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MINERAL RECOVERY FROM GEOTHERMAL BRINE

FINAL REPORT

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I. INTRODUCTION

This is the Final Report for the MidAmerican Energy Holdings Company (MEHC) project entitled "Mineral Recovery from Geothermal Brine". The project was designed with two major objectives: (1) to test the commercial viability of amorphous silica that was being produced as a byproduct by the geothermal facilities at the Salton Sea Geothermal Field, and (2) to develop a process for the extraction of manganese from the brines and then produce commercially valuable electrolytic manganese dioxide. The final funding agreement (the Agreement) with the California Energy Commission (CEC) for this project was signed on March 9, 2000, and technical work continued until the end of calendar year 2000. Both the silica and manganese projects were carried out simultaneously.

PROJECT BACKGROUND

The resources of the Salton Sea Geothermal Field produce very high temperature fluids that are rich in a variety of dissolved minerals. These include the alkali and alkaline earths, many transition metals, and a high concentration of dissolved silica, an important constituent that must be dealt with in brine handling. The primary focus of development of this hydrothermal resource until recently has been on utilizing the heat and steam for electrical power generation. Extraction of the energy for electrical power generation has had to overcome the severe problems of corrosion and silica scaling during the processing of these geothermal fluids. Having had significant success in developing and commercializing the techniques for power production, MEHC initiated a program aimed at recovering useful minerals from the brines. Development studies have been completed on a process for the recovery of high-purity zinc from geothermal brine, and construction of a commercial plant that will produce 30,000 metric tons per year of this metal was underway at the end of 2000. The goal of the project described here was to develop and refine chemical processing methods for extracting two other important constituents from the geothermal brines – silica and manganese. A large world-wide market exists for both of these constituents, the former as amorphous silica powder, and the latter in the form of manganese dioxide for batteries.

TYPES OF POWER PLANTS

When the geothermal brines are processed to generate electricity, the hot, pressurized fluid is flowed from the well through a series of vessels where it is depressurized and allowed to boil or "flash" to produce steam for the turbines. Flashing and cooling causes amorphous silica and other compounds to precipitate naturally from the fluids. If not controlled, buildup of deposits in the vessels and piping from precipitation would quickly render the power plants inoperable. In addition, the hot brines are highly corrosive to mild steels. Two fundamentally different designs of geothermal power plant are presently being used by MEHC to handle the brines and avoid or mitigate the effects of scaling and corrosion (Featherstone, et al, 1995).

One basic type of power plant is known as the Crystallizer/Reactor/ Clarifier (CRC) Process, in which the brine is seeded with previously precipitated silica to deliberately cause further precipitation, and the flashing to obtain steam is performed with fluid/solid suspensions. In the first step of this process, brine from the production wells is flashed to steam in a series of vessels called flash crystallizers, in which particulate amorphous silica (from a later stage of the process) is added to the fluid. This so-called "seeding" process has the effect of precipitating some of the amorphous silica from the brine, thus reducing its concentration to saturation and therefore its propensity to form scale. The steam flows to the turbines to generate power. The brine, which is then a suspension of amorphous silica particles, next goes to a reactor-clarifier, where more precipitation of the silica takes place, and then finally to a polishing clarifier, where the particulate silica is separated from the brine. This silica is continuously fed back to the flash crystallizers as seed material. The concentration of silica in the brine is thus maintained at saturation levels appropriate to the temperatures of the fluid at each stage of the process, and the brine-handling equipment remains free of scale. Finally, the clarified brines are reinjected into the ground by means of injection wells and most of the excess impure amorphous silica that is produced is discarded in landfills. MEHC's affiliated facilities commonly known as Elmore (Elmore) and Leathers (Leathers) are examples of the CRC Process.

In another type of power plant now in operation, known as the pH Mod Process, the brine from the production wells is progressively acidified with hydrochloric acid, which completely retards the precipitation of silica and the formation of scale in the system. This acidified brine is flashed to steam for the turbines, with the steam being separated in more conventional, high-pressure and low-pressure geothermal separators. In the classic pH Mod Process, such as the MEHC-affiliated plants in the area commonly known as Region 1 (Region 1), the acidified brine is reinjected with its silica concentration still well above saturation levels, and no silica precipitates because of the inhibiting effects of the low pH of the brine. If it is desirable to remove solid, amorphous silica from pH Mod effluent brine for industrial use, it is necessary to provide an additional operation to treat this fluid.

A third type of facility for power generation combines the operations of both pH Mod and CRC processes. This "hybrid" plant has a pH Mod front end, and silica precipitation is induced at an intermediate high pressure stage (15-20 psig, where steam is taken off) by

introducing lime and silica seed as in a CRC plant. Thus, like the CRC process, particulate silica is produced as a byproduct and the effluent fluid is also similar.

SILICA RECOVERY

As can be seen, the CRC and the pH Mod/CRC Hybrid Processes naturally produce solid, amorphous silica that has potential as an industrial material. As noted above, in the case of the pH Mod Process, to recover the silica, since the silica is still in solution, a means must be provided to remove it. In general this is done by raising the pH of the effluent brine with an alkali such as lime, while seeding the brine with previously precipitated silica, in an overall operation analogous to that of a CRC Process plant. The solid silica is then recovered by fluid clarification and filtration. Some of the critical characteristics of amorphous silica that determine its potential use as an industrial material are its purity, particle size, and surface properties, and it is known that *these characteristics are quite different depending on the history of silica particle growth in the fluid and how the silica is precipitated*, and hence on the type of process from which it comes. The initial effort in this project was to select a potential use for the silica already available, and then test it in that application. The plan was to continue work that would be focused on modifying the precipitation processes to improve the properties of the silica.

MANGANESE RECOVERY

The first phase of this work was the development of a process for transferring the manganese from the brine to a solution that would be suitable for the electrolytic production of solid, battery-grade manganese dioxide. The process had to be designed to separate manganese in solution from several other elements (such as iron and calcium) that would interfere in its subsequent use. Solvent extraction was the primary process selected, and it was designed to operate with brine effluent from which both silica and zinc had previously been removed.

A second phase of this work was an investigation of the production of manganese dioxide using the solution from the manganese extraction process. Manganese dioxide for use in batteries is produced on an industrial scale by anodic deposition in electrolytic cells. The present industrial process utilizes a sulfate electrolyte derived from manganese ore. The electrolytically-produced manganese dioxide (commonly known as EMD) is a unique material which has a very rigorous set of specifications that must be met for it to be useful as a battery material (Glover, et al, 1989; Anthony, 1999). The primary objective of the MEHC work was to demonstrate that battery-grade EMD could be produced from a chloride solution derived from geothermal brine.

II. PROJECT OVERVIEW

SILICA

Task 2.1 Process for Production of Marketable Silica

This task was divided into the three following subtasks corresponding to the type of power-plant process from which the silica would be obtained. The objective was to maximize the value of the silica for a given use for each geothermal process. It was envisioned that in optimizing the variables in the production of commercially-viable silica, both pilot-scale, and probably laboratory-scale studies would have to be conducted.

Subtask 2.1.1 Crystallizer/Reactor/Clarifier (CRC) Process
Subtask 2.1.2 pH Mod Process
Subtask 2.1.3 Pilot-Scale pH Mod/CRC Unit
(This subtask was further subdivided into two additional subtasks:
Subtask 2.1.3.1 Laboratory-Scale Study: Study of Silica Precipitation Process Variables
Subtask 2.1.3.2 Laboratory-Scale Study of Leaching, Washing, and Drying Variables

Prior to the start of the work reported here, there were ongoing investigations of the chemical and physical characteristics of the silica produced at all of the various MEHC facilities. A market survey had been conducted to determine the many potential uses for amorphous silica. One of these uses of interest was, at the high (purity and value) end, as a filler in the making of rubber for tires. A second use, at the lower end, was as a material for making cement and the production of concrete. A pilot-scale silica-removal system had also been developed and was in operation at one of the pH Mod facilities, which corresponds to the work envisioned for **Subtask 2.1.2**. It was decided at the outset of the project that the major effort would first be placed on testing silica from this process and from the full-scale, hybrid pH Mod/CRC Process (**Subtask 2.1.3**), and that the emphasis would be on the use of the geothermal silica in cement and concrete. Because of power-plant related problems associated with the CRC Process facilities during the work period, no testing of the silica or attempts to maximize its value (**Subtask 2.1.1**) were accomplished for this subtask.

Silica samples from the pH Mod and the hybrid geothermal processes were subjected to a series of tests by subcontractors, first to determine whether it had "pozzolanic" activity (Swaddle, 1990) as an ingredient in Portland cement. In these formulations, the pozzolan replaces an equivalent amount of cement. Siliceous materials from various sources (e.g., natural pozzolans such as volcanic ash) are commonly used in cement, and by reacting with the calcium hydroxide to form hydrated calcium silicates and aluminates, they help to impart strength to the hardened concrete product. The following tests of MEHC geothermal silica were conducted. Silica from the pH Mod Process was used in Tests 1-3, and silica from the Hybrid Process was used in Tests 4-6.

1. American Society for Testing Materials (ASTM) C618, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete." In these tests (using ASTM C311), the compressive strength of

concrete prepared from the geothermal silica was compared to that of fly ash as a reference material, and it was concluded (a) that the geothermal silica did have pozzolanic activity, and (b) that its performance in the compressive strength tests was satisfactory.

2. Additional tests of compressive strength as well as measurements of "slump" and air content at 7- and 28-day cure intervals for mixtures containing 15, 35, and 55% silica. Again, the performance of silica compared favorably with fly ash, but there were some interesting differences between the two additives. Slump decreased with higher percentages of silica, but since replacements higher than about 20% are seldom used in the industry, the degree of slump was not a concern.

3. Measurements of the temperature rise as the concrete cures. This occurs because of exothermic reactions in the mixture, and is potentially detrimental because it may lead to excessive expansion and shrinkage, and then later cracking of the concrete Here it was found that there was very little difference between silica and fly ash up to 35% loading, but at 55%, the temperature of the concrete mixture increased earlier with silica than with fly ash. Both admixtures reached the same maximum temperature. This indicated that the chemical reactions were occurring more rapidly with silica than with fly ash, but again, the results appeared to be acceptable for the geothermal silica.

4. Resistance to chloride ion permeability. This characteristic is particularly important when concrete is used in high chloride environments such as sea water, where intrusion of chloride ion may weaken the concrete. These test followed the procedures in ASTM C1202-97, "Standard Test Method for Determination of Chloride Permeability of Concrete." The test specimens were cast in accordance with ASTM C192-98. "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory." A 20% replacement level of silica was used. It was found that the chloride permeability of the concrete containing silica was lower than the concrete without pozzolan by 33-69%, a very satisfactory result.

5. Large-scale test of concrete mix. A large batch (8 cubic yards) of concrete containing 15% geothermal silica was prepared at a commercial concrete plant. A test slab of about 20 x 20 ft. size was poured with this concrete, as well as some cylinders for measurement of strength-vs.-time development. The handling of the concrete and the initial appearance of the slab were observed to be excellent. The slab is still in good condition after two and a half years' use as a truck shop driveway.

6. Reaction with alkali. In this test, ASTM 1260, "Accelerated Mortar Bar Test," concrete bars are cast, cured, and then immersed in a 1 mol/L sodium hydroxide solution at 80° C. The dimensions of the bars are measured periodically, and if there is a reaction between the concrete and the alkali, the bars expand. Expansions greater than 0.20% after 16 days are indicative of potentially deleterious behavior. Geothermal silica was tested at replacement levels of 20 and 30%, and for 20%, expansions reached as much as 1.6% after only 7 days. There was less expansion at the higher replacement, but the results were clearly unsatisfactory and demonstrate that the concrete containing geothermal silica was highly reactive toward alkali. The mechanism of this reaction is not known, but is believed to be due to minor constituents in the silica, which, as obtained from the hybrid pH Mod/CRC Process, was only about 87% pure SiO_2.

The results of the use of geothermal silica as an admixture for concrete thus were quite promising, but the failure of the material in the alkali reactivity test points to further

research and development in this area. Two major aspects should be investigated: (a) additional concrete tests employing silica samples from the other geothermal processes, and (b) treatment of the pH Mod/CRC silica (such as by leaching and/or washing) to increase its purity.

The laboratory studies embodied in **Subtask 2.1.3.1** were expected to shed more light on the variables involved in the precipitation of silica from geothermal brine, so that a more acceptable product could obtained. As noted in the original work plan, this investigation was being conducted primarily by the Lawrence Livermore National Laboratory (LLNL), and MEHC was following their studies. Autoclave tests were being initiated, but by the time the MEHC tests were terminated, no information on silica precipitation useful for the MEHC studies had been obtained. At larger scale, as noted above, the pilot scale silica precipitation and removal system installed at the pH Mod facility was in operation during the CEC work period, and while producing silica for the concrete tests, it also yielded information on the effects of some of the important process variables.

For **Subtask 2.1.3.2**, a number of studies of the treatment of the silica after precipitation were conducted. One of the potential uses of the geothermal silica is as "clinker" additive for cement manufacture. In this application, the silica is not required to possess pozzolanic activity. It was demonstrated that silica from the CRC Process (which is the least pure of all of the silicas) could be leached with dilute acid, removing some of the impurities, and providing a suitable product for cement clinker. Discussions are underway at this writing to market this silica to a local company. The results of these studies also provided information for the design of larger-scale facilities. For example, a new precipitation, leaching, and vacuum-belt filtration system is being installed at the pH Mod facility, and it is expected that the silica it produces will have greatly improved chemical and physical properties.

MANGANESE

Task 2.2 Process for Production of Marketable Electrolytic Manganese Dioxide

This task was subdivided into four subtasks, corresponding to the three basic unit operations of the envisioned process, followed by a subtask in which a pilot-scale facility of the whole process would be tested. These subtasks were entitled:

Subtask 2.2.1 Laboratory-Scale Study: Solvent Extraction of Manganese
Subtask 2.2.2 Laboratory-Scale Study: Separation of Manganese from Iron and Calcium
Subtask 2.2.3 Laboratory Scale Study: Electrodeposition of Manganese Dioxide
Subtask 2.2.4 Devise Design Parameters for Large Scale Pilot Plant

The development of the process for recovery of manganese from geothermal brine was predicated on treatment of the effluent from the power generation facilities –downstream of the processes for the removal of silica and zinc. The type of power production facility (CRC, pH Mod, or Hybrid) from which the fluid comes is irrelevant as far as manganese

recovery and production of manganese dioxide (EMD) is concerned. There may be minor differences in the chemical composition of the spent brine from the silica and zinc processes, but they are not expected to be important in the subsequent manganese process operations.

Extraction of Manganese. Laboratory-scale studies at MEHC revealed that the best technique for removal of the manganese from the spent brine was solvent extraction. The medium selected was an organic, aliphatic-hydrocarbon solvent (trade name, Orfom SX-11), containing di-(2-ethylhexyl) phosphoric acid and a long-chain quaternary amine (trade name, Aliquat 336). Prior to use, the organic phase is equilibrated with aqueous NaOH so that the extractant solution contains the ion-pair, QL, where Q is the quaternary amine and L is the organic phosphate. When the solvent is mixed with the aqueous brine, the ligand L^- complexes manganese and transfers it to the organic phase. The metal is then stripped from the organic phase with aqueous HCl. This separates manganese from all of the significant constituents of the brine except iron and calcium. These metals in high concentrations interfere in the electrolytic production of EMD, thus additional studies were conducted on their removal.

Data from the laboratory-scale extraction studies were employed to specify a bench-scale (2 gpm) extraction unit that was obtained from Koch Technologies, Inc. The Koch equipment was operated successfully at one of the CRC Process facilities where an ion-exchange system was also installed to remove zinc from the effluent brine. With the spent zinc process fluid as a feed for the Koch system, the characteristics of the extraction process were further examined, and solutions were provided for tests of methods for the removal of iron and calcium.

Separation of Iron and Calcium. Lakefield Research in Ontario, Canada (Lakefield) was engaged to investigate methods for the separation of the iron and calcium. Several approaches were examined for iron, in which the iron is first oxidized to Fe(III). Several reagents were investigated for the oxidation including hydrogen peroxide and sodium hypochlorite. One promising method for iron separation is solvent extraction as the Fe(III)-chlorocomplex, but the best method that was developed now appears to be hydrolytic precipitation as form of the compound, FeOOH, and then removal as a solid. The solvent extraction method might be preferable if the byproduct $FeCl_3$ solution is marketable.

The technique for the removal of calcium that was developed was to use the spent solution from the EMD electrolysis to scrub the initial Mn-loaded, organic-extractant solution. The high concentration of manganese in the scrub solution effectively competes for the QL and "crowds" out the calcium, thus reducing it to an acceptable level in the subsequent processing.

EMD Electrolysis. Manganese dioxide is produced by electrolytic oxidation of manganese ion in the following reaction:

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^- \qquad (1)$$

In the electrolytic cell, solid MnO_2 is deposited on the anode, and hydrogen is liberated at the cathode. In the standard industrial process, in sulfate media, a small amount of oxygen is also produced at the anode as a side reaction. Certain properties of the EMD

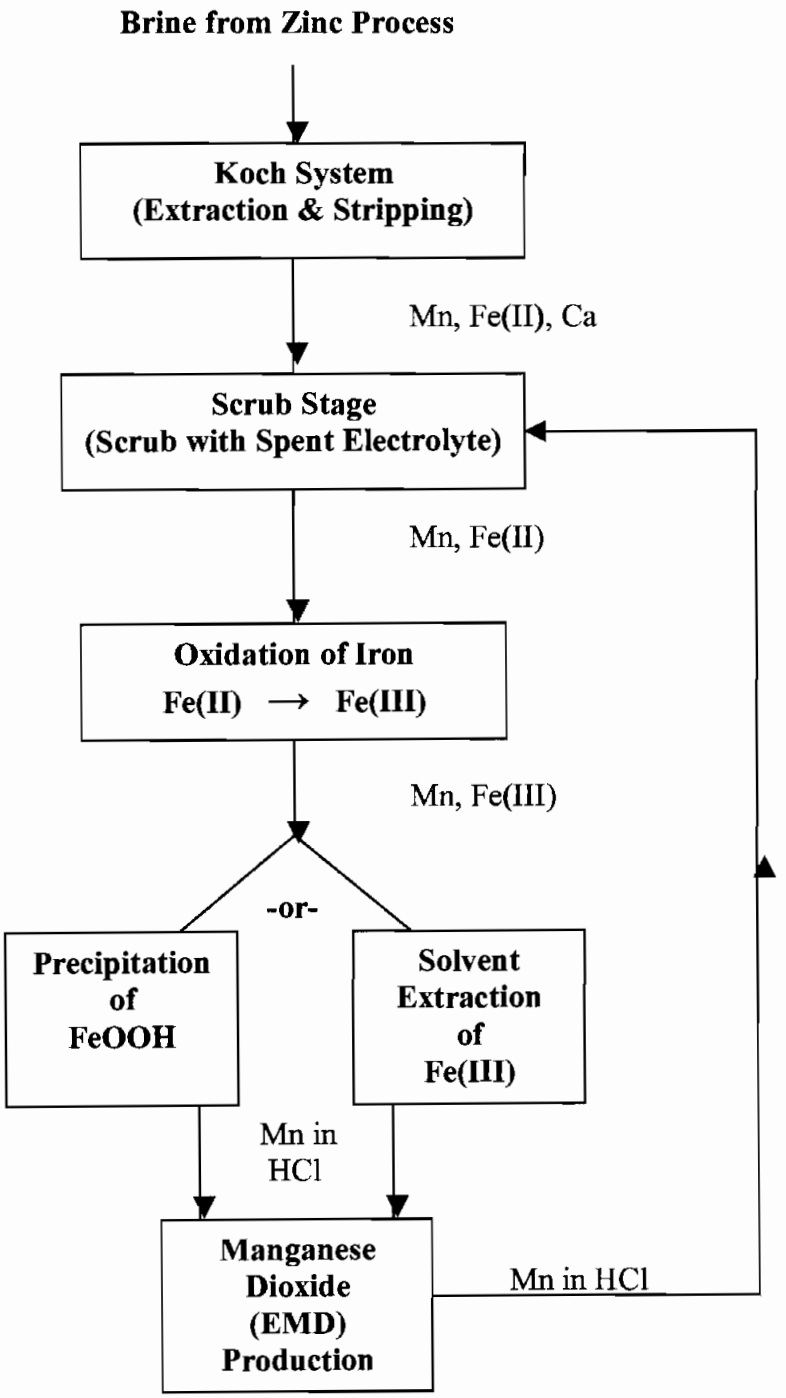
that is produced are important for its marketability as a material for alkaline batteries. For example, its crystal structure must correspond to that of γ-MnO_2 and there are a variety of other specifications. In the conventional industrial process, the electrolyte solution is dilute sulfuric acid. At MEHC, the objective was to demonstrate the process in the hydrochloric acid medium from the extraction, which introduces the complication that another side reaction occurs at the anode – the oxidation of chloride ion to chlorine. The concentration of chloride as a contaminant in the final product also may be an issue.

The process to be implemented at MEHC was investigated in several stages. The first stage was in the laboratory at the University of Missouri, Rolla, where a small electrolytic cell was employed. Examined were variables such as solution composition, electrode current density, current efficiency, evolution of chlorine, and the crystal structure of the EMD produced. At MEHC, a bench-scale electrolytic cell of approximately 50 gal. capacity, containing four anodes and five cathodes, was then constructed and operated for several months using the product from the Koch extraction system as a feed solution.

Subsequently, a smaller scale apparatus was operated at Lakefield Research using simulated brine. Lakefield produced 1.0-1.7 kg batches of EMD in a cell with one anode and one cathode. Detailed measurements were made of the electrolysis parameters, the specific energies (1.3-1.8 kWh/kg) the current efficiencies (90-100%), the rate of evolution of chlorine, and the quality of EMD produced. Some experiments on crushing and washing of the EMD, and measurement of the residual chloride in the product were also conducted. The characteristics of these electrolyses and the resulting EMD were generally excellent and comparable to those of the industrial process. As expected, significant quantities of chlorine are produced when the current efficiency is lower. In a full-scale process, this chlorine would have to be scrubbed for safety reasons, but it might also be possible to use it as the oxidant for Fe(II) in the iron separation step.

All of these experiments comprised a preliminary demonstration that an EMD meeting most of the required specifications can be produced from the chloride media derived from geothermal brine. What still needs to be done is to confirm that a complete iron and calcium separation process, based on the proposed flowsheets, is capable of producing a feed electrolyte that can in turn yield battery-grade EMD. Using the information developed thus far, MEHC is now in a position to design and test a pilot-scale facility with a brine processing capability of 50-75 gpm and the corresponding production rate of EMD. A simplified block diagram of the process that would be designed is shown on the next page in Figure 1. As shown in this diagram, there is still a choice to be made for the iron removal process. In the overall process, the concentration of manganese is raised from ~1.5 g/L to ~60 g/L going into the EMD electrolyzer. The spent electrolyte is ~50 g/L in Mn, thus it is quite effective for displacing the calcium in the scrubbing step.

Figure 1. Schematic diagram of the Process for the Production of Electrolytic Manganese Dioxide (EMD)



III. TECHNICAL TASKS – DETAILED DISCUSSION

TASK 2.1 PROCESS FOR PRODUCTION OF MARKETABLE SILICA

As noted above, because the silica produced at each type of geothermal facility is fundamentally different , this task was originally divided into three subtasks corresponding to the type of power-plant process from which the silica would be obtained. Moreover, the amorphous silica recovery processes that are being developed eventually must be compatible with each of these power generation systems. For marketing the silica as a commercial product, the silica product handling and finishing systems must also be optimized. With these constraints, the immediate goal of this task was to test a given type of silica and then attempt to modify the specific silica recovery and handling processes to optimize the characteristics of the silica. A strong incentive for finding a commercial outlet for the silica is that on the order of 100 tons of dry silica per day is generated as a byproduct at the MEHC facilities.

Subtask 2.1.1 Crystallizer/Reactor/Clarifier (CRC) Process

At the time the silica project was initiated, the facilities at Elmore were undergoing change for the zinc process, and they were the site for the manganese extraction systems. Among the most serious problems encountered during the startup of the new zinc facilities were the zinc/power plant interfaces. Even minor changes in power plant brine properties, especially to more oxidized conditions, adversely affects zinc operations. Conversely, effluent streams from the zinc plant proved to be very difficult to handle without producing negative impacts on power plant operations. All attempts to modify upstream brine properties were discontinued (other than those necessary to operate zinc) because of these problems. Further use will be considered only after successful startup of the commercial zinc facilities. In addition, the silica that was produced routinely here was of a lower purity than that available elsewhere. Thus as noted in Section II., Project Overview, no work was done utilizing silica from this type of process. The major progress in the recovery and use of marketable silica thus will be discussed under the headings of Subtasks 2.1.2 and 2.1.3.

Subtask 2.1.2 pH Mod Process

Silica recovery from the pure, pH Mod power-production process requires an additional system for precipitation and removal of the silica. As noted in Section II, Project Overview, a pilot-scale silica-removal system had been developed and was in operation at one of the pH Mod facilities. Thus it afforded a readily available material for the experiments in this subtask. This facility was a pilot scale reactor/clarifier/filtration system at which a variety of treatment methods and conditions for recovery of silica could be examined. The product from this facility was used in many of the tests to be described here. Geothermal silica was subjected to some preliminary tests as a filler for rubber manufacture, but they indicated that the geothermal silica, as currently produced, was not suitable for that application. Attention was then shifted to an application in which the purity and surface properties were not as critical, namely, in the manufacture of cement and concrete.

In the manufacture of Portland cement (Swaddle, 1990), limestone is fired with various clays and silicate materials at a high temperature. First of all, geothermal silica could provide a material for this process, i. e. as a "clinker." When the cement is then used with an aggregate to react with water and produce concrete, a second possible use for the geothermal silica is as a substitute, or replacement, for a certain fraction of the cement. In this application, the replacement material must have "pozzolanic" activity. This is a property (possessed by certain natural pozzolans such as volcanic ash) that is related to its reactivity and ability to form hydrated silicates in the final concrete product as it hardens. The silica recovered from the geothermal pH Mod Process was subjected to a number of tests to determine its potential as an additive for cement and concrete. The results of these tests will be described under the next subtask heading.

Subtask 2.1.3 Pilot-Scale pH Mod/CRC Unit

This facility was not constructed and put in operation *per se*; rather, silica from the full-scale, Hybrid pH Mod/CRC Process at the MEHC-affiliated plants commonly known as Vulcan (Vulcan) and Hoch (Hoch) in the area commonly known as Region 2 (Region 2) was employed, along with the silica from the pH Mod Process, for the tests of silica as a pozzolan in the manufacture of concrete.

Pozzolonic Activity Tests. Preliminary tests (see Attachment 1) were conducted according to the ASTM specification C618, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete." The procedure used was ASTM C311, "Test methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete." It was found that the geothermal silica had considerable potential for use as a pozzolanic material.

After determining that the geothermal silica passed the criteria stipulated in ASTM C618, it was decided that actual concrete testing should be performed, in order to evaluate the geothermal silica in a typical application in construction. The purpose of concrete testing, as opposed to ASTM mortar testing, is that the pozzolan in question is tested in the presence of aggregate material in the mix. There is considerable dispute in the industry as to what type and size of aggregate is suitable for this evaluation. Nonetheless, an investigation was performed at Southland Geotechnical (Southland) in El Centro, California, using an aggregate that is locally produced in the Imperial Valley of California, and at the Materials Technology Laboratory at the Canada Centre for Mineral and Energy Technology (CANMET) in Ottawa, Ontario, Canada, using their in-house testing aggregate.

The initial concrete tests were conducted at Southland, using the mixture proportions detailed in Table 1. Note that the replacement of cement by geothermal silica was in the order of 20%. The fresh concrete mixture was set in 4 x 8 inch cylinder molds in triplicate and allowed to cure for 7 and 28 days. The results of these tests are shown in Table 2.

Table 1: Proportions of Components in Fresh Concrete in Southland Experiments (Lb./Yd^3)

COMPONENT	CONTROL MIXTURE	TEST MIXTURE
Water	280	280
Cement	560	448
Geothermal Silica	0	112
Coarse Aggregate	1904	1904
Fine Aggregate	1268	1268

Table 2: Results of Compressive Strength Measurements in Southland Experiments

	COMPRESSIVE STRENGTH, psi	
MIXTURE TYPE	7 DAY CURE	28 DAY CURE
Control 1	3730	5830
Control 2	3550	4520
Control 3	3330	4110
Test 1	2480	4120
Test 2	1900	2310
Test 3	1970	4230

As can be seen in Table 2, the compressive strength of the concrete using silica was comparable to that of the controls, but because of the fairly large variation in the results for the controls, this test was considered not completely valid.

In order to verify the results of the Southland experiments, a sample of geothermal silica was sent to CANMET for testing. Apart from the compressive strength measurement, CANMET carried out a more in-depth examination of the geothermal silica, as well as testing it against a commercially available Class F fly ash (see Attachment 2). CANMET prepared several concrete mixtures as shown in Table 3. For each fresh concrete mixture, six 4 x 8 inch cylinders were cast for compressive strength determinations (for the 7 and 28 day curing in triplicate) and one 6 x 12 inch cylinder was cast for temperature rise determination.

Table 3: Proportions of Components in Fresh Concrete in CANMET Experiments (Lb./Yd^3)

MIXTURE TYPE	WATER	CEMENT	POZZOLAN	COARSE AGGREGATE	FINE AGGREGATE
15% Fly Ash	280	475	83	1950	1303
15% Silica	280	477	83	1938	1289
35% Fly Ash	280	364	197	1950	1300
35% Silica	280	362	196	1911	1271
55% Fly Ash	278	249	308	1923	1284
55% Silica	276	248	307	1856	1237
Control	280	560	0	1965	1311

The results of the CANMET tests are presented in Table 4. As can be seen in the compressive strength data, replacement of cement with geothermal silica added more strength to the concrete specimens than the replacement with fly ash. However, in excess of

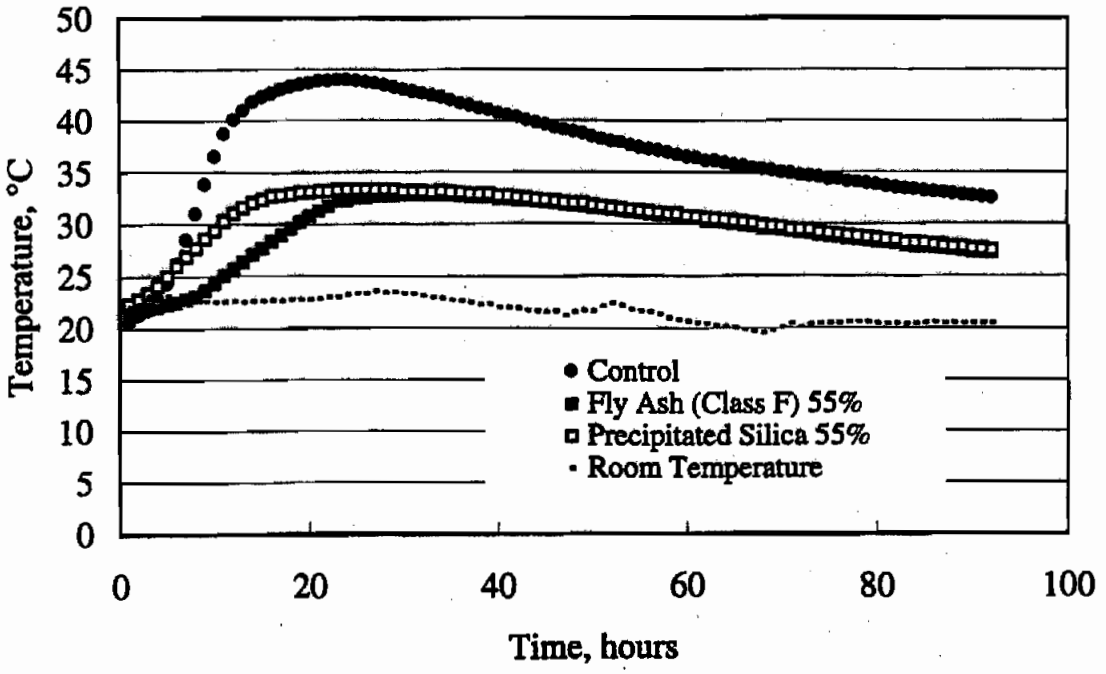
Table 4: Physical Properties of Fresh and Hardened Concrete

Mixture Type	Slump, inch	% Air Content	Unit Weight, Lb./Yd^3	Compressive Strength at 7 day cure, psi	Compressive Strength at 28 day cure, psi
15% Fly Ash	2.5	1.5	4091	4743	6106
15% Silica	2.2	1.5	4067	4656	6179
35% Fly Ash	3.5	1.3	4091	3800	5323
35% Silica	2.0	1.5	4020	3974	6077
55% Fly Ash	5.5	1.2	4044	1987	3365
55% Silica	1.5	1.7	3924	2234	4076
Control	1.5	1.5	4115	5628	6846

15% silica replacement, the slump decreases compared to an increasing slump for the concrete containing fly ash. In the measurement of "slump," a cylinder is prepared from the wet concrete mixture, and then inverted to note how the mixture slumps down, as an indication of its viscosity. The effect of decreasing slump is probably due to differences in particle morphology and specific surface area, and it signifies that the water consumption rate for silica replacement will be higher than that of fly ash replacement. However, more than 20% replacement of pozzolan is seldom employed in the industry. Therefore, this data does not raise a concern. Even though there is considerable dispute in the industry as to what are the exact chemical reactions between pozzolans and cement, there is an agreement that oxygen plays an important role. As illustrated in Table 4, fly ash reduces the air content in the mix, while geothermal silica increases it. This demonstrated another positive attribute that concrete acquires with the incorporation of geothermal silica.

Temperature Rise Tests. As concrete cures, its temperature rises because of exothermic reactions in the mixture. Excessive temperature rise is potentially detrimental because it may lead to excessive expansion and shrinkage, and then later cracking of the concrete. CANMET carried a series of measurements of the temperature of the mixes containing 15, 35, and 55% of geothermal silica. A temperature curve for 55% replacement is shown in Figure 2. The complete report can be found in Attachment 3. There was very little difference between silica and fly ash at 15 and 35%, but with increasing amount of both pozzolans, there was a decrease in the maximum temperature reached. The temperature of the concrete mixture increased earlier with silica than with fly ash, but both reached the same maximum temperature. This indicated that the chemical reactions were occurring more rapidly with silica than with fly ash, but again, the results appeared to be quite acceptable.

Figure 2: Semi-adiabatic Temperature Rise of Concrete at 55% Replacement Level



Resistance to Chloride Ion Permeability. Resistance to chloride ion permeability is another important aspect of the benefits of pozzolan usage in concrete. Pozzolans are used in high chloride environments, such as seawater, and intrusion of chloride ion may weaken the concrete. These tests of geothermal silica were conducted at Construction Technology Laboratories, Inc. (CTL) in Skokie, Illinois. The "test mix" was composed of a 20% replacement of cement with geothermal silica. The concrete mix designs are shown in Table 5. CTL utilized their in-house fine and coarse aggregates and

Table 5: Mix Design of Fresh Concrete for Chloride Permeability Determination

COMPONENT	CONTROL MIX	TEST MIX
Cement, lb./Y^3	517	414
Geothermal Silica, lb./Y^3	0	103
Eau Claire Fine Aggregate, SSD, lb./Y^3	1345	1345
Eau Claire Coarse Aggregate, SSD, lb./Y^3	2000	2000
Water, lb./Y^3	233	233
Daravair 1400, oz per 100 lb. cement	0.6	0.7
Slump, in.	2.5	1
Air Content, %	4.6	3.8
Unit Weight, lb./$ft.^3$	146.4	146.4
ASTM C 39 Compressive Strength, psi*	5430	5023

* Average of three specimens

commercially available Type I/II Portland cement. The test work followed the procedures in ASTM C1202-97, "Standard Test Method for Determination of the Chloride Permeability of Concrete". Concrete mixes were cast in accordance with ASTM C192-98 "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory."

Fifteen 4 x 8 inch concrete cylinders were cast from each mix. All specimens were moist cured (73 ± 3° F and 100% relative humidity) until time of rest. Measurements in accordance with ASTM C1202 were performed on both the control and geothermal silica specimens at ages 29, 43 and 57 days. Test results indicate the addition of the geothermal silica to the concrete mix reduced the measured charge passed, and hence the chloride ion permeability, at all test ages. Total charge passed on test specimens as compared to the control specimens were reduced by an average of 33% at 29 days, 54% at 43 days and 69% at 57 days. This was a very satisfactory result.

Large-Scale Test of Concrete Mix. In a more rigorous attempt to evaluate the geothermal silica, a concrete mixing test was conducted at a commercial concrete batch plant in the Imperial Valley, on the morning of Thursday, June 8, 2000. A representative from Southland was present and oversaw the collection and handling of fresh concrete samples. The samples were also cured and evaluated by Southland.

The concrete mix design was supplied by Jeff Lyon of Southland. The basic design incorporated geothermal silica at a 15% replacement of cement, with an additional 1.2 lb. of pozzolan per 1 lb. of cement (per CalTrans specifications). A water-reducing admixture (Grace Daracem) and city (potable) water were used for the mixture, and no air entrainment admixtures were employed. Riverside Cement (available locally) was used at a water to cement ratio of 0.5. Due to the sticky nature of fresh concrete, deviation from the 0.5 ratio had occurred. Extra water was added, producing a slump of 6.5 inches. Air entrainment in the fresh concrete was measured at 1.8%.

A total of 8 cubic yards of fresh concrete was batched. Following the specifications of the mix design, the correct weight of sand, rock and geothermal silica was charged into the feed hopper. The hopper was equipped with a weight scale, in order to measure each component accordingly. The cement, which was stored in the silo, was screw fed into the hopper. The conveyor fed all the measured components into a concrete mixer truck. The fine geothermal silica had enough moisture content so that dusting did not occur during handling. Water and the water-reducing admixture were added to the contents in the mixer truck, and then all of the components were blended.

A test slab of about 20 x 20 ft. was poured as shown in Figure. 3 In addition, specimens were collected in 4 x 8 in. cylinders, as shown in Figure 4. These samples were collected in order to measure the strength development of the concrete at 1, 3, 7, 28, 56 and 90-day cure. The test cylinders were capped, labeled and placed on a sheet of plywood. They were then buried in moistened dirt. The plywood was used to keep the specimens level and stable, and the moistened dirt was employed to keep the specimens from drying out during curing.

Figure 3. Pouring of fresh concrete into a test slab.

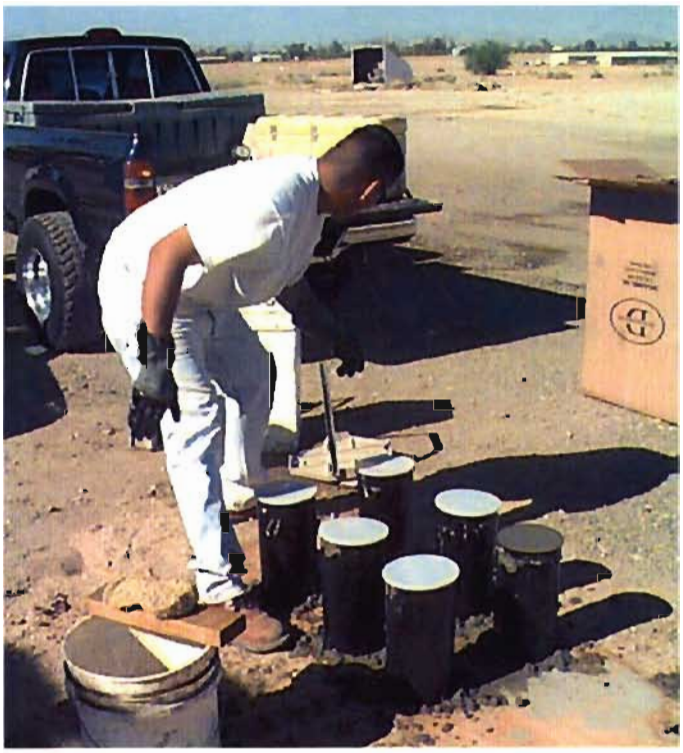


Figure 4. Preparation of 4 x 8 inch cylinder samples.

After the concrete was poured, the first step in finishing the slab was the depression of the aggregate. This created a smooth to layer for surface finishing. Immediately after the depression of coarse aggregate, a floater was passed on top of the fresh slab, as shown in Figure 5. This gave the slab a rough finish. A cross pattern was then embedded into the slab (creating four approximately 10 x 10 ft. planes). The floater was then wetted with water and passed once again on the surface, creating a very smooth finish. The concrete was left to set for 30 minutes to allow it to harden sufficiently to support the weight of a worker. Then there was a final trowel finish of the entire slab to ensure that the surface was even and smooth.

Figure 5. Second, final pass with floater.

The surface texture and sheen on the concrete was excellent. The floater slid across the slab with much ease, without collecting paste on its sides. This not only rendered a well-finished product, but also decreased the amount of time for the work to be performed. Moreover, a curing compound was not employed on this test slab. Curing compounds are commonly used in construction and act as sealants, protecting the concrete from uneven drying (due to wind and sun). However, it was observed that in this situation, the geothermal silica enhanced the performance of the fresh concrete and therefore curing compounds were not necessary. In addition, the geothermal silica demonstrated that it had excellent handling properties. By pure coincidence, this test was conducted on a windy day, which accentuated the factors that give rise to handling problems. In the loading/conveying operation, there was no dusting problem, and when incorporated in the fresh concrete, the geothermal silica enhanced the surface finish. Thus in this application, geothermal silica proved its worth as an ingredient in concrete.

Figure 6 is a photograph of the slab as it appears more recently, after 2 years since pouring. The installation is still in good condition after being driven over by numerous

trucks. Figure 7 shows the brush marks that are still present, indicating the durability of the concrete.

Figure 6. The slab as it appeared in 2002.

Figure 7. Close-up of slab showing texture of surface.

Reaction of Concrete with Alkali. Further testing was conducted in accordance with ASTM 1260, "Accelerated Mortar Bar Test." The testing was done by CANMET in Canada and Construction Technology Laboratories, Inc. in the USA (see Attachments 4 and 5. In this test, concrete bars are cast, cured, and then immersed in a 1 mol/L sodium hydroxide solution at 80° C. The dimensions of the bars are measured periodically, and if there is a reaction between the concrete and the alkali, the bars expand. Expansions greater than 0.20% after 16 days are indicative of potentially deleterious behavior. Geothermal silica was tested at replacement levels of 20 and 30%, and for 20%, expansions reached as much as 1.6% after only 7 days. Oddly enough, there was less expansion at the higher replacement, but the results were clearly unsatisfactory and demonstrate that the silica was highly reactive toward alkali. The mechanism of this reaction is not known, but is believed to be due to minor constituents in the silica, which, as obtained from the hybrid pH Mod/CRC Process, was only about 87% pure SiO_2. In particular, it is possible that unreacted lime in the silica (from the hybrid power-plant) influenced the performance of the concrete.

A proposal to further study the alkali-silica reactivity problem was submitted by CANMET and may be considered at a later time. This proposal is included as Attachment 6. The failure of Salton Sea geothermal silica to pass this last critical test has ended, at least for now, the possibility of utilizing this material as a pozzolanic-mineral admixture in concrete. Looking ahead, a new horizontal vacuum belt filter system has been installed at the pH Mod facilities. This new system employs filter feed slurry acidification. Solids produced from the system should have improved properties for use in cement and concrete. In particular, the material will not contain significant concentrations of occluded lime.

As mentioned above, another potential use of the geothermal silica is as additive to the "clinker" in cement manufacture. In this application, the silica is not required to possess pozzolanic activity. It has been demonstrated that silica from the CRC Process (which is the least pure of all of the silicas) can be leached with dilute acid, removing some of the impurities, and providing a suitable product for cement clinker. Discussions are underway at this writing to market this silica to a local company.

Subtask 2.1.3.1 Laboratory-Scale Study: Study of Silica Precipitation Process Variables

A variety of inorganic powder products are used as reinforcing fillers in silicones and rubber. They range from expensive, high degree of reinforcement, to low cost, inert extenders and coloring agents. Approximately five years ago, MEHC employed BFGoodrich Polymer Testing Laboratory, in Akron, Ohio, to investigate the use of geothermal silica as a rubber filler in a typical tire formulation. It was found that geothermal silica alone did not reinforce the rubber compound. After further investigation, it was determined that the silica required surface modification, as well as a change in particle morphology.

One form of surface modification involves the use of 'coupling agents'. A coupling agent is a compound that has the ability to bond to the surface of a silica particle and the molecules in the rubber matrix. Organofunctional silanes are commonly used as coupling agents for silica surface modifications. Suitable organofunctional silanes, and methods of binding the silanes to the silica surface, were briefly investigated. Particle morphology is controlled in the precipitation process in geothermal brine. There are several clues as to

which variables may render a smaller, more porous silica particle. These variables, and the effect of grinding, were to be studied in detail to facilitate reactions with the coupling agents.

At this time, MEHC has done no further studies of the geothermal silica for this application. However, we were, and still are, closely following a related laboratory investigation that is being carried out at LLNL, in a project that was funded by the U.S. Department of Energy, and now also by the CEC. Initially using synthetic solutions that simulated the composition of the geothermal brines, and a high-temperature autoclave, the LLNL investigators examined the effect of solution conditions on the particle characteristics of the precipitated silica. Some studies were also underway toward the goal of producing silica that would undergo silane coupling reactions. However, by the time the MEHC silica studies were terminated, no information was forthcoming from these studies that pointed to the process variables that were critical, or provided the key to producing silica amenable to the silane coupling reaction.

It should noted that it may not be reasonable to expect to modify the properties of the silica precipitated in the CRC process. By design, precipitated silica acts as seed material in the CRC process to enhance further precipitation for the control of scaling. The silica particles build on themselves in a layered fashion similar to layers of an onion. The result is a dense particle with very little pore volume. All commercial precipitated amorphous silicas have pore volumes at least an order of magnitude greater than Salton Sea geothermal silica. Electron microscope photographs (see Attachment 7) of precipitated Salton Sea silica from Elmore show the dense layered effect of the seeding process. In the case of the hybrid plants, and especially the pH Mod plants, there is the possibility of more proactive control over the silica precipitation process and work has continued in this area.

Subtask 2.1.3.2 Laboratory-Scale Study of Leaching, Washing, and Drying Variables

The principal objectives in this subtask were not only to examine methods of rendering the silica suitable for marketing applications, but also to develop methods that could be used to treat the silicas so they would pass the mandated tests for disposal as so-called non-hazardous waste material. For this subtask, MEHC focused primarily on the latter objective. If the filter cake composition is classified as hazardous, according to the criteria of the California Waste Extraction Test, the material must be trucked to a hazardous waste landfill, where the cost is 5 times that of disposal at a non-hazardous material landfill. Those relatively infrequent occasions (5-10% of the time) when testing indicates that the filter cake is hazardous are generally due to the concentrations of arsenic and/or lead exceeding the prescribed limits. Washing studies using plain water and dilute acid demonstrated that the concentrations of these elements could be reduced to acceptable levels, and the process has been scaled up. The aim is to leach as much of the heavy metals (namely lead and arsenic) as possible while using the least amount of hydrochloric acid.

During the test period, vacuum belt filter test units (with approximately 10 ft^2 filter cloth area) were installed at both the CRC and pH Mod plants. It has been determined that the vacuum belt filtration operation produces a filter cake with a few percent more moisture than the Pneumapress filtration units (which utilize pressure, rather than vacuum) that were previously employed in both the CRC and pH Mod plants. However, with steam drying of the vacuum belt filter cake, the two different filter operations produce equivalent cake with

respect to critical liquefaction properties. Vacuum filtration has the great advantage of being a continuous operation as opposed to the batch filter-press operation. It has also been shown that the vacuum belt filter requires less wash water (with and without acidification) than the batch operation for the amount of silica filter cake that is produced. The use of acid washing the filter belt to prolong its use is also being investigated. The acid washing and vacuum filtration system is currently in operation at the Region 1 pH Mod plant commonly known as Unit 5 (Unit 5) but has not yet been installed at the Region 2 Vulcan and Hoch hybrid plants.

TASK 2.2 PROCESS FOR PRODUCTION OF MARKETABLE ELECTROLYTIC MANGANESE DIOXIDE

As more fully described below with respect to each respective subtask (including relevant schematic diagrams, methods employed, and results), MEHC has nearly completed all of Task 2.2. All of the individual components of the overall process (extraction of Mn, separation of Fe and Ca, and electrodeposition of EMD) have been thoroughly examined. Work remaining to be completed (as Subtask 2.2.4) is to design a pilot scale facility to test the entire process.

The general objective of this task was to develop a process for separating manganese from geothermal brine in a form suitable for electrowinning as EMD. A conventional process for electrodeposition may be used, if a concentrated aqueous solution of manganese can be obtained that is low in base- and heavy-metal concentrations. Preliminary studies in the laboratory showed that brine effluent from the zinc process can be processed to recover manganese using a unique solvent extraction procedure. Manganese is extracted with excellent efficiency, but the metals calcium and iron are also extracted. Iron could be separated from the manganese in an additional step using solvent extraction techniques, although the practicality and applicability of this step is questionable. A second intermediate processing step was developed in which manganese is separated from iron by using selective precipitation techniques. By a modification of the primary manganese solvent extraction steps, it was demonstrated that calcium can also be removed from the feed solution for the electrowinning step. The electrodeposition of EMD in chloride containing media was investigated in the laboratory and at bench-scale.

Subtask 2.2.1 Laboratory-Scale Study: Solvent Extraction of Manganese

The studies under this subtask were conducted during the first and second quarters of calendar year 2000. Both laboratory, and somewhat larger bench-scale studies were conducted, the latter using apparatus in the field at a CRC geothermal facility.

The investigations focused on a solvent system consisting of two compounds in an organic, hydrocarbon solvent. The two compounds are used in equimolar concentrations in the solvent. They are abbreviated "Q" and "L," and are the following:

Q $R_3CH_3N^+Cl^-$, where R is a mixture of straight chain C_8 and C_{10} groups, with the C_8:C_{10} ratio being about 2.
Trade Name: Aliquat 336. Supplier: Henkel Corp., Minerals Industry Div.

L Di-(2-ethylhexyl) phosphoric acid
Also known as D2EHPA or "Deppa" Supplier: Albright & Wilson, Americas

The solvent is an aliphatic, high boiling point, hydrocarbon having the trade name, Orfom SX-11.

The original idea for using the QL reagent was obtained by MEHC from three U.S. Patents (see Attachment 8). Q and L are believed to exist as an ion pair in the organic phase, and Mn, Ca and Fe are extracted as the divalent chloride salts ($MnCl_2$, $CaCl_2$ and $FeCl_2$) at a self-buffering pH of ~3.5, possibly by a solvating mechanism. pH buffering is an essential feature of the QL reagent. Without this feature, the extraction of manganese would not be very efficient (less than 25%). The reagent extracts Fe and Mn approximately equally (~50% in one stage) and is also selective against Ca [i.e., the reagent shows the same selectivity trend (Fe ~ Mn > Ca)] as with L alone. However, because of the higher concentration of Ca (30 to 40 g/L) in the Salton Sea geothermal brine relative to Mn and Fe (1.5-2 g/L), the loaded organic after the extraction is found to contain approximately equal concentration of all three metals (3-4 g/L).

Ion pairing the deprotonated ligand (L^-) with the quaternary ammonium cation (Q^+) results in the formation of the extractant, QL. Complexation with a metal (M^{2+}) in the presence of chloride ions leads to ML_2 and QCl in the organic phase as shown in Equation 1.

$$M^{2+} + 2Cl^- + 2\,\underline{QL} \leftrightarrow \underline{ML_2} + 2\underline{QCl} \qquad (2)$$

Underscoring denotes species in the organic phase.

The metal can then be stripped from the organic phase with acid, as shown in Equation 3.

$$\underline{ML_2} + 2\underline{QCl} + 2H^+ \leftrightarrow M^{2+} + 2\underline{HL} + 2\underline{QCl} \qquad (3)$$

And finally, the ion pair can be reconstituted by treatment of the stripped organic phase with an alkali, as shown in Equation 4.

$$\underline{HL} + \underline{QCl} + NaOH \leftrightarrow \underline{QL} + NaCl + H_2O \qquad (4)$$

The novelty and cost benefit of this process lies in the fact that Equation 4 can be driven to the right hand side with a minimal (sub-stoichiometric) amount of alkali.

The formulation for 50.45 L of extractant containing 0.495 mol/L QL is given below. The proportions would the same for both the laboratory and the bench-scale studies.

- D2EHPA: 8.33L (17.84 lb.)
- Aliquat 336: 12.23 L (24.25 lb.)
- Orfom SX-11: 29.9 L

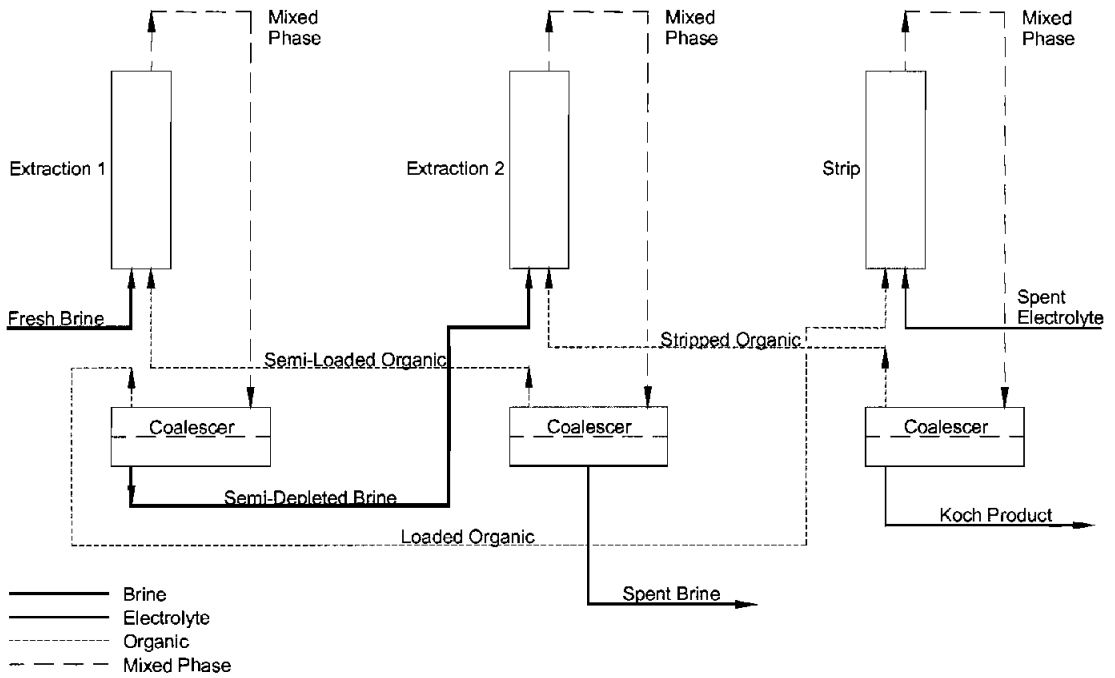
This organic phase is subsequently pre-equilibrated by contacting it with a NaOH/NaCl solution (0.495 mol/L NaOH, 0.1 mol/L NaCl) at an organic/aqueous (O/A)

ratio of 1 for 30 minutes at 65° C. The two phases are allowed to separate and the aqueous phase is discarded. An additional 5.03 L of DBBP (di-butyl butyl phosphonate) is then added and mixed in. The resulting organic phase is labeled QL (0.495 M) and stored.

The result of the laboratory studies led to a series of graphical isotherms (see Attachment 9) that defined the optimum conditions for the extraction and stripping of the manganese. Based on these data, a larger extraction unit was purchased (with CEC funds) from the Koch Technologies Co. (Parsippany, NJ). This unit was connected to the brine effluent from an ion-exchange system which removed the zinc from the brine. The feed for the zinc system was in turn the effluent from the Elmore CRC plant, thus silica was also depleted in the fluid.

A diagram of the Koch unit is shown in Figure 8, and its operation illustrates the extraction process. The unit was operated at a flow rate of 2 gpm (1 gal. brine + 1 gal. extractant). The unit is a complete modular system consisting of three co-current vertical, one-inch diameter, glass mixing columns. Each mixing column contains a stack of perforated Teflon® plates and spacers mounted centrally on a reciprocating moving shaft.

Figure 8. Koch Liquid-Liquid Extraction System for Manganese Recovery



The extraction is performed in two stages. In each stage, aqueous brine is mixed with the QL extractant. The mixed phase from each stage is collected in 3-inch diameter horizontal glass coalescers where separation of organic from aqueous solution occurs. Stripping then produces the manganese/iron/calcium/chloride solution (Koch Product). Initially, the Koch unit was operated with a single extraction stage to assess the rate of recovery. After two months of operation, the unit was reconfigured, as shown in Figure 8, to include two extraction stages and one stripping stage.

Not shown in Figure 8 is a secondary equilibration process in which the stripped organic solvent is contacted with a basic solution to neutralize its acidity and regenerate the extractant compounds. As mentioned earlier, a novelty and cost benefit of this process is that the neutralization and regeneration require a sub-stoichiometric amount of alkali. The second essential feature is that the reagent is pH buffered as it captures manganese.

It was demonstrated both in the laboratory and in experiments with the Koch unit (as in the laboratory) that manganese and iron were extracted and stripped with high efficiency; however, it was found that the concentration of calcium in the production solution could not be reduced to an acceptable level. Although the QL reagent is more selective for iron and manganese, the equilibria cause an unacceptably high concentration of calcium in the brine. The concentration of calcium in the raw brine is very high (approximately 30,000 mg/kg), and its concentration in the solution ultimately provided for the electrodeposition of EMD must be less than 500 mg/kg. Thus additional studies were performed on methods for removing iron and calcium from the Koch product.

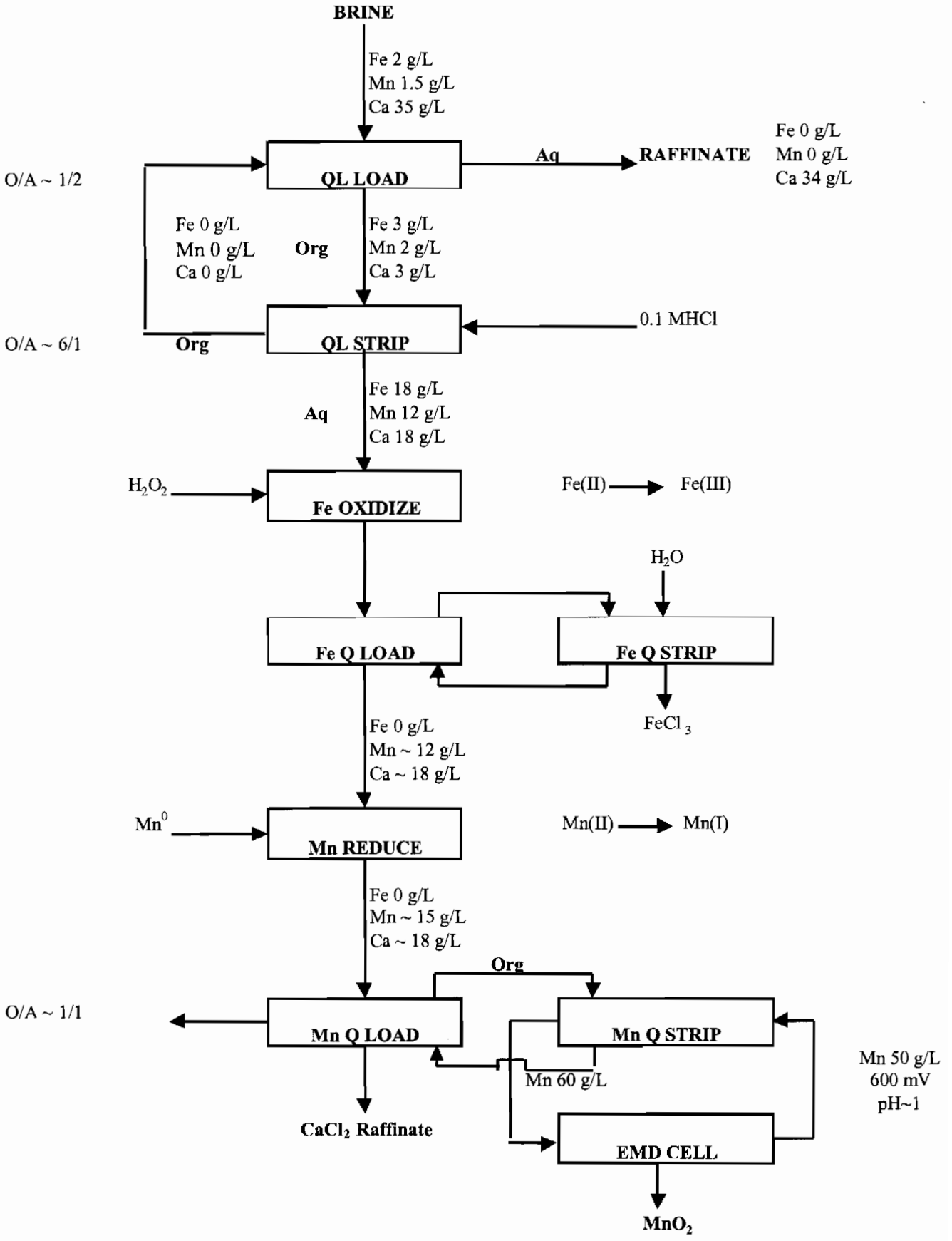
Subtask 2.2.2 Laboratory-Scale Study: Separation of Manganese from Iron and Calcium

Iron. An extensive literature search was conducted to screen potential technologies for the separation of iron from the Koch unit manganese-chloride product. It was found that solvent extraction processes have been used to extract iron from chloride solutions in commercial plants worldwide. Some facilities use precipitation for iron removal. A modified ion exchange technology using crown ether complexing has also been proposed, but has not been commercially applied.

Laboratory shakeout tests of five commercially available extractants and two diluents were conducted in the first quarter of work to select organic solutions for iron extraction. Efficient extraction as the chlorocomplex first requires oxidation of the iron, present in geothermal brine as Fe(II), to Fe(III). Various oxidants were investigated. Two extractants produced promising results. Both are amines available from Henkel Corporation (Tucson, AZ). One was Alamine 336, a tertiary amine, which removed 98-99% of the iron from the Koch Product; and the second, Aliquat 336, the same quaternary amine used in the primary brine extraction (used alone – not with L) produced similar results. Three other extractants, from Albright-Wilson and Cytec, did not produce acceptable results.

An overall process flowsheet was proposed based on that work, and is shown in Figure 9. However, no additional work on separation of manganese from iron by solvent extraction has been done since the first quarter. The practicality of utilizing iron removal system based on solvent extraction is somewhat in doubt. It would depend in part on finding a market for the $FeCl_3$ solution byproduct, which is a possibility.

Figure 9. MEHC/Lakefield Flowsheet



Attention was next turned to a method for separating iron based on selective hydrolytic precipitation. Initial work was done at MEHC, and then Lakefield was engaged to carry out additional studies. Tests were conducted using batch precipitation procedures, with some work carried out on a continuous bench-scale system.

The basis of the separation of iron from manganese by selective precipitation is that manganese hydroxide precipitates at a higher pH than iron hydroxide or its cogeners. Thus, as base (alkali) is added to an acid solution containing both iron and manganese, iron compounds should precipitate first, leaving the manganese in solution. To effect a good separation, however, both the type of base used and its mode of addition are very important. Another factor is the oxidation state of the iron. As already noted, in the geothermal brine and Koch unit process solutions, the iron is present as Fe(II). In the hydrolytic precipitation, Fe(II) precipitates at a higher pH than Fe(III), thus for more effective separation of the iron from the manganese, it is desirable that the iron be oxidized to Fe(III).

In laboratory work at MEHC, a variety of alkalis, including different types of hydroxides and carbonates, and various solution handling conditions were tested to effect selective precipitation of the iron. In the process finally developed, using $CaCO_3$ at elevated temperature, and air oxidation of the ferrous iron, it was found that a very good separation, better than 99.9%, is feasible. The iron precipitate was magnetic and had the approximate composition of Fe_2O_3, which indicated that it was probably the mineral maghemite. The precipitate was readily settled and filtered and had potential to be marketable to Portland cement companies. The aqueous solution resulting from the precipitation contained less than 10 ppm of iron and, if needed, could be used as a feedstock to a final purification stage.

A second hydrolytic precipitation process for iron removal has also been proposed and it will be compared to that we have developed. Lakefield was engaged to perform this work. The second process involves the precipitation of a form of FeOOH known as akaganeite [β-Fe(O,OH,Cl)], by a step-wise neutralization method that is based on the solubility of the precipitate, control of nucleation regimes, and on pH variation. The overall process is also heavily depended on seed addition and the number of process stages; these two variables were tested to determine final operating parameters for a pilot plant study. Settling and filterability tests also were performed to obtain information about solid/liquid separation properties.

In initial tests at Lakefield, a batch of synthetic seed of iron hydroxide was made at an elevated temperature of 180° F from a concentrated solution of ferric chloride. This seed material was filtered, washed thoroughly, and then used in a matrix of oxidation/precipitation experiments. The first set of tests using this synthetic seed, and Koch strip solution produced at the MEHC Pilot Plant, were designed to find the correct pH levels for operation of a potentially two-stage iron-removal circuit. Preliminary results showed that: (1) each stage must be controlled in a very narrow range of pH and oxidation potential, and (2) hydrogen peroxide is not a very efficient oxidant and should be replaced by sodium hypochlorite. Work continued at Lakefield on the sodium hypochlorite method to optimize the oxidation and precipitation and filtration steps. Solubility experiments were performed to establish the pH dependent curves as well as to determine the induction pH as a function of dissolved iron. Operating pH volumes were determined for the oxidation/precipitation steps, and the result was a multistage process. Figure 10 is a proposed flowsheet for this separation process.

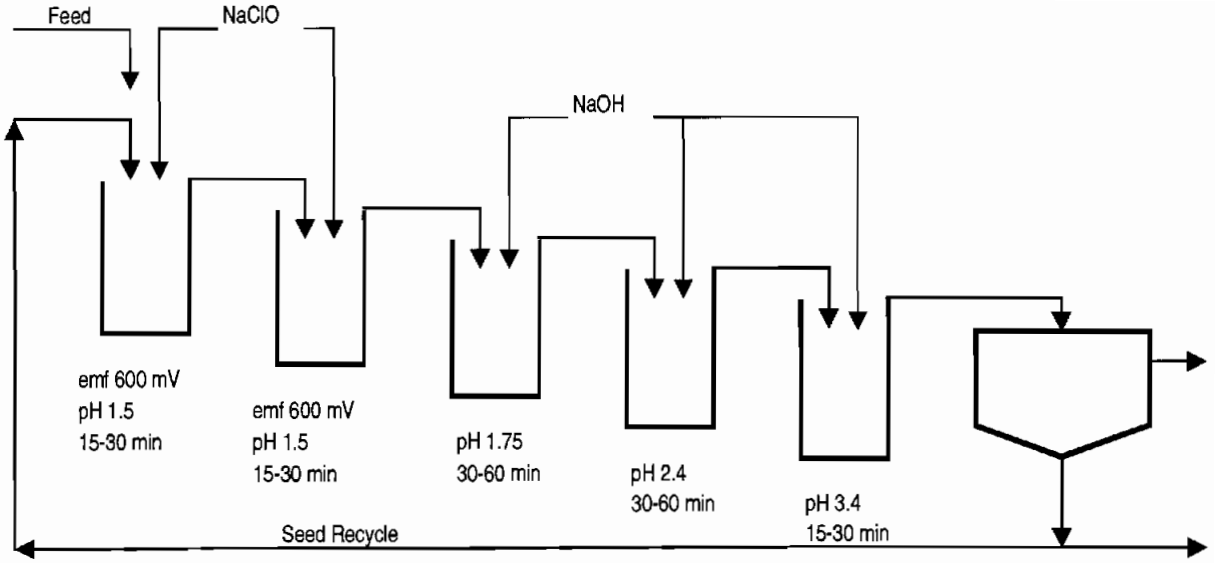


Figure 10. Proposed flowsheet for iron oxidation and precipitation.

As shown in Figure 10, it was found that a two-stage precipitation process operating at about pH 1.7 to pH 1.8 and pH 2.3 to 2.4 followed by a polishing stage operating at pH 3.4 were the optimum conditions for Fe(III) precipitation as akaganeite.

Six oxidation experiments were carried out to investigate the influence of stoichiometric excess of oxidant on the residual iron concentration, uptake of manganese in the iron precipitate (loss of manganese), as well as the crystal properties of the iron precipitate. Because of its filterability and handling properties, akaganeite was the desired crystalline phase of iron. Initial attempts to oxidize ferrous iron with hydrogen peroxide again failed in this particular chloride system. Sodium hypochlorite proved to be a very efficient oxidant reacting almost 99% according to stoichiometry. Although manganese concentration decreased somewhat as the iron was oxidized by sodium hypochlorite during the experiments, the uptake of manganese in the solids was found to be minimal. In terms of less manganese: in all tests, less than 1.5% manganese was reported in the akaganeite solids.

X-ray diffraction analysis of the precipitate formed in the sodium hypochlorite precipitations confirmed the formation of akaganeite as the major phase. Scanning electron microscopy showed akaganeite as compact anhedral aggregates. Individual crystals were sub-micron in size. Qualitative filtration test work indicated that akaganeite that precipitated in QL strip liquor filtered more easily than akaganeite precipitated in eluate solution. Although filtration rates were somewhat slow, it is assumed that in a continuous operation, crystals will grow larger and will have improved filtration properties. Further details of the Lakefield work on iron removal from manganese chloride can be found in Attachments 10 and 13.

Calcium. To reduce the concentration of calcium in the Koch unit product, an alternative extraction scheme was proposed, and Lakefield was engaged to test the process at laboratory scale. The basic changes in the main scheme are the addition of an extra

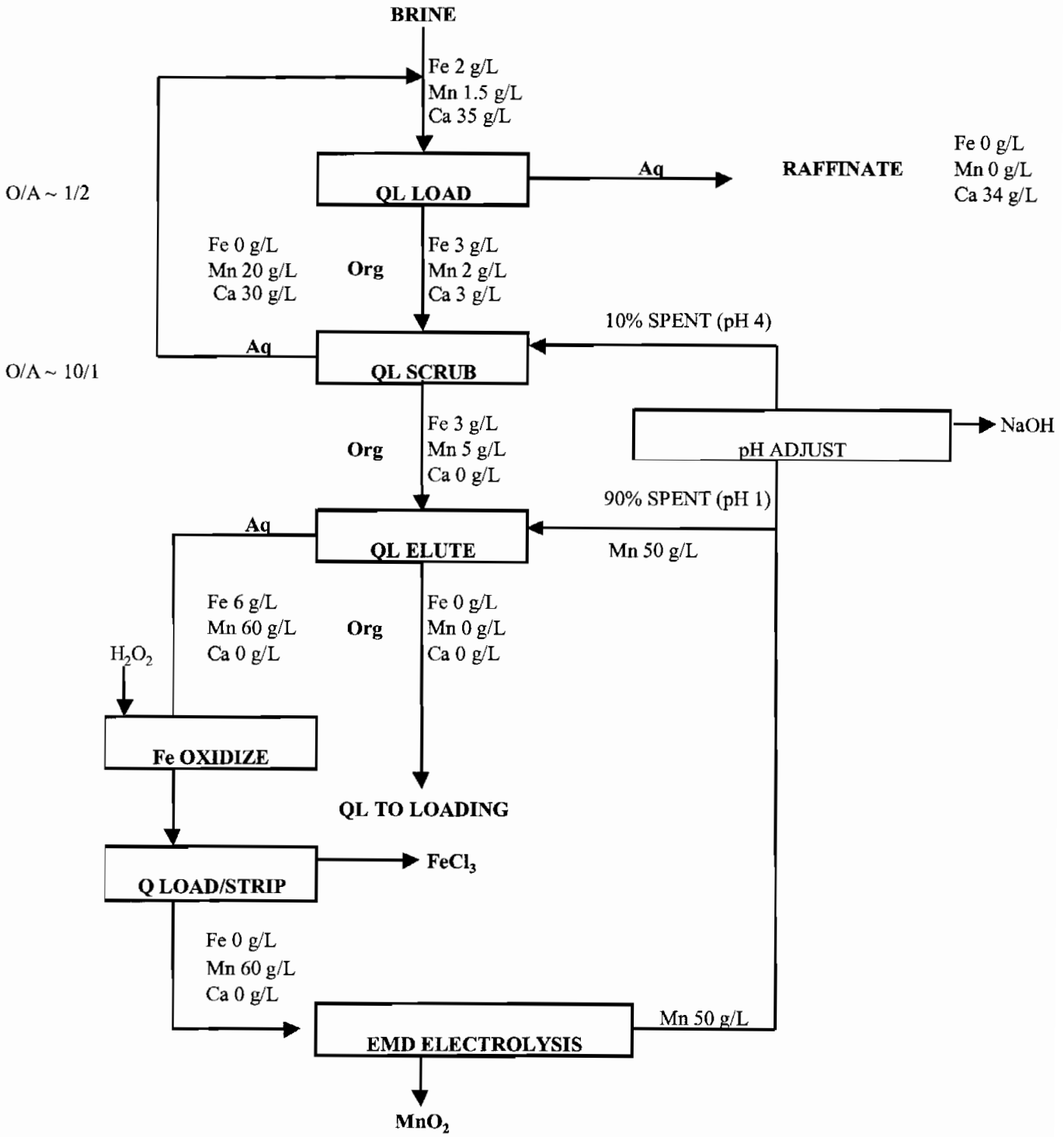
scrubbing stage, and a modification of the stripping stream. In the modified process, the organic solvent with QL, and loaded with Mn, Fe, and Ca, is scrubbed with a small bleed stream (5-15%) of the spent electrolyte from the EMD electrolysis. Because of the high concentration of Mn in this solution, ~50 g/L vs. ~2 g/L in the geothermal brine, and the more favorable equilibrium, the Mn displaces Ca by a mechanism known as "crowding". The calcium-loaded aqueous solution from this step is discarded while the organic phase advances to the stripping process. The scrubbed organic is then stripped with the balance (85-95%) of the spent electrolyte to produce a semi-final product of manganese/iron chloride solution. In this scrubbing step, iron is not displaced from the loaded organic, which reinforced the conclusion that the only practical method for removing iron is the oxidation/precipitation route.

Bench test work and three continuous scrubbing runs were undertaken to investigate the removal of calcium from loaded QL organic phase by scrubbing with a bleed of simulated spent electrolyte from EMD production. The bench test work and the continuous test work were performed with organic (QL) prepared at Lakefield according to MEHC's instructions. The scrub feed (aqueous phase) was taken from the spent electrolyte of the EMD electrowinning work. Variables that were tested during the continuous piloting included organic/aqueous (O/A) ratio (10 to 20) and scrub feed acidity (7.4 to 20 g/L HCl). The major findings were the following:

- Continuous scrubbing of calcium with an acidic $MnCl_2$ solution was successful. In all three runs, more than 99.5% of the calcium was removed;
- Calcium appears to be removed by a combined manganese/hydrogen ion cation exchange displacement mechanism. The relative contributions of the manganese cations and protons depends on the O/A and acid/metal ratios in the scrub feed;
- No manganese is stripped from the loaded organic phase during calcium scrubbing with the acidic $MnCl_2$ scrub feed solution. In fact, during runs 1 and 2, there was a net loading of manganese onto the organic phase;
- Calcium removal from the QL organic phase appears to be a flexible and robust process as it was able to handle different compositions of spent electrolyte (7.4 g/L HCl and 20 g/L HCl) as well as different O/A ratios, without a detrimental effect on calcium removal efficiency;
- At the maximum O/A ratio tested (20), the residual calcium concentration in the scrubbed organic was 13 mg/L, as opposed to <2 mg/L in a run in which the O/A ratio was 10;
- Iron scrubbing from the loaded QL organic by contacting it with a bleed stream from the spent electrolyte from EMD production was not successful. This was not unexpected since the equilibrium constant for Fe(II) and manganese bonding to D2EHPA are approximately equal.

The details of the Lakefield calcium removal work can be found in Attachment 11. A basic flow sheet incorporating the calcium scrubbing technique is shown in Figure 11.

Figure 11. MEHC/Lakefield Flowsheet for Manganese Extraction.



Subtask 2.2.3 Laboratory Scale Study: Electrodeposition of Manganese Dioxide

Manganese dioxide is produced by electrolytic oxidation of manganese ion in the following reaction:

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^{+} + 2e^{-} \qquad (5)$$

In the electrolytic cell, solid MnO_2 is deposited on the anode, and hydrogen is liberated at the cathode. In the standard industrial process, a small amount of oxygen is also produced at the anode as a side reaction. Certain properties of the EMD that is produced are important for its marketability as a material for alkaline batteries. For example, its crystal structure must correspond to that of γ-MnO_2 and there are a variety of other specifications. In the conventional industrial process, the electrolyte solution is dilute sulfuric acid. At MEHC, the objective was to demonstrate the process in the hydrochloric acid medium from the extraction, which introduces a complication that another side reaction occurs at the anode – the oxidation of chloride ion to chlorine.

Under contract to MEHC, the initial experiments on the production of EMD from manganese chloride solutions at laboratory scale were performed at the University of Missouri, Rolla. Factors such as the type of electrode material, optimum current density, and purity of the electrolyte were examined. A report on the University of Missouri results can be found in Attachment 12.

Based on the encouraging initial results from the University of Missouri experiments, a small-scale EMD electrolysis facility was designed at MEHC. It was used to determine the feasibility of producing alkaline-grade EMD in a continuous mini-plant type operation. Figure 12 is a diagram of the EMD electrodeposition unit and Figure 13 is a photograph of the setup at MEHC.

Figure 12. Electrolytic Manganese Dioxide Electrodesposition Unit

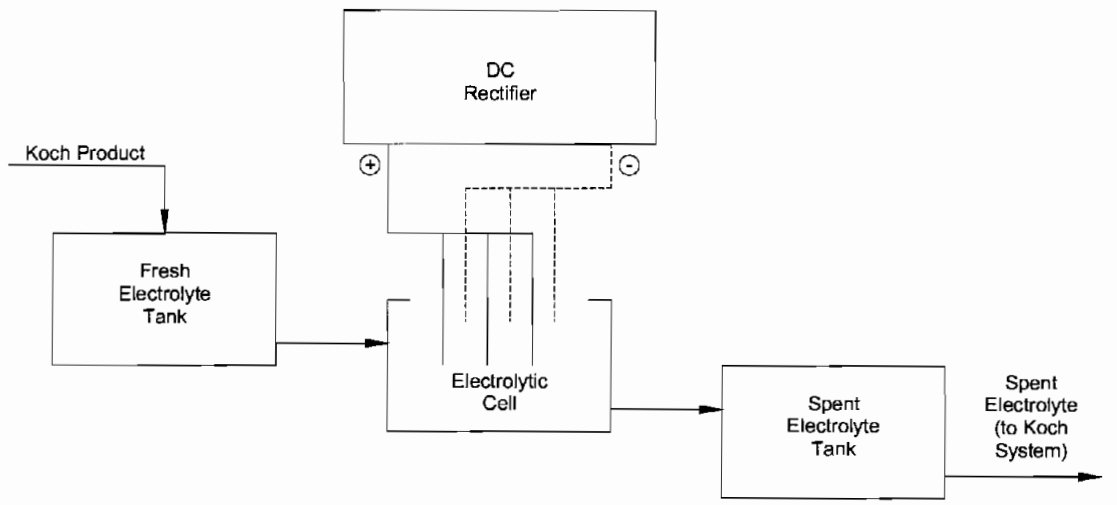


Figure 13. Apparatus used at MEHC for electrowinning of EMD. The white box is the electrolytic cell

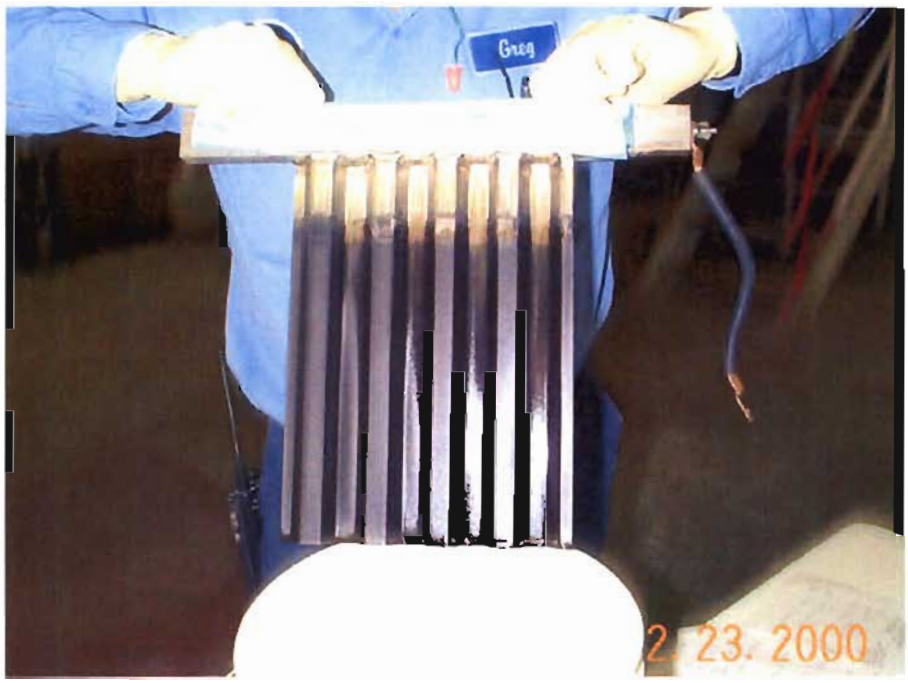


Figure 14. Anodes after deposition of EMD in MEHC cell.

This electrolyzer comprised 4 titanium anodes and 5 graphite cathodes, and it was operated with about 50 gal. of electrolyte. Six electrolysis campaigns were completed using three different compositions of simulated electrolyte, each operating for about 120 hours and producing about 12.6 lb of EMD. Figure 14 is a photograph of an anode coated with EMD. Crystallographic analysis at the University of Missouri demonstrated that the crystal structure of our product was typical of commercial-grade EMD. During the course of this work, a number of analytical procedures and specifications were written for use in the EMD project; these are listed in Appendix C.

During the later phases of testing, the EMD electrodeposition research was continued under contract with Lakefield. The objective of this study, which was also conducted at bench scale in hydrochloric acid media, was to examine more carefully the effects of key variables (such as anode current density, cell voltage, and acid concentration) on the current efficiency of EMD deposition process, and on the quality of the EMD product. The matrix of experimental conditions employed by Lakefield was designed by Kevin Anthony of MarTech Consulting. In addition, an effort was made to determine the rate of evolution of chlorine, which is the principal side reaction at the anode during the electrodeposition of the manganese dioxide. The electrolyzer comprised one titanium anode of 0.08 m^2 total area and one graphite cathode. The electrolyses were carried out for 120 h and 1.0-1.7 kg of EMD was produced.

Both the electrolysis controls and the techniques for chlorine measurement were checked out, and seven experimental runs were completed. An abbreviated table of the results is presented in Table 6. It was found that the most important variable in determining

Table 6. Some characteristics of the EMD electrodeposition and EMD product from the Lakefield experiments. (For complete data, see Attachment 12.)

Run:	1	2	3	4	5	6	7
Ave. Current Density, A/m^2	59.9	99.8	60.5	59.8	99.9	100.	99.5
Current Efficiency, %	102	101	100	90	91	102	100
Specific Energy, kWh/kg EMD	1.34	1.46	1.30	1.49	1.90	1.64	1.84
Cl_2 Evol. Rate, g/min.	< 0.1	0.8	0.8	3.5	7.4	2.8	1.8
EMD Product Analysis:							
Loss on Ignition at 105° C, %	0.10	0.40	0.35	0.45	0.50	0.30	0.20
Mn-total, %	61.6	61.2	61.8	61.3	60.4	61.1	61.7
x for MnO_x	2.02	1.99	2.00	2.01	2.01	1.99	1.99
Chloride, ppm	< 10	50	30	30	60	50	70

the current efficiency was the concentration of acid. The chlorine evolution rates correlate as expected with the current efficiency for production of EMD – higher chlorine rates correspond to lower current efficiencies. In the better runs (e.g., Nos. 1-3) both the Current and Energy Efficiency was quite good. As can be seen in the table the product EMD from these runs was analyzed and appears to be satisfactory. Not all of the standard analytical measurements were made on the EMD product, but among those that were performed, the results were within or near specifications. EMD is required to be a minimum of 61.2%. The value of x in MnO_x should be close to 2.00. Chloride should be <50 ppm.

The Lakefield experiments were performed with "pure" manganese chloride solution that simulated the product the iron and calcium separation steps. Work remaining to be done in this subtask is to show that the proposed, entire manganese, iron, and calcium separation process, in a completely integrated operation, can produce a feed electrolyte that can in turn yield battery-grade EMD.

