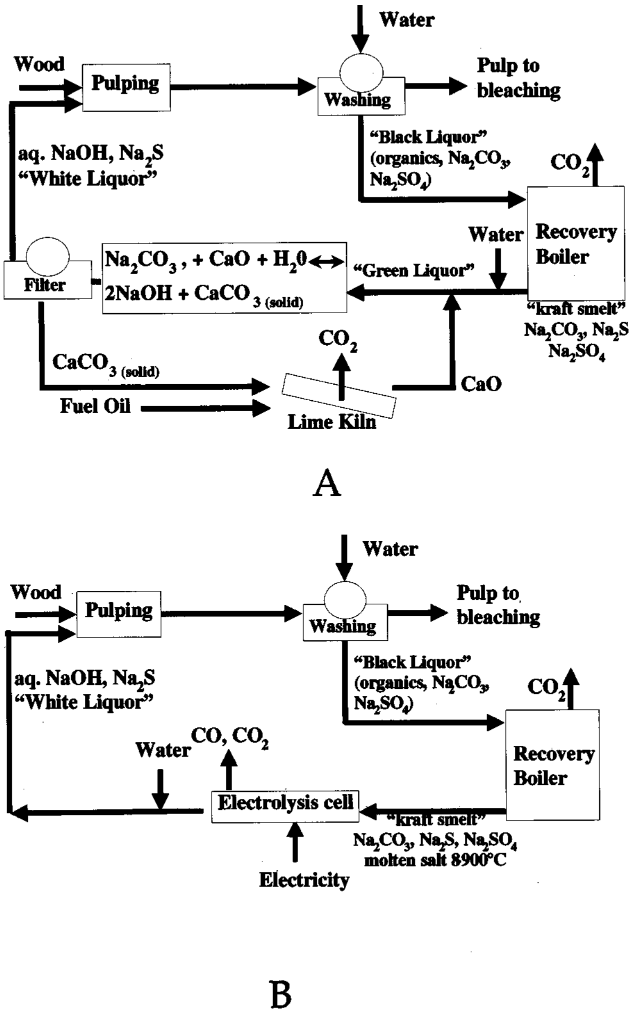

Figure 1. (A) The conventional kraft chemical recovery cycle. (B) Kraft chemical recovery via molten salt electrolysis (only the main chemicals and reactions shown).

The results of the analysis are compared to the expected composition based upon the hypothesized electrochemistry and electrical 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) into molten precursors of pulping solutions of mainly sodium hydroxide and sodium sulfide.[4,5] At the limit of the potential window for the positive branch of the cyclic voltammograms (Fig. 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 (Fig. 2)[4]

$$CO_3^{2-} \rightarrow CO_2 + \tfrac{1}{2}\ O_2 + 2e^- \quad E^0_{900°C} = 0\ \ V \qquad [5]$$

$$Na^+ + 1e^- \rightarrow Na^0 \quad E^0_{900°C} = -2.19\ \ V \qquad [6]$$

$$CO_3^{2-} + 4e^- \rightarrow 3\ \ O^{2-} + C \quad E^0_{900°C} = -2.28\ \ V \qquad [7]$$

$$CO_3^{2-} + 2e^- \rightarrow 2\ O^{2-} + CO \quad E^0_{900°C} = -2.625\ \ V \qquad [8]$$

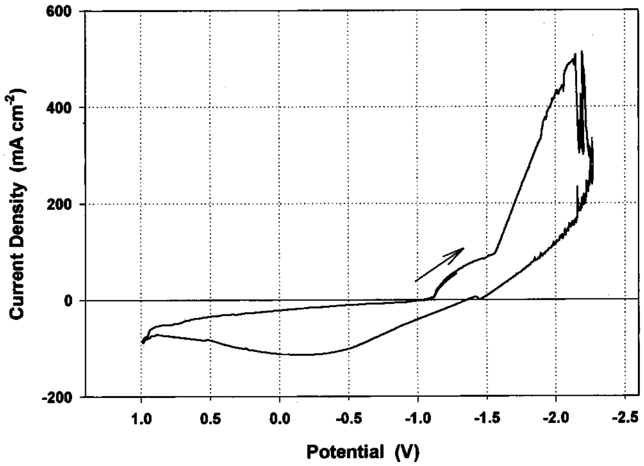

Figure 2. Cyclic voltammogram *vs.* carbonate reference electrode scanned at 0.1 V/s of a pure sodium carbonate melt on gold electrodes at 860°C under an argon atmosphere. The carbonate oxidizes at the positive limit of the voltammogram while carbonate reduces at the negative limit. Intermediate reactions of sodium reduction and oxide oxidation also occur.[4]

