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Analytical Chemistry Division

IN-LINE SENSORS FOR ELECTROLYTIC MAGNESIUM CELLS

QUARTERLY REPORT

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ABSTRACT

This report summarizes progress for the first three months of FWP CEED020, "In-Line Sensors for Electrolytic Magnesium Cells." The next report is due February 15, 1991.

TECHNICAL HIGHLIGHTS

The program is fully staffed.

An annotated bibliography of the pertinent literature has been started and will be expanded.

$MgCl_2$ purification and molten salt preparation facilities have been completed at both the University of Tennessee, Knoxville, and Oak Ridge National Laboratory.

The purification of $MgCl_2$ is being studied.

Initial Raman spectral results have been obtained at both facilities.

Two analytical spectral techniques involving near-infrared (NIR) and IR reflectance spectral measurements show promise for identifying and quantifying OH^- species in solid salts of interest.

A sealed IR reflectance cell has been developed for use in the project.

An electrochemical cell for use in voltammetric studies concerned with the project has been designed and fabricated.

BACKGROUND INFORMATION

The program staff currently includes two full-time postdoctoral employees, Sheng Dai and J. E. Coffield, a graduate student, R. L. Richardson, a part-time employee, T. R. Mueller, a consultant in Raman techniques, G. M. Begun, and the P.I.'s Gleb Mamantov and J. P. Young. An annotated bibliography has been started listing reports of interest in three areas: purification of $MgCl_2$, spectral and electrochemical studies of molten salts containing $MgCl_2$, and application of fiber optics to our analytical interests. The bibliography will continually be updated.

MELT PURIFICATION AND PREPARATION

(Sheng Dai, J. E. Coffield, and R. L. Richardson)

Two general techniques are being used to purify $MgCl_2$; the products of these purifications are being compared to develop a routine purification procedure. For early work, $MgCl_2 \cdot 6H_2O$ was first heated in a vacuum, followed by treatment with semiconductor grade HCl gas at reduced pressure. Ultimately the solid was melted; HCl gas bubbled through melt for 6 hours followed by a flow of N_2 to aid the degassing of HCl. Finally, the melt was heated to 1000°C under a vacuum for a short period of time. Problems with this technique include the necessary removal of large amounts of water and consumption of a large volume of HCl. The product $MgCl_2$ did not appear to attack SiO_2 during subsequent Raman studies of the molten salt contained in SiO_2. A four component molten salt, NaCl-KCl-$CaCl_2$-$MgCl_2$ was also prepared from the purified $MgCl_2$; the melt was also treated with HCl and N_2 gas. In Raman studies of this molten mixture, it was found that the SiO_2 container was attacked. It is possible that HCl still remained in the mixture and was responsible for the corrosion. Further studies are necessary; in the commercial melt that our sensors will be designed for, it is possible that HCl will be present since $MgCl_2 \cdot 2H_2O$ is added to maintain the Mg(II) concentration in the cell.

Another procedure for preparing $MgCl_2$ is based on a combination and modification of several methods.[1-3] The dehydration procedure is applied to ammonium carnallite, $MgCl_2 \cdot NH_4Cl_2 \cdot 6H_2O$, and involves a two step heating process, the first to remove most of the water and the next to allow NH_4Cl to dissociate and purify $MgCl_2$. The product of this procedure is then distilled under vacuum at 850°C based on the work of Smith and Boston.[3] This procedure separates any residual oxide and produces a product which is said to be compatible with fused quartz at 900°C.