Subtask 2.2.4 Devise Design Parameters for Large Scale Pilot Plant

In this subtask, all of the unit operations that have been individually evaluated should next be fully integrated and demonstrated in a pilot-plant or mini-pilot plant. The detailed design work has not been done; however, based on the data obtained thus far, MEHC believes it is now in a position to design a pilot plant that would operate at a geothermal brine feed rate of 50-75 gpm.

APPENDIX A REFERENCES

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(Featherstone, et al, 1995) J. Featherstone, S. Butler, and E. Bonham, "Comparison of Crystallizer Reactor Clarifier and pH Mod Process Technologies Used at The Salton Sea Geothermal Field," *Proceedings of the World Geothermal Congress, 1995*, Florence, Italy, Vol. 4, pp. 2391-2396.

(Glover, et al, 1989) D. Glover, B. Schumm, Jr., and A. Kozawa, Eds., *Handbook of Manganese Dioxides, Battery Grade*, International Battery Materials Association,

(Swaddle, 1990) T. W. Swaddle, "Portland Cement," in *Inorganic Chemistry*, Academic Press, New York, 1990, pp. 207-210.

APPENDIX B ABBREVIATIONS

ASTM	American Society for Testing and Materials
CANMET	Canada Centre for Mineral and energy Technology, Materials Technology Laboratory
CEC	California Energy Commission
CRC	Crystallizer Reactor Clarifier, Process in which seed silica is used to reduce dissolved silica to saturation level
D2EHPA	Di-(2-ethylhexyl) phosphoric acid; used in extraction of manganese
EMD	Electrolytic Manganese Dioxide
L	Di-(2ethyl-hexyl) phosphoric acid; used in extraction of manganese
LLNL	Lawrence Livermore National Laboratory
MEHC	MidAmerican Energy Holdings Company
pH Mod	Process in which acid is used to retard the precipitation of silica
Org	Organic phase in extraction process
O/A	Ratio of organic to aqueous phase in liquid-liquid solvent extraction
Q	Quaternary amine, Aliquat 336™ (Henkel); used in solvent extraction of manganese

APPENDIX C ANALYTICAL PROCEDURES AND RELATED REPORTS WRITTEN FOR THE SILICA AND MANGANESE PROJECTS

1. Standard Operating Procedure for Sampling and Analysis for Soluble Silica in Geothermal Process Streams.

2. Spectrophotometric Determination of Chloride in EMD Process Solutions

3. Procedures for Measurement of Chlorine and Oxygen Produced by an EMD Electrolytic Cell

4. Procedure for Alkaline Discharge Testing of EMD Samples

5. Analytical Procedure for Iron (III) in Brine

6. Procedure for Determination of Manganese and MnO_2 (and x in MnO_x) in Electrolytic Manganese Dioxide (EMD)

7. Experimental Procedure for the Determination of the Formal Potential of the Fe(III)/Fe(II) Couple in Hypersaline Geothermal Brines, and Its Use to Estimate Fe(III) Concentrations

8. Report on the Development of Specifications for EMD Process
   - Table 1. Industry Specifications for Alkaline-Grade EMD and CalEnergy Analysis Capabilities
   - Table 2. Impurity Specifications for Alkaline-Grade EMD from New CalEnergy Process and CalEnergy Analysis Capabilities
   - Table 3. Impurity Specifications for the EMD Process Electrolyte vs. New ICP-ES Capability

APPENDIX D. LIST OF ATTACHMENTS

Attachment 1	Evaluation of Precipitated Silica as a Pozzolanic Material for Use in Concrete
Attachment 2	Physical Properties and Strength Activity Index of Precipitated Silica
Attachment 3	Semi-Adiabatic Temperature Rise in Precipitated Silica Concrete
Attachment 4	Summary Report – Accelerated Mortar Bar Test (AMBT – ASTM C 1260) Data, CalEnergy Project (October 2000)
Attachment 5	ASTM C 1260 Results – Cement and Mortar Laboratory
Attachment 6	Proposal for In-Depth Investigation of the Potential Alkali-Silica Reactivity of Precipitated Silica Material from CalEnergy
Attachment 7	Electron Microscope Photographs of Elmore Plant Filter Cake by the McCrone Group, Chicago, Illinois
Attachment 8	QL Reagent Patents
Attachment 9	Manganese Loading and Stripping Isotherms
Attachment 10	Iron Removal from Manganese Chloride Liquors by Precipitating as Akaganeite.
Attachment 11	Calcium Scrubbing from a Loaded Organic with Spent Electrolyte from Electrolytic Manganese Dioxide Processing
Attachment 12	Final Report – Evaluation of the EMD Process from Chloride Bath, University of Missouri, Rolla
Attachment 13	Executive Summary of CalEnergy Projects: EMD production, Calcium Scrubbing from QL Organic, and Iron Removal from $MnCl_2$ Liquors.

1

EVALUATION OF PRECIPITATED SILICA AS A POZZOLANIC MATERIAL FOR USE IN CONCRETE

By

V. Mohan Malhotra, P.Eng.

January 27, 2000

Ottawa, Ontario, Canada

EVALUATION OF PRECIPITATED SILICA AS A POZZOLANIC MATERIAL FOR USE IN CONCRETE

By

V. Mohan Malhotra

Summary:

This report deals with the evaluation of precipitated silica as a pozzolanic material for use in concrete. The chemical analysis and particle size distribution of the precipitated silica fume are included, and the results of the pozzolanic tests in accordance with ASTM C 618 are presented. Also presented are the limited data on compressive strength of concrete incorporating 20 per cent of precipitated silica fume as a partial replacement for cement.

Notwithstanding the limited nature of the investigation, it is concluded that the precipitated silica investigated has considerable potential for use as a pozzolanic material for partial replacement of cement in concrete. A comprehensive research program is needed to develop data on the mechanical properties and durability of non air-entrained and air-entrained precipitated silica concrete.

EVALUATION OF PRECIPITATED SILICA AS A POZZOLANIC MATERIAL FOR USE IN CONCRETE

Introduction

The manufacturing of portland cement is a highly energy intensive process, and after aluminum and steel it consumes the highest energy per unit tonne of production. In addition to the high energy demand, the production of each tonne of portland cement releases one tonne of CO_2 into the atmosphere. Thus both from the resource conservation and environmental protection issues, attempts should be made to replace part of portland cement in concrete by supplementary cementing materials. Precipitated silica is one such material. Other supplementary cementing materials currently being used include fly ash, blast-furnace slag and silica fume.

Precipitated Silica

The spent brine recovered in the production of geothermal power contains large quantities of zinc, silica and other minerals. During the recovery of zinc from the brine, silica is removed and precipitated as powdered amorphous silica.

Colour and Specific Gravity of Precipitated Silica

The precipitated silica is light yellowish in colour and has a specific gravity of 2.04. The bulk density of the geothermal silica at 3% moisture content or less is 0.7 g/cc.

Chemical Analysis of Precipitated Silica

The XRF analysis and the oxide composition of the precipitated silica are given in Table 1.

Particle-Size Distribution of Precipitated Silica

The particle size distribution of the precipitated silica is shown in Figure 1. About 50% of the material is smaller than 8.56 μm. The range of particle sizes is between 0 and 30 μm, and the percentage passing 45 μm is 97.5%.

Particle Shape

Unlike silica fume and fly ash, the particles of the precipitated silica are agglomerates of sub-micron primary particles (Fig.2).

Pozzolanic Activity Index with Portland Cement

The test performed to determine the pozzolanic activity index with portland cement are given in Table 2. The test results show that the precipitated silica meets the strength

requirements of ASTM C618 both at 7 and 28 days in the case of an investigation performed by the CTL laboratory, and at 28 days in the case of the investigation performed by the Southland Geotechnical laboratory.

Mixture proportions and compressive strength of concrete

The mixture proportioning data for the control and concrete incorporating 20 per cent precipitated silica as replacement for portland cement are given in Table 3, and the compressive strength data are shown in Table 4.

At 20% replacement, the compressive strength of the 4x8 in. cylinders of precipitated silica concrete at 7 and 28 days is about 70 and 80% of the control strength, respectively. This is in line with strength of concrete incorporating other pozzolanic materials such as fly ash. The gain in strength from 7 to 28 days is considerable, and this gain is expected to continue with age, though no data are available at present.

Concluding Remarks

Limited investigations performed to date indicate that the precipitated silica has pozzolanic properties, and should have use in concrete. The suggested replacement level is between 15 to 20 percent as partial replacement for portland cement.

The following additional investigations are needed to determine:

- The uniformity of Precipitated Silica
- Adiabetic temperature rise in concrete incorporating precipitated silica.
- Long-term durability of concrete incorporating various percentages of precipitated silica as a partial replacement for cement. The suggested percentage levels are 15, 20 and 25 percent. The durability tests should include carbonation, ASTM 1202 test method for electrical-indication of concrete, ability to resist chloride-ion penetration, ASTM C1260, test method for alkali reactivity of aggregates, and tests for determining resistance to sulfate attack.
- Properties of high-performance concrete incorporating precipitated silica.
- Compatibility between precipitated silica concrete and chemical admixtures.
- Stability of air in air-entrained concrete incorporating precipitated silica.

Table 1

XRF Analysis and Oxide Composition of Precipitated Silica*

XRF Analysis of Precipitated Silica		Oxide Composition	
Sample dried at 115 C during 2 hours.			
Mg	0.00 Wt%	**SiO_2**	92.14%
Na	3378.86 ppm	**Al_2O_3**	0.18%
Al	479.02 ppm	**Fe_2O_3**	3.74%
Si	42.98 Wt%	**CaO**	0.16%
S	44.76 ppm	**Na_2O**	0.91%
Cl	3638.17 ppm	**K_2O**	0.50%
K	2078.20 ppm	**P_2O_5**	0.11%
Ca	1119.94 ppm	**MnO**	0.05%
Cr	2.65 ppm	**BaO**	0.01%
Mn	400.50 ppm	**SO_3**	0.01%
Fe	1.31 Wt%		
Ni	0.00 ppm		
Cu	31.79 ppm		
Zn	23.22 ppm		
As	127.01 ppm		
Sr	7.10 ppm		
Mo	0.00 ppm		
Ag	88.51 ppm		
O	54.49 Wt% (Floater)		
Sb	489.15 ppm		
Ba	52.74 ppm		
Pb	0.00 ppm		
Cd	0.00 ppm		
P	247.19 ppm		
Total	100.00 Wt%		
*** 5 iterations, Convergence error 0.10%**			

Provided by CalEnergy; sample dried at 115°C for two hours.

Table 2

Results of Pozzolanic Tests with Precipitated Silica

Laboratory	Water Requirement, % of control		Activity Index with Portland Cement*			
			Test Sample		ASTM C618 Requirement, % of Control	
	Test	ASTM C618 Limits	7 days	28 days	7 days	28 days
CTL	105	110 ± 5	Compressive Strength, PSI Control = 5620 Test = 4290 Activity Index 76%	Compressive Strength, PSI Control = 7160 Test = 6970 Activity Index 97%	75	75
Southland Geotechnical	104	110 ± 5	Compressive Strength, PSI Control = 4990 Test = 3200 Activity Index 64%	Compressive Strength, PSI Control = 6660 Test = 6000 Activity Index 91%	75	75

* Chemical analysis of the cements used by the two laboratories is given in attachment 2.

Table 3

Mixture Proportioning Data and Properties of Fresh

Concrete for Precipitated Silica Concrete.

		Quantities, lbs/Yd^3	
		Control	Test*
Water content		280	280
Cement content		560	448
Precipitated Silica content		---	112
C.A. (maximum size = 0.5 in.)	0.5 in.	1432	1432
	0.25 in.	472	472
F.A.		1268	1268
W/cm		0.5	0.5
Slump, in.		1.5 in.	0.0

* Incorporates 20% silica fume.

Note : Data provided by Southland Geotechnical Laboratory.

Table 4

Compressive Strength of Precipitated Silica Concrete

Mixture Type	W/CM	Cement, lbs/Yd^3	Precipitated Silica lbs/Yd^3	Compressive strength of 4 x 8 in. cylinders, psi	
				7 days	28 days
Control Mixtures:					
25	0.5	560	—	3730	5830
27	0.5	560	—	3550	4520
28	0.5	560	—	3330	4110
Precipitated Silica Mixtures:					
25	0.5	448	112	4120	4515
27	0.5	448	112	2310	2375
28	0.5	448	112	4230	4230

- Data supplied by Southland Geotechnical laboratoryAttachement 1

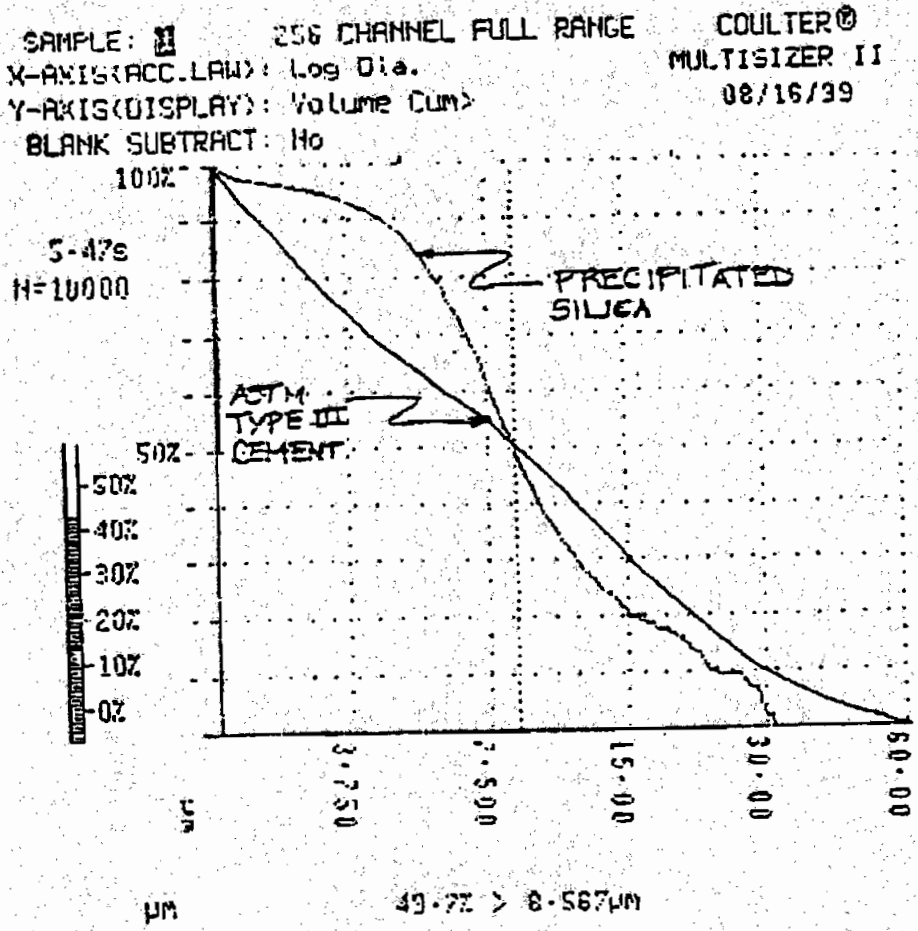

Figure 1: Particle Size Distribution of Precipitated Silica (Supplied by CalEnergy)

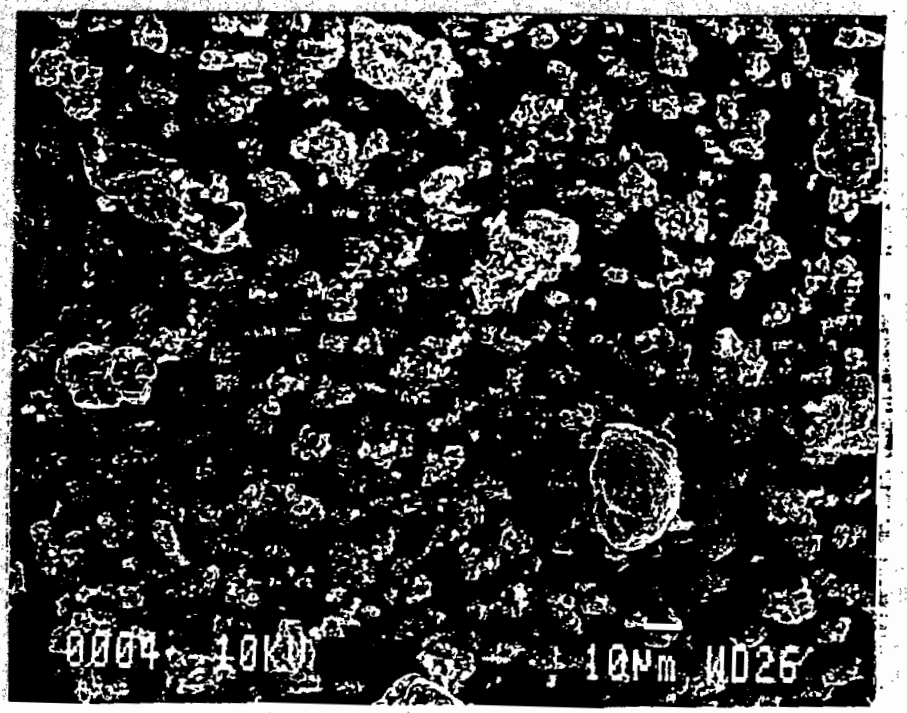

Fig. 2a Product T-03 Mag. X500

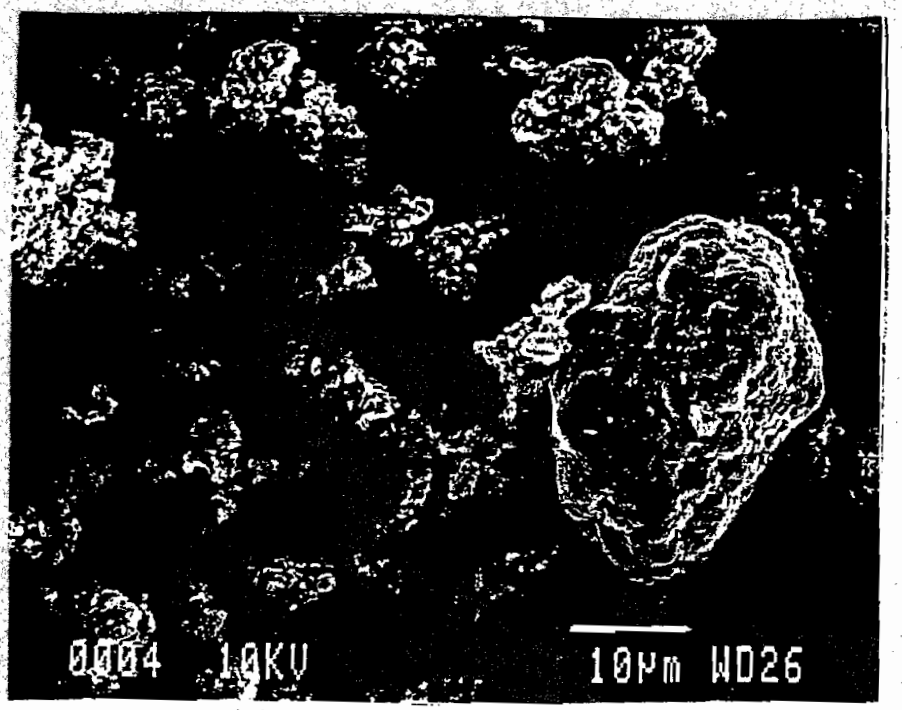

Fig. 2b Product T-03 Mag.X1500

Figure 2: Photomicrographs of precipitated silica at different magnifications (courtesy of CalEnergy)

Attachment 1

Chemical Analysis of the Cements Used in Pozzolanic Tests and Concrete

	CTL	Southland Geotechnical
	99-2 Cem Cement 938038	Southdown Cement 937398
Analyte	**Weight %**	**Weight %**
SiO_2	20.58	20.70
Al_2O_3	4.71	4.08
Fe_2O_3	3.08	3.71
CaO	62.16	61.54
MgO	2.90	4.53
SO_3	3.22	2.47
Na_2O	0.16	0.15
K_2O	0.55	0.40
TiO_2	0.25	0.26
P_2O_5	0.08	0.08
Mn_2O_3	0.07	0.07
SrO	0.09	0.06
L.O.I. (950°C)	1.60	1.93
Total	99.43	99.99
Alkalies as Na_2O	0.52	0.42
Insoluble Residue		
Free CaO		

Calculated Compounds per ASTM C150-97

C3S	51	53
C2S	20	19
C3A	7	5
C4AF	9	11
Ss(C4AF + C2F)	---	---

Notes: 1. This analysis represents specifically the sample submitted.
2. Oxide analysis by X-ray fluorescence spectrometry. Samples fused at 1000°C with $Li_2B_4O_7$
3. Values for TiO_2 and P_2O_5 are not added to Al_2O_3 when the compounds are calculated, in accordance with ASTM C 150-97.
4. X-ray Fluorescence oxide analysis meets the precision and accuracy requirements for rapid methods per ASTM C114-97. Most recent re-qualification date is May 18, 1999.
5. This report may not be reproduced except in its entirety.

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Physical Properties and Strength Activity Index of Precipitated Silica

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March 24, 2000

Mr. Fiorella Sist
CalEnergy Operating Co.
950 West Lindsey Road
Calipatria, CA
92233
USA

Dear Mr. Sist:

Re: Report "Physical Properties and Strength Activity Index of Precipitated Silica"

I am pleased to submit to you two copies of the above report.

If you would like to discuss any aspect of this report, please contact Ray Chevrier at (613) 996-4933.

We look forward to being of further assistance to your organization in the near future.

Sincerely,

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cc: Mr. Frederick Vallee

Materials Technology Laboratory

Physical Properties and Strength Activity Index of Precipitated Silica

PROTECTED BUSINESS INFORMATION

MTL 2000-19(CF)

R. Chevrier

March 2000

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MATERIALS TECHNOLOGY LABORATORY
REPORT MTL 2000-19(CF)

PHYSICAL PROPERTIES AND STRENGTH ACTIVITY INDEX OF PRECIPITATED SILICA

by

R. Chevrier*

SCOPE

The purpose of this study was to confirm that the precipitated silica (amorphous silica powder) supplied by CalEnergy Operating Company, California, meets the requirements of ASTM C 618 for strength-activity index with portland cement (ASTM C311). The strength activity index with portland cement is an indication that a product is suitable for use as a mineral admixture in portland-cement concrete. In this study the precipitated silica was compared with an ASTM Class F fly ash from a source in western Canada. The sample of the precipitate silica as received contained approximately 10% moisture, it was tested in both the wet condition for strength activity, and in the dry condition after being dried for 24 hours at 100 °C. The physical properties were determined on the dry sample. For strength-activity index, a series of four mortar mixtures was repeated three times. Each series included one control mixture with 100% portland cement, one mixture with 20% replacement of cement with wet precipitated silica, one mixture with 20% replacement of cement with dry precipitated silica and one mixture with 20% replacement of cement with fly ash.

TEST RESULTS

The physical properties of the cement, fly ash and precipitated silica are presented in Table 1. The chemical analysis of cement and fly ash are shown in Table 2, and the XRF analysis and oxide composition of precipitated silica are given in Table 3.

The results from the strength-activity index as seen in Tables 4, 5 and 6 show that the precipitated silica meets the requirements of ASTM C 618 (Appendix A) at both 7 and 28 days, for strength-activity index with portland cement. They also show that the strength development pattern of the precipitated silica mortars is similar to that of the fly ash mortars (Fig. 1). For strength-activity index, the coefficient of variation (Table 7) for the results with precipitated silica ranges from 2.2 to 4.1. This indicates that the repeatability of the strength-activity index test using precipitated silica is satisfactory, and it also reflects an excellent degree of control in the laboratory.

---

* Senior Technologist, International Center for Sustainable Development of Cement and Concrete (ICON), CANMET, Natural Resources Canada, Ottawa, Canada

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Table 1 - Physical Properties of Cement, Precipitated Silica and Fly Ash

Physical Test	Portland Cement CT 09	Silica Powder	Fly Ash CT 80
Specific Gravity (ASTM C188)	3.15	2.04	2.08
Bulk Density, g/mL	-	0.7*	-
Fineness			
Passing 45μm (ASTM C430), %	93.1	97.5	83.6
Blaine (ASTM C204), cm^2/g	4020	3450	3205
BET Surface Area, m^2/g	-	30*	-
Average Particle Size, μm	-	10*	-

* Values from MSDS supplied with material

Table 2 - Chemical Analysis of Cement and Fly Ash

%	Portland Cement CT 09	ASTM Class F Fly Ash CT 80
Silicon dioxide (SiO_2)	20.33	52.40
Aluminum oxide (Al_2O_3)	4.36	23.40
Ferric oxide (Fe_2O_3)	2.99	4.70
Calcium oxide (CaO)	62.92	13.40
Magnesium oxide (MgO)	2.72	1.30
Sodium oxide (Na_2O)	0.27	3.60
Potassium oxide (K_2O)	0.83	0.60
Titanium dioxide (TiO_2)	0.19	0.80
Manganese oxide (MnO)	0.04	-
Phosphorous pentoxide (P_2O_5)	0.21	0.20
Sulphur trioxide (SO_3)	3.23	0.21
Loss on Ignition (LOI)	2.32	0.30

* ASTM class F fly ash requirement is $SiO_2 + Fe_2O_3 + Al_2O_3$ content of minimum 70%.

Table 3 - XRF Analysis and Oxide Composition of Precipitated Silica

XRF Analysis of Precipitated Silica		Oxide Composition	
Sample dried at 115 C during 2 hours.			
Mg	0.00 Wt%	SiO_2	92.14%
Na	3378.86 ppm	Al_2O_3	0.18%
Al	479.02 ppm	Fe_2O_3	3.74%
Si	42.98 Wt%	CaO	0.16%
S	44.76 ppm	Na_2O	0.91%
Cl	3638.17 ppm	K_2O	0.50%
K	2078.20 ppm	P_2O_5	0.11%
Ca	1119.94 ppm	MnO	0.05%
Cr	2.65 ppm	BaO	0.01%
Mn	400.50 ppm	SO_3	0.01%
Fe	1.31 Wt%		
Ni	0.00 ppm		
Cu	31.79 ppm		
Zn	23.22 ppm		
As	127.01 ppm		
Sr	7.10 ppm		
Mo	0.00 ppm		
Ag	88.51 ppm		
O	54.49 Wt% (Floater)		
Sb	489.15 ppm		
Ba	52.74 ppm		
Pb	0.00 ppm		
Cd	0.00 ppm		
P	247.19 ppm		
Total	100.00 Wt%		
* 5 iterations, Convergence error 0.10%			

Provided by CalEnergy; sample dried at 115°C for two hours.

Table 4 - Mixture Proportions, Flow and 7-day Strength Activity Index with Portland Cement (ASTM C311)

Mixture No.	Designation	Cement g	SCM g	Water mL	Flow %	7-day Compressive Strength, Mpa *				7-day Activity Index, % **
						Cube 1	Cube 2	Cube 3	Average	
C1	Control	500	-	243	117	38.5	38.6	38.2	38.4	-
C2	Silica Wet	400	111	225	115	29.6	28.6	29.4	29.2	75.3
C3	Silica Dry	400	100	238	115	30.5	30.1	29.5	30.0	77.5
C4	Fly Ash	400	100	225	120	32.5	34.8	33.8	33.7	86.9
C5	Control	500	-	243	117	38.1	37.9	37.5	37.8	-
C6	Silica Wet	400	111	225	116	30.8	30.9	31.0	30.9	79.7
C7	Silica Dry	400	100	238	116	32.6	32.6	32.0	32.4	83.6
C8	Fly Ash	400	100	225	118	33.1	32.9	33.0	33.0	85.1
C9	Control	500	-	243	118	41.0	39.6	39.5	40.0	-
C10	Silica Wet	400	111	225	117	28.6	28.4	28.7	28.6	73.7
C11	Silica Dry	400	100	238	115	32.1	32.2	31.5	31.9	82.4
C12	Fly Ash	400	100	225	118	34.0	32.6	34.0	33.5	86.5

* Measured on 2-inch cubes

** Activities [(Test/Control) x 100 = %] were calculated with the average of three controls - (C1, C5, C9)

Notes:

- Silica as received contained approx. 10% moisture - The proportions for mixtures with the wet silica were calculated accordingly.
- The water for test mixtures (Silica - Fly Ash) is adjusted to produce a flow within ±5% of control mixture flow.
- 1375 grams of Silica Sand (C109) was used in all mixtures - Cement is a Type 10 (CT 09).
- All cubes were stored in lime saturated water until test after initial 24-hour moist-curing period (ASTM C311 - C109).

Table 5 - Mixture Proportions, Flow and 28-day Strength Activity Index with Portland Cement (ASTM C311)

Mixture No.	Designation	Cement g	SCM g	Water mL	Flow %	28-day Compressive Strength, Mpa *				28-day Activity Index, % **
						Cube 1	Cube 2	Cube 3	Average	
C1	Control	500	-	243	117	49.3	47.5	49.1	48.6	-
C2	Silica Wet	400	111	225	115	40.4	40.5	39.7	40.2	85.0
C3	Silica Dry	400	100	238	115	42.3	39.6	42.6	41.5	87.7
C4	Fly Ash	400	100	225	120	44.3	45.2	46.0	45.2	95.5
C5	Control	500	-	243	117	47.5	45.8	45.7	46.3	-
C6	Silica Wet	400	111	225	116	42.5	40.6	42.1	41.7	88.2
C7	Silica Dry	400	100	238	116	43.2	44.9	45.1	44.4	93.8
C8	Fly Ash	400	100	225	118	45.2	46.6	45.4	45.7	96.7
C9	Control	500	-	243	118	47.5	44.9	48.5	47.0	-
C10	Silica Wet	400	111	225	117	40.6	39.5	40.3	40.1	84.8
C11	Silica Dry	400	100	238	115	43.2	43.9	43.5	43.5	92.0
C12	Fly Ash	400	100	225	118	42.9	46.5	45.7	45.0	95.2

* Measured on 2-inch cubes

** Activities [(Test/Control) x 100 = %] were calculated with the average of three controls - (C1, C5, C9)

Notes:

- Silica as received contained approx. 10% moisture - The proportions for mixtures with the wet silica were calculated accordingly.
- The water for test mixtures (Silica - Fly Ash) is adjusted to produce a flow within ±5% of control mixture flow.
- 1375 grams of Silica Sand (C109) was used in all mixtures - Cement is a Type 10 (CT 09).
- All cubes were stored in lime saturated water until test after initial 24-hour moist-curing period (ASTM C311 - C109).

Table 6 - Summary of Strength Activity Index with Portland Cement (ASTM C311)

Mixture No.	Designation	Cement g	SCM g	Water mL	Flow %	Compressive Strength, Mpa *		Strength Activity Index, % **	
						7 days	28 days	7 days	28 days
C1	Control	500	-	243	117	38.4	48.6	-	-
C2	Silica Wet	400	111	225	115	29.2	40.2	75.3	85.0
C3	Silica Dry	400	100	238	115	30.0	41.5	77.5	87.7
C4	Fly Ash	400	100	225	120	33.7	45.2	86.9	95.5
C5	Control	500	-	243	117	37.8	46.3	-	-
C6	Silica Wet	400	111	225	116	30.9	41.7	79.7	88.2
C7	Silica Dry	400	100	238	116	32.4	44.4	83.6	93.8
C8	Fly Ash	400	100	225	118	33.0	45.7	85.1	96.7
C9	Control	500	-	243	118	40.0	47.0	-	-
C10	Silica Wet	400	111	225	117	28.6	40.1	73.7	84.8
C11	Silica Dry	400	100	238	115	31.9	43.5	82.4	92.0
C12	Fly Ash	400	100	225	118	33.5	45.0	86.5	95.2
Average Values of 3 Series	Control	500	-	243	117.3	38.8	47.3	-	-
	Silica Wet	400	111	225	116.0	29.6	40.7	76.2	86.0
	Silica Dry	400	100	238	115.3	31.5	43.1	81.1	91.2
	Fly Ash	400	100	225	118.7	33.4	45.3	86.2	95.8

* Average value of 3 mortar cubes (2-inch cube)

** Activities [(Test/Control) x 100 = %] were calculated with the average of three controls - (C1, C5, C9)

Table 7 - Coefficient of Variation of the Strength Activity Index

Designation	Age	Strength Activity Index, %				Coefficient of Variation, %
		Series 1	Series 2	Series 3	Average	
Silica Wet	7 days	75.3	79.7	73.7	76.2	4.1
Silica Wet	28 days	85.0	88.2	84.8	86.0	2.2
ca Dry	7 days	77.5	83.6	82.4	81.1	4.0
Silica Dry	28 days	87.7	93.8	92.0	91.2	3.5
Fly Ash	7 days	86.9	85.1	86.5	86.2	1.1
Fly Ash	28 days	95.5	96.7	95.2	95.8	0.8

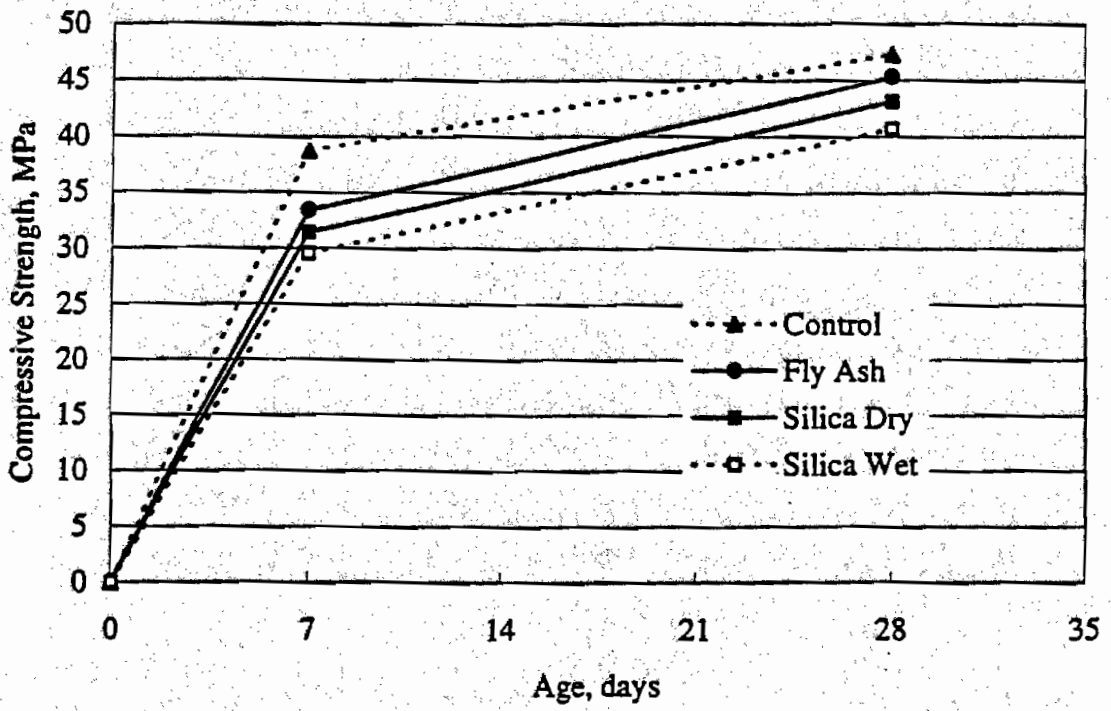

Fig. 1 - Compressive Strength Development of Precipitated Silica and Fly Ash Mortars

APPENDIX A

ASTM C 618 - Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete

Designation: C 618 – 91

Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete[1]

This standard is issued under the fixed designation C 618; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This specification has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This specification covers fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete where cementitious or pozzolanic action, or both, is desired, or where other properties normally attributed to finely divided mineral admixtures may be desired or where both objectives are to be achieved.

NOTE 1—Finely divided materials may tend to reduce the entrained air content of concrete. Hence, if a mineral admixture is added to any concrete for which entrainment of air is specified, provision should be made to ensure that the specified air content is maintained by air content tests and by use of additional air-entraining admixture or use of an air-entraining admixture in combination with air-entraining hydraulic cement.

1.2 The values stated in inch-pound units are to be regarded as the standard.

2. Referenced Documents

2.1 *ASTM Standards:*

C 260 Specification for Air-Entraining Admixtures for Concrete[2]

C 311 Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *fly ash*—finely divided residue that results from the combustion of ground or powdered coal.

NOTE 2—This definition of fly ash does not include, among other things, the residue resulting from: (*1*) the burning of municipal garbage or any other refuse with coal; or (*2*) the injection of lime directly into the boiler for sulfur removal; or (*3*) the burning of industrial or municipal garbage in incinerators commonly known as "incinerator ash."

3.1.2 *pozzolans*—siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

4. Classification

4.1 *Class N*—Raw or calcined natural pozzolans that comply with the applicable requirements for the class as given herein, such as some diatomaceous earths; opaline cherts and shales; tuffs and volcanic ashes or pumicites, any of which may or may not be processed by calcination; and various materials requiring calcination to induce satisfactory properties, such as some clays and shales.

4.2 *Class F*—Fly ash normally produced from burning anthracite or bituminous coal that meets the applicable requirements for this class as given herein. This class fly ash has pozzolanic properties.

4.3 *Class C*—Fly ash normally produced from lignite or subbituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Some Class C fly ashes may contain lime contents higher than 10 %.

5. Chemical Composition

5.1 Fly ash and natural pozzolans shall conform to the requirements as to chemical composition prescribed in Table 1. Supplementary optional chemical requirements are shown in Table 1a.

6. Physical Properties

6.1 Fly ash and natural pozzolans shall conform to the physical requirements prescribed in Table 2. Supplementary optional physical requirements are shown in Table 2a.

7. Methods of Sampling and Testing

7.1 Sample and test the mineral admixture in accordance with the requirements of Test Methods C 311.

7.2 Use cement of the type proposed for use in the work and, if available, from the mill proposed as the source of the cement, in all tests requiring the use of hydraulic cement.

8. Storage and Inspection

8.1 The mineral admixture shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment. Every facility shall be provided the purchaser for careful sampling and inspection, either at the source or at the site of the work as may be specified by the purchaser.

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[1] This specification is under the jurisdiction of ASTM Committee C-9 on Concrete and Concrete Aggregates, and is the direct responsibility of Subcommittee C09.03.10 on Fly Ash, Slag, Mineral Admixtures, and Supplementary Cementitious Materials.

Current edition approved April 15, 1991. Published June 1991. Originally published as C 618 – 68 T to replace C 350 and C 402. Last previous edition C 618 – 89a.

[2] *Annual Book of ASTM Standards*, Vol 04.02.

TABLE 1 Chemical Requirements

	Mineral Admixture Class		
	N	F	C
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70.0	70.0	50.0
Sulfur trioxide (SO_3), max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	10.0	6.0[A]	6.0

[A] The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

TABLE 1A Supplementary Optional Chemical Requirement

NOTE—This optional requirement applies only when specifically requested.

	Mineral Admixture Class		
	N	F	C
Available alkalies, as Na_2O, max, %[A]	1.5	1.5	1.5

[A] Applicable only when specifically required by the purchaser for mineral admixture to be used in concrete containing reactive aggregate and cement to meet a limitation on content of alkalies.

TABLE 2 Physical Requirements

	Mineral Admixture Class		
	N	F	C
Fineness:			
Amount retained when wet-sieved on 45 μm (No. 325) sieve, max, %[A]	34	34	34
Strength activity index:[B]			
With portland cement, at 7 days, min, percent of control	75[D]	75[D]	75[D]
With portland cement, at 28 days, min, percent of control	75[D]	75[D]	75[D]
With lime, at 7 days min, psi (kPa)	800 (5500)	800 (5500)	...
Water requirement, max, percent of control	115	105	105
Soundness:[C]			
Autoclave expansion or contraction, max, %	0.8	0.8	0.8
Uniformity requirements:			
The specific gravity and fineness of individual samples shall not vary from the average established by the ten preceding tests, or by all preceding tests if the number is less than ten, by more than:			
Specific gravity, max variation from average, %	5	5	5
Percent retained on 45-μm (No. 325), max variation, percentage points from average	5	5	5

[A] Care should be taken to avoid the retaining of agglomerations of extremely fine material.

[B] Neither the *strength* activity index with portland cement nor the pozzolanic activity index with lime is to be considered a measure of the compressive strength of concrete containing the mineral admixture. The *strength* activity index with portland cement is determined by an accelerated test, and is intended to evaluate the contribution to be expected from the mineral admixture to the longer strength development of concrete. The weight of mineral admixture specified for the test to determine the *strength* activity index with portland cement is not considered to be the proportion recommended for the concrete to be used in the work. The optimum amount of mineral admixture for any specific project is determined by the required properties of the concrete and other constituents of the concrete and should be established by testing. *Strength* activity index with portland cement is a measure of reactivity with a given cement and may vary as to the source of both the fly ash and the cement.

[C] If the mineral admixture will constitute more than 20 % by weight of the cementitious material in the project mix design, the test specimens for autoclave expansion shall contain that anticipated percentage. Excessive autoclave expansion is highly significant in cases where water to mineral admixture and cement ratios are low, for example, in block or shotcrete mixes.

[D] Meeting the 7 day or 28 day *strength* activity index will indicate specification compliance.

9. Rejection

9.1 The mineral admixture may be rejected if it fails to meet any of the requirements of this specification.

9.2 Packages varying more than 5 % from the stated weight may be rejected. If the average weight of the packages in any shipment, as shown by weighing 50 packages taken at random, is less than that specified, the entire shipment may be rejected.

9.3 Mineral admixture in storage prior to shipment for a period longer than 6 months after testing may be retested and may be rejected if it fails to meet the fineness requirements.

TABLE 2A Supplementary Optional Physical Requirements

NOTE—These optional requirements apply only when specifically requested.

	Mineral Admixture Class		
	N	F	C
Multiple factor, calculated as the product of loss on ignition and fineness, amount retained when wet-sieved on No. 325 (45-μm) sieve, max, %[A]	....	255	....
Increase of drying shrinkage of mortar bars at 28 days, max, %[B]	0.03	0.03	0.03
Uniformity Requirements:			
In addition, when air-entraining concrete is specified, the quantity of air-entraining agent required to produce an air content of 18.0 vol % of mortar shall not vary from the average established by the ten preceding tests or by all preceding tests if less than ten, by more than, %	20	20	20
Reactivity with Cement Alkalies:[C]			
Reduction of mortar expansion at 14 days, min, %	75	....	....
Mortar expansion at 14 days, max, %	0.020	0.020	0.020

[A] Applicable only for Class F mineral admixtures since the loss on ignition limitations predominate for Class C.

[B] Determination of compliance or noncompliance with the requirement relating to increase in drying shrinkage will be made only at the request of the purchaser.

[C] The indicated tests for reactivity with cement alkalies are optional and alternative requirements to be applied only at the purchaser's request. They need not be requested unless the fly ash or pozzolan is to be used with aggregate that is regarded as deleteriously reactive with alkalies in cement. The test for reduction of mortar expansion may be made using any high-alkali cement in accordance with Test Methods C 311, Section 30.1 on Reduction of Mortar Expansion, if the portland cement to be used in the work is not known, or is not available at the time the mineral admixture is tested. The test for mortar expansion is preferred over the test for reduction of mortar expansion if the portland cement to be used in the work is known and available. The test for mortar expansion should be performed with each of the cements to be used in the work.

10. Packaging and Package Marking

10.1 When the mineral admixture is delivered in packages, the class, name, and brand of the producer, and the weight of the material contained therein shall be plainly marked on each package. Similar information shall be provided in the shipping invoices accompanying the shipment of packaged or bulk mineral admixture.

11. Keywords

11.1 fly ash; mineral admixture; natural pozzolan

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3

Materials Technology Laboratory

Semi-Adiabatic Temperature Rise in Precipitated Silica Concrete

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MTL 2000-20(CF)

R. Chevrier

March 2000

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MATERIALS TECHNOLOGY LABORATORY
REPORT MTL 2000-19(CF)

SEMI-ADIABATIC TEMPERATURE RISE IN PRECIPITATED SILICA CONCRETE

by

R. Chevrier*

SCOPE

This paper presents the results of a study comparing the semi-adiabatic temperature rise in precipitated-silica concrete with that in fly ash concrete at various replacement levels. The precipitated silica (amorphous silica powder) was supplied by CalEnergy Operating Company, California. As received, the precipitated silica contained approximately 10% moisture, this was dried for 24 hours at 100 °C prior to incorporating it in the concrete. The fly ash used was an ASTM Class F from a source in eastern Canada. In this study, seven non-air entrained concrete mixtures, with a constant cementitious materials content of 330 kg/m^3 and a constant W/(C+CM) of 0.50, were made. These included: one control mixture with 100% portland cement, three concrete mixtures with precipitated silica at 15%, 35% and 55% replacement levels, and three concrete mixtures with fly ash at 15%, 35% and 55% replacement levels. From each concrete mixture, one 6 x 12-inch cylinder was cast for temperature rise determination and six 4 x 8-inch cylinders were cast for compressive strength determination at 7 and 28 days.

TEST RESULTS

The physical properties and the chemical analysis of the cement, fly ash and precipitated silica are presented in Table 1 and 2, respectively. The mixture proportions of the concrete are given in Table 3.

The results from the semi-adiabatic temperature rise as seen in Figs. 1, 2 and 3 show that at each replacement level the temperature rise curve of the precipitated silica concrete is very similar to that of the corresponding fly ash concrete. Apart from a slightly faster rise at the beginning, especially at the 55% replacement level, the maximum temperature is virtually the same. This would indicate that this product would be suitable for use in applications where heat of hydration of concrete is a concern. The strength development pattern for the precipitated silica concrete is comparable to that of the fly ash concrete, except at 28 days for 35 and 55% replacement levels,

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where the compressive strength of the precipitated silica concrete is approximately 5 MPa higher than the compressive strength of the corresponding fly ash concrete (Fig. 4). It should be noted that with increasing amounts of the precipitated silica, the slump of the concrete decreases (Table 4) as compared with an increasing slump for the fly ash concrete. This is probably due to the more angular shape of the precipitated silica particles and the higher specific surface area. We can therefore conclude that, as opposed to fly ash concrete, the water demand for concretes made with replacement levels of precipitated silica in excess of 10%, would be higher. Further studies would be needed in order to optimize the use of this product in concrete.

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TEST RESULTS 1

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Table 1 - Physical Properties of Cement, Precipitated Silica and Fly Ash

Physical Test	Portland Cement CT 03	Precipitated Silica	Fly Ash CT 95
Specific Gravity (ASTM C188)	3.17	2.04	2.58
Bulk Density, g/mL	-	0.7*	-
Fineness			
Passing 45μm (ASTM C430), %	94.3	97.5	75.2
Blaine (ASTM C204), cm^2/g	4074	3450	2260
BET Surface Area, m^2/g	-	30*	-
Average Particle Size, μm	-	10*	-

* Values from MSDS supplied by CalEnergy Operating Company

Table 2 - Chemical Analysis of Cement, Precipitated Silica and Fly Ash

Major Oxides, %	Portland Cement CT 03	Precipitated Silica	Fly Ash CT 95
Silicon dioxide (SiO_2)	20.30	92.14	42.74
Aluminum oxide (Al_2O_3)	4.23	0.18	20.29
Ferric oxide (Fe_2O_3)	3.01	3.74	23.71
Calcium oxide (CaO)	62.02	0.16	4.17
Magnesium oxide (MgO)	2.80	-	1.22
Sodium oxide (Na_2O)	0.26	0.91	0.88
Potassium oxide (K_2O)	0.90	0.50	2.56
Titanium dioxide (TiO_2)	0.17	-	0.86
Manganese oxide (MnO)	0.05	0.05	0.11
Phosphorous pentoxide (P_2O_5)	0.22	0.11	0.68
Sulphur trioxide (SO_3)	3.46	0.01	1.60
Loss on Ignition (LOI)	2.04	0.30	2.44

Table 3 - Concrete Mixture Proportions

Mixture No.	Mixture Designation	W/(C+CM)	Water, kg/m³	Cement, kg/m³	CM, kg/m³	Aggregates, kg/m³	
						Coarse	Fine
TR2	Fly Ash 15%	0.50	166	282	49	1157	773
TR3	Silica 15%	0.50	166	283	49	1150	765
TR4	Fly Ash 35%	0.50	166	216	117	1157	771
TR5	Silica 35%	0.50	166	215	116	1134	754
TR6	Fly Ash 55%	0.50	165	148	183	1141	762
TR7	Silica 55%	0.50	164	147	182	1101	734
TR8	Control	0.50	166	332	0	1166	778

Table 4 - Properties of Fresh and Hardened Concrete

Mixture No.	Mixture Designation	Slump, mm	Air Content, %	Unit Weight, kg/m³	Compressive Strength, Mpa*	
					7 days	28 days
TR2	Fly Ash 15%	64	1.5	2427	32.7	42.1
TR3	Silica 15%	57	1.5	2413	32.1	42.6
TR4	Fly Ash 35%	89	1.3	2427	26.2	36.7
TR5	Silica 35%	51	1.5	2385	27.4	41.9
TR6	Fly Ash 55%	140	1.2	2399	13.7	23.2
TR7	Silica 55%	38	1.7	2328	15.4	28.1
TR8	Control	38	1.5	2441	38.8	47.2

* Average of 3 - 4" x 8" concrete cylinders (1 Mpa = 145 psi)

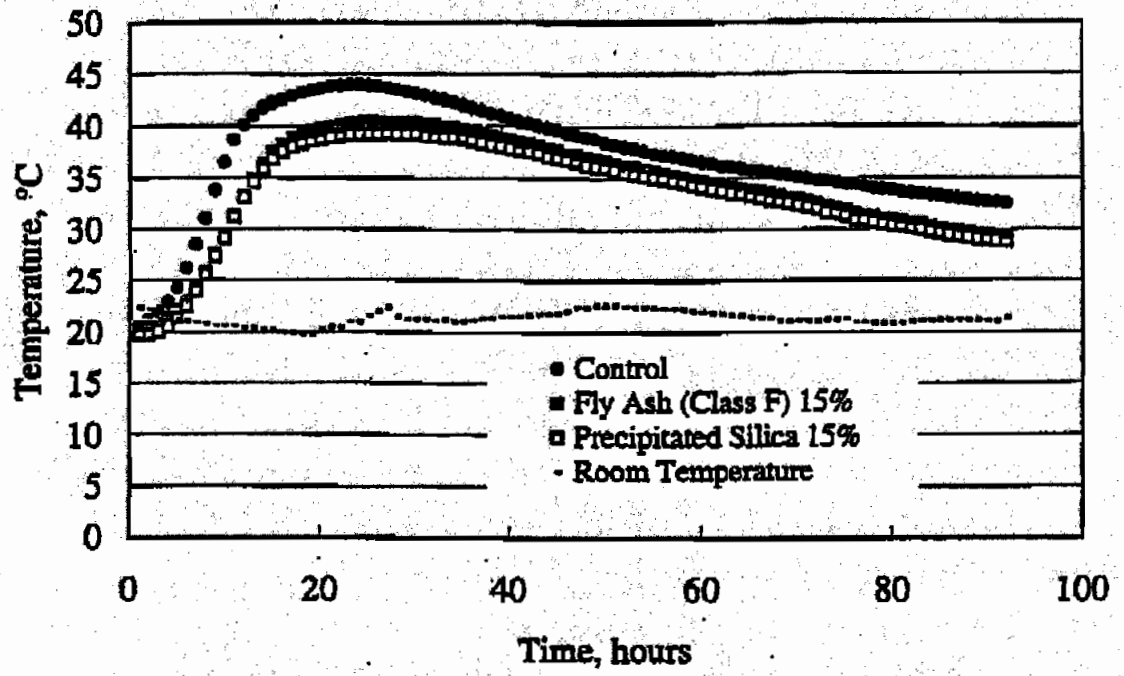


Fig. 1 - Semi-adiabatic Temperature Rise of Concrete at 15% Replacement Level

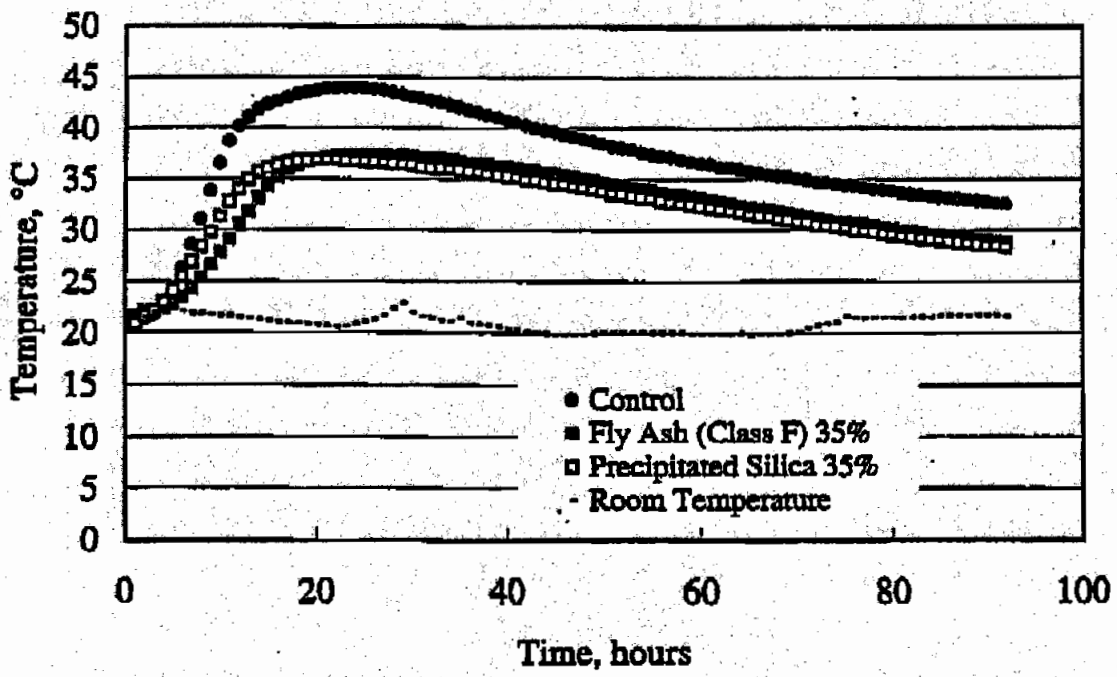


Fig. 2 - Semi-adiabatic Temperature Rise of Concrete a 35% Replacement Level

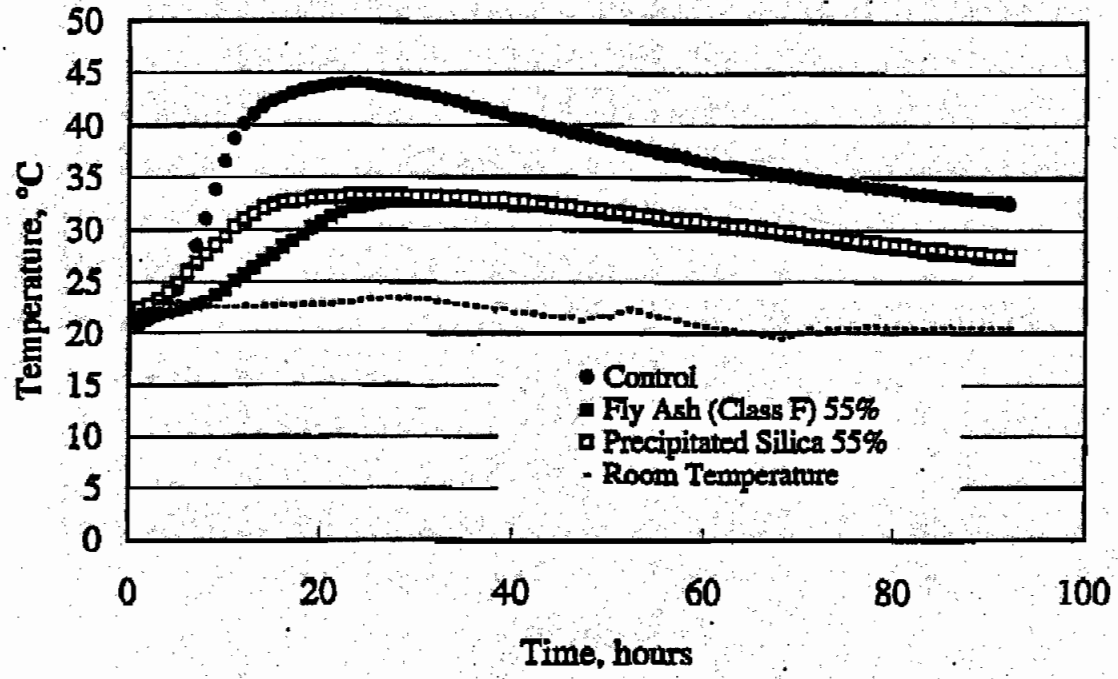


Fig. 3 - Semi-adiabatic Temperature Rise of Concrete at 55% Replacement Level

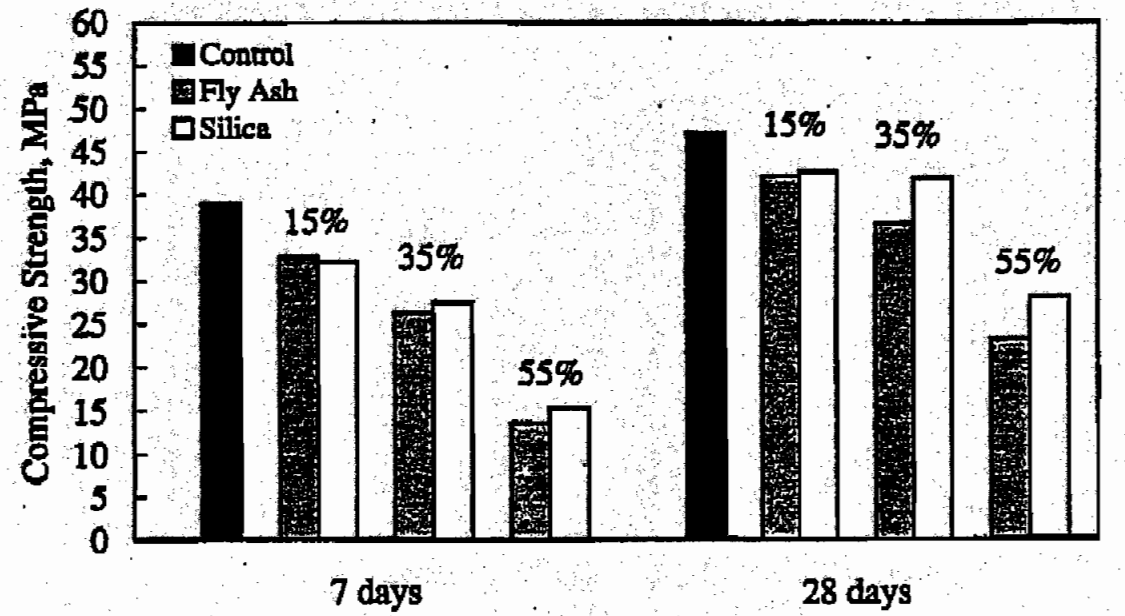


Fig. 4 - Compressive Strength Development of Precipitated Silica and Fly Ash Concrete

4

Natural Resources Canada | Ressources naturelles Canada

Minerals and Metals Sector | Secteur des minéraux et des métaux

Ottawa, Ontario K1A 0E4 | Ottawa (Ontario) K1A 0E4

Mrs Fiorella Sist
Cal Energy Minerals LLC
950 West Lindsey Road
Calipatria, CA 92233, USA

Object: Testing of the Cal Energy "pozzolan" for potential alkali-silica reactivity using the Accelerated Mortar Bar Test (ASTM C 1260)

Dear Mrs. Sist,

Please find enclosed a summary report for the test program on the Accelerated Mortar Test (ASTM C 1260) using the Cal Energy "pozzolan".

If you have any questions, please do not hesitate to contact me.

Yours sincerely,

Benoit Fournier

Benoit Fournier, Ph.D.
Manager
ICON/CANMET
405 Rochester Street
Ottawa, ON, Canada, K1A 0G1
Tel: (613) 992 8394
Fax: (613) 992 9389
Email: bfournie@nrcan.gc.ca

Summary Report
Accelerated Mortar Bar Test (AMBT – ASTM C 1260) Data
Cal Energy Project (October 2000)

The information below summarizes the test program performed to date in the project. The testing is still under progress and a final report will be issued when the expansion testing will be completed, i.e. by the end of October 2000.

Scope of the Project

A total of seven mortar mixtures were made with three aggregates, two reactive (NM and Sp) and one non-reactive (HP); these included control mortar mixtures and mixtures incorporating 20 and 30% of a powder material provided by Cal Energy. Mortar bars were made and tested in accordance with the Accelerated Mortar Bar Test ASTM C 1260.

Aggregates Used

The following three aggregates have been used in the test program:

- New Mexico reactive gravel (from Albuquerque, New Mexico)
- Siliceous limestone (Control reactive aggregate used in Canada and in the USA)
- High-purity non-reactive limestone from Newfoundland, Canada

The aggregates were crushed and sieved as recommended in ASTM C 1260.

Cement Used

A high-alkali control ASTM Type I cement was used in the mortar mixtures. The alkali content of the cement is 0.90% Na_2O equivalent.

Pozzolanic Material

A powder material was provided to CANMET by Cal Energy Minerals LLC in September 2000. The material was dried in the oven at 105°C for 24 hours and then gently passed over a 300 micron sieve to break the lumps. Those broke very easily.

Tests Performed

The Accelerated Mortar Bar Test (AMBT) (ASTM C 1260) was performed using the various materials listed above. A total of seven mixtures were made, as follows:

1. Control mixture with the reactive Spratt limestone (**Sp Control**)
2. Mixture incorporating the reactive Spratt limestone and 20% Cal Energy "pozzolan" as replacement, by mass, of the portland cement (**Sp CE 20**)
3. Control mixture with the reactive New Mexico gravel (**NM Control**)
4. Mixture incorporating the reactive New Mexico gravel and 20% Cal Energy "pozzolan" as replacement, by mass, of the portland cement (**NM CE 20**)
5. Mixture incorporating the reactive New Mexico gravel and 30% Cal Energy "pozzolan" as replacement, by mass, of the portland cement (**NM CE 30**)

6. Control mixture with the non-reactive high-purity limestone (**HP Control**)
7. Mixture incorporating the non-reactive high-purity limestone and 20% Cal Energy "pozzolan" as replacement, by mass, of the portland cement (**HP CE 20**)

In the AMBT, mortar bars, 25 by 25 by 285 mm in size, are prepared using specified aggregate size fractions, mixture proportions and mixing procedures (ASTM C 1260). After 24 hours moist curing in their moulds, the bars are placed in a sealed plastic container filled with water at 23°C, and the container stored in an oven at 80°C. The next day, an initial length measurement is taken, the bars transferred in a 1N NaOH solution at 80°C and measured hot periodically over a two-week time period.

ASTM C 1260 states that:

- Expansions < 0.10% at 16 days after casting (i.e. 14 days of testing in the 1N NaOH solution) are indicative of innocuous behavior in most cases.
- Expansions > 0.20% at 16 days after casting (i.e. 14 days of testing in the 1N NaOH solution) are indicative of potentially deleterious expansion.
- Expansions between 0.10 and 0.20% at 16 days after casting (i.e. 14 days of testing in the 1N NaOH solution) include both aggregates that are known to be innocuous and deleterious in field performance.

The AMBT can also be used to evaluate the effectiveness of supplementary cementing materials (or pozzolans) to control expansion due to ASR. A 14-day 0.10% expansion limit is then used as a limit for "non-reactive" systems.

Preliminary Test Results

Figure 1 give the X-ray diffraction pattern for the Cal Energy "pozzolan". The material is basically composed of amorphous material and some NaCl. A samples has been sent for chemical analysis.

Table 1 summarizes the expansion data obtained to date, i.e. after 7 days of immersion in the 1N NaOH at 80°C. Figures 2 to 4 illustrates the expansion results. The following observations can be made at this stage:

- The control mortar incorporating the reactive aggregates SP and NM have already reached expansion levels > 0.15%, i.e. confirming their reactive character.
- The control mortar incorporating the non-reactive aggregates HP have not shown any expansion to date, which was expected considering the non-reactive character of this aggregate.
- With both aggregates NM and SP, the use of the Cal Energy "pozzolan" (as received) at the 20% level actually increased the expansion of the mortar bars compared to the control systems made of portland cement only. The use of 20 and 30% Cal Energy "pozzolan" contributed in reducing the expansion of the mortar specimens incorporating the aggregate NM compared to the control at early ages. However, higher expansions are obtained at later ages.
- With the non-reactive aggregate HP, the use of the Cal Energy "pozzolan" at the 20% level actually resulted in tremendous amount of expansion that reached 1.6% after only 7 days of testing. The limit for reactive material is 0.15% at 14 days. One of the three bars actually broke because of expansion and cracking, and could not be measured.

Conclusions to date

The expansion results obtained to date in the AMBT suggests that the powder material provided by Cal Energy is actually acting as a highly-reactive material in the mortar bars tested. This is confirmed by the huge amount of expansion obtained in the case of the mortar made with the non-reactive high-purity limestone and 20% CE powder (i.e. HP CE 20). Petrographic examination of the mortar bars will be performed to confirm the above hypothesis and other possible explanation for the behavior observed.

Accelerated Mortar Bar Test (CSA A23.2-25A; ASTM C 1260)

Mixed on October 4 2000

Spratt ,New Mexico and high purety Aggregates

Expansion in %		Time (days)						
Sample no.	**Ther choc**	**T1**	**T3**	**T5**	**T7**	**T10**	**T12**	**T14**
Sp Control - 1	0.0602	0.0170	0.0932	0.1543	0.1974			
Sp Control - 2	0.0652	0.0150	0.0942	0.1533	0.1933			
Sp Control - 3	0.0602	0.0130	0.0953	0.1544	0.1966			
AVERAGE	**0.062**	**0.015**	**0.094**	**0.154**	**0.196**			
Sp CE 20 - 1	0.0612	0.0100	0.0632	0.3639	0.8521			
Sp CE 20 - 2	0.0631	0.0140	0.0390	0.2922	0.7666			
Sp CE 20 - 3	0.0612	0.0110	0.0652	0.3209	0.7470			
AVERAGE	**0.062**	**0.012**	**0.056**	**0.326**	**0.789**			
NM Control - 1	0.0886	0.2434	0.4134	0.5582	0.6598			
NM Control - 2	0.0832	0.1481	0.4214	0.5706	0.6767			
NM Control - 3	0.0862	0.1332	0.4045	0.5547	0.6559			
AVERAGE	**0.086**	**0.175**	**0.413**	**0.561**	**0.664**			
NM CE 20 - 1	0.0782	0.0080	0.2064	0.6133	1.1004			
NM CE 20 - 2	0.0812	0.0080	0.2153	0.6660	1.2228			
NM CE 20 - 3	0.0761	0.0060	0.1992	0.6096	1.1281			
AVERAGE	**0.079**	**0.007**	**0.207**	**0.630**	**1.150**			
NM CE 30 - 1	0.0731	0.0070	0.0330	0.2591	0.6841			
NM CE 30 - 2	0.0742	0.0070	0.0290	0.1802	0.5978			
AVERAGE	**0.074**	**0.007**	**0.031**	**0.220**	**0.641**			
Hp Control - 1	0.0571	0.0020	0.0010	0.0050	0.0050			
Hp Control - 2	0.0571	0.0010	0.0000	0.0050	0.0040			
Hp Control - 3	0.0592	-0.0010	-0.0020	0.0040	0.0020			
AVERAGE	**0.058**	**0.001**	**0.000**	**0.005**	**0.004**			
Hp CE 20 - 1	0.0591	0.0170	0.3724	0.9800	1.6106			
Hp CE 20 - 2	0.0601	0.0180	0.3746	1.0207	1.6998			
Hp CE 20 - 3	0.0674	0.0111	0.4326	1.1589	.....			
AVERAGE	**0.062**	**0.015**	**0.393**	**1.053**	**1.655**			

Table 1

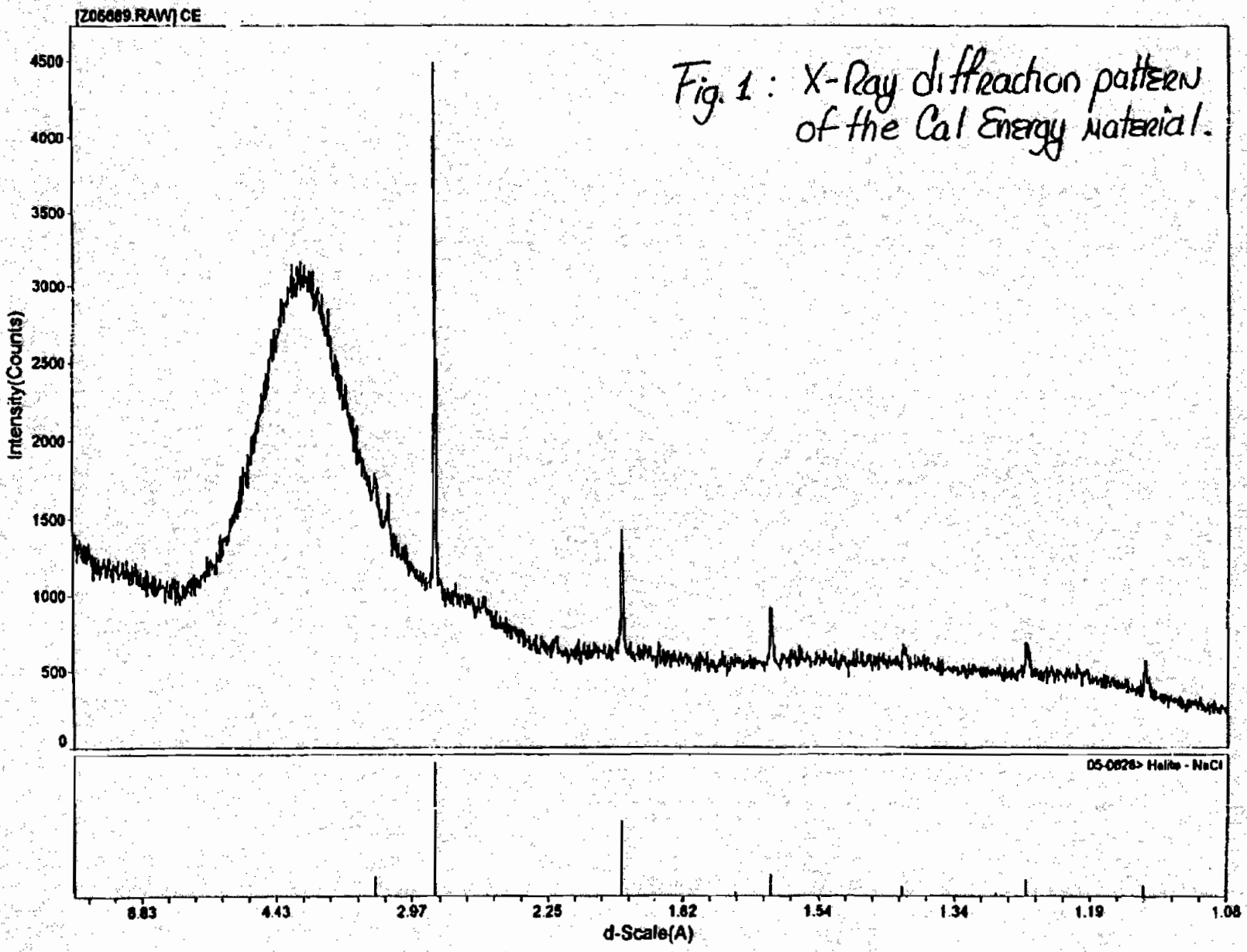


Fig. 1 : X-Ray diffraction pattern of the Cal Energy material.

Fig. 2

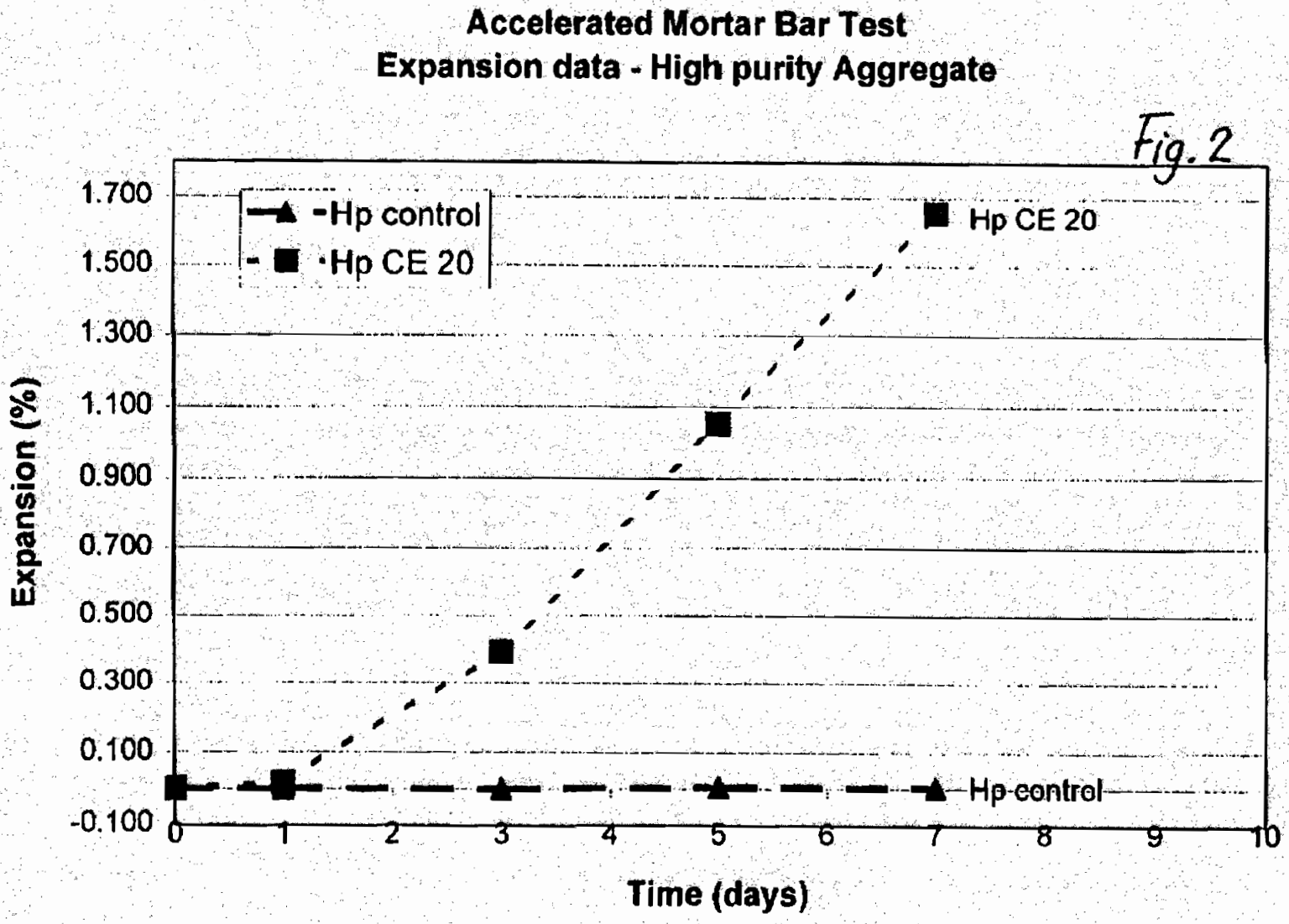
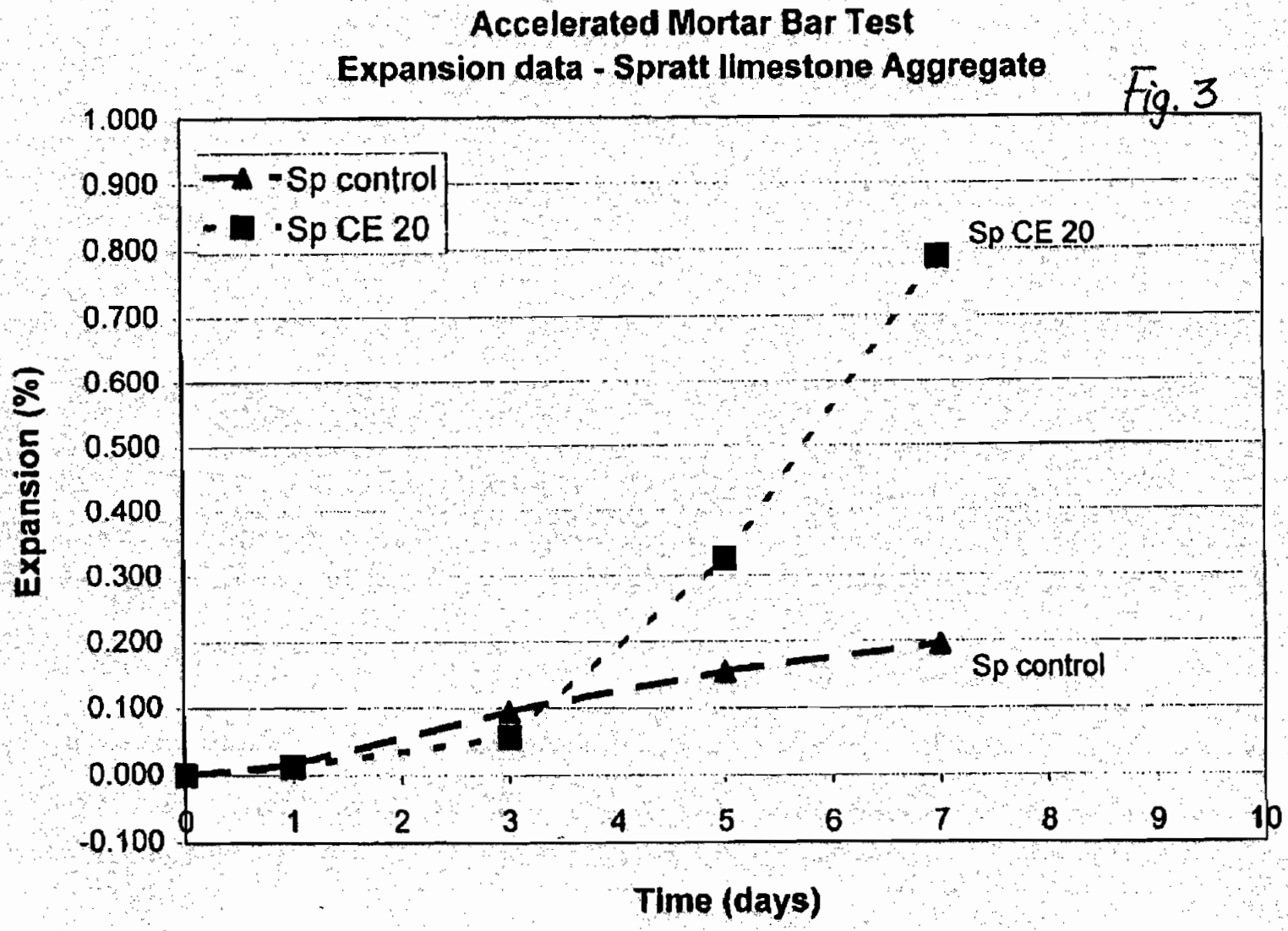

Accelerated Mortar Bar Test
Expansion data - High purity Aggregate
Hp control
Hp CE 20
Hp CE 20
Hp control
Expansion (%)
1.700
1.500
1.300
1.100
0.900
0.700
0.500
0.300
0.100
-0.100
0
1
2
3
4
5
6
7
8
9
10
Time (days)

Fig. 3


Accelerated Mortar Bar Test
Expansion data - Spratt limestone Aggregate
Sp control
Sp CE 20
Sp CE 20
Sp control
Expansion (%)
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
-0.100
0
1
2
3
4
5
6
7
8
9
10
Time (days)

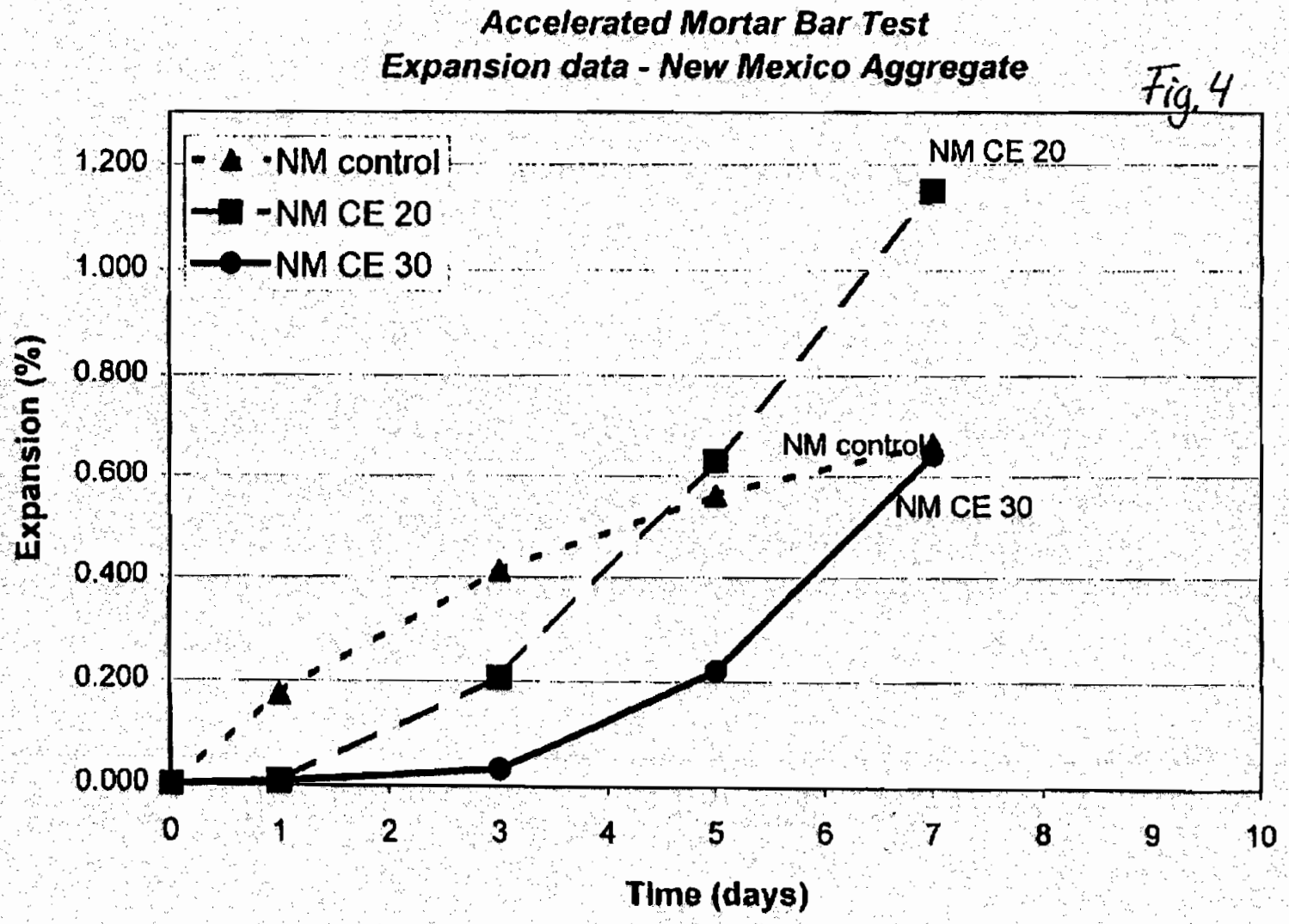

Accelerated Mortar Bar Test
Expansion data - New Mexico Aggregate
NM control
NM CE 20
NM CE 30
Expansion (%)
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
1
2
3
4
5
6
7
8
9
10
Time (days)

Fig. 4

5

Construction Technology Laboratories, Inc.
5420 Old Orchard Road, Skokie, IL 60077-1030
(847) 965-7500 Fax (847) 965-6541

FACSIMILE TRANSMITTAL SHEET

To: **Ms. Fiorella Sist**
Of: **Cal Energy**
Fax: **760-348-4073**

October 20, 2000

From: ***Michael Morrison***

CTL Project No.: **409087**

If you do not receive all the pages, please contact Helene Acker at (847) 965-7500 ext. 414

Re: Data for Precipitated Silica

Attached are un-reviewed drafts of ASTM C 1260 results. As we discussed, the mix containing 20% of your product expanded beyond the measuring capacity of our length comparator. These are repeat tests verifying our initial ASTM C 1260 results from about one month ago. The "Test Mix" expanded more and also faster then the "Control Mix." This confirms our findings from the first run of tests. Additionally, we performed ASTMC 1260 testing using a known non-reactive material to prove that your material was reacting with the alkalis. Limestone from the Thornton, IL pit was used. We have worked extensively with this coarse aggregate over the last 12 years and have used it as "Control Mixes" in FHWA work. You can see by the results of this Thornton Control mix how reactive your material is. We observed an average expansion of 0.64% at 14 days. Usually this material by itself has expansions well below .05%.