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 (Fig. 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 (Fig. 3). The reduction of sulfate occurs in many steps as suggested by Rapp and Goto[7]

$$SO_4^{2-} + 2e^- \rightarrow SO_3^{2-} + O^{2-} \quad E^0_{900°C} = -1.822\ \ V \qquad [9]$$

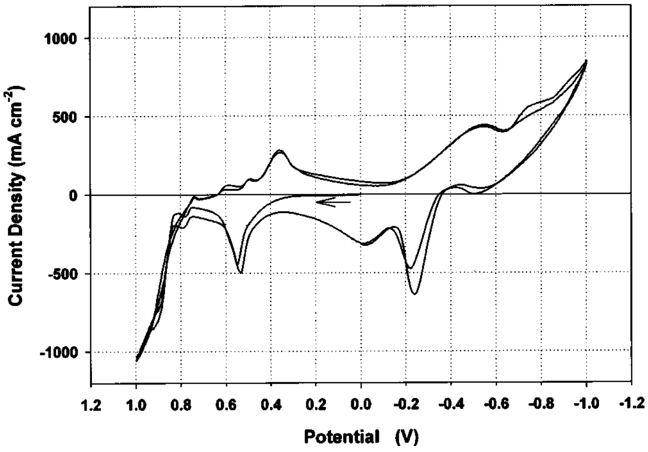

Figure 3. Cyclic voltammogram *vs.* Pt/PtS scanned at 0.1 V/s of a melt containing sodium carbonate, sodium sulfide, sodium sulfate, and sodium oxide on platinum electrodes at 820°C under an argon atmosphere. The carbonate oxidizes at the positive limit of the voltammogram while sulfate reduces at the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

$$SO_3^{2-} + 2e^- \rightarrow SO_2^{2-} + O^{2-} \qquad [10]$$

$$SO_2^{2-} + 2e^- \rightarrow \tfrac{1}{2}\ S_2^0 + 2\ O^{2-} \qquad [11]$$

$$\tfrac{1}{2}S_2^0 + 2e^- \rightarrow S^{2-} \quad E^0_{900°C} = -0.701\ \text{V} \qquad [12]$$

The cyclic voltammogram in Fig. 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 Fig. 3[5]

$$O^{2-} \rightarrow \tfrac{1}{2}\ O_2 + 2e^- \quad E^0_{900°C} = -0.888\ \text{V} \qquad [13]$$

$$S^{2-} \rightarrow \tfrac{1}{2}\ S_2 + 2e^- \quad E^0_{900°C} = -0.701\ \text{V} \qquad [14]$$

$$xS^o + S^{2-} \leftrightarrow S_{x+1}^{2-} \qquad [15a]$$

$$\tfrac{1}{2}S_2 + Na_2S \leftrightarrow Na_2S_2 \quad K_{900°C} = 1.27 \cdot 10^2 \qquad [15b]$$

$$S_2^{2-} + 2e^- \leftarrow 2S^{2-} \quad E^0_{900°C} = -0.988\ \text{V} \qquad [16]$$

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 Eq. 5 and 13 serve to oxidize sulfide to sulfate, which is an undesirable process

$$Na_2S + 2\ O_2 \leftrightarrow Na_2SO_4 \quad K_{900°C} = 1.29 \cdot 10^{28} \qquad [17]$$

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]

$$SO_4^{2-} \rightarrow SO_3 + \tfrac{1}{2}\ O_2 + 2e^- \quad E^0_{900°C} = +1.203\ \text{V} \qquad [18]$$