Typically, about 40g of ammonium carnallite is used as the starting material. This is heated under vacuum at 175°C for approximately 4 hours in a fused quartz double bulb tube. The volume (ca. 18 ml) of water removed during this heating was roughly consistent with that expected for complete dehydration of the hexahydrate. The temperature was then raised to approximately 350°C to remove the ammonium chloride. After heating at this temperature for 3 hours, the reaction tube was cooled and the lower section (containing the $MgCl_2$) was sealed off under vacuum. This raw $MgCl_2$ was transferred in

a dry box to a second quartz double bulb tube, placed under vacuum, and heated rapidly to 850°C to distill $MgCl_2$. A small amount of white solid (presumably MgO) remained in the bottom of the tube. Other modifications of this procedure are also being investigated such as simply mixing NH_4Cl with $MgCl_2 \cdot 6H_2O$, changes in the temperature-time procedure, etc. The usefulness of all these techniques will await tests to determine the purity of the $MgCl_2$.

RAMAN SPECTROSCOPY

(Sheng Dai, J. E. Coffield, G. Mamantov, and G. M. Begun)

Raman spectra of solid and molten $MgCl_2$ (commercial and our anhydrous preparation) and of $MgCl_4^{2-}$ in molten NaCl-KCl-$CaCl_2$-$MgCl_2$ have been obtained. Our spectra compare well with that reported by Huang & Brooker.[4] Our initial Raman spectral work was carried out with a consultant to the Chemistry Department of the University of Tennessee, Professor Bernard Gilbert, University of Liege. He pointed out that one of the peaks assigned earlier[5] to $MgCl_4^{2-}$ was actually an instrumental artifact. The spectrum of molten $MgCl_2$ is shown in Figure 1 and consists of a single broad band (192.1 cm^{-1}, possibly composed of several bands); the spectrum of solid $MgCl_2$ has two sharp bands (154 and 242.9 cm^{-1}).

In the molten mixture of NaCl-KCl-$CaCl_2$-$MgCl_2$ (35-35-15-15 mole %) the $MgCl_4^{2-}$ exhibits a Raman band at 249 cm^{-1}; this melt is similar in composition to that used in the Dow electrochemical Mg production. Attempts are underway to measure some simulated industrial multi-component melts involving various mixtures of MgO, NaOH, NaCl, KF, KCl, $CaCl_2$, and $MgCl_2$.

REFLECTANCE SPECTRAL MEASUREMENTS

(Sheng Dai and J. P. Young)

It should be possible to utilize infrared (IR) or near IR (NIR) absorption spectra to detect and determine possible impurities (hydroxide and water) of interest to our project. The former involves a measurement of fundamental vibration modes while the latter depends on overtone transitions. Whether these species exist in the melts we use is also not known. To answer these points we have developed analytical techniques to obtain diffuse reflectance spectral measurements on solids. We have developed capabilities to make these measurements in sealed cells since many of the chloride samples we have will be hygroscopic. An IR diffuse reflectance cell has been designed and fabricated for this purpose. The operation of both the NIR and IR cells has been checked with $Ca(OH)_2$-K_2CO_3 mixtures.

The fundamental hydroxide band in $Ca(OH)_2$, at 3634 cm^{-1}, measured using this technique is shown in Figure 2. In the NIR, overtone bands of water and OH^- are better resolved than the bands in the IR region allowing for the detection of hydroxide species in the

presence of water. In the IR range, the bands for water and OH^- overlap; however, the broad characteristic fundamental water band can be employed to detect water impurity in melt components. Calibration curves will be prepared, and various chloride samples, of our own or Dow Chemical Company origin, will be analyzed.

ELECTROCHEMICAL STUDIES

(T. R. Mueller, J. E. Coffield, and G. Mamantov)

Glassy carbon seems to offer the best combination of chemical inertness and electrical conductivity for electrochemical investigations in the proposed melts. Under some conditions, platinum is known to form chlorides; therefore, we plan to carry out our electrochemical investigations in glassy carbon vessels.

We have procured glassy carbon crucibles for containment of the melts. Discussions with the manufacturer of this carbon material, Sigri Corporation, indicate that the crucibles should be compatible with the proposed anhydrous melts. Carbon materials have been ordered for use as electrodes. We propose to use these and selected metal electrodes in preliminary studies of melts of interest.