We are starting the work on the two new samples you submitted at the beginning of the month. I will keep you posted, as results become available.

Should you have any questions, please contact me.

Michael Morrison

Michael Morrison
Sr. Materials Technologist, Supervisor
Cement & Mortar Laboratory
847-965-7500 x 511
e-mail:mmorrison@ctlgroup.com

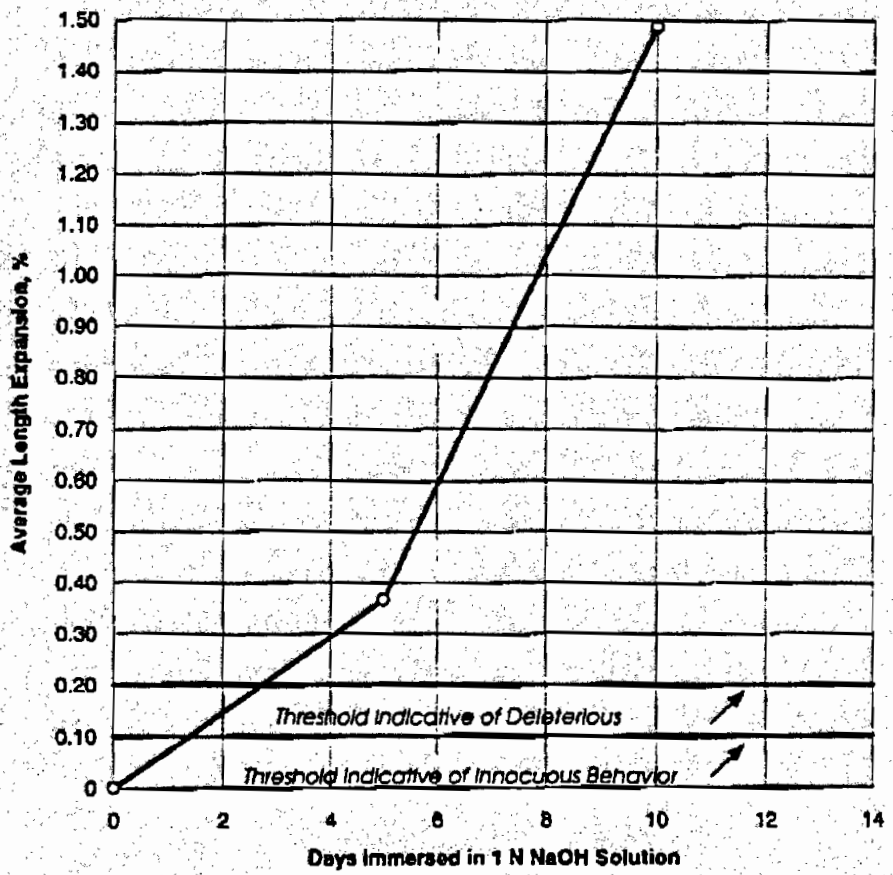
- CONFIDENTIALLY NOTE -

The information contained in this facsimile is legally privileged and confidential information intended only for the use of the individual or entity named above. If the reader of this message is not the intended recipient, you are hereby notified that any dissemination, distribution, or copy of this communication is strictly prohibited. If you have received this communication in error, please immediately notify us by telephone and return the original message to us via the United States Postal Service at our expense. Thank you.

Client: Cal Energy, Inc.
Project: ASR of Precipitated Silica
Contact: Ms. Fiorella Sist
Submitter: Ms. Fiorella Sist

CTL Project No.: 409087
CTL Project Mgr.: M. Morrison
Technician: Mortar Lab
Approved: H. Kanare
Date: October 13, 2000

ASTM C 1260 Length Change Due to Alkali-Silica Expansion of a Fine Aggregate Identified as Albuquerque Sand Using CTL Provided Lab Blend Cement (Lot #18L0014)



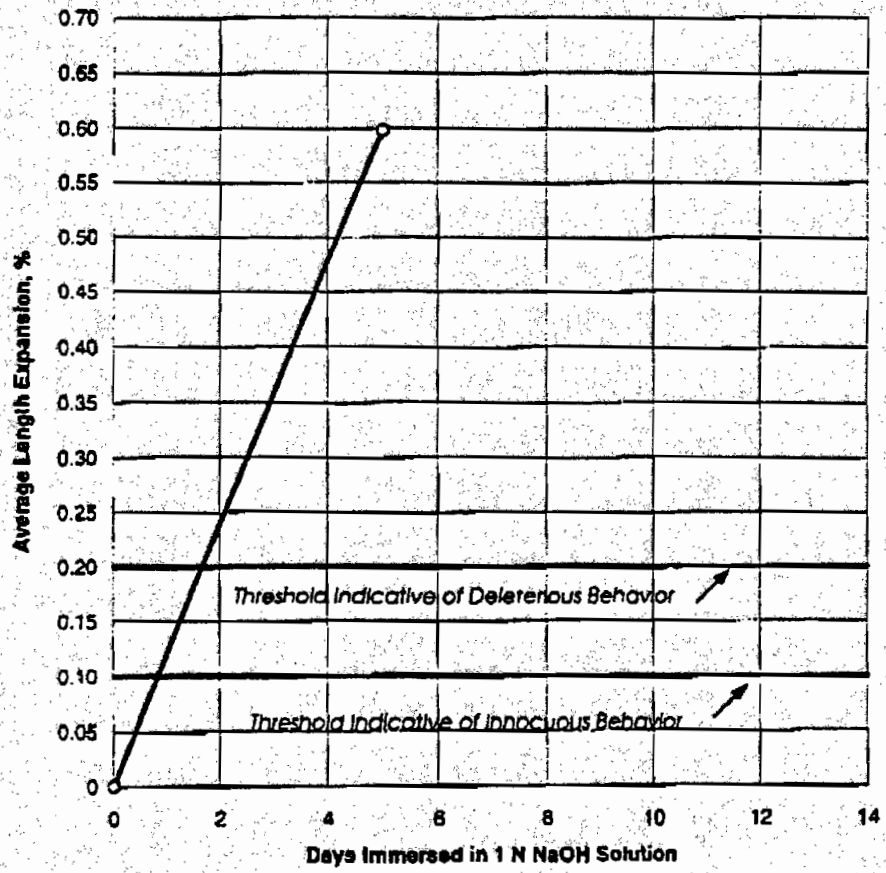
Expansion, %			Specimen IDs			
Date	Age, days	Condition	A	B	C	Average
09/21/00	0	1 N NaOH	0.000	0.000	*	0.00
09/26/00	5	1 N NaOH	0.348	0.386	*	0.37
10/01/00	10	1 N NaOH	**	1.487	*	1.49
10/05/00	14	1 N NaOH	**	**	*	

* Specimen broke during de-molding.
** Specimen broke during test.

Client: Cal Energy, Inc.
Project: ASR of Precipitated Silica
Contact: Ms. Fiorella Sist
Submitter: Ms. Fiorella Sist

CTL Project No.: 409087
CTL Project Mgr.: M. Morrison
Technician: Mortar Lab
Approved: H. Kanare
Date: October 13, 2000

ASTM C 1260 Length Change Due to Alkali-Silica Expansion of a Fine Aggregate Identified as Albuquerque Sand Using CTL Provided Lab Blend Cement (Lot #18L0014) Containing a 20% Precipitated Silica Replacement by Weight of Cement



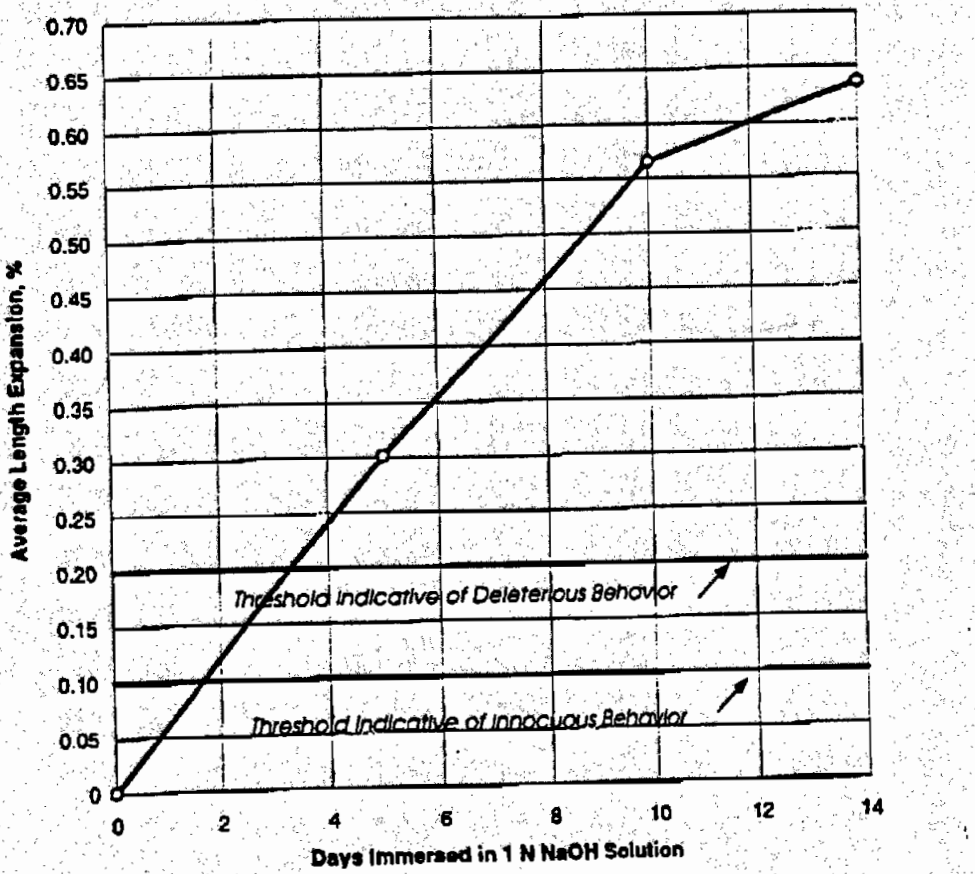
Expansion, %			Specimen IDs			
Date	Age, days	Condition	A	B	C	Average
09/21/00	0	1 N NaOH	0.000	0.000	0.000	0.00
09/26/00	5	1 N NaOH	0.629	0.523	0.643	0.60
10/01/00	10	1 N NaOH	*	*	*	
10/05/00	14	1 N NaOH	*	*	*	

* Specimen expansion exceeded the capacity of the comparator used to measure length change.

Client: Cal Energy, Inc.
Project: ASR of Precipitated Silica
Contact: Ms. Fiorella Sist
Submitter: Ms. Fiorella Sist

CTL Project No.: 409087
CTL Project Mgr.: M. Morrison
Technician: Mortar Lab
Approved: H. Kanare
Date: October 13, 2000

ASTM C 1260 Length Change Due to Alkali-Silica Expansion of a Coarse Aggregate Identified as Thorton Using CTL Provided Lab Blend Cement (Lot #18L0014) Containing a 20% Precipitated Silica Replacement by Weight of Cement



Expansion, %			Specimen IDs			
Date	Age, days	Condition	A	B	C	Average
09/21/00	0	1 N NaOH	0.000	0.000	*	0.00
09/26/00	5	1 N NaOH	0.313	0.290	*	0.30
10/01/00	10	1 N NaOH	0.575	0.556	*	0.57
10/05/00	14	1 N NaOH	0.644	0.628	*	0.64

* Specimen broke during de-molding.

6

Proposal for In-Depth Investigation of the Potential Alkali-Silica Reactivity of Precipitated Silica Material from Cal Energy

Background and Objective

Testing performed to date at CANMET has identified the highly-reactive character of the material. Additional testing would be necessary to better understand the process involved. The following activities are proposed to clarify the mechanisms involved and find potential solutions to this issue.

Proposed testing Program

The following tests are proposed:

1. **Evaluation of the pessimum effect**
   - Some highly-reactive mineral phases (e.g. opale, cristobalite) show what is called a pessimum effect; it means that maximum expansion is obtained with a certain proportion of the material in concrete or mortar and when the material is used at higher or lower levels, reduced expansion is observed.
   - The testing we did in the previous study was done according to ASTM standards, i.e. at a fixed 20% replacement level of the cement in the mortar mixtures. It is possible that higher or lower expansion values be obtained at different proportions. Maybe the material would produce less expansion at proportions < 10%.
   - It is proposed to run the Accelerated mortar bar test (ASTM C 1260) with the following proportions of precipitated silica, as replacement of the high-alkali cement: 1, 3, 5, 10, 15 and 25%. Mortar mixtures using a non-reactive aggregate will be made. Expansions will be measured over a 14-day period to determine how the material performs in different proportions in the test.
   - A total of 6 mixtures will be made in this part and the bars will be examined petrographically for signs of reactivity.

2. **Effect of the particle size**
   - The precipitated silica investigated has a mean particle size of about 10 to 15 μm. Grinding the material to finer sizes is likely to reduce expansion due to alkali-silica reaction and to increase the pozzolanic activity of the material.
   - The average particle size of silica fume particles is 0.1μm. Silica fume is a very active pozzolan and is not alkali-silica reactive.
   - It is proposed to grind the precipitated silica material to increase its fineness and then evaluate its potential alkali-silica reactivity as a function of fineness. However, in practice, grinding this material may not be technically practical or a viable economic solution because of the cost involved in grinding.
   - It is proposed to run the Accelerated mortar bar test (ASTM C 1260) using the precipitated silica material ground at two different fineness (< 10μm, but to be determined according to feasability). The material will be tested at three different replacement levels, i.e. 5, 10 and 15%, as replacement of the high-alkali cement. Mortar mixtures using a non-reactive aggregate will be made

Proposal for In-Depth Investigation of the Potential Alkali-Silica Reactivity of Precipitated Silica Material from Cal Energy

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- A total of 6 mixtures will be made in this part and the bars will be examined petrographically for signs of reactivity.

3. **Concrete Prism Testing**
   - The most promising results obtained using the Accelerated Mortar Bar Test (ASTM C 1260), i.e. the lowest expansion levels obtained as a function of the particle size and the proportion of precipitated silica, will need to be validated using the Concrete Prism Test ASTM C 1293. This test, unfortunately, is a minimum one-year test.
   - A total of 3 concrete mixtures will most likely be necessary for this part of the project.

4. **Additional mineralogical characterization**
   The precipitated silica material is mainly a silicate glass. We suggest to run some additional mineralogical characterization through thermal analysis and/or infrared spectroscopy to characterize in more details the glassy phase(s) present. This may contribute in a better understanding of the behavior of the material in the tests described above.

5. **Potential uses of the material other that in concrete**
   Investigations will be made to find potential other utilization for the precipitated silica material as a raw material in chemical or metallurgical processes.

Cost of the Proposed Program

The cost of the various work elements are given below:

1.	Evaluation of the pessimum effect:	$4.2K (Can)
2.	Effect of the particle size	$4.2K(Can)
3.	Concrete Prism Testing	$3.0K(Can)
4.	Mineralogical Characterization	$1.0K (Can)
5.	Potential Uses (research of information)	$2.0K (Can)
6.	Report (progress and final reports)	$3.0K (Can)
	Total	**$17.4K (Can)**

Scheduling

Some work could be started in December 2001, i.e. element 1, grinding of element 2. The AMBT would be completed in January/February 2001 and the Concrete Prism Testing started in early March following data analysis from the AMBT.

Prepared by B. Fournier, Ph.D.
Manager, ICON/CANMET
November 27th, 2000

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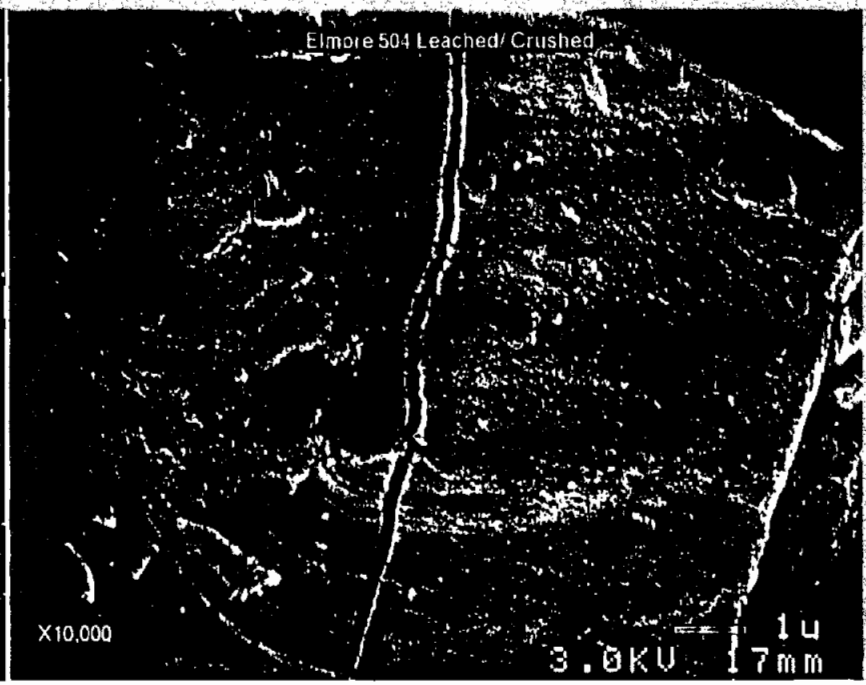
Manager, ICON/CANMET
November 27th, 2000

7

Elmore 504 Leached/ Crushed
X1000
10u
3.0KV 17mm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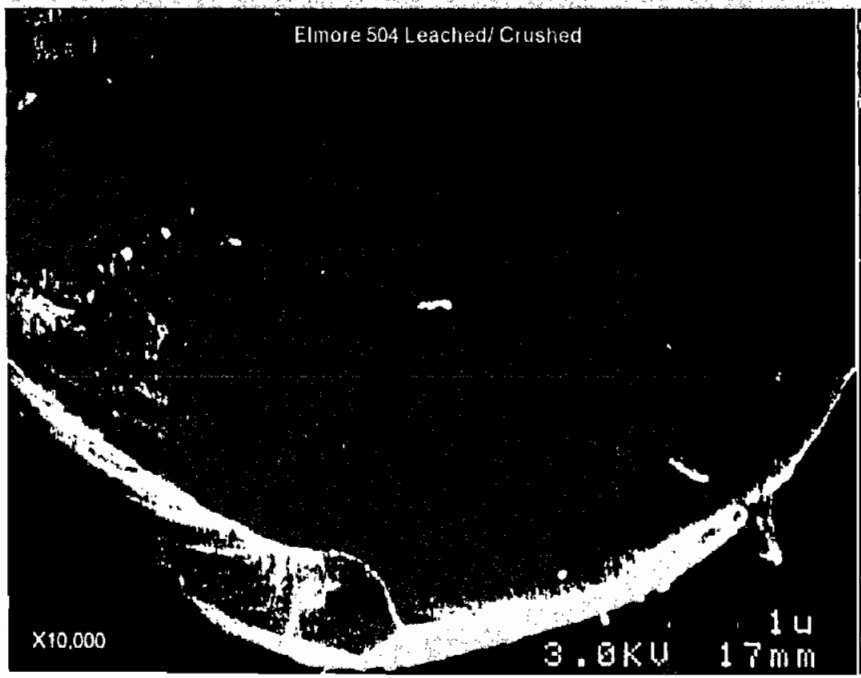
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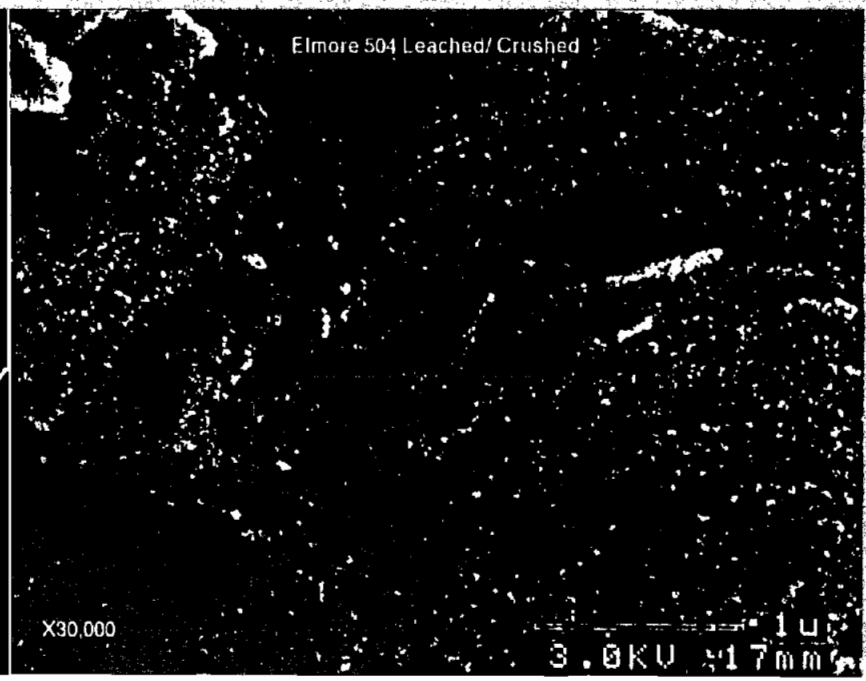
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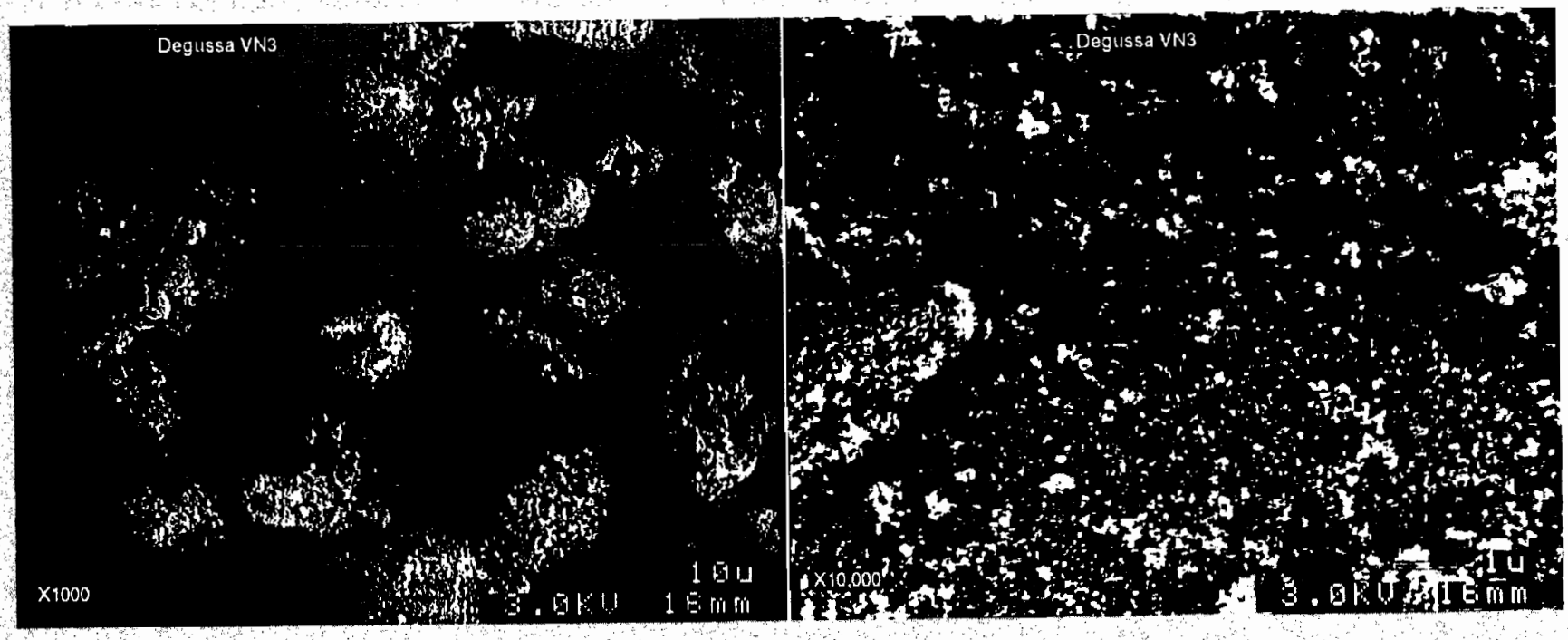
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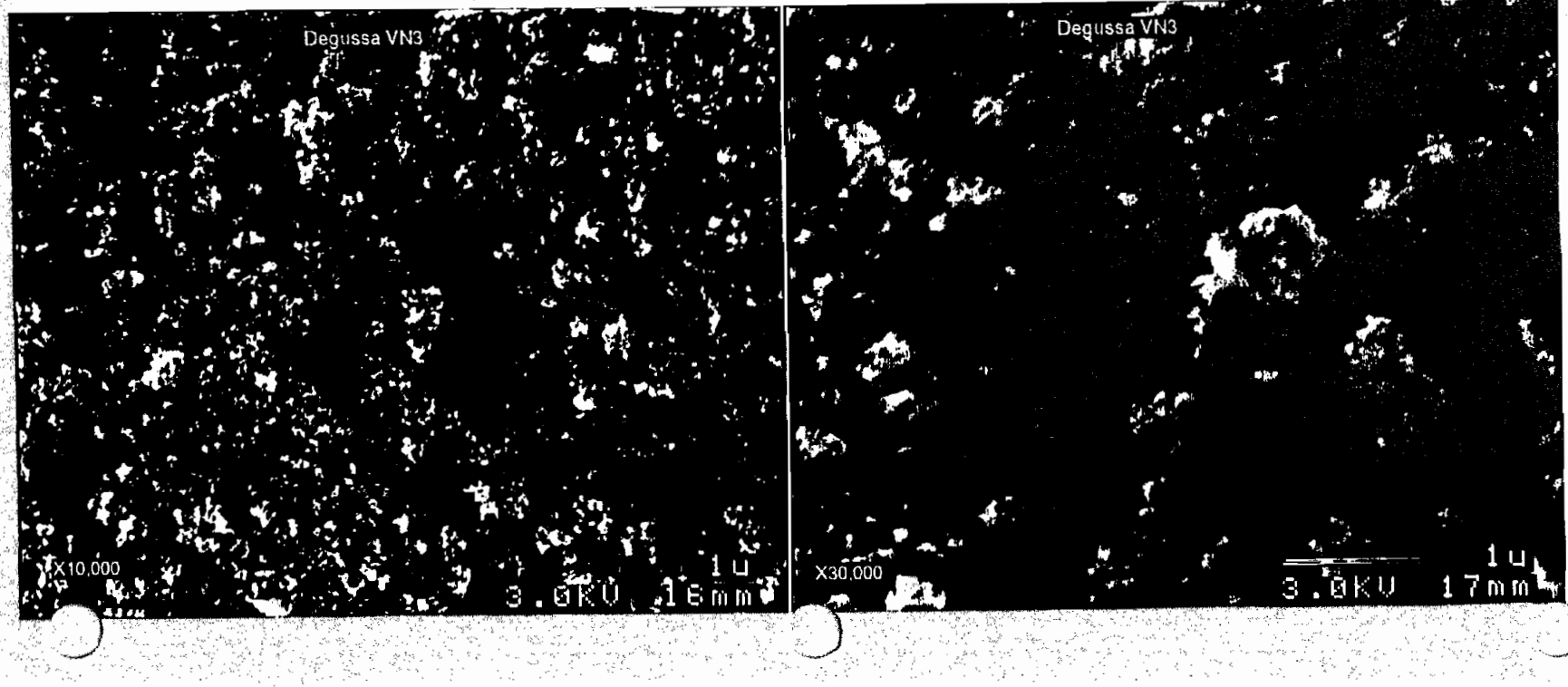
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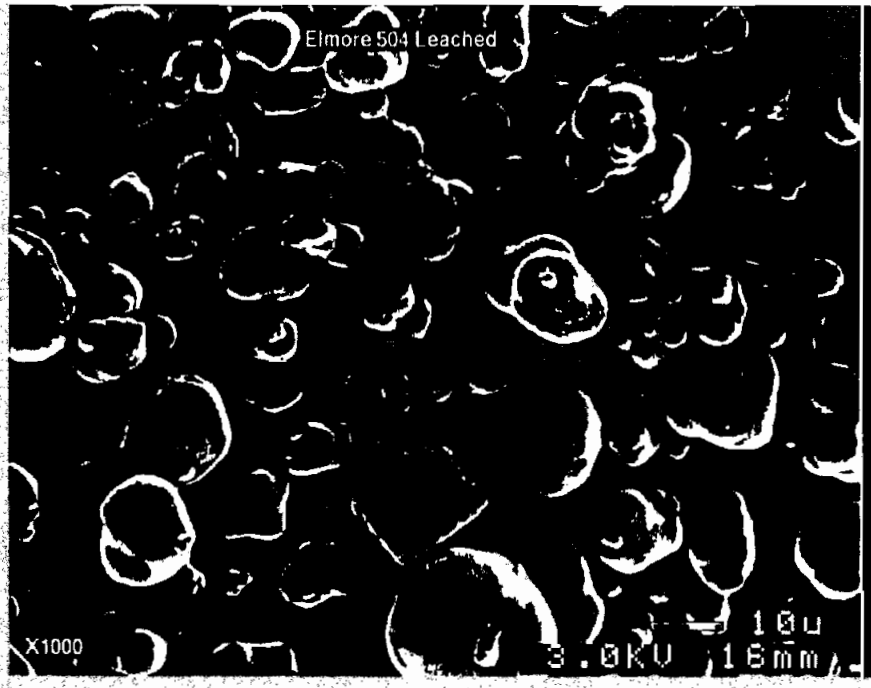
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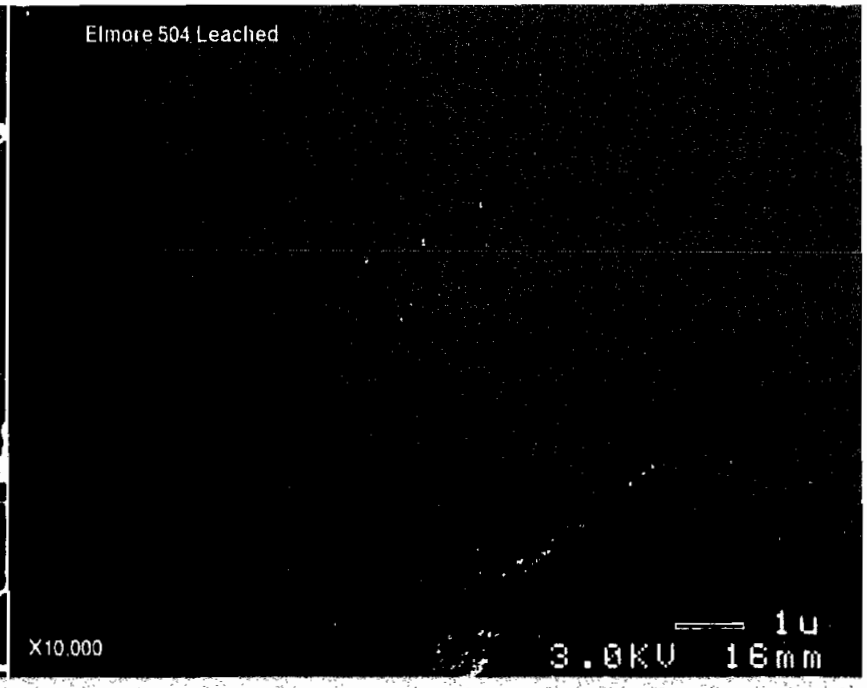
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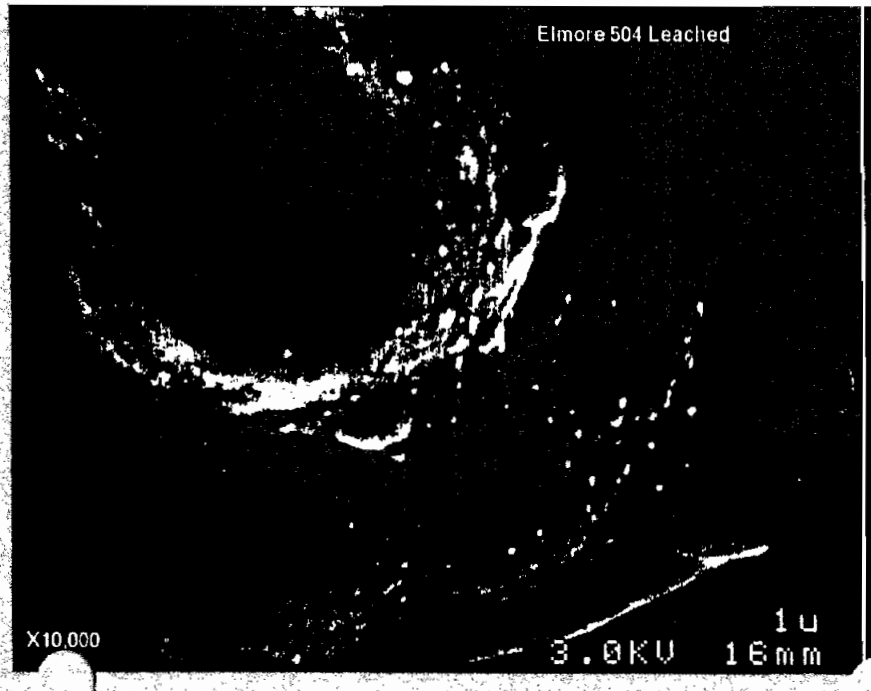
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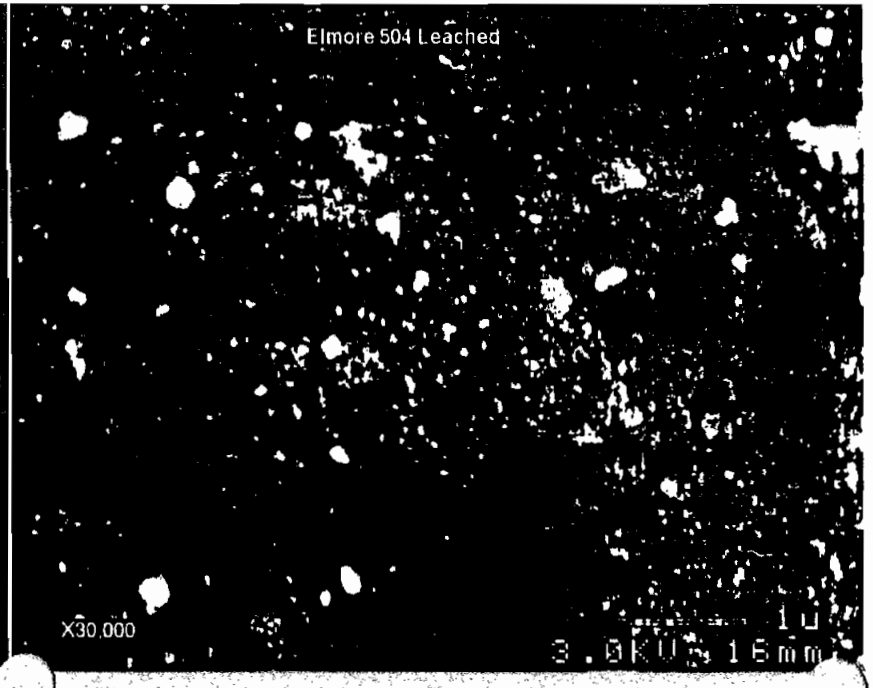
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United States Patent [19]
MacKay

[11] **4,051,223**
[45] **Sept. 27, 1977**

[54] **PROCESS FOR THE RECOVERY OF MAGNESIUM**

[75] Inventor: Kenneth D. MacKay, Circle Pines, Minn.

[73] Assignee: General Mills Chemicals, Inc., Minneapolis, Minn.

[21] Appl. No.: 638,599

[22] Filed: Nov. 10, 1975

[51] Int. Cl.[2] B01D 11/04
[52] U.S. Cl. ..... 423/197; 75/101 BE
[58] Field of Search ..... 423/157; 75/101 BE

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Stary, "The Solvent Extraction of Metal Chelates," The MacMillan Co., 1965, pp. 51–78.

Primary Examiner—O. R. Vertiz
Assistant Examiner—Wayne A. Langel
Attorney, Agent, or Firm—Gene O. Enockson; Patrick J. Span

[57] **ABSTRACT**

Magnesium values are selectively extracted from aqueous solutions thereof also containing calcium using quaternary ammonium salts of selected hydrogen ion exchange reagents. Magnesium is stripped from the resulting organic phase with acids.

23 Claims, No Drawings

PROCESS FOR THE RECOVERY OF MAGNESIUM

The present invention relates to the recovery of magnesium from aqueous solutions thereof such as sea water which also contain calcium ions. More particularly, it relates to such a process using certain salts of quaternary ammonium compounds and selected hydrogen ion exchange agents.

Presently, most of the magnesium sold in the United States is derived from sea water where it is present at about 1.3 g./l. Processing involves several steps: precipitation, decantation, filtration, neutralization, drying, evaporation and electrolysis. Processing is said to be difficult and to require equipment of high capital cost (see Encyclopedia of Chemical Technology, 2nd Ed., Vol. 12, pp. 661–675, Wiley Interscience; 1967). It would be highly desirable to provide a process of less complexity and cost for the recovery of magnesium from sea water.

I have now discovered that magnesium can be selectively recovered from aqueous solutions also containing calcium ions by using certain salts of quaternary ammonium compounds and selected hydrogen ion exchange agents. Thus the magnesium and calcium containing aqueous solution is contacted with a solution of the quaternary ammonium salt in an essentially water-immiscible organic solvent to selectively extract magnesium values into the organic phase. The magnesium values can then be conventionally stripped from the loaded organic phase.

The starting quaternary ammonium salts can be formed by washing the corresponding solution of the hydrogen ion exchange reagent and the quaternary ammonium compound with water or aqueous base. Each neutralization or salt formation step can be illustrated by the following equation (where a base is used):

$$LH_{org} + QX_{org} + B_{aq} \rightarrow QL_{org} + BHX_{aq}$$

where L is the anion of the hydrogen ion exchange agent, Q is the quaternary ammonium cation, X is the inorganic anion of the starting quaternary ammonium compound and B is the base. This can be further illustrated in respect of the use of a specific base as follows:

$$2LH_{org} + Q_2X + 2NaHCO_{3aq} \rightarrow 2QL_{org} + Na_2X_{aq} + 2CO_2$$

This formed salt solution is then used to contact the aqueous magnesium and calcium containing solution to extract at least part of the magnesium values into the organic phase. The extraction step in its simplest form can be illustrated (for example with $MgCl_2$ in the aqueous solution) by the following equation:

$$2QL_{org} + MgCl_{2aq} \rightarrow L_2Mg_{org} + 2QCl_{aq}$$

However, the following reactions may also be taking place:

$$4QL_{org} + MgCl_{2aq} \rightarrow L_2MgQ_{2org} + 2QCl_{aq}$$

$$3QL_{org} + MgCl_{2aq} \rightarrow L_2MgQ_{org} + 2QCl_{aq}$$

The loaded organic phase can then be stripped of magnesium values by contacting the same with acid-ie. aqueous acidic solutions. This can be illustrated (in the simplest form) by the following equation:

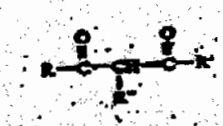
$$L_2Mg_{org} + 2QCl_{aq} + 2HCl_{aq} \rightarrow 2LH_{org} + 2QCl_{aq} + MgCl_{2aq}$$

The concentrated magnesium values are then recovered from the aqueous phase by conventional techniques, especially electrodeposition. Following the stripping stage, the organic phase can again be neutralized as previously indicated to form the salt of the hydrogen ion exchange reagent and the quaternary ammonium compound, and the thus neutralized organic phase recycled for use for further magnesium extractions.

The entire process can be operated continuously as in past practices with the results being selective extraction of magnesium over calcium and the production of a relatively pure, concentrated magnesium containing solution (i.e. the stripping solution) from which magnesium can be recovered by conventional techniques. The equations given above are illustrative only and it will become apparent from the following description that several groups of hydrogen ion exchange agents can be used as well as various quaternary ammonium compounds, neutralizing solutions and the like.

The hydrogen ion exchange reagents usable in the present invention include β-diketones, fluorinated β-diketones, 8-hydroxyquinolines, chloro or bromo substituted 8-hydroxyquinolines, hydroxamides and mixtures thereof. All of such reagents have acceptable solubility of at least 2% by weight in the essentially water-immiscible organic solvents.

β-diketones desirably used in the present invention have the formula:



where r is phenyl or alkyl substituted phenyl, R' is alkyl, alkyl substituted phenyl or chloro substituted phenyl and R'' is H or —CN with the provison that: (1) when R is phenyl, R' is a branched chain alkyl group of at least seven carbon atoms and (2) when R is alkyl substituted phenyl, the number of carbon atoms in the alkyl substituent or substituents is at least 7 and at least one such alkyl substituent is branched chain. Compounds of this group are further described in MacKay and Kopicz U.S. patent application Ser. No. 381,432, filed Aug. 24, 1973 and the corresponding Belgian Pat. No. 819,130 which descriptions is incorporated herein by reference.

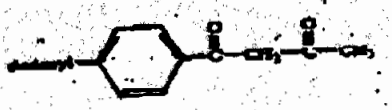
The said diketones of the aforementioned MacKay et al. application are prepared by known techniques. A preferred procedure is that generally described by Swamer and Hauser in J. Amer. Chem. Soc., 72, 1352 (1950). Thus a lower alkyl ester is condensed with a compound containing an acetyl moiety in the presence of sodium hydride and an inert organic solvent. Typical inert organic solvents are diethyl ether and tetrahydrofuran.

The said diketone preparations can be further described by the following examples.

EXAMPLE A

A dispersion of 16.9 g. (0.4 mole) of 57% by weight sodium hydride in mineral oil was washed with n-pentane under nitrogen and the supernatant liquid was removed by suction through a sintered glass tip tube. The process was repeated three times before 300 ml. of

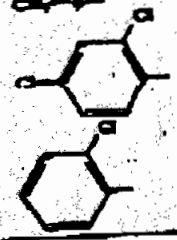
dry diethyl ether was added at once. The mixture was stirred and 35.2 g. (0.4 mole) of ethyl acetate was rapidly added. Then about 2 mL of dodecylacetophenone (the dodecyl group is branched chain and was derived from tetrapropylene via alkylation therewith) was added to the slurry. No gas evolution was indicated on a wet test meter, so two drops of absolute ethanol were added. After about an hour, vigorous gas evolution occurred and the remaining dodecylacetophenone was added as a 25% by weight solution in diethyl ether. The total ketone added was 57.4 g. (0.2 mole) and the addition was performed at such a rate as to maintain solvent reflux. When the addition was complete, the mixture was stirred until gas evolution ceased—1 to 2 hours. Another 150 mL diethyl ether was added and the excess sodium hydride was neutralized by the careful addition of absolute ethanol. When the sodium hydride failed to react, the reaction mixture was poured onto a mixture of ice and conc. hydrochloric acid with vigorous stirring. The phases then were separated and the upper organic phase was washed twice with water, once with 10% sodium bicarbonate, and finally once with water. After drying over anhydrous magnesium sulfate, the solvent was distilled under reduced pressure. The product distilled at 96°–160° C. (0.5 mm. Hg.) and 39.2 g. of product was obtained (yield of 59%). The β-diketone product had the following structure (confirmed by its infrared spectrum):



The generalized reaction for preparing the diketones is as follows:

Examples B–K were carried out in essentially the same manner as Example A with the reactants, mole ratios and solvents set forth in the following Table A:

Table A

Example	R	R'	R''	Mole Ratio $R''CH_2R'$	Mole Ratio $R'CO_2R''$	NaH	Solvent	% Yield	B.P. °C
A	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
B	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
C	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
D	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
E	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
F	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
G	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
H	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
I	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
J	$C_{12}H_{25}$—	$C_{12}H_{25}$—	C_2H_5	0.5	1.0	1.0	Et_2O	59	150–160 (0.5 mm.)
K	$C_{12}H_{25}$—		C_2H_5	0.77	0.87	1.33	Et_2O	71	233–250 (13–35 mm.)[2]

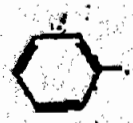
[1]The acyl group is $(CH_3)_2CHCH_2CH(CH_3)CH_2$— and is derived from Isovaleric Acid (Aldrich Chemical Corp.)

[2]The bowl group is a mixture of isomeric dodecyl acetyl groups and is derived from Neodecanoic Acid (American Hoechst Corp.) which proved to be satisfactory shown in a vpt distillation. The particular distillation conditions recorded from Isovaleric Acid (Eastman Kodak Co.) - A mixture of isomeric, branched C_{12} acids.

[3]The second group is that obtained from alkylation of benzene with tripropylene.

[4]The highest yield in these distillations during the recovery of materials which distillable was with on the reaction solvent. Multiple-film still distillation.

[5]The symbol "Ar" designates a benzene ring.



and all alkyl groups are primarily in the para position.

EXAMPLE L

A dispersion of 16.9 (0.4 mole) of 57% by weight sodium hydride in mineral oil was slurried with n-pentane under nitrogen and the dispersing liquid was removed by suction through a sintered glass tip tube. The process was repeated three times before 500 mL of dry diethyl ether was added at once. The mixture was slurried and 40.8 g. (0.2 mole) of methyl dodecylbenzene (the dodecyl group is as obtained in the alkylation of benzene with tetrapropylene) was rapidly added. Then 20.0 g. (0.02 mole) of pinacolone and two drops of methanol were rapidly added. Only a slow evolution of gas was observed on the wet test meter. After three days of continuous stirring, 7.5 L of gas was evolved and the remaining sodium hydride was neutralized by the careful addition of absolute ethanol. When no further reaction was observed, the mixture was poured onto a mixture of ice and concentrated hydrochloric acid with vigorous stirring. The phases then were separated and the upper organic phase was washed twice with water, once with 10% sodium bicarbonate, and finally once with water. After drying over anhydrous magnesium

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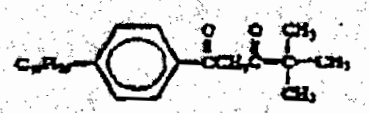
sulfate, the solvent was distilled under reduced pressure. The product distilled at 110°-180° C. (0.3 mm. Hg.) and 54.1 g. of product was obtained. The infrared spectrum and gas-liquid chromatograph of the distillate indicated that 70% of it had the following structure.

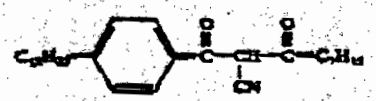


while the remainder was mostly methyl dodecylbenzoate.

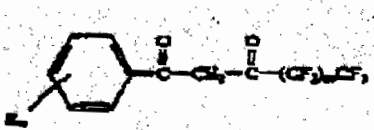
EXAMPLE M

A solution of 80.6 g. (0.195 mole) of the β-diketone of Example C in 1 l. of cyclohexane was shaken with an equal volume of aqueous solution containing 0.2 M copper sulfate, 0.5 M ammonia, and 0.5 M ammonium carbonate. After a few minutes of shaking, the phases were separated and the organic phase was shaken again with fresh aqueous solution. After phase separation, the copper rich organic phase was dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration.

A stream of cyanogen chloride gas was slowly bubbled through the solution of copper-β-diketone complex. Copious quantities of solids were precipitated during the addition. The reaction was followed by infrared spectroscopy and when the ratio of absorbances at 1615 cm^{-1} to 2220 cm^{-1} became constant at about 2.1, the addition was terminated. The time of addition was about two hours. A portion of the reaction mixture was clarified by filtration, the remainder was centrifuged. After decanting the supernatant, it was combined with the filtrate and washed twice with 3 N sulfuric acid. The organic phase was then dried over anhydrous sodium sulfate. The solvent was removed by distillation under reduced pressure leaving 79.5 g. (99% yield) of residue. A GLC analysis of the product indicated that it was at least 97% pure and infrared analysis confirmed the following structure:

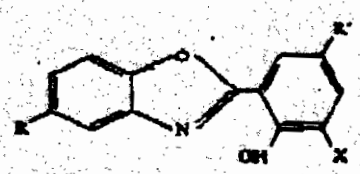


Fluorinated β-diketones also find use in the invention, such compounds having the formula:



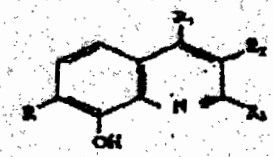
where n is a whole integer of 1 to 4, m is 0, 1 or 2 and R is an alkyl group of 1–25 carbons. Fluorinated β-diketones are variously described in U.S. Pat. Nos. such as 2,916,349; 2,632,763; 2,830,066; etc.

Another group of hydroxon ion exchange agents useful in the present invention are benzoxazoles of the formula:

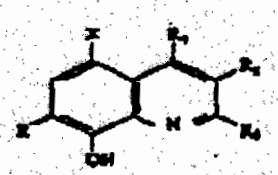


where R is hydrogen or an alkyl group having from 1 to 20 carbon atoms, R' is hydrogen, chlorine or an alkyl group containing from 1 to 20 carbon atoms, X is H or chlorine and the total number of carbon atoms in R and R' is 6 to 40 with the proviso that one of R and R' must be an alkyl group of at least 4 carbon atoms. These compounds are further described in MacKay and Regier U.S. patent application Ser. No. 518,011, filed Oct. 25, 1974 which description is incorporated herein by reference.

Substituted β-hydroxyquinolines also find use in the invention. The basic structure of these compounds is



where R is a branched chain alkyl or alkenyl radical containing about 8 to 20 carbon atoms and R_1, R_2 and R_3 are hydrogen or alkyl groups of 1 to 4 carbon atoms. The corresponding 5-chloro or bromo compounds of the formula



are also useful in the invention and are described in Mattison U.S. patent application Ser. No. 447,629, filed Mar. 4, 1974 which description is incorporated herein by reference.

The 7-alkenyl substituted compounds of the said Mattison application may be prepared by reacting 5-chloro (or bromo) -8-hydroxyquinoline with an alkenyl chloride in the presence of sodium hydroxide and dimethylsulfoxide with subsequent heating. The 7-alkyl substituted compounds of the said Mattison application are desirably prepared by reacting 8-hydroxyquinoline with an alkenyl chloride in the presence of sodium hydroxide and the dimethylsulfoxide solvent (heating to rearrange as above). The product is then hydrogenated and chlorinated or brominated. The compounds wherein R_1, R_2, or R_3 are alkyl are desirably prepared by reacting 2-amino-4-chloro (or bromo) phenol with an α,β-unsaturated aldehyde in the presence of 2-nitro-4-chloro (or bromo) phenol, ferrous sulfate and sulfuric acid. Such R_1, R_2, or R_3 substituted 5-chloro (or bromo)-8-hydroxyquinoline is then reacted as above with an alkenyl chloride. The details of these reactions are further set forth in the examples to follow.

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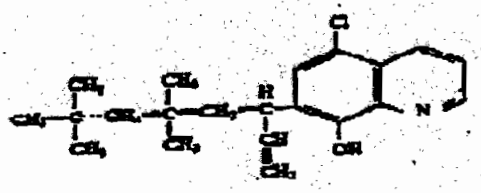
EXAMPLE N

Five hundred ml. dimethyl sulfoxide, 179 gm. (1.0 mole) 5-chloro-8-hydroxyquinoline, 40 gm. sodium hydroxide and 243 gm. (1.2 Mole) dodecenyl chloride (5,5,7,7-tetramethyl-1-chloro-2-octene available from Rohm & Haas) were combined with stirring in that order in a one liter round bottom flask. Stirring was continued overnight at 70° C. (18 hr.). Five hundred ml. H_2O and 500 ml. Skellysolve B (a normal hexane solvent) were added and the mixture shaken. The aqueous layer was extracted with another 250 ml. Skellysolve B. The total organic layer was washed to pH 5 with water and then with about 1 liter Claisen's alkali (in portions). It was again washed with H_2O until neutral and then with aqueous NaCl and dried. The product was stripped of solvent to yield 369.3 gm. of a dark oil. Of this amount, 365.3 gm. was distilled through a one foot Vigreux column. A 231.8 gm. fraction distilling off between 160°–170° C. at .06 mm Hg consisted in excess of 97% of 5-chloro-7-dodecenyl-8-hydroxyquinoline having the structure:



EXAMPLE O

Part A — Preparation of 7-dodecenyl-8-hydroxyquinoline.

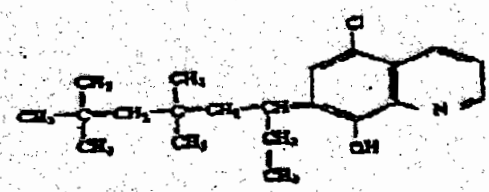
One hundred forty five grams (1.0 mole) 8-hydroxyquinoline, 40 gm. sodium hydroxide, 500 ml. methanol and 5 gm. potassium iodide were combined in a two liter round bottom flask. To this was added 243 gm. dodecenyl chloride (as used in Example D) and the mixture stirred under reflux overnight. The product was filtered, taken up in ether and washed with 500 ml. Claisen's alkali (in five portions). The ether solution was washed several times with water until neutral, dried and the solvent stripped to yield 317.9 gm. of crude product. Of this amount, 310.9 gm. was distilled through a one foot Vigreux after being heated in the pot to 230° C. and cooled to about 100° C. The fractions coming off at 197°–202° C., 0.7 mm. Hg. (51.1 gm.) and 202°–251° C., 0.8 mm. Hg. (96.8 gm.) consisted almost entirely of 7-dodecenyl-8-hydroxyquinoline.

Part B — Hydrogenation of 7-dodecenyl-8-hydroxyquinoline.

Ten grams 7-dodecenyl-8-hydroxyquinoline were dissolved in 90 ml. 95% ethanol and 1.0 gm. hydrogenation catalyst (palladium on carbon) was added. This was charged to a Parr Bomb which was degassed and charged to 35 psig with H_2. The pressure fell to 14 psig in 16 min. and was then repressurized to 29 psig. Over 1½ hours this fell to 19.5 psig. The reactor was degassed at aspirator vacuum, N_2 bled in and the mixture filtered giving a plum purple solution. Solvent stripping left 9.0 gm. of product which was a dark oil. Infrared analysis showed the product to be 7-dodecyl-8-hydroxyquinoline.

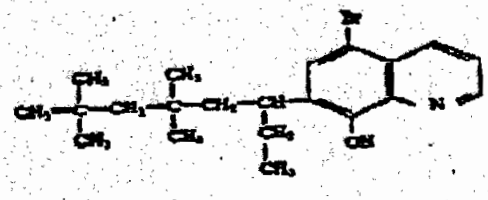
Part C — Chlorination of 7-dodecyl-8-hydroxyquinoline.

Forty five grams (0.144 mole) 7-dodecyl-8-hydroxyquinoline prepared as in Part B was dissolved in 180 ml. methanol (absolute) at 25° C. and then 12.8 gm. Cl_2 (0.180 mole) was bubbled in over ½ hr. at 21°–25° C. with good stirring. Stirring was continued 30 min. and the solvent stripped on a rotary evaporator. The residue was taken up in ether and washed with H_2O to pH 5, dried and the ether stripped. The residue weighed 48.3 gm. of which 43 gm. was recrystallized from absolute ethanol giving 24.5 gm. of gold colored platelets (m.p. 88.5°–90° C.). The product was 5-chloro-7-dodecyl-8-hydroxyquinoline having the structure:



EXAMPLE P

To 5.0 gm. 7-dodecyl-8-hydroxyquinoline as prepared in Part B of Example O dissolved in 12 ml. methanol was added 2.56 gm. Br_2 over a ten minute period at 25°–30° C. with stirring. The solution was stirred for an additional hour at 25° C. and was then taken up in ether and washed with water to pH 5. The product solution was further washed with saturated aqueous NaCl, dried and the ether stripped to give 6.0 gm. of a brown solid. The 5-bromo-7-dodecyl-8-hydroxyquinoline had the structure:



EXAMPLE Q

Example N was essentially repeated using triisobutenyl chloride in place of the indicated dodecenyl chloride. The triisobutenyl chloride was prepared as follows. To a two liter, three neck round bottom flask equipped with a stirrer, dry ice condenser and a gas inlet tube was charged 700 g. (4.16 mole) triisobutylene (available from Eastman Kodak). The flask was heated to 95° C. and 266 gm. (3.75 mole) Cl_2 was added over 3½ hr. at 95°–105° C. The reaction mixture was cooled overnight and then distilled through a 1 ft. Vigreux column. The product obtained from the triisobutylene chloride had the structure:

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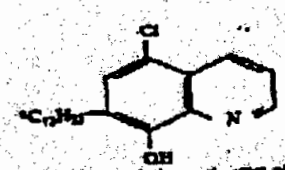
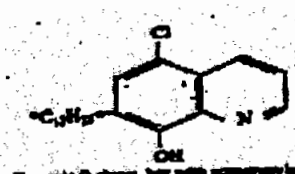


*The $C_{12}H_{25}$ radical is highly branched, the exact nature of the branching being dependent on the particular starting chemical (isobutylene) and conditions of its preparation.

EXAMPLE R

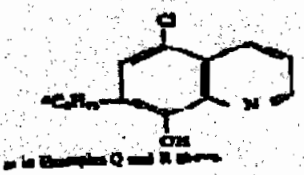
Example Q was essentially repeated using tetrapropenyl chloride in place of the indicated dodecenyl chloride of Example N. The tetrapropenyl chloride was prepared as follows: Into the reaction flask was charged 1000 gm. (5.91 mole) tetrapropylene (available from Enjay Chemical). The flask was heated to 95° C. and 377 gm. (5.37 mole) Cl_2 was added over three hours at 95°–100° C. The product was distilled through a 1 ft. Vigreaux column. The product had the structure:



*Same compound as Example Q above, but with tetrapropylene

EXAMPLE S

Example Q was essentially repeated using diisobutenyl chloride in place of the indicated dodecenyl chloride of Example N. The diisobutenyl chloride was prepared as follows: Into the reaction flask was charged 1000 g. (8.91 mole) of diisobutylene. The flask was heated to 95° C. and the Cl_2 (566 gm., 7.98 mole) was added over 5 hours at 95°–100° C. The product was then distilled through a 1 ft. Vigreaux column. The product had the following structure:

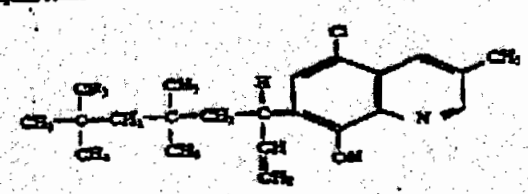


*Same isomer as in Examples Q and R above.

EXAMPLE T

Into a one liter, three neck round bottom flask fitted with a stirrer, condenser and thermometer was charged 72 gm. (0.5 mole) 2-amino-4-chlorophenol, 43.4 gm. (.25 mole) 2-nitro-4-chlorophenol, 5 gm. ferrous sulfate and 70 ml. sulfuric acid (conc.). This mixture was heated to 140° C., the thermometer was replaced with an addition funnel and 112 gm. (1.6 mole) methacrolein was added dropwise over 40 min. so as to maintain moderate reflux (initial temp. 140° C., 80° C. at completion of addition). The reaction mixture was refluxed for four hours, water was added and excess 2-nitro-4-chlorophenol was steam distilled off. The solids recovered from the neutralized (50% KOH solution followed by saturated Na_2CO_3) pot residue were dissolved in 1.4 liter of methanol and filtered to remove insoluble tars. After stripping the methanol, the residue was extracted with hot 10% HCl, filtered to remove solids, and the solids were twice treated with hot acid. The combined acid solutions were washed twice with chloroform, neutralized (KOH-Na_2CO_3 solutions as above) and the resulting precipitate was filtered off and air-dried. This material was dissolved in ether, filtered and evaporated to give 15.7 g. of crude product. Crystallization of a portion from ether - petroleum ether gave white needles, m.p. 125°–127° C.

The procedure of Example N was essentially repeated using 15.7 gm. (0.08 mole) 3-methyl-5-chloro-8-hydroxyquinoline as above prepared in place of the 5-chloro-8-hydroxyquinoline and 20 gm. of dodecenyl chloride. The product, 3-methyl-5-chloro-7-dodecenyl-8-hydroxyquinoline had the structure:

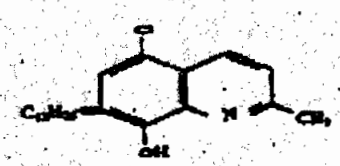


EXAMPLE U

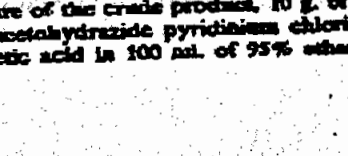
Example N was essentially repeated using 2-methyl-8-hydroxyquinoline in place of 5-chloro-8-hydroxyquinoline. The resultant 2-methyl-7-dodecenyl-8-hydroxyquinoline was hydrogenated by the procedure of Example O, Part B to give 2-methyl-7-dodecyl-8-hydroxyquinoline.

Chlorination: A stirred suspension of 23.7 g. (0.073 mole) of 2-methyl-7-dodecyl-8-hydroxyquinoline in 100 ml. of methanol was maintained at 0°–5° C. during the addition of a solution of 5.3 g. (0.074 mole) of Cl_2 in 100 ml. of methanol over 5–10 min. After addition was complete, the mixture was stirred at 0° C. for 1 hr., then at room temperature overnight.

The mixture was poured into an ice-cold $NaHCO_3$ solution (final aq. pH 7–8) and extracted with ether. The extract was washed with water, dried over $MgSO_4$, filtered and evaporated to give 19.3 g. of product containing



plus a carbonyl-containing impurity (probably

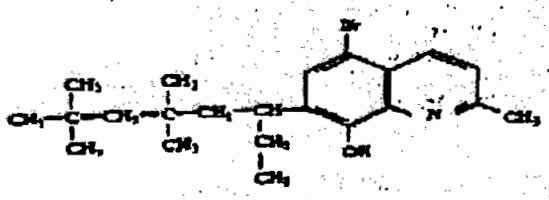


A mixture of the crude product, 10 g. of Girard's P reagent (acetohydrazide pyridinium chloride) and 10 ml. of acetic acid in 100 ml. of 95% ethanol was re-

stained for 45 min., cooled and neutralized with saturated Na_2CO_3 solution. After addition of water and ether extraction the extract was washed with water, dried over $MgSO_4$, filtered and evaporated to give 15.6 g. of product as a clear red oil.

EXAMPLE V

Example U was essentially repeated except that Br_2 was used in place of Cl_2. The product, 2-methyl-5-bromo-7-dodecyl-8-hydroxyquinoline had the structure:

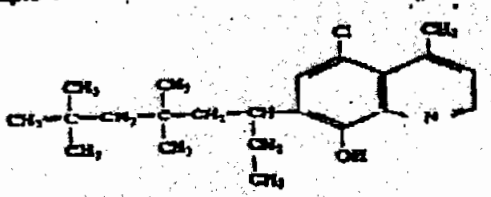


EXAMPLE W

Example U was essentially repeated except that 4-methyl-8-hydroxyquinoline was used in place of 2-methyl-8-hydroxyquinoline. The 4-methyl starting material was prepared as follows: In a 1 liter 3 neck round bottom flask fitted with a stirrer, thermocouple, addition funnel and reflux condenser was placed 300 g. of polyphosphoric acid. The acid was heated to 90° C. and 109 g. (1.0 mole) of o-aminophenol was added over 2.5 hrs. in 7–8 portions with vigorous stirring. After addition was complete, the mixture was stirred at 90°–100° C. for 10 min., then 105 g. (1.5 mole) of methyl vinyl ketone was added portionwise over 1.5 hrs. With each addition the temperature rose to 120°–130° C. After addition was complete, the mixture was stirred at 110° C. for 45 min., then cooled to 70° C. and 200 ml. of water was added. The mixture was stirred at room temperature for 30 min., then allowed to sit overnight.

Volatile materials were steam-distilled off and the precipitate from the neutralized residue (50% KOH followed by saturated Na_2CO_3 solution) was filtered, washed with water and air-dried. The dried precipitate was triturated with chloroform, filtered, and the remaining solid (o-aminophenol) was washed with chloroform.

The combined chloroform solutions were washed with water, dried over $MgSO_4$, filtered and evaporated to give 74.8 g. of crude product. Crystallization from ethanol gave 58.2 g. of light brown solid, m.p. 137°–139° C., and an additional 9.1 g. was obtained by sublimation (130°–140° C. and 0.1 mm.) of the mother liquors. The product after alkylation and hydrogenation as in Example O followed by chlorination and purification as in Example U had the structure:



As indicated previously, the selected hydrogen ion exchange agents are neutralized with the quaternary ammonium salt. Quaternary ammonium salts are well known and a wide variety of the same may be used in the present invention. The cation proportion of such quaternary ammonium compounds can be illustrated as follows:

where R_1 is a hydrocarbon radical such as alkyl, alkenyl, aryl, alkaryl, arylalkyl and the like of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms. Representative anions X^- and X^- are chloride, bromide, iodide, sulfate, bisulfate and the like.

Representative of the above quaternary ammonium compounds are lauryltrimethyl ammonium chloride, myristyltrimethyl ammonium chloride, palmityltrimethyl ammonium choloride, lauryltrimethyl ammonium sulfate, myristyltrimethyl ammonium bromide, palmityltrimethyl ammonium iodide, stearyltrimethyl ammonium chloride, stearyltrimethyl ammonium sulfate, oleyltrimethyl ammonium chloride, oleylbutyldimethyl ammonium sulfate, dilauryldimethyl ammonium chloride, distearyldimethyl ammonium sulfate, trilaurylmethyl ammonium chloride, trioctylmethyl ammonium bromide, tridecylmethyl ammonium chloride, stearylbenzyldimethyl ammonium sulfate, oleylbenzyldiethyl ammonium chloride and the like.

The hydrogen ion exchange reagent, the quaternary ammonium salt, and the magnesium complex of the hydrogen ion exchange reagent must all be soluble in the essentially water-immiscible organic solvents to an extent of at least 2% by weight in order to practically recover metal values on a commercial scale. The organic solvents are preferably aliphatic or aromatic hydrocarbons such as the petroleum derived liquid hydrocarbons including kerosene, fuel oil, etc. In addition to the simple hydrocarbon solvents, chlorinated hydrocarbons may also be used. Accordingly, both the unsubstituted and the chlorinated solvents are contemplated by the term "liquid hydrocarbon".

It is essential in my process to use the salt of the selected hydrogen ion exchange agents and the quaternary ammonium compounds. This salt is prepared by dissolving the hydrogen ion exchange agent and the starting quaternary ammonium salt in the organic solvent and then neutralizing (i.e., removing inorganic acid therefrom) by washing with water or aqueous base. In use, the said salt will preferably be present in an amount of about 2 to 15% by weight in the solvent. Also, in continuous extraction processes, the quaternary ammonium salt of the hydrogen ion exchange reagent will be continuously regenerated as a separate step in the overall process subsequent to stripping of the magnesium loaded phase and prior to use for further extraction. The hydrogen ion exchange reagent and the starting quaternary ammonium compound will preferably be used in essentially equimolar amounts, although excesses of either in the nature of mole ratios of quaternary to reagent of about 3:5 to 7:5 have been found to not appreciably effect the degree of extraction or selectivity.

As indicated, the neutralization is carried out by water washing or with aqueous solutions of bases. The latter are preferred with representative bases being

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sodium bicarbonate, sodium hydroxide, sodium carbonate, potassium hydroxide, calcium hydroxide, potassium carbonate, ammonia or ammonium hydroxide, and the like. For some of the selected hydrogen ion exchange reagents, it may be necessary to use a strong base such as sodium hydroxide in preference to sodium bicarbonate for example.

In its general aspects, the magnesium recovery process of the present invention comprises contacting an aqueous magnesium and calcium containing solution with an organic solvent solution of the quaternary ammonium salt of the selected hydrogen ion exchange reagent to extract at least a portion of the magnesium values into the organic phase, separating the magnesium pregnant organic phase from the aqueous phase and stripping at least a portion of the magnesium values from the organic phase by contacting same with an acid stripping agent. In most, if not all, commercial operations, the organic phase must be regenerated for economic purposes. As such, the process of the invention will then comprise the steps of neutralizing the stripped organic phase and recycling the organic phase for contacting further quantities of the magnesium and calcium containing aqueous solution. The phase ratios in these steps can be varied widely as it will be apparent that the contacting, for example, of any quantity of the organic phase with the aqueous magnesium and calcium containing phase will result in extraction of magnesium into the organic phase. However, for commercial practicality, the various organic:aqueous phase ratios are preferably in the range of 10:1 to 1:10. After for practical purposes, the extractions (and stripping and neutralization) are normally carried out at ambient temperatures and pressures.

The magnesium loaded organic is preferably stripped using acid stripping mediums which are desirably aqueous such as aqueous sulfuric acid, hydrochloric acid and the like. The starting magnesium and calcium containing solution has a pH of from about 4 to 12, and preferably from about 6 to 9. The optimum pH will vary depending especially upon the particular extractant salt being used therefor.

In order to achieve enhanced selectivity of magnesium extraction over calcium, it is necessary that some magnesium values remain in the starting aqueous solutions after the extraction step. In this regard, the concentration of the quaternary ammonium salt of the selected hydrogen ion exchange reagent in the organic phase and/or the organic:aqueous phase ratios and/or contact times will be so controlled as to extract less than 100% of the magnesium values. When the starting aqueous solution is depleted of magnesium values, significant calcium extraction occurs. This is of course undesirable.

The following Examples illustrate preferred embodiments of the invention without being limiting:

EXAMPLE I

Organic solutions containing equal molar concentrations of selected hydrogen ion exchange reagents and starting quaternary ammonium compound in an aromatic petroleum solvent (Aromatic 150 available from Exxon) were first prepared. The starting quaternary (Aliquat®336) was a trialkyl monomethyl ammonium chloride wherein the alkyl groups contained 8 and 10 carbons, such alkyl groups being straight chained and randomly distributed in the quaternary cation. These organic solutions were then mixed with equal volumes of aqueous base (5% wt./vol.) for 60 minutes with shaking to form the salts of the quaternary and the selected hydrogen ion exchange reagents. After phase separation, the respective organic solutions were contacted with shaking for a period of one hour with an equal volume of a synthetic sea water solution of the following composition: 1.40 g/l. Mg^{++}, 0.37 g./l. Ca^{++}, 12.0 g./l. Na^{+}, 0.5 g./l. K^{+}, 21.6 g./l. Cl^{-}, 5.6 g./l. Br^{-}, pH 6.6 (such solution was made up by dissolving 11.4 g. of $MgCl_2.6H_2O$, 1.4 g. of $CaCl_2.2H_2O$, 26.8 g. of NaCl, 7.2 g. of NaBr and 0.9 g. of KCl in distilled water to a volume of one liter). After the above contacting, the phases were separated and the organic and aqueous layers were analyzed for magnesium and calcium by atomic absorption. The results of these extractions are given in Table 1.

Table 1

Hydrogen Ion Exchange Agent	Molar conc.	Base Used to Neutralization	Organic (ppm) Mg^{++}	Organic (ppm) Ca^{++}	Aqueous (ppm) Mg^{++}	Aqueous (ppm) Ca^{++}
[illegible][1]	.05	$NaHCO_3$	334	1.1	1040	374
β-Diketone[2]	0.1	NaOH	443	1	—	—
1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione[3]	0.1	NaOH	710	1.3	820	400
1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione[4]	0.025	$NaHCO_3$	168	<0.5	1188	375
β-Diketone[2]	0.5	$NaHCO_3$	75	<0.5	1320	384
β-Diketone[2]	0.1	NaOH	680	0.8	680	410

[1] 1-phenyl-3-butyl-4,5-pyrazolidinedione wherein the methyl group in the para position was then derived from a synthetic alcohol mixture, Carbowax alcohol 26, in which the alkyl chain is branched and consists on average of 12 carbon atoms.

[2] 2-thenoyltrifluoroacetone

[3] 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione wherein the thienyl group is branched chain

[4] 1-phenyl-3-butyl-4,5-pyrazolidinedione wherein the butyl group is branched chain.

The magnesium loaded organic is preferably stripped using acid stripping mediums which are desirably aqueous such as aqueous sulfuric acid, hydrochloric acid and the like. The starting magnesium and calcium containing solution has a pH of from about 4 to 12, and preferably from about 6 to 9. The optimum pH will vary depending especially upon the particular extractant salt being used therefor.

In order to achieve enhanced selectivity of magnesium extraction over calcium, it is necessary that some magnesium values remain in the starting aqueous solutions after the extraction step. In this regard, the concentration of the quaternary ammonium salt of the selected hydrogen ion exchange reagent in the organic phase and/or the organic:aqueous phase ratios and/or contact times will be so controlled as to extract less than 100% of the magnesium values. When the starting aqueous

EXAMPLE II

The process of Example 1 was partially repeated except using only the fluorinated β-diketone at a concentration of 0.1M with various starting quaternary ammonium compounds (neutralization by $NaHCO_3$). The quaternaries used were as follows:

A. Dihydrogenated tallow dimethyl ammonium chloride (Aliquat®H226)

B. Dicocos dimethyl ammonium chloride (Aliquat®221)

C. Lauryl trimethyl ammonium chloride (Aliquat®4).

Results are set forth in the following Table 2.

Table 2

Quaternary	Organic (ppm) Mg++	Organic (ppm) Ca++	Aqueous (ppm) Mg++	Aqueous (ppm) Ca++
A	663	37	634	373
B	1057	46	970	339
C	798	21	711	301

EXAMPLE III

The process of Example I was partially repeated except using only the fluorinated β-diketone with varying concentrations of the salt prepared from said β-diketone and the starting quaternary ammonium compound (neutralization by $NaHCO_3$). Results are set forth in the following Table 3.

Table 3

Molar Concentration of Diketone-Quat Salt	Organic (ppm) Mg++	Organic (ppm) Ca++	Aqueous (ppm) Mg++	Aqueous (ppm) Ca++
1.0	1480	460	824	448
0.8	1378	395	813	425
0.6	1398	323	735	367
0.5	1335	282	675	328
0.4	1350	280	675	341
0.3	1350	278	818	334
0.2[a]	1338	256	788	324
0.1	443	54	288	167

[a]Shows that with the reagent salt and starting aqueous solution, selectivity of magnesium over calcium is optimized at 0.2M or lower.

EXAMPLE IV

The process of Example I was partially repeated except using only the fluorinated β-diketone and the salt thereof was prepared by neutralization (with the $NaHCO_3$ solution) of mixtures of varying quantities of 0.2M solutions of the diketone and the starting quaternary ammonium compound (there is more mixtures there is either an excess of the diketone or the starting quaternary ammonium compound). Fifty ml. of the synthetic sea water solution was contacted with the combined quantities of quaternary and diketone used in the neutralization step and as indicated in the following Table 4.

Table 4

Volume (ml) Used in 50% Neutralization Quaternary	Diketone	Organic (ppm) Mg++	Organic (ppm) Ca++	Aqueous (ppm) Mg++	Aqueous (ppm) Ca++
5	20	370	87	883	385
10	15	1144	276	1282	381
15	10	1315	325	1282	381
20	5	1480	460	1282	381
25	0	1378	395	1282	381
30	0	1398	323	1282	381
35	0	1335	282	1282	381
40	0	1350	280	1282	381
45	0	1350	278	1282	381
50	0	1338	256	1282	381

EXAMPLE V

Extraction kinetics were studied by partially repeating Example I except using only the fluorinated β-diketone and quaternary at concentrations of 0.1M. Samples were removed at various time intervals and the organic phases were analyzed for magnesium and calcium. Results are set forth in Table 5 which follows.

Table 5

Time, min.	Organic (ppm) Mg++	Organic (ppm) Ca++
1	236	167
2	328	121
3	376	86
4	467	33
5	551	11.5
6	569	2.0

The above data indicate that calcium is initially extracted but is subsequently displaced from the organic phase by magnesium.

EXAMPLE VI

Portions of a loaded organic prepared as in the Examples above containing 650 ppm Mg++ were shaken for one hour with 5% aqueous hydrochloric acid at various organic:aqueous phase ratios. The separated organics were then analyzed for magnesium. Results are set forth in the following Table 6.

Table 6

O/A Ratio	Mg++ (ppm) Organic
10/10	650
10/8	650
10/6	650
10/4	650
10/2	650
10/1	650

The above data illustrate that essentially complete stripping of magnesium is possible with dilute hydrochloric acid even at high O/A phase ratios. The loaded organic as above described was also readily stripped by sparging with HCl gas. In each case, a precipitate formed which was found to be $MgCl_2.6H_2O$ with less than 1% sodium and calcium present. Analysis of the stripped organic showed no magnesium remaining.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

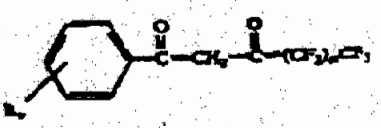
1. The process of selectively recovering magnesium from an aqueous solution thereof which also contains calcium ions which comprises contacting said solution with a solution of a quaternary ammonium salt of a hydrogen ion exchange reagent in an essentially water-immiscible organic solvent to extract at least a portion of but less than 100% of the magnesium values into the organic phase, separating the magnesium loaded organic phase from the aqueous phase and stripping magnesium from the organic phase, said hydrogen ion exchange reagent being selected from the group consisting of:

A. β-diketones having the formula

where R is phenyl or alkyl substituted phenyl, R' is alkyl, alkyl substituted phenyl or chloro substituted phenyl and R'' is H or — CN with the provisos that (1) when R is phenyl, R' is a branched chain alkyl group of at least seven carbon atoms and (2) when R is alkyl substituted phenyl, the number of carbon atoms in the alkyl substituent or substituents is at

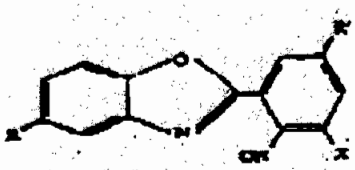
least 7 and at least one such alkyl substituent is branched chain;

B. fluorinated β-diketones having the formula



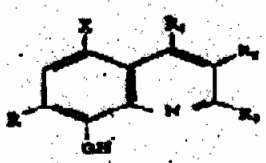
where n is a whole integer of 1 to 4, m is 0, 1 or 2 and R is an alkyl group of 1–25 carbon atoms;

C. benzoxazoles having the formula



where R is hydrogen or an alkyl group having from 1 to 20 carbon atoms, R' is hydrogen, chlorine or an alkyl group containing from 1 to 20 carbon atoms, X is H or chlorine and the total number of carbon atoms in R and R' is 6 to 40 with the proviso that one of R and R' must be an alkyl group of at least 6 carbon atoms; and

D. 8-hydroxyquinolines of the formula



where R is a branched chain alkyl or alkenyl radical containing about 8 to 20 carbon atoms, R_1, R_2 and R_3 are hydrogen or alkyl groups of 1 to 4 carbon atoms and X is H, chlorine or bromine.

2. The process of claim 1 wherein the hydrogen ion exchange reagent is a fluorinated β-diketone (B).

3. The process of claim 2 wherein the fluorinated β-diketone (B) is 1-dodecylphenyl-3-trifluoromethyl-1,3-propanedione.

4. The process of claim 1 wherein the magnesium is stripped using an acid stripping medium.

5. The process of claim 4 wherein the acid stripping medium is an aqueous solution of an acid selected from sulfuric and hydrochloric acid.

6. The process of claim 1 wherein the magnesium and calcium containing aqueous solution has a pH of from about 4 to 12.

7. The process of claim 6 wherein the solution has a pH of from about 4 to 9.

8. The process of claim 1 wherein the quaternary ammonium salt of the hydrogen ion exchange reagent is present in the essentially water-immiscible organic solvent in an amount of about 2 to 15% by weight.

9. The process of claim 1 wherein the essentially water-immiscible organic solvent is a liquid hydrocarbon.

10. The process of claim 1 wherein quaternary ammonium cation of the salt of the hydrogen ion exchange reagent has the formula:

where R_1 is a hydrocarbon radical of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms.

11. The process of claim 1 wherein the salt is prepared by the neutralization of the hydrogen ion exchange reagent with the starting quaternary ammonium compound in a mole ratio of the latter to the former of about 3:5 to 7:5.

12. The process of claim 1 wherein the stripped organic phase is separated from the acid stripping medium, neutralized to reform the quaternary ammonium salt of the hydrogen ion exchange reagent and recycled for contacting further quantities of the magnesium and calcium containing aqueous solution.

13. The process of claim 1 wherein the hydrogen ion exchange reagent is a fluorinated β-diketone (B), the essentially water-immiscible organic solvent is a liquid hydrocarbon, the pH of the magnesium and calcium containing aqueous solution is from about 6 to 9 and the stripping medium is aqueous sulfuric acid.

* * * * *

United States Patent [19]
MacKay et al.
[11] 4,058,585
[45] Nov. 15, 1977

[54] SOLVENT EXTRACTION OF METALS FROM ACIDIC SOLUTIONS WITH QUATERNARY AMMONIUM SALTS OF HYDROGEN ION EXCHANGE AGENTS

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[21] Appl. No.: 630,600

[22] Filed: Nov. 10, 1975

[51] Int. Cl.² C01G 3/00; C01G 9/00; C01G 51/00; C01G 53/00

[52] U.S. Cl. ..... 423/24; 423/100; 423/139; 423/157; 252/182; 260/307 D; 260/566 A; 260/567.6 M; 260/270 Q; 260/501.15; 260/287 XA

[58] Field of Search ..... 423/24, 100, 139, 157; 260/567.5, 567.6 R, 287 O, 307 D, 566 A, 586 R, 468 H, 924, 567.6 M, 270 O, 501.15; 75/101 BE

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[57] ABSTRACT

Process of extracting metals using organic solvent solutions of salts of hydrogen ion exchange agents and quaternary ammonium compounds. Organic solvent solutions of such quaternary ammonium salts of hydrogen ion exchange agents.

14 Claims, No Drawings

517 638-9331

SOLVENT EXTRACTION OF METALS FROM ACIDIC SOLUTIONS WITH QUATERNARY AMMONIUM SALTS OF HYDROGEN ION EXCHANGE AGENTS

This invention relates to the recovery of metal values from aqueous acidic solutions thereof. More particularly, it relates to such a process using hydrogen ion exchange reagents with an improved procedure for controlling pH and to the new compositions providing such improved procedure.

Liquid ion exchange recovery of metal values from their aqueous solutions has become increasingly important in the commercial production of high quality metal on a large scale. These exchange recovery systems generally involve contacting the aqueous metal containing solution with an exchange reagent dissolved in an essentially water-immiscible organic solvent whereby at least part of the metal values are transferred to the organic phase, separating the metal pregnant organic phase from the aqueous phase and then contacting the metal pregnant organic phase with an aqueous stripping solution to transfer the metal values to the stripping solution. The net effect is generally to arrive at a more concentrated metal containing solution (i.e. the metal pregnant strip solution) from the starting relatively dilute metal containing aqueous solution. The metal pregnant strip solution is of controllable composition or purity and the metal values can be directly recovered therefrom, most generally by electrolysis. The entire process is generally continuous with recycle of the stripped organic phase for contacting further quantities of metal containing aqueous solutions. Counter-current, multiple stage extractions are generally included in these continuous circuits.

Various metal values are optimally extracted at defined pH ranges using particular hydrogen ion exchange reagents. In this respect, the entire system will be designed around the use of a particular liquid ion exchange reagent optimally operable with a designated pH range for the specific metal involved. Thus the pH of the aqueous leach solution will be altered if necessary to fall within the optimum extraction range. In this respect, acid or base may be added to bring the pH into the desired range.

Despite the above initial pH adjustment, an additional problem is often encountered. Thus the acidity of the solution being extracted is progressively increased (i.e. the pH is lowered) by the exchange of metal ions in the solution for hydrogen ions on the liquid ion exchange reagent as the process proceeds. This can cause loss of efficiency as the pH of the solution being extracted drops below the optimum range for the particular hydrogen ion exchange reagent and metal being extracted. One prior procedure used in attempting to attack this problem has been the addition of alkaline reagents, such as ammonia, lime or the like, to neutralize the forming acid. This can require careful monitoring. Additionally, such neutralization increases the overall cost of the recovery process due to the cost of the neutralizing reagents which are added and also because of the loss of acid through said neutralizing.

A more recent suggested procedure is that of U.S. Pat. No. 3,876,106 to Wayne C. Hazen. In the process suggested in this patent, the acidity of the leach solution is controlled during the process by contacting same with a solvent extractant for the acid when the acidity of the leach solution has reached a point at which the recovery of metal ions is no longer efficient. The Patent discloses that long chain secondary and tertiary amines are preferred extractants for the hydrogen ions. The acid can be stripped from this amine extractant solution and the latter then reused. The water strip containing acid can then be used for further ore leaching if desired. This process thus involves an additional step for treating the leach solution as well as the step of recovering acid from the amine containing solvent extractant. If the latter were not carried out, substantial increased costs could be incurred due to loss of amine and the solvent therefor.