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

The gas and chemical analyses are 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 Eq. 9 to 12 is assumed to occur, along with carbonate oxidation

$$\text{Cathode}\quad SO_4^{2-} + 8e^- \rightarrow S^{2-} + 4\ O^{2-} \quad E^0_{900°C} = -1.663\ \text{V} \qquad [19]$$

The anode follows Eq. 5 and leads to the overall reaction

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

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

Experimental

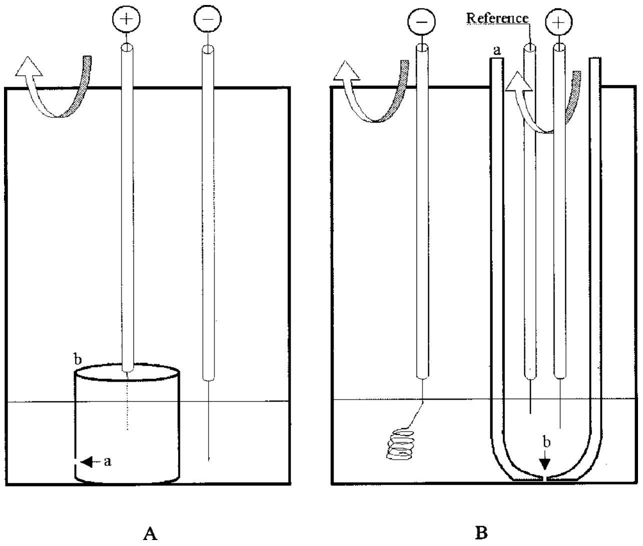

Figure 4. Configurations of electrochemical cells for divided melt-undivided atmosphere (A) and divided melt-divided atmosphere (B).

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 0.25 in. 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 (Fig. 4A). This was accomplished by drilling a hole (0.051 cm diam) on the sidewall near the bottom (Fig. 4A, a) of an alumina crucible (Fig. 4A, b; 3 cm outside diam, 4.1 cm outside height, 0.2 cm wall thickness, CoorsTek, Golden, CO). This alumina crucible served as the anolyte chamber and fits into another alumina crucible of larger diameter (8.3 cm diam, 16 cm tall, 99.8% Al_2O_3, 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 (Fig. 4B). A closed-end alumina tube (Fig. 4B, a; 61 cm in length and 2.54 cm diam) had a hole drilled in the end with a diameter of 0.051 cm (Fig. 4B, 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 Fig. 4. The electrode materials were all platinum wires (0.05 cm diam) (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 h 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 % Na_2O, 15 wt % Na_2O_2). 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% Al_2O_3, 8.3 cm diam, 16 cm tall, Coors Technical Ceramics, Golden, CO). A larger diameter crucible (99.8% Al_2O_3, 10.5 cm diam, 19.4 cm tall, Coors Technical Ceramics) was used to contain the melt in the event of crucible failure.

Reactor setup and heating.—Solid, granular sodium salts were placed in the alumina crucible and tube. The electrodes were inserted into the top of the reactor and lowered above the melt. The loaded alumina crucible was positioned in the bottom of the reactor, the lower part of the reactor was raised into place, and the flange was closed. The ceramic purge port was secured 20-30 cm above the material in the crucible while the sheathed thermocouple was positioned 1 cm from the bottom of the melt crucible. The system was purged with argon (0.5-1.2 L_{STP}/min for the outer system, 0.05-0.15 L_{STP}/min for the tube) for 3 h before heating. The electrochemical cell was heated at approximately 100°C h^{-1} to the operating temperature (±5°C).

Electrolysis experiments.—During the electrolysis experiments the following quantities were measured: time (±60 s), 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.—Purging the electrochemical cell, either as a whole or by compartment, assisted the removal of gases produced during electrolysis. Both the inlet and the outlet flow rates were measured; deviations between the two were significant due system resistance. The outlet flow rate closest to the gas analyzers was used to calculate the rate of gas being produced by the electrolysis.

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 flow rates 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 flow rate was measured with a bubble flow meter (±1 mL) and a stopwatch (±0.01 s).