The vessel that will provide atmospheric isolation of the electrochemical cell has been designed and fabricated. The lower section is quartz; the upper section is glass. The container has been designed with seven entry ports into the melt container. These will be used for insertion of electrodes, salt additions, purge gas, and stirring. Initial loading of the salt and assembly will be done in an inert atmosphere box.

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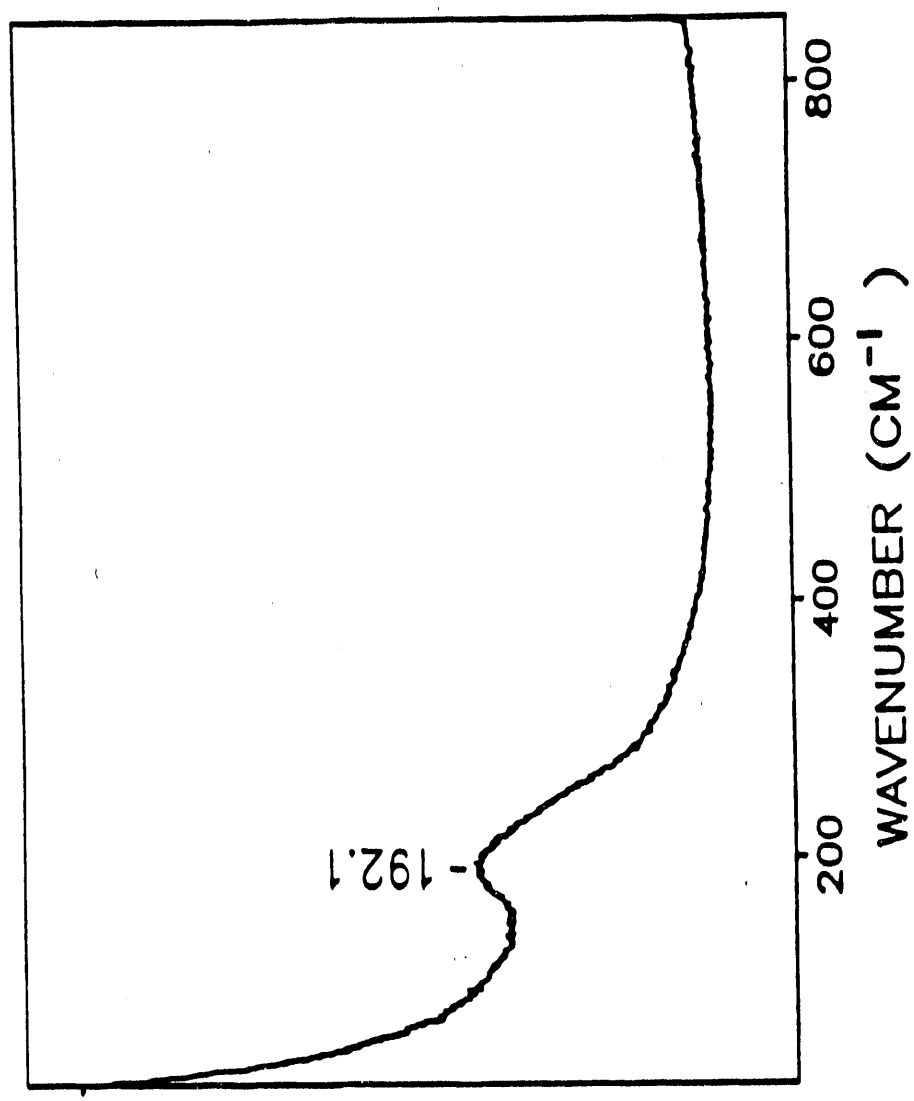

Figure 1. Raman Spectrum of Molten $MgCl_2$; Temperature 750°C.