We have now discovered a new procedure for avoiding a decrease in aqueous pH during extraction and compositions useful in this improved process. Our process employs a solution of a salt of a hydrogen ion exchange agent and a quaternary ammonium compound in an essentially water-immiscible organic solvent. Such salts can be formed by washing the corresponding solution of the hydrogen ion exchange reagent and the quaternary ammonium compound with water or aqueous bases. Such neutralization or salt formation step can be illustrated by the following equation (when a base is used):

$$LH_{org} + QX_{org} + B_{aq} \rightarrow QL_{org} + BHX_{aq}$$

where L is the anion of the hydrogen ion exchange agent, Q is the quaternary ammonium cation, X is the inorganic anion of the starting quaternary ammonium compound and B is the base. This can be further illustrated in respect of the use of a specific base as follows:

$$2LH_{org} + Q_2X_{org} + 2NaHCO_{3aq} \rightarrow 2QL_{org} + Na_2X_{aq} + 2CO_2$$

This formed salt solution is then used to contact the acidic aqueous metal containing solution to extract at least part of the metal values into the organic phase. The extraction step can be illustrated by the following equation:

$$2QL_{org} + MX_{aq} \rightarrow L_2M_{org} + Q_2X_{aq}$$

where M is a divalent cation (e.g., Ni^{++}, Co^{++}) and X is a divalent anion (e.g., SO_4^{--}). From this equation, it is readily apparent that there is no net transfer of hydrogen ions (protons) from the organic phase to the aqueous phase during the extraction. Accordingly, pH decrease is eliminated by our process.

The loaded organic phase can then be stripped of metal values by contacting same with aqueous acidic solutions. This can be illustrated by the following equation:

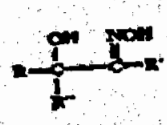
$$L_2M_{org} + Q_2X_{org} + H_2X_{aq} \rightarrow 2LH_{org} + Q_2X_{aq} + MX_{aq}$$

The metal values are then recovered from the aqueous phase by conventional techniques, especially electrodeposition. Following the stripping stage, the organic phase can again be neutralized by washing as previously indicated to form the salt of the hydrogen ion exchange reagent and the quaternary ammonium salt and the thus neutralized organic phase recycled for use for further metal extractions. Where the neutralization is effected by water washing, the wash solution will be acidic and

can be used for leaching purposes. The entire process can be operated continuously as in past practices except that in the process of the invention, pH reduction on extraction is eliminated making certain extractions feasible and/or more efficient in some cases and processing flexibility is increased. The equations given above are illustrative only and it should be clearly evident that the invention has a general application to hydrogen ion exchange reagents and quaternary ammonium salts which are soluble in essentially water-immiscible organic solvents, extractable metal values, neutralizing solutions and acid stripping mediums.

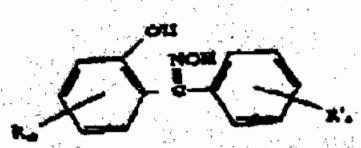
A wide variety of hydrogen ion exchange reagents can be used in the present invention. These reagents are capable of being deprotonated by reaction with the quaternary ammonium salts. Representative of various of these hydrogen ion exchange reagents are α-hydroxy oximes, benzophenoximes, β-diketones, fluorinated β-diketones, benzoxazoles, 8-hydroxyquinolines, organo phosphoric acids, naphthenic acids and the like. A number of these groups of reagents are described in more detail hereinbelow.

The α-hydroxy oximes have the following general formula:

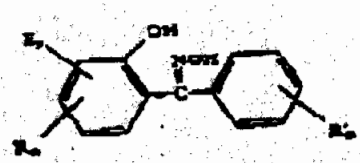


where R, R' and R'' may be any of a variety of organic hydrocarbon radicals such as aliphatic and alkylaryl radicals. R'' may also be hydrogen. These compounds are further described in Swanson U.S. Pat. No. 3,224,873 which description is incorporated herein by reference.

Benzophenoximes useful in the present invention may have the formula:



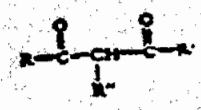
in which R and R' may be individually alike or different and are preferably saturated aliphatic groups and m and n are 0, 1, 2, 3 or 4 with the proviso that m and n are not both 0. The total number of carbon atoms in R_m and R'_n is from 3-25. R and R' contain 1-25 carbon atoms. These compounds are further described in Swanson U.S. Pat. No. 3,592,775 which description is incorporated herein by reference. 2-Hydroxybenzophenoximes of the above type containing electron withdrawing substituents have the formula:



where E is an electron withdrawing substituent, p is 1, 2, 3 or 4 and m is 0 or a whole integer up to 4—p. R, R' and n are as previously described. These compounds are

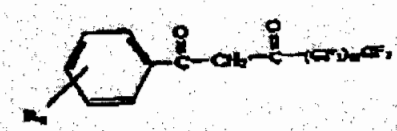
further described in Mattison and Swanson U.S. Pat. No. 3,655,347.

β-diketones desirably used in the present invention have the formula:



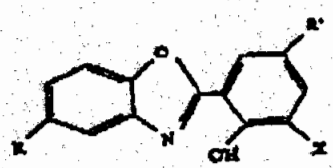
where R is phenyl or alkyl substituted phenyl, R' is alkyl, alkyl substituted phenyl or chloro substituted phenyl and R'' is H or —CN with the provisos that: (1) when R is phenyl, R' is a branched chain alkyl group of at least seven carbon atoms and (2) when R is alkyl substituted phenyl, the number of carbon atoms in the alkyl substituent or substituents is at least 7 and at least one such alkyl substituent is branched chain. Compounds of this group are further described in MacKay and Rogier U.S. patent application Ser. No. 391,432, filed Aug. 24, 1973 and the corresponding Belgian Pat. No. 819,136 which description is incorporated herein by reference.

Fluorinated β-diketones also find use in the invention one preferred group having the formula:



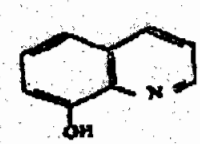
where n is a whole integer of 1 to 4, m is 0, 1 or 2 and R is an alkyl group of 1-25 carbons. Fluorinated β-diketones are variously described in U.S. Pat. Nos. such as: 3,894,803; 2,916,349; 2,632,763; 2,330,066; etc.

Another group of hydrogen ion exchange agents useful in the invention are benzoxazoles of the formula:



where R is hydrogen or an alkyl group having from 1 to 20 carbon atoms, R' is hydrogen, chlorine or an alkyl group containing from 1 to20 carbon atoms, X is H or chlorine and the total number of carbon atoms in R and R' is 6 to 40 with the proviso that one of R and R' must be an alkyl group of at least 6 carbon atoms. These compounds are further described in MacKay and Rogier U.S. patent application Ser. No. 518,011, filed Oct. 25, 1974 which description is incorporated herein by reference.

Substituted 8-hydroxyquinolines also find use in the invention. The basic structure of these compounds is

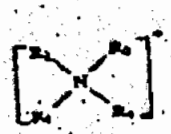


where the same will have hydrocarbon solubilizing groups such as in the 7 position where alkyl and alkenyl groups find effective use. Chloro or bromo substituted compounds (5 position) are described in Mattison U.S. patent application Ser. No. 447,629, filed Mar. 4, 1974 which description is incorporated herein by reference.

The organo phosphoric acids may have the formula

where R is an organic group, preferably hydrocarbon such as alkyl, aryl, alkylaryl and the like. These reagents are also well known in the liquid ion exchange recovery of metal values.

As indicated previously, the hydrogen ion exchange agent is neutralized with a quaternary ammonium salt. Quaternary ammonium salts are well known and a wide variety of the same may be used in the present invention. The cation portion of such quaternary ammonium compounds can be illustrated as follows:



where R_1 is a hydrocarbon radical such as alkyl, alkaryl, aryl, alkaryl, arylalkyl and the like of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms. Representative anions X^- and $X^=$ are chloride, bromide, iodide, sulfate, bisulfate and the like.

Representative of the above quaternary ammonium compounds are lauryltrimethyl ammonium chloride, myristyltrimethyl ammonium chloride, palmityltrimethyl ammonium chloride, lauryltrimethyl ammonium sulfate, myristyltrimethyl ammonium bromide, palmityltrimethyl ammonium iodide, stearyltrimethyl ammonium chloride, stearyltrimethyl ammonium sulfate, oleyltrimethyl ammonium chloride, oleylbutyldimethyl ammonium sulfate, dilauryldimethyl ammonium chloride, distearyldimethyl ammonium sulfate, trilauryldimethyl ammonium chloride, triocylmethyl ammonium bromide, tridecylmethyl ammonium chloride, stearylbenzyldimethyl ammonium sulfate, oleylbenzyldiethyl ammonium chloride and the like. In the examples to follow, the quaternary ammonium salt used was a trialkyl monomethyl ammonium chloride wherein the alkyl groups contained 8 and 10 carbons, such alkyl groups being straight chained and randomly distributed in the quaternary cation.

The hydrogen ion exchange reagent, the quaternary ammonium salt, and the metal complex of the hydrogen ion exchange reagent must all be soluble in the essentially water-immiscible organic solvents to an extent of at least 2% by weight in order to practically recover metal values on a commercial scale. The organic solvents are preferably aliphatic or aromatic hydrocarbons such as the petroleum derived liquid hydrocarbons including kerosene, fuel oil, etc. In addition to the simple hydrocarbon solvents, chlorinated hydrocarbons may also be used. Accordingly, both the unsubstituted

and the chlorinated solvents are contemplated by the term "liquid hydrocarbon."

An essential step in our process is the formation of the quaternary ammonium salt of the hydrogen ion exchange agents. This step is carried out by dissolving the hydrogen ion exchange agent and the starting quaternary ammonium salt in the organic solvent and then neutralizing (i.e., removing inorganic acid therefrom) by washing with water or aqueous base. The resulting neutralized solutions form part of the present invention and comprise at least about 2 percent of the so-formed quaternary ammonium salt of the hydrogen ion exchange agent in the organic solvent. In use, the said salt will preferably be present in an amount of about 2 to 15% by weight in the solvent. However, the said salt solution may be sold as a concentrate for later dilution prior to using same in the metal recovery process. In such instance, the salt will generally be present in the solvent in amounts of 15% or more, preferably 25–75% by weight. Also, in continuous extraction processes, the quaternary ammonium salt of the hydrogen ion exchange reagent will be continuously regenerated as a separate step in the overall process subsequent to stripping of the metal loaded phase and prior to use for further extraction. The hydrogen ion exchange reagent and the starting quaternary ammonium salt will preferably be used in essentially equimolar amounts in the formation of the new hydrogen ion exchange reagent salt solutions.

As indicated, the neutralization is carried out by water washing or with aqueous solutions of bases. The latter are preferred with representative bases being sodium bicarbonate, sodium hydroxide, sodium carbonate, potassium hydroxide, calcium hydroxide, potassium carbonate, ammonia or ammonium hydroxide and the like. Preferably also only relatively dilute solutions of base need be used.

In its general aspects, the metal recovery process of the present invention comprises contacting an aqueous metal value containing solution with an organic solvent solution of the quaternary ammonium salt of the hydrogen ion exchange reagent to extract at least a portion of the metal values into the organic phase, separating the metal pregnant organic phase from the aqueous phase and stripping at least a portion of the metal values from the organic phase by contacting same with an aqueous acidic stripping solution. In most, if not all, commercial operations, the organic phase must be regenerated for economic purposes. As such, the process of the invention will then comprise the steps of neutralizing the stripped organic phase and recycling the organic phase for contacting further quantities of the metal containing aqueous solution. The phase ratios in these steps can be varied widely as it will be apparent that the contacting, for example, of any quantity of the organic phase with the aqueous metal containing phase will result in extraction of metal into the organic phase. However, for commercial practicality, the various organic:aqueous phase ratios are preferably in the range of 10:1 to 1:10. Also for practical purposes, the extractions (and stripping and neutralization) are normally carried out at ambient temperatures and pressures.

The loaded organic is stripped using aqueous acidic stripping medium such as aqueous sulfuric acid, hydrochloric acid and the like. The starting metal containing solution has a pH of less than 7.0 and, as indicated, the optimum pH will vary depending especially upon the metal being extracted and the particular extractant

therefor. A wide variety of metal values may be extracted according to our process including, without being limited thereto, copper, nickel, cobalt, zinc, magnesium, cadmium, iron, mercury, lithium, silver(I), and the like. Divalent metal recovery is especially facilitated by the invention.

The following Examples illustrate preferred embodiments of the invention without being limiting:

EXAMPLE I-A

Equal volumes of a solution of both the quaternary ammonium chloride (0.1M) and 1-dodecylphenyl-3-trifluoromethyl-1,3-propanedione (0.1M) in an aromatic petroleum solvent (Aromatic 150 available from Exxon) and aqueous $NaHCO_3$ (5% by weight) were shaken together for 2 minutes. The aqueous phase was drawn off and the organic contacted a second time with an equal volume of the $NaHCO_3$ solution. The organic was then washed with water to a pH of 7–8 and filtered through filter paper to remove trace amounts of water. In the diketone reagent, the dodecyl group is in the para position and was derived from a synthetic alkylbenzene, Chevron alkylate 21, in which the alkyl chain is branched and contains an average of 12 carbon atoms.

The quaternary ammonium salt of the diketone as above prepared was contacted at various organic:aqueous phase ratios with an aqueous solution containing 5.10 g./l. Cu^{++} (as $CuSO_4$) and having an initial pH of 2.0 (the solutions were combined in a bottle and shaken for 30 minutes). The organic and aqueous phases were analyzed for Cu^{++} content and the pH of the separated aqueous was measured. Results are set forth in the following Table I-A:

Table I-A

Org. ml.	Aq. ml.	O/A Phase Ratio	pH initial	pH final	Cu^{++} (org.) g./l.	Cu^{++} (aq.) g./l.
10	40	1/4	2.0	1.32	2.14	4.57
10	20	1/2	2.0	2.48	2.34	3.58
10	10	1/1	2.0	2.67	2.50	2.60
20	10	2/1	2.0	2.68	2.33	0.44
30	10	3/1	2.0	2.70	1.69	0.88
38	10	3/1	2.0	4.38	1.82	0.00
100	10	10/1	2.0	4.62	0.50	0.00

For comparison purposes, the first six runs as set forth above were repeated except that the diketone alone was used at a concentration of 0.1M in the aromatic solvent (the quaternary ammonium chloride was not used and the solution was not contacted with the $NaHCO_3$ solution). Results are set forth in the following Table I-A Comparative:

Table I-A Comparative

Org. ml.	Aq. ml.	O/A Phase Ratio	pH initial	pH final	Cu^{++} (org.) g./l.	Cu^{++} (aq.) g./l.
10	40	1/4	2.0	1.30	1.31	4.77
10	20	1/2	2.0	1.82	1.11	4.60
10	10	1/1	2.0	1.78	0.88	4.21
20	10	2/1	2.0	1.86	0.66	2.94
30	10	3/1	2.0	1.85	0.51	2.47
39	10	3/1	2.0	1.90	0.51	1.97

EXAMPLE I-B

The diketone salts as prepared in Example I-A was used to extract nickel by contacting (with shaking for 30 minutes) 10 milliliter portions thereof with 5 milliliter portions of a 1.0M solution of aqueous $NiSO_4$ plus various amounts of water and/or pH adjusting solutions.

Results of these extractions are set forth in the following Table I-B:

Table I-B

Org. ml.	$NiSO_4$ Solution ml.	H_2O ml.	pH Adjusting Solution ml.	pH Final	Ni^{++} (aq.) g./l.
10	5	5	—	4.15	2.14
10	5	—	5 (5 g./l. H_2SO_4)	2.38	1.28
10	5	4	1 (0.1M $NaHCO_3$)	6.82	2.12
10	5	3	3 (2.5 g./l. H_2SO_4)	2.10	0.45
10	5	2	3 (5 g./l. H_2SO_4)	2.98	1.79
10	5	3	2 (5 g./l. H_2SO_4)	2.83	1.67

EXAMPLES II – XI

Salts of various hydrogen ion exchange reagents and the quaternary ammonium chloride were prepared in Aromatic 150 as in Example I-A and used to extract divalent copper, nickel, cobalt and zinc. Equal volumes of acid solutions of salts were used with various aqueous solutions of the metal values (1.0M of the respective aqueous metal sulfate solutions diluted with an equal volume of water and/or pH adjusting solutions as in Example I-B). The hydrogen ion exchange agents used were as follows:

Example	Agent
II	5,8-diethyl-7-hydroxydodecane-6-oxime
III	2-hydroxy-5-nonylbenzophenoxime (the nonyl group was branched chain)
IV	6-n-butyl-5-hydroxyhexadecane-7-oxime
V	2-hydroxy-3-chloro-5-nonylbenzophenoxime (the nonyl group was branched chain)
VI	Diketone as used in Example I-A
VII	1-(4-dodecylphenyl)-3-heptyl-1,3-propanedione (the dodecyl and heptyl groups were branched chain)
VIII	2-(2-hydroxy-3,5-dichlorobenzyl)-5-dodecylbenzenesulfonic acid (dodecyl group was branched chain)
IX	2-undecyl-4,6-dinitrophenol
X	di-2-ethylhexylphosphoric acid
XI	naphthenic acid

Results of these extractions are set forth in the following Tables, each table numbers corresponding to the hydrogen ion exchange reagent numbers above:

TABLE II

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.30	1.92	4.55	0.60	3.70	0.32	3.65	0.27
2.05	1.15	4.08	0.28	2.75	0.21	4.80	0.29
1.45	0.80	2.50	0.23	3.40	0.21	3.40	0.28
1.20	0.48	2.50	0.17	2.92	0.19	2.19	0.14
0.80	0.18	2.08	0.09	2.17	0.19	1.70	0.05
		1.20	0.03	1.20	0.02	1.20	0.03

TABLE III

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.98	2.12	4.80	2.10	6.02	1.65	6.80	0.11
2.40	2.23	2.15	1.19	5.78	0.80	5.80	0.13
2.00	1.30	4.65	0.73	3.70	0.48	2.40	0.07
1.72	1.01	4.65	0.43	5.80	0.19	1.90	0.08
1.40	0.60	3.40	0.11	3.28	0.12	1.40	0.01
1.18	0.18	2.80	0.06	2.40	0.07	2.15	0.04
0.78	0.04	1.85	0.02	1.85	0.05		

Table IV

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.50	2.50	5.70	5.64	6.60	0.47	5.60	0.48

Table IV-continued

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
2.90	2.02	3.10	0.41	3.95	0.36	4.10	0.35
2.70	1.25	3.32	0.33	3.70	0.38	3.25	0.23
1.24	0.56	2.33	0.30	3.20	0.25	2.15	0.16
0.56	0.21	2.50	0.24	2.90	0.25	1.13	0.08
		1.75	0.08	2.15	0.12		
		1.20	0.02	1.20	0.02		

Table V

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
4.25	3.08	5.40	2.76	5.32	1.90	3.73	0.83
2.20	3.60	4.49	1.87	5.13	0.74	4.78	0.30
1.25	1.52	4.08	0.68	4.72	0.42	2.52	0.30
0.63	3.13	3.93	1.13	3.30	0.08	1.90	0.02
0.38	0.78	2.35	0.08	1.40	0.01	1.40	0.04
0.30	0.46	1.85	0.024				

Table VI

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
4.10	3.31	6.88	2.12	6.80	1.91	5.80	2.42
2.47	3.04	6.64	2.14	6.35	1.92	4.53	2.48
1.92	2.19	4.15	2.14	5.48	1.86	2.90	1.39
1.52	1.37	2.98	1.79	4.31	1.86	1.98	0.18
1.00	0.36	2.83	1.67	2.45	0.87	1.70	0.10
		2.58	1.38	2.00	0.23		
		2.10	0.46				

Table VII

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
3.40	2.66	6.78	1.48	7.10	1.34	5.70	0.79
3.00	1.84	5.90	0.51	6.78	1.91	4.80	0.63
1.35	0.11	6.52	0.52	6.30	0.53	2.48	0.46
		2.55	0.45	4.80	0.50	1.35	.13
		2.33	0.37	3.10	0.49		
		1.25	0.05	2.14	0.23		
				1.32	0.05		

Table VIII

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L
3.55	2.97	5.00	2.17	5.00	1.91
2.45	3.22	3.82	1.83	4.18	1.48
2.15	2.91	3.45	1.17	3.70	1.05
1.29	1.17	2.70	0.45	2.72	0.42
0.60	0.15	1.70	0.12	1.60	0.10

Table IX

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
2.20	3.10	3.57	1.45	4.17	1.09	4.52	1.77
1.90	2.95	3.82	1.35	4.12	0.95	4.32	1.27
1.38	2.98	3.72	1.13	4.05	1.01	3.20	0.65
0.60	2.33	2.80	0.56	3.10	0.53	2.39	0.37
0.30	1.96	1.52	0.04	2.62	0.32	1.55	0.14
0.02	1.44	0.85	0.02	1.55	0.07	0.60	0.06

Table X

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
4.00	0.33	5.40	0.20	5.00	0.22	3.80	0.91
2.53	0.08	5.40	0.09	4.60	0.11	2.50	0.11
1.70	0.02	4.50	0.03	3.10	0.03	2.00	0.04
1.35	0.01	3.70	0.01	2.50	0.02	1.60	0.05

Table X-continued

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
		3.90	0.01	1.96	0.02	0.95	0.01

Table XI

pH Final	[Cu] Org. g/L	pH Final	[Ni] Org. g/L	pH Final	[Co] Org. g/L	pH Final	[Zn] Org. g/L
3.70	0.64	6.80	0.36	5.60	0.17	4.99	0.49
3.60	0.38	5.65	0.21	3.75	0.22	3.82	0.36
2.52	0.46	3.80	0.28	1.50	0.05	3.65	0.23
1.40	0.04	1.50	0.08	1.40	0.04	2.60	0.21
		1.40	0.02			1.45	0.03

EXAMPLES XII – XV

Loaded organic solutions prepared as in Examples I–XI were stripped of metal values with aqueous sulfuric acid (1.50 g/L H_2SO_4). Equal volumes of the loaded organics and the stripping solution were contacted with shaking for two minutes. After separation of the phases, the stripped organic was analyzed for metal value content. In the present Examples, the loaded organics are identified by reference to the hydrogen ion exchange reagent salts of Examples II–XI used in contacting the metal values. Results of the stripping operations are set forth in the following Tables XII–XV:

Table XII

Loaded Organic: Reagent Salt Exp.	Loaded Organic: Cu^{++} g/L	Stripped Organic: Cu^{++} g/L	% Cu^{++} Stripped
II	1.77	0.08	98
III	2.13	0.004	99.5
IV	2.43	0.004	99.5
V	3.08	0.071	97.8
VI	3.04	0.002	99.7
VIII	2.57	0.002	100
IX	3.10	0.228	92.5
X	0.324	0.0001	100
XI	0.330	<0.0001	100

Table XIII

Loaded Organic: Reagent Salt Exp.	Loaded Organic: Ni^{++} g/L	Stripped Organic: Ni^{++} g/L	% Ni^{++} Stripped
II	1.41	0.34	76
III	2.16	0.0006	100
IV	0.304	0.0016	100
V	1.63	0.03	98.3
VI	2.14	0.0006	100
VII	1.48	0.0012	100
VIII	2.17	0.0032	100
IX	1.14	0.0028	100
X	0.204	<0.0005	100
XI	0.34	<0.0005	100

Table XIV

Loaded Organic: Reagent Salt Exp.	Loaded Organic: Co^{++} g/L	Stripped Organic: Co^{++} g/L	% Co^{++} Stripped
II	0.322	0.081	74.4
III	1.73	1.12	34.6
IV	0.327	0.065	83
V	1.50	1.31	51.4
VI	1.86	<0.0005	100
VII	1.01	0.248	75
VIII	1.05	0.0018	100
IX	0.83	0.705	24.6
X	0.214	0.0001	100
XI	0.225	<0.0005	100

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Table XV

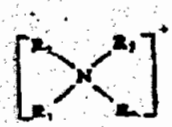
Loaded Organic		Stripped Organic	
Reagent Salt Exp.	Zn^{++} g/l.	Zn^{++} g/l.	% Zn^{++} Stripped
II	0.137	<0.0001	100
III	0.188	0.001	100
IV	0.345	0.0005	100
V	0.765	0.007	99
VI	2.42	0.0007	100
VII	0.790	<0.0005	100
IX	1.77	0.0007	100
X	0.014	<0.0001	100
XI	0.436	<0.0005	100

EXAMPLE XVI

Example 1 A was essentially repeated except kerosene was used as the solvent, the diketone and quaternary ammonium compound were used at levels of 10 and 11.2% weight/volume, respectively, and the resulting solution of the diketone salt was used to extract nickel (4 g./l. Ni^{++} as $NiSO_4$, pH 4.2) and cobalt (4 g./l. Co^{++} as $CoSO_4$, pH 3.9). Analyses indicated that 4.1 g./l. Ni^{++} and 2.6 g./l. Co^{++} were extracted with raffinate (metal barren aqueous) pH values of 6.8 and 7.2, respectively.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process of extracting divalent metal values from an aqueous acidic solution thereof comprising contacting said solution with a solution of a quaternary ammonium salt of a hydrogen ion exchange agent in an essentially water-immiscible organic solvent to extract at least a portion of the said divalent metal values into the organic phase, separating the loaded organic phase from the aqueous phase and stripping the divalent metal values from the loaded organic phase by contacting same with an aqueous acidic stripping medium, said divalent metal values being capable of being extracted from an aqueous acidic solution thereof, said quaternary ammonium salt of the hydrogen ion exchange agent having the formula QL where Q is a quaternary ammonium cation and L is the deprotonated moiety or anion of the hydrogen ion exchange agent and said quaternary ammonium cation having the formula



where R_1 is a hydrocarbon radical of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms.

2. The process of claim 1 wherein the stripped organic phase is neutralized to regenerate the quaternary ammonium salt of the hydrogen ion exchange reagent and the resulting organic phase is recycled for extracting further quantities of metal values.

3. The process of claim 1 wherein both the quaternary ammonium compound and the hydrogen ion exchange agent used in the preparation of the quaternary ammonium salt of the said hydrogen ion exchange agent are soluble to the extent of at least about 2.0% by weight of the essentially water-immiscible organic solvent.

4. The process of claim 3 wherein L is derived from an α-hydroxy oxime.

5. The process of claim 3 wherein L is derived from a 2-hydroxybenzophenoxime.

6. The process of claim 3 wherein L is derived from a beta-diketone.

7. The process of claim 3 wherein L is derived from a fluorinated beta-diketone.

8. The process of claim 3 wherein L is derived from a hydroxy containing benzotriazole.

9. The process of claim 3 wherein L is derived from a substituted 8-hydroxyquinoline.

10. The process of claim 3 wherein L is derived from an organo phosphoric acid.

11. The process of claim 3 wherein L is derived from naphthenic acid.

12. The process of claim 1 wherein the organic solvent is a liquid hydrocarbon.

13. The process of claim 1 wherein the divalent metal values are selected from copper, nickel, cobalt and zinc.

14. The process of claim 2 wherein the neutralization is effected by contacting the stripped organic phase with water or an aqueous solution of a base.

* * * * *

United States Patent [19]

MacKay et al.

[11] **4,128,493**

[45] **Dec. 5, 1978**

[54] **COMPOSITIONS USEFUL IN PROCESS FOR EXTRACTION OF METAL VALUES FROM ACIDIC SOLUTIONS**

[75] Inventors: **Kenneth D. MacKay, Circle Pines; Edgar R. Rogier, Minnetonka, both of Minn.**

[73] Assignee: **General Mills Chemicals, Inc., Minneapolis, Minn.**

[21] Appl. No.: **822,765**

[22] Filed: **Aug. 8, 1977**

Related U.S. Application Data

[62] Division of Ser. No. 630,600, Nov. 10, 1975, Pat. No. 4,058,585.

[51] Int. Cl.² C09K 3/00

[52] U.S. Cl. ..... 252/184; 252/182; 260/307 D; 260/501.15; 260/566 A; 260/567.6 M; 260/567.6 H; 260/567.6 F; 546/134; 546/181

[58] Field of Search ..... 252/184, 182; 260/307 D, 566 A, 567.6 R, 567.6 M, 567.6 H, 567.6 F, 286 Q, 287 XA, 501.15

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Primary Examiner—Benjamin R. Padgett
Assistant Examiner—Deborah L. Kyle
Attorney, Agent, or Firm—Patrick J. Span; Gene O. Enockson

[57] **ABSTRACT**

Process of extracting metals using organic solvent solutions of salts of hydrogen ion exchange agents and quaternary ammonium compounds. Organic solvent solutions of such quaternary ammonium salts of hydrogen ion exchange agents.

4 Claims, No Drawings

COMPOSITIONS USEFUL IN PROCESS FOR EXTRACTION OF METAL VALUES FROM ACIDIC SOLUTIONS

This application is a division of application Ser. No. 630,600, filed Nov. 10, 1975 now U.S. Pat. No. 4,058,585.

This invention relates to compositions useful in liquid ion exchange recovery of metals.

Liquid ion exchange recovery of metal values from their aqueous solutions has become increasingly important in the commercial production of high quality metal on a large scale. These exchange recovery systems generally involve contacting the aqueous metal containing solution with an exchange reagent dissolved in an essentially water-immiscible organic solvent whereby at least part of the metal values are transferred to the organic phase, separating the metal pregnant organic phase from the aqueous phase and then contacting the metal pregnant organic phase with an aqueous stripping solution to transfer the metal values to the stripping solution. The net effect is generally to arrive at a more concentrated metal containing solution (i.e. the metal pregnant strip solution) from the starting relatively dilute metal containing aqueous solution. The metal pregnant strip solution is of controllable composition or purity and the metal values can be directly recovered therefrom, most generally be electrolysis. The entire process is generally continuous with recycle of the stripped organic phase for contacting further quantities of metal containing aqueous solutions. Counter-current, multiple stage extractions are generally included in these continuous circuits.

Various metal values are optimally extracted at defined pH ranges using particular hydrogen ion exchange reagents. In this respect, the entire system will be designed around the use of a particular liquid ion exchange reagent optimally operable with a designated pH range for the specific metal involved. Thus the pH of the aqueous leach solution will be altered if necessary to fall within the optimum extraction range. In this respect, acid or base may be added to bring the pH into the desired range.

Despite the above initial pH adjustment, an additional problem is often encountered. Thus the acidity of the solution being extracted is progressively increased (i.e. the pH is lowered) by the exchange of metal ions in the solution for hydrogen ions on the liquid ion exchange reagent as the process proceeds. This can cause loss of efficiency as the pH of the solution being extracted drops below the optimum range for the particular hydrogen ion exchange reagent and metal being extracted. One prior procedure used in attempting to attack this problem has been the addition of alkaline reagents, such as ammonia, lime or the like, to neutralize the forming acid. This can require careful monitoring. Additionally, such neutralization increases the overall cost of the recovery process due to the cost of the neutralizing reagents which are added and also because of the loss of acid through said neutralizing.

A more recent suggested procedure is that of U.S. Pat. No. 3,676,106 to Wayne C. Hazen. In the process suggested in this patent, the acidity of the leach solution is controlled during the process by contacting same with a solvent extractant for the acid when the acidity of the leach solution has reached a point at which the recovery of metal ions is no longer efficient. The Patent discloses that long chain secondary and tertiary amines

are preferred extractants for the hydrogen ions. The acid can be stripped from this amine extractant solution and the latter then reused. The water strip containing acid can then be used for further ore leaching if desired. This process thus involves an additional step for treating the leach solution as well as the step of recovering acid from the amine containing solvent extractant. If the latter were not carried out, substantial increased costs could be incurred due to loss of amine and the solvent therefor.

We have now discovered a new procedure for avoiding a decrease in aqueous pH during extraction and compositions useful in this improved process. Our process employs a solution of a salt of a hydrogen ion exchange agent and a quaternary ammonium compound in an essentially water-immiscible organic solvent. Such salts can be formed by washing the corresponding solution of the hydrogen ion exchange reagent and the quaternary ammonium compound with water or aqueous bases. Such neutralization or salt formation step can be illustrated by the following equation (when a base is used):

$$LH_{org.} + QX_{aq.} + B_{aq.} \rightarrow QL_{org.} + BHX_{aq.}$$

where L is the anion of the hydrogen ion exchange agent, Q is the quaternary ammonium cation, X is the inorganic anion of the starting quaternary ammonium compound and B is the base. This can be further illustrated in respect of the use of a specific base as follows:

$$2LH_{org.} + Q_2X_{org.} + 2NaHCO_{3aq.} \rightarrow 2QL_{org.} + Na_2X_{aq.} + 2CO_2$$

This formed salt solution is then used to contact the acidic aqueous metal containing solution to extract at least part of the metal values into the organic phase. The extraction step can be illustrated by the following equation:

$$2QL_{org.} + MX_{aq.} \rightarrow L_2M_{org.} + Q_2X_{org.}$$

where M is a divalent cation (e.g., Ni^{++}, Co^{++}) and X is a divalent anion (e.g., SO_4^{--}). From this equation, it is readily apparent that there is no net transfer of hydrogen ions (protons) from the organic phase to the aqueous phase during the extraction. Accordingly, pH decrease is eliminated by our process.

The loaded organic phase can be stripped of metal values by contacting same with aqueous acidic solutions. This can be illustrated by the following equation:

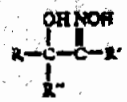
$$L_2M_{org.} + Q_2X_{org.} + H_2X_{aq.} \rightarrow 2LH_{org.} + Q_2X_{org.} + MX_{aq.}$$

The metal values are then recovered from the aqueous phase by conventional techniques, especially electrodeposition. Following the stripping stage, the organic phase can again be neutralized by washing as previously indicated to form the salt of the hydrogen ion exchange reagent and the quaternary ammonium salt and the thus neutralized organic phase recycled for use for further metal extractions. Where the neutralization is effected by water washing, the wash solution will be acidic and can be used for leaching purposes. The entire process can be operated continuously as in past practices except that in the process of the invention, pH reduction on extraction is eliminated making certain extractions feasi-

ble and/or more efficient in some cases and processing flexibility is increased. The equations given above are illustrative only and it should be clearly evident that the invention has a general application to hydrogen ion exchange reagents and quaternary ammonium salts which are soluble in essentially water-immiscible organic solvents, extractable metal values, neutralizing solutions and acid stripping mediums.

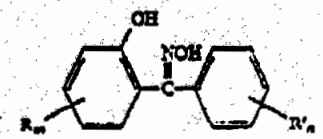
A wide variety of hydrogen ion exchange reagents can be used in the present invention. These reagents are capable of being deprotonated by reaction with the quaternary ammonium salts. Representative of various of these hydrogen ion exchange reagents are α-hydroxy oximes, benzophenoxmes, β-dikerones, fluorinazed β-diketones, benzoxazoles, 8-hydroxyquinolines, organo phosphoric acids, naphthenic acids and the like. A number of these groups of reagents are described in more detail hereinbelow.

The α-hydroxy oximes have the following general formula:

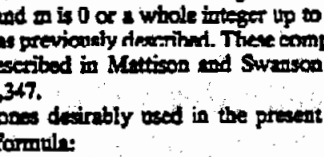


where R, R' and R" may be any of a variety of organic hydrocarbon radicals such as aliphatic and alkylaryl radicals. R" may also be hydrogen. These compounds are further described in Swanson U.S. Pat. No. 3,224,873 which description is incorporated herein by reference.

Benzophenoximes useful in the present invention may have the formula:

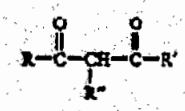


In which R and R' may be individually alike or different and are preferably saturated aliphatic groups and m and n are 0, 1, 2, 3 or 4 with the proviso that m and n are not both 0. The total number of carbon atoms in R_m and R'_n is from 3–25. R and R' contain 1–25 carbon atoms. These compounds are further described in Swanson United States Patent 3,592,775 which description is incorporated herein by reference. 2-Hydroxybenzophenoximes of the above type containing electron withdrawing substituents have the formula:



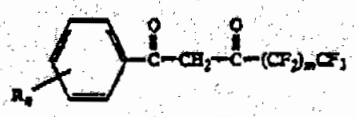
where E is an electron withdrawing substituent, p is 1, 2, 3 or 4 and m is 0 or a whole integer up to 4-p. R, R' and n are as previously described. These compounds are further described in Mattison and Swanson U.S. Pat. No. 3,655,347.

β-diketones desirably used in the present invention have the formula:



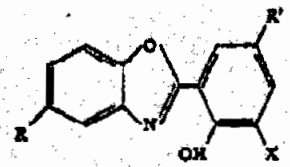
where R is phenyl or alkyl substituted phenyl, R' is alkyl, alkyl substituted phenyl or chloro substituted phenyl and R" is H or —CN with the provisos that: (1) when R is phenyl, R' is a branched chain alkyl group of at least seven carbon atoms and (2) when R is alkyl substituted phenyl, the number of carbon atoms in the alkyl substituent or substituents is at least 7 and at least one such alkyl substituent is branched chain. Compounds of this group are further described in Mackay and Rogier United States patent application Ser. No. 391,432, filed Aug. 24, 1973 and the corresponding Belgian Pat. No. 819,136 which description is incorporated herein by reference.

Fluorinated β-diketones also find use in the invention one preferred group having the formula:



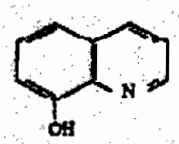
where n is a whole integer of 1 to 4, m is 0, 1 or 2 and R is an alkyl group of 1–25 carbons. Fluorinated β-diketones are variously described in U.S. Pat. Nos. 3,894,803; 2,916,349; 2,632,763; 2,130,066; etc.

Another group of hydrogen ion exchange agents useful in the invention are benzoxazoles of the formula:



where R is hydrogen or an alkyl group having from 1 to 20 carbon atoms, R' is hydrogen, chlorine or an alkyl group containing from 1 to 20 carbon atoms, X is H or chlorine and the total number of carbon atoms in R and R' is 6 to 40 with the proviso that one of R and R' must be an alkyl group of at least 6 carbon atoms. These compounds are further described in MacKay and Rogier United States patent application Ser. No. 518,011, filed Oct. 25, 1974 which description is incorporated herein by reference.

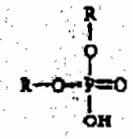
Substituted 8-hydroxyquinolines also find use in the invention. The basic structure of these compounds is



where the same will have hydrocarbon solubilizing groups such as in the 7 position where alkyl and alkenyl groups find effective use. Chloro or bromo substituted compounds (5 position) are described in Mattison U.S.

patent application Ser. No. 447,629, filed Mar. 4, 1974 which description is incorporated herein by reference.

The organo phosphoric acids may have the formula



where R is an organic group, preferably hydrocarbon such as alkyl, aryl, alkylaryl and the like. These reagents are also well known in the liquid ion exchange recovery of metal values.

As indicated previously, the hydrogen ion exchange agent is neutralized with a quaternary ammonium salt. Quaternary ammonium salts are well known and a wide variety of the same may be used in the present invention. The cation portion of such quaternary ammonium compounds can be illustrated as follows:

where R_1 is a hydrocarbon radical such as alkyl, alkenyl, aryl, alkaryl, arylalkyl and the like of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms. Representative anions X^- and X^{--} are chloride, bromide, iodide, sulfate, bisulfate and the like.

Representative of the above quaternary ammonium compounds are lauryltrimethyl ammonium chloride, myristyltrimethyl ammonium chloride, palmityltrimethyl ammonium chloride, lauryltrimethyl ammonium sulfate, myristyltrimethyl ammonium bromide, palmityltrimethyl ammonium iodide, stearyltrimethyl ammonium chloride, stearyltrimethyl ammonium sulfate, oleyltrimethyl ammonium chloride, oleylbutyldimethyl ammonium sulfate, dilauryldimethyl ammonium chloride, distearyldimethyl ammonium sulfate, trilaurylmethyl ammonium chloride, trioctylmethyl ammonium bromide, tridecylmethyl ammonium chloride, stearylbenzyldimethyl ammonium sulfate, oleylbenzyldiethyl ammonium chloride and the like. In the examples to follow, the quaternary ammonium salt used was a trialkyl monomethyl ammonium chloride wherein the alkyl groups contained 8 and 10 carbons, such alkyl groups being straight chained and randomly distributed in the quaternary cation.

The hydrogen ion exchange reagent, the quaternary ammonium salt, and the metal complex of the hydrogen ion exchange reagent must all be soluble in the essentially water-immiscible organic solvents to an extent of at least 2% by weight in order to practically recover metal values on a commercial scale. The organic solvents are preferably aliphatic or aromatic hydrocarbons such as the petroleum derived liquid hydrocarbons including kerosene, fuel oil, etc. In addition to the simple hydrocarbon solvents, chlorinated hydrocarbons may also be used. Accordingly, both the unsubstituted and the chlorinated solvents are contemplated by the term "liquid hydrocarbon".

An essential step in our process is the formation of the quaternary ammonium salt of the hydrogen ion exchange agents. This step is carried out by dissolving the hydrogen ion exchange agent and the starting quaternary ammonium salt in the organic solvent and then neutralizing (i.e. removing inorganic acid therefrom) by washing with water or aqueous base. The resulting neutralized solutions form part of the present invention and comprise at least about 2 percent of the so-formed quaternary ammonium salt of the hydrogen ion exchange agent in the organic solvent. In use, the said salt will preferably be present in an amount of about 2 to 15% by weight in the solvent. However, the said salt solution may be sold as a concentrate for later dilution prior to using same in the metal recovery process. In such instance, the salt will generally be present in the solvent in amounts of 15% or more, preferably 25–75% by weight. Also, in continuous extraction processes, the quaternary ammonium salt of the hydrogen ion exchange reagent will be continuously regenerated as a separate step in the overall process subsequent to stripping of the metal loaded phase and prior to use for further extraction. The hydrogen ion exchange reagent and the starting quaternary ammonium salt will preferably be used in essentially equimolar amounts in the formation of the new hydrogen ion exchange reagent salt solutions.

As indicated, the neutralization is carried out by water washing or with aqueous solutions of bases. The latter are preferred with representative bases being sodium bicarbonate, sodium hydroxide, sodium carbonate, potassium hydroxide, calcium hydroxide, potassium carbonate, ammonia or ammonium hydroxide and the like. Preferably also only relatively dilute solutions of base need be used.

In its general aspects, the metal recovery process of the present invention comprises contacting an aqueous metal value containing solution with an organic solvent solution of the quaternary ammonium salt of the hydrogen ion exchange reagent to extract at least a portion of the metal values into the organic phase, separating the metal pregnant organic phase from the aqueous phase and stripping at least a portion of the metal values from the organic phase by contacting same with an aqueous acidic stripping solution. In most, if not all, commercial operations, the organic phase must be regenerated for economic purposes. As such, the process of the invention will then comprise the steps of neutralizing the stripped organic phase and recycling the organic phase for contacting further quantities of the metal containing aqueous solution. The phase ratios in these steps can be varied widely as it will be apparent that the contacting, for example, of any quantity of the organic phase with the aqueous metal containing phase will result in extraction of metal into the organic phase. However, for commercial practicality, the various organic:aqueous phase ratios are preferably in the range of 10:1 to 1:10. Also for practical purposes, the extractions (and stripping and neutralization) are normally carried out at ambient temperatures and pressures.

The loaded organic is stripped using aqueous acidic stripping mediums such as aqueous sulfuric acid, hydrochloric acid and the like. The starting metal containing solution has a pH of less than 7.0 and, as indicated, the optimum pH will vary depending especially upon the metal being extracted and the particular extractant therefor. A wide variety of metal values may be extracted according to our process including, without being limited thereto, copper, nickel, cobalt, zinc, magnesium, cadmium, iron, mercury, lithium, silver(I), and

the like. Divalent metal recovery is especially facilitated by the invention.

The following Examples illustrate preferred embodiments of the invention without being limiting:

EXAMPLE I-A

Equal volumes of a solution of both the quaternary ammonium chloride (0.1M) and 1-dodecylphenyl-3-trifluoromethyl-1,3-propanedione (0.1M) in an aromatic petroleum solvent (Aromatic 150 available from Exxon) and aqueous $NaHCO_3$ (5% by weight) were shaken together for two minutes. The aqueous phase was drawn off and the organic contacted a second time with an equal volume of the $NaHCO_3$ solution. The organic was then washed with water to a pH of 7–8 and filtered through filter paper to remove trace amounts of water. In the diketone reagent, the dodecyl group is in the para position and was derived from a synthetic alkylbenzene, Chevron alkylate 21, in which the alkyl chain is branched and contains an average of 12 carbon atoms.

The quaternary ammonium salt of the diketone as above prepared was contacted at various organic:aqueous phase ratios with an aqueous solution containing 5.10 g./l. Cu^{++} (as $CuSO_4$) and having an initial pH of 2.0 (the solutions were combined in a bottle and shaken for 30 minutes). The organic and aqueous phases were analyzed for Cu^{++} content and the pH of the separated aqueous was measured. Results are set forth in the following Table I-A:

Table I-A

Org. ml.	Aq. ml.	O/A Phase Ratio	pH initial	pH final	Cu^{++} (org.) g./l.	Cu^{++} (aq.) g./l.
10	40	1/4	2.0	2.33	2.14	4.5
10	20	1/2	2.0	2.40	2.34	3.93
10	10	1/1	2.0	2.67	2.50	2.60
20	10	2/1	2.0	3.09	2.33	0.44
30	10	3/1	2.0	3.70	1.67	0.03
50	10	5/1	2.0	4.20	1.03	0.00
100	10	10/1	2.0	4.62	0.50	0.00

For comparison purposes, the first six runs as set forth above were repeated except that the diketone alone was used at a concentration of 0.1M in the aromatic solvent (the quaternary ammonium chloride was not used and the solution was not contacted with the $NaHCO_3$ solution). Results are set forth in the following Table I-A Comparative:

Table I-A

			Comparative			
Org. ml.	Aq. ml.	O/A Phase Ratio	pH initial	pH final	Cu^{++} (org.) g./l.	Cu^{++} (aq.) g./l.
10	40	1/4	2.0	1.90	1.31	4.77
10	20	1/2	2.0	1.82	1.11	4.60
10	10	1/1	2.0	1.70	0.88	4.21
20	10	2/1	2.0	1.60	0.64	3.74
30	10	3/1	2.0	1.55	0.51	3.47
50	10	5/1	2.0	1.50	0.31	3.07

EXAMPLE I-B

The diketone salt as prepared in Example I-A was used to extract nickel by contacting (with shaking for 30 minutes) ten milliliter portions thereof with five milliliter portions of a 1.0M solution of aqueous $NiSO_4$ plus various amounts of water and/or pH adjusting solutions. Results of these extractions are set forth in the following Table I-B-

Table I-B

Org. ml.	$NiSO_4$ Solution ml.	H_2O ml.	pH Adjusting Solution ml.	pH Final	Ni^{++} (org.) g./l.
10	5	5	—	4.15	2.14
10	5	—	5 (6 g./l. H_2SO_4)	2.58	1.38
10	5	4	1 (0.1M $NaHCO_3$)	6.82	2.12
10	5	2	3 (25 g./l. H_2SO_4)	2.10	0.46
10	5	2	3 (6 g./l. H_2SO_4)	2.98	1.79
10	5	3	2 (6 g./l. H_2SO_4)	2.85	1.67

EXAMPLES II–XI

Salts of various hydrogen ion exchange reagents and the quaternary ammonium chloride were prepared in Aromatic 150 as in Example I-A and used to extract divalent copper, nickel, cobalt and zinc. Equal volumes of said solutions of salts were used with various aqueous solutions of the metal values (1.0M of the respective aqueous metal sulfate solutions diluted with an equal volume of water and/or pH adjusting solutions as in Example I-B). The hydrogen ion exchange agents used were as follows:

Example	Agent
II	5,8-diethyl-7-hydroxydodecane-6-oxime
III	2-hydroxy-5-nonylbenzophenoxime (the nonyl group was branched chain)
IV	6-n-butyl-6-hydroxydodecane-5-oxime
V	2-hydroxy-3-chloro-5-nonylbenzophenoxime (the nonyl group was branched chain)
VI	diketone as used in Example I-A
VII	1-(4-dodecylphenyl)-3-heptyl-1,3-propanedione (the dodecyl and heptyl groups were straight chain)
VIII	2-(2-hydroxy-3,5-dichlorophenyl)-5-dodecylbenzenesulfonic (the dodecyl group was branched chain)
IX	7-dodecenyl-8-hydroxyquinoline
X	di-2-ethylhexylphosphoric acid
XI	naphthenic acid

Results of these extractions are set forth in the following Tables, such table numbers corresponding to the hydrogen ion exchange reagent numbers above:

Table II

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.50	1.92	4.95	0.40	5.70	0.32	5.65	0.27
2.05	1.15	4.08	0.28	3.75	0.21	4.80	0.29
1.49	0.80	2.90	0.23	3.40	0.21	3.40	0.28
1.20	0.48	2.50	0.17	2.92	0.19	2.19	0.14
0.60	0.19	2.00	0.09	2.17	0.10	1.70	0.05
		1.20	0.03	1.20	0.02	1.20	0.02

Table III

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.98	3.12	5.90	2.10	6.02	1.63	6.00	0.11
2.60	2.13	5.15	1.19	5.78	0.80	5.00	0.13
2.00	1.39	4.85	0.73	5.70	0.42	2.50	0.07
1.72	1.04	4.65	0.43	5.60	0.19	1.90	0.03
1.40	0.62	3.40	0.11	5.20	0.12	1.40	0.01
1.18	0.12	2.40	0.06	2.40	0.07	2.15	0.04
0.07	0.04	1.85	0.02	1.85	0.05		

Table IV

pH Final	[Cu] Org. g./l.	pH Final	[Ni] Org. g./l.	pH Final	[Co] Org. g./l.	pH Final	[Zn] Org. g./l.
2.50	2.30	5.70	0.64	6.40	0.47	5.60	0.48
2.50	2.02	5.10	0.41	5.95	0.36	4.10	0.35
2.10	1.25	3.32	0.33	5.70	0.33	3.25	0.33

Table IV-continued

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
1.24	0.56	2.85	0.30	3.20	0.25	2.15	0.16
0.58	0.21	2.50	0.24	2.90	0.25	1.19	0.02
		1.75	0.09	2.15	0.12		
		1.20	0.02	1.20	0.02		

Table V

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
4.25	3.08	5.40	2.76	5.32	1.90	5.75	0.81
2.20	3.69	4.49	1.83	5.13	0.74	4.70	0.20
1.25	1.92	4.08	0.65	4.78	0.42	2.32	0.10
0.63	1.13	3.95	1.15	3.10	0.09	1.90	0.02
0.38	0.78	2.55	0.09	1.40	0.01	1.40	0.01
0.10	0.46	1.80	0.024				

Table VI

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
4.10	3.51	6.82	2.12	6.80	1.91	5.80	2.42
2.47	3.04	6.64	2.14	6.55	1.92	4.53	2.45
1.62	2.19	4.15	2.14	5.48	1.88	2.90	1.39
1.52	1.27	2.98	1.79	4.33	1.86	1.98	0.18
1.00	0.36	2.85	1.67	2.50	0.87	1.70	0.10
		2.48	1.18	2.00	0.23		
		2.10	0.45				

Table VII

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
3.40	2.58	6.72	1.48	7.10	1.34	5.70	0.79
3.00	1.84	5.90	0.51	6.70	1.01	4.80	0.63
1.35	0.11	4.52	0.52	6.30	0.53	2.48	0.46
		2.55	0.45	4.80	0.50	1.33	.13
		2.12	0.27	3.10	0.48		
		1.25	0.05	2.16	0.23		
				1.52	0.09		

Table VIII

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l
3.50	3.57	3.50	2.17	3.10	1.91
2.45	3.22	3.32	1.65	4.10	1.48
2.15	2.91	3.45	1.17	3.70	1.05
1.29	1.17	2.70	0.48	2.72	0.42
0.60	0.15	1.70	0.12	1.60	0.10

Table IX

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
2.20	3.10	3.97	1.45	4.17	1.09	4.52	1.77
1.90	2.95	3.82	1.35	4.12	0.95	4.32	1.27
1.58	2.78	3.72	1.13	4.05	1.01	3.20	0.65
0.80	2.33	2.60	0.36	3.10	0.53	2.32	0.37
0.30	1.96	1.52	0.04	2.62	0.32	1.55	0.14
0.02	1.46	0.85	0.02	1.55	0.07	0.60	0.04

Table X

pH Final	[Co] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
4.00	0.33	5.60	0.20	5.00	0.22	3.80	0.91
2.53	0.08	5.40	0.09	4.40	0.11	2.50	0.11
1.70	0.02	4.50	0.03	3.10	0.03	2.00	0.04
1.35	0.01	3.70	0.01	2.50	0.02	1.68	0.03
		3.50	0.01	1.48	0.02	0.94	0.01

Table XI

pH Final	[Cu] Org. g/l	pH Final	[Ni] Org. g/l	pH Final	[Co] Org. g/l	pH Final	[Zn] Org. g/l
3.70	0.44	6.80	0.36	5.60	0.17	4.99	0.49
3.00	0.38	5.45	0.21	3.75	0.22	3.82	0.26
2.52	0.34	3.80	0.28	1.90	0.05	3.45	0.23
1.40	0.04	1.50	0.06	1.40	0.02	2.60	0.21
		1.40	0.02			1.45	0.03

EXAMPLES XII–XV

Loaded organic solutions prepared as in Examples I–XI were stripped of metal values with aqueous sulfuric acid (1.50 g./l. H_2SO_4). Equal volumes of the loaded organics and the stripping solution were contacted with shaking for two minutes. After separation of the phases, the stripped organic was analyzed for metal value content. In the present Examples, the loaded organics are identified by reference to the hydrogen ion exchange reagent salts of Examples II–XI used in extracting the metal values. Results of the stripping operations are set forth in the following Tables XII–XV:

Table XII

Loaded Organic		Stripped Organic	
Reagent Salt Exp.	Cu^{++} g/l	Cu^{++} g/l	% Cu^{++} Stripped
II	3.77	0.08	98
III	2.13	0.004	99.5
IV	2.43	0.004	99.5
V	3.08	0.071	97.8
VI	3.04	0.002	99.7
VIII	3.57	0.002	100
IX	3.10	0.228	92.5
X	0.334	0.0001	100
XI	0.339	<0.0001	100

Table XIII

Loaded Organic		Stripped Organic	
Reagent Salt Exp.	Ni^{++} g/l	Ni^{++} g/l	% Ni^{++} Stripped
II	1.41	0.34	76
III	2.16	0.0005	100
IV	0.504	0.0016	100
V	1.83	0.03	98.3
VI	2.14	0.0006	100
VII	1.48	0.0012	100
VIII	2.17	0.0032	100
IX	1.14	0.0008	100
X	0.204	<0.0005	100
XI	0.36	<0.0005	100

Table XIV

Loaded Organic		Stripped Organic	
Reagent Salt Exp.	Co^{++} g/l	Co^{++} g/l	% Co^{++} Stripped
II	0.322	0.081	74.4
III	1.73	1.12	34.6
IV	0.327	0.045	85
V	1.90	1.31	31.4
VI	1.96	<0.0005	100
VII	1.01	0.248	75
VIII	1.05	0.0018	100
IX	0.93	0.705	24.6
X	0.214	0.0001	100
XI	0.226	<0.0005	100

Table XV

Loaded Organic		Stripped Organic	
Reagent Salt Exp.	Zn^{++} g/l	Zn^{++} g/l	% Zn^{++} Stripped
II	0.157	<0.0001	100
III	0.101	0.003	100
IV	0.346	0.0005	100
V	0.760	0.007	99

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Table XV-continued

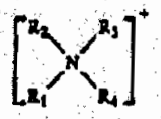
Loaded Organic Reagent Salt Exp.	Zn^{++} g./l.	Stripped Organic Zn^{++} g./l.	% Zn^{++} Stripped
VI	2.42	0.0007	100
VII	0.790	<0.0005	100
IX	1.77	0.0009	100
X	0.014	<0.0005	100
XI	0.486	<0.0005	100

EXAMPLE XVI

Example I-A was essentially repeated except kerosene was used as the solvent, the diketone and quaternary ammonium compound were used at levels of 10 and 11.2% weight/volume, respectively, and the resulting solution of the diketone salt was used to extract nickel (4 g./l. Ni^{++} as $NiSO_4$, pH 4.2) and cobalt (4 g./l. Co^{++} as $CoSO_4$, pH 3.9). Analyses indicated that 4.1 g./l. Ni^{++} and 2.6 g./l. Co^{++} were extracted with raffinate (metal barren aqueous) pH values of 6.8 and 7.2, respectively.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition consisting essentially of an essentially water-immiscible organic solvent containing dissolved therein at least about 2% by weight of a quaternary ammonium salt of a hydrogen ion exchange agent wherein the salt has the formula QL where Q is the quaternary ammonium cation of the formula



where R_1 is a hydrocarbon radical of 6 to 24 carbon atoms and R_2, R_3 and R_4 are hydrocarbon radicals of 1 to 24 carbon atoms and L is the deprotonated moiety of anion of the hydrogen ion exchange reagent, L being derived from reagents selected from the group consisting of

(a) an α-hydroxy oxime

(b) a 2-hydroxybenzophenoxime

(c) a βdiketone

(d) a hydroxy containing benzoxazole and

(e) a substituted 8-hydroxyquinoline.

2. The composition of claim 1 wherein the salt is present in the solvent in an amount of about 2 to 75% by weight.

3. The composition of claim 2 wherein the solvent is a liquid hydrocarbon.

4. The composition of claim 1 wherein said β-diketone is a fluorinated beta-diketone.

* * * * *

** TOTAL PAGE.25 **

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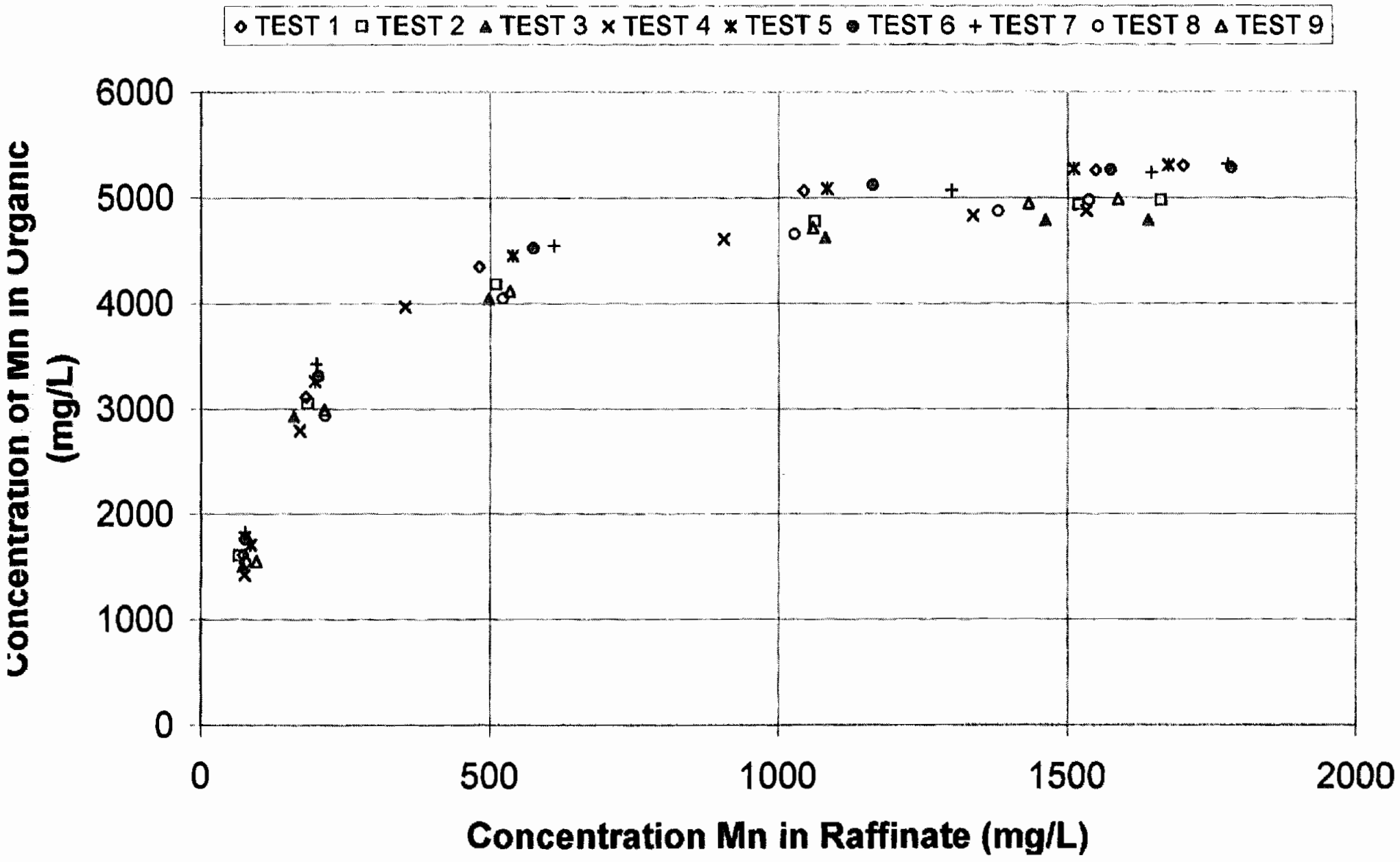
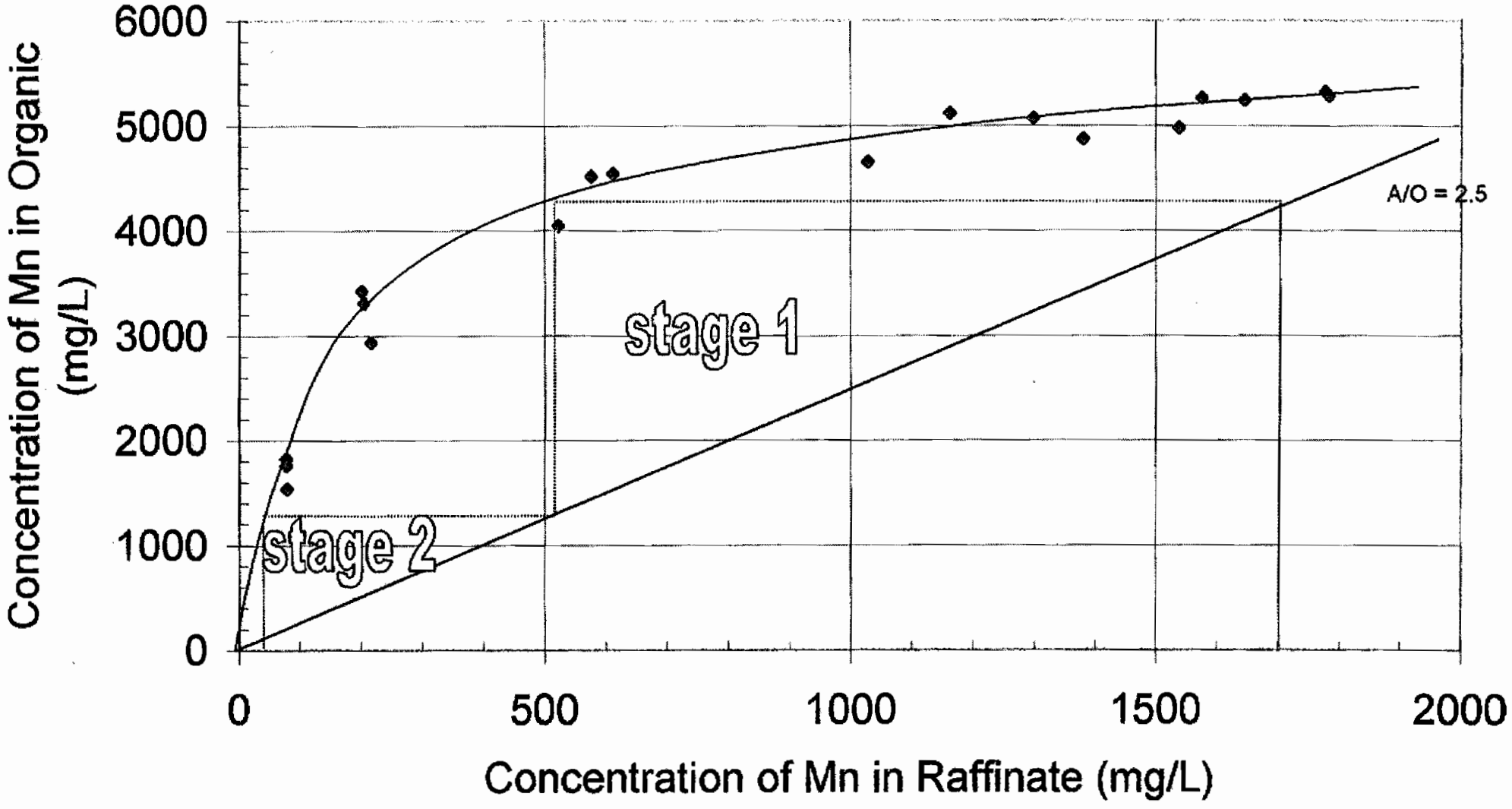
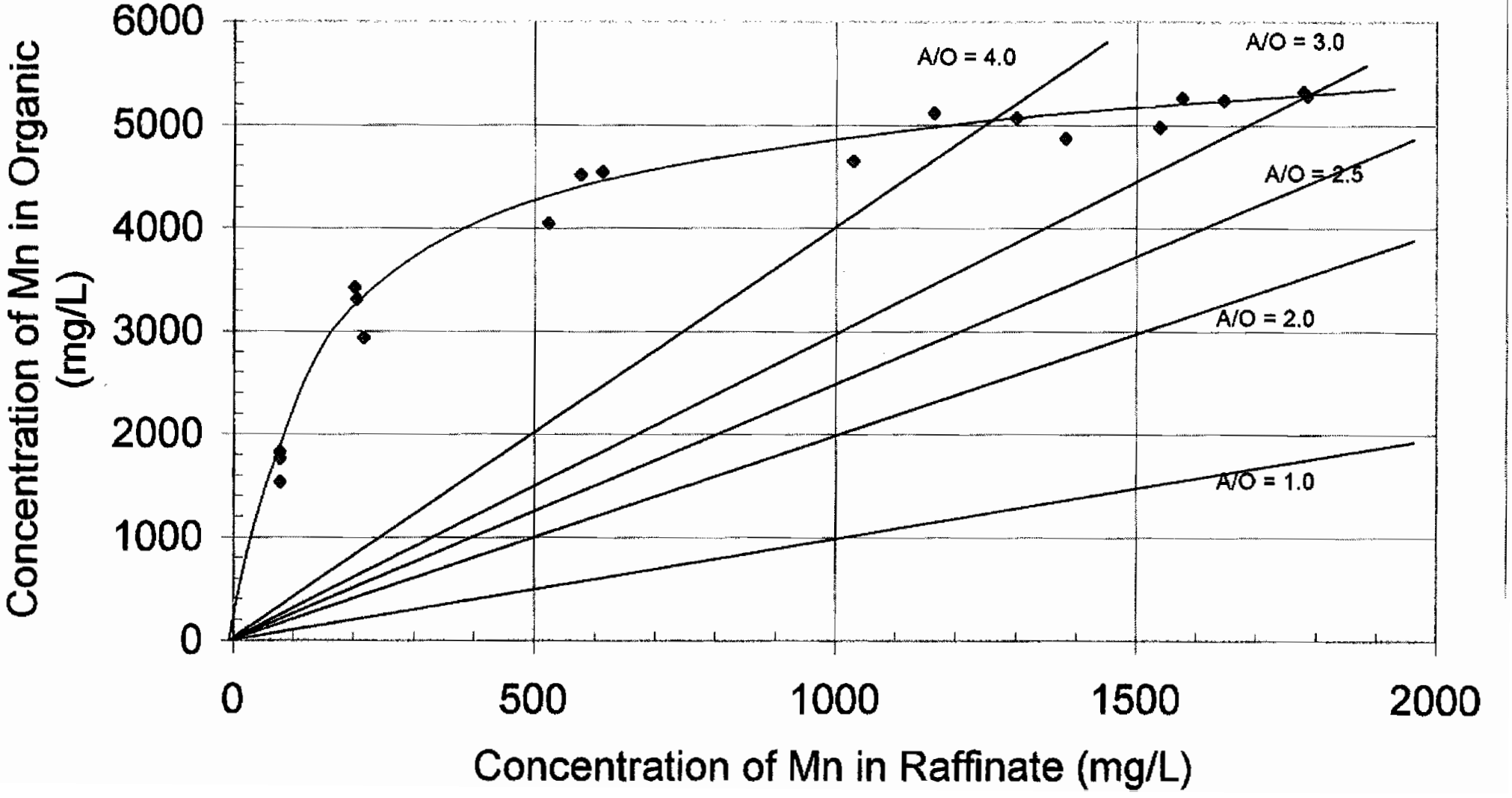
Overall Manganese Loading Isotherm



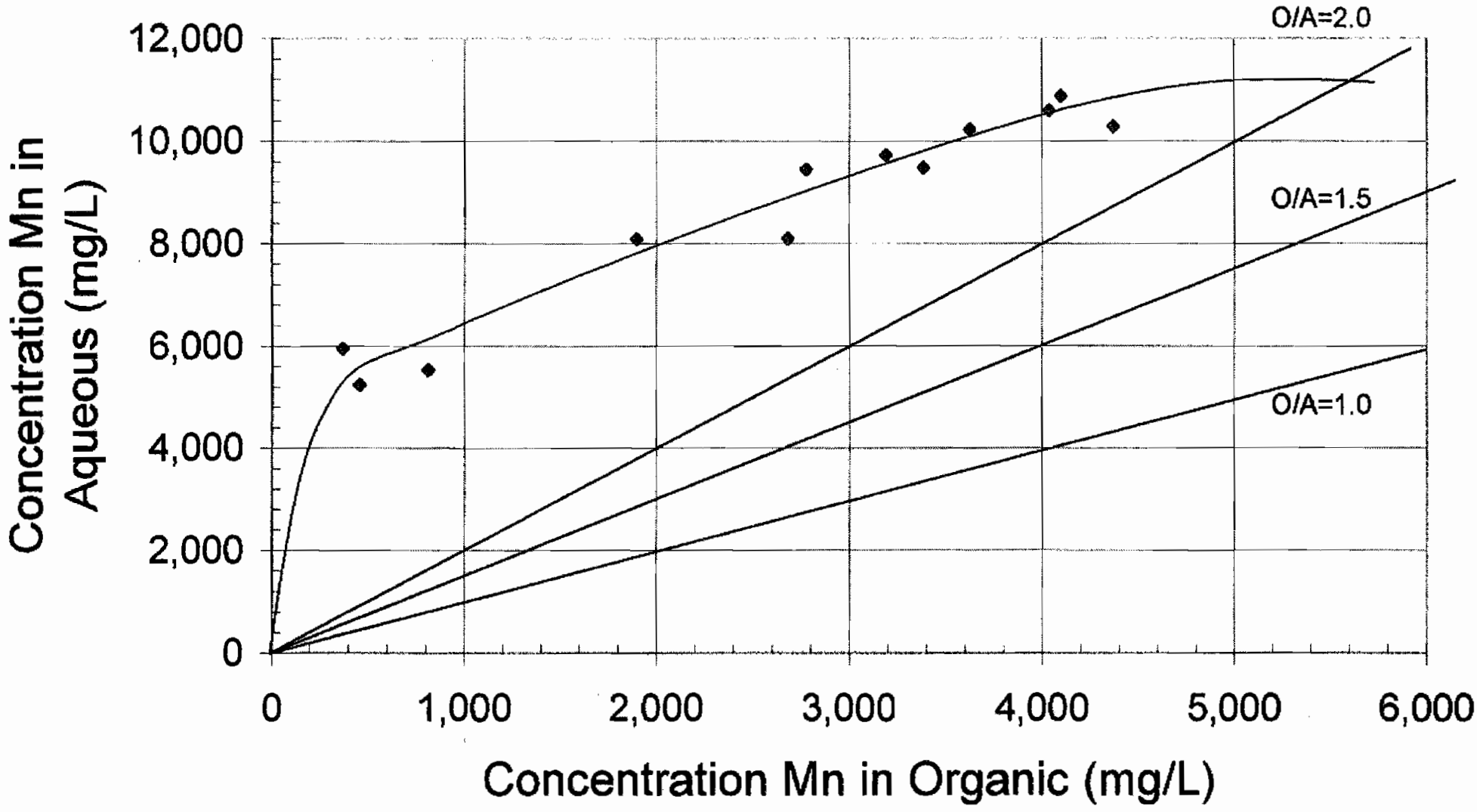
Manganese Loadi..g Isotherm Using Q=0.45M, L=0.45M and 0% TBP



Manganese Loading Isotherm Using Q=0.45M, L=0.45M and 0% TBP



Manganese Stripping Isotherm of Q=0.45M, L=0.45M, 0% TBP Using 0.1M HCl Solution



10

IRON REMOVAL FROM MANGANESE CHLORIDE LIQUORS BY PRECIPITATING AS AKAGANEITE

PREPARED FOR

CAL ENERGY OPERATING CO.

Progress Report No. 1 LR Project: 10138-001

NOTE: This report refers to the samples as received.
The practice of this Company in issuing reports of this nature is to require the recipient not to publish the report or any part thereof without the written consent of Lakefield Research.

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EXECUTIVE SUMMARY

Iron removal from two manganese chloride process streams (CalEnergy strip liquor and Lakefield Flowsheet # 1, eluate) from the CalEnergy Salton Sea project was evaluated by ferrous oxidation and precipitation as akaganeite. Iron could be removed from both process streams. The use of hydrogen peroxide as an oxidant appeared to be ineffective. Sodium hypochlorite, however could selectively oxidise ferrous iron from both the strip liquor and the eluate process stream.

Seed crystals were produced from a concentrated ferric chloride solution. XRD analysis of the seed material confirmed akaganeite ($Fe_8(O,OH)_{16}Cl_{1.3}$) as the major crystalline phase with traces of lepidocrocite (FeO(OH)) and magnetite (Fe_3O_4).

Solubility experiments were performed to establish the pH dependent curves as well as to determine the induction pH as a function of dissolved iron. Based on these results operating pH values were determined for the oxidation/precipitation experiments. It was found that a two-stage process operating around pH 1.7 to pH 1.8 and pH 2.3 to 2.4 followed by a polishing stage operating at pH 3.4 were the optimum conditions for iron precipitation as akaganeite.

Six oxidation experiments were carried out to investigate the influence of stoichiometric excess of oxidant on the residual iron concentration, uptake of manganese in akaganeite, as well as crystal properties. Initial attempts to oxidise ferrous iron with hydrogen peroxide failed in this particular chloride system; sodium hypochlorite proved to be a very efficient oxidant reacting almost (99 %) according to stoichiometry. Though manganese concentration decreased somewhat as the iron was oxidised by sodium hypochlorite during the experiments, the uptake of manganese in the solids was minimal. In terms of loss of manganese: in all tests less than 1.5 % manganese reported to the akaganeite solids.

XRD analysis confirmed formation of akaganeite as the major phase in all oxidation tests with traces of lepidocrocite, hematite and magnetite. SEM imaging showed akaganeite as compact anhedral aggregates. Individual crystals were sub-micron in size.

Qualitative filtration testwork indicated that akaganeite precipitated in QL strip liquor filtered more easily than akaganeite precipitated in the eluate solution. It is suggested that the higher ionic strength of the eluate (60 g/L Mn) plays an important role in this. Though filtration is still slow it is assumed that in a continuous operation crystals will grow larger and thus have improved filtration properties.

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INTRODUCTION

This report contains the results of the laboratory bench scale testwork conducted on the CalEnergy strip liquor and a synthetically made up eluate solution. The main objective of the testwork was to evaluate the removal of iron from the process stream by precipitation of akaganeite.

The testwork was requested by Mr. George Furmanski of CalEnergy and by Dr. Kevin Anthony of MarTech Consulting Pty Ltd.

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SUMMARY OF RESULTS

1. Project Overview

Iron removal from manganese containing chloride solutions was studied in two cases. The first case study dealt with the CalEnergy Flowsheet in which iron was to be removed from a strip liquor containing 6 – 7 g/L Mn, 6 – 7 g/L Fe(II) and 5 g/L Ca. The second case study dealt with iron removal from an eluate process stream according to Lakefield Flowsheet # 1, containing 6 g/L Fe(II) and 60 g/L Mn.

Seed material was produced from a concentrated ferric chloride solution that was slowly neutralised with sodium hydroxide. The seed material produced during this testwork was subjected to solubility testwork to determine the solubility pH dependence as well as the critical supersaturation. This information provided operating design parameters for the oxidation/precipitation testwork.

2. Feed/Reagent Characterisation

Table 1: Composition of Strip Liquor as received from CalEnergy

mg/L	pH	FAT (g/L HCl)	Fe^{2+}	Fe(tot)	Mn	Ca	Cl
Drum 1	2.36	< 1	7400	7400	6090	3730	26700
Drum 2	2.60	< 1	8400	8400	6910	3810	27500

Table 2: Composition of synthetic eluate (Lakefield Flowsheet # 1)

	Fe^{2+}	Mn	Ca
mg/L	6010	55600	0

Table 3: Sodium Hypochlorite concentration in domestic bleach solution (Javex, s.g. = 1.07)

Sample ID	wt % NaClO reported	wt % NaClO analysed
Javex 5.25%	5.25	2.57

The wt% NaClO was determined by measuring residual chlorine and back-calculating to obtain hypochlorite concentration according to:

$$Cl_2 + 2NaOH \leftrightarrow NaOCl + NaCl + H_2O$$

Though the hypochlorite concentration has decreased 50% compared to its reported value, sodium hypochlorite (2.57 wt % NaClO) still oxidised all iron according to stoichiometry. Further analysis of this particular hypochlorite stock solution indicated that the hypochlorite decomposed into another potent oxidising chloride compound. Comparison tests with fresh hypochlorite confirm similar stoichiometry conditions; hypochlorite is a very efficient oxidant capable of oxidising ferrous iron according to stoichiometry.

3. *Seed Preparation*

A crucial part of precipitating crystalline akaganeite under supersaturated conditions is the presence of seed crystals. Since akaganeite is not commercially available, it had to be prepared in the lab. The following equation describes the precipitation of ferric hydroxide/akaganeite from a chloride system:

$$FeCl_3 + 2H_2O \rightarrow FeOOH + 3HCl$$

A concentrated ferric chloride (70 g/L Fe) solution was heated to 80 – 85 °C. The pH of the feed solution was 0.6. Precipitation of ferric hydroxide was visible during heating due to decreased solubility of ferric hydroxide at elevated temperatures. The solution was acidified (pH 0.21) with HCl to re-dissolve the precipitate. Sodium hydroxide crystals were then added slowly

to raise the pH to the target levels. Following neutralisation initial crystallisation was visible at pH 0.60 – 0.68. Neutralisation with sodium hydroxide continued up to pH 3 – 3.5 over a time span of 4 hours. At the end of the test the slurry was filtered. The solids were contacted again next day with fresh ferric chloride solution and the previous procedure was repeated. In total three of these tests were performed. The assumption was that the solids added to the second and third test would act as seed material and form crystalline akaganeite particles. XRD analysis confirmed the formation of akaganeite as the major phase. Test procedures and results are presented in Appendix A.

4. Solubility Testwork

Solubility testwork was performed with the seed material prepared as described in the previous section. The objective of these tests was to establish the pH dependence of the solubility dependence of akaganeite in both process liquors. These tests were performed in 500 mL fleakers filled with 200 mL slurry (25 g/L solids) at 80 °C. The slurries were equilibrated for 3 hours. At the end of the test the complete volume was filtered and the filtrate was re-heated and slowly neutralised by drop-wise addition of 1 M NaOH to establish the induction pH. Prior to induction pH determination a sample of the filtrate was taken and analysed for Fe(II) and Fe.

4.1 QL Strip Liquor

The solubility of akaganeite in the strip liquor is expressed as total iron versus pH. Since the iron in the strip liquor mainly consists of ferrous iron (see Table 1) this had to be oxidised beforehand in order to obtain data that would reflect on the actual process. Hydrogen peroxide was initially selected as an oxidant, since it would not introduce any impurity ions into the system. Table 4 presents the results obtained with hydrogen peroxide as an oxidant. Full details of the tests are available in Appendix B. From the data it can be concluded that a stoichiometric addition of 150 % did not oxidise the ferrous iron. Hydrogen peroxide was not an effective oxidant and its use was not pursued.

Table 4: Solubility of akaganeite in strip liquor; hydrogen peroxide oxidant.

	Target pH	pH (t=0)	pH (t=3)	T(t=3), °C	pH_i	Fe^{2+}, mg/L	Fe, mg/L
Test 1-0		1.00				8070	10100
Test 1-1	1.5	1.47	1.38	80	1.6	4640	5960
Test 1-2	2.0	1.33	1.88	80	2.2	2680	2880
Test 1-3	2.5	1.35	2.37	80	2.7	4050	4260
Test 1-4	3.0	1.35	2.60	80	3.0	4440	4870
Test 1-5	3.5	1.35	3.07	80	3.5	4110	4380

For the next series of tests, sodium hypochlorite (NaClO) was selected as an oxidant. The following equation describes the reaction stoichiometry:

$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$$

$$ClO^-_{(aq)} + H_2O + 2e^- \rightarrow Cl^-_{(aq)} + 2OH^-_{(aq)}$$

$$2Fe^{2+}_{(aq)} + ClO^-_{(aq)} + H_2O \rightarrow 2Fe^{3+}_{(aq)} + Cl^-_{(aq)} + 2OH^-_{(aq)}$$

Qualitative tests Sol 1-6 and Sol 1-7 were performed to confirm that hydrogen peroxide is not working in this particular chloride system as well as to confirm the oxidation of ferrous iron by sodium hypochlorite. Full details of both tests are reported in Appendix B. The first test (Sol 1-6) started with hydrogen peroxide addition, while monitoring E_h of the solution. Initially after the addition of H_2O_2 the emf increased to 450 mV (versus Ag/AgCl electrode). At that point sodium hypochlorite was added while monitoring emf which readily increased up to 650 – 780 mV. Another test (Sol 1-7) was performed in parallel monitoring the exact quantity of sodium hypochlorite over a period of 2 hours taking care not to exceed 600 mV, where Mn^{2+} may oxidise.

Table 5: Test results of Sol 1-6 and Sol 1-7

	Target pH	pH (t=3)	NaClO, % stoich.	% Fe oxidised	Mn mg/L	Fe^{2+} mg/L	Fe mg/L
Test 1-6	3.0	3.5	unknown	99.86%	7520	10	12.7
Test 1-7	1.5	1.5	82.24%	78.27%	10100	1608	4310

Calculations showed that based on 7400 mg/L Fe(II) and an 82.2 % stoichiometric addition of sodium hypochlorite, 78.2 % of ferrous iron had been oxidised to ferric iron. On this basis it was decided to continue further testwork with sodium hypochlorite as an oxidant (25 % stoichiometric excess). The test series Sol 1-0 to Sol 1-5 were repeated (Sol 1-8 to Sol 1-11) using this oxidant and the results are presented in Table 6.

Table 6: Akaganeite solubility in QL strip liquor; NaClO oxidant

	Target pH	pH (t=3)	T(t=3)	pH_i	Mn, mg/L	Fe^{2+}, mg/L	Fe, mg/L
Test 1-head			80		6440	8000	7950
Test 1-8	1.5	1.40	80	1.7	6980	20	3230
Test 1-9	2.0	1.86	80	2.3	6770	10	241
Test 1-10	2.5	2.32	80	2.8	7120	< 10	19.6
Test 1-11	3.5	3.87	80	5.0	6310	< 10	< 0.10

Based on these results it is possible to draw the solubility/supersaturation curves presented in Figure 1.

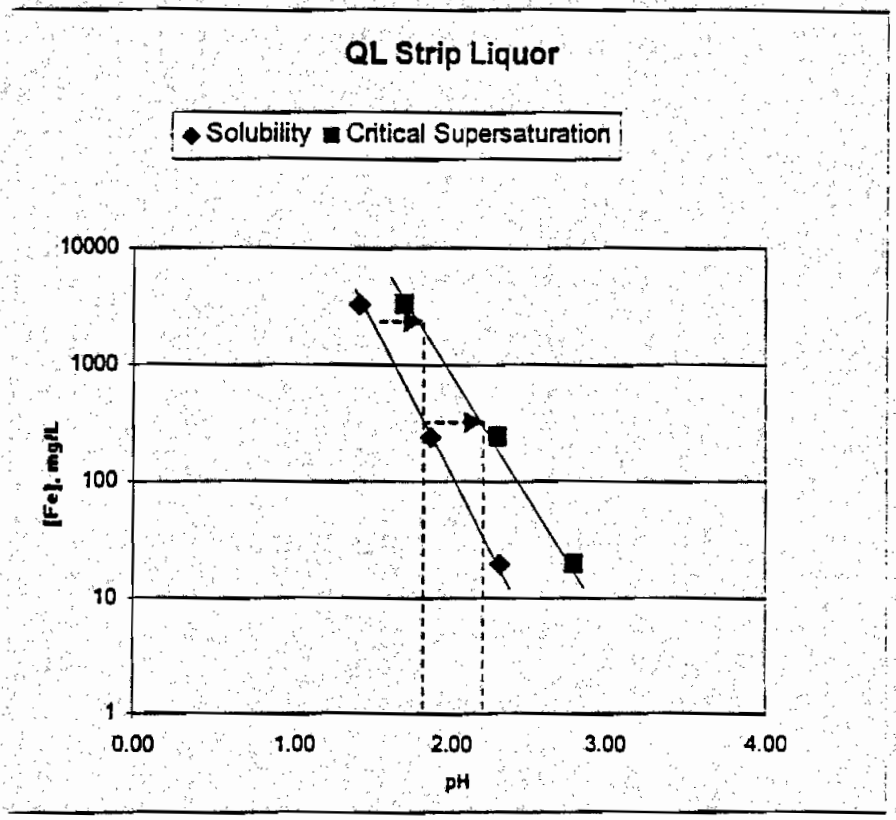


Figure 1: Solubility of akaganeite in QL strip liquor

On this basis it was concluded that a two stage (pH 1.8 – pH 2.4) precipitation process followed by a polishing stage at pH 3.4 – 3.6 to remove residual iron would yield optimum conditions for crystallisation of crystalline akaganeite.