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

Postelectrolysis 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. Analysis was performed as soon as possible to minimize atmospheric oxidizing and carbonating of the solutions. 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 the 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 (Eq. 9 through 12) are explained by the participation of sulfide and polysulfide in a current shuttle between the electrodes (Eq. 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 V.

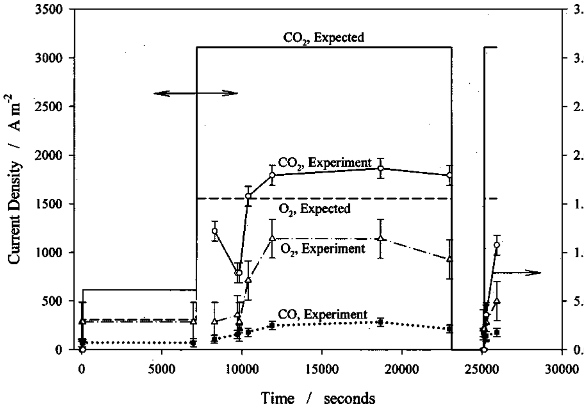

Figure 5. Gas evolution data as a function of time for an electrolysis experiment of sodium carbonate, sodium sulfide, and sodium sulfate in a divided melt and common atmosphere at 820°C.

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 (*i*) the anolyte and catholyte molten salts were separated but their atmospheres were not and (*ii*) 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 (Fig. 4A). 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 (Fig. 4B).

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, column 1, Table I). A total of 26,766 ± 918 C were transferred, equating to a 15.4 ± 0.5% (extent of conversion) conversion of carbonate loaded into the cell based upon carbonate oxidation.

In Fig. 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 s. when the current was turned off. It began to rise again at 25000 s. 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 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

$$\text{Na}_2\text{CO}_3 \leftrightarrow \text{Na}_2\text{O} + \text{CO}_2 \quad K_{900^\circ\text{C}} = 7.23 \cdot 10^{-8} \qquad [21]$$

Table I. Material balance for divided melt-undivided atmosphere experiment with initial components of Na_2CO_3, Na_2S, and Na_2SO_4.

		Postelectrolysis analysis					
	Initial ±<1%	Expected[a] ±3.4%	Total Cat + An ±10%[b] Moles	Catholyte ±10%	Anolyte ±10%	% [(Cat + An)/ Expected] × 100 ±13.4%	Method
Na_2CO_3	0.900	0.761	0.903	0.814	0.089	118.7	ABC
			0.864	0.781	0.083	113.5	ABC
			0.758	0.686	0.072	99.6	CIE
Na_2S	0.232	0.267	0.016	0.015	0.001	6.0	ABC
Na_2SO_4	0.231	0.196	0.467	0.409	0.058	238.3	CIE
Na_2O	-	0.139	0.063	0.058	0.005	45.3	ABC
			0.057	0.053	0.004	41.0	
Na	2.726	2.726	2.962			108.7	ICP
			2.543			93.3	ICP
			2.924			107.3	ABC and CIE[c]
			2.808			103.0	ABC and CIE
S	0.463	0.463	0.507			109.5	ICP
			0.418			90.3	ICP
			0.482			104.1	ABC and CIE
Al	-	-	0.041	0.030	0.011		ICP
CO_2	-	0.139	0.047			33.8	Trapezoidal[d]
			±0.004[e]			±11.9%	
O_2	-	0.069	0.030			43.5	Trapezoidal
			±0.005			±20.1%	
CO	-	-	0.008			-	Trapezoidal
			±0.002				

[a] Based upon stoichiometry of carbonate oxidation and sulfate reduction and coulombs passed during experiment (26,766 ± 918 C or ±3.4%).

[b] Unless otherwise noted, acid titration (ABC), capillary ion electrophoresis (CIE), and inductively coupled plasma (ICP) were reported to have an error less than ±10%.

[c] Moles of metal are determined by considering NaOH, Na_2S, and Na_2CO_3 from ABC acid titrations and Na_2SO_4 from CIE.

[d] Trapezoidal rule was used to integrate the rate of evolution ($mol\ min^{-1}$) with time.

[e] Gas analysis error was propagated from the flow rate and smallest increment of the analyzer.