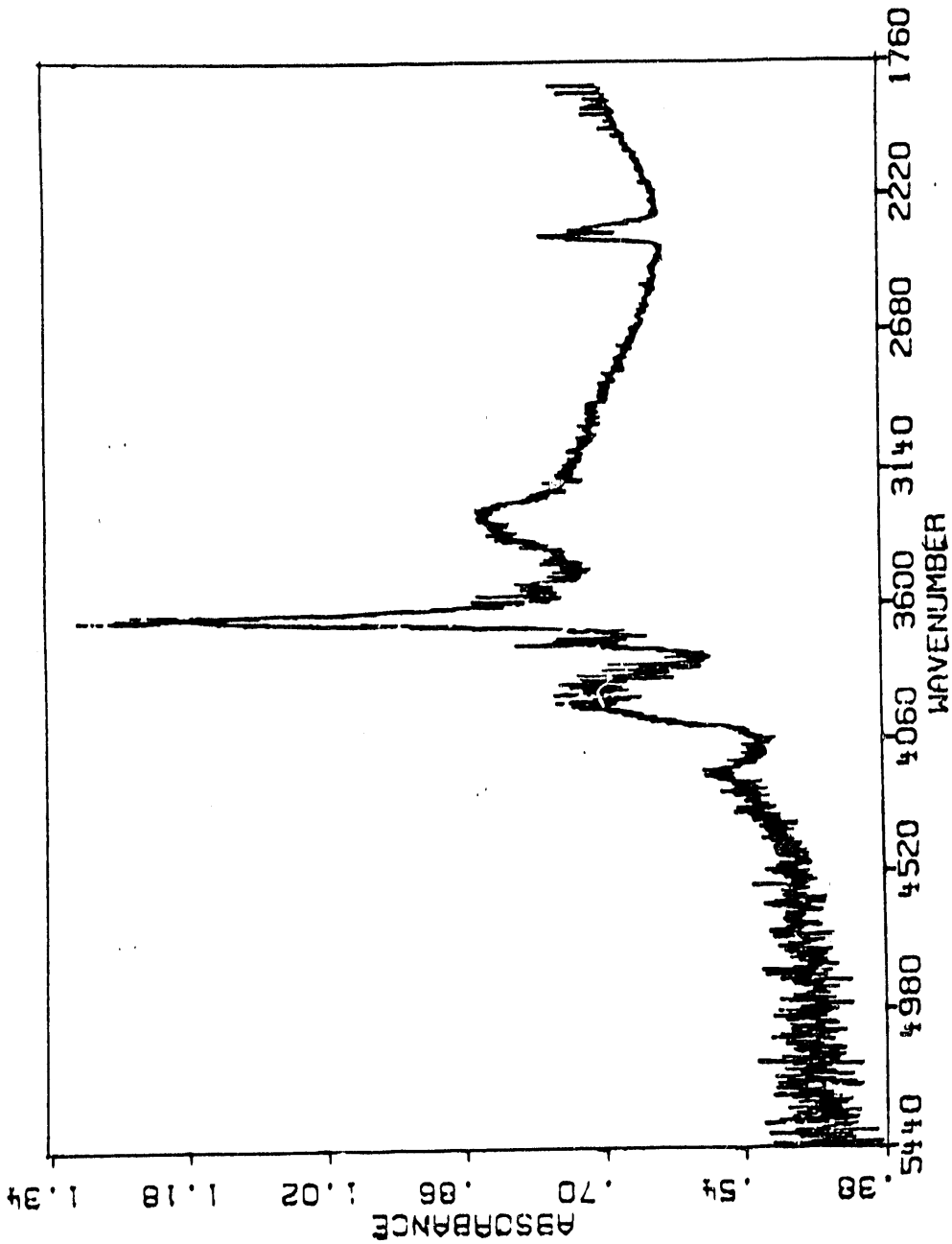

Figure 2. Diffuse Reflectance Infrared Spectrum of $Ca(OH)_2$ in a Sealed Cell; Yttrium Oxide Window.

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