4.2 QL eluate, Lakefield Flowsheet # 1.

Similar experiments were performed with akaganeite in the synthetically prepared QL eluate from Lakefield Flowsheet # 1. The composition of the eluate is presented in Table 2, however for these series of solubility tests the ferrous chloride had not been added, effectively removing ferrous oxidation prior to performing the solubility tests. Table 7 presents the results of tests Sol 2-1 to Sol 2-5 and Figure 2 presents the matching solubility/supersaturation curves.

Table 7: Akaganeite solubility in QL eluate; NaClO oxidant

	Target pH	pH (t=0)	pH (t=3)	T(t=3), °C	pH_i	Mn, mg/L	Fe, mg/L
Test 2-head						59400	0
Test 2-1	1.5	1.5	1.48	80	1.8		177
Test 2-2	2.0	1.9	1.79	82	2.2		21
Test 2-3	2.5	2.5	2.45	82	3.0		< 0.50
Test 2-4	3.0	2.9	3.09	82	3.6		< 0.50
Test 2-5	3.5	3.4	3.59	82	?		< 0.50

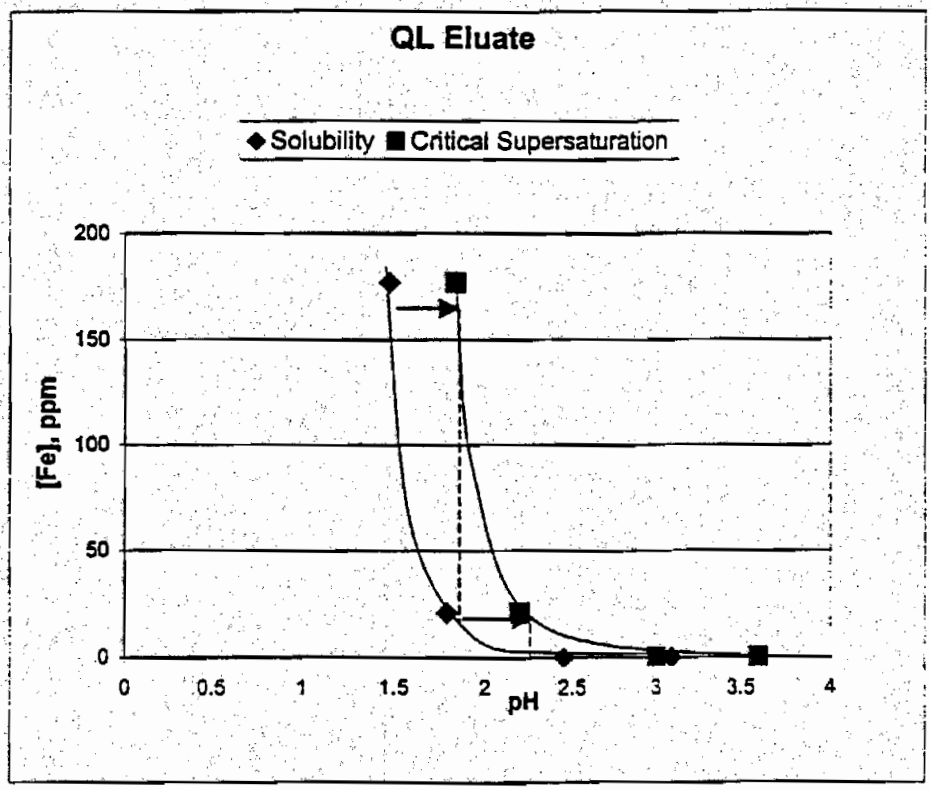


Figure 2: Solubility of akaganeite in QL eluate

5. *Oxidation/Precipitation Tests*

Six oxidation experiments were performed to investigate the influence of the stoichiometric addition of sodium hypochlorite on the quality of precipitate, residual iron left in solution as well as uptake of manganese in akaganeite. Conditions of the six tests are presented in Table 8.

solution as well as uptake of manganese in akaganeite. Conditions of the six tests are presented in Table 8.

Table 8: Test conditions oxidation experiments (Ox 1-1 to Ox 1-3 and Ox 2-1 to Ox 2-3)

Common conditions			Ox 1-1	Ox 1-2	Ox 1-3	Ox 2-1	Ox 2-2	Ox 2-3
Volume	0.7	L						
Agitation	300	rpm						
Temperature	80 - 82	°C						
Seed conc.	25	g/L						
Total seed added	17.5	g/L						
Base	2	M NaOH						
Oxidant	5.14%	wt% NaClO						
Stoichiometry	0.5	mol NaClO/mol Fe						
Test specific conditions								
Feed solution				QL Strip Liquor			QL Eluate	
Oxidant stoichiometric addition		%	100	150	80	120	180	80
Time at stage 1		min	60	60	60	60	60	60
Stage 1 target pH			1.8	1.8	1.8	1.7	1.7	1.7
Time at stage 2		min	60	60	60	60	60	60
Stage 2 target pH			2.4	2.4	2.4	2.3	2.3	2.3
Time at stage 3		min	30	30	30	30	30	30
Stage 3 target pH			3.4	3.4	3.4	3.4	3.4	3.4

The uptake of manganese is influenced by the addition of hypochlorite since once all ferrous iron has been oxidised, some of the manganese will oxidise. The influence of the stoichiometric excess of hypochlorite addition on the uptake of manganese on the residue solids (akaganeite) is presented in Table 9. A recovery percentage for manganese, calculated based upon uptake of manganese in the residue and quantity of solids recovered, is shown in Table 10. The uptake of manganese in akaganeite also depends on the washing of the solids. During tests Ox 1-3 and Ox 2-3 samples were taken of the wash filtrate and analysed for Mn and Ca (Ox 1-3). These results are also discussed in the individual test results below. The efficiency of sodium hypochlorite expressed as percent ferrous oxidised over percent stoichiometric addition of hypochlorite is presented in Table 11.

The filtration characteristics of each test are presented in Table 12. It must be noted though, that this data is mainly qualitative and the tests have not been replicated. Descriptions of the filtration (and where applicable settling tests) tests are reported in Appendix C.

Table 9: Characterisation of residue solids

test solution	Test id.	Fe, %	Mn, %	Cl, %	Planned Stoich.	Actual Stoich.
strip liquor	Test 1-1	58.4	0.10	5.24	100.0%	97.8%
strip liquor	Test 1-2	58.5	0.12	4.59	150.0%	146.8%
strip liquor	Test 1-3	59.5	< 0.05	7.37	80.0%	78.3%
eluate	Test 2-1	54.6	2.54	9.02	100.0%	120.5%
eluate	Test 2-2	54.2	2.05	7.36	150.0%	180.7%
eluate	Test 2-3	59.9	0.13	5.78	80.0%	78.3%

Table 10: Manganese recovery

	wt % Mn residue	total solids, g	Mn in solids, mg	Mn, aq mg/L	Mn, aq mg	% Mn lost in residue	Mn recovery %
Test 1-1	0.1	15.7	15.7	6090	4263	0.4%	99.6%
Test 1-2	0.12	15.9	19.1	6090	4373	0.4%	99.6%
Test 1-3	0.05	17.4	8.7	6090	3532	0.2%	99.8%
Test 2-1	2.54	14.8	375.9	55600	26688	1.4%	98.6%
Test 2-2	2.05	18.2	373.1	55600	26688	1.4%	98.6%
Test 2-3	0.13	16.4	21.3	55600	30580	0.1%	99.9%

Table 11: Oxidation of ferrous iron in experiments Ox 1-1 to Ox 2-3

	Fe^{2+} Feed mg/L	Added NaClO, g	% stoich. NaClO	Fe^{2+} t=60 mg/L	% Fe oxidized at 60 min	NaClO efficiency	Peak emf (mV)	Time of peak emf (min)
Test 1-1	7400	65.75	97.84%	19	99.7%	101.9%	715	120
Test 1-2	7400	98.63	146.76%	10	99.9%	68.0%	845	60
Test 1-3	7400	52.60	78.27%	1760	76.2%	97.4%	600	15
Test 2-1	6010	65.75	120.47%	39	99.4%	82.5%	915	60
Test 2-2	6010	98.63	180.70%	28	99.5%	55.1%	1031	30
Test 2-3	6010	42.72	78.27%	316	94.7%	121.0%	624	30

Table 12: Filtration characteristics

	filter paper	Vacuum, inch Hg	Filter time min	cake % solids
Test 1-1	Whatman # 42	21.5	15	47.92
Test 1-2	Whatman # 42	21.5	30	48.09
Test 1-3	Whatman # 42	21.5	17	49.07
Test 2-1	Whatman # 42	21.5	55	47.24
Test 2-2	Whatman # 42	21.5	55	47.51
Test 2-3	Whatman # 42	21.5	40	50.93

5.1 Discussion of oxidation test results

The complete test procedures and results are presented in Appendix C. The decrease in manganese concentration, observed in all tests, is partly due to dilution effect of adding 5.14 %(w/w) NaClO, as well as adding base (2M NaOH) during the experiment. A similar decrease in concentration is observed with calcium, which in fact practically simulates a tracer.

Nearly 99 % of ferrous iron oxidised within the first 15 to 30 minutes of the tests (Ox 1-2 and Ox 1-3): approximately half of the ferric iron formed at pH 1.6, precipitates as akaganeite upon oxidation, which makes the presence of seed crystals important in the oxidation stage. The difference in emf values in tests Ox 1-1 to Ox 1-3 as well as tests Ox 2-1 to Ox 2-3 is related to the different levels of sodium hypochlorite addition. Residual iron concentration at pH 3.4 - 3.6 (stage 3) is less than 0.5 mg/L, whereas residual iron concentration in test Ox 1-3 is 1260 mg/L, due to the low addition of sodium hypochlorite (78 % NaClO stoichiometric addition). In this test 81% of the ferrous iron oxidised after 30 minutes.

During tests Ox 1-3 and Ox 2-3 the solids were washed after filtration with a one-displacement wash (50 mL DI). Samples were taken and analysed for Mn and Ca. In test Ox 1-3 manganese and calcium concentrations are 1890 and 1110 mg/L respectively. In test Ox 2-3 manganese concentration was 16.3 g/L, which is an indication that an efficient washing strategy may recover much of the manganese lost to the iron precipitate

5.2 Solids characterisation

X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis were performed on selected samples. The reports are attached in Appendix D. In all submitted samples (solids collected at end of tests Ox 1-1, Ox 1-3, Ox 2-2) akaganeite was identified as the major crystalline phase with traces of lepidocrocite, magnetite and hematite tentatively identified. SEM imaging showed the majority of akaganeite as compact, anhedral aggregates. Individual crystals were sub-micron in size. Energy dispersive spectral (EDS) analysis confirmed the presence of minor amounts of chlorine present within the structure of akaganeite.

PROPOSED FLOWSHEET FOR IRON OXIDATION / PRECIPITATION

Based on the results reported here, a flowsheet is proposed that consists of one to two stage iron oxidation by sodium hypochlorite followed by two-stage akaganeite precipitation. The addition of oxidant can be E_h controlled or based on stoichiometry. The latter case would entail feeding from a large surge tank with known ferrous concentration that also serves to diminish feed composition fluctuations. A percentage of the iron precipitate will be recycled back to the oxidation stage to provide seeding, since some of the iron will precipitate upon oxidation. Figure 3 presents a schematic of the proposed flowsheet.

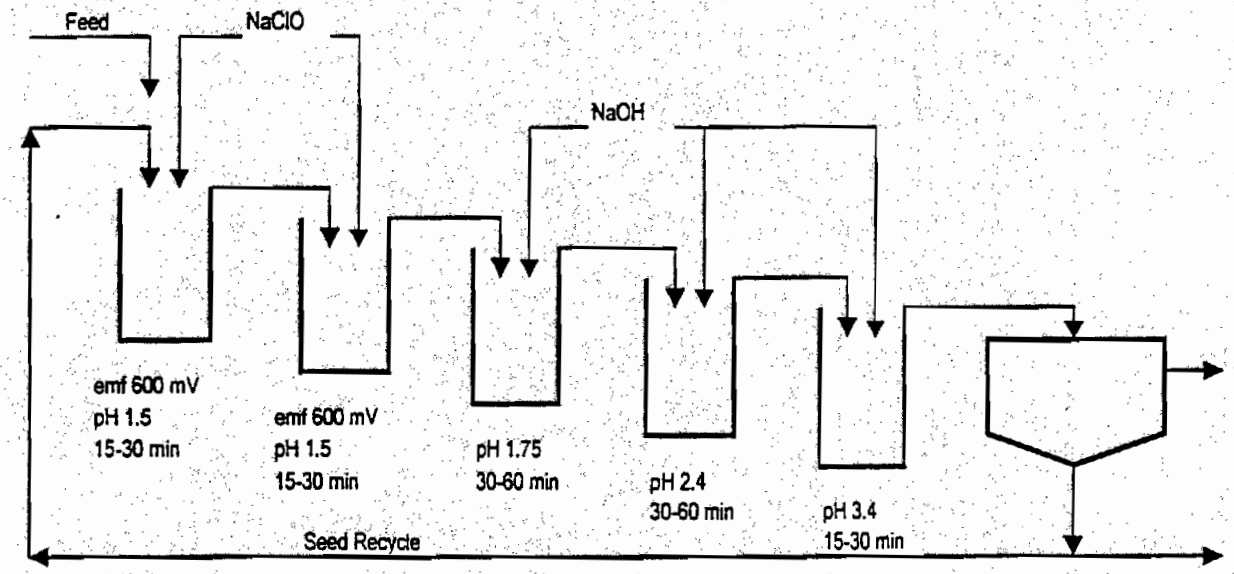


Figure 3: Proposed flowsheet for iron oxidation and precipitation

RECOMMENDATIONS FOR FURTHER TESTWORK

- High volume test to produce sufficient quantity of slurry,to enable quantitativve settling and filtration to be carried out.
- Study of use of flocculant to improve settling, effect of this on MnEW.
- Study of choice of base (MnO vs NaOH)
- Small scale pilot plant study. Suggest 2.5 L (with possibility for 5 L) reactors for oxidation, 10 L reactors for precipitation. Using recommended retention times, around 500 L of feed is required for a 48 hours run. Continuous testwork will determine which method of solid liquid separation is most suitable for this process.

Appendix A

Seed Preparation

Procedure .....

Results.....

ct: 10138-001
nt: CalEnergy

Niels Verbaan
6-Nov-00

ective: Preparation of seed material for precipitation tests
t: Seed prep 1

rocedure:

1 Heat ferric chloride solution to 80 C
2 Measure pH
3 Slowly neutralise using NaOH (1 M NaOH) till precipiation is visible (pH will start to go down)
4 Note pH (this is the induction pH)
5 Continue to neutralise till all iron has precipitated (Let's say pH 3.5)
6 Let solids settle. Decant as much as possible. Filter and repulp solids if necessary
7 Refill reactor with ferric chloride solution and repeat steps 1 to 6 (2 times)
8 Filter and wash solids using 500 mL water
9 Record wet weight
10 Dry in oven at 100 C
11 Submit sample for XRD, FeXRF, Cl

Project: 10138-001
Client: CalEnergy
Test: Cycle 1

Niels Verbaan
6-Nov-00

Time					NaOH (g)			
hour	minutes	elapsed (min)	Temp (C)	pH	reading	Refill	added	Observations
14	15	0	76.8	0.58	0		0	Precipitation visible. V = 1.5 L, agitation 300 rpm
14	30	15	75.9	0.21	0		0	Acidified slurry to remove solids
14	40	25		0.21	77.56		77.56	Started with 1 M NaOH, switched to dry NaOH crystals
14	44	29	75.7	0.26	74.65		80.47	
15	0	45	75.7	0.47	72.81		82.31	No precipitation
15	5	50		0.6	65.13		89.99	Solution getting darker
15	15	60	76.9	0.68	57.04		98.08	pH going down. Precipitation started
15	40	85		0.61	57.04		98.08	Precipitate clearly visible, brown orange
15	45	90	80.1	0.66	45.22		109.9	
15	55	100	80	0.67	26.8	86.17	128.32	Recovered metal scoop from slurry (2-4 minutes submersed)
		-855			112.97			
16	10	115	79.2	0.69	103.01		138.28	
16	45	150	80.8	0.78	66.4		174.89	
17	0	165		0.82	37.02		204.27	
17	5	170	82.6	0.83	19.12	91.57	222.17	
17	20	185	83.6	0.9	86.73		227.01	
17	40	205		1.03	62.78		250.96	
17	49	214	82.4	1.24	45.77		267.97	
18	20	245		2.75	30.46		283.28	Stop test

10138-001
CalEnergy
Cycle 2

Niels Verbaan
7-Nov-00

Time					NaOH (g)			
hours	min	total min	Temp °C	pH	reading	refill	added	Observations
11	22	0	73.8	0.61				Filtered solids from Seed prep 1 were used as seed.
11	37	15	75	0.6	105.04		0	pH went down after solids were added (0.79 to 0.6), which
11	40	18		0.64	96.71		8.33	is an indication of the precip reaction.
11	48	26	81.2	0.67	80.6		24.44	pH = 0.77 (reset T in pH meter)
12	40	78	82	0.78	65.86		39.18	
12	45	83	78.5	0.76	65.86		39.18	
12	50	88	79.6	0.79	49.2		55.84	
12	58	96		0.85	46.44		58.6	
13	10	108	80.5	0.86	29.62		75.42	
13	15	113		0.86	24.62		80.42	
13	22	120		0.87	16.28	88.88	88.76	
13	39	137	80.1	0.91	79.54		98.1	
13	50	148	80.1	0.94	73.71		103.93	
14	5	163		0.96	64.99		112.65	
14	7	165	82.6	0.99	59.82		117.82	
14	15	173	83.6	1.06	41.74		135.9	
14	22	180	82.4	1.13	27.5		150.14	
14	40	198	82.4	1.17	24.49		153.15	
14	43	201		1.31	14.62	124.82	163.02	
14	49	207		2.56	112.43		175.41	
14	51	209		3.12	111.05		176.79	

Project: 10138-001
Client: CalEnergy
Test: Cycle 3

Niels Verbaan
8-Nov-00

Time					NaOH (g)			
hour	minutes	cum. min	T, °C	pH	reading	refill	added	Observations
8	57	0	76	0.66	111.26			Left stirring overnight (at temperature)
10	32	95	80	0.72	87.78		0	
10	41	104		0.72	60.36		27.42	
11	5	128		0.82	25.52		62.26	Split up sample due to high % solids (problem with stirring)
11	12	135	78	0.96	25.57		62.21	T-adjustment pH meter
11	22	145		0.98	21.27	117.76	66.51	
11	30	153		1.06	93.19		91.08	
11	47	170	80	1.32	61.71		122.56	
				3				end test
								Solids filtered and washed

Appendix B

Solubility – Saturation Testwork

Procedures.....

Results.....

Project: 10138-001
Client: CalEnergy

Niels Verbaan
10-Nov-00

Objective: Procedure solubility experiments
Tests: Sol 1-0 to Sol 1-5
Liquor: QL Strip Liquor

Conditions:

			Comments
Number of experiments (data points)	5		
Variable	pH		
Slurry	25	g/L	
Volume	200	mL	Use 500 mL fleakers
Agitation			Marine type impellers
Solids	5	g/200 mL	
Temperature	80	C	
Duration of solubility exp.	3	hr	
pH modifiers	HCl or NaOH		Make up 1 M HCl and 1 M NaOH
Peroxide addition			Required to remove ferrous from solution. Ferrous will affect iron analys, as some will oxidize to ferric.
Feed:	6	g/L Fe(II)	
Reaction:			$Fe^{2+} + H^+ + 0.5\ H_2O_2 = Fe^{3+} + H_2O$
Stoichiometry	0.5	mol H_2O_2/mol Fe^{2+}	
Excess:	150	%	
To add:	0.02	mol H_2O_2	Per 200 mL
Strength:	35.00	wt %	
To add:	0.55	g H_2O_2 (100 %)	per 200 mL
	1.57	g H_2O_2 (30 %)	per 200 mL
Filtration	millipore		
Induction pH detrmination	0.5 or 1 M NaOH		

Procedure:

1 Heat up 200 mL of process liquor.
2 Once T has been reached add seed (5 g).
3 Wait 5 minutes, add the required amount of oxidant
4 Measure pH (pH t=0).
5 Wait 10 minutes and adjust pH with apropriate pH modifier
6 Equilibrate for 3 hours
7 Filter pulp. Take sample of filtrate for Fe analysis (ICP)
8 Heat up filtrate back to 80 C (use a millipore setup if necessary). Solution may not contain any solids
9 Start neutralising (SLOWLY) with 1 M NaOH (or less concentrated), until solids are visible or pH starts decreasing
10 This pH is the induction pH (pHi)

Note: When testing solubility of akaganeite in in synthetic made up solution (QL eluate), do not add any ferrous chloride as this needs to be oxidized again with hydrogen peroxide. Naturally this is not the case when doing the oxidation/precipitation trial runs.

Results:

	Target pH	pH (t=0)	pH (t=3)	T(t=3), °C	pH i	Fe^{2+}, ppm	Fe, ppm
Test 1-0		1				8070	10100
Test 1-1	1.5	1.47	1.38	80	1.55	4640	5960
Test 1-2	2	1.33	1.88	80	2.2	2680	2880
Test 1-3	2.5	1.35	2.37	80	2.7	4050	4260
Test 1-4	3	1.35	2.6	80	3	4440	4870
Test 1-5	3.5	1.35	3.07	80	3.45	4110	4380

Project: 10138-001
Client: CalEnergy

Niels Verbaan
16-Nov-00

Objective: Investigate oxidation of ferrous iron by monitoring EMF
Test: Sol 1-6 Sol 1-7
Liquor: QL Strip Liquor

Conditions:

Volume	200	mL	
pH	2		
Seeding	25	g/L	
Seed to add	5	g	
Temperature	80		
Peroxide addition			Required to remove ferrous from solution.
			Ferrous will affect iron analysis, as some will oxidize to ferric.
Feed:	7400	ppm Fe(II)	(Drum 1)
Reaction:			$Fe^{2+} + H^+ + 0.5\ H_2O_2 = Fe^{3+} + H_2O$
Stoichiometry	0.5	mol H_2O_2/mol Fe^{2+}	
Excess:	150	%	
To add:	0.02	mol H_2O_2	Per 200 mL
Strength:	30.00	wt %	
To add:	0.68	g H_2O_2 (100 %)	per 200 mL
	2.25	g H_2O_2 (35 %)	per 200 mL

Procedure: Idem as previous solubility experiments (sol 1-0 to sol 1-5)
Monitor EMF. If EMF below 600 mV, add more H_2O_2
Perform experiments on hot plate to speed up process.
Analyze samples for Fe(2) and Fe(tot)

	Test 1-6					Test 1-7					
Targets	3.5					1.5					Notes
Time, min	pH	(30wt%) H_2O_2, g (cum)	(5.25wt%) Javex, g	emf, mV	Temp, °C	pH	(30wt%) H_2O_2, g	(5.25wt%) Javex, g (cum)	emf, mV	Temp, °C	
0	2	0	0	410	80	2	0	0	420	80	1
10	2	2.25		450							2
		4.77		476							3
		6.92		486							
60	1.7	7		450							4
											5
											6
90				450	80			0	430	80	7
105			??	600							8
120	1.4			650							
	1.7										9
150				780				2.72	490		
180	3.5							5.59	519		10
190						1.6		9.38	542		
200								13.86	565		
210								15.31	581		
240	3.5					1.5		15.45	611		

	Notes
1	Added 5 g Akaganeite to test1-6 and test 1-7
2	Added calculated amount of peroxide to test 1-6
3	Decided to add extra hydrogen peroxide
4	EMF initially going up after addition of H2O2, but decreasing shortly after
5	Hydrogen peroxide obviously does not work.
6	Decided to try out something else: sodium hypochlorite (NaClO)
7	Used household bleach (Javex, 5.25 wt % NaClO)
8	I did not measure the quantity of added Javex
9	Started adding Javex to test 1-7, this time more careful not to overshoot EMF
10	Black precipitate visible in local area where NaClO is added. It seems to re-dissolve however.

...ions:

Total Javex added	15.45	g
Javex strength	5.25	wt%
Reaction		$2Fe^{2+} + NaClO + H_2O = 2Fe^{3+} + NaCL + 2OH^-$
Stoichiometry	0.50	mole NaClO / mole Fe(II)
	0.81	g NaClO
	0.011	mole NaClO
This oxidizes	0.022	mol Fe(II)
	1.2	g Fe
We have	7400	ppm Fe(II)
in	200	mL
gives	1.48	g Fe(II)
% stoichiometric	82.24%	

Results:

QL Strip Liquor

	Target pH	pH (t=3)	NaClO, % stoich.	% Fe oxidised	Mn ppm	Fe^{2+} ppm	Fe ppm
Sol 1-6	3	3.5	unknown	99.86%	7520	10	12.7
Sol 1-7	1.5	1.5	82.24%	78.27%	10100	1608	4310

Niels Verbaan
20-Nov-00

Project: 10138-001
Client: CalEnergy

Objective: Procedure
Tests: Sol 1-8 to Sol 1-11
Liquor: QL Strip Liquor

Conditions

Volume:	200	mL
Javex strength	5.25	wt%
Reaction		$2Fe^{2+} + NaClO + H_2O = 2Fe^{3+} + NaCL + 2OH^-$
Stoichiometry	0.50	mole NaClO / mole Fe(II)
We have	7400	ppm Fe(II)
in	200	mL
gives	1.48	g Fe(II)
Excess:	25	% stoichiometry
Oxidant to add:	23.48	g NaClO (5.25 %)

Procedure: See Sol 1-0 to Sol 1-5

Results:

	Target pH	pH (t=3)	T(t=3)	pH i	Mn, ppm	Fe^{2+}, ppm	Fe, ppm
Test 1-head			80		6440	8000	7950
Test 1-8	1.5	1.4	80	1.69	6980	20	3230
Test 1-9	2	1.86	80	2.3	6770	10	241
Test 1-10	2.5	2.32	80	2.8	7120	< 10	19.6
Test 1-11	3.5	3.87	80	5	6310	< 10	< 0.10

Project: 10138-001
Client: CalEnergy

Niels Verbaan
14-Nov-00

Objective: Procedure
Tests: Sol 2-1 to Sol 2-5
Liquor: Lakefield Flowsheet # 1 eluate (no ferrous chloride added yet)

Conditions: idem as previous solubility experiments

Volume	200	mL
pH	2	
Seeding	25	g/L
Seed to add	5	g
Temperature	80	

Procedure: See Sol 1-0 to Sol 1-5
do not execute line 3 (oxidant addition)
Ferrous chloride was not added uyet to the the synthetically made up eluate solution, since it would have to be oxidised again in order to perform the solubility experiments

Results:

	Target pH	pH (t=0)	pH (t=3)	T(t=3), °C	pH i	Mn, ppm	Fe, ppm
						59400	
Test 2-head							177
Test 2-1	1.5	1.5	1.48	80	1.84		21
Test 2-2	2	1.9	1.79	82	2.2		< 0.50
Test 2-3	2.5	2.5	2.45	82	3		< 0.50
Test 2-4	3	2.9	3.09	82	3.6		< 0.50
Test 2-5	3.5	3.4	3.59	82	?		

Appendix C

Oxidation testwork

Procedures.....

Results.....

10138-001
CalEnergy - Fe removal

Niels Verbaan
22-Nov-00

Objective: Oxidation/Precipitation experiments
Ox 1-1 Ox 1-2 Ox 1-3

Solution: QL strip Liquor

Conditions:

Volume	0.7	L
Agitation	300	rpm
Temperature	80 -90	°C
Variable		hypochlorite addition (1x, 1.5x, 0.8x)
Seed concentration	25	g/L
Total seed added	17.5	g
Base	2	M NaOH or stronger
Oxidant	5.25	wt % sodium hypochlorite
Reaction:		$2Fe^{++} + NaClO + H_2O = 2Fe^{+++} + NaCL + 2OH^-$
Stoichiometry:	0.5	mole NaClO/mole Fe
Ferrous (feed)	7400	ppm (Drum 1)
Excess		
NaClO to add		

F

F

	1x	1.5x	0.8x
mol NaClO	0.05	0.07	0.04
g NaClO	3.45	5.18	2.76
g NaClO, 5.25 wt%	65.75	98.63	52.60
Test id	Ox 1-1	Ox 1-2	Ox 1-3

Sampling schedule

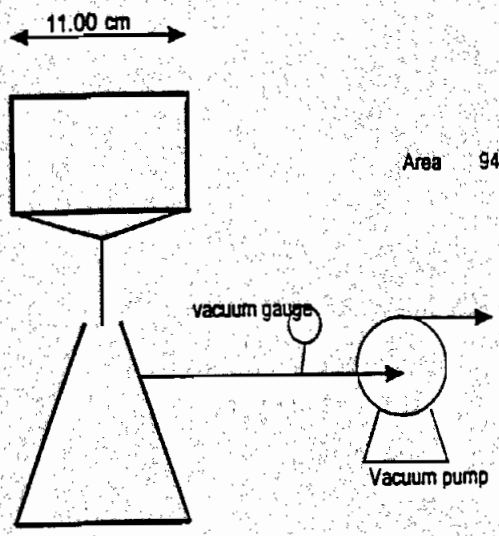
Procedure:

1 Heat up solution to 80 C
2 Some precipitate will form as the temp is increased.
3 Add the seed material (25 g/L): 17.5 g
4 Measure pH and EMF, take sample — t = 0
5 Add required amount of oxidant. Do this slowly over a period of 15 minutes
Time zero is time when all oxidant has been added to the slurry
6 Measure pH and EMF
7 Maintain conditions for 60 minutes, take samples — t = 15, 30, 60
8 Adjust pH to pH(A) (depends on solubility data)
9 Measure pH and EMF, take sample — t = 75, 90, 120
10 Maintain pH at that level for 60 minutes
11 Adjust pH to pH(B) (depends on solubility data)
12 Measure pH and EMF, take sample — t= 135, 150, 180
13 Maintain pH at that level for 60 minutes
14 Adjust pH to pH(C) (depends on solubility data)
15 Maintain pH at that level for 30 minutes
16 End of test
17 Set aside 100 mL for qualitative settling tests
18 Filter remaining slurry according to attached procedure.
19 Take sample of final filtrate — t = 210
20 Analyse all sol'n samples for Fe(2), Fe, Mn, Ca
21 Submit solid sample for XRD, SEM, FeXRF, MnXRF, CaXRF, ClXRF

Note: submit samples for XRD and SEM only for selected tests

pH A =	1.8
pH B =	2.4
pH C =	3.4

Semi-quantitative filter test



Area 94.99 cm2

Conditions:			
	Seeding	25	g/L
	Volume	0.7	L
	Per volume	17.5	g
	Solids produced:	7.4	g/L Fe
		5.18	g Fe
		8.24	g FeOOH
	Total solids to be filtered	25.74	g FeOOH
	Cake moisture	65.00	wt %
	Wet weight	73.54	
	Estimate sg wet cake	2.00	kg/L
	Volume wet cake	36.8	mL
	Cake thickness	0.39	cm
	Displacement wash	47.80	g liquor
	Use	50	mL DI water

Procedure:

1 Pour sample onto Buchner.
2 Turn vacuum pump. Note time and vacuum (inch Hg)
3 Measure time to filter complete sample
4 Note down any observations such as cake cracks etc
5 Measure volume of filtrate. Take sample (t = 210).
6 Wash with 1 displacement wash. Measure time it takes till cake is dry
7 Measure cake thickness

Results:

Test: Ox 1-1 **Liquor:** QL Strip Liquor **Oxidant addition:** 1x

Log sheet

Time hr	Time min	cum	pH	emf mV	Temp °C	Sample	Notes
10	50						Solution into reactor, heating up
10	55				60		Seed added
12	5					t-0	
12	10	0	2.4	370	80		All NaClO added (after sample t-0 had been taken)
12	20	10		636			
12	25	15	1.6			t-15	
12	40	30		680	80	t-30	
12	50	40	1.55		80.9		
13	10	60		710		t-60	After sampling pH 1.55 ↑ 1.8
13	25	75		710		t-75	
13	30	80	1.75				pH 1.7 ↑ pH 1.8
13	40	90	1.75			t-90	pH 1.7 ↑ pH 1.8
14	0	110	1.75	715	81		pH 1.7 ↑ pH 1.8
14	10	120			81	t-120	After sampling pH 1.8 ↑ 2.4
14	20	130	2.45	640	81		
14	25	135				t-135	
14	40	150	2.55			t-150	
14	55	165		640	81		
15	10	180	2.55			t-180	After sampling pH 2.5 ↑ 3.4
15	40	210	3.4	420	81		
						t-210	sample taken after filtration

End of test:

Volume slurry:	700 mL
Settling test	97 mL
Filtration test	603 mL
Filtrate	600 mL

Assay summary

Solution:

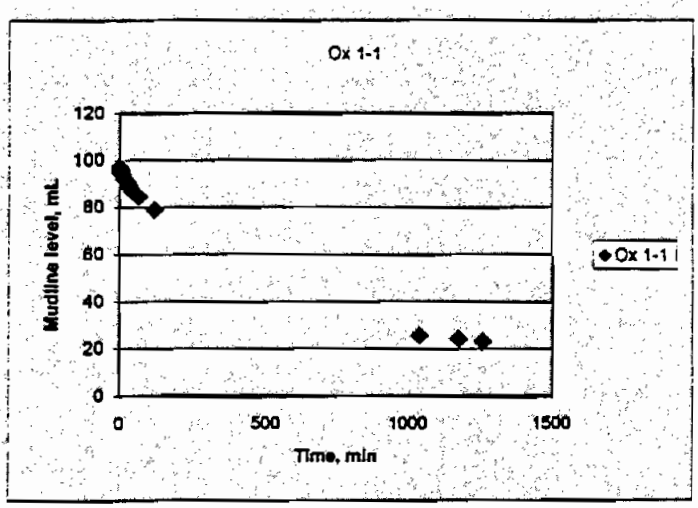
pH	Time min	Sample ID	Mn mg/L	Fe mg/L	Fe^{2+} mg/L	Ca mg/L
2.4	0	t-0	6860	7910	7910	3910
1.6	15	t-15	6200	3730	93	3650
1.6	30	t-30	6120	3460	17	3620
1.55	60	t-60	6190	3300	19	3540
1.75	75	t-75	5920	1810	17	3420
1.75	90	t-90	5600	1330	17	3260
1.75	120	t-120	5240	883	< 10	3130
2.45	135	t-135	5240	23.8	11	3090
2.45	115	t-115	5170	7.88	< 10	3020
2.45	180	t-180	4520	5.37	< 10	2670
3.4	210	t-210	4670	< 0.50	< 10	2700

Solids:

Sample ID	Buck. Wt g	Fe %	Mn %	Ca %	Cl g/t
OX 1-1	15.7	58.4	0.1	0.076	52385

Settling test

Time hr	min	cum	height, mL	Notes
		0	97	22-Nov
		3	96	Mudline clearly visible
		5	95	Supernatant fairly clear
		8	94	
		16	92	
		22	91	
		27	90	
		32	89	
		42	87	
16	52	62	84.5	
17	44	114	79	
9	6	1036	25.5	23-Nov
11	25	1175	24	
12	50	1260	23	



Filtration test:

Filtered slurry:	603.0	mL
Dry weight:	15.7	g
Solids concentration	26.0	g/L
Filter paper:		Whatman # 42, 110 mm
Vacuum	21.5	"Hg
Filter time:	15	min
Washing	50	mL DI
Washing time:	11	min
Wet weight cake	43.8	g
Tare	11.0	g
Dry weight	15.7	g
% solids	47.9	%
Cake thickness	1.5	mm

Akaganeite balance		
2.6	g	settling test
5.7	g	samples
15.7	g	Filtration
24.0	g	recovered.
25.7	g	total solids accordin

Niels Verbaan

Test: Ox 1-2 **Liquor:** QL Strip Liquor **Oxidant addition:** 1.5x 22-Nov-00

Log sheet

Time hr	Time min	Time cum	pH	emf mV	Temp °C	Sample	Notes
10	50						Sol'n added
10	55						Seed added
12	5					t-0	
12	10	0	2.4	365	80		All NaClO added
12	20	10		800			
12	25	15	1.6			t-15	
12	40	30		820		t-30	
12	50	40	1.55		81		
13	10	60		845		t-60	After sampling pH 1.49 - 1.8
13	25	75		795		t-75	
13	30	80	1.75				pH 1.7 - pH 1.8
13	40	90	1.75			t-90	pH 1.7 - pH 1.8
14	0	110	1.75	755	81		pH 1.7 - pH 1.8
14	10	120			81	t-120	After sampling pH 1.8 - 2.4
14	20	130	2.4	520	81		faulty EMF reading ???
14	25	135				t-135	
14	40	150	2.45		81	t-150	
14	55	165		710			
15	10	180	2.5			t-180	After sampling pH 2.5 - 3.4
15	40	210	3.6	420	81		
						t-210	sample diluted with 50 mL DI washwater by mistak

End of test:

Volume slurry:	718 mL	
Settling test	92 mL	
Filtration test	626 mL	
Filtrate	665 mL	(filtrate + wash)

Assay summary

Solution:

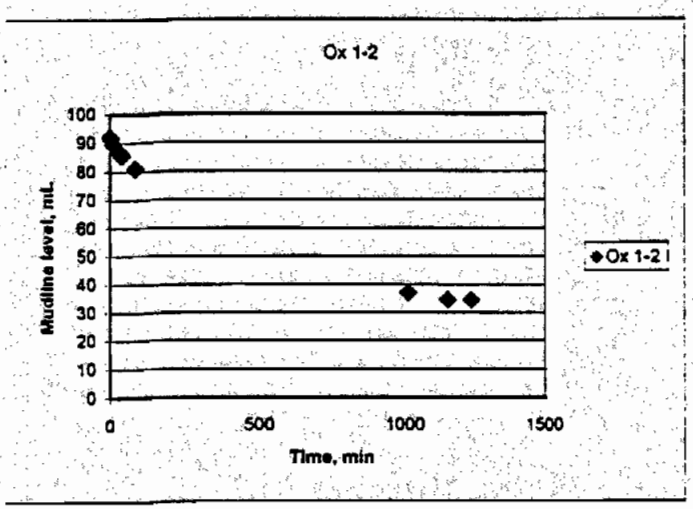
Time min	Sample ID	pH	emf mV	T °C	Mn mg/L	Fe mg/L	Fe^{2+} mg/L	Ca mg/L
0	t-0	2.4	365	80	6930	7950	7950	3860
15	t-15	1.6	800		6400	3430	80	3420
30	t-30	1.6	820		6620	3330	< 10	3490
60	t-60	1.55	845		6190	3050	< 10	3340
75	t-75	1.75	795		6020	1640	< 10	3270
90	t-90	1.75			5770	1180	< 10	3200
120	t-120	1.75	755		5600	756	< 10	3040
135	t-135	2.4	520		5490	52.7	10	3000
150	t-150	2.45	710		5310	11.3	< 10	2960
180	t-180	2.5			4710	7.45	< 10	2670
210	t-210	3.6	420		4440	< 0.50	< 10	2510

Solids:

Sample ID	Buck. Wt g	Fe %	Mn %	Ca %	Cl g/t
OX 1-2	15.9	58.5	0.12	0.12	45905

Settling test:

Time hr	Time min	cum	height, mL	Notes
16	19	0	92	22-Nov
16	22	3	91.5	Mudline clearly visible
16	29	10	89.5	Supernatant fairly clear
16	52	33	86.5	
16	59	40	85.5	
17	44	85	81	
9	6	1007	37	23-Nov
11	25	1146	34.5	
12	50	1231	34.5	



Filtration test

Filtered slurry:	626.0	mL
Dry weight	15.9	g
Density	25.4	g/L
Filter paper:		Whatman # 42, 110 mm
Vacuum	21.5	"Hg
Filter time:	30	min
Washing	50	mL DI
Washing time:	12	min
Wet weight cake	43.3	g
Tare	10.2	g
Dry weight	15.9	g
% solids	48.1	%
Cake thickness	1.5	mm

Akaganeite balance		
2.5	g	settling
5.7	g	samples
15.9	g	Filtration
24.2	g	recovered.
25.7	g	total solids accordin

Results:

Niels Verbaan

Test: Ox 1-3 **Liquor:** QL Strip Liquor **Oxidant addition:** 0.8x 24-Nov-00

Log sheet

Time hr	min	cum	pH	emf mV	Temp °C	Sample	Notes
10	0						Seed added
11	6		2.4	370	80	t-0	
11	15	0					t = 0, Javex added
11	25	10		596			
11	30	15				t-15	
11	33	18	1.68	600			
11	45	30	1.62	598	80	t-30	
12	15	60		598		t-60	After sampling pH ↑ 1.8
12	30	75	↑ 1.8		80	t-75	
12	35	80		589			
12	40	85	1.7 ↑ 1.8		80		Filtrate is reddish in colour
12	45	90				t-90	
13	0	105		578			
13	10	115	1.75 ↑ 1.8		80.1		
13	15	120				t-120	After sampling pH 1.8 ↑ 2.4
13	30	135	2.38	495	80	t-135	
13	45	150	2.45	445	80	t-150	
14	10	175	2.41	454	80		
14	15	180				t-180	After sampling pH 2.4 ↑ 3.4
14	45	210	3.2	325			

End of test:

Volume slurry:	580 mL
Settling test	99.5 mL
Filtration test	480.5 mL
Filtrate	mL

Assay summary

Solution:

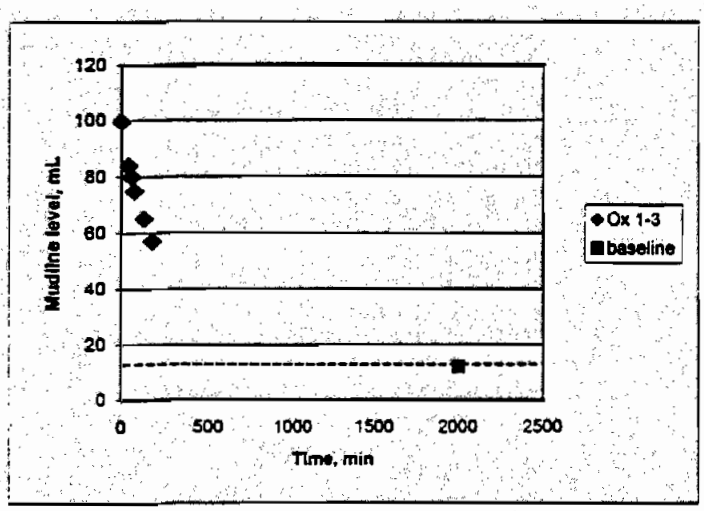
Time min	Sample ID	pH	emf mV	T °C	Mn mg/L	Fe mg/L	Fe^{2+} mg/L	Ca mg/L
0	t-0	2.4	370	80	6900	8180	8240	3970
15	t-15	1.68	600		6460	4820	1650	3750
30	t-30	1.62	598		5950	4150	1510	3600
60	t-60	1.62	598		6330	4100	1760	3860
75	t-75	1.8	589		5580	3290	1500	3400
90	t-90	1.75			5500	2630	1540	3360
120	t-120	1.75	578		6180	2400	1600	3800
135	t-135	2.38	495		5660	1960	1400	3470
150	t-150	2.45	445		5490	1750	1410	3420
180	t-180	2.41	454		5220	1080	1080	3210
210	t-210	3.2	325		5450	1040	1260	3340
	wash				1890	370	370	1110

Solids:

Sample ID	Buck. Wt. g	Fe %	Mn %	Ca %	Cl g/t
OX 1-3	17.4	59.5	< 0.05	0.02	73665

Settling test:

Time hr	min	cum	height, mL	Notes
15	1	0	99.5	
15	42	41	84	cloudy supernatant
15	58	57	80	
16	13	72	75	
17	7	126	65	
17	53	172	57	
9	0	3479	12	27-Nov-00
		2000	12	



Filtration test:

Filtered slurry:	480.5	mL
Dry weight	17.4	g
Density	36.2	g/L
Filter paper:		Whatman # 42, 110 mm
Vacuum	21.5	"Hg
Filter time:	17	min
Washing	50	mL DI
Washing time:	29	min
Wet weight cake	46.0	g
Tare	10.5	g
Dry weight	17.4	g
% solids	49.1	%
Cake thickness	1.5	mm

Akaganeite calance		
3.6	g	settling
5.7	g	samples
17.4	g	Filtration
26.7	g	recovered.
25.7	g	total solids accordin

Niels Verbaan
21-Nov-00

Project: 10138-001
Client: CalEnergy - Fe removal

Objective: Oxidation/Precipitation experiments
Test: Ox 2-1 Ox 2-2 Ox 2-3
Solution: Synthetic eluate

Conditions:

Volume	0.7	L
Agitation	300	rpm
Temperature	80 -90	C
Variable		hypochlorite additio (1x, 1.5x, 2x)
Seed concentration	25	g/L
Total seed added	17.5	g
Base	2	M NaOH or stronger
Oxidant	5.25	wt % sodium hypochlorite
Reaction:		$2Fe^{++} + NaClO + H_2O = 2Fe^{+++} + NaCL + 2OH^-$
Stoichiometry:	0.5	mole NaClO/mole Fe
Ferrous (feed)	6010	ppm (Drum 1)

F

F

Excess NaClO to add	1x	1.5x	0.8x
mol NaClO	0.05	0.07	0.03
g NaClO	3.45	5.18	2.24
g NaClO, 5.25 wt%	65.75	98.63	42.72
Test id	Ox 2-1	Ox 2-2	Ox 2-3

Sampling schedule

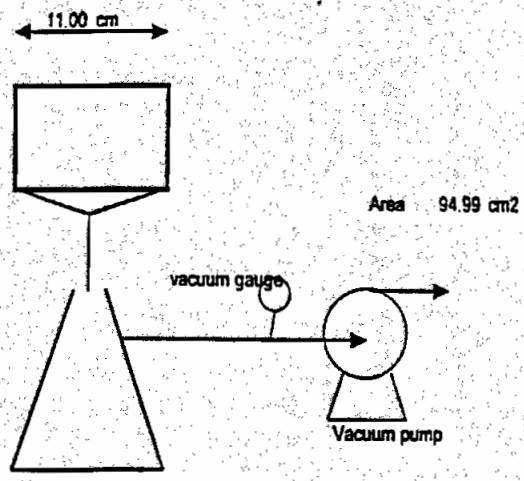
Procedure:

1 Heat up solution to 80 C
2 Some precipitate will form as the temp is increased.
3 Add the seed material (25 g/L): 17.5 g — t = 0
4 Measure pH and EMF, take sample
5 Add required amount of oxidant. Do this slowly over a period of 15 minutes
Time zero is time when all oxidant has been added to the slurry
6 Measure pH and EMF — t = 15, 30, 60
7 Maintain conditions for 60 minutes, take samples
8 Adjust pH to pH(A) = (depends on solubility data) — t = 75, 90, 120
9 Measure pH and EMF, take sample
10 Maintain pH at that level for 60 minutes
11 Adjust pH to pH(B) = (depends on solubility data) — t= 135, 150, 180
12 Measure pH and EMF, take sample
13 Maintain pH at that level for 60 minutes
14 Adjust pH to pH(C) = (depends on solubility data)
15 Maintain pH at that level for 30 minutes
16 End of test
17 Set aside 100 mL for qualitative settling tests
18 Filter remaining slurry according to attached procedure. — t = 210
19 Take sample of final filtrate
20 Analyse all sol'n samples for Fe(2), Fe, Mn
21 Submit solid sample for XRD, SEM, FeXRF, MnXRF, ClXRF

Note: submit samples for XRD and SEM only for selected tests

pH A = 1.7
pH B = 2.3
pH C = 3.4

Semi-quantitative filter test



Conditions:			
	Seeding	25	g/L
	Volume	0.7	L
	Per volume	17.5	g
	Solids produced:	6	g/L Fe
		4.2	g Fe
		6.68	g FeOOH
	Total solids to be filtered	24.18	g FeOOH
	Cake moisture	65.00	wt %
	Wet weight	69.09	
	Estimate sg wet cake	2.00	kg/L
	Volume wet cake	34.5	mL
	Cake thickness	0.36	cm
	Displacement wash	44.91	g liquor
	Use	50	mL DI water

Procedure:

1 Pour sample onto Buchner.
2 Turn vacuum pump. Note time and vacuum (inch Hg)
3 Measure time to filter complete sample
4 Note down any observations such as cake cracks etc
5 Measure volume of filtrate. Take sample.
6 Wash with 1 displacement wash. Measure time it takes till cake is dry
7 Measure cake thickness

Results:

Niels Verbaan
21-Nov-00

Test: Ox 2-1 Liquor: Lakefield Flowsheet # 1, eluate Oxidant addition: 1x

Log sheet

Time hr	Time min	Time cum	pH	emf mV	T °C	Sample	Notes
13	45		1.96	440	79.8		30 minutes after seed addition
13	55					t-0	
14	8						All NaClO added
14	10	0		641			Time zero
14	25	15	1.55			t-15	
14	40	30	1.45	830		t-30	
15	10	60	1.41	915	80	t-60	After sampling pH 1.41 - 1.7
15	15	65	1.7				
15	30	80	1.65				pH 1.6 - pH 1.7
15	45	95		820		t-90	
15	55	105	1.65		79		pH 1.6 - pH 1.7
16	15	125	1.7	615		t-120	After sampling pH 1.7 - 2.3
16	30	140	2.7			t-135	
16	50	160				t-150	
17	15	185	2.63	610		t-180	After sampling pH 2.7 - 3.3
17	40	210	3.3	500	80	t-210	

End of test:

Volume slurry:	480 mL
Settling test	0 mL
Filtration test	480 mL
Filtrate	450 mL

Assay summary

Solution:

Time	Sample ID	pH	emf mV	T °C	Mn mg/L	Fe mg/L	Fe^{2+} mg/L
	head				55600	6010	6010
0	t-0	1.96	440	80	61500	6560	6560
15	t-15	1.55	641		47400	2750	56
30	t-30	1.45	830		49600	2850	56
60	t-60	1.41	915		49200	2830	39
75	t-75	1.7			49200	2020	17
90	t-90	1.65	820		49000	1290	73
120	t-120	1.65			50600	679	73
135	t-135	2.7	615		48500	< 0.30	< 10
150	t-150	2.6			47500	< 0.3	< 10
180	t-180	2.6	610		47800	< 0.3	< 10
210	t-210	3.3	500		46200	< 0.3	< 10

Solids:

Sample ID	Buck. Wt. g	Fe %	Mn %	Cl g/t
OX 2-1	14.8	54.6	2.54	90173

Filtration test:

Filtered slurry:	480.0	mL
Dry weight	14.8	g
Density	30.8	g/L
Filter paper:	Whatman # 42, 110 mm	
Vacuum	21.5	"Hg
Filter time:	55	min
Washing	50	mL DI
Washing time:	3.5	min
Wet weight cake	42.1	g
Tare	10.7	g
Dry weight	14.8	g
% solids	47.2	%
Cake thickness	1.5	mm

Akaganeite balance		
0.0	g	setting
5.7	g	samples
14.8	g	Filtration
20.5	g	recovered.
24.2	g	total solids accordin

Results:

Niels Verbaan

Test: Ox 2-2 Liquor: Lakefield Flowsheet # 1, eluate Oxidant addition: 1.5x 21-Nov-00

Time hr	Time min	Time cum	pH	emf mV	T °C	Sample	Notes
13	45		1.96	440	79.8		30 minutes after seed addition
13	55					t-0	
14	10	0					Time zero. All NaClO added
14	25	15		641		t-15	
14	40	30	1.55			t-30	
15	10	60	1.45	830		t-60	
15	15	65	1.7				
15	45	95	1.65			t-90	
15	55	105		820			
16	15	125	1.7	615		t-120	
16	30	140	2.7			t-135	
16	50	160				t-150	
17	15	185	2.63	610		t-180	
17	40	210	3.3	500	80	t-210	

End of test:

Volume slurry:	480 mL
Settling test	0 mL
Filtration test	480 mL
Filtrate	450 mL

Assay summary

Solution:

Time	Sample ID	pH	emf mV	T °C	Mn mg/L	Fe mg/L	Fe^{2+} mg/L
0	t-0	2	440	80	56300	6240	6240
15	t-15	1.58			42500	2210	45
30	t-30	1.5	1031		48000	2530	28
60	t-60	1.45	960		46600	2300	28
75	t-75	1.7			47700	1860	< 10
90	t-90	1.65	830		49400	1240	11
120	t-120				52500	722	11
135	t-135	2.8	605		48100	< 0.50	< 10
150	t-150				48300	< 0.50	< 10
180	t-180	2.75	605		56900	< 0.50	< 10
210	t-210	3.2	530		60900	< 0.50	< 10

Solids:

Sample ID	Dry. Wt. g	Fe %	Mn %	Cl g/t
OX 2-2	18.2	54.2	2.05	73559

Filtration test

Filtered slurry:	480.0	mL
Dry weight	18.2	g
Density	37.9	g/L
Filter paper:	Whatman # 42, 110 mm	
Vacuum	21.5	"Hg
Filter time:	55	min
Washing	50	mL DI
Washing time:	13	min
Wet weight cake	47.4	g
Tare	9.1	g
Dry weight	18.2	g
% solids	47.5	%
Cake thickness	1.5	mm

Akaganeite balance		
0.0	g	settling
5.7	g	samples
18.2	g	Filtration
23.9	g	recovered.
24.2	g	total solids accordin

Results:

Niels Verbaan

Test: Ox 2-3 Liquor: Lakefield Flowsheet # 1, eluate Oxidant addition: 0.8x 24-Nov-00

Time hr	Time min	Time cum	pH	emf mV	T °C	Sample	Notes
10	0						Seed added
11	6		1.9	443	80	t-0	
11	15	0					t = 0, Javex added
11	25	10		596			
11	30	15				t-15	
11	33	18	1.59	614			
11	45	30	1.52	624	80	t-30	
12	15	60		630		t-60	After sampling pH - 1.8
12	30	75	- 1.7			t-75	
12	35	80		620			
12	40	85	1.6 - 1.7				Filtrate is reddish in colour
12	45	90				t-90	
13	0	105		615	80		
13	10	115	1.65 - 1.7				
13	15	120				t-120	After sampling pH 1.8 - 2.4
13	30	135	2.26	500	80	t-135	
13	45	150	2.32	475	80	t-150	
14	10	175	2.28	486	80		
14	15	180				t-180	After sampling pH 2.4 - 3.4
14	45	210	3.4	296	80		

End of test:

Volume slurry:	550	mL
Settling test	99	mL
Filtration test	451	mL
Filtrate		mL

Assay summary

Solution:

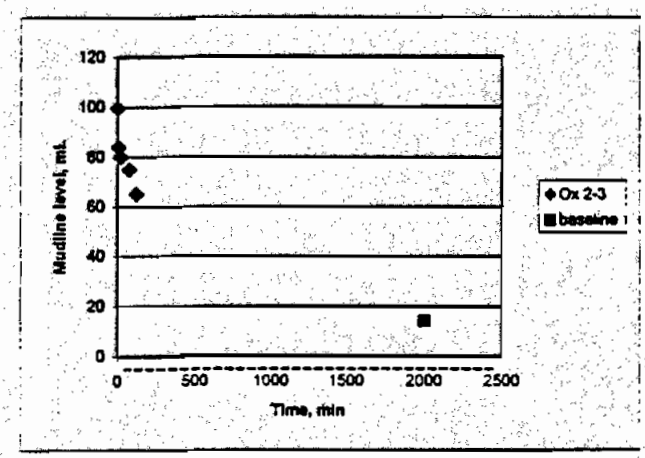
Time	Sample ID	pH	emf mV	T °C	Mn mg/L	Fe mg/L	Fe^{2+} mg/L
	head				52900	5480	5480
0	t-0	1.9	443	80	55200	5810	5810
15	t-15	1.59	614		50100	2990	360
30	t-30	1.52	624		46800	2630	327
60	t-60		630		47200	2520	316
75	t-75	1.7	620		45600	2150	330
90	t-90	1.65			46400	1850	326
120	t-120	1.65	615		46200	1410	335
135	t-135	2.26	500		47200	280	327
150	t-150	2.32	475		48000	239	311
180	t-180	2.28	486		39600	260	337
210	t-210	3.4	290		44900	203	296
	wash				16300	85	85

Solids:

Sample ID	Dry. Wt. g	Fe %	Mn %	Cl g/t
OX 2-3	16.4	59.9	0.13	57827

Settling test:

Time hr	Time min	cum	height mL	Notes
15	51	0	99.5	
15	58	7	84	cloudy supernatant
16	13	22	80	
17	7	76	75	
17	53	122	65	
9	0	2469	14	27-Nov-00
		2500	14	



Filtration test:

Filtered slurry:	451.0	mL
Dry weight	16.4	g
Density	36.4	g/L
Filter paper:	Whatman # 42, 110 mm	
Vacuum	21.5	"Hg
Filter time:	40	min
Washing	50	mL DI
Washing time:	25	min
Wet weight cake	42.3	g
Tare	10.1	g
Dry weight	16.4	g
% solids	50.9	%
Cake thickness	1.5	mm

Akaganeite balance		
3.6	g	settling
5.7	g	samples
16.4	g	Filtration
25.8	g	recovered.
0.0	g	total solids accordin

Appendix D

Mineralogy Report

XRD graphs .....

SEM / EDS analysis.....

Lakefield Research

Mineralogical Services

X-ray Diffraction Analysis and Scanning Electron Microscope Examination of Fe Precipitates

submitted by

Calenergy Operating Company – Salton Sea

Project Managed By: Nichola McKay, M.Sc., Senior Mineralogist

Date: December 7, 2000

Project No: 10138-001 NOV4510.R00 / DEC4501.R00

Note

This report refers to the samples as received. The practice of this Company in issuing reports of this nature is to require the recipient not to publish the report or any part thereof without the written consent of Lakefield Research Limited.

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X-ray Diffraction Analysis and Scanning Electron Microscope Examination of Fe Precipitates

Summary Report

Three Fe precipitate samples, identified as OX1-1, OX1-3, and OX2-2 were submitted for mineralogical study. A portion of each sample was pulverized and subjected to X-ray diffraction (XRD) analysis for qualitative identification of crystalline phases. A portion of each sample was mounted, as-received, for scanning electron microscopy (SEM) analysis. The objectives of the SEM study were determination of bulk composition by energy dispersive spectral (EDS) analysis and examination and comparison of precipitate crystallinity.

The samples were virtually identical in mineral assemblage and morphology. The samples consisted primarily of akaganeite ($Fe_8(O,OH)_{16}Cl_{1-3}$). Trace amounts of lepidocrocite (FeO(OH)), magnetite (Fe_3O_4) and hematite (Fe_2O_3) were tentatively identified. SEM-EDS analysis confirmed the presence of minor amounts of chlorine within the structure of the akaganeite. The akaganeite in OX2-2 also contained minor amounts of manganese. Akaganeite formed compact, anhedral aggregates, with minor amounts of angular cleavage or parting. Individual crystals were sub-micron in size, and were not visually resolvable. A summary of XRD and SEM analyses is presented in Table 1. SEM photomicrographs, EDS spectra and XRD charts are appended.

Sample	XRD mineral identification		EDS composition		SEM Imaging
	Major	Trace/Tentative	Major	Minor	Morphology
OX1-1	akaganeite	lepidocrocite magnetite hematite	Fe	Cl	Compact, anhedral masses. Minor sub-angular cleavage or parting. Sub-micrometer crystals.
OX1-3	akaganeite	lepidocrocite magnetite hematite	Fe	Cl	Compact, anhedral masses. Minor sub-angular cleavage or parting. Sub-micrometer crystals.
OX2-2	akaganeite	lepidocrocite magnetite hematite	Fe	Cl, Mn	Compact, anhedral masses. Minor sub-angular cleavage or parting. Sub-micrometer crystals.

LAKEFIELD RESEARCH LIMITED
December 7, 2000

Nichola A. McKay, M.Sc.
Senior Mineralogist

Lisa Ryan
X-ray Diffraction Technologist

Bruce Jago, Ph.D.
Manager, Mineralogical Services

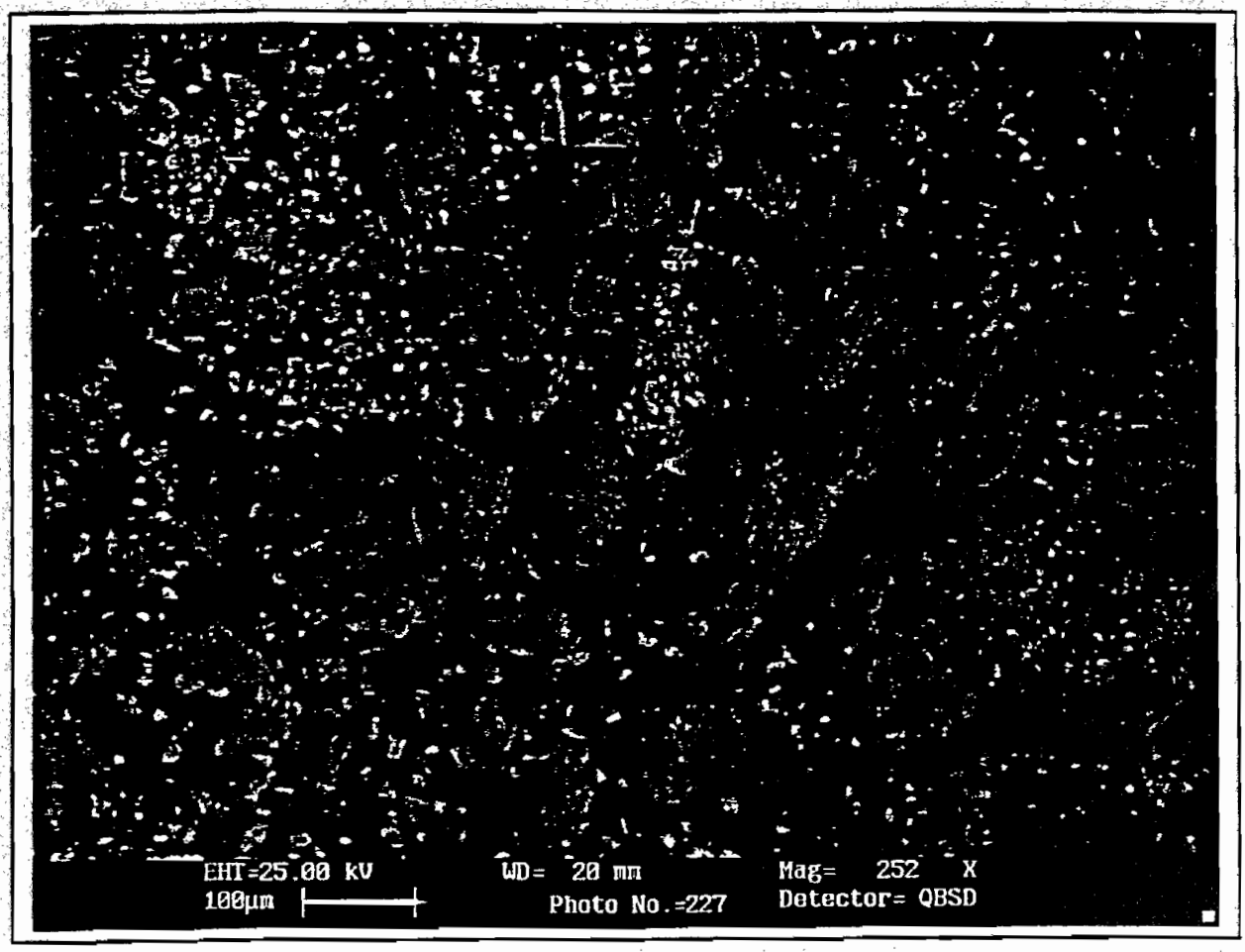
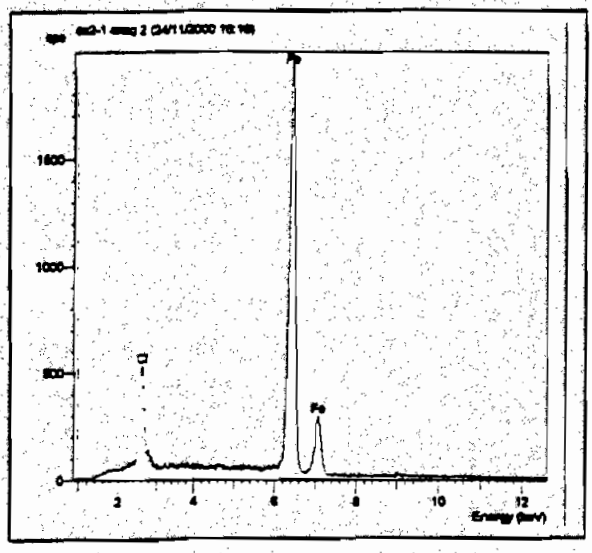


Photo 1: OX1-1. Overview of sample showing akaganeite aggregates. The akaganeite forms compact, anhedral masses. Sub-angular cleavages are visible on some of the grains. No discrete crystals could be identified. EDS analysis identified minor and variable quantities of chlorine associated with the akaganeite. BEI. 252x.



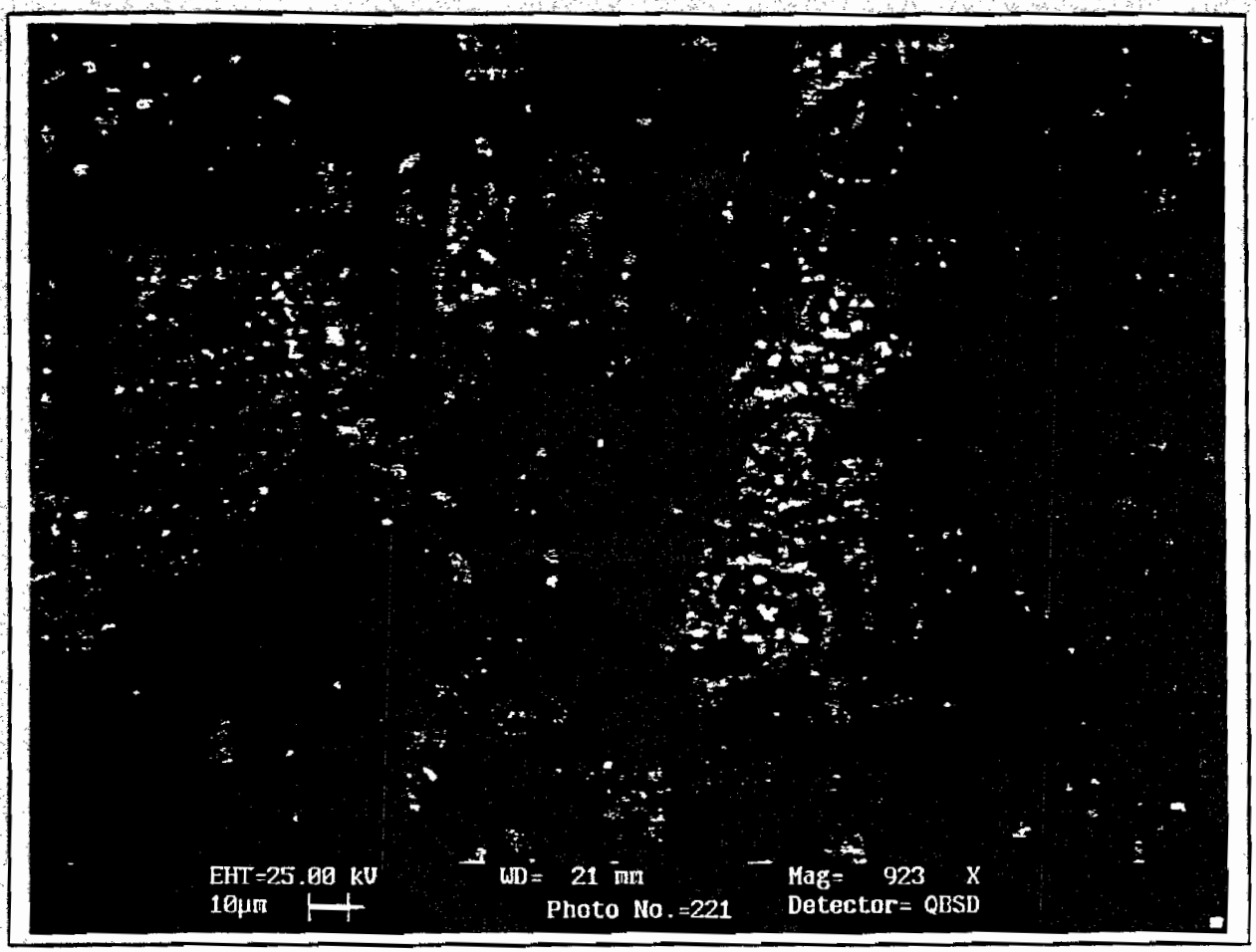


Photo 2: OX1-1. High magnification view of akaganeite aggregates. Individual crystals could not be resolved, and must be less than <0.5 µm in diameter. BEI. 923x.

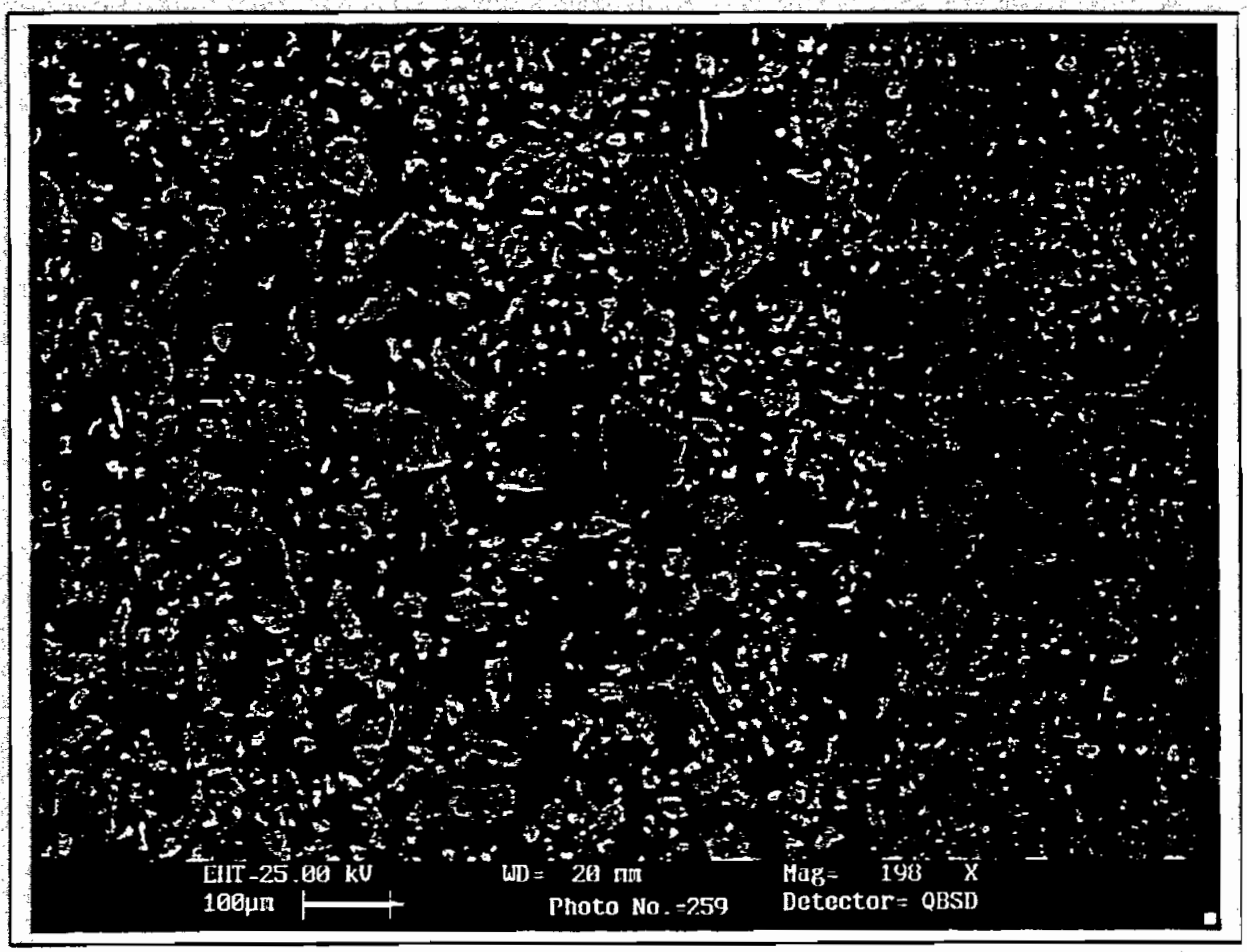
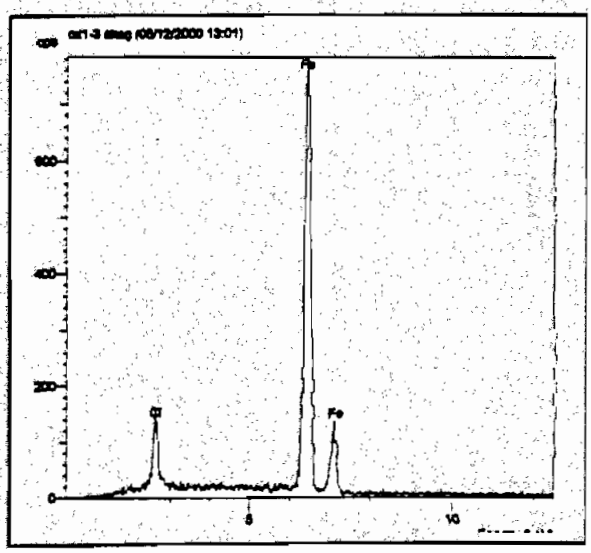
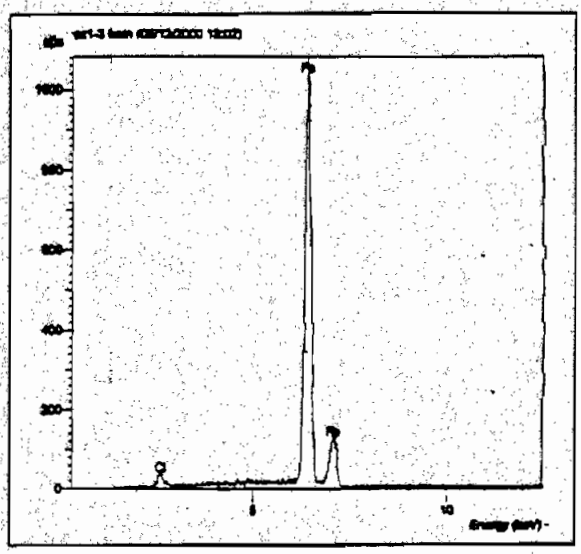


Photo 3: OX1-3. Low magnification view of akaganeite aggregates. The akaganeite grains are compact and anhedral. Angular cleavages can be seen. EDS analysis (below left) identified minor amounts of chlorine within the akaganeite structure. Rare iron oxide/oxyhydroxide grains, which contained significantly less chlorine, were also identified (below right). BEI. 198x.





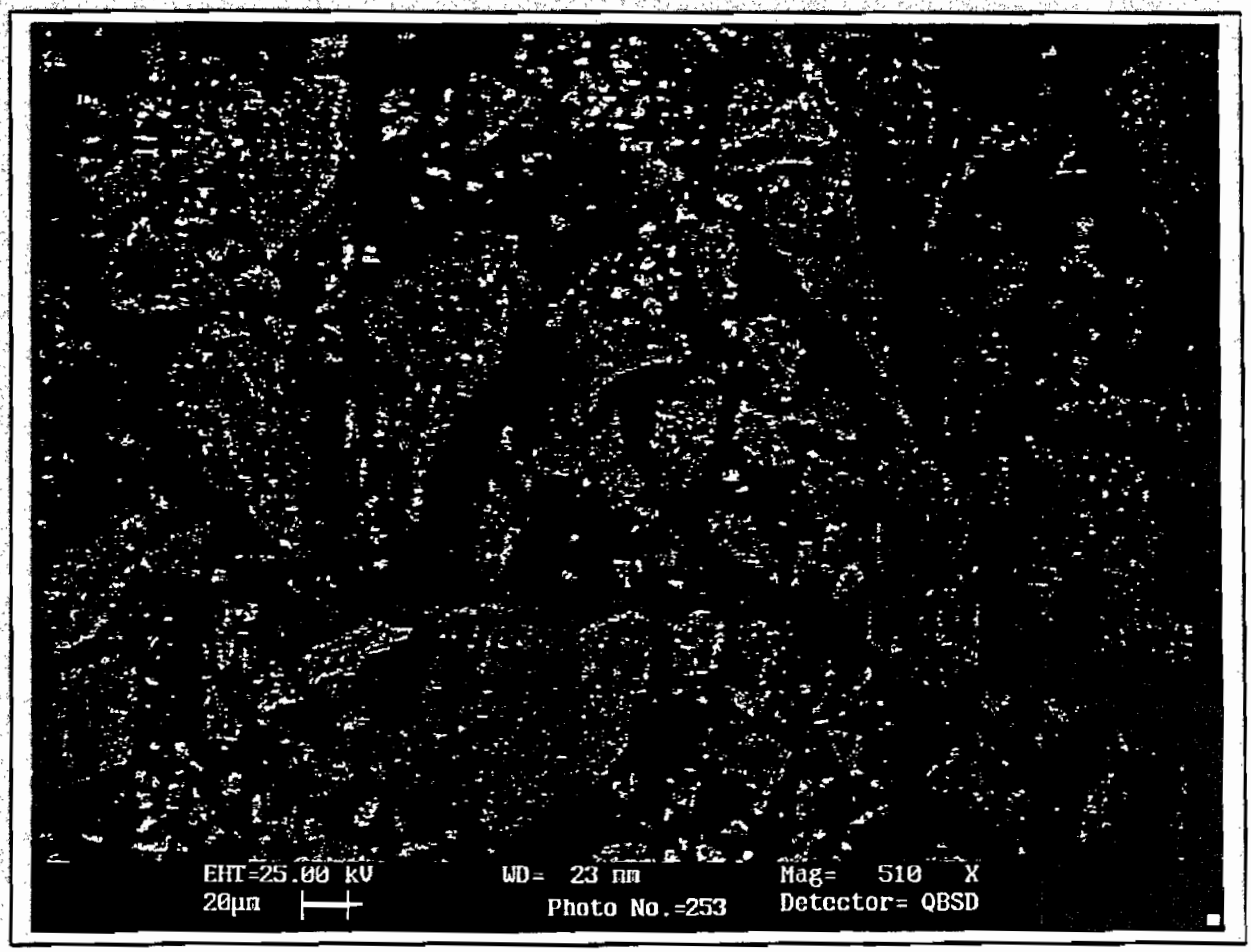


Photo 4: OX1-3. Higher magnification view of akaganeite aggregates. Individual crystals could not be resolved, and must be less than <0.5 µm in diameter. BEI. 510x.

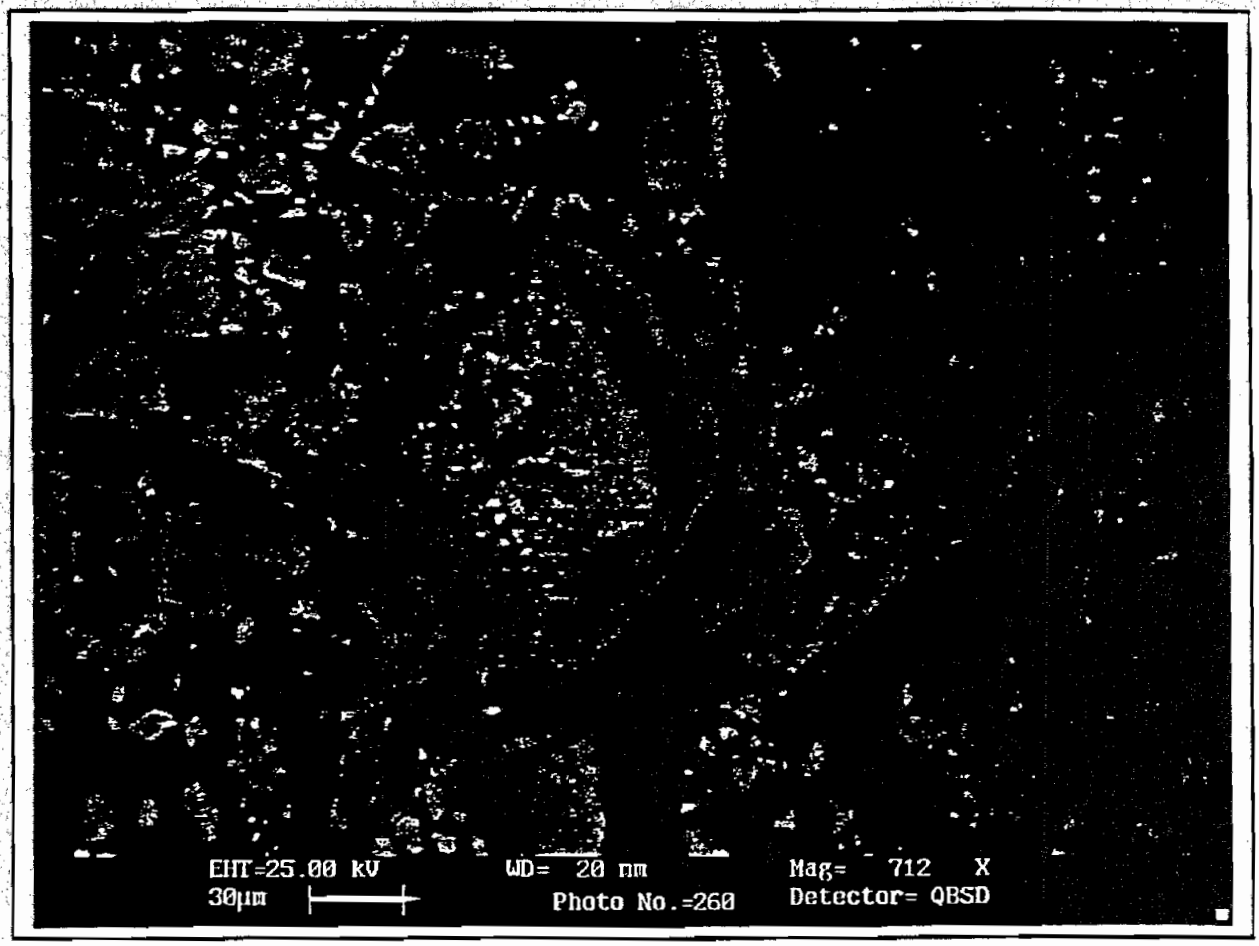


Photo 7: OX1-3. High magnification view of an akaganeite aggregate exhibiting angular cleavages. BEI. 712x.