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]

$$SO_2^{2-} + 2CO_3^{2-} \rightarrow SO_4^{2-} + 2\ O^{2-} + 2CO \qquad [22]$$

which is an intermediate in the sulfate reduction sequence.

The postelectrolysis chemical analysis and integrated gas are summarized in Table I; the method of analysis is indicated in the last column. The second to last column of Table I provides the percentage of combined anolyte and catholyte moles present to the expected moles based upon stoichiometry of Eq. 20, charge passed and assuming a mass balance of sodium and sulfur in the melt. Since chemical separation between the anolyte and catholyte is not expected to be completely efficient, the combined moles found in each compartment are compared. The postelectrolysis sodium carbonate determined by ABC titration and CIE range from indicating no oxidation of carbonate to stoichiometric conversion. From the carbon dioxide gas analysis data that evolves proportionally to the applied current, it is inferred 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 (Eq. 14 through 16). A majority of the sulfide was oxidized to sulfate (Eq. 17) during the experiment by oxygen generated at the anode (Eq. 5 and 13) and due to atmospheric oxidation during dissolving the chemicals and 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

$$Na_2CO_3 + Al_2O_3 \leftrightarrow 2NaAlO_2 + CO_2 \quad K_{900°C} = 2.13 \cdot 10^1 \qquad [23]$$

$$Na_2O + Al_2O_3 \leftrightarrow 2NaAlO_2 \quad K_{900°C} = 8.04 \cdot 10^8 \qquad [24]$$

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 6 summarizes the electrochemical reactions, and subsequent chemical reactions, occurring in a melt-separated cell of mixtures containing Na_2CO_3, Na_2SO_4, Na_2S. 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

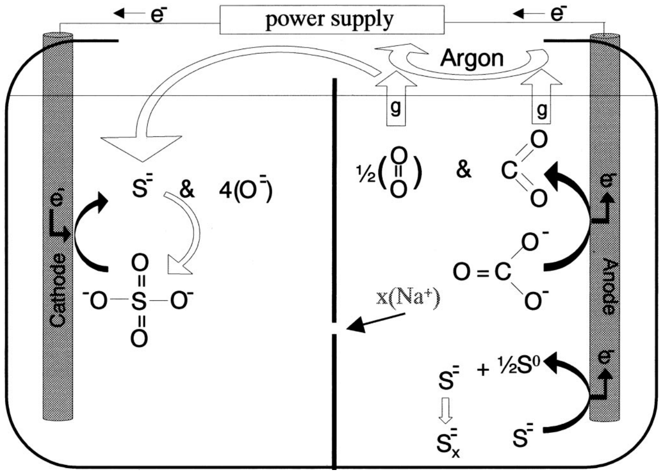

Figure 6. Electrochemical reactions occurring at the limits of the potential window in mixtures containing sodium carbonate, sodium sulfide, and sodium sulfate at 840 ± 20°C in a cell where the melt of the anolyte and catholyte are separated, but the atmospheres are not.

the electrodes in an electrolysis experiment of sodium carbonate and sodium sulfate to determine individual gas contributions and to minimize sulfide oxidation.

Figure 7 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 at 840 ± 10°C of a mixture containing sodium carbonate and sodium sulfate (1:0.33 mol ratio, column 1, Table II). Carbon dioxide was not detected in the catholyte off-gas. The total charge transferred was 44,015 ± 1,564 C, equating to a 22.8 ± 0.8% conversion of carbonate loaded into the cell, based upon carbonate oxidation (Eq. 5).

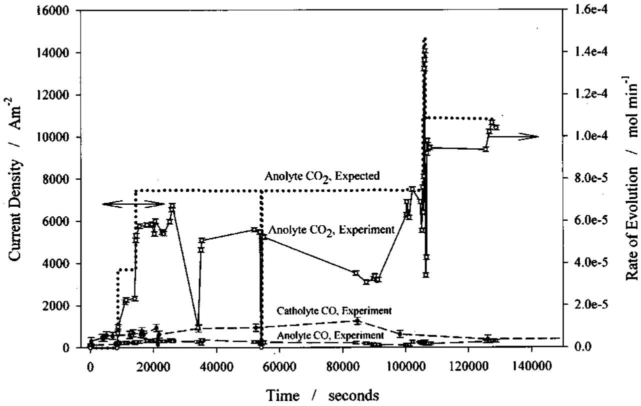

Figure 7. Gas evolution data as a function of time for an electrolysis experiment of sodium carbonate and sodium sulfate in a divided melt and atmosphere at 840°C.

