INVESTIGATION OF MELTS CONTAINING Na_2CO_3, Na_2SO_4, Na_2S/Na_2S_x and Na_2O/Na_2O_2 FOR THE ELECTROLYTIC RECYCLE OF PULPING CHEMICALS

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The purpose of this work is to verify the electrochemical reactions could occur in a molten kraft melt. This will aid in developing an alternative process to the traditional equilibrium-limited wet chemical method [1] for recovery of pulping chemicals. This work is an extension to include sodium sulfides and oxides into the mix with sodium carbonate and sulfate (2).

Cyclic voltammetry (CV) and electrolysis conditions have been applied to molten salt mixtures between the initial and anticipated final compositions for electrolytic recycling of pulping chemicals. Thermodynamic potentials have been fitted to the cyclic voltammograms. Gas detection and post-electrolysis chemical analysis support the conclusions drawn from the CVs.

A mixture composed to simulate the initial conditions (sodium carbonate, sodium sulfide/polysulfide and sodium sulfate) exhibited carbonate ion oxidation and sulfate ion reduction at the limits of the potential window by CV. Gas analysis during electrolysis confirms the carbonate ion oxidation (Figure 2). At potentials inside the positive limit, oxidation of sulfide to sulfur occurs with subsequent chemical reaction to polysulfide. Mixtures with added sodium oxide and peroxide, prepared to simulate a near-final composition, had similar spans of the potential window and had an additional oxidation peak attributed to oxide and peroxide oxidation (Figure 1). All major peaks were found to be scan-rate dependent except for one attributed to an intermediate of sulfate reduction, presumably chemically reacting with another species in the melt.

We conclude the electrolytic recycle process is feasible since carbonate oxidation cleans the melt of carbon and sulfide reduction produces the desired sulfide and oxide ions. This investigation also demonstrates that separation is necessary between the anolyte and the catholyte so the reduction products are not consumed by oxidation (Figure 3).

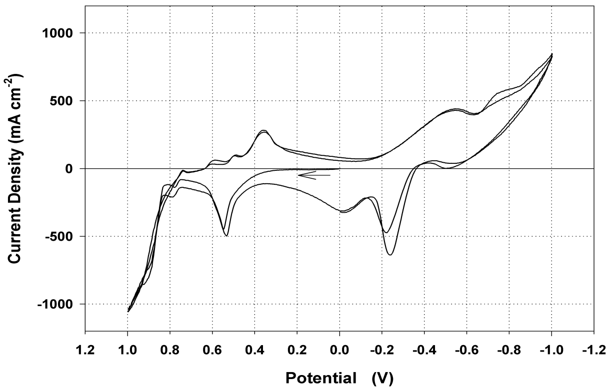

Figure 1: CV versus Pt/PtS scanned at 0.1 V/s of a melt containing Na_2CO_3, Na_2SO_4, Na_2S/Na_2S_x and Na_2O/Na_2O_2 on Pt electrodes at 820°C under an Ar atmosphere. The $CO_3^=$ oxidizes at the positive limit of the CV while $SO_4^=$ reduces at the negative limit. Intermediate reactions of sulfide and oxide oxidations also occur.

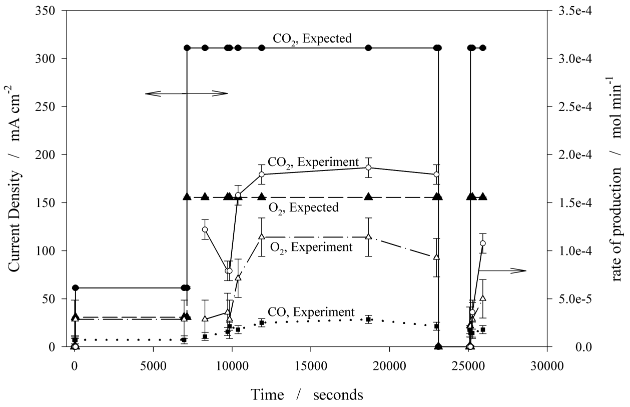

Figure 2: Gas evolution data as a function of time for an electrolysis experiment Na_2CO_3, Na_2SO_4, Na_2S/Na_2S_x in a divided melt and common atmosphere at 820°C.

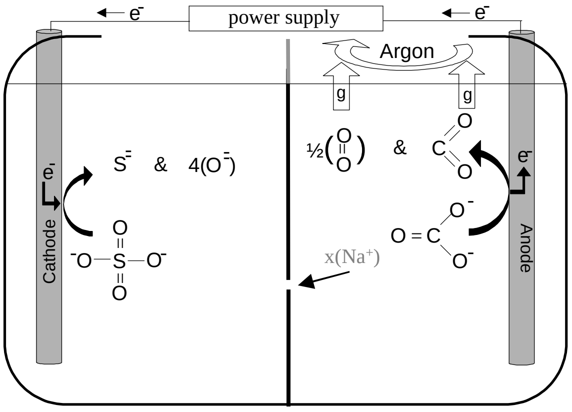

Figure 3: The electrochemical reactions which occur at the limits of the potential window in mixtures containing Na_2CO_3 and Na_2SO_4 at 840±20°C. Both the melt and the atmospheres of the anolyte and catholyte are separated.

ACKNOWLEDGEMENTS

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REFERENCES

1. T. M. Grace, B. Leopold, and E. W. Malcolm, Alkaline Pulping, in ‘Pulp and Paper Manufacture’ (edited by M. J. Kocurek and F. Stevens), Vol. 5, Joint Textbook Committee of the Paper Industry of the United States and Canada, Atlanta, (1991).

2. R. Wartena, J. Winnick and P.H. Pfromm, ‘Recycling Wood Pulping Chemicals by Molten Salt Electrolysis: Cyclic Voltammetry of Mixtures Containing Na_2CO_3 and Na_2SO_4’, *Journal of Applied Electrochemistry*, in review, June 2001.