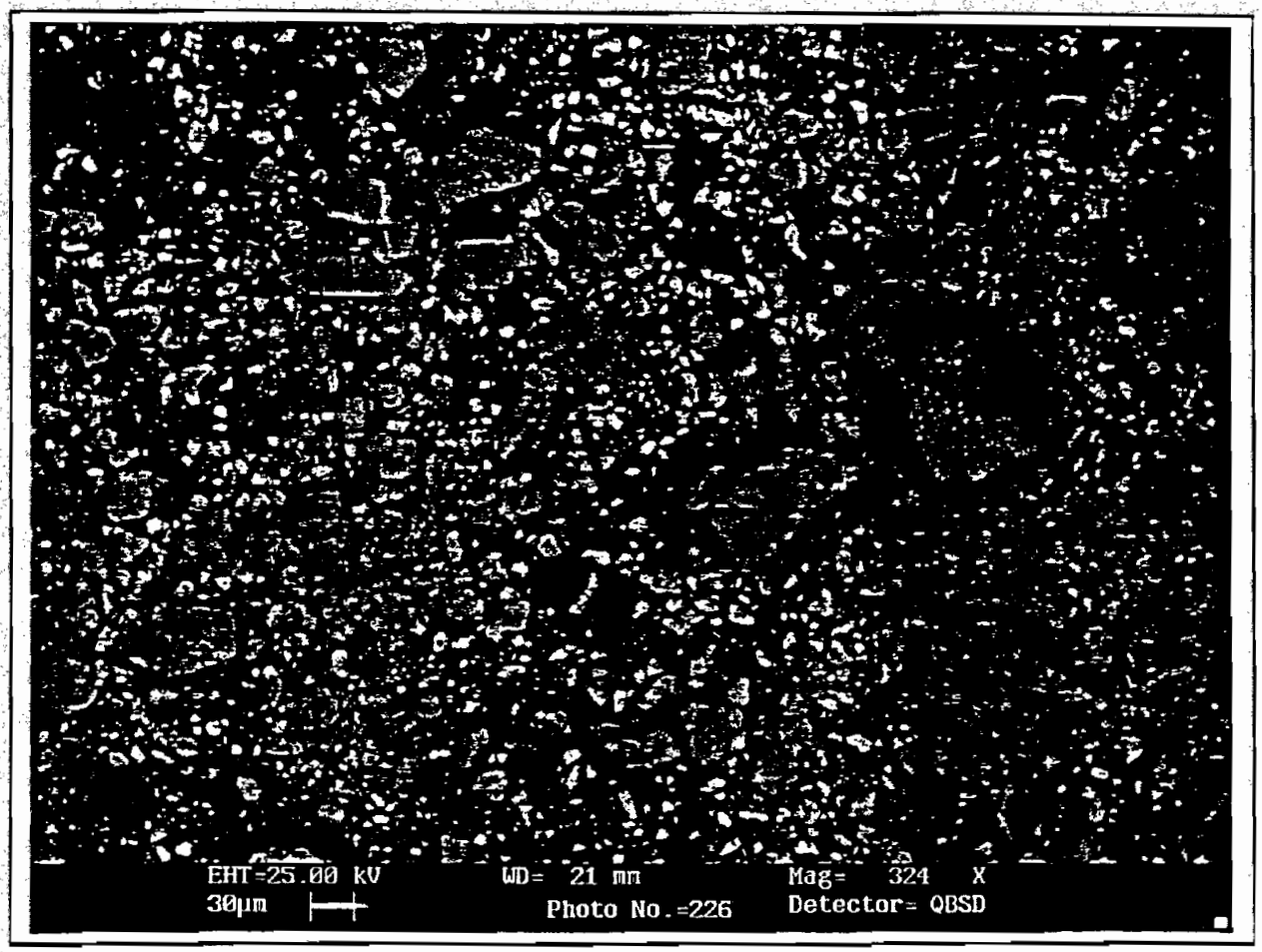
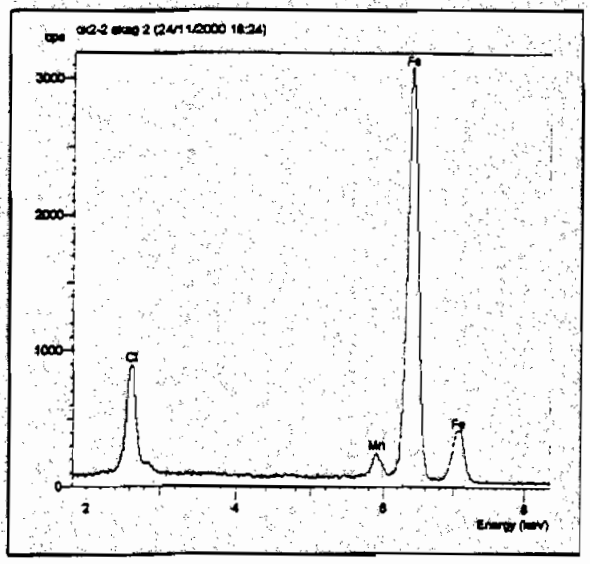


Photo 3: OX2-2. Overview of sample showing aggregates of akaganeite. The akaganeite forms compact, anhedral masses with sub-angular cleavages. EDS analysis identified minor and variable amounts of chlorine and manganese associated with the akaganeite. BEI. 252x.



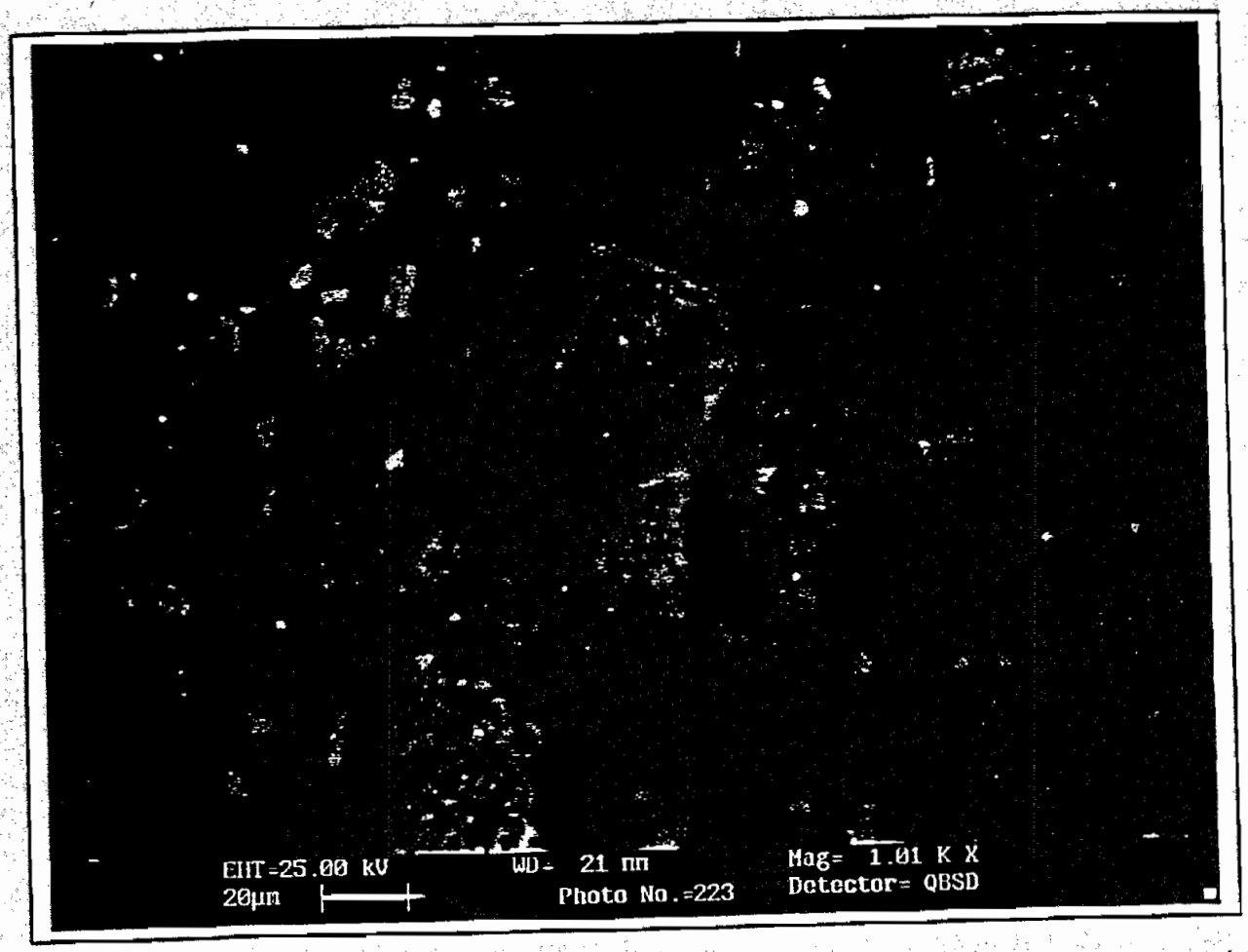


Photo 4: OX2-2. High magnification view of an akaganeite aggregate. Individual crystals cannot be resolved, and must be less than <0.5 µm in diameter. BEI. 252x.

Appendix 1: XRD Analyses

Summary of Qualitative X-ray Diffraction Results

Sample	Crystalline Mineral Assemblage (relative proportions based on peak height)			
	Major	Moderate	Minor	Trace
OX 1-3	akaganeite	-	-	*lepidocrocite *magnetite, *hematite

*Tentative identification due to low concentrations, diffraction line overlap or poor crystallinity

Instrument: Siemens D5000 diffractometer
Scan Conditions: Co radiation, graphite monochromator, 40Kv, 30mA. Step: .02°. Step time: 1.0s
Interpretations: JCPDS / ICDD powder diffraction files. Siemens Search / Match software.
Detection Limit: 0.5-2%. Strongly dependent on crystallinity.
Interpretations do not reflect the presence of non-crystalline / amorphous compounds. Mineral proportions are based on relative peak heights and may be strongly influenced by crystallinity, structural group or preferred orientations. Interpretations and relative proportions should be accompanied by supporting petrographic and geochemical data (WRA, ICP-OES).

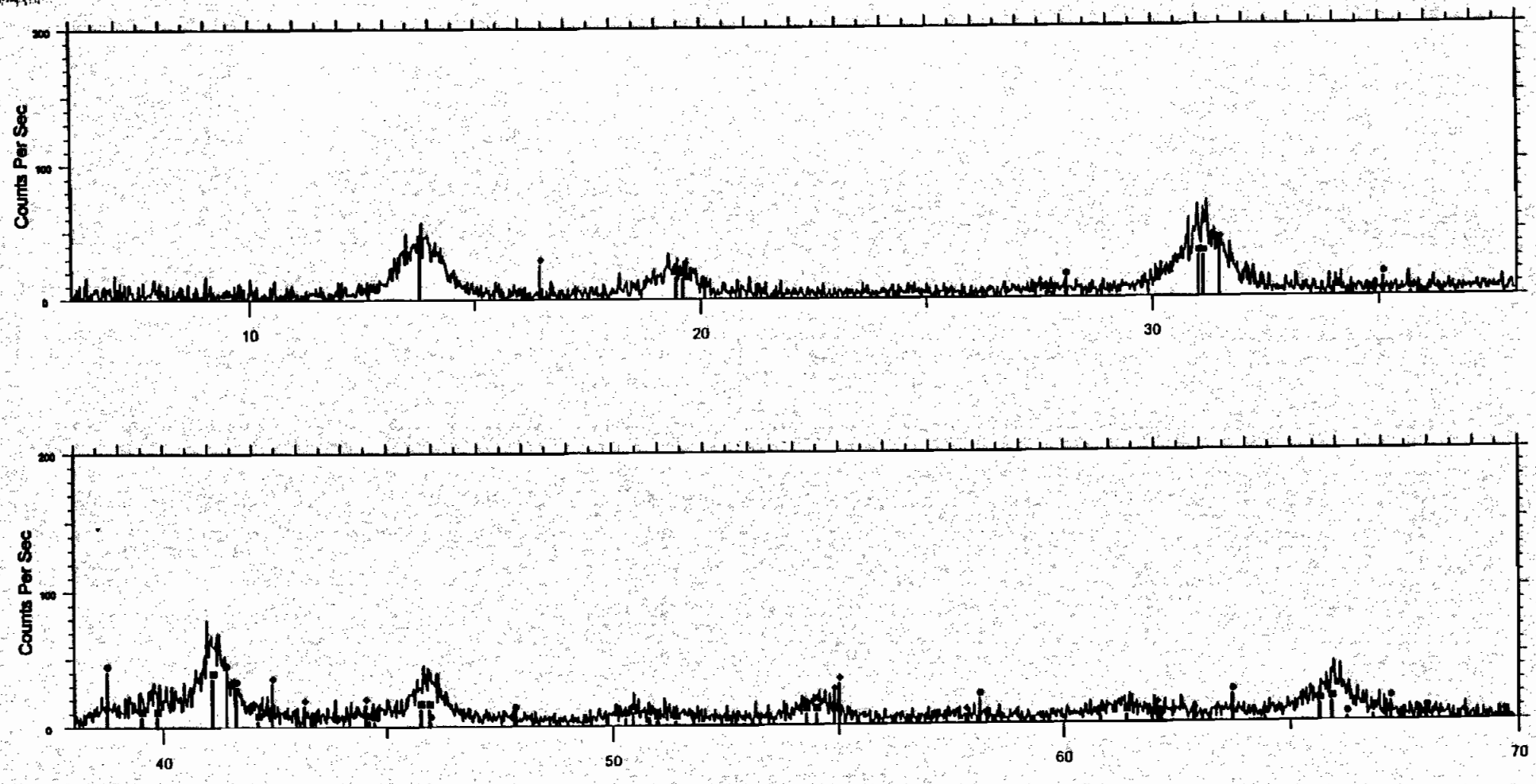
Mineral	Composition
Akaganeite	$Fe_8(O,OH)_{16}Cl_{1.3}$
Hematite	Fe_2O_3
Lepidocrocite	FeO(OH)
Magnetite	Fe_3O_4

Note:
The main diffraction lines of lepidocrocite and magnetite overlap with the diffraction pattern of akaganeite.

Lisa Ryan
XRD Technician

Nichola McKay, M.Sc.
Senior Mineralogist

The (Indicative XRD) method (METH 8.8-I) used by Lakefield Research Limited Mineralogical Services is accredited to the ISO/IEC 17025 standard by the Standards Council of Canada. Mini-method available upon request.



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File: dec4501-1.RAW - Start: 6.000 ° - End: 70.000 ° - Step: 0.020 ° - Step time: 1.0 s
42-1315 (I) - Akaganeite-M - Fe8(O,OH)16Cl1.3
44-1415 (*) - Lepidocrocite, syn - FeO(OH)
33-0664 (*) - Hematite, syn - Fe2O3
19-0629 (*) - Magnetite, syn - FeFe2O4

Summary of Qualitative X-ray Diffraction Results

Sample	Crystalline Mineral Assemblage (relative proportions based on peak height)			
	Major	Moderate	Minor	Trace
OX1-1	akaganeite	-	-	*lepidocrocite *magnetite, *hematite
OX2-2	akaganeite	-	-	*lepidocrocite *magnetite, *hematite

*Tentative identification due to low concentrations, diffraction line overlap or poor crystallinity

Instrument: Siemens D5000 diffractometer
Scan Conditions: Co radiation, graphite monochromator, 40Kv, 30mA. Step: .02°. Step time: 1.0s
Interpretations: JCPDS / ICDD powder diffraction files. Siemens Search / Match software.
Detection Limit: 0.5-2%. Strongly dependent on crystallinity.

Interpretations do not reflect the presence of non-crystalline / amorphous compounds. Mineral proportions are based on relative peak heights and may be strongly influenced by crystallinity, structural group or preferred orientations. Interpretations and relative proportions should be accompanied by supporting petrographic and geochemical data (WRA, ICP-OES).

Mineral	Composition
Akaganeite	$Fe_8(O,OH)_{16}Cl_{1.3}$
Hematite	Fe_2O_3
Lepidocrocite	FeO(OH)
Magnetite	Fe_3O_4

Note:

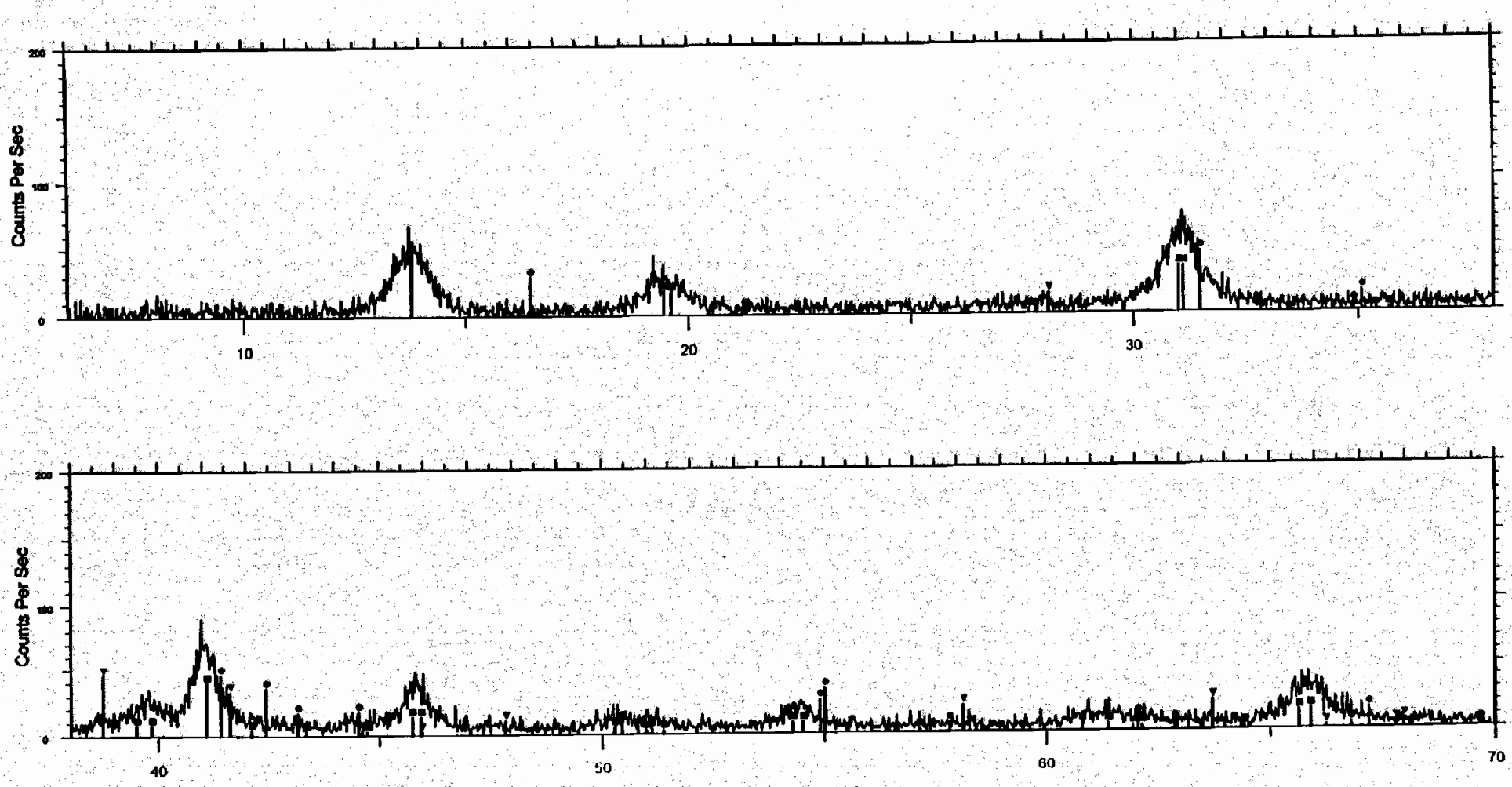
Sample OX2-2 exhibited a trace unidentified peak at 2.83Å.

The main diffraction lines of lepidocrocite and magnetite overlap with the diffraction pattern of akaganeite.

Lisa Ryan
XRD Technician

Nichola McKay, M.Sc.
Senior Mineralogist

The Qualitative XRD method (METH 8-X-1) used by Lakefield Research Limited Mineralogical Services is accredited to the IEC / ISO Guide 25 standard by the Standards Council of Canada. Mini-method available upon request.



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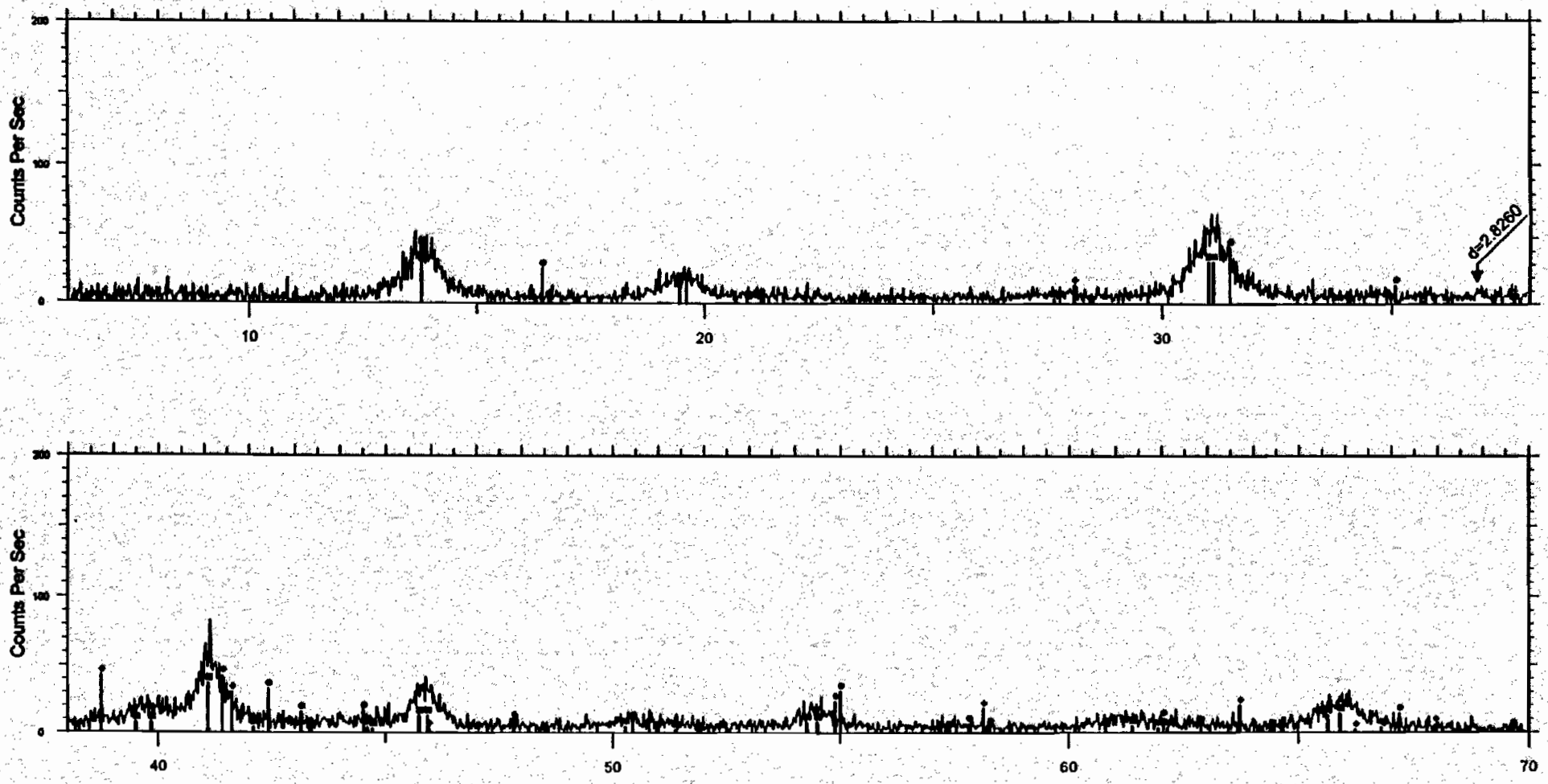
42-1315 (I) - Akaganeite-M - Fe8(O,OH)16Cl1.3
44-1415 (*) - Lepidocrocite, syn - FeO(OH)
19-0629 (*) - Magnetite, syn - FeFe2O4
33-0664 (*) - Hematite, syn - Fe2O3



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File: nov4510-2.RAW - Start: 6.000 ° - End: 70.000 ° - Step: 0.020 ° - Step time: 1.0 s
42-1315 (I) - Akaganeite-M - Fe8(O,OH)16Cl1.3
33-0664 (*) - Hematite, syn - Fe2O3
44-1415 (*) - Lepidocrocite, syn - FeO(OH)
19-0629 (*) - Magnetite, syn - FeFe2O4

11

CALCIUM SCRUBBING

from a

LOADED ORGANIC

with

SPENT ELECTROLYTE

from

ELECTROLYTIC MANGANESE DIOXIDE PROCESSING

Progress Report No. 1 LR Project: 10088-001

NOTE: This report refers to the samples as received.
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July, 2001

ABSTRACT

Bench testwork and three continuous scrubbing runs were undertaken to investigate the removal of calcium from loaded QL organic phase by scrubbing with a bleed of simulated spent electrolyte from electrolytic manganese dioxide (EMD) production. The bench testwork and the continuous testwork were performed with organic (QL) prepared according to CalEnergy's instructions. The scrub feed (aqueous phase) was taken from the spent electrolyte of the EMD electrowinning work (1). Variables that were tested during the continuous piloting included O/A ratio (10 to 20) and scrub feed acidity (7.4 to 20 g/L HCl). The major findings were the following:

- Continuous scrubbing of calcium with an acidic $MnCl_2$ solution was successful. In all three runs more than 99.5% of the calcium was removed;
- Calcium appears to be removed by a combined manganese / hydrogen ion cation exchange displacement mechanism. The relative contributions of manganese cations and protons depends on the O/A and acid/metal ratios in the scrub feed;
- No manganese is stripped from the loaded organic phase during calcium scrubbing with the acidic $MnCl_2$ scrub feed solution. In fact, during PP1 and PP2, there was a net loading of manganese onto the organic phase;
- Calcium removal from the QL organic phase appears to be a flexible and robust process as it was able to handle different spent electrolyte compositions (7.4 g/L HCl and 20 g/L HCl) as well as different O/A ratios, without a detrimental effect on calcium removal efficiency;
- At the maximum O/A ratio tested (20), the residual calcium concentration in the scrubbed organic was 13 mg/L, as opposed to <2 mg/L in PP1, which was achieved with an O/A of 10;
- Iron scrubbing from the loaded QL organic by contacting it with a bleed stream from the spent electrolyte from EMD production was unsuccessful.

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INTRODUCTION

At the request of Mr. George Furmanski of CalEnergy Operating Company, Lakefield Research conducted bench and continuous testwork on the removal of calcium from a manganese-loaded organic, using a bleed stream of EMD (Electrolytic Manganese Dioxide) spent electrolyte. The results of the testwork are presented in this report.

All results were submitted as they became available to Mr. George Furmanski and Mr. John Featherstone of CalEnergy, and Mr. Kevin Anthony (MarTech Consulting), consultant for CalEnergy.

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Report

1. Project Overview

A spent brine from the CalEnergy zinc plant will be treated by solvent extraction with an organic phase (QL) that consists of equal molar portions of D2EHPA (di-2-ethylhexyl phosphoric acid)and Aliquat 336 quaternary amine. The reagent is believed to exist as an ion pair in the organic phase, and extracts Mn, Ca and Fe as the divalent chloride salts ($MnCl_2$, $CaCl_2$ and $FeCl_2$) at a self-buffering pH of ~3.5, possibly by a solvating mechanism. The reagent extracts Fe and Mn approximately equally (~50% in one stage) and is quite selective against Ca (i.e. the reagent shows the same selectivity trend (Fe ~ Mn > Ca) as D2EHPA). However, because of the high concentration of Ca (30 to 40 g/L) in the CalEnergy brine relative to Mn and Fe (1.5 – 2 g/L), the loaded organic contains approximately equal concentration of all three metals (3-4 g/L).

In a proposal from Lakefield Research to CalEnergy (Appendix E), several flowsheets were suggested, for handling the co-extracted Fe and Ca in the most economical manner.

The conceptual flowsheet that was tested in a continuous pilot circuit in this program was the Lakefield Flowsheet # 1 (QL Extraction, QL Scrub, QL Strip and iron removal from strip liquor). As iron removal through an SX route had been shown in earlier testwork to be unsuccessful, it was decided to remove iron from the extraction feed brine prior to the QL loading stage. This was done by oxidation with hypochlorite and precipitation as akaganeite (2).

2. QL Organic

2.1. Production of QL

Ion pairing a deprotonated ligand (L^-) with a quarternary ammonium cation (Q^+) results in the formation of extractant of QL (3). Complexation with metal (M^{2+}) in the presence of chloride ions leads to ML_2 and QCl in the organic phase as shown in Equation 1.

$$M^{2+} + 2Cl^- + 2\,\underline{QL} \leftrightarrow \underline{ML_2} + 2\underline{QCl} \qquad (1)$$

Underscoring denotes species in the organic phase.

The metal can then be stripped from the organic phase with acid, as shown in Equation 2.

$$\underline{ML_2} + 2\underline{QCl} + 2H^+ \leftrightarrow M^{2+} + 2\underline{HL} + 2\underline{QCl} \quad (2)$$

And finally, the ion pair can be reconstituted by treatment of the stripped organic phase with an alkali, as shown in Equation 3.

$$\underline{HL} + \underline{QCl} + NaOH \leftrightarrow \underline{QL} + NaCl + H_2O \quad (3)$$

The novelty and cost benefit of this process lies in the fact that Equation 3 can be driven to the right hand side with a minimal (sub-stoichiometric), amount of alkali.

The organic phase (QL) was prepared according to instructions given by George Furmanski of CalEnergy. The following procedure describes the generation of 50.45 L of 0.495 M QL.

The following components were mixed to make up the QL:

- D2EHPA: 8.33 L (17.84 lbs)
- Aliquat 336: 12.23 L (24.25 lbs)
- Orfom SX-11 (aliphatic high boiling point solvent): 29.9 L

This organic phase was subsequently pre-equilibrated by contacting it with a NaOH/NaCl solution (0.495 M NaOH, 0.1 M NaCl) at an O/A ratio of 1 for 30 minutes at 65°C. The two phases were allowed to separate and the aqueous phase was discarded. An additional 5.03 L of DBBP (di-butyl butyl phosphonate) was added and mixed in. The resulting organic phase was labelled QL (0.495 M) and stored.

2.2. Loading of QL

A synthetic brine solution was prepared for the extraction of Mn and Ca by the freshly prepared QL organic phase. Table 1 describes the composition of the synthetic extraction feed brine.

Table 1 Extraction feed brine composition

brine	Mn	Ca	Na	K	Cl
mg/L	1490	42000	67	21.7	216

The organic phase was contacted with the brine solution at an O/A ratio of one, at about 80°C for 30 minutes. The initial loading was done in a two stage contact, counter-current manner. In between pilot plant campaigns, the organic was contacted once with the raffinate remaining from the previous loading, to re-equilibrate. The first contact loaded 300 mg/L Mn; the second contact increased the Mn concentration to approximately 1750 mg/L. Calcium was extracted in one stage. The high calcium concentration in the raffinate was sufficient to load the organic to approximately 2000 mg/L Ca in one contact each time the organic was reloaded.

In a normal operational cycle, the organic would be loaded, scrubbed, stripped and subsequently regenerated. A 0.15 M NaOH solution would be used for the final regeneration. In the present testwork, manganese was not stripped, and an interesting observation was made when by mistake the scrubbed organic was contacted with a caustic regeneration solution,(i.e. without having stripped the manganese). Manganese precipitated in the organic phase in this test and subsequent phase separation behaviour was extremely slow. This means that prior to regeneration it will be important to ensure the organic phase is completely stripped of manganese, in order to prevent this type of situation.

3. *SX pilot plant design and operation*

3.1. Physical set-up and operation

Three stages of scrubbing were applied in this mini pilot plant. The individual stages consisted of glass-jacketed mixers and settlers. Nominal volume in the mixers was 230 mL and in the settlers 600 mL. Mixers and settlers were heated by circulating hot (95 °C – 100 °C) water through the jackets. Two heated water reservoirs were installed, one for heating the three mixers, the other for heating the three settlers. Heating was controlled by either adjusting the water circulation rate, or by adjusting the water temperature in the reservoirs. As well, the organic phase was preheated in a 1 L upflow settler fitted with a 750 W quartz immersion heater. Organic phase was continuously preheated before entering the pilot plant. Preheating in this

ensured that only cold organic was pumped, since the feed to the circuit was the gravimetric overflow of the organic preheater. A constant temperature profile across the mixers and settlers was achieved by adjusting individual flows entering the mixer / settler jackets. A schematic flowsheet of the pilot is shown in Figure 1, and in Figure 2 a close up of a mixer settler unit is presented.

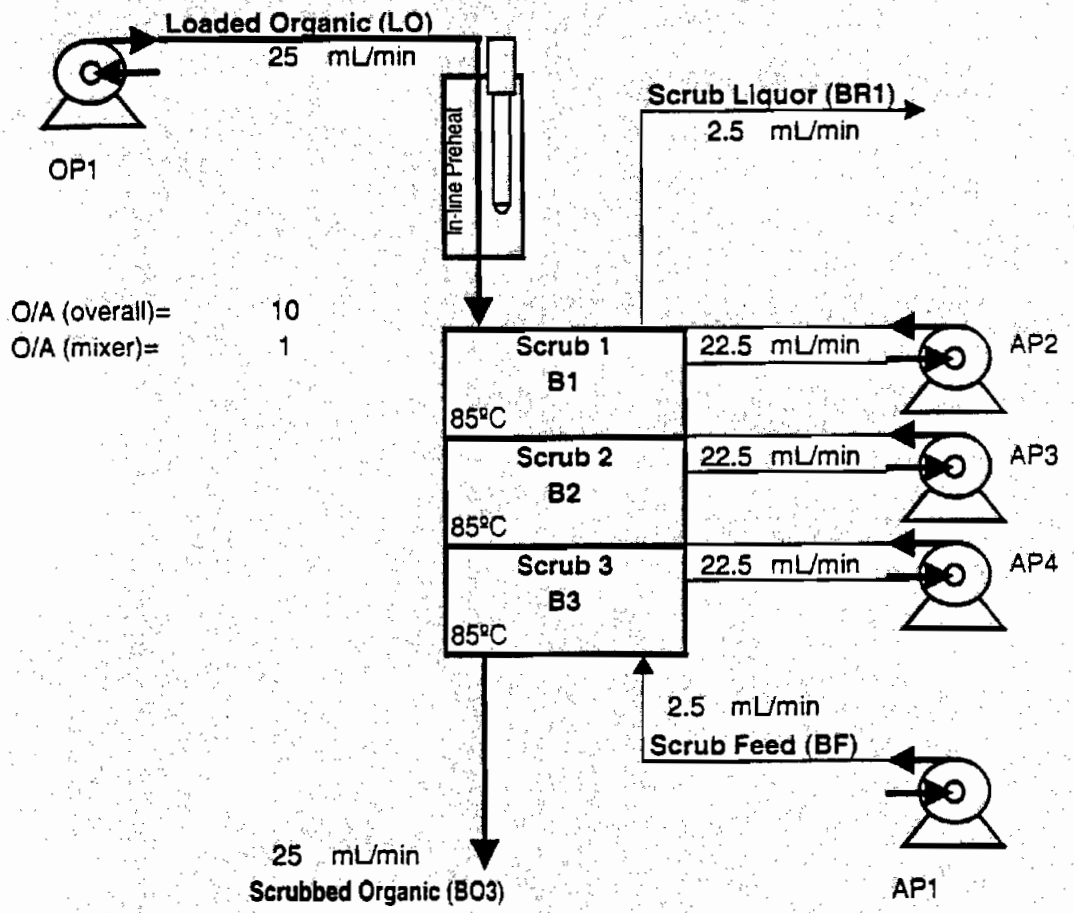

Figure 1 Schematic of pilot plant

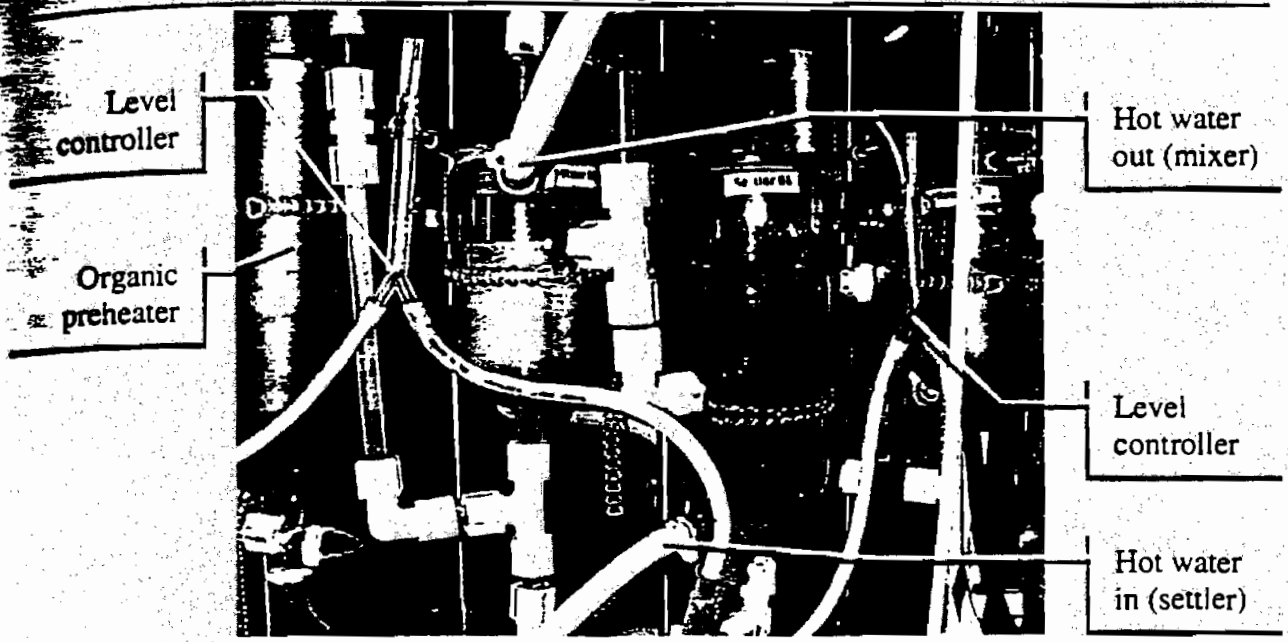

Figure 2 Mixer-settler unit

Due to the high temperature targeted in the pilot plant. all organic. aqueous and water circulating flowlines were made of polypropylene or neoprene tubing. Organic phase was pumped using a positive displacement metering pump. All other aqueous flows were pumped using peristaltic pumps with the appropriate sized neoprene tubing. In order to obtain the targeted O/A ratio in the mixers, aqueous recycle flows were installed.

Aqueous advance flows from settler to preceding mixer were achieved using level controllers. The level controllers were inverted 'Y' s. These were set as soon as the pilot plant was running steadily. The levels were set have more organic layer in the B3 settler in order to provide ample settling time in the organic and more aqueous in B1 in order to produce an organic-free scrub liquor.

Each mixer was fitted with a 3.15 cm diameter pump-mix agitator driven by a variable speed motor. The agitators were of polypropylene construction. and the stainless steel agitator shafts were also sheathed in polypropylene tubing welded to the agitator heads.

In order to minimise loss of organic and aqueous phase due to evaporation, covers were installed (tight fit, but not sealed) on the mixers and settlers. Settler covers were closed except for a sampling port that was normally closed during operation. The mixer cover had an opening

impeller shaft, which was a tight - but not sealed - fit. An accurate record was kept of the ueous volume entering as well as exiting the pilot plant in order to estimate the percentage ueous loss due to evaporation. Scrub feed was pumped out of a 2 L graduated cylinder and rub liquor flowed into another 2 L graduated cylinder. Record was also kept of the volume of queous inside the cells by measuring the height of the organic layer in the settlers to estimate queous hold-up within the system.

3.2. Start-up procedures

Prior to start up, the circuit was filled the appropriate amount of aqueous solution to provide an O/A of 1 in the mixers and settlers. Water circulation pumps and water heaters were turned on to heat up the circuit. As soon as the circuit reached temperature, the organic was introduced (entering B1) through the inline preheater. Aqueous recycle flows and pump mixers were turned on as the organic advanced through the circuit from B1 to B3. Time zero was taken as the moment when the organic overflowed from B3 settler into the scrubbed organic reservoir.

4. *Bench Testwork - Results*

A total of 16 bench tests was performed to investigate the scrubbing of calcium and iron from the loaded organic. All tests, unless otherwise indicated, were performed at 85°C – 90°C and had a retention time of 60 minutes. The tests can be divided into the following series:

- Tests 1 – 5: t = 30 min. No volume or pH adjustment. O/A varying from 5 to 20;
- Tests 6 – 10: Volume adjustment with DI water and pH control (with NaOH) at pH 4. O/A varying from 5 to 20;
- Tests 11 – 13: Volume adjustment with DI water, no pH control. O/A varying from 5 to 20;
- Tests 14-16: Volume adjustment with DI, no pH control, addition of Mn metal to maintain a reducing environment. O/A ratio varying from 5 to 10 and Mn° stoichiometry varying from 1.5 to 3.8 (with respect to Fe(III)).

Volume adjustment was necessary during these tests as a large fraction of the aqueous phase would evaporate due to the high temperature and long retention time. During tests 5 to 16 DI water was added to address this problem. Detailed data sheets are available in Appendix A.

Ten litres of organic solution was prepared according to the specified method and subsequently loaded by contacting it with synthetic brine solution. Table 2 presents the results of the batch loading of the organic phase. Thirty litres of synthetic brine solution was prepared using analytical grade reagents and DI water. The pH of the scrub feed stock solution (spent electrolyte from EMD processing) was adjusted to pH 4 prior to the test work.

Table 2 Composition of synthetic brine, raffinate and loaded organic

mg/L	Extraction Feed	Extraction Raffinate	Loaded Org Comp	Scrub Feed
Zn	47	8	115	
Fe	1190	470	2180	
Mn	1250	816	1340	~ 50000
Ca	32200	32235	1500	
Na	83600	84975	124	
K	20300			

The scrubbing tests were performed in 500 mL Fleakers inserted in a hot water bath. A summary of the results is presented in Table 3. In tests 6 – 10 some iron precipitation was visible, which was not filtered.

Calcium was removed from the organic phase to varying extents by displacement with manganese. Besides manganese loading by displacing calcium, manganese also appeared to load onto the organic by displacing hydrogen ions, since the final pH was consistently lower than the initial. Though the percentage of calcium scrubbed was as high as 97%, assay values in the final scrubbed organic were consistently higher than 25 mg/L. The target value for calcium was < 2 mg/L. At the higher O/A ratios not enough manganese was available to displace all the calcium from the organic, which translated into a lower percentage of scrubbed calcium.

Iron removal was not found to be feasible by scrubbing with EMD spent electrolyte. In all tests the iron concentration in the scrubbed organic remained greater than 2 g/L. The reductive scrub (tests 14-16) also failed to remove any iron from the organic phase.

In conclusion, the batch tests showed that although calcium removal appeared to be feasible, the removal of iron by scrubbing with EMD spent electrolyte was not. Iron will have to be removed by a different method or will have to be dealt with prior to the extraction, by oxidation with hypochlorite and precipitation as akaganeite, for example.

Table 3 Summarised results of bench test work

Test		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
O/A		20	15	10	7.5	5	20	15	10	7.5	5	20	10	5	10	5	5
Initial pH		4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	3.42	3.6	3.45	4.01	4.01	4.01
Final pH		1.4	1.4	1.3	1.3	1.2	4.1	4.0	4.2	3.9	4.0	1.3	1.3	1.3	2.1	1.1	1.7
% Ca scrubbed		46	68	90	-	96	90	93	96	97	98	71	90	97	88	97	96
Scrubbed Organic mg/L	Mn	1900	2130	2380	nss	2430	3120	4180	4270	3470	3800	1290	1420	1560	2640	1670	3030
	Fe	2390	2540	2390	nss	2300	3290	3900	4110	3250	3380	2030	2140	2145	3540	2510	3480
	Ca	803	482	154	nss	59	156	102	60	42	26	464	153	41	198	49	58
Aqueous (scrub liquor) mg/L	Mn	8420	12200	24500	36200	46000	28500	26000	28200	31600	40600	19700	29200	38200	42500	43100	44500
	Fe	340	141	167	185	146	124	83	54	54	48	43	60	76	25	107	169
	Ca	42700	37100	25200	18400	12100	19300	17000	12600	9520	7610	20800	9630	7650	13350	7270	7720

Note: nss = not sufficient sample

5. *Continuous Testwork - Results*

In total, three short campaigns (designated PP1, PP2 and PP3) were performed to investigate the scrubbing of calcium from loaded QL. The operating conditions of PP1, PP2 and PP3 are listed in Table 4. PP1, the first trial run, was also meant to determine the physical performance of the plant operating at the targeted elevated temperature.

Table 4 Operating conditions of PP1, PP2 and PP3

	PP1	PP2	PP3
Overall O/A	10	20	10
Mixer O/A	1	1	1
Total Operating time (h)	24	15.5	15.5
Mixer retention time (min)	4.6	2.3	2.3
Mixer temperature (°C)	85	85	85
Scrub feed acidity (g/L HCl)	7.4	7.4	20
DI addition to compensate for evaporation	No	No	Yes

In order to compare the results, all three runs are discussed together. Detailed data sheets of assays are presented in Appendix B (PP1), Appendix C (PP2) and Appendix D (PP3).

5.1. Evaporation

As PP2 and PP3 ran with a higher flowrate of loaded organic (50 mL/min) than PP1 (25 mL/min), PP2 and PP3 ran for only 15.5 hours, while PP1 operated for 24 hours exactly. In PP1 the aqueous phase would have had nearly 3 complete turnovers, versus 2 and 4 turnovers in PP2 and PP3 respectively.

After considering the loss of organic by sampling, organic build-up in the mixers and settlers and an accurate record of total organic fed to the system, it was possible to calculate loss of organic due to evaporation. Expressed in percents, 2 to 5 % of the organic was lost due to evaporation.

As mentioned, flows of aqueous in and out were also closely monitored. Considering aqueous build-up in the mixer-settlers and sampling, it was found that around 10 to 20% of the aqueous phase was lost due to evaporation. In PP3, a DI water drip was installed to compensate for this effect. Most likely the aqueous is evaporated in the mixers, since the aqueous is covered by the organic phase in the settlers. It was observed that bubbles of steam rose through the organic phase in the settlers. Upon exiting the organic phase, the steam condensed onto the top inside wall and ran back down the cell wall into the aqueous phase. It is therefore possible that the organic phase may entrain some aqueous as it overflows into the next mixer or scrubbed organic reservoir. The scrubbed organic reservoir, upon emptying, was examined for evidence of aqueous accumulation, but only minor quantities were found (approximately 30 mL per 14 L org.). Aqueous transfer will be a function of the settler geometry and can be avoided in a commercial plant by appropriate mechanical design of the organic outflows.

It was found that the targeted temperature profile could be reached and maintained without difficulty, as can be seen in Figure 3, which shows the temperature profile across the mixers as well as the temperature of the organic preheater in campaign PP1. The temperature was not changed during the three continuous runs that were performed.

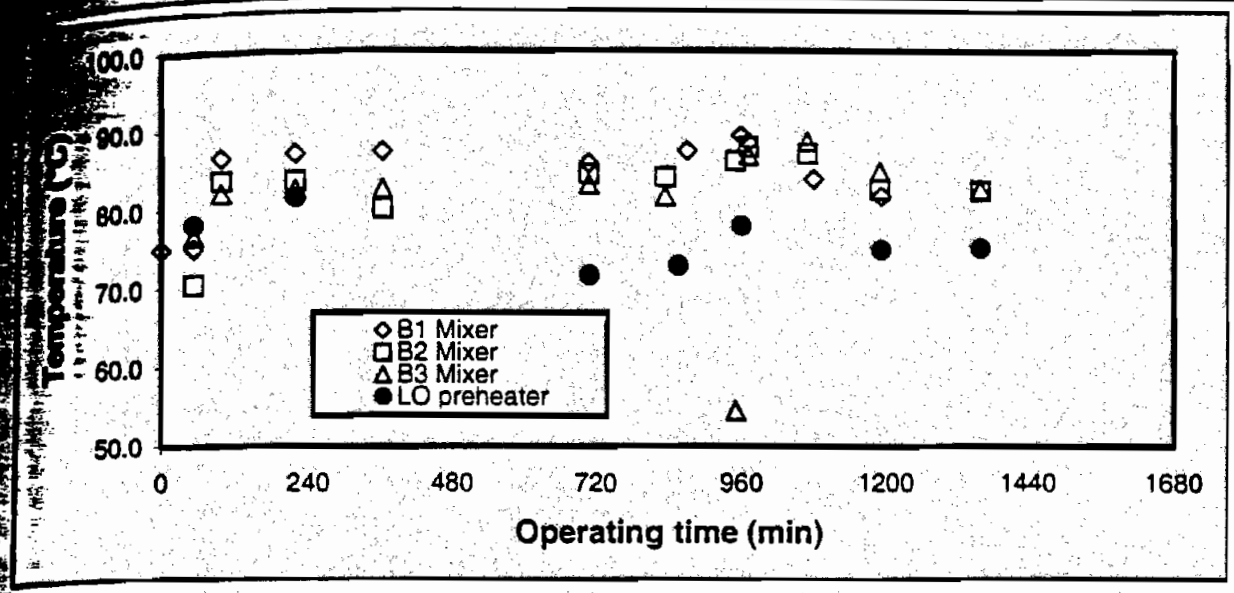

Figure 3 Mixer Temperature (PP1)

5.2. Flowrates

Flowrates were monitored on a regular basis (every 2-3 hours). Complete operating data sheets can be found in the Appendices (B, C and D). It was found that once the pumps were calibrated and set, they showed no tendency to drift.

An attempt was made to quantify the flowrate of scrub liquor produced. This was difficult with the low aqueous flowrates. The advance of aqueous through the system appeared to be in surges. Prior to advancing from the settler to the preceding mixer through the level controller, there appeared to be an aqueous build-up, most likely due to the surface tension of the aqueous phase inside the level controller. Once the aqueous started flowing a surge would follow. Arrangements were made to insert a piece of filtration paper inside the level controller (on both sides of the 'Y') to decrease the surface tension. Although this proved quite helpful, it did not completely eliminate the problem.

5.3. pH

No pH adjustments in the mixers were performed in the three runs. Scrub feed contained 7.4 g/L HCl (pH 0.7) in PP1 & PP2 and 19.3 g/L HCl in PP3. The higher acidity of the scrub feed in PP 3 was chosen to represent a spent electrolyte stream from EMD electrolysis, which

contain around 20 g/L HCl. Whereas most of the acid in was consumed in B3 in PP1 and cid consumption took place in stages in B3 and B2 during PP3.

Table 5 pH profile for PP1 – PP3

Average pH	PP1	PP2	PP3
B1	1.6	2.0	1.6
B2	1.6	1.9	1.6
B3	1.5	1.8	1.2
Feed (g/L HCl)	7.4	7.4	19.3

In Figure 4, pH is plotted *versus* the operating time of PP3, which covered four turnovers. The pH, however, did not appear to change with time, which led to the conclusion that steady state had been reached.

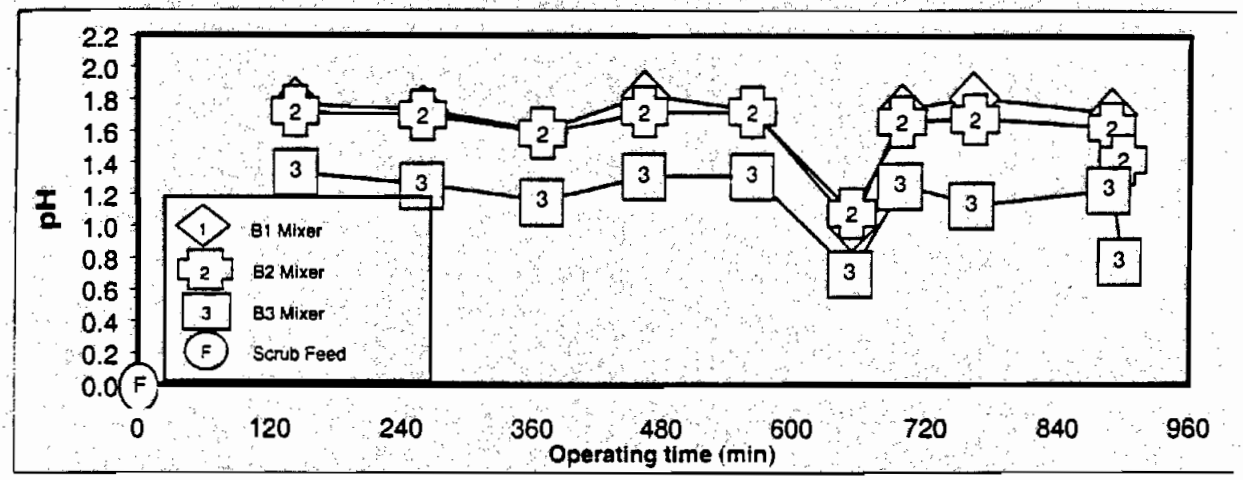

Figure 4 pH profile in PP3

5.4. Chemical performance

The main objective of this investigation was to scrub calcium from the organic phase without stripping any manganese. The average assays of calcium and manganese in the organic and aqueous phase are presented for PP1 to PP3 are presented in Table 6. The average assay results are corrected for the evaporation of aqueous phase: the actual assays are reported in

Appendix B (PP1), Appendix C (PP2) and Appendix D (PP3). In PP1 and PP3, operating at an O/A of 10, calcium removal was close to the analytical detection limit (< 2 mg/L Ca in PP1 and 3 mg/L Ca in PP3). In PP2, which operated with an O/A of 20, complete removal of calcium was not achieved. In B3, calcium in the organic was lowered to 13 mg/L. In fact all three stages consistently operated with Ca levels in the organic 5 to 10 times higher than PP3 or PP1. It was clear in all cases that all three stages were required to decrease the calcium level to an acceptable value.

Calcium appeared to be removed by two mechanisms: 1) calcium displacement by hydrogen ions, as can be seen in Table 5, which shows the pH profile across the three stages; 2) calcium displacement by manganese. The latter effect can be seen in Table 6: manganese concentration in the loaded organic increased from around 1.3 g/L in the feed to more than 2.5 g/L in B1. In all three runs, this high Mn concentration decreases again as the organic advances from B2 to B3, likely due to the acid stripping in B3 (and B2 during PP3). This phenomenon is confirmed by monitoring manganese in the aqueous phase. In PP1 Mn levels remained constant through B3 and B2, but decreased in B1, which suggests that Mn primarily displaced calcium in B1. In PP2 there is a different situation. Mn in the aqueous phase decreased from its feed concentration of around 55 g/L Mn to around 8 g/L Mn exiting B1.

Table 6 Average assays (Org and Aq) of PP1 to PP3

Average assays, mg/L		PP1		PP2		PP3	
		Ca	Mn	Ca	Mn	Ca	Mn
Feed	ORG↓	2110	1180	2580	1620	1800	1350
B1	ORG	243	2700	845	2523	114	2703
	AQ	23833	29405	33773	8273	15525	48364
B2	ORG	9	2563	157	2930	17	2687
	AQ	2673	56485	14160	35007	2420	61252
B3	ORG	2	2178	13	2792	3	1610
	AQ	99	56062	3323	55714	417	63720
Feed	AQ↑	17.5	56000	18	54850	33.8	53700
% calcium scrubbed		99.9		99.5		99.8	

More than 99.5% of the calcium was removed from the organic in all three runs.

5.5. Acid/metal balance

The amounts of metal displaced and the amount of acid consumed are summarised in Table 8. The results were calculated by establishing an elemental balance (see Table 7) over the three stages. The results are expressed in moles of cation per litre of organic processed. Two moles of acid strip one mole of metal. The total amount of acid consumed is calculated by subtracting the residual amount of acid in the scrub liquor from the initial amount of acid. Amount of metal displaced is calculated based on assays of the organic as well as assays of the aqueous phase. It is clear from the data that the elemental balance does not close well. This can be attributed to two factors: the small size of the pilot plant and inaccuracies in analyses.

Table 7 Elemental balance for PP1, PP2 and PP3

	In (mol)		Out (mol)		Balance (Out/In), %	
	Ca	Mn	Ca	Mn	Ca	Mn
PP1	0.05	0.11	0.05	0.09	102.7	77.4
PP2	0.06	0.08	0.04	0.06	64.0	74.6
PP3	0.04	0.12	0.04	0.12	85.4	96.0

Note: numbers are based on 1 litre of organic processed

The results indicate that the predominant mechanism of calcium removal is by displacement with manganese. However, when there is sufficient acid available, calcium removal by hydrogen ion displacement appears to be the predominant mechanism (PP3). When the calculation is based on the aqueous assays, the calculated amount of calcium displaced agrees well with the actual amount of calcium displaced.

Table 8 Calcium displacement by manganese and by hydrogen protons

Calculation based on:		PP1 ORG	PP1 AQ	PP2 ORG	PP2 AQ	PP3 ORG	PP3 AQ
Actual calcium displaced	mol	**0.053**	**0.054**	**0.064**	**0.041**	**0.045**	**0.038**
Mn displaced	mol	0.018	0.044	0.021	0.041	0.005	0.010
Acid Consumed	mol	0.018		0.009		0.051	
2 mol acid/1 mole Ca	mol	0.009		0.005		0.026	
Calculated Ca displaced based on Mn and acid consumption	mol	**0.027**	**0.053**	**0.026**	**0.046**	**0.030**	**0.035**

Note: numbers are based on 1 litre of organic processed

5.6. Phase separation

Phase separation was good in all stages of the circuit during all three runs. It was observed that in B1 both the organic and the aqueous phase were slightly opaque. Organic and aqueous phases in B2 and B3 were clear (see Figure 5). During PP3 both phases in the B1 and B2 settlers were opaque, while both phases were clear in the B3 settler. An emulsion band was observed (never more than 0.5 cm thick), but only at times when there was an aqueous surge through the circuit. At steady aqueous flow through the circuit, phase separation was instantaneous and no emulsion was observed.

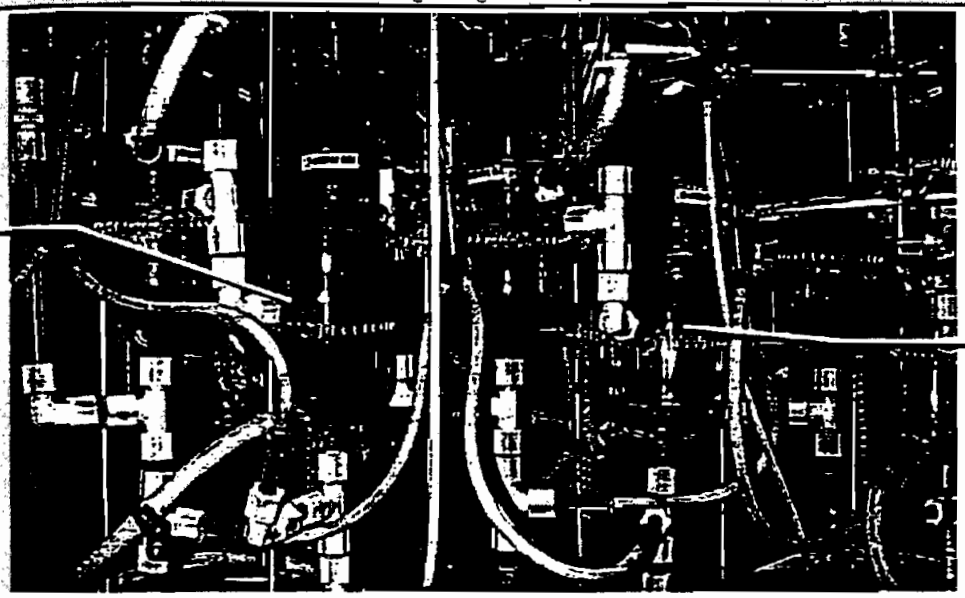

Figure 5 Close-up of mini pilot plant set-up (stage B1 and B2 during PP1)

Conclusions

In conclusion, the following can be stated:

- Iron removal from a loaded organic by contacting it with a bleed stream of spent electrolyte from EMD production was found to be unfeasible;
- Continuous scrubbing of calcium with an acidic $MnCl_2$ solution was successful. In all three continuous pilot circuit runs more than 99.5% of the calcium in the loaded organic was removed;
- Calcium appears to be removed by cation exchange by a combined manganese/ hydrogen ion displacement mechanism. The relative contributions of manganese ions and protons to the displacement of calcium depends on the O/A ratio and acid/metal ratio in the scrub feed;
- No manganese is stripped by the acid in the scrub feed solution. In fact, during PP1 and PP2 there was a net loading of manganese onto the organic phase during calcium scrubbing;
- Calcium removal from the QL organic phase appears to be a flexible, robust process. Good results were obtained with different spent electrolyte compositions (7.4 g/L HCl and 20 g/L HCl) as well as different O/A ratios;
- The maximum O/A ratio tested was 20, producing a residual calcium concentration of 13 mg/L as opposed to <2 mg/L in PP1, which operated with an O/A of 10. In order to reduce Ca levels in the scrubbed organic to below 10 mg/L, scrubbing needs to be carried out at O/A < 20. A fourth scrub stage may permit attainment of good results at O/A ratios approaching 20.

Recommendations

Although calcium removal appears to be quite feasible and flexible, some optimisation may be necessary in terms of optimum O/A ratio, acid concentration and staging requirements;

This work has shown that it is possible to scrub calcium from a loaded organic with the spent electrolyte from manganese electrolysis, without prior neutralisation of the scrub feed. The next logical step will be to integrate the process with manganese stripping using the remaining spent electrolyte, (i.e. only a small bleed of spent electrolyte will be needed to scrub the calcium, if this is done at an O:A ration of ~20:1). The following questions should then be addressed:

- Is the amount of acid produced in the EMD EW sufficient to strip off the manganese from the organic? (i.e. Is there a closed acid balance in stripping and electrolysis.)
- What would be an appropriate O/A ratio for the manganese stripping stage, bearing in mind an optimum ΔMn is required in order to balance Mn removed in the EMD EW? Based on a ΔMn of 6 to 13 g/L Mn, an O/A ratio of 3 to 6 should be sufficient.
- What will be the acid concentration in the strip liquor? Partial neutralisation of excess acid may be required prior to EMD EW, as the EW is not efficient at high acid concentration.

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3) Progress Report CalEnergy. Synthetic Brine Recipe and QL Reagent. June 17 – July 15, 1997

Appendix A

Bench Test Work

Tests 1 to 16 .....

CALENERGY 10088-001
Scrubbing Tests of the Loaded Organic

	Head Organic ppm	Head Scrub Soln ppm
Zn	115	0.0
Mn	1340	47000
Fe	2180	0.0
Ca	1500	0.0

Test Conditions: Time = 30 min No pH or volume re-adjustment.
Temp = 85 - 90°C

Test Number				1	2	3	4	5
Date of Test								
Target Scrubbing A:O				1:20	1:15	1:10	1:7.5	1:5
pH	Initial			4.8	4.8	4.8	4.8	4.8
	Final			1.37	1.37	1.32	1.27	1.17
Volumes	Initial	Organic	mL	300	300	200	225	200
		Aqueous	mL	15	20	20	30	40
	Final	Organic	mL	300	300	200	225	200
		Aqueous	mL	4	9	9	19	26
Organic		Zn	mg/L	91	98	91	nss	85
		Mn		1900	2130	2380	nss	2430
		Fe		2390	2540	2390	nss	2300
		Ca		803	482	154	nss	59
Organic Gained or Lost		Zn	mg	-7	-5	-5		-6
		Mn		168	237	208		218
		Fe		63	108	42		24
		Ca		-209	-305	-269		-288
Percent Scrubbed		Ca	mg	46	68	90		96
Mn/Ca wt. ratio in organic		Feed		0.89	0.89	0.89	0.89	0.89
		Scrubbed		2	4	15		41
Aqueous		Zn	mg/L	0	0	0	0	0
		Mn		8420	12200	24500	36200	46000
		Fe		340	141	167	185	146
		Ca		42700	37100	25200	18400	12100
Aqueous Gained or Lost		Zn	mg	0	0	0	0	0
		Mn		-671	-830	-720	-722	-684
		Fe		1.4	1.3	1.5	3.5	3.8
		Ca		171	334	227	350	315

Notes:

ENERGY 10088-001
bbing Tests of the Loaded Organic

	Head Organic	Head Scrub Soln
	ppm	ppm
	138	0.0
n	1990	54300
	2780	0.0
	1500	0.0
Na	83.7	

Test Conditions: Time = 60 min; Temp = 85 - 90°C. pH and aqueous adjusted to 4.0 and added DI to return to initial volume every 5 min.

Test Number				6	7	8	9	10
Date of Test				30-Aug	30-Aug	01-Sep	01-Sep	03-Sep
Target Scrubbing A:O				1:20	1:15	1:10	1:7.5	1:5
pH	Initial			4.8	4.8	4.8	4.8	4.8
	Final			4.1	4.0	4.2	3.9	4.0
Volumes	Initial	Organic	mL	400	400	200	225	200
		Aqueous	mL	20	25.4	20	30	40
	Final	Organic	mL	400	400	200	225	200
		Aqueous	mL	20	25.4	20	30	40
Organic		Zn	mg/L	233	205	211	165	188
		Mn		3120	4180	4270	3470	3800
		Fe		3290	3900	4110	3250	3380
		Ca		156	102	60	42	26
Organic Gained or Lost		Zn	mg	38	27	15	6	10
		Mn		452	876	456	333	362
		Fe		204	448	266	106	120
		Ca		-538	-559	-288	-328	-295
Percent Scrubbed		Ca	mg	90	93	96	97	98
Mn/Ca wt. ratio in organic		Feed		1.33	1.33	1.33	1.33	1.33
		Scrubbed		20	41	72	82	145
Aqueous		Zn	mg/L	0	0	0	0	0
		Mn		28500	26000	28200	31600	40600
		Fe		124	83	54	54	48
		Ca		19300	17000	12600	9520	7610
Aqueous Gained or Lost		Zn	mg	0	0	0	0	0
		Mn		-516	-719	-522	-681	-548
		Fe		2.5	2.1	1.1	1.6	1.9
		Ca		386	432	252	286	304

Notes: When adjust pH back to 4.0, Fe precipitates during adjustment. Ppte was not filtered out between adjustments.
(No Fe precipitation took place during the loading of QL.)

CALENERGY 10088-001
Repeat Scrubbing Tests of the Loaded Organic

	Head Organic ppm	Head Scrub Soln ppm
Zn	120	0.1
Mn	760	51150
Mn reassay	915	
Fe	1830	<0.1
Ca	1600	11

Test Conditions: Time = 60 min, Temp = 85 - 90°C. Aqueous soln. volume adjusted every 5 min. No pH adjustment

Test Number				11	12	13
Date of Test				25-Sep	25-Sep	26-Sep
Target Scrubbing A:O				1:20	1:10	1:5
pH	Initial			3.42	3.6	3.45
	Final			1.26	1.28	1.25
Volumes	Initial	Organic	mL	400	200	200
		Aqueous	mL	20	20	40
	Final	Organic	mL	390	200	200
		Aqueous	mL	20	20	40
Organic		Zn	mg/L	214	231	176
		Mn		1100	1250	1150
		Mn reassay		1290	1420	1560
		Fe		2030	2140	2145
		Ca		464	153	41
Organic Gained or Lost		Zn	mg	35	22	11
		Mn		125	98	78
		Mn reassay		137	101	129
		Fe		60	62	63
		Ca		-459	-289	-312
Percent Scrubbed		Ca	mg	71	90	97
Mn/Ca wt. ratio in organic		Feed		0.48	0.48	0.48
		Scrubbed		2	8	28
Aqueous		Zn	mg/L	<0.05	<0.05	0.17
		Mn		19700	29200	38200
		Fe		43	60	76
		Ca		20800	9630	7650
Aqueous Gained or Lost		Zn	mg	0	0	0
		Mn		-629	-439	-518
		Fe		0.9	1.2	3.0
		Ca		416	192	306

CALENERGY 10088-001
Repeat Scrubbing Tests of the Loaded Organic

	Head Organic ppm	Head Scrub Soln ppm
Zn	120	0.1
Mn	760	51150
Fe	1830	<0.1
Ca	1600	11

Test Conditions: Time = 60 min; Temp = 85 - 90°C; Aqueous soln. volume adjusted every 5 min. No pH adjustment; Mn powder added to maintain reducing conditions.

Test Number				**14**	**15**	**16**
Date of Test				04-Oct	04-Oct	04-Oct
Target Scrubbing A:O				**1:10**	**1:5**	**1:5**
Mn Powder Added			g	0.556	0.556	1.37
Stoichiometric Ratio Mn^{o}/Fe^{3+}				1.5	1.5	3.8
pH	Initial			4.01	4.01	4.01
	Final			2.07	1.13	1.67
Volumes	Initial	Organic	mL	200	200	200
		Aqueous	mL	20	40	40
	Final	Organic	mL	200	200	200
		Aqueous	mL	20	40	40

Organic	Zn	mg/L	199	203	212
	Mn		2640	1670	3030
	Fe		3540	2510	3480
	Ca		198	49	58
Organic Gained or Lost	Zn	mg	16	17	18
	Mn		376	182	454
	Fe		342	136	330
	Ca		-280	-310	-308
Percent Scrubbed	Ca	mg	88	97	96
Mn/Ca wt. ratio	Feed		0.48	0.48	0.48
in organic	Scrubbed		13	34	52
Aqueous	Zn	mg/L	<0.05	1.17	<0.05
	Mn		42500	43100	44500
	Fe		25	107	169
	Ca		13350	7270	7720
Aqueous Gained or Lost	Zn	mg	0	0	0
	Mn		-173	-322	-266
	Fe		0	4	7
	Ca		267	290	308

Notes: Mn metal not effective in removing Fe.

Appendix B

Pilot plant 1 (PP1)

Operating data sheets .....

Assays.....

Project: 10088-001
Client: CalEnergy

Niels Verbaan
March 30-2001

Run: PP1

Objective: Operating Log

Temperature (°C)									
Time	Operating	LO	B1		B2		B3		
dd hh:mm	time (min)	Preheater	Mixer	Settler	Mixer	Settler	Mixer	Settler	Notes
29 07:29									Start feeding hot LO into B1O
29 08:20	0								Org o/f B3 settler: Time zero.
29 09:15	55	78.0	74.9	78.0	70.5	60.0	76.6	67.0	
29 10:00	100		75.0		83.6		82.0		
29 12:00	220	81.5	86.5	88.0	83.6	82.5	82.5	83.0	
29 14:25	365		87.0		80.0		82.5		
29 20:10	710	71.5	87.2		84.4		83.1		
29 22:15	835		85.7		84.0		81.6		
29 22:35	855	72.8							
29 22:50	870			88.6		87.3		88.0	
30 00:10	950		87.3		86.0		54.5		
30 00:20	960	77.8		89.8		88.9		80.7	
30 00:32	972		89.2	86.5	87.8	85.7	86.7	84.5	
30 02:10	1070		88.4		87.0		88.5		
30 02:20	1080			81.9		81.2		82.6	
30 04:10	1190		83.7		82.4		84.7		
30 04:12	1192	74.8		87.5		86.8		88.9	
30 07:00	1360	75.0	81.6	83.4	82.3	83.0	82.5	84.5	
30 08:20	1440								Shut down PP1

pH - Mixers						
Time	Operating					
dd hh:mm	time (min)		B1	B2	B3	Notes
29 07:29						Start feeding hot LO into B1O
29 08:20	0					Org o/f B3 settler: Time zero.
29 10:00	100		1.68	1.73	1.35	
29 14:25	365		1.80	1.72	1.55	
29 18:20	600		1.53	1.48	1.39	pH measured in sample (set 3)
29 20:10	710		1.85	1.68	1.56	
29 22:15	835		1.54	1.70	1.54	
30 00:10	950		1.74	1.66	1.50	
30 02:10	1070		1.83	1.69	1.57	
30 02:20	1080		1.47	1.57	1.55	pH measured in sample (set 5)
30 04:10	1190		1.39	1.51	1.35	
30 07:00	1360		1.64	1.35	1.29	
30 08:15	1435		1.57	1.51	1.40	pH measured in sample (set 7)
30 08:20	1440					Shutdown
		Avg	1.64	1.60	1.46	pH (feed): 0.7

Organic holdup												
		(in settler)										
Time	Operating	Organic holdup (mL)				Total Org		Total Aq		Organic Height (cm)		
dd hh:mm	time (min)	B1	B2	B3		mL		mL		B1	B2	B3
29 07:29												
29 08:20	0											
29 08:25	5											
29 09:06	46											
29 09:50	90											
29 10:00	100	354.1	365.6	423.3		1143		627.3		9.2	9.5	11
29 10:10	110											
29 11:15	175											
29 13:00	280	357.9	381	327.1		1066		704.3		9.3	9.9	8.5
29 13:30	310											
29 14:45	385											
29 15:50	450											
29 15:55	455	342.5	384.8	508		1235		534.9		8.9	10	13.2
29 16:35	495											
29 18:45	625											
29 19:25	665											
29 20:25	725	323.3	357.9	377.1		1058		712		8.4	9.3	9.8
29 21:25	785											
29 22:20	840	319.4	365.6	388.7		1074		696.6		8.3	9.5	10.1
29 22:25	845											
29 23:35	915											
29 23:40	920	346.4	346.4	384.8		1078		692.7		9	9	10
30 00:48	988											
30 02:20	1080											
30 02:50	1110	400.2	319.4	361.8		1081		688.9		10.4	8.3	9.4
30 03:00	1120											
30 04:15	1195											
30 05:25	1265											
30 07:00	1360											
30 08:10	1430	307.9	338.7	384.8		1031		738.9		8	8.8	10
30 08:20	1440	shutdown										

Calculated flowrates for aqueous and organic							
Total Aqueous in:	3150	mL	Total Org. in	31.72	L		
Total Aqueous out:	2330	mL	Total Org out	30.85	L		
Aquous buildup in circuit:	111.6	mL	Org buildup	-112	mL	in	1330 min
Sampling	255	mL	Sampling	240	mL		
out + buildup + samples	2697	mL	out + buildup + samples	30.98	L		
Aq. Evaporation:	453.4	mL					
Time span:	1330	min	Time span	1314	min		
Evaporation rate:	0.341	mL/min	Org loss:	0.742	L		
Average BF	2.188	mL/min	Org. loss rate	0.564	mL/min		
Average B1R	1.618	mL/min	Average LO	24.14	mL/min		
% evaporation	15.58	%	% loss	2.338	%		
Actual total O/A	11.04						

PP1

Batch Loading: O/A = 1

Date hh:mm	Operating time (hr)			Mn mg/L	Mn corr mg/L	Ca mg/L	Ca corr mg/L	FAT g/L HCl	TOC %
		Extraction Feed		1490					
		Raffinate (E1R)		67.8		41400			
		Loaded Organic (after 3 batches)		1650		1970			
		Loaded Organic Comp(LOC)		1180		2110			

Continuous Scrubbing: (O/A = 10)

Aqueous

		BFC-1	Scrub Feed Comp	56000		17.5		7.4	
29 08:20	0	startup							
		Scrub 1							
29 18:20	10	B1R-3	B1 Scrub Liquor	35400	29883	29100	24565		
30 02:20	18	B1R-5	B1 Scrub Liquor	31600	26875	29800	25156		
30 08:15	24	B1R-7	B1 Scrub Liquor	37500	31656	25800	21779		
Proportional evaporation (%)			15.6						
			Average B1R		29405		23833		
		Scub 2							
29 18:20	10	B2R-3	B2 Scrub Liquor	64400	57709	2520	2258		
30 02:20	18	B2R-5	B2 Scrub Liquor	63400	56813	3290	2948		
30 08:15	24	B2R-7	B2 Scrub Liquor	61300	54931	3140	2814		
Proportional evaporation (%)			10.4						
			Average B2R		56485		2673		
		Scub 3							
29 18:20	10	B3R-3	B3 Scrub Liquor	65400	62003	77.6	74		
30 02:20	18	B3R-5	B3 Scrub Liquor	63600	60296	96.3	91		
30 08:15	24	B3R-7	B3 Scrub Liquor	48400	45886	140	133		
Proportional evaporation (%)			5.2						
			Average B3R		56062		99		
30 08:15	24	BLC-7	Scrub Liquor Comp	36100	30474	19900	16799	0.7	0.034
30 08:20	24	shutdown							
Overall evaporation (%)			15.6						

Organic

		LOC-2	Loaded Organic Comp	1180		2110			
29 08:20	0	startup							
		Scrub 1							
29 18:20	10	B1O-3	B1 Scrubbed Organic	2610		257			
30 02:20	18	B1O-5	B1 Scrubbed Organic	2700		304			
30 08:15	24	B1O-7	B1 Scrubbed Organic	2790		168			
			Average B1O	2700		243			
		Scrub 2							
29 18:20	10	B2O-3	B2 Scrubbed Organic	2500		8.6			
30 02:20	18	B2O-5	B2 Scrubbed Organic	2460		9.9			
30 08:15	24	B2O-7	B2 Scrubbed Organic	2730		8.4			
			Average B2O	2563		9.0			
		Scrub 3							
29 14:20	6	B3O-2	B3 Scrubbed Organic	1450		< 2.0			
29 18:20	10	B3O-3	B3 Scrubbed Organic	2600		< 2.0			
29 22:20	14	B3O-4	B3 Scrubbed Organic	2370		< 2.0			
30 02:20	18	B3O-5	B3 Scrubbed Organic	2350		< 2.0			
30 05:20	21	B3O-6	B3 Scrubbed Organic	2120		< 2.0			
30 08:15	24	B3O-7	B3 Scrubbed Organic	2180		< 2.0			
			Average B3O	2178		<2.0			
30 08:15	24	BOC-7	Scrubbed Organic Comp	2100		< 2.0			
30 08:20	24	shutdown							

Appendix C

Pilot plant 2 (PP2)

Operating data sheets .....

Assays .....

Project: 10088-001
Client: CalEnergy

Niels Verbaan
April 19-2001

Run: PP2

Objective: Operating Log

Temperature (°C)									
Time dd hh:mm	Operating time (min)	LO Preheater	B1 Mixer	B1 Settler	B2 Mixer	B2 Settler	B3 Mixer	B3 Settler	Notes
19 07:27									Start feeding hot LO into B1O
19 07:52	0								Org o/f B3 settler: Time zero.
19 08:45	53	77.0	76.7	72.0	80.0	77.0	90.0	74.5	
19 11:00	188		81.5	80.1	82.6	87.3	91.1	78.1	
19 14:30	398	81.0	80.0	79.2	76.0	80.0	72.0	70.0	
19 17:00	548		85.0		85.4		77.0		
19 19:10	678		85.3	88.2	84.9	90.5	84.3	81.5	
19 21:10	798	84.0	84.1	85.0	83.5	89.2	84.5	86.1	
19 23:20	928	85.0	86.6	88.0	85.8	90.2	86.6	83.2	
19 23:20	928								SHUT DOWN
		average	82.7		82.6		83.6		

pH - Mixers						
Time dd hh:mm	Operating time (min)		B1	B2	B3	Notes
19 07:27						Start feeding hot LO into B1O
19 07:52	0					Org o/f B3 settler: Time zero.
19 08:45	53		1.91	1.89	1.83	
19 11:00	188		2.08	1.87	1.82	
19 13:50	358		1.64	1.55	1.50	pH Sample Set 2 (Scrub Feed pH = 0.66)
19 14:30	398		2.09	1.85	1.73	
19 17:00	548		2.07	1.90	1.77	
19 18:50	658		2.14	1.91	1.79	pH Sample Set 4
19 19:10	678		2.23	1.95	1.83	
19 21:15	803		1.80	1.94	1.81	
19 23:20	928		1.98	1.85	1.74	pH Sample Set 6
19 23:20	928					SHUT DOWN
	Average		2.0	1.9	1.8	BF pH 0.66

Flowrates (mL/min)

Time dd hh:mm	Operating time (min)	LO	B1RR	B2RR	B3RR	BF	Notes
-19 07:27							Start feeding hot LO into B1O
-19 07:52	0						Org o/f B3 settler: Time zero.
-19 08:25	33	50	50	52	50	2.4	
19 08:25	33		47.5	47.5	47.5	2.5	Flow adjust to
19 14:50	418	50	47.5	47.5	47.5	2.5	
19 19:00	668	50	46.0	47.5	47.5	2.5	
19 21:00	788	50	46.5	47.5	47.0	2.6	
19 23:20	928						SHUT DOWN

Organic holdup

Time dd hh:mm	Operating time (min)	Organic holdup (mL) (in settler) B1	B2	B3		Total Org mL		Total Aq mL		Organic Height (cm) B1	B2	B3
19 07:52	0											
19 08:50	58											
19 09:55	123	277.1	431	346.4		1054		715.8		7.2	11.2	9
19 12:00	248	331	431	377.1		1139		631.1		8.6	11.2	9.8
19 14:20	388	315.6	388.7	423.3		1128		642.7		8.2	10.1	11
19 16:40	528	250.1	438.7	404.1		1093		677.3		6.5	11.4	10.5
19 19:25	693	361.8	396.4	396.4		1155		615.8		9.4	10.3	10.3
19 19:35	703											
19 21:20	808	307.9	442.6	342.5		1093		677.3		8	11.5	8.9
19 21:30	818											
19 23:20	928	404.1	523.4	446.4		1374		396.4		10.5	13.6	11.6
		shutdown										

Calculated flowrates for aqueous and organic

Total Aqueous in:	2250	mL	Total Org. in	46.4	L	(based on 50
Total Aqueous out:	1290	mL	Total Org out	44.6	L	mL/min flow)
Aquous buildup in circuit:	0	mL	Org buildup	319.4	mL	in 928 min
Sampling	240	mL	Sampling	240	mL	
out + buildup + samples	1530	mL	out + buildup + samples	45.16	L	
Aq. Evaporation:	720	mL				measured
Time span:	928	min	Time span	928	min	
Evaporation rate:	0.776	mL/min	Org loss:	1.241	L	
Average BF	2.425	mL/min	Org. loss rate	1.337	mL/min	
Average B1R	1.39	mL/min	Average LO	50	mL/min	50
% evaporation	32	%	% loss	2.674	%	
Actual total O/A	20.62					

PP2

Batch Loading: (O/A) = 1

Time dd hh:mm	Operating time (hr)			Mn mg/L	Mn corr	Ca mg/L	Ca corr	FAT g/L HCl	TOC mg/L
		Extraction Feed (raffinate from previous loading)							
		Raffinate (E1R)							
		Loaded Organic (after 3 batches)							
		Loaded Organic Comp(LOC)		1620		2580			
Continuous Scrubbing: O/A = 20									
			Aqueous						
		BFC-2	Scrub Feed Comp	*54850*		18		7.4	
19 07:52	0	startup		avg PP1, PP2					
		Scrub 1							
19 13:50	6	B1R-2	B1 Scrub Liquor	19700	13396	43200	29376		
19 18:50	11	B1R-4	B1 Scrub Liquor	7950	5406	44300	30124		
19 23:20	15	B1R-6	B1 Scrub Liquor	8850	6018	61500	41820		
Proportional evaporation (%)			32						
			Average B1R		8273		33773		
		Scrub 2							
19 13:50	6	B2R-2	B2 Scrub Liquor	52100	40985	12700	9991		
19 18:50	11	B2R-4	B2 Scrub Liquor	44000	34613	18500	14553		
19 23:20	15	B2R-6	B2 Scrub Liquor	37400	29421	22800	17936		
Proportional evaporation (%)			21.3						
			Average B2R		35007		14160		
		Scrub 3							
19 13:50	6	B3R-2	B3 Scrub Liquor	62200	55565	2100	1876		
19 18:50	11	B3R-4	B3 Scrub Liquor	67300	60121	3930	3511		
19 23:20	15	B3R-6	B3 Scrub Liquor	57600	51456	5130	4583		1200
Proportional evaporation (%)			10.7						
			Average B3R		55714		3323		
19 23:20	15	BLC-7	Scrub Liquor Comp	12100		26400		0.74	
19 23:20	15	shutdown							
Overall Evaporation			32						
			Organic						
		LOC-2	Loaded Organic Comp	1620		2580			
19 07:52	0	startup							
		Scrub 1							
19 13:50	6	B1O-2	B1 Scrubbed Organic	3030		681			
19 18:50	11	B1O-4	B1 Scrubbed Organic	2300		947			
19 23:20	15	B1O-6	B1 Scrubbed Organic	2240		906			
			Average B1O	2523		845			
		Scrub 2							
19 13:50	6	B2O-2	B2 Scrubbed Organic	2940		106			
19 18:50	11	B2O-4	B2 Scrubbed Organic	2930		175			
19 23:20	15	B2O-6	B2 Scrubbed Organic	2920		191			
			Average B2O	2930		157			
		Scrub 3							
19 10:50	3	B3O-1	B3 Scrubbed Organic	2870		4.9			
19 13:50	6	B3O-2	B3 Scrubbed Organic	2870		10.5			
19 15:50	8	B3O-3	B3 Scrubbed Organic	2840		14.5			
19 18:50	11	B3O-4	B3 Scrubbed Organic	2820		13.8			
19 20:50	13	B3O-5	B3 Scrubbed Organic	2760		15			
19 23:20	15	B3O-6	B3 Scrubbed Organic	2590		17			
			Average B3O	2792		13			
19 23:20	15	BOC-7	Scrubbed Organic Comp	2350		20.7			
19 23:20	15	shutdown							

Appendix D

Pilot plant 3 (PP3)

Operating data sheets .....

Assays .....

Project: 10088-001
Client: CalEnergy
Run: PP3
Objective: Operating Log

Niels Verbaan
April 26-2001

Temperature (°C)									
Time	Operating	LO	B1		B2		B3		
dd hh:mm	time (min)	Preheater	Mixer	Settler	Mixer	Settler	Mixer	Settler	Notes
26 07:38									Start feeding hot LO into B1O
26 08:06	0								Org o/f B3 settler: Time zero.
26 08:40	34	80.0	86.5		83.9		86.9		
26 10:30	144		87.0		85.0		88.0		
26 12:25	259	80.0	84.6	87.2	83.6	89.6	86.5	89.5	
26 15:50	464		80.0		80.0		82.6		
26 17:30	564		83.0		80.0		85.2		
26 19:40	694	73.0	82.8	86.0	81.9	87.1	85.5	89.5	
26 20:50	764	78.0	80.5	83.0	78.9	84.3	83.0	86.9	
26 22:53	887	81.7	83.1	87.0	79.5	86.6	85.0	90.9	
26 23:25	919								Shut Down

pH - Mixers					
Time	Operating				
dd hh:mm	time (min)	B1	B2	B3	Notes
26 07:38					Start feeding hot LO into B1O
26 08:06	0				Org o/f B3 settler: Time zero.
26 10:30	144	1.77	1.72	1.34	
26 12:25	259	1.73	1.70	1.26	
26 14:15	369	1.60	1.59	1.16	Sample Set 2
26 15:50	464	1.83	1.72	1.32	
26 17:30	564	1.73	1.72	1.32	
26 19:00	654	1.01	1.09	0.71	Sample Set 4
26 19:45	699	1.74	1.66	1.26	
26 20:50	764	1.81	1.68	1.13	
26 22:55	889	1.71	1.62	1.23	
26 23:05	899	1.42	1.42	0.78	Sample Set 6
26 23:25	919				SHUT DOWN
Average		1.64	1.592	1.151	0

Flowrates (mL/min)							
Time	Operating						
dd hh:mm	time (min)	LO	B1RR	B2RR	B3RR	BF	Notes
26 07:38							Start feeding hot LO into B1O
26 08:06	0						Org o/f B3 settler: Time zero.
26 08:40	34	50				5	
26 11:40	214	50	50-45	46.0	46.0	5	
26 16:10	484	50	45.0	46.0	46.0	5	
26 19:30	684	51	45.0	46.0	45.0	5.1	
26 20:50	764	50	45.0	46.0	45.0	5	
26 22:45	879	50	45.00	46.00	45.00	5	
26 23:25	919						SHUT DOWN

Organic holdup

	Operating time (min)	Organic holdup (mL) (in settler)			Total Org	Total Aq	Organic Height (cm)		
		B1	B2	B3	mL	mL	B1	B2	B3
06:06	0	435	331	327	1093	677.3	11.3	8.6	8.5
06:45	39	404.1	392.5	307.9	1105	665.8	10.5	10.2	8
10:35	149								
11:30	204	311.7	392.5	423.3	1128	642.7	8.1	10.2	11
11:50	224								
12:35	269								
13:00	294								
13:40	334	338.7	415.6	407.9	1162	608.1	8.8	10.8	10.6
15:10	424								
15:45	459	346.4	434.9	423.3	1205	565.7	9	11.3	11
15:55	469								
17:35	569	384.8	404.1	423.3	1212	558	10	10.5	11
19:10	664	407.9	407.9	454.1	1270	500.3	10.6	10.6	11.8
19:45	699	384.8	365.6	469.5	1220	550.3	10	9.5	12.2
20:38	752	311.7	431	481.1	1224	546.5	8.1	11.2	12.5
21:35	809	307.9	404.1	450.3	1162	608.1	8	10.5	11.7
22:35	869	396.4	415.6	396.4	1208	561.9	10.3	10.8	10.3
23:00	894	396.4	431	404.1	1232	538.8	10.3	11.2	10.5
23:25	919	392.5	415.6	461.8	1270	500.3	10.2	10.8	12
				buildup	177	-177			
		shutdown							

Calculated flowrates for aqueous and organic

Total Aqueous in:	4550	mL		Total Org. in	47.1	L	
Total Aqueous out:	4150	mL		Total Org out	44.25	L	
Aquous buildup in circuit:	-177	mL		Org buildup	177	mL	in 919 min
Sampling	240	mL		Sampling	240	mL	
out + buildup + samples	4213	mL		out + buildup + samples	44.67	L	
Aq. Evaporation:	337	mL					measured
Time span:	919	min		Time span	919	min	
Evaporation rate:	0.367	mL/min		Org loss:	2.433	L	
Average BF	4.951	mL/min		Org. loss rate	2.647	mL/min	
Average B1R	4.516	mL/min		Average LO	51.25	mL/min	50
% evaporation	7.407	%		% loss	5.166	%	
Actual total O/A	10.1						

PP3

Batch Loading: (O/A) = 1

Time dd hh:mm	Operating time (hr)			Mn mg/L	Mn corr mg/L	Ca mg/L	Ca corr mg/L	FAT g/L HCl	TOC %
		Extraction Feed (raffinate from previous loading)							
		Raffinate (E1R)							
		Loaded Organic (after 3 batches)							
		Loaded Organic Comp(LOC)							
Continuous Scrubbing: O/A = 10. DI addition to make up for evaporation									
			Aqueous						
26 08:00	0	BFC-2 startup	Scrub Feed Comp	53700		33.8		19.3	
		Scrub 1							
26 14:15	6	B1R-2	B1 Scrub Liquor	54100	50093	16000	14815		
26 19:00	11	B1R-4	B1 Scrub Liquor	52600	48704	16400	15185		
26 23:05	15	B1R-6	B1 Scrub Liquor	50000	46296	17900	16574		<250.00
Proportional evaporation (%)			7.40722519						
			Average B1R	52233	48364	16767	15525		
		Scrub 2							
26 14:15	6	B2R-2	B2 Scrub Liquor	65300	62075	2428	2308		
26 19:00	11	B2R-4	B2 Scrub Liquor	66800	63501	2520	2396		
26 23:05	15	B2R-6	B2 Scrub Liquor	61200	58178	2690	2557		
Proportional evaporation (%)			4.9						
			Average B2R	64433	61252	2546	2420		
		Scrub 3							
26 14:15	6	B3R-2	B3 Scrub Liquor	65900	64273	385	375		
26 19:00	11	B3R-4	B3 Scrub Liquor	66700	65053	528	515		
26 23:05	15	B3R-6	B3 Scrub Liquor	63400	61835	371	362		
Proportional evaporation (%)			2.5						
			Average B3R	65333	63720	428	417		
26 23:05	15 -888176	BLC-7 shutdown	Scrub Liquor Comp	53100		16200		0.7	
Overall Evaporation			7.41						
			Organic						
26 08:00	0	LOC-2 startup	Loaded Organic Comp	1350		1800			
		Scrub 1							
26 14:15	6	B1O-2	B1 Scrubbed Organic	2710		109			
26 19:00	11	B1O-4	B1 Scrubbed Organic	2670		120			
26 23:05	15	B1O-6	B1 Scrubbed Organic	2730		112			
			Average B1O	2703		114			
		Scrub 2							
26 14:15	6	B2O-2	B2 Scrubbed Organic	2690		16			
26 19:00	11	B2O-4	B2 Scrubbed Organic	2600		17			
26 23:05	15	B2O-6	B2 Scrubbed Organic	2770		17			
			Average B2O	2687		17			
		Scrub 3							
26 11:00	3	B3O-1	B3 Scrubbed Organic	1650		2.9			
26 14:15	6	B3O-2	B3 Scrubbed Organic	1620		3.0			
26 16:00	8	B3O-3	B3 Scrubbed Organic	1650		3.1			
26 19:00	11	B3O-4	B3 Scrubbed Organic	1620		2.6			
26 21:00	13	B3O-5	B3 Scrubbed Organic	1540		2.3			
26 23:05	15	B3O-6	B3 Scrubbed Organic	1570		2.6			
			Average B3O	1610		2.8			
	-888176 -888176	BOC-7 shutdown	Scrubbed Organic Comp	1440		9.6			

Appendix E

CALENERGY PROPOSAL

CALENERGY PROPOSAL

Background

The spent brine from the Calenergy zinc plant will be treated by solvent extraction with an organic phase (QL) that consists of equal molar portions of DEHPA and Aliquat 336 quaternary amine. The reagent is believed to exist as an ion pair in the organic phase, and extracts Mn, Ca and Fe as the divalent chloride salts ($MnCl_2$, $CaCl_2$ and $FeCl_2$) at a self-buffering pH of ~3.5 – possibly by a solvating mechanism. The reagent extracts Fe and Mn approximately equally (~50% in one stage) and is quite selective against Ca (i.e. the reagent shows the same selectivity trend (Fe ~ Mn > Ca) as DEHPA). However, because of the high concentration of Ca in the Calenergy brine (30-40 g/L) relative to Mn and Fe (1.5 – 2 g/L), the loaded organic contains approximately equal concentration of all three metals (3-4 g/L).

The conceptual flowsheet that has been developed by Calenergy to treat the loaded organic is shown in Figure 1, and consists of the following steps:

- Stripping of all the metals simultaneously with weak acid solution (0.1M HCl)
- Oxidation of the Fe(II) to Fe(III) with H_2O_2, followed by extraction of $FeCl_4^-$ with Aliquat 336.
- Reduction of Mn(II) to Mn(I) with manganese metal, followed by extraction of $MnCl_2^-$ with Aliquat 336
- Elution of the loaded organic phase with spent electrolyte from the EMD cells.

In addition, the following alternative flowsheets have been proposed for testing by Lakefield.

The first flowsheet (Figure 2) consists of the following steps:

- The loaded organic is scrubbed with a small bleed stream (5-15%) of spent electrolyte (preneutralized to pH 4) to displace calcium. Depending on the Mn content of the bleed, it could either be discarded or recycled to the brine feed to QL solvent extraction.

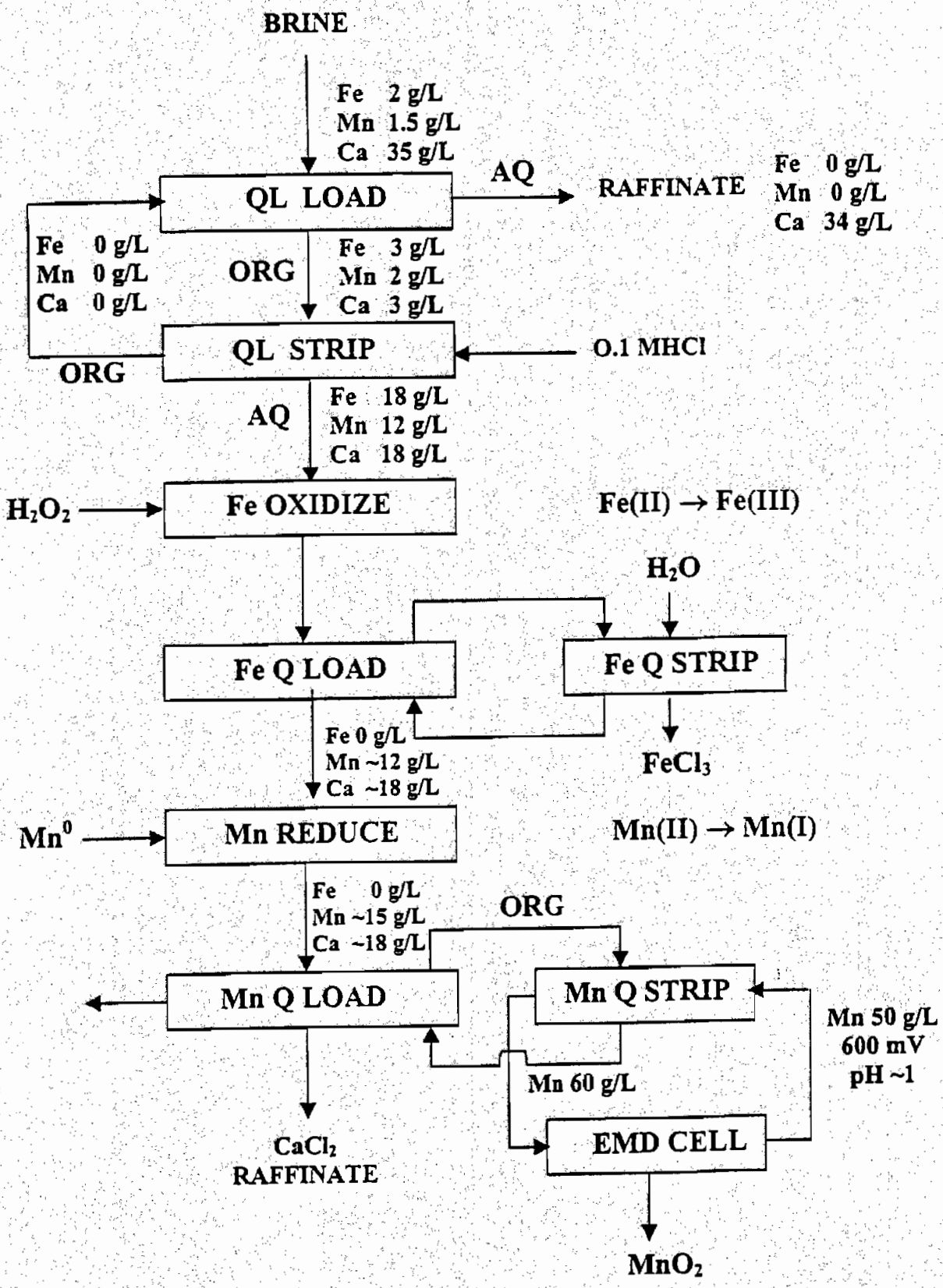

Figure 1 CALENERGY FLOWSHEET

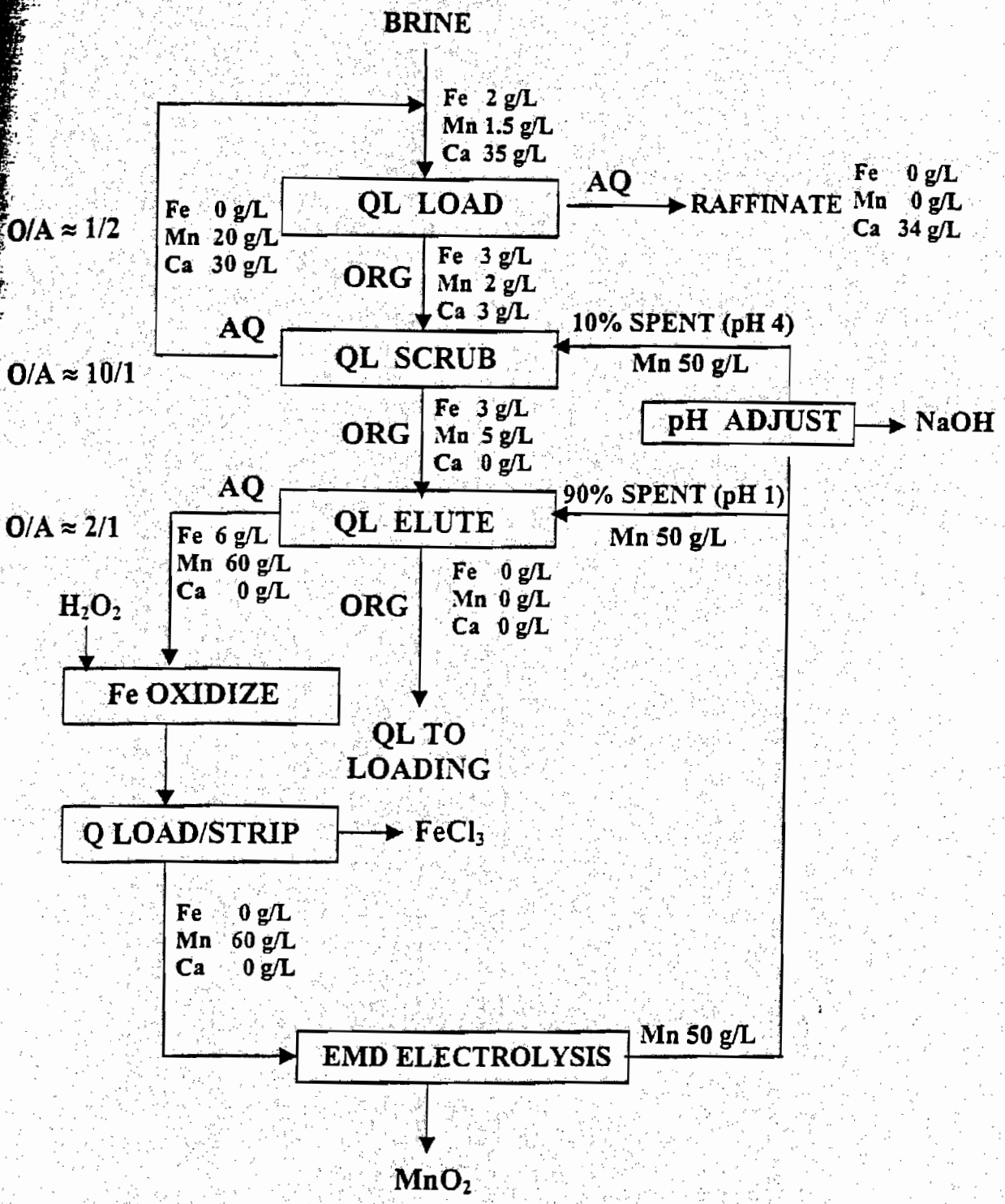

Figure 2 LAKEFIELD FLOWSHEET #1

- The scrubbed organic is stripped with the balance of the spent electrolyte (85-95%) at its natural pH (~pH 1) to strip the Fe and Mn.
- The strip liquor is treated with H_2O_2 to oxidize Fe(II) → Fe(III). The iron is then either extracted with Aliquat 336 or precipitated (as $Fe(OH)_3$ or $FePO_4$).
- The iron-depleted strip liquor is then fed to the EMD cells.

The second Lakefield flowsheet (Figure 3) incorporates the following features:

- A preliminary scrubbing stage (as in Fig 2) to remove Ca from the loaded organic.
- A second scrubbing stage at slightly higher pH (~pH 5) to remove as much of the iron as possible. This scrub solution would either be treated to separate Fe and Mn, as shown in Figure 2, (if there is significant Mn value in the solution) or discarded.
- Elution of the Mn from the loaded organic with spent electrolyte in a closed loop with the EMD cells.

The third Lakefield flowsheet (Figure 4) is a hybrid of the Lakefield calcium scrubbing idea and the Calenergy manganese reduction idea, and consists of the following features:

- A preliminary scrubbing stage (as in Figures 2 and 3) to remove Ca from the loaded organic.
- A second scrubbing stage in which the loaded organic is treated with a small bleed of spent electrolyte that has been reduced to ~-300 mV with manganese metal, and the pH adjusted (if necessary) to ~1. In this scrubbing stage, Fe will be stripped from the organic because of the low pH, but Mn will remain loaded (switching from DEHPA to Aliquat) because of the formation of anionic $MnCl_2^-$. Depending on the Mn content of the scrub solution, it would either be discarded or treated to separate Fe and Mn (as shown in Figure 2 and 3).
- Elution of the Mn from the loaded organic with spent electrolyte in a closed loop with the EMD cells. Under these conditions, $MnCl_2^-$ will be oxidized back to $MnCl_2$, which will strip from the organic phase at the low pH of the spent electrolyte.

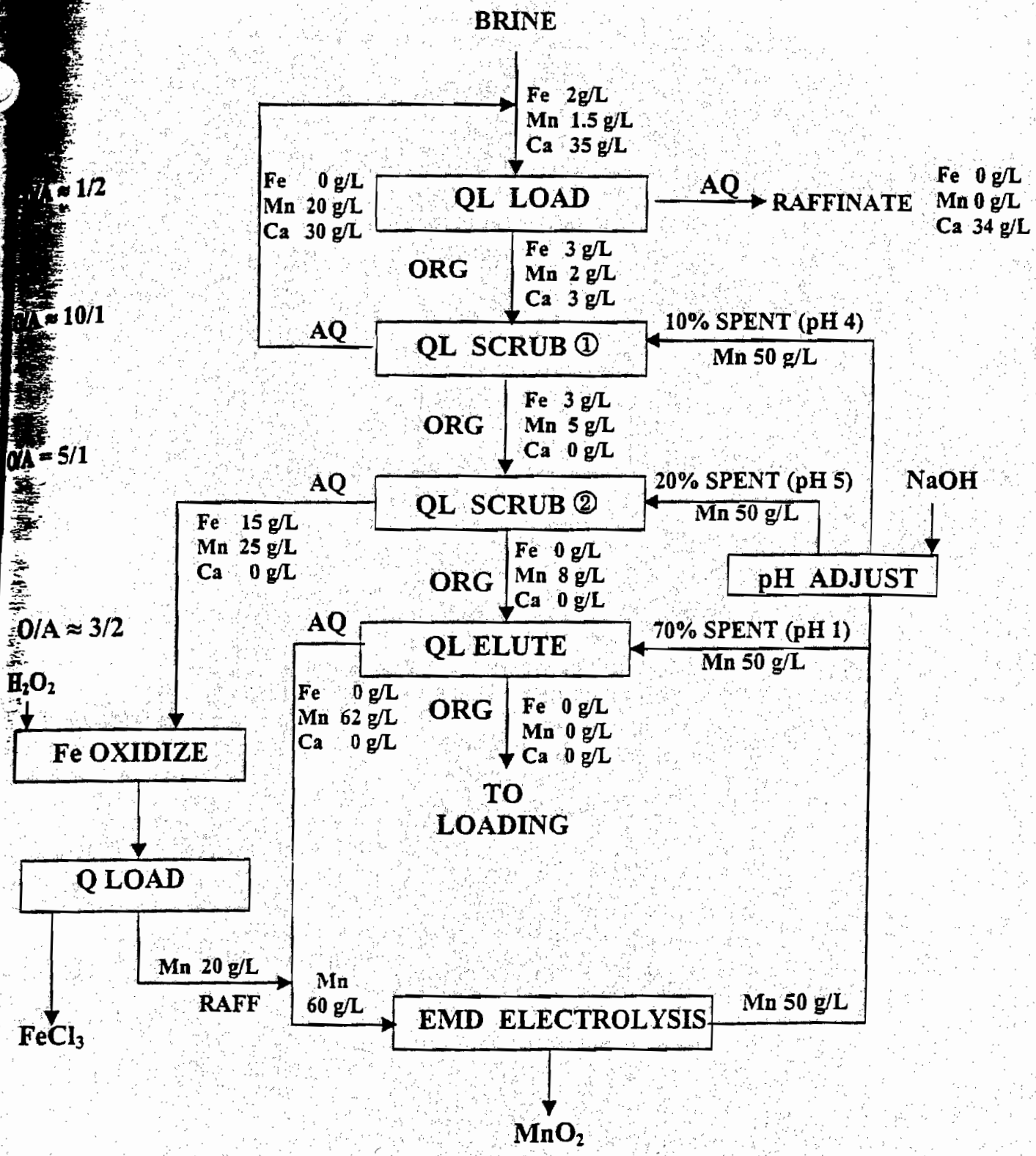

Figure 3 LAKEFIELD FLOWSHEET #2

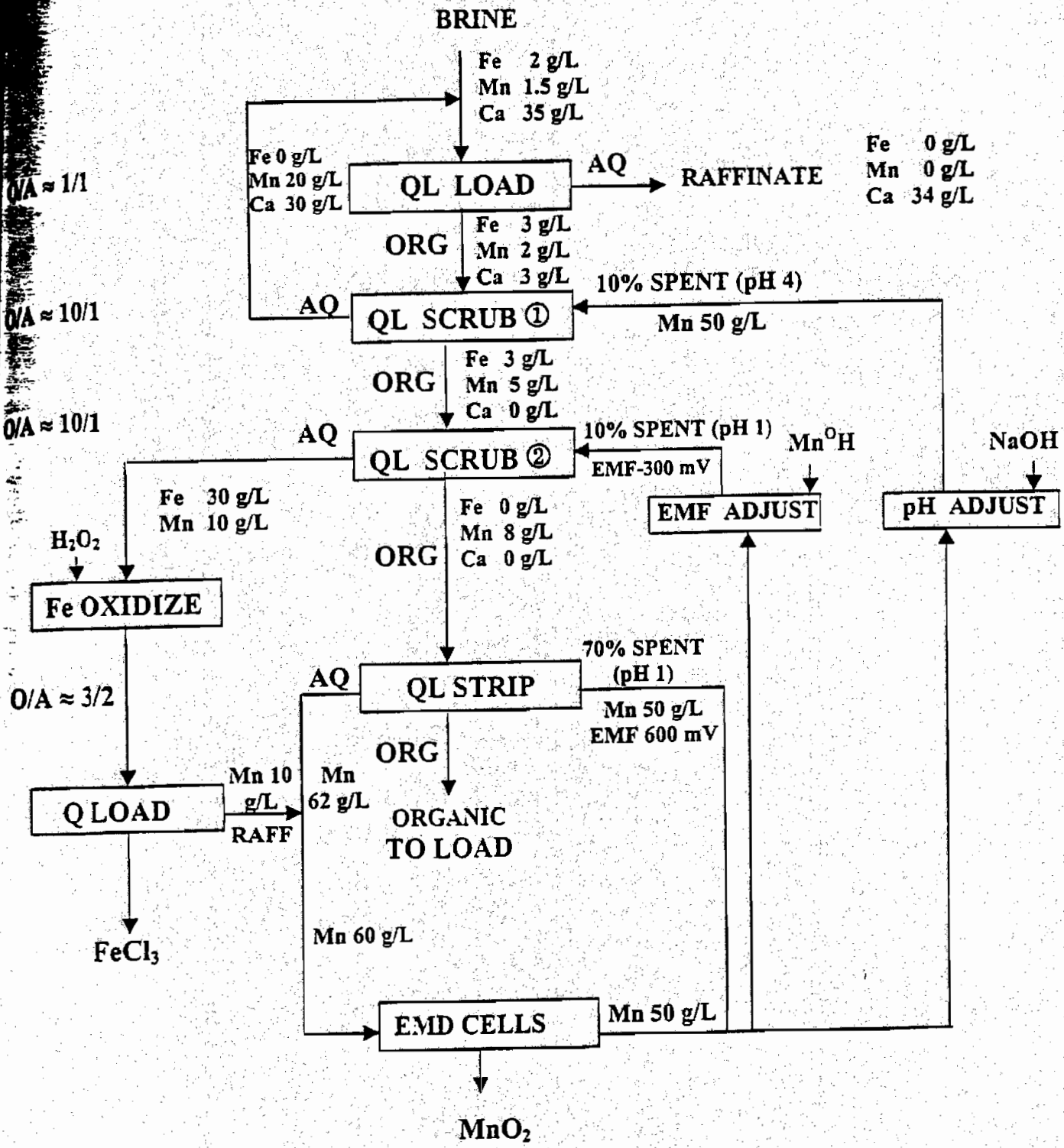

Figure 4 LAKEFIELD FLOWSHEET #3

The objective of the testwork at Lakefield will be to test the 3 Lakefield flowsheets, initially in batch shake out tests, and then in mini, continuous runs, with a view to:

(1) determining optimum operating conditions for each flowsheet (pH, O:A ratio, number of stages etc).

(2) determining (if possible) the best flowsheet for comparison with the Calenergy flowsheet, prior to integrated, larger-scale piloting at the Calenergy facilities using the best of the 4 flowsheets.

Testwork Details

The tests at Lakefield will be done with synthetic solutions made up to the approximate compositions of the Calenergy brine, spent electrolyte, and loaded QL organic phase. These compositions will be provided by George Furmanski (of SNC, seconded to Calenergy) along with the recipe for preparation of the QL reagent.

Synthetic loaded organic will be made up fresh, when needed, by contacting synthetic brine with QL reagent organic phase, at a 3:1 A:O ratio and ~90°C. A small amount of Fe powder will be suspended in the synthetic brine to ensure that iron remains in the ferrous state. The target loading on the organic phase will be 2 g/L Mn, 3 g/L Fe, 3 g/L Ca.

Synthetic spent electrolyte will be made up by dissolving the purest grade of commercial manganese compound ($MnCl_2$) in HCl, to produce a solution containing ~50 g/L Mn and 14 g/l HCl.

Wherever possible, a temperature of 80-90°C will be maintained in all the tests (batch shake out tests as well as mini continuous runs).

Batch Tests

(1) Loaded organic will be scrubbed with spent electrolyte, pre-adjusted to pH 4 with NaOH, at O:A ratios of 20:1, 15:1, 10:1, 7.5:1, 5:1. If the pH drifts during the shake out tests, it will be readjusted back to pH 4 with HCl or NaOH. Further tests may be done outside this range of O:A ratios, or as intermediate points, once the results of the first 5 shake outs have been assessed. At the end of each test the organic and aqueous phase will be analysed for Mn, Fe and Ca.

(2) A second series of 5 or more points on an isotherm will be developed using exactly the same methodology as above, except with the spent electrolyte pre-adjusted to pH 5 (and maintained at pH 5 during the shake out).

(3) If there is a significant different between the isotherms, particularly with respect to Fe displacement by Mn, a wider range of pHs will be tested (pH 3.5, 4.5, 5.5) at the optimum O:A ratio.

(4) A large batch of loaded organic will be prepared and then scrubbed with spent electrolyte using the best conditions established in (1), (2) and (3) above, to remove all the Ca. The Ca-depleted organic phase will then be treated as follows:

a) with spent electrolyte pre-adjusted to pH 5, at O:A ratios of 20:1, 15:1, 10:1, 7.5:1 and 5:1.

b) with spent electrolyte pre-adjusted with Mn metal to an EMF of –300 mV and pre-adjusted (if necessary) to pH <1, at O:A ratios of 20:1, 15:1, 10:1, 7.5:1 and 5:1.

Mini Continuous Tests

Based on the batch shake out test results, the best flowsheet configuration will be selected, using the following criteria as guidelines:

- The initial scrubbing stage should use the minimum amount of spent electrolyte (maximum O:A ratio) and produce a scrubed organic containing ~0 g/L Ca (and minimum Fe), and an aqueous scrub solution containing minimum Mn.

- The subsequent scrubbing stage should also use minimum spent electrolyte and produce a scrubbed organic containing ~0 g/L Fe plus an aqueous scrub solution, containing minimum Mn.

It is hoped that the second objective (scrubbing Fe) will be achieved either with the high pH (pH 5) spent electrolyte scrub or with the low emf (-300 mV), low pH (~pH 1) spent electrolyte scrub. It is likely that both routes will have to be tested in the mini, continuous pilot plant at Lakefield. It is envisaged that a minimum of two and possibly as many as four or five short (~24 hours) mini, continuous runs will be needed to define the optimum operating conditions for the scrubbing flowsheet.

The number of scrubbing stages and the O:A ratio will be varied, with the objectives of maximizing the O:A ratio, maximizing Ca and Fe removal and minimizing the Mn concentration in the spent scrub solution.

The pH of the spent electrolyte will be fixed at the optimum value established in the batch tests, and the initial O:A ratio will be based on the results from the batch tests. The O:A ratio will then be varied in response to the results achieved in the first run with continuous, countercurrent flow of aqueous and organic.

The number of scrubbing stages will initially be set at 6, (three for Stage 1 scrubbing, and three for Stage 2), but this number will be increased or decreased based on the results achieved in the initial continuous test. (Inter-stage sampling and analysis will be conducted to determine single stage scrubbing efficiencies).

Both types of scrubbing solution will be tested in the mini-continuous tests, namely –

- spent electrolyte adjusted to pH 4 to 5, to scrub Ca and possibly Fe
- spent electrolyte reduced with manganese metal and adjusted to <pH 1 to scrub Fe.

Once the best scrubbing flowsheet has been established, a longer continuous run will be carried out (2-4 days) in which scrubbing and elution (with synthetic spent electrolyte at ~50 g/L Mn and ~14 g/L HCl) will be integrated.

The objectives of the longer run will be to:

- determine the purity of the advance electrolyte/strip solution with respect to Fe, Ca.
- produce advance electrolyte for a (possible) iron removal investigation (either by oxidation / solvent extraction or by oxidation / precipitation. (These iron removal studies are not included in the present cost estimate).
- determine the optimum O:A ratio in stripping with respect to the ΔMn and ΔHCl values that are compatible with EMD electrolysis.

Note – it is planned to produce synthetic loaded organic for all the continuous runs, by batch loading the QL reagent from a synthetic brine solution.

Cost Estimate

1. Equipment set up for continuous runs, preparation of solutions, preparation of synthetic loaded organic		
2 technicians (at $80/h) for 2 weeks		$12,800
2. Batch tests		
1 technician for 2 weeks	= $8000	
0.33 engineers for 2 weeks	= $3500	
analysis (25% of labour)	= $2900	$14,400
3. Mini continuous tests		
(assume 5 x 24 hr, 1 x 96 hr runs = 216 hrs)		
2 technicians at $80/hr for 216 hrs	= $34600	
0.33 engineers at $130/hr for 216 hrs	= $9400	
analysis (25% of labour)	= $11000	$55,000
Testwork plus analysis sub-total		$82,200
Supervision, consulting (20%)		$16,400
Reporting, meetings (10%)		$8,200
Miscellaneous (chemicals, equipment, (5%)		$4,100
Contingency (10%)		$8,200
4. Customizing Equipment for high temp SX (jacketed SX cells etc). At cost		$10,000
Overall Total		**$129,100**
		~US $90,000

Schedule

It is estimated that the work will take ~8 weeks to complete, with a final report issued approximately 3 weeks after the testwork. Results will be faxed/e-mailed to Calenergy throughout the testwork program.

12

GRADUATE CENTER FOR MATERIALS RESEARCH

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July 21, 2000

Mr. John Featherstone
Manager, Minerals Extraction
Cal Energy Co., Inc.
950 W. Lindsey Road
Calipatria, CA 92233

Dear John:

The final report is enclosed and we hope it is clear. We tried to give an overall summary-type analysis of some of the more salient points. In general, the process seems feasible, with the critical item being how well the EMD performs in the battery test.

Thanks for involving us in the program and we hope we were of help. As you know, Zhang is leaving, so the timing for the end of the project is just about right. Contact me if there are any questions or comments.

Sincerely yours,,

Thomas J. O'Keefe
Curators' Professor of Metallurgical Engineering
and Senior Investigator, Graduate Center
for Materials Research

Enclosure

Final Report

Evaluation of the EMD Process from Chloride Bath

July 20, 2000

Introduction

Manganese dioxide is an essential cathodic ingredient in a dry cell. Although electrolytic manganese dioxide (EMD) can be made from a couple of high temperature aqueous electrolytes composed of manganese (II) salts and respective acids, such as $Mn(NO_3)_2/HNO_3$, $MnCl_2/HCl$, $Mn(ClO_4)_2/HClO_4$, $MnSO_4/H_2SO_4$, $Mn(SiO_6)_2/H_2SiO_6$, and $Mn(SO_3NH_2)_2/HSO_3NH_2$, currently most of the commercial EMD products are produced from the sulfate bath. A 98 °C solution of manganese sulfate and sulfuric acid with anodes such as lead, lead based alloys, graphite and titanium is used. It was also reported that the chloride route could result in superior quality EMD, plus improved physical, chemical, catalytic and electrochemical properties, as compared with the conventional sulfate route [J.P. Rethinaraj, et al, Hydrometallurgy, 34 (1993), 119-133].

The main objectives of this research was:

1. To verify the feasibility of the EMD process from chloride bath
2. To define the structures of electrolytic manganese dioxide made from chloride electrolyte

(CEMD) using XRD technique and to study the thermal decomposition behavior of CEMD using the DTA technique

3. To evaluate the influences of various operating conditions such as anode pretreatment, anode current density, electrolyte temperature and pH, and Mn concentration etc., on the EMD morphology and structure

4. To optimize the operating parameters for the CEMD process and to provide technical reference and characterizations for CalEnergy miniplant tests and pilot plant runs

Experimental

A small scale test apparatus composed of a 1 liter cell with a condenser on the top, a constant temperature circulating bath, a power supply unit, and a safety control unit was built up at UMR, as illustrated in Figure 1. Two graphite plates with an exposed area of about 6 cm^2/each were used as the cathodes, and a titanium plate (Grade 7 or 16) with an exposed area of about 6 cm^2 was used as the anode. A HP 6634B unit was used as power supply. The set-up was designed to allow all gases to vent through a KI solution with small amount of starch as indicator, so that the evolution of chlorine gas or/and oxygen gas during the deposition can be tested by the discoloration of the KI solution.

Unless specified elsewhere, the general conditions for the chloride EMD deposition tests were:

Initial Mn^{2+} (from $MnCl_2 4H_2O$): 52g/L

Final Mn^{2+}: ~47-49 g/L depending on the operating conditions

Initial HCl: 10g/L

Final HCl: ~13-16 g/L depending on the operating conditions

Anode: Grade 7 Ti, polished to grit #240, degreased with acetone

Cathode: Graphite

Electrolyte temperature: 98 °C

Preconditioning: Anode CD 10A/m^2 for 1 hour

Anode CD for deposition: 100A/m^2

XRD tests were conducted on both the EMD samples made at UMR and at the CalEnergy miniplant using a Scitag unit. Differential thermal analysis (DTA) tests were done using a NETZSCH STA409 analyzer.

Technical Summary

A summary of the test conditions, anode current efficiency, and the surface morphology of deposit of the EMD deposition tests conducted at UMR lab is given in Table 1. XRD and DTA tests were also made with the EMD samples. The more complete results were shown in the 4 Interim Reports which are attached as Appendix A.

A technical summary, of the main conclusions derived from this research is as follows:

- Reasonably good MnO_2 deposits could be made from chloride electrolyte

- No extensive Cl_2 gas evolution was noted during deposition if conditions were proper
- XRD patterns using the γ(110) for comparison showed some slight difference in peak location and degree of diffusivity. Also differences in the Qi value were shown on different samples
- For comparison, sulfate EMD was also made at UMR lab, and it was similar to the chloride EMD, but the morphology of sulfate EMD was much more dense and smooth than the chloride EMD.
- Morphology of chloride EMD was more sensitive to parameters than sulfate EMD, but reasonable morphology of deposit from chloride bath could be obtained
- DTA tests showed similar trends, but some specific variations for the different deposits. The CalEnergy samples had a lower weight loss when heating from 110 °C to 400 °C, as compared to the Eveready sample or UMR samples.
- Anode current density seemed to have a critical influence on the EMD growth and surface morphology. Deposits made at lower current densities of 60 or 80 A/m^2 were usually uniform, smooth and dense, while at 100A/m^2, the deposits obtained showed differences in thickness, and sometimes showed a layered structure or flaky morphology
- At lower electrolyte temperatures, the chlorine or/and oxygen evolution reactions may be enhanced. Also low electrolyte temperature was unfavorable to the deposit morphology
- Lower acid concentration may cause nodular and brittle deposits but the γ phase may be enhanced
- Calcium in the range of 100ppm to 5g/L did not cause any major changes of the deposits in terms of deposit surface morphology and XRD patterns

- Iron in the range of 10-500 ppm did not show noticeable influences on deposit structure according to the XRD tests, but at 500 ppm, the anode current efficiency decreased to 88%

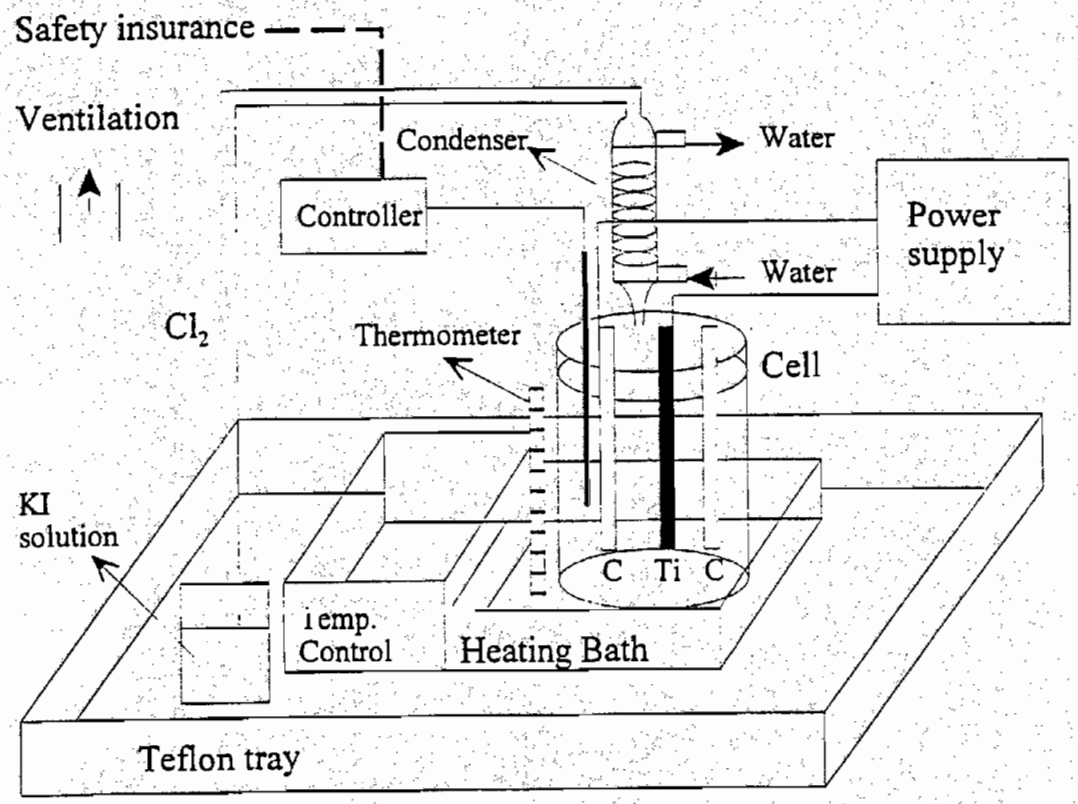

Figure 1 Illustration of EMD lab test set-up

Table 1 Summary of UMR Lab EMD Deposition Tests

Date	Preconditioning	Deposition	ACE(%)	Note
11/17-11/18, 99	5A/m^2, 1hr	100A/m^2, 48hrs	101	Nonuniform in thickness
11/29-12/03, 99	5A/m^2, 1hr	100A/m^2, 96hrs	99	Nonuniform in thickness
12/07-12/10, 99	5A/m^2, 1hr	100A/m^2, 72hrs	-*	Reasonably good
12/15-12/21, 99	5A/m^2, 1hr	60A/m^2, 144hrs	-*	Good
12/28-12/30, 99	5A/m^2, 1hr	100A/m^2,43.5hrs	98*	Nonuniform in thickness
1/4-1/6, 00	5A/m^2, 1hr	100A/m^2, 50hrs	100*	Reasonably good
1/10-1/12, 00	5A/m^2, 1hr	100A/m^2, 48hrs	102*	Nonuniform in thickness
1/18-1/19, 00	10A/m^2, 3hr	100A/m^2, 24hrs	104	Nonuniform in thickness
1/20-1/21, 00	10A/m^2, 15min	100A/m^2, 24hrs	102	Reasonably good
1/24-1/25, 00	10A/m^2, 20min, 50A/m^2, 40min	100A/m^2, 24hrs	103	Uniform in thickness
1/26-1/27, 00	-	60A/m^2, 24hrs	100	Uniform in thickness
2/01-2/04, 00	10A/m^2, 1hr **Sulfate**	100A/m^2, 64hrs **Sulfate**	109	Very good, uniform and smooth
2/04-2/06, 00	-	100A/m^2, 48hrs	101	Nonuniform in thickness, powdery **On used G7 Ti of 1/26-27**
2/07-2/08, 00	50A/m^2, 1hr	100A/m^2, 24hrs	100	Better than above **On used G7 Ti of 1/24-25**
2/10-2/11, 00	-	100A/m^2, 24hrs	94	Non-uniform in thickness, 50% area adhered EMD
2/15-2/17, 00	50A/m^2, 1hr **Sulfate**	100A/m^2, 48hrs	98	Reasonably OK, edges are thicker. **KI sol'n with starch changed to blue**
2/18-2/21, 00	50A/m^2, 1hr **(500ppm Fe, 150ppm Ca)**	100A/m^2, 72hrs **(500ppm Fe, 150ppm Ca)**	89	Bad deposit, non-uniform and flaking
2/24-2/25, 00	50A/m^2, 3.4hrs **(500ppm Fe)**	100A/m^2, 24hrs **(500ppm Fe)**	88	Non-uniform and flaking, most area shinny
2/29-3/03, 00	50A/m^2, 1hr **(50ppm Fe)**	100A/m^2, 72hrs **(50ppm Fe)**	99	Non-uniform and flaking
3/06-3/08, 00	50A/m^2, 1hr **(20ppm Fe)**	100A/m^2, 48hrs **(20ppm Fe)**	102	Non-uniform in thickness, dense

(Table 1 continued)

3/09-3/13, 00	50A/m², 1hr **(10ppm Fe)**	100A/m², 96hrs **(10ppm Fe)**	100	Big thickness variation over surface
3/14-3/17, 00	50A/m², 1hr	100A/m², 72hrs	-	Non-uniform in thickness, better than above
3/22-3/25, 00	50A/m², 1hr **Sulfate+chloride**	100A/m², 80hrs **Sulfate+chloride**	-	Relatively uniform in thickness **KI sol'n with starch changed to blue**
4/25-4/28, 00	10A/m², 1hr	100A/m², 66hrs	110	Very nice, smooth and dense
5/1-5/4, 00	10A/m², 1hr	100A/m², 72hrs **93 °C**	99	Non-uniform in thickness, thicker edges
5/11-5/15, 00	10A/m², 1hr	80A/m², 91hrs	100	Very nice, like SEMD
5/16-5/19, 00	10A/m², 1hr	100A/m², 72hrs **96 °C**	98	Non-uniform in thickness, thicker edges, flaky
5/22-5/25, 00	10A/m², 1hr	**90A/m²**, 69hrs	103	Reasonably good
5/31-6/4, 00	10A/m², 1hr	**80A/m²**, 95hrs	102	Uniform, gas holes on surface
6/5-6/9, 00	10A/m², 20m	**60A/m²**, 89hrs **96 °C**	102	Uniform, gas holes on surface
6/9-6/13, 00	10A/m², 45m	60A/m², 95hrs **18g/L HCl**	94	Uniform and dense
6/13-6/16, 00	10A/m², 45m	**60A/m²**, 72.5hrs **0g/L HCl**	105	Very nodular, brittle
6/20-6/23, 00	10A/m², 45m	**80A/m²**, 76hrs	-*	Uniform and dense, sent to CalEnergy
6/26-6/29, 00	10A/m², 40m	100A/m², 21hrs 80A/m², 56hrs	-*	Nonuniform, sent to CalEnergy
6/30-7/3, 00	10A/m², 50m	**80A/m²**, 76hrs	-*	Uniform and dense, sent to CalEnergy
7/7-7/10, 00	10A/m², 1.5hr	**60A/m²**, 76hrs **40g/L Mn**	101	Uniform and dense

* Samples sent to CalEnergy

Appendix A

Interim Report (I)

Preliminary Summary of Features of EMD

October, 1999

1. Chemical formula and Crystalline Structures

Over 20 manganese dioxide minerals have been reported. Only two of these, ramsdellite and β-MnO_2 or pyrolusite, are stoichiometric. The remainder exhibit defect structures to varying degrees, and most contain large cavities which accommodate various foreign cations such as Ba^{2+}, Pb^{2+}, K^+, Na^+, Ca^{2+}, and Mn^{2+}, as well as water molecules.

For natural manganese dioxide minerals, they were classified as following 8 groups by V. M. Burns[1] et al:

a) The α-MnO_2, Cryptmelane, or Hollandite Group

b) β-MnO_2 or Pyrollusite

c) Ramsdellite

d) γ-MnO_2 or Nsutite (hydroxide) only on Ti

e) δ-MnO_2 and birnessite

f) Todorokite

g) Psilomelane

h) The MnOOH Polymorphs

The γ-MnO_2 most widely used for dry cells, either naturally occurring or prepared by electrolytic means, consists of ramsdellite matrix with statistically distributed intergrown microdomains of pyrolusite.

Its chemical formula can be written as:

$(MnO_2)_{2n-3}(MnOOH)_{4-2n}\ mH_2O$

where $1.5<n<2$

The presence of (OH) group in γ-MnO_2 may be evidenced by infrared spectroscopy. Ramsdellite and pyrolusite do not exhibit the characteristic absorption bands for OH.

XRD Data for Manganese Dioxide

The term γ-MnO_2 had been historically used ambiguously.

The International Center for Diffraction Data has published the XRD data for 86 manganese oxides and 33 manganese hydroxides, manganites or hydrated manganese oxides since 1930s. Among these, some were already deleted or/and updated. The XRD data for the α-,ϵ-, λ-, and ρ-MnO_2 can be obtained from PDF card numbers 44-0141, 30-0820, 44-0992 and 12-0714, respectively. There is no PDF number for the γ- or β- MnO_2.

However, there has been considerable published XRD data for the γ-MnO_2 and β-MnO_2 in the

literature on EMD. According to M. Fukuda[2], there are 3 types of structures for the synthetic γ-MnO_2 and 4 for the natural γ-MnO_2, as well as 3 β-MnO_2 structures. With heating, all phases which belong to the γ-series are transformed finally to β-MnO_2. They are shown in the "Reverse-Y diagram" (see Figure I-1).

The main orientations for γ-, β- and ∈- MnO_2 are listed in Table I-1:

2. Properties of EMD

The International Common Sample (I.C.) Office summarized the main properties of the I.C. MnO_2 samples and characteristics of interests in EMD for battery applications[3], including

a) Typical chemical analysis

b) Density

c) Surface areas and pore diameter

d) Discharge curves of typical EMD, CMD, NMD in 9M KOH

e) Discharge performance of dry cells and the ratio of OCV/SCC

f) Conductivity

h) XRD pattern

i) Potential in 1M KOH and 2M NH_4Cl +0.1M ZnO

These published data from different investigators provide a good reference for the EMD study.

K. Takashaki and Y. Nakayama[4] summarized the functional properties demanded in battery grade EMD as following.

1) Harmful heavy metal cumulative limit

Sb, Mo, As: Most harmful, cumulative limit 5ppm max.

V, Cr, Co, Ni, Cu, Ag: Harmful, cumulative limit 10-20ppm max.

Pb, Cd: Harmful, cumulative limit 100ppm max.

Fe: Harmful, cumulative limit 500ppm max.

2) Alkaline earth, alkali metal and surface ions

Mg + Ca (as sulfate and carbonate): cumulative limit 500ppm max.

K, Na (in lattice defect tunnel): cumulative limit 3000ppm max.

SO_4^{2-} (in lattice defect tunnel): cumulative limit 12000ppm max.

CO_3^{2-}: limit 2000ppm max.

3) Bound water

a) Free water which can be removed by drying at 110-120°C

b) Bound water which can be removed by drying at 120-350°C

c) Lattice water which can be removed by drying at 350-750°C

Muddy EMD	→ Powder	→ Product
(~11-15% H_2O)	(~8% H_2O)	(~3% H_2O)

(Sticky state) (Powder state) (Dry state)

4) XRD

MnO_2 suitable for dry cells:

γ-ramsdellite (acidic property), psilomelane, Nsutite (δ or ρ)

δ-vernadite (or biirnnesite) (bound water, high, 5-40% ex. CMD)

ϵ-fibrous EMD (Mn modules are ϵ type)

MnO_2 unsuitable for dry cells (deficient in activity)

β-pyrolusite (basic property)

α-cryptomelane (contains K^+... typical)

Hollandite (contains Ba, Fe)

Coronadite (contains Pb)

Manjiroite (contains Na)

Rating by stability probably is as follows: β>α>γ>δ>ϵ

5) BET area

EMD generally had BET areas of 30-45 m^2/g, CMD 45-100, ACM 200-60, HCMD 200, NMD 10-20.

6) Porosity

EMD porosity is usually 50-60% (mercury intrusion under pressure by mercury intrusion

porosimeter).

7) Tapping density

Normally 2g/cc, or higher 2.6-2.8g/cc.

8) Grain size distribution and grain shape

Grain shapes that are more regular have higher activity.

-200 mesh (=74μ) 90%, coarse

-325 mesh (=44μ) 90%, fine

Proper grain size distribution range is roughly 5-60 μm . And it is desired that the distribution peak being around 30-40 μ.m.

9) Resistivity

37-77 Ω cm for EMD.

MnO_2 is a semiconductor, and depending on the manufacturing method, its conductivity varies over a wide range of 10^{-6}-10^{-1} Ω^{-1} cm^{-1}.

3. Electrolytic Process

EMD can be made in different bathes, such as sulfate, nitrate, chloride, and chlorate, with compositions of 0.2-0.4M free acid and 0.6-1.0M its salt and temperatures above 90°C, on a couple of anode substrates, such as graphite, titanium , lead, etc. The main reactions are:

On anode: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e$

On cathode: $2H^+ + 2e \rightarrow H_2\uparrow$

Overall reaction: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2\uparrow$

At present, most EMD products are made from the sulfate bath. Since large quantities of by-product commercial hydrochloric acid, obtained from the chlor-alkali and/or PVC industries, and pyrolusite ore are available, the preparation of EMD through the intermediate formation of $MnCl_2$ could provide cheaper production route, due to this ready available of indigenous raw materials. In addition, chloride electrolyte possesses a higher conductivity and solubility than sulfate.

The electrolytic conditions for producing EMD from the chloride bath is as follows according to J. P. Rethinaraj[5] et al.

90-120 g/L $MnCl_2$ or 40-52g/L Mn^{2+}

14-18 g/L HCl

C.D.: 12-16 mA/cm^2

Temperature: 90-100°C

The anode material is titanium, and cathode material graphite. The crystalline structure of the EMD belongs to the γ variety.

4. Summary of UMR Lab Test Results

The manganese oxide/hydroxide samples with different heat treatment including the EMD samples made at UMR from the sulfate and chloride bathes, Eveready battery sample, and the precipitated sample from CalEnergy, as well as a Baltimore Plant MED sample, were analyzed by the XRD techniques. Table I-2 summarizes the main results.

According to E. Preisler [6], The ratio of peak heights of the most characteristic peaks of γ- and ϵ-MnO_2 at θ=11.0° and θ=18.5° defined as Q_i, can be as an estimation of the relative amounts of γ- and ϵ-MnO_2. In the sulfate bath with suspended particles, at a current density of 30mA/cm^2 a rather pronounced γ-MnO_2 pattern is obtained having Q_i ~1.5 while a typical ϵ-MnO_2 gives Q_i ~0.35.

It can be seen from Table I-2 that almost all the EMD samples made at UMR from both chloride bath and sulfate bath, the Eveready battery sample (mixed with graphite powder), and the Baltimore Plant EMD sample, were mixture of γ- and ϵ-MnO_2. With lower Mn^{2+} content and higher current densities, growth of ϵ-MnO_2 could be enhanced.

Heating at 70°C and 110°C, which are used to remove the free water or moisture from the sample, did not make difference. But heating at 250°, which is thought to remove the bound water, did make a change in the XRD patterns of the UMR made samples, which indicates a change in the structure. No major structural change was found for the Eveready battery sample with a heating temperature of 250°. The precipitated sample from CalEnergy showed a dramatic change in the XRD patterns with heating. The original manganite MnOOH was changed to the MnO_2 pyrolusite

after heating at 250°.

Selected XRD patterns for the Eveready battery sample, Baltimore Plant EMD sample, UMR lab EMD sample, and CalEnergy precipitated sample, are put in Appendix I-A.

The effect of calcium in the electrolyte on EMD was also investigated. Preliminary tests using a electrolyte (50g/L Mn^{2+}, 3.6g/L HCl) containing 1 or 5 g/L Ca^{2+} were conducted. An initial current density of 0.5mA/cm^2 was used for the preconditioning of the Ti anode, which is thought to help the adhesion of deposit. Then a current density of 10mA/cm^2 was used for the deposition. The results showed that the EMD coatings made with 1 or 5g/L Ca^{2+} had a even better adherence and less cracks on the deposit surface compared with no Ca^{2+}. Figure I-2 shows the SEM micrographs of a piece of EMD crystal sample made in the presence of 1g/L Ca^{2+}. A fibrous microstructure can be seen at high magnification. This is in consistent with the results reported by K. Matsuki et al[7]. The XRD pattern of the crystal sample (see Appendix I-A) shows that no γ peaks appear and strongly preferred orientations of (100) and (110) of ϵ-MnO_2 are evident. However, its powder sample also gave a similar XRD pattern (see Appendix I-A, characteristic of mixture of γ and ϵ-MnO_2) to those with no Ca^{2+}.

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1. V. M. Burns and R.G. Burns, Maganese Dioxide Symposium, Cleveland, USA. Vol.1 (1975). 288-309.

2. M. Fukuda, Third Manganese Dioxide Symposium, Graz, 1985, IBA, Cleveland. 181–189.

3. Manganese Dioxide Symposium, Vol.2 (1980). Tokyo, Japan. 561-574.

4. K. Takahashi and Y. Nakayama, Third Manganese Dioxide Symposium, Graz, 1985, IBA, Cleveland. 208-220.

5. J. P. Rethinaraj et al, Hydromatallurgy, 34 (1993), 119-133.

6. E. Peisler, J. Applied Elctrochemistry, 19(1989), 540-546.

7. K. Matsuki, E. Endo, and H. Kamada, Electrochimica Acta, 29(1994), 983-9993.

Table I-1 The main orientations for γ-, β- and ϵ- MnO_2

EMD	2θ (λ=1.5406) (Degree)				
γ-MnO_2	22.2°	37.2°	42.6°	56.3°	67.6°
β-MnO_2	28.8°	37.5°	42.9°	56.7°	59.5°
ϵ-MnO_2	-	37.1°	42.4°	56.0°	66.8°

Table I-2 Summary of XRD Results

Sample	Q_i	Possible phases	Remarks
Eveready battery sample			
As received	0.59	ϵ- + γ- MnO_2	PDF 30-0820 matches most
Drying at 110°	0.69	ϵ- + γ- MnO_2	Similar XRD pattern to above
Drying at 250°	0.71	ϵ- + γ- MnO_2	Similar XRD pattern to above
Baltimore Plant sample			
As received	0.59	ϵ- + γ- MnO_2	PDF 30-0820 matches most
SEMD (0.64M $MnSO_4$ +0.37M H_2SO_4)			
Drying at 70°	0.64	ϵ- + γ- MnO_2	PDF 30-0820 matches most
Drying at 110°	0.54	ϵ- + γ- MnO_2	Similar XRD pattern to above
Drying at 250°	0.71	ϵ- + γ- MnO_2	Peaks moved 1-2°, a new peak at ~34°
CEMD (50g/L Mn, 15g/L HCl, 6mA/cm^2)			
Drying at 70°	0.56	ϵ- + γ- MnO_2	PDF 30-0820 matches most
CEMD (50g/L Mn, 3.6g/L HCl, 10mA/cm^2)			
Drying at 70°	0.53	ϵ- + γ- MnO_2	PDF 30-0820 matches most
CEMD (50g/L Mn, 3.6g/L HCl, 1g/L Ca^{2+} , 10mA/cm^2)			
Crystal, Drying at 70°	0	ϵ- MnO_2	PDF 30-0820 matches most

Powder, Drying at 70°	0.59	ϵ- + γ- MnO_2	PDF 30-0820 matches most
CEMD (20g/L Mn, 15g/L HCl, 15mA/cm^2)			
Drying at 70°	0.45	ϵ- + γ- MnO_2	PDF 30-0820 matches most
Drying at 110°	0.34	Mainly ϵ-MnO_2	Similar XRD pattern to above
Drying at 250°	050	ϵ- + γ- MnO_2	Peaks moved 1-2°, a new peak at ~32°
CEMD (10g/L Mn, 15g/L HCl, 15mA/cm^2)			
Drying at 70°	0.43	ϵ- + γ- MnO_2	PDF 30-0820 matches most
PMD (CalEnergy)			
As received	-	MnOOH or MnO(OH)	Both PDF 74-1842 and 41-1379 match most
Drying at 110°	-	MnOOH or MnO(OH)	Similar XRD pattern to above
Drying at 250°	-	MnO_2	Pyrolusite-synthetic (81-2261)

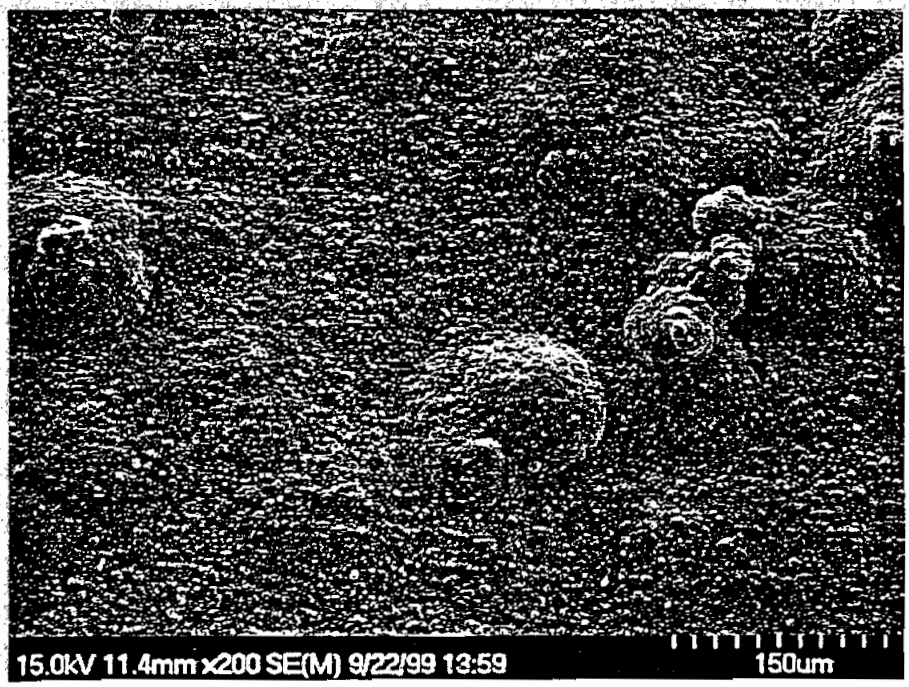


Figure I-1 SEM micrographs of EMD crystal made from 50g/L Mn, 3.6g/L HCl and 1g/L Ca, a) 200X

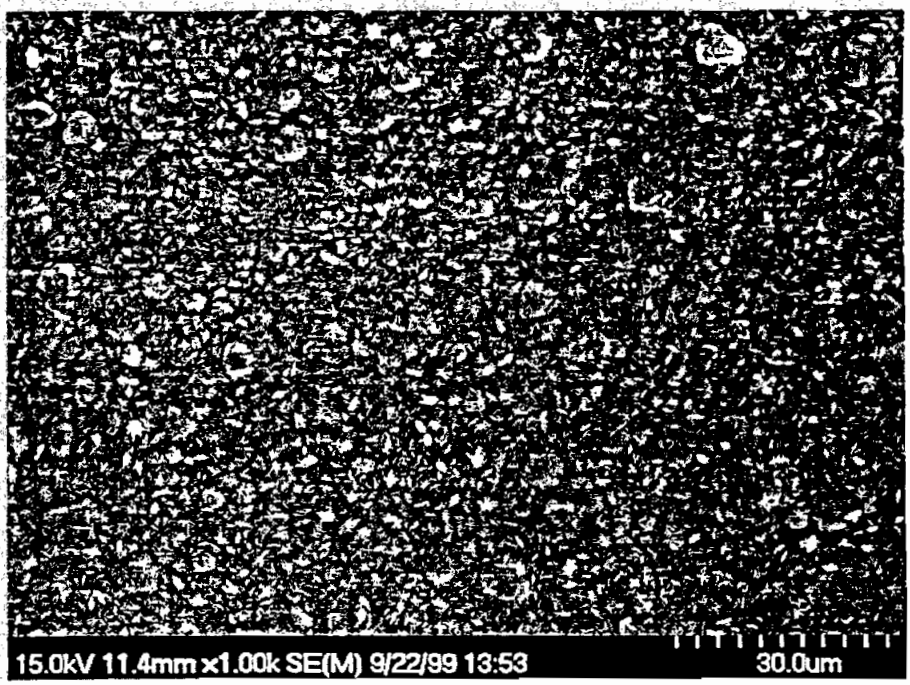


Figure I-2 (Continued), b)1000X

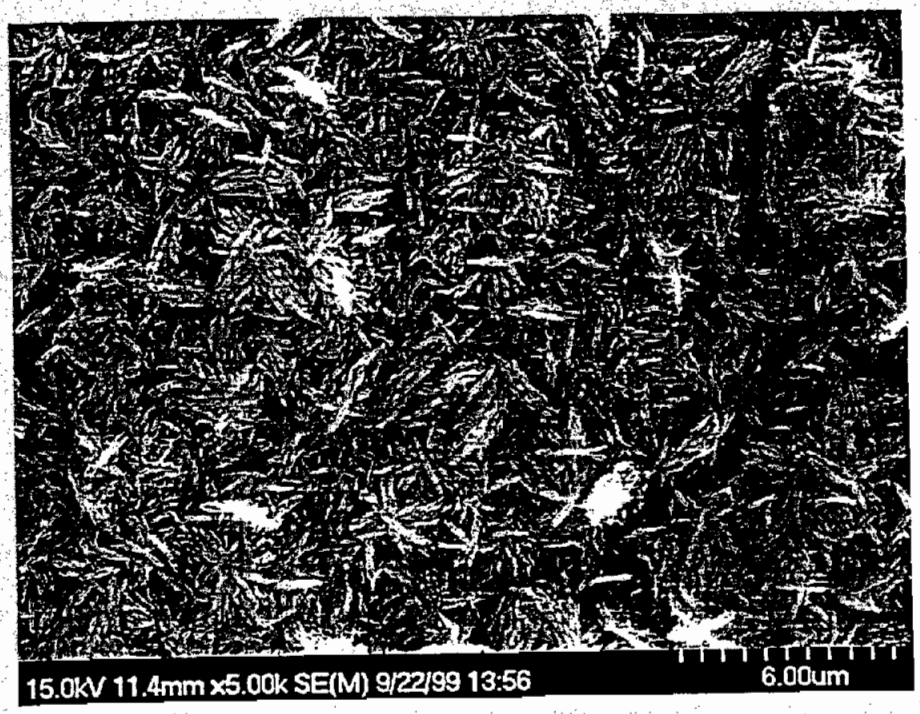


Figure I-2 (Continued), c) 5000X

Appendix I-A

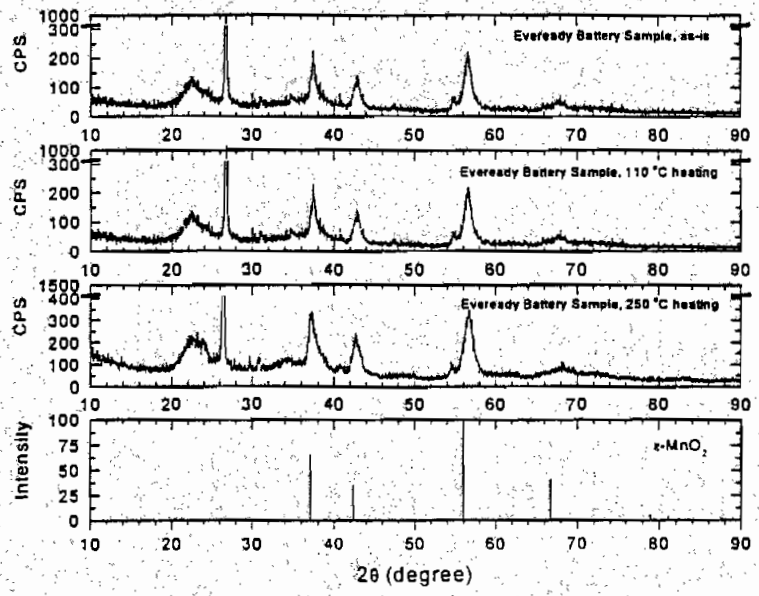


Figure I-1 XRD patterns for the Eveready battery sample

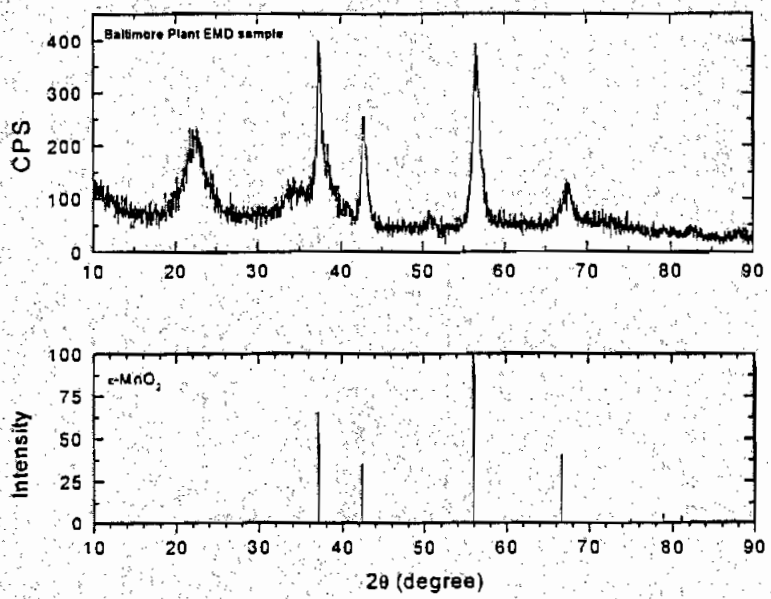


Figure I-2 XRD patterns for the Baltimore plant EMD sample

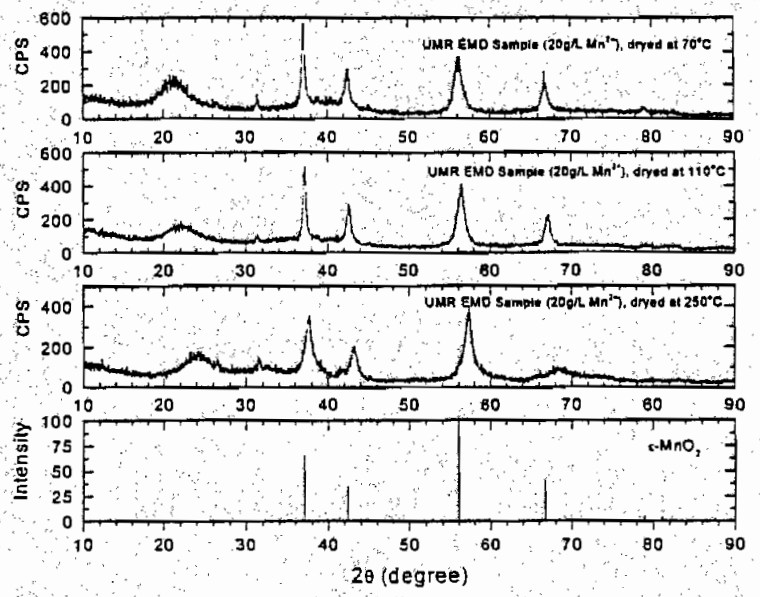


Figure I-3 XRD patterns for UMR lab EMD sample made from an electrolyte containing 20g/L Mn^{2+} and 15g/L HCl at 15mA/cm^2, 95°C

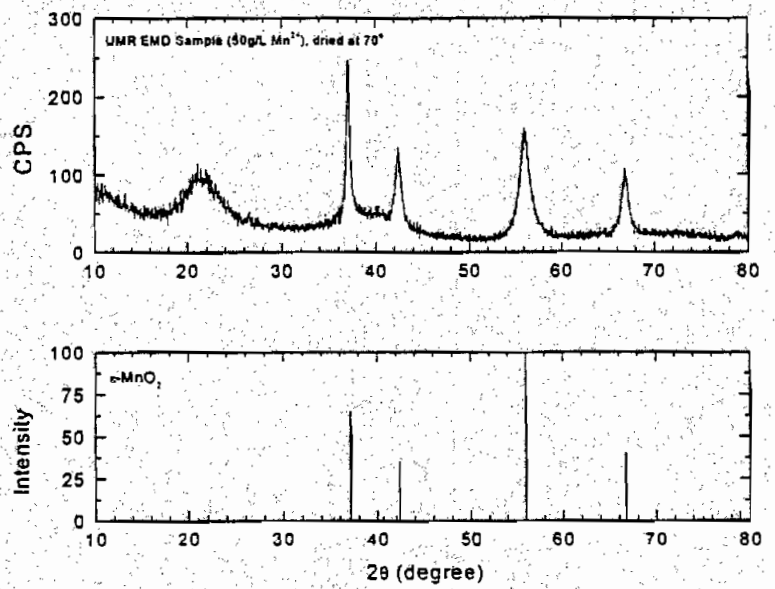


Figure I-4 XRD pattern for UMR lab EMD sample made from an electrolyte containing 50g/L Mn^{2+} and 3.6g/L HCl at 10mA/cm^2, 95°C

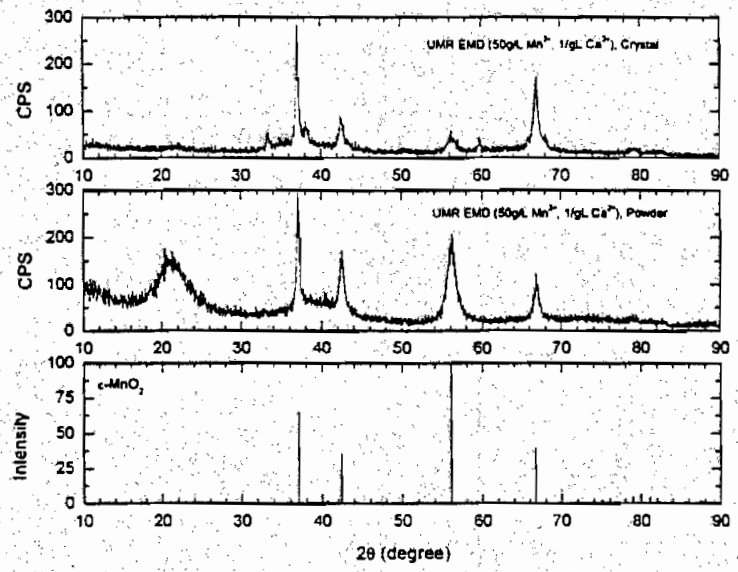


Figure I-5 XRD patterns for UMR lab EMD sample made from an electrolyte containing 50g/L Mn^{2+}, 1g/L Ca^{2+} and 3.6g/L HCl at 10mA/cm^2, 95°C

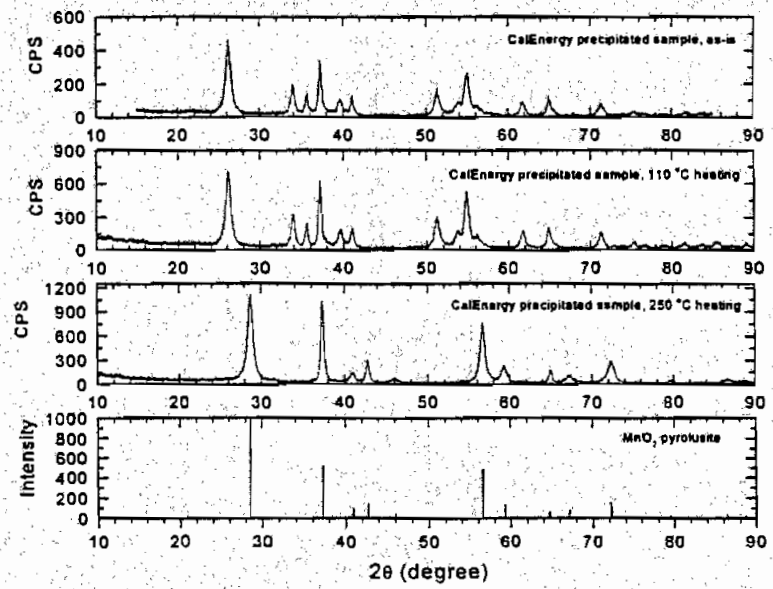


Figure I-6 XRD patterns for the CalEnergy precipitated sample with different heating temperature

Interim Report (II)

Summary of UMR Lab Tests

January 25, 2000

A couple of preconditioning tests, deposition tests, and polarization tests were conducted based on discussions at the meeting at UMR on Oct. 26th, 1999. Some XRD and DTA tests with the EMD samples were also done.

1. Preconditioning

Precoating at lower anode current densities seems to be a necessary step for making a uniform EMD deposit with good adhesion to the titanium substrate, particularly when using an ACD of 100A/m^2. In order to get a better precoating condition, different current densities (5, 10, 20 A/m^2) and holding times (10min, 15min, 1hr, 3hr, 5hr) were tested. It was found that for EMD deposition at 100A/m^2, shorter time precoating at 5 or 10A/m^2 seemed better. Moreover, with an intermediate layer made first at 10A/m^2 for 20 minutes and then at 50A/m^2 for 40 minutes, a even better deposit was obtained in terms of the overall surface morphology and the uniformity in thickness on both sides. For the EMD deposition at an ACD of 60A/m^2, a dense and uniform (in thickness) deposit could be made using a preconditioning current density of 5A/m^2 for 1 hour or even without preconditioning. It seems advisable to define the preconditioning step more

specifically, as it does seem to have a strong influence on not only adhesion but subsequent MnO_2 growth uniformity as well.

2. EMD Tests

To get a better EMD deposit, the graphite plate cathode was wrapped with Teflon tape to have an exposed area of about $3cm^2$ facing the titanium anode. The distance between anode and cathode is about 4cm. The titanium anode plate was sealed with a heat-shrink teflon tubing to leave each side an exposed area of about $3cm^2$.

Some longer term (3-6 days) EMD deposits were made in order to have a thickness of 3-5 mm. In other cases, screening tests of 1 or 2 days were also conducted and focused on optimizing the precoating conditions and identifying the short term phases obtained. The main test results are summarized in Table II-1.

It is seen that at an ACD of $100A/m^2$, the EMD deposit uniformity is very dependent on the preconditioning step. At $60A/m^2$ or lower, a smooth and uniform deposit could be made even without preconditioning. Longer time preconditioning at lower current densities seemed to increase the adherence.

3. Polarization

Polarization tests on both precoated and coated titanium electrodes (Grade 7 or Grade 16) were conducted in the electrolyte containing 52g/L Mn^{2+} and 10g/L HCl at 80°C. Similar trends can be seen from the polarization curves with precoated Grade 7 and Grade 16 titanium, as shown in Figure II-1. Also, a deposit layer made at 60A/m^2 for 30 minutes after precoating did not cause any major difference in polarization behavior, as shown in Figure II-2. It is seen that at 100A/m^2, the electrode potential is 1.40, 1.38, and 1.41 V (vs NHE), respectively for precoated Grade 7, precoated Grade 16, and precoated + coated Grade 7. But when the current density is close to 300A/m^2, a sudden potential increase happens, and vigorous gas (chlorine and oxygen) evolution can be observed on the electrode surface. Galvanostatic tests also revealed that at 100A/m^2, anode potential was about 1.37V and no gas bubbling was observed. At 300A/m^2 or higher, the anode potential was 1.52V and increased substantially, and vigorous gas evolution could be seen.

4. Chlorine Test

To test if chlorine is generated during electrowinnng, the existing current set-up for lab tests was designed to allow all the gases to vent through a 0.1N KI solution. After the eletrowinning test, the KI solution can be titrated with sodium thiosulfate to determine the total amount of elemental iodine in the KI solution produced by the reactions with oxygen or chlorine gas. Further analysis of chloride can be done by the ionic selective electrode (ISE). However, when the 1% starch indicator solution was added to the vented KI solutions after deposition tests, no discoloration was ever noted. If the solutions were exposed to air and light for some time, they gradually

changed to a light blue color. This indicates that very little chlorine, if any, was generated during the EMD electrowinning at current densities of 100A/m^2 or lower. This observation is also consistent with the polarization measurement results. The anode potential is not high enough to provide the required overpotential for oxygen or chlorine evolution at anode current densities of 100A/m^2 or lower. On the other aspect, in most tests, the anodic current efficiency was near 100% (calculated based on MnO_2). Chlorine gas is evolved if the current density goes to 300A/m^2 or at an anode potential near 1.75V (vs NHE).

5. XRD and DTA

DTA tests were conducted using a NETZSCH STA409 (simultaneous thermal analysis) Analyzer. In each test only 200 to 400mg powder sample is needed. The increase rate of temperature was 10 °C/min. The thermogravimetric (TG) analysis and differential scanning calorimetric (DSC) curves are shown in Figure II-3 and II-4, respectively, for UMR lab EMD sample (made at 100A/m^2 in an electrolyte containing 52g/L $Mn^{2+}$and 10g/L HCl), and for the Baltimore Plant EMD (made from a sulfate bath). The weight loss at several selected temperatures is listed in Table II-2, and the two peak temperatures on DSC curve are listed in Table II-3. It is seen that the percent weight losses of sample from 110 to 400 °C, which were due to the loss of "combined water", are 3.66% and 4.20% for the UMR and Baltimore EMD samples, respectively. On the DSC-Temperature curve, the two DSC peak temperatures, which are 559 and 958 °C for UMR sample, and 572 and 987 °C for the Baltimore sample, set up the two regions for the decomposition of MnO_2 into the lower oxides, Mn_2O_3 and Mn_3O_4,

respectively. More tests are needed in order to more precisely characterize the decomposition process of MnO_2. The final products after DTA tests being Mn_3O_4 were also confirmed by XRD analysis, as shown in Figure II-5 and II-6 for UMR and Baltimore Plant EMD samples, respectively.

Several UMR Lab made EMD samples were already sent to CalEnergy for the chemical analysis. More XRD tests will be conducted to get the structural data for the EMD made with different conditions.

Table II-1 Summary of UMR Lab EMD Deposition Tests

Date	Preconditioning	Deposition	ACE(%)	Note
11/17-11/18, 99	5A/m^2, 1hr	100A/m^2, 48hr	101	Nonuniform in thickness
11/29-12/03, 99	5A/m^2, 1hr	100A/m^2, 96hr	99	Nonuniform in thickness
12/07-12/10, 99	5A/m^2, 1hr	100A/m^2, 72hr	-*	Reasonably good
12/15-12/21, 99	5A/m^2, 1hr	60A/m^2, 144hr	-*	Good
12/28-12/30, 99	5A/m^2, 1hr	100A/m^2, 43.5hr	98*	Nonuniform in thickness
1/4-1/6, 00	5A/m^2, 1hr	100A/m^2, 50hr	100*	Reasonably good
1/10-1/12, 00	5A/m^2, 1hr	100A/m^2, 48hr	102*	Nonuniform in thickness
1/18-1/19, 00	10A/m^2, 3hr	100A/m^2, 24hr	104	Nonuniform in thickness
1/20-1/21, 00	10A/m^2, 15min	100A/m^2, 24hr	102	Reasonably good
1/24-1/21, 00	10A/m^2, 20min, 50A/m^2, 40min	100A/m^2, 24hr	103	Uniform in thickness
1/26-1/27, 00	-	60A/m^2, 24hr	100	Uniform in thickness

* Samples sent to CalEnergy

Table II-2 Percent Weight Loss at Selected Temperatures in DTA Tests

	110°C	400°C	1000°C
UMR EMD	0.16%	3.82%	15.00%
Baltimore EMD	0.18%	3.38%	15.24%

Table II-3 Peak Temperatures on DSC Curves

UMR EMD (Chloride)	305°C	559°C	958°C
Baltimore EMD (Sulfate)	-	572°C	987°C
Ref.1 (Chloride)*	317°C	572°C	983°C

* Ref.1: **Hydrometallurgy, 34, 119-133(1993).**

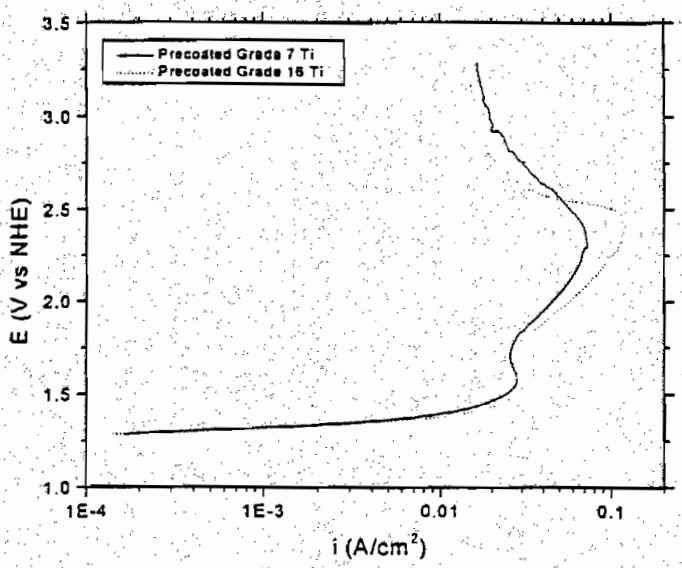


Figure II-1 Polarization curves for Grade 7 and Grade 16 titanium electrode in the electrolyte containing 52g/L Mn^{2+} and 10g/L HCl at 80°C. Prior to test, preconditioning at 5A/m² for 1hour was applied

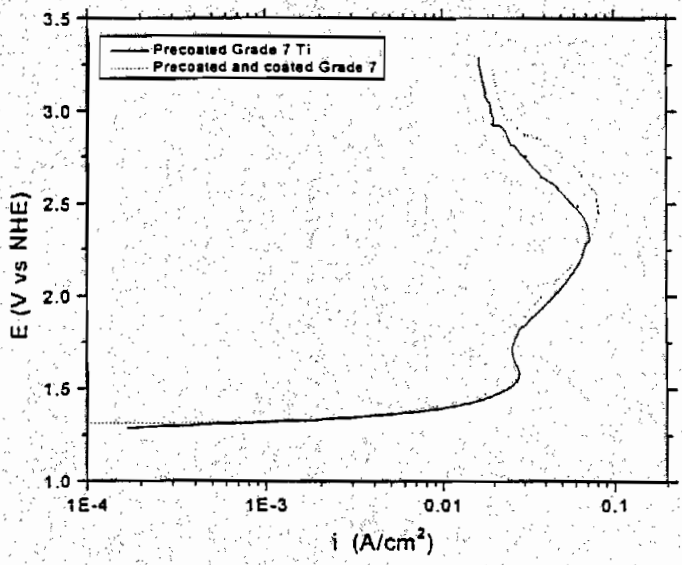


Figure II-2 Polarization curves for Grade 7 titanium electrode in the electrolyte containing 52g/L Mn^{2+} and 10g/L HCl at 80°C. Prior to tests, preconditioning at 5A/m² for 1hour and deposition at 60A/m² for 30 minutes were applied

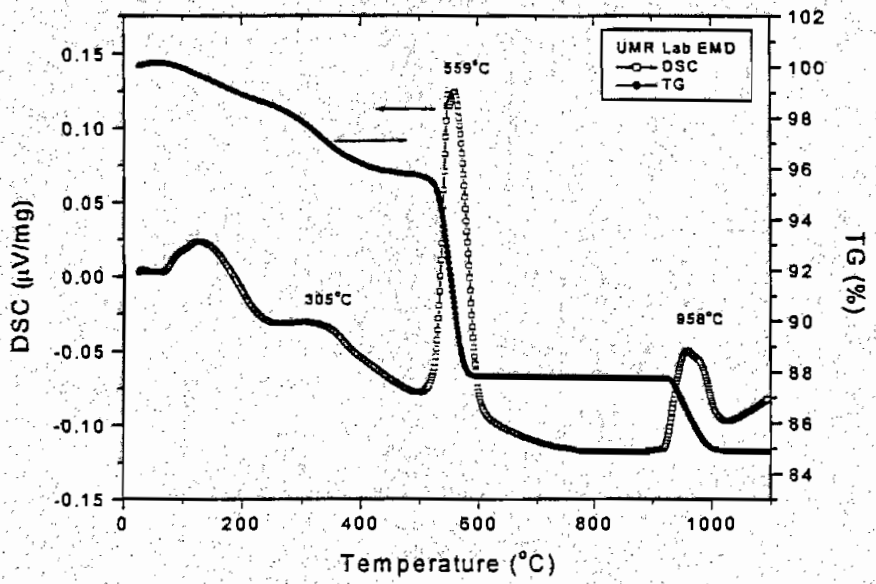


Figure II-3 DTA test curves of an EMD sample made at UMR lab in the electrolyte containing 52g/L Mn^{2+} and 10g/L HCl at 100A/m^2 and 97°C for 2 days

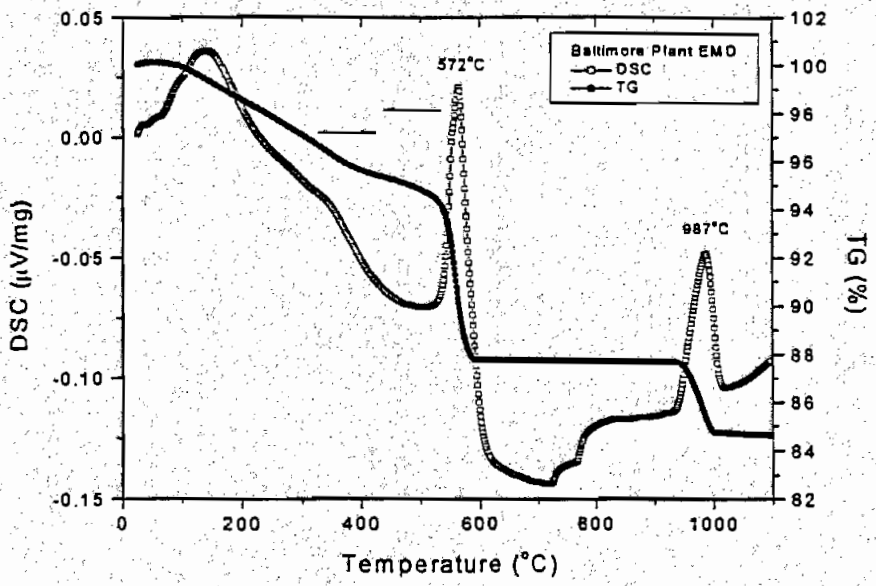


Figure II-4 DTA test curves of a EMD sample made at Baltimore Plant in a sulfate bath

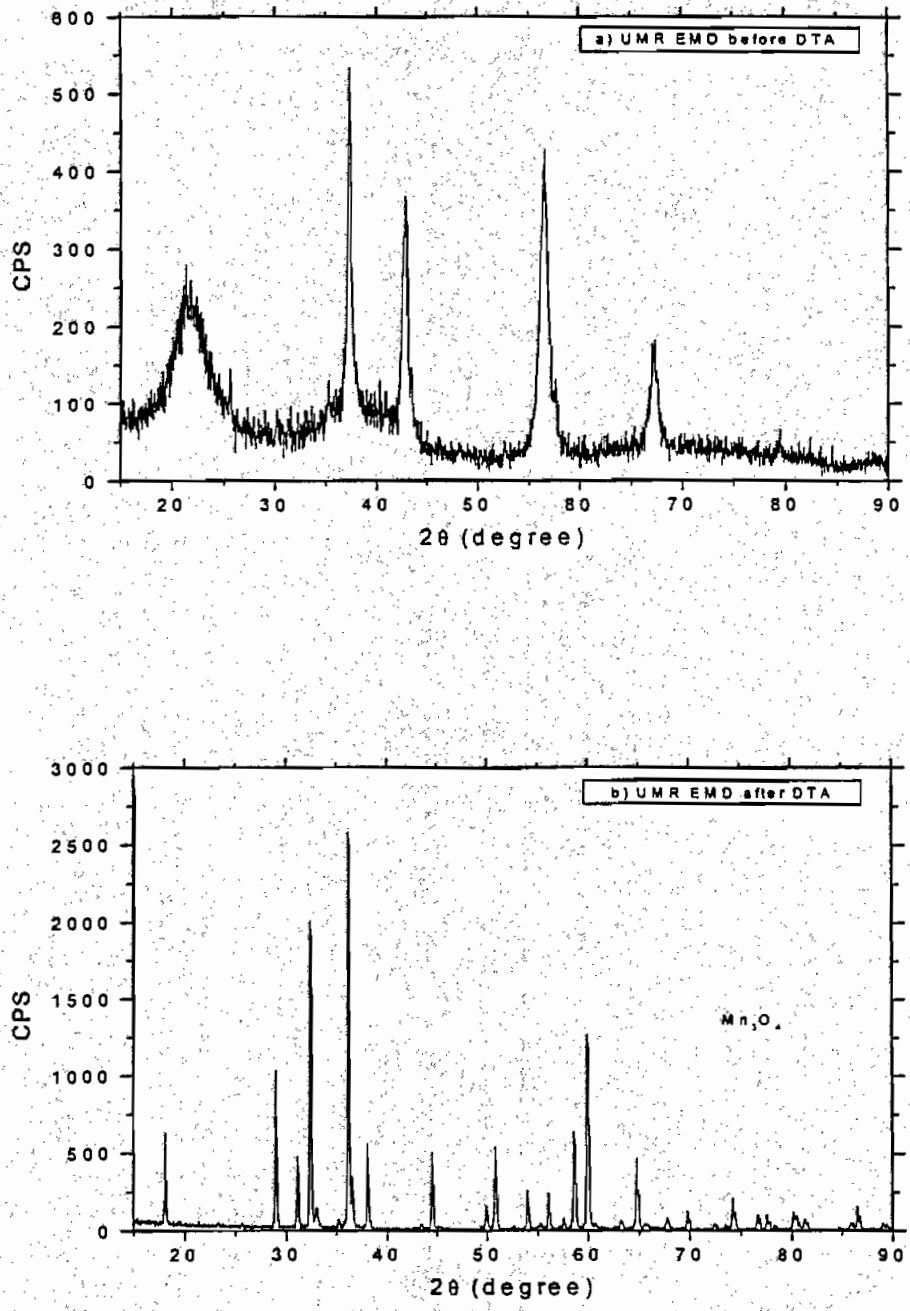


Figure II-5 XRD patterns for an EMD sample made at UMR lab in the electrolyte containing 52g/L Mn^{2+} and 10g/L HCl at 100A/m^2 and 97°C for 2 days, a) before DTA test, and b) after DTA test

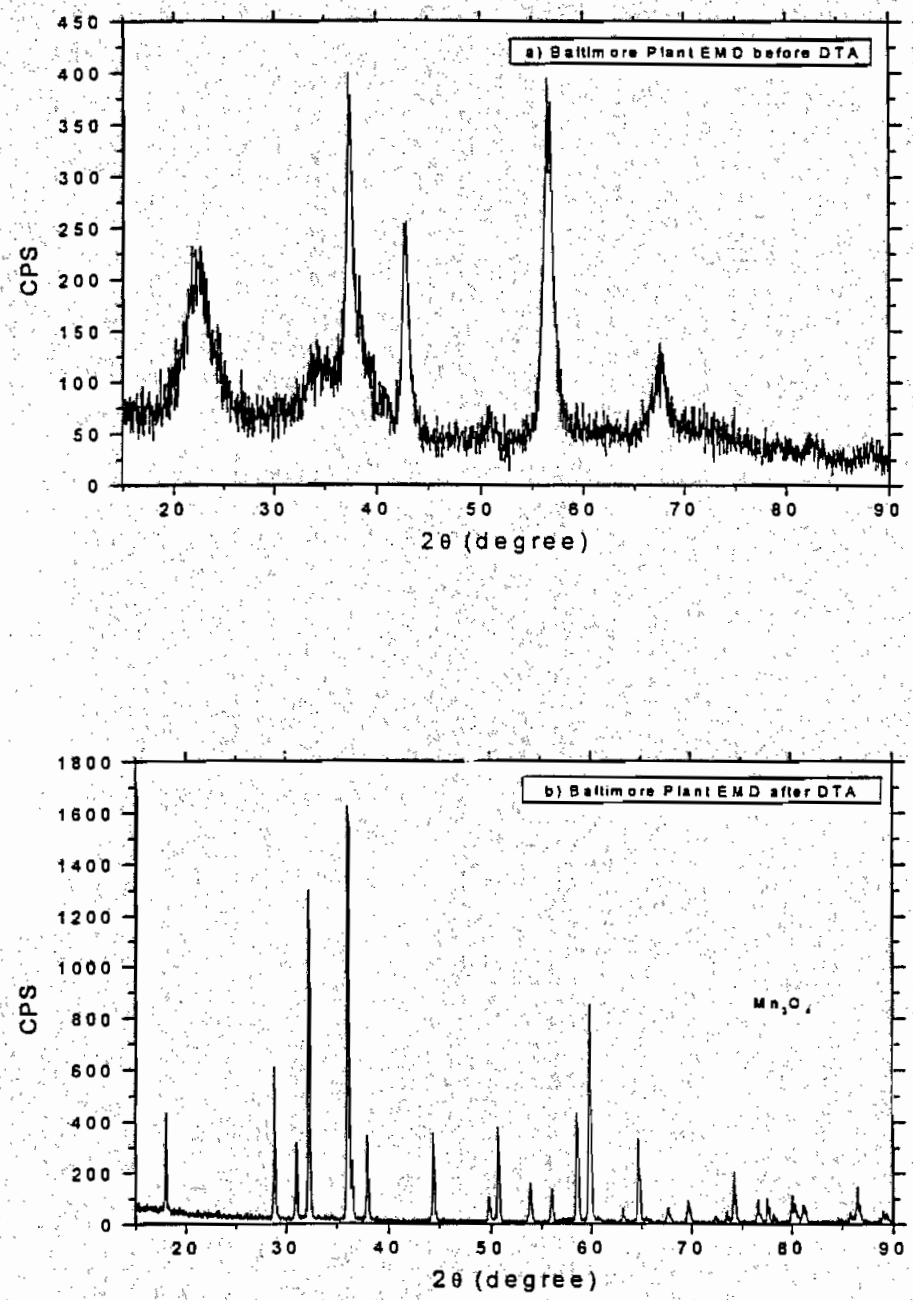


Figure II-6 XRD patterns for an EMD sample made at Baltimore Plant in a sulfate bath, a) before DTA test, and b) after DTA test

Interim Report (III)

Summary of UMR Lab Tests

April 21, 2000

To determine the effects of iron and calcium impurities in the electrolyte on the EMD structure and properties, a couple of deposition tests were conducted at UMR. Deposition from sulfate bath and the mixed bath of sulfate and chloride were also carried out for comparison. Deposit morphology and structure, deposit adhesion to substrate, as well as chlorine evolution during deposition etc., were evaluated. Most of the deposit samples, including an Eveready EMD sample, CalEnergy EMD samples of 5 runs, were analyzed by Scitag X-ray and Netzsch STA 409 DTA units. A summary of 2θ values of the γ (110) peak, half-height-width of the γ (110) peak, values of Qi product, and the values of initial and final cell voltage during deposition are listed in Table III-1 based on XRD tests. The percent weight loss from 110-400°C, and two peak temperatures indicating phase changes from MnO_2 to Mn_2O_3, and from Mn_2O_3 to Mn_3O_4, respectively, are summarized in Table III-2 based on the DTA tests. Most XRD and DTA curves for different samples are put in the Appendices III-A and III-B.

Unless specified elsewhere, the general conditions for the chloride EMD deposition tests were:

Mn^{2+} (in $MnCl_2 4H_2O$): 52g/L

HCl: 10g/L

Anode: Grade 7 Ti, polished to grit #240, degreased with acetone

Cathode: Graphite

Electrolyte temperature: 97°

Preconditioning: Anode CD 10A/m^2 for 1 hour

Anode CD for deposition: 100A/m^2

The sulfate bath had the following compositions:

Mn^{2+} (in $MnSO_4H_2O$): 52g/L

H_2SO_4: 24.5g/L

The mixed bath was composed of half chloride and half sulfate and the other conditions were identical to chloride EMD deposition.

No major structural difference can be seen from the XRD curves with the EMD samples made from electrolytes containing different concentrations of iron, as well as a combination of 500ppm Fe^{2+} and 150ppm Ca^{2+} . The 2θ values of γ (110) peaks of all samples are about 21.5°, and the values of Qi product range from 0.42 (10ppm Fe^{2+}) to 0.55 (0 ppm Fe^{2+}). However, the current efficiency dropped to about 88% with additions of 500 ppm Fe^{2+} or 500ppm Fe^{2+} and 150 ppm Ca^{2+} due to the Fe redox reaction. In fact, a discoloration from pink (Mn^{2+}) to brown (Fe^{3+}) for solutions containing higher than 20ppm Fe^{2+} can usually be observed after the deposition tests. With additions of Fe^{2+} and Ca^{2+}, an increase in percent weight loss from 110 to 400°C was evident, as can be seen from Table 2. Changes in the peak temperatures in DSC curves can also be observed, but no specific trend is noted.

For the other tests, the XRD pattern of a UMR EMD sample made from a sulfate bath is almost identical to that obtained with Eveready EMD sample in terms of the 2θ values of the γ (110) peak, half-height-width of γ (110) peak, and values of Qi product. A similar XRD curve was obtained with an EMD sample made from mixed bath of chloride and sulfate. Most other EMD samples made from chloride bath with or without Fe showed what appeared to be a slight shift to lower angles of the γ (110) peak. It was also shown that γ-EMD is favored at low current density and high Mn^{2+} concentration as reported in the literature. The typical values of Qi product are in the range of 0.45-0.60.

Compared to the Eveready sample, a shift to higher angles of the γ (110) peak was observed with the CalEnergy samples, except for the sample of Test #2 which was unusual due to the shutdown during the deposition. The Test #1 deposit was dense, smooth and relatively uniform in thickness, and had a high Qi of 0.66. The deposits of the later runs were made with used substrate which had adherent EMD residues from previous runs. Multi-layered morphology could be observed and the deposit thickness variations were more evident. As can be seen from Appendix A, the X-ray patterns obtained with the inner layer of the Test #3 and Test #4 deposits showed more peaks and were more complicated, indicating different structures than the bulk deposit.

In the DTA tests, CalEnergy deposits except for Test #2 had lower values of percent weight loss when heating from 110 to 400°C, particularly the sample of Test #3, which had a weight loss of 1.57% compared to 3.5% or higher for the samples from Eveready or made at UMR. These data might be correlated with the operating parameters and product finishing procedure.

In summary, all CalEnergy EMD samples had similar structures in terms of the XRD tests, but the sample of Test #1 was most similar to the Eveready sample and had a highest Q value. The inner layer of the deposits which contained the EMD from previous runs had different structures than the bulk EMD and may have influences on the growth. The DTA tests showed that all the CalEnergy EMD samples except Test #2 had an apparently low weight loss from 110 to 400°C compared to the Eveready and UMR EMD samples.

Iron and calcium did not show a noticeable influence on the deposit structures according to the XRD tests, but with the addition of 500ppm Fe or a combination of 500ppm Fe and 150ppm Ca, the anodic current efficiency dropped to about 88%. Also, with increased amounts of impurity Fe in electrolyte, the weight loss from 110 to 400°C increased, which may indicate an increase of the content of combined water in the deposits.

TABLE III-1 Summary of $2\theta_{\gamma(110)}$, Half Height Width and Q_i Values from XRD Results as well as values of the initial and final cell voltage during deposition

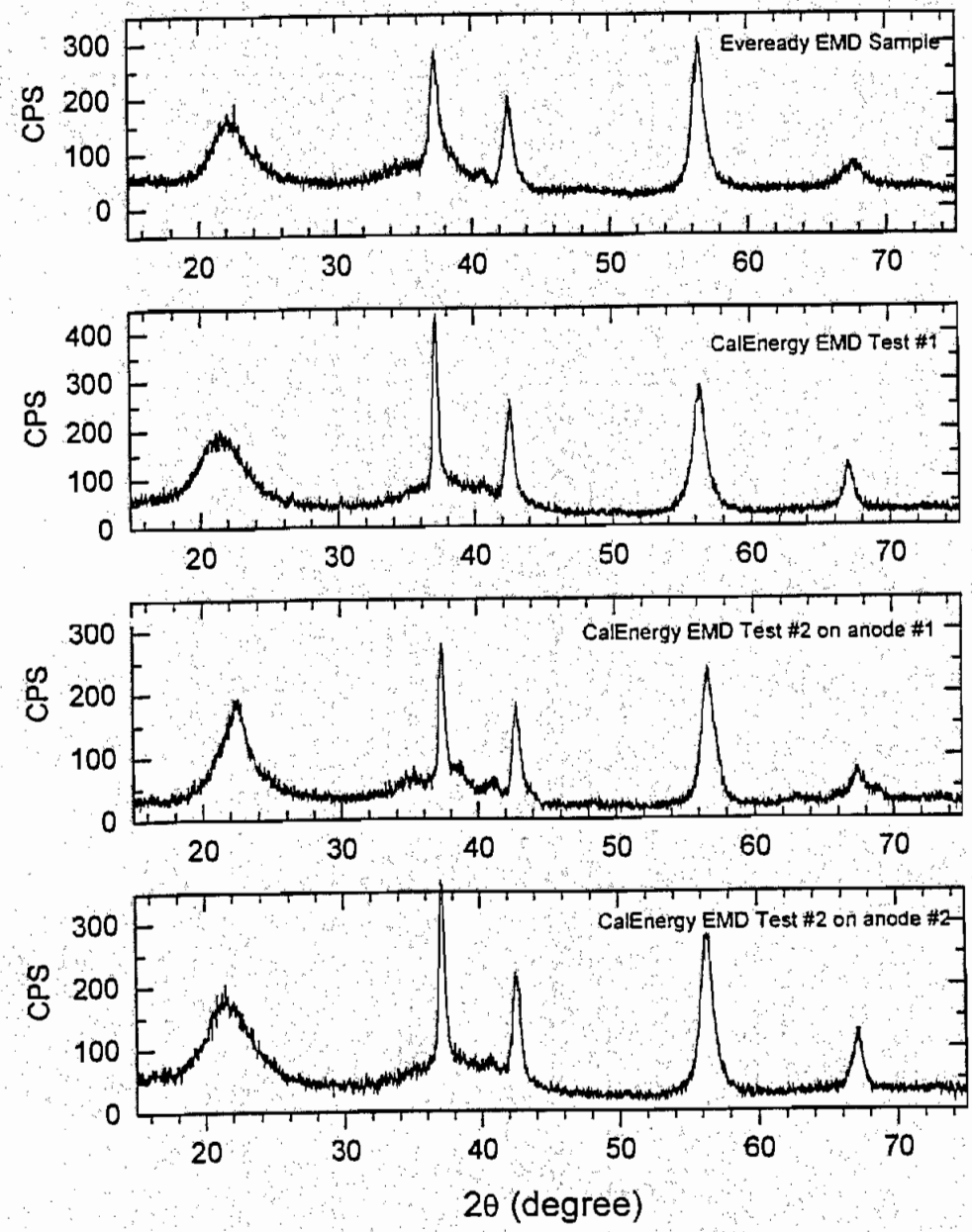
Deposit samples	$2\theta_{\gamma(110)}$ (°)	$2\theta_{\gamma(110)\,htw}$ (°)	Qi	E_{cell} (V)
Eveready	22.0	2.9	0.58	-
CalEnergy, Test #1	22.3	2.1	0.66	2.3-2.5
CalEnergy, Test #2 On Anode 1	21.5	3.8	0.53	2.3-2.9
CalEnergy, Test #2 On Anode 2	21.5	3.5	0.48	2.3-2.9
CalEnergy, Test #3	23.0	3.8	0.53	2.3-3.0
CalEnergy, Test #3, Inner layer	22.8	2.7	0.88	2.3-3.0
CalEnergy, Test #4	23.0	3.1	0.49	2.3-3.3
CalEnergy, Test #5	23.2	3.6	0.54	-
UMRsemd (sulfate)	22.1	2.7	0.60	1.98-2.00
UMRscemd (sulfate+chloride)	22.0	3.5	0.54	2.13-2.19
UMRcemd	21.5	3.2	0.55	2.13-2.17
UMRcemd10Fe (chloride+10ppm Fe)	21.5	3.5	0.42	2.10-2.24
UMRcemd20Fe (chloride+20ppm Fe)	21.5	4.0	0.50	1.80-2.21
UMRcemd50Fe (chloride+50ppm Fe)	21.5	3.5	0.50	2.09-1.81
UMRcemd500Fe (chloride+500ppm Fe)	21.5	3.7	0.47	2.08-2.02
UMRcemd500Fe150Ca (500Fe+150Ca) in ppm	21.4	3.5	0.53	2.18-2.49

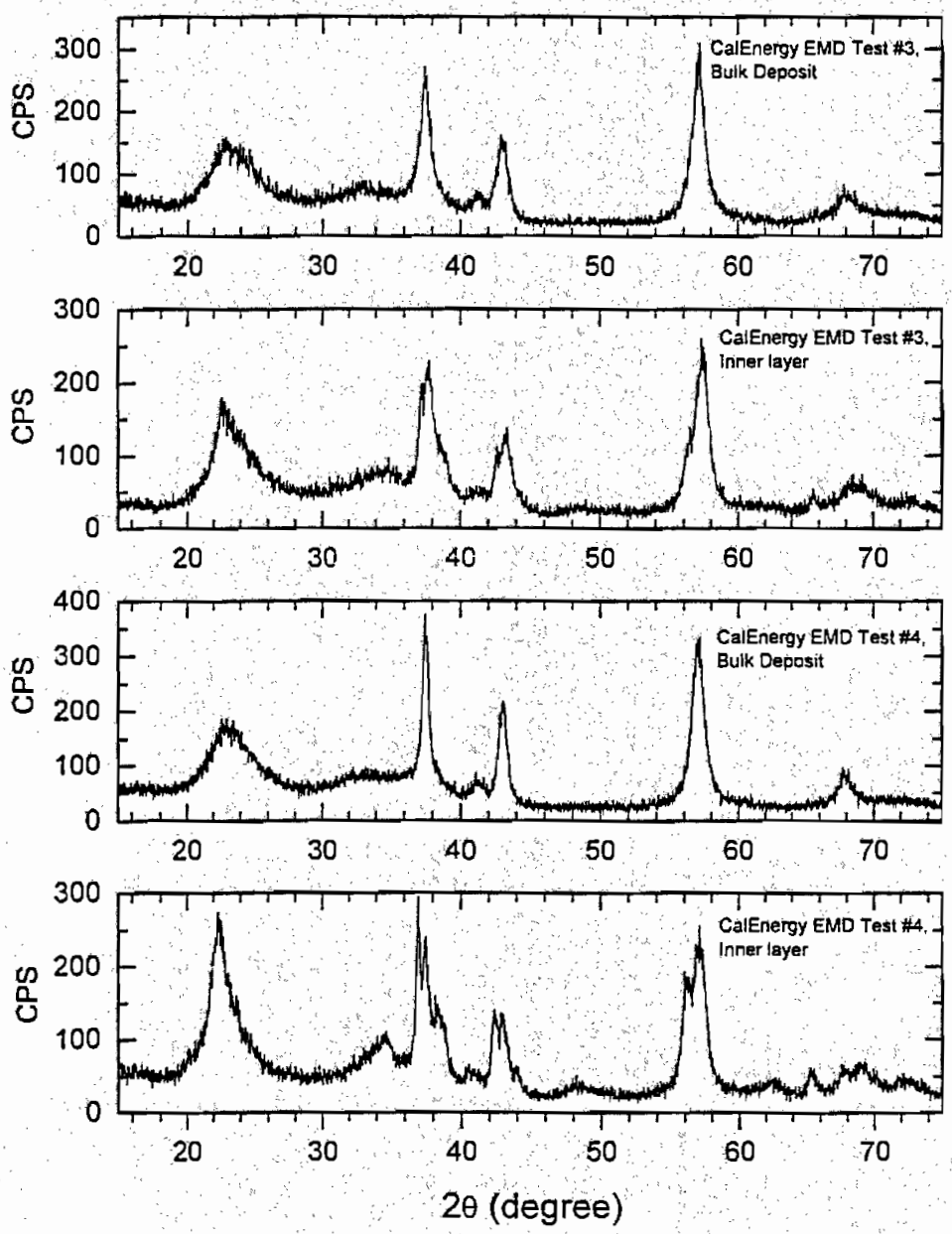
UMRcemdi15 (at i=15mA/cm2)	21.7	4.0	0.47	1.90-2.78
UMRcemdgraphite (on graphite, i=2.5mA/cm2)	21.7	2.7	0.57	-

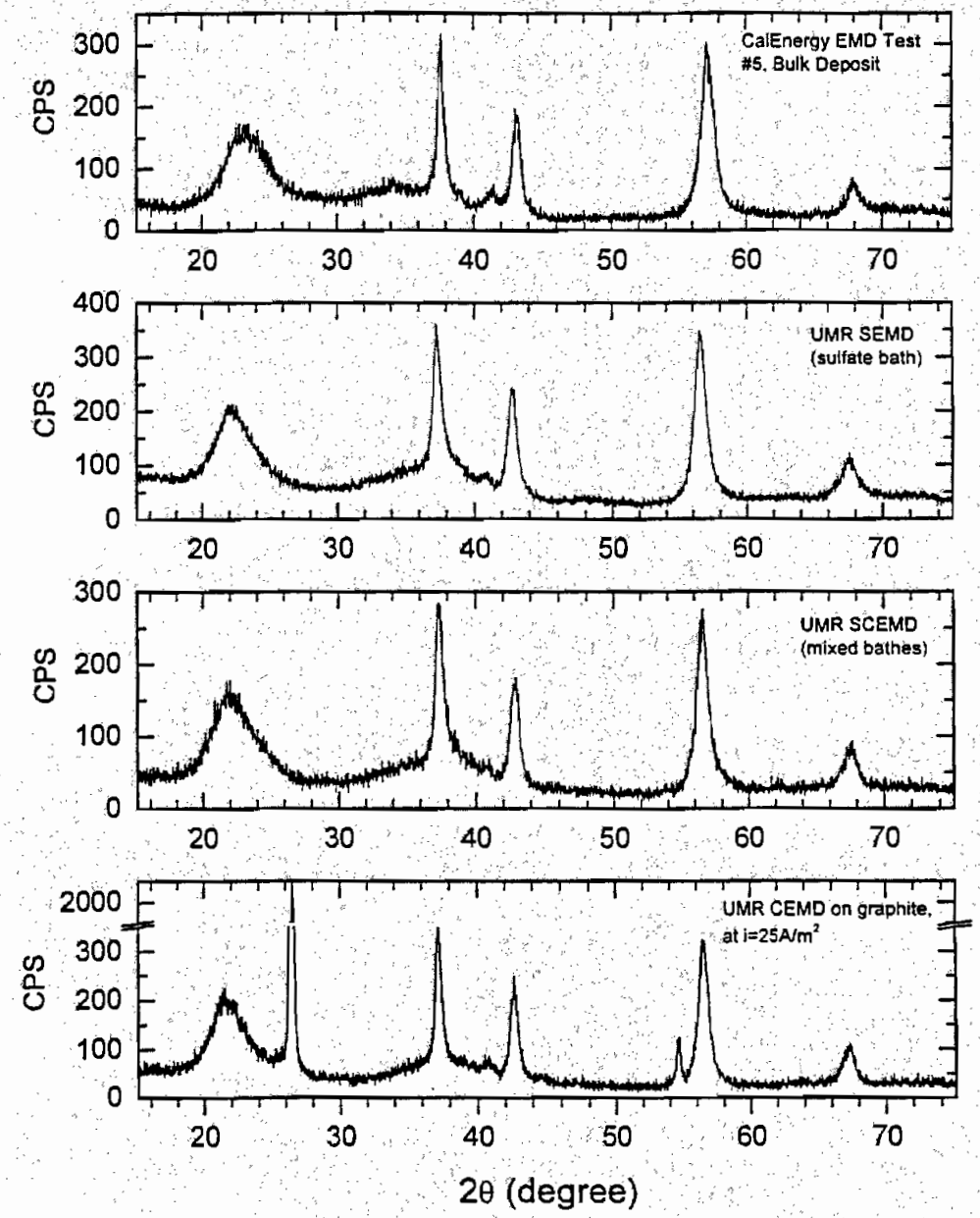
TABLE III-2 Summary of Weight Losses and Peak Temperatures From DTA tests

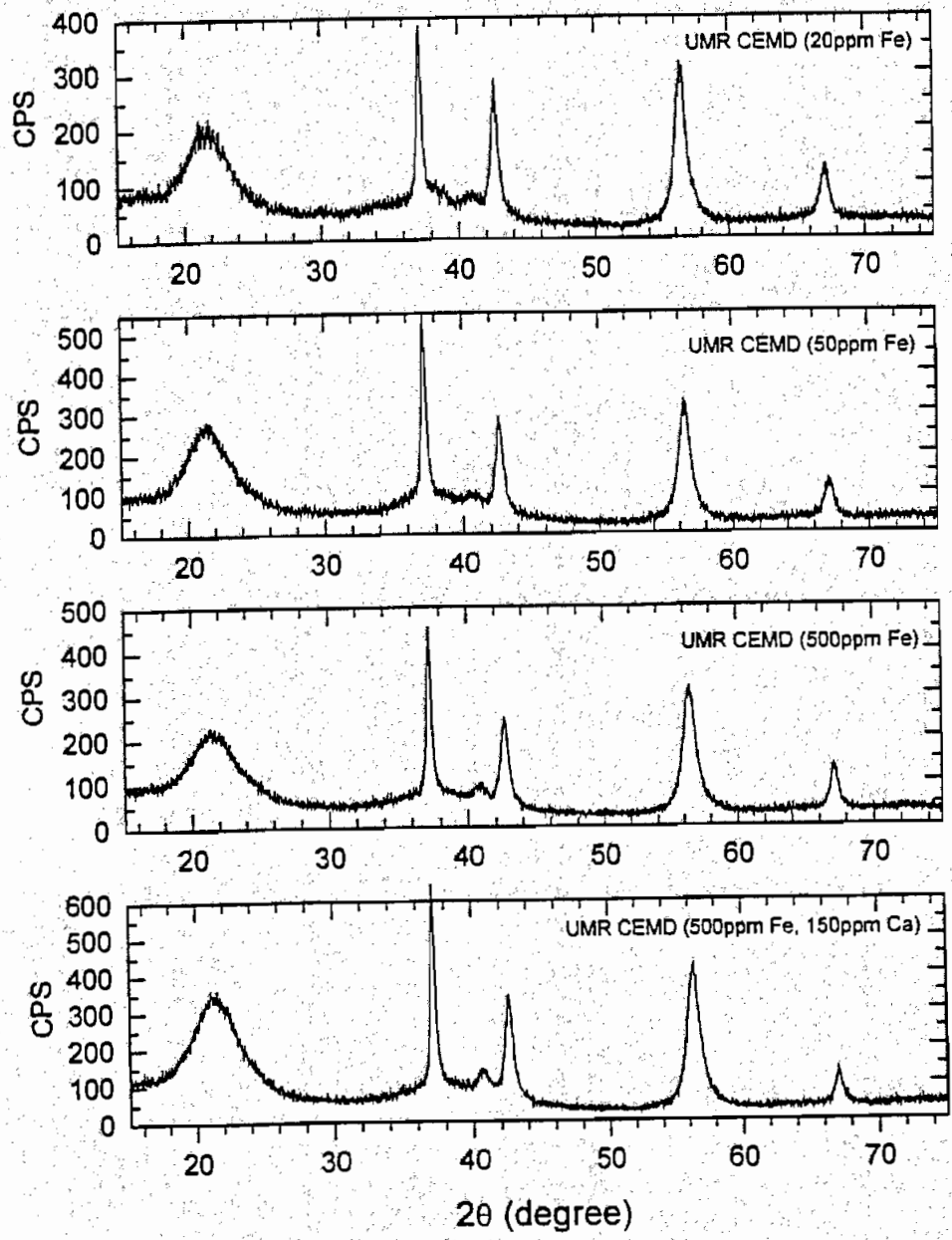
Deposit samples	Weight Loss (%) (110-400 °C)	T_{p1} (°C) MnO_2/Mn_2O_3	T_{p2} (°C) Mn_2O_3/Mn_3O_4
Eveready	3.80	560.5	968.7
Calt1	2.39	559.2	972.3
Calt21	4.35	553.7	978.3
Calt22	4.02	555.2	980.3
Calt3	1.57	560.9	981.1
Calt3in	1.57	562.3	971.5
Calt4	2.38	562.9	979.1
Calt4in	1.68	563.6	972.7
Calt5	2.50	561.2	974.4
UMRsemd (sulfate)	4.26	564.0	952.4
UMRscemd (sulfate+chloride)	4.43	563.6	954.1
UMRcemd (chloride)	3.23	555.9	969.5
UMRcemd20Fe (+20ppm)Fe	3.71	562.8	975.0
UMRcemd50Fe (+50ppm)Fe	4.21	555.9	971.5
UMRcemd500Fe (+5000ppm)Fe	4.76	570.1	990.8
UMRcemd500Fe150Ca (500Fe+150Ca)	4.93	543.0	963.1

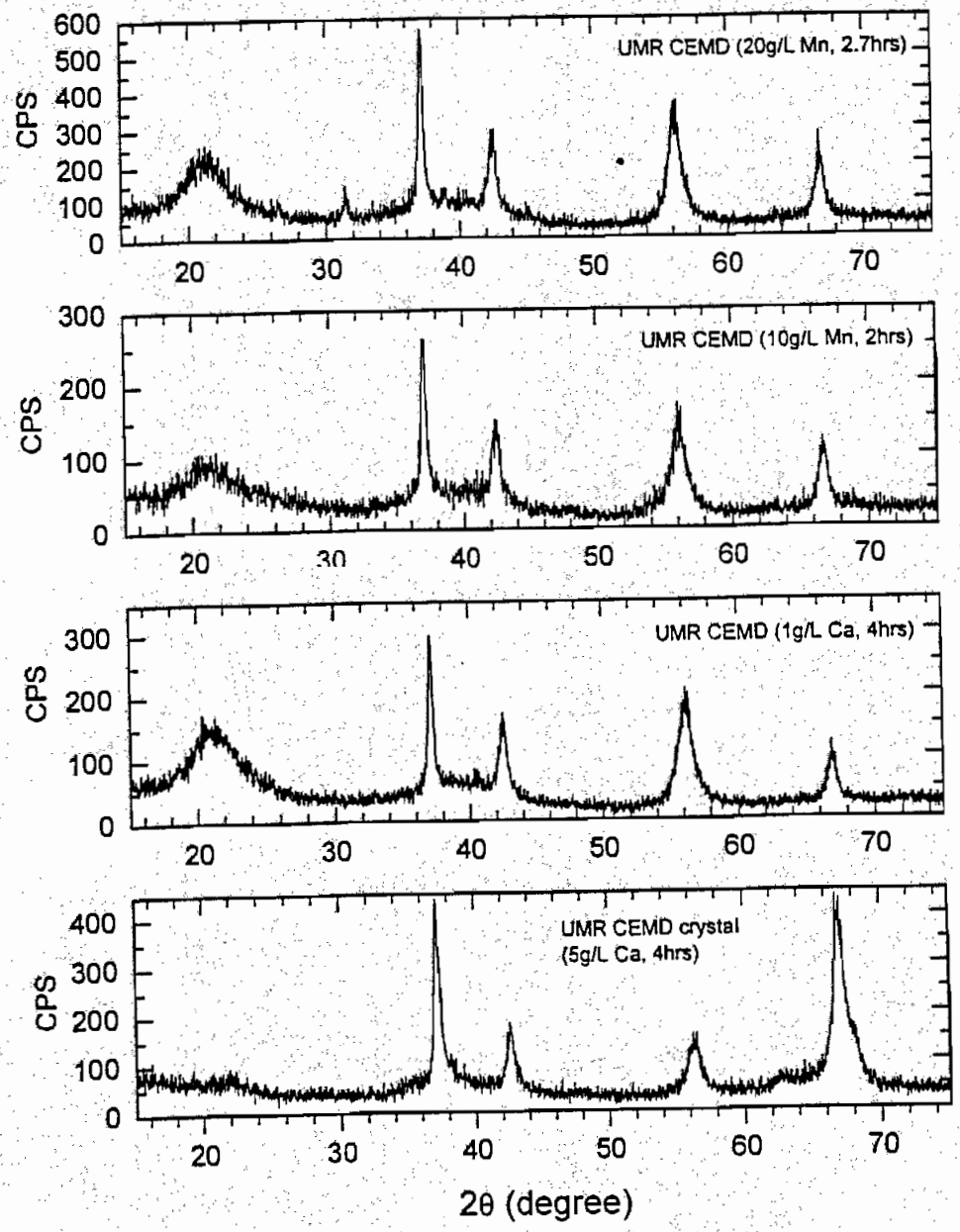
Appendix III-A
XRD Patterns



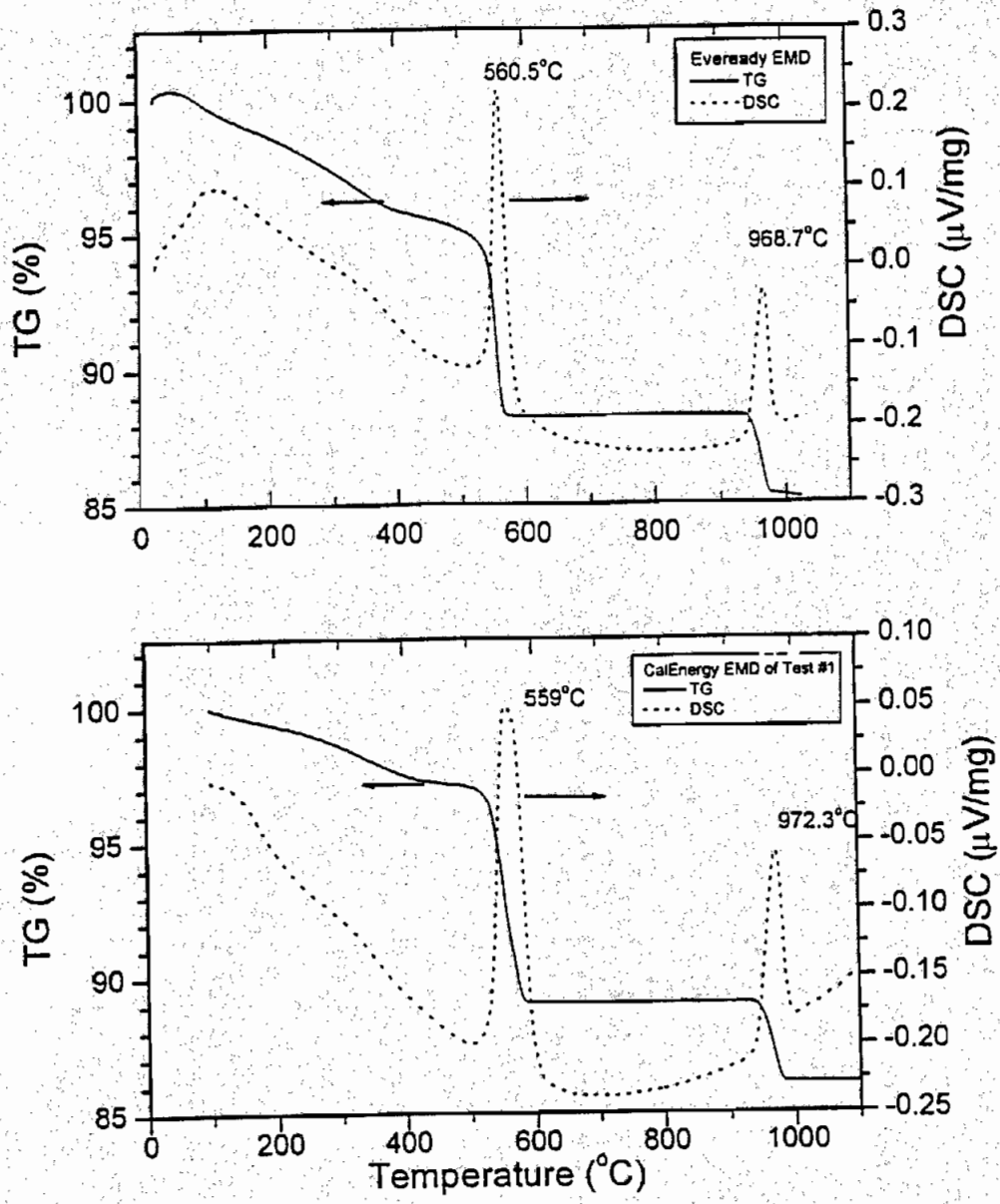

CalEnergy EMD Test #3, Bulk Deposit
CalEnergy EMD Test #3, Inner layer
CalEnergy EMD Test #4, Bulk Deposit
CalEnergy EMD Test #4, Inner layer
CPS
2θ (degree)

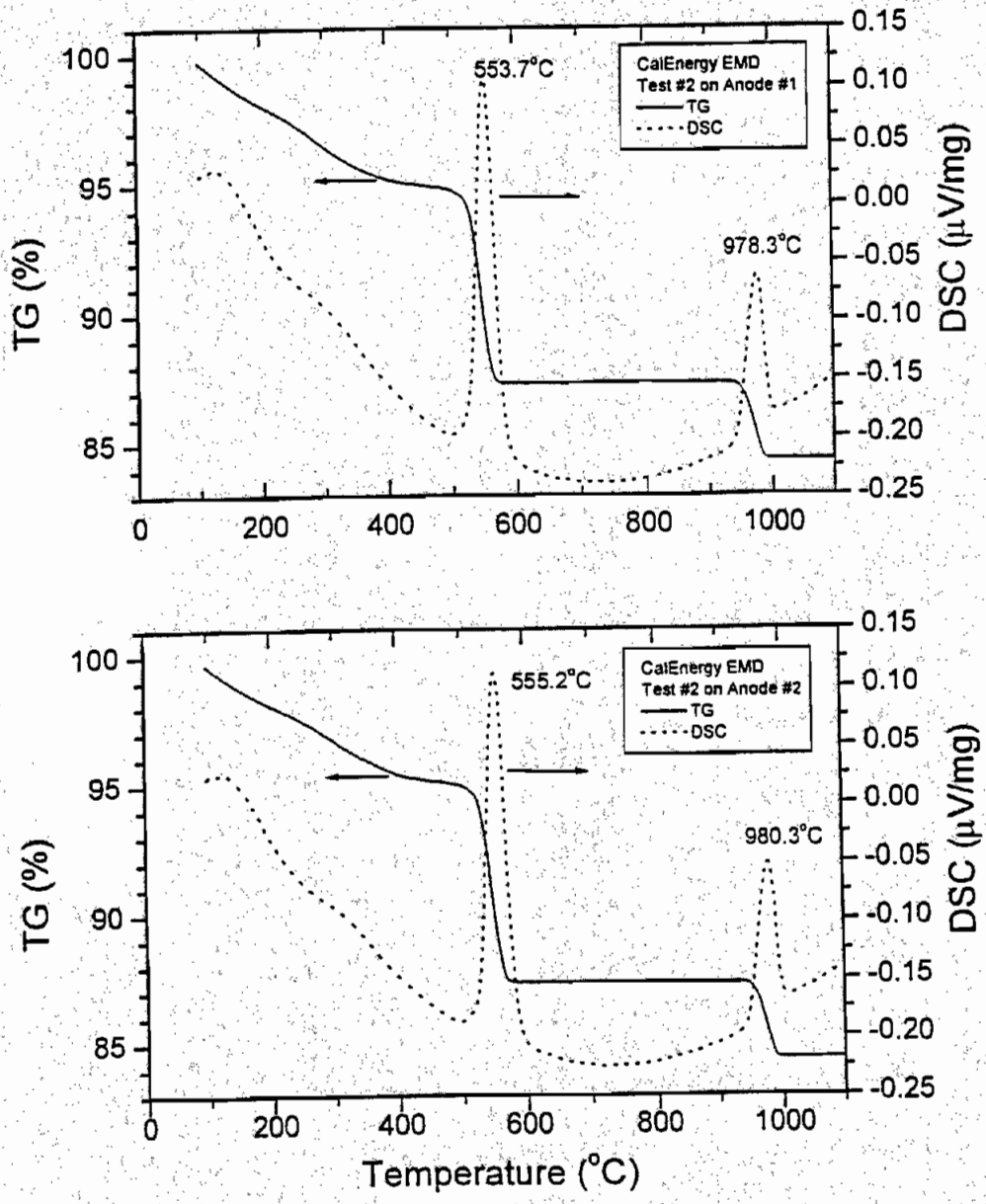

CalEnergy EMD Test
#5, Bulk Deposit
UMR SEMD
(sulfate bath)
UMR SCEMD
(mixed bathes)
UMR CEMD on graphite,
at i=25A/m²
CPS
2θ (degree)

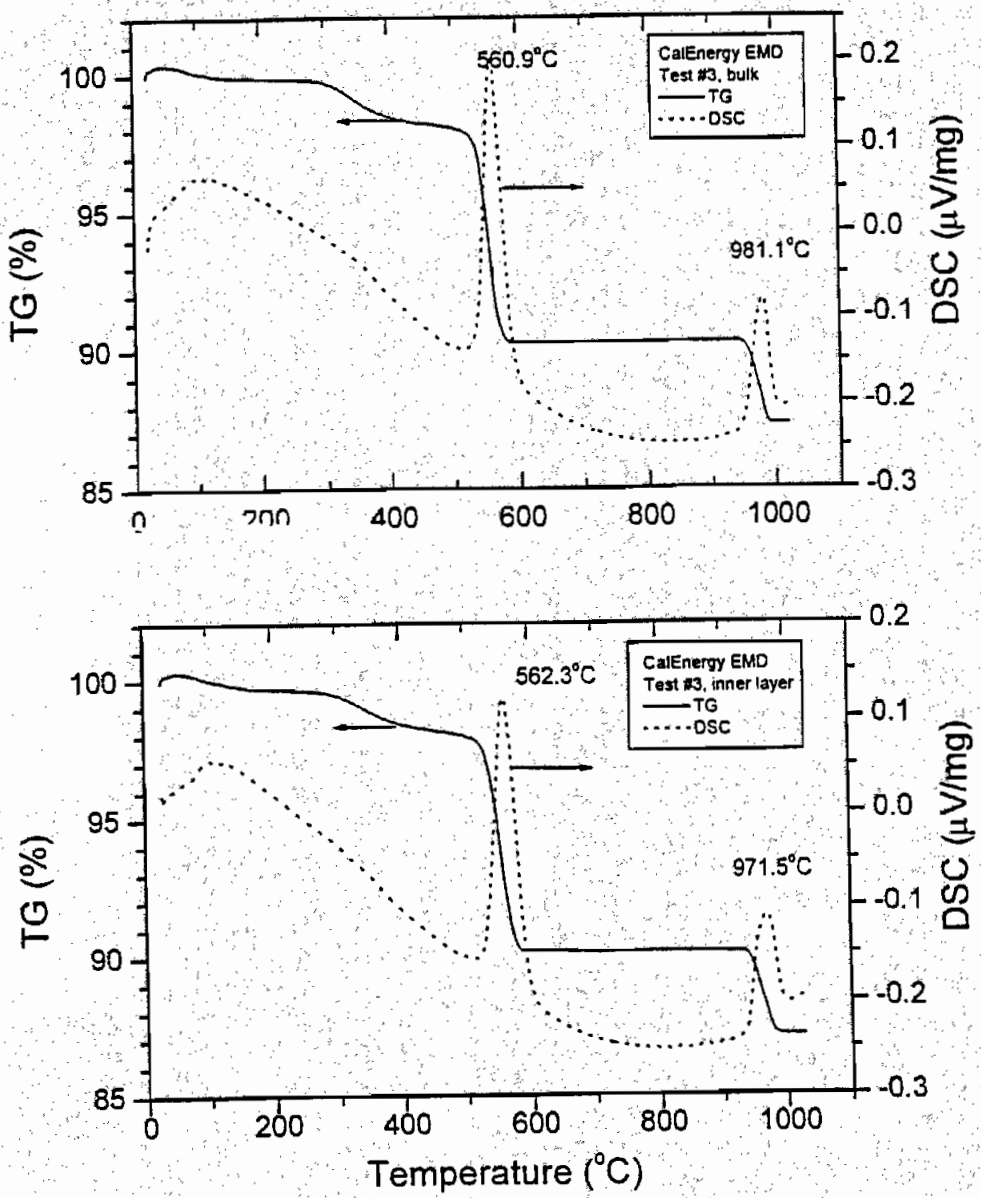

UMR CEMD (20ppm Fe)
UMR CEMD (50ppm Fe)
UMR CEMD (500ppm Fe)
UMR CEMD (500ppm Fe, 150ppm Ca)
CPS
2θ (degree)

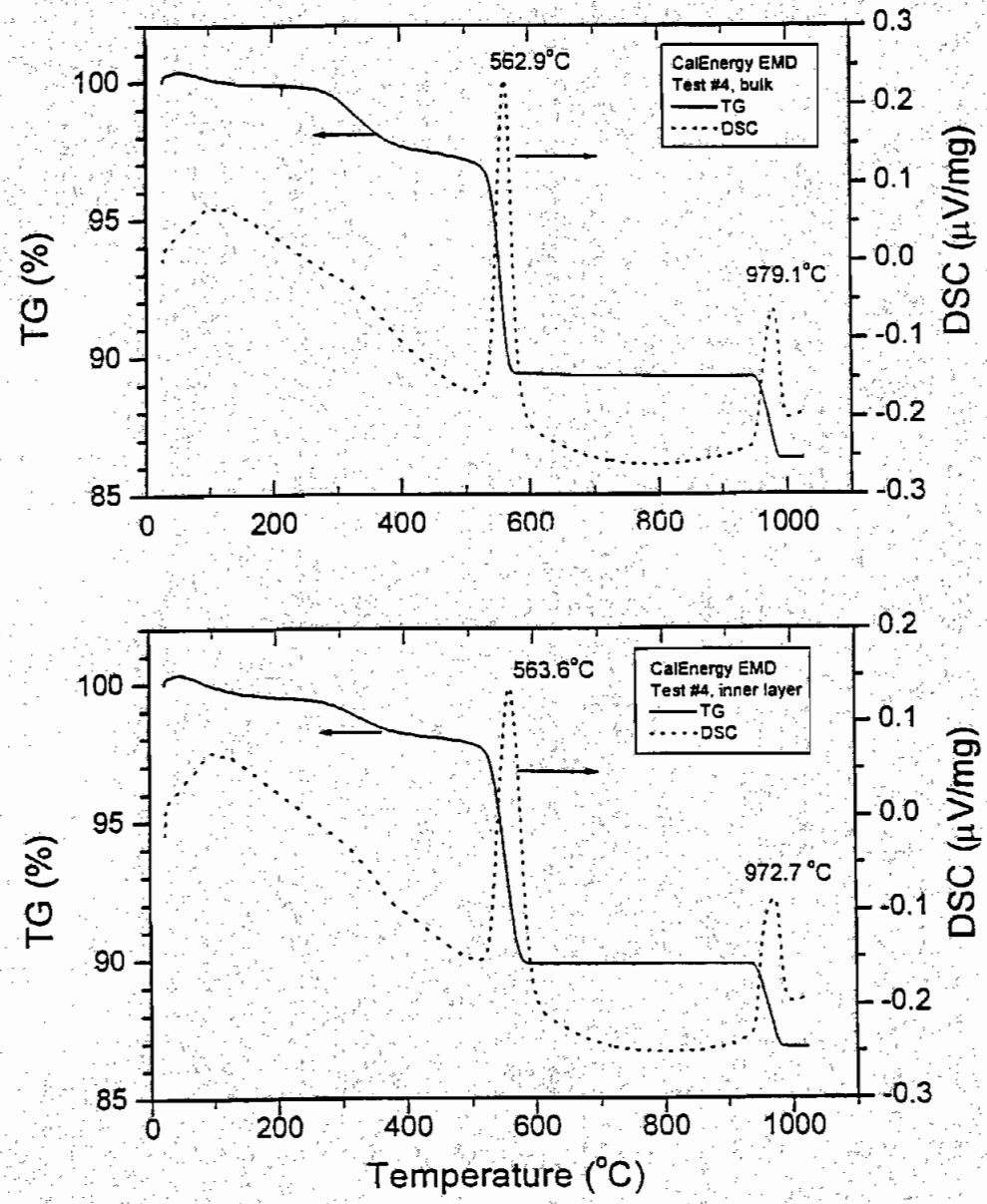

UMR CEMD (20g/L Mn, 2.7hrs)
UMR CEMD (10g/L Mn, 2hrs)
UMR CEMD (1g/L Ca, 4hrs)
UMR CEMD crystal
(5g/L Ca, 4hrs)
CPS
2θ (degree)

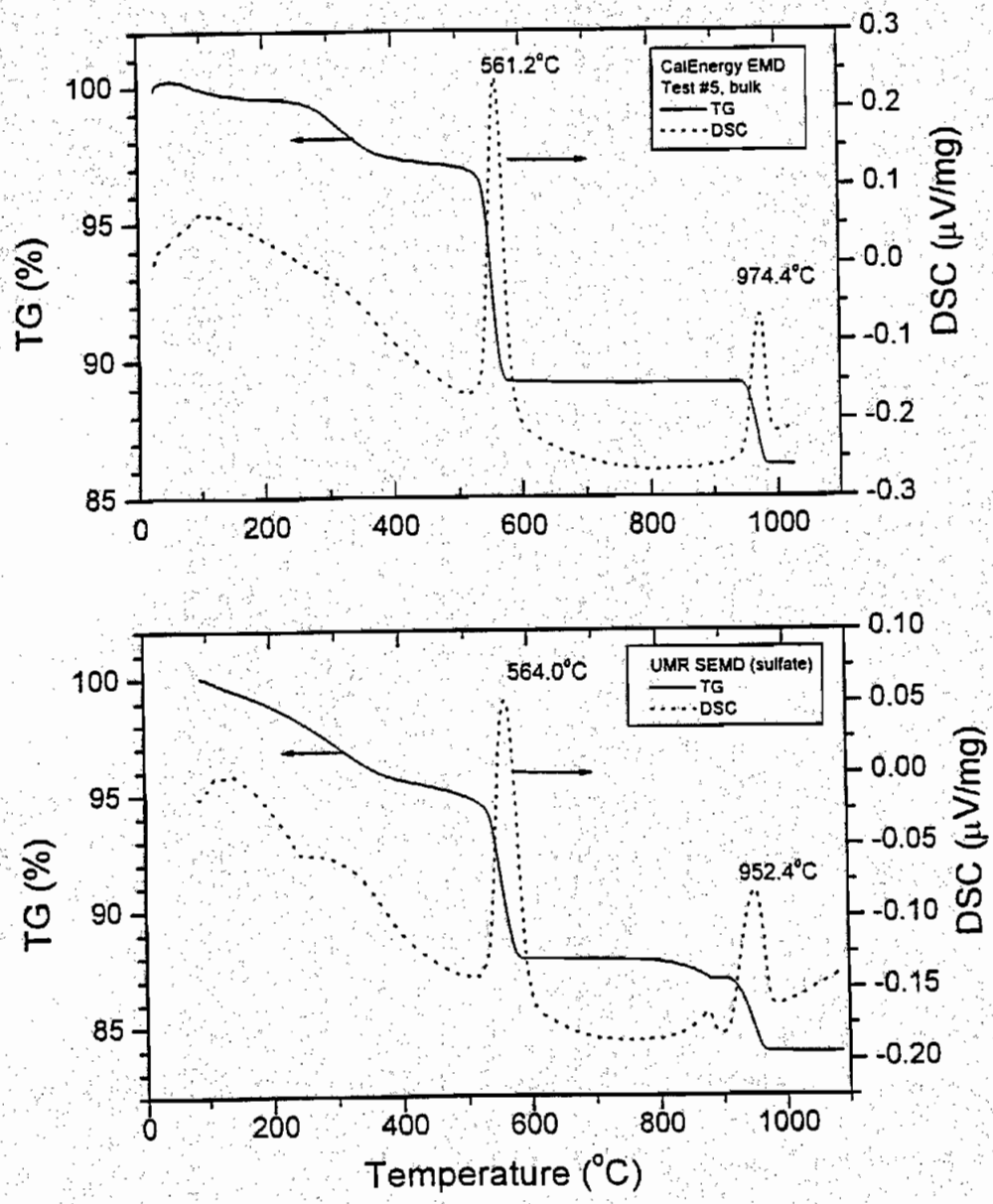
Appendix III-B
DTA Curves

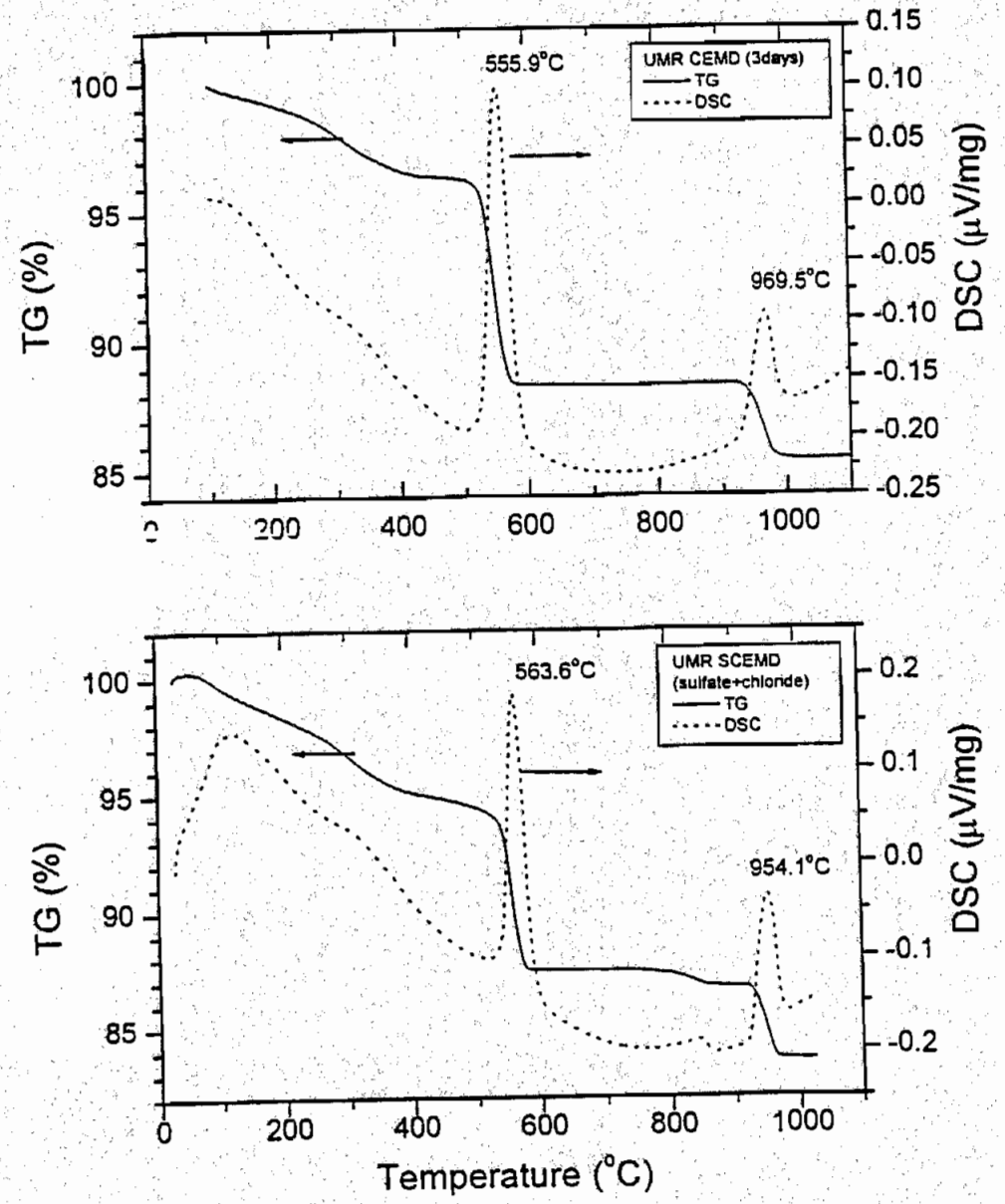



CalEnergy EMD
Test #2 on Anode #1
TG
DSC
553.7°C
978.3°C
TG (%)
DSC (μV/mg)
CalEnergy EMD
Test #2 on Anode #2
TG
DSC
555.2°C
980.3°C
TG (%)
DSC (μV/mg)
Temperature (°C)


560.9°C
CalEnergy EMD
Test #3, bulk
TG
DSC
981.1°C
TG (%)
DSC (μV/mg)
562.3°C
CalEnergy EMD
Test #3, inner layer
TG
DSC
971.5°C
TG (%)
DSC (μV/mg)
Temperature (°C)


562.9°C
CalEnergy EMD
Test #4, bulk
TG
DSC
979.1°C
TG (%)
DSC (μV/mg)
100
95
90
85
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
200
400
600
800
1000
563.6°C
CalEnergy EMD
Test #4, inner layer
TG
DSC
972.7 °C
TG (%)
DSC (μV/mg)
100
95
90
85
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
200
400
600
800
1000
Temperature (°C)


CalEnergy EMD
Test #5, bulk
TG
DSC
561.2°C
974.4°C
TG (%)
DSC (μV/mg)
100
95
90
85
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
200
400
600
800
1000
UMR SEMD (sulfate)
TG
DSC
564.0°C
952.4°C
TG (%)
DSC (μV/mg)
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
Temperature (°C)


555.9°C
UMR CEMD (3days)
TG
DSC
969.5°C
TG (%)
DSC (μV/mg)
100
95
90
85
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
200
400
600
800
1000
563.6°C
UMR SCEMD
(sulfate+chloride)
TG
DSC
954.1°C
TG (%)
DSC (μV/mg)
100
95
90
85
0.2
0.1
0.0
-0.1
-0.2
0
200
400
600
800
1000
Temperature (°C)

Interim Report (IV)

Summary of UMR Lab Tests

July 15, 2000

During recent meeting at UMR with Kevin on May 8th and 9th, it was determined to continue more screening tests at UMR. The variables to be evaluated included the anode current density, electrolyte temperature and pH, and Mn concentration with XRD and DTA tests aslo being conducted on the samples. A summary of XRD phase 2θ values of the γ (110) peak $2\theta_{\gamma(110)}$, half-height-width of γ(110) peak $2\theta_{\gamma(110)\,htw}$, and values of Qi product are listed in Table IV-1 based on XRD tests. The percent weight loss from 110-400°C, and two peak temperatures indicating phase changes from MnO_2 to Mn_2O_3 (T_{P1}), and from Mn_2O_3 to Mn_3O_4 (T_{P2}), respectively, are summarized in Table IV-2 based on the DTA tests. Various examples of the XRD and DTA curves with different samples are in the Appendices IV-A and IV-B.

Unless specified elsewhere, the general conditions for the chloride EMD deposition tests were:

Initial Mn^{2+} (from $MnCl_2 4H_2O$): 52g/L

Final Mn^{2+}: ~47-49 g/L depending on the operating conditions

Initial HCl: 10g/L

Final HCl: ~13-16 g/L depending on the operating conditions

Anode: Grade 7 Ti, polished to grit #240, degreased with acetone

Cathode: Graphite

Electrolyte temperature: 98°

Preconditioning: Anode CD 10A/m^2 for 1 hour

Anode CD for deposition: 100A/m^2

The x-ray pattern obtained with the CalEnergy EMD sample of Test #7 was similar to these of the previous runs such as Tests #4 and #5, but the Qi had a lower value of about 0.44. The deposit showed thickness variations, and some parts of the deposit had the layered structure (multi-layers), which had a more complicated and quite different XRD pattern than that of the dense bulk deposit, indicating that different phases were present, as can be seen in the Appendix IV-A. The differences in the weight losses and phase transformation temperatures between the dense bulk deposit and the layered deposit can also be seen in the DTA tests. The dense bulk deposit had a total percent weight loss of about 8% when heating from 100 to 1100 °C, while for the samples of other runs the total percent weight loss was about 14%.

In the UMR lab tests, at lower electrolyte temperatures of 93 and 96 °C, the deposits made at 100A/m^2 were non-uniform in thickness and had a flaky morphology, and had a similar XRD pattern but with a quite diffuse $\gamma(110)$ peak. The chlorine evolution reaction and/or oxygen evolution reaction on the anodes were easier to happen at lower temperatures, as indicated by discoloration of the KI solution containing starch indicator during the tests. Also, the deposits may contain more combined water when made at lower electrolyte temperatures as evidenced by

the percent weight loss when heating from 110 to 400 °C in the DTA tests, which were 3.55% and 4.82%, at 96 °C and 93 °C, respectively.

Anode current density seemed to have a critical influence on the EMD growth and surface morphology. Previous tests have showed that most deposits made at 100A/m^2 were non-uniform in thickness and even flaky, while smooth and dense EMD deposits could be made at 60A/m^2 even with no preconditioning of the anode. Similarly, most deposits made at 80A/m^2 were uniform, smooth and dense. The deposit made at 80 and 60 A/m^2 had a similar XRD pattern to that of the Eveready EMD sample.

The influences of parameters such as electrolyte temperature, initial acid concentration and Mn^{2+} concentration, were evaluated at 60A/m^2. Smooth and dense deposits were obtained at 96 °C, initial HCl concentration of 18g/L (compared to 10g/L), and initial Mn^{2+} concentration of 40 g/L (compared to 52g/L), respectively. At an initial HCl concentration of 0g/L, however, the deposit showed a totally different surface morphology. It was very nodular and brittle. However, it is interesting that the deposit obtained in this case had a much higher Qi value, of about 0.95 in terms of the XRD result. This is different from the results reported in the literature where low acid levels usually cause low Qi values. The DTA test results seemed to show that less combined water was present in the deposits when made at lower acid levels. An initial Mn^{2+} concentration of 40 g/L seemed acceptable for the EMD deposition at 60A/m^2. More screening tests are required in order to optimize the ranges of various operating parameters.

TABLE IV-1 Summary of $2\theta_{\gamma(110)}$, Half Height Width and Q_i Values from XRD Tests

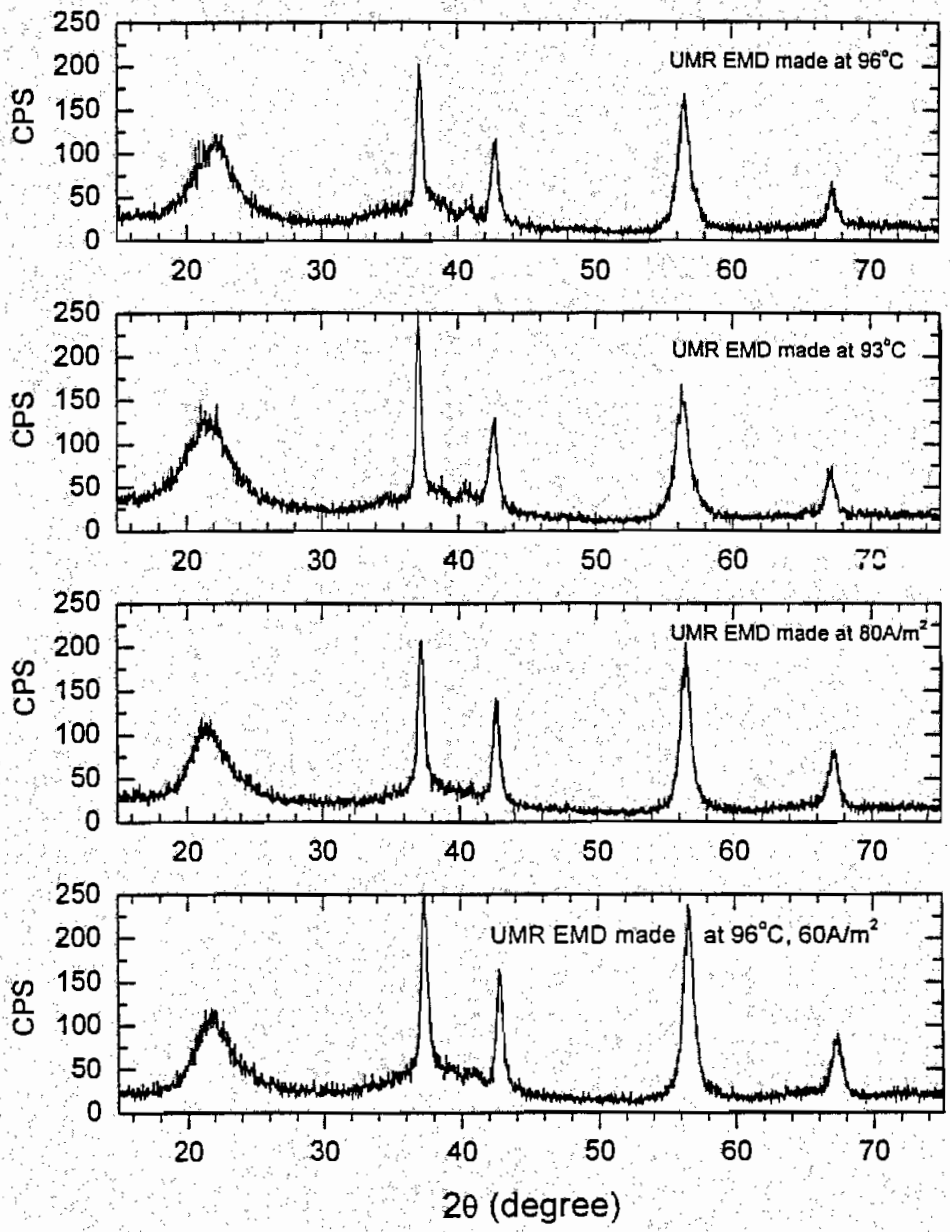
Deposit samples	$2\theta_{\gamma(110)}$ (°)	$2\theta_{\gamma(110)\,htw}$ (°)	Qi
Eveready	22.0	2.9	0.58
CalE-Test 7	23.2	3.8	0.44
CalE-Test 7ml	-	-	-
UMR-Temp93C	21.5	3.8	0.49
UMR-Temp96C	22.1	3.6	0.50
UMR-i80	21.5	3.0	0.53
UMR-i60-Temp96C	21.8	3.2	0.45
UMR-i60-[HCl]0	23.0	2.0	0.95
UMR-i60-[HCl]18	21.5	2.8	0.55

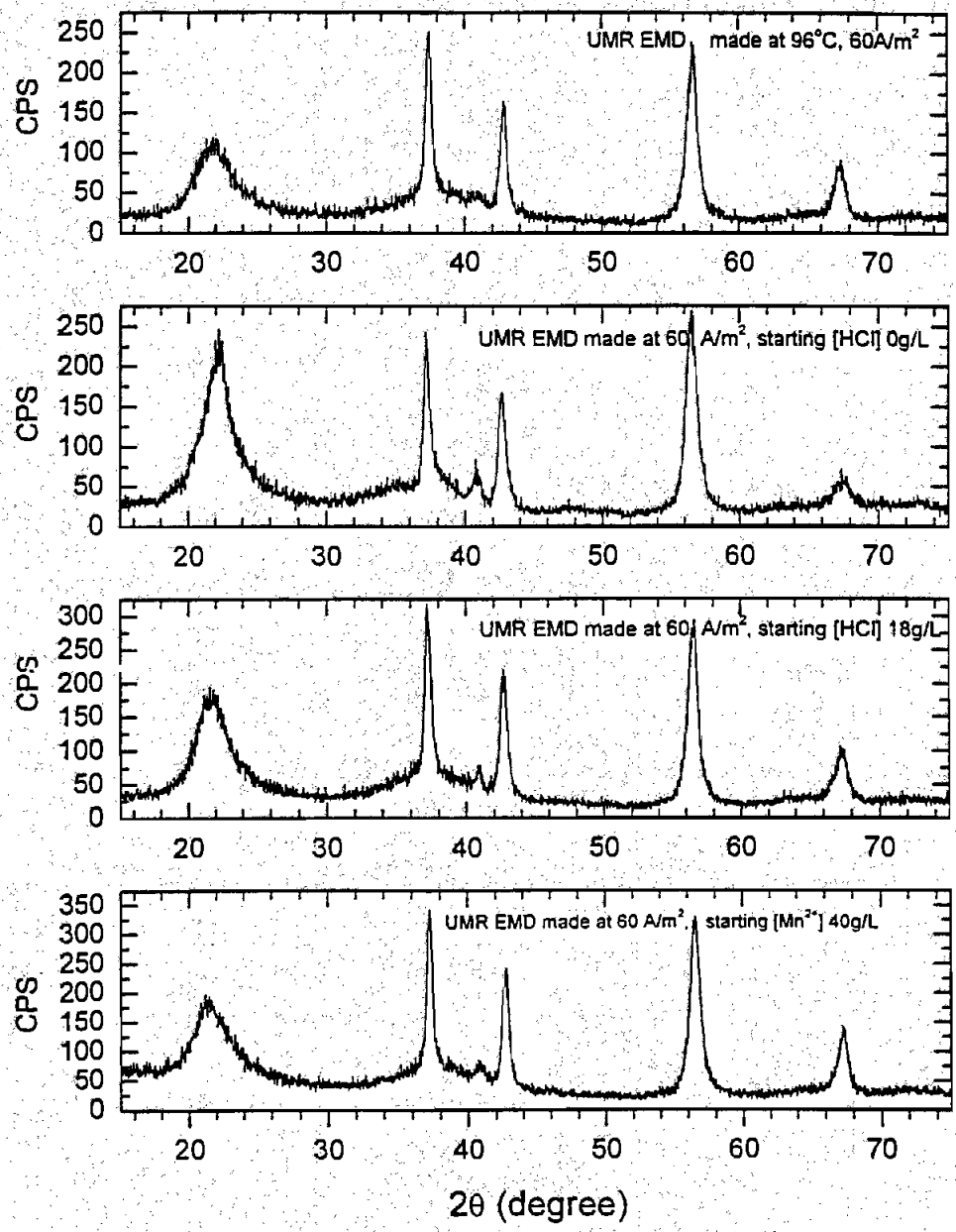
TABLE IV-2 Summary of Weight Losses and Peak Temperatures From DTA tests

Deposit samples	Weight Loss (%) (110-400 °C)	T_{p1} (°C) MnO_2/Mn_2O_3	T_{p2} (°C) Mn_2O_3/Mn_3O_4
Eveready	3.80	560.5	968.7
CalE-Test 7	1.47	556.0	964.7
CalE-Test 7ml	1.05	579.8	977.1
UMR-Temp93C	4.82	561.0	978.3
UMR-Temp96C	3.55	565.6	979.7
UMR-i80	3.53	567.7	975.2
UMR-i60-Temp96C	3.43	568.5	981.4
UMR-i60-[HCl]0	2.43	571.3	980.7
UMR-i60-[HCl]18	3.06	567.0	979.0

Appendix IV-A

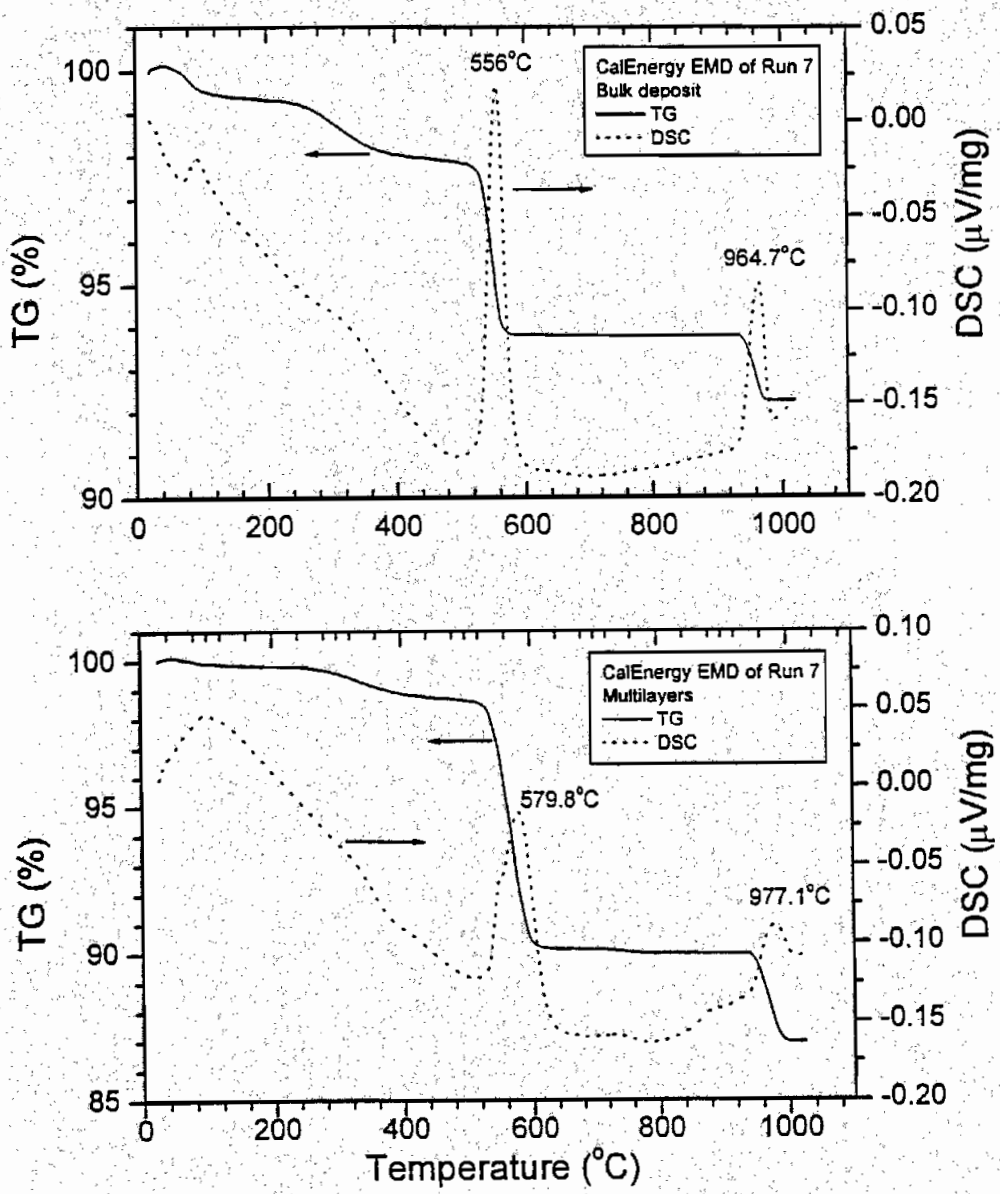
XRD Patterns

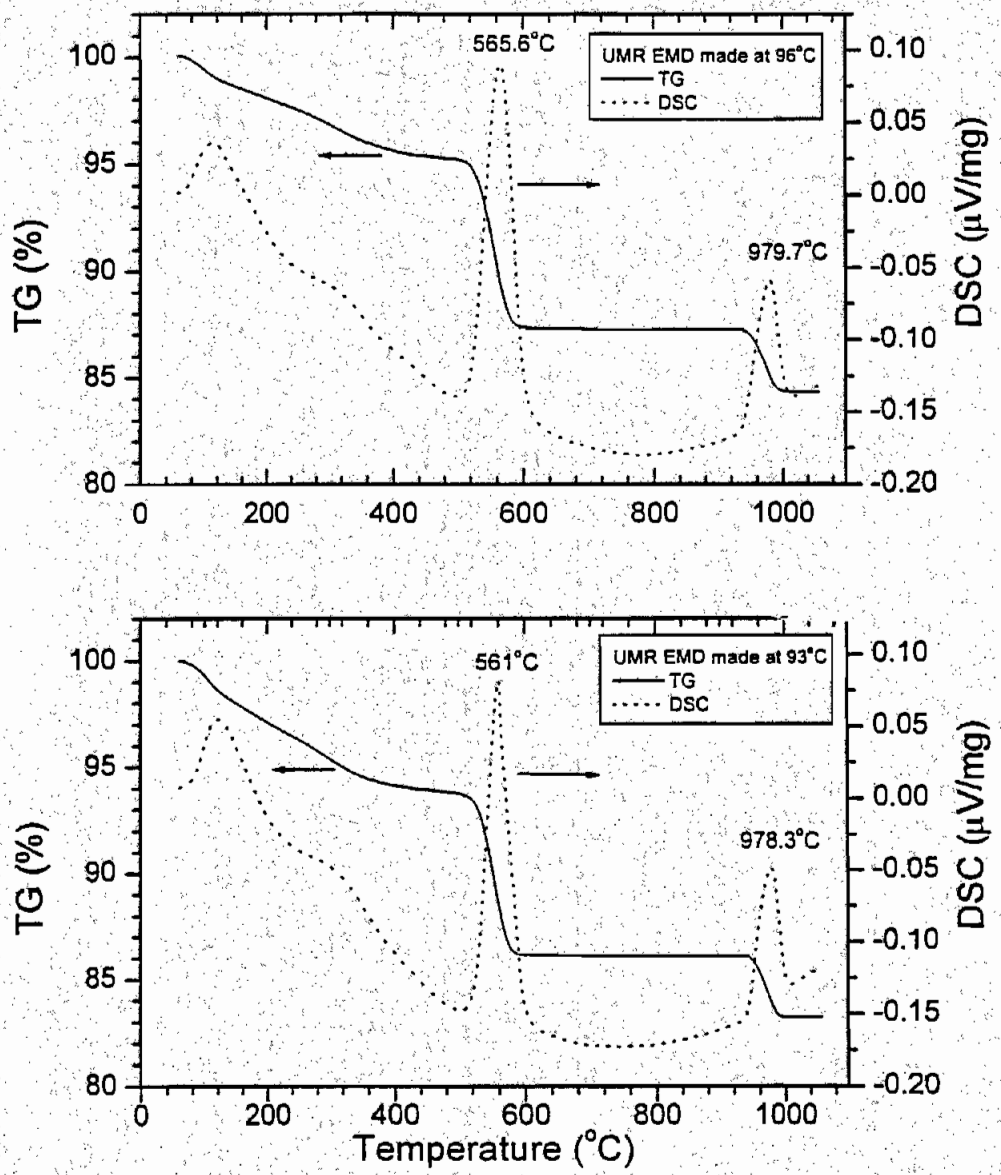