This experiment differs from the experiment described in the previous section by division not only of the melt, but also of the atmosphere.

In Fig. 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 (Eq. 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

Table II. Material balance for divided melt-divided atmosphere experiment with initial components of Na_2CO_3 and Na_2SO_4.

		Postelectrolysis analysis					
	Initial ±<1%	Expected[a] ±3.6%	Total Cat + An ±10%[b] Moles	Catholyte ±10%	Anolyte ±10%	% [(Cat + An)/ Expected] × 100 ±13.6%	Method
Na_2CO_3	0.998	0.770	0.763	0.707	0.056	99.1	ABC
			0.736	0.681	0.055	95.6	ABC
Na_2S	-	0.057	0.035	0.013	0.022	61.4	ABC
Na_2SO_4	0.329	0.272	0.306			112.5	Difference[c]
Na_2O	-	0.228	0.090	0.090	0	39.5	ABC
Na	2.654	2.654	2.489	2.272	0.217	93.8	ICP
			2.388			90.0	ABC and CIE[c,d]
S	0.329	0.329	0.341	0.313	0.028	103.6	ICP
Al	-	-	0.072	0.058	0.014		ICP
CO_2	-	0.228	0.150	0.003	0.147	65.8	Trapezoidal[e]
			±0.014[f]	±0.001	±0.013	±12.9%	
O_2	-	0.114	NA				
CO	-	-	0.026	0.019	0.007		Trapezoidal
			±0.007	±0.005	±0.002		

[a] Based upon stoichiometry of carbonate oxidation and sulfate reduction and coulombs passed during experiment (44,015 ± 1,564 C or ±3.6%).

[b] Unless otherwise noted, acid titration (ABC), capillary ion electrophoresis (CIE), and inductively coupled plasma (ICP) were reported to have an error less than ±10%.

[c] Sodium sulfate by difference between the sulfur determined by ICP and sodium sulfide determined by ABC titration.

[d] Moles of metal are determined by considering NaOH, Na_2S, and Na_2CO_3 from ABC acid titrations and Na_2SO_4 from CIE.

[e] Trapezoidal rule was used to integrate the rate of evolution (mol min^{-1}) with time.

[f] Gas analysis error was propagated from the flow rate and smallest increment of the analyzer.

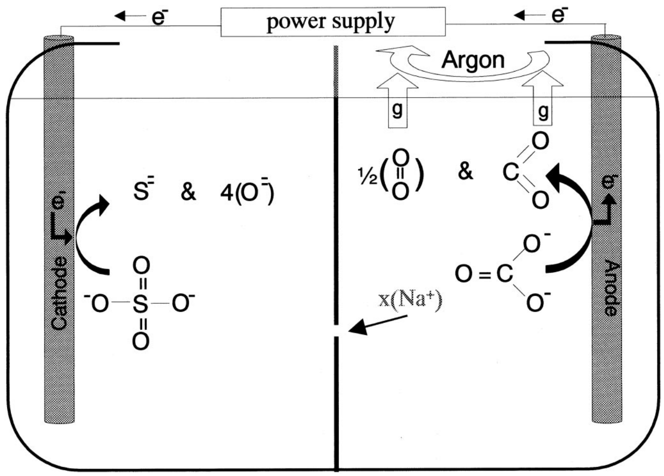

Figure 8. Electrochemical reactions occurring at the limits of the potential window in mixtures containing sodium carbonate and sodium sulfate at 840 ± 20°C in a cell where both the melt and the atmospheres of the anolyte and catholyte are separated.

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 postelectrolysis analysis of the melt and gas evolution is summarized in Table II; it is of the same format as Table I. The carbonate loss was again 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/polysulfide (Eq. 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 (Eq. 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.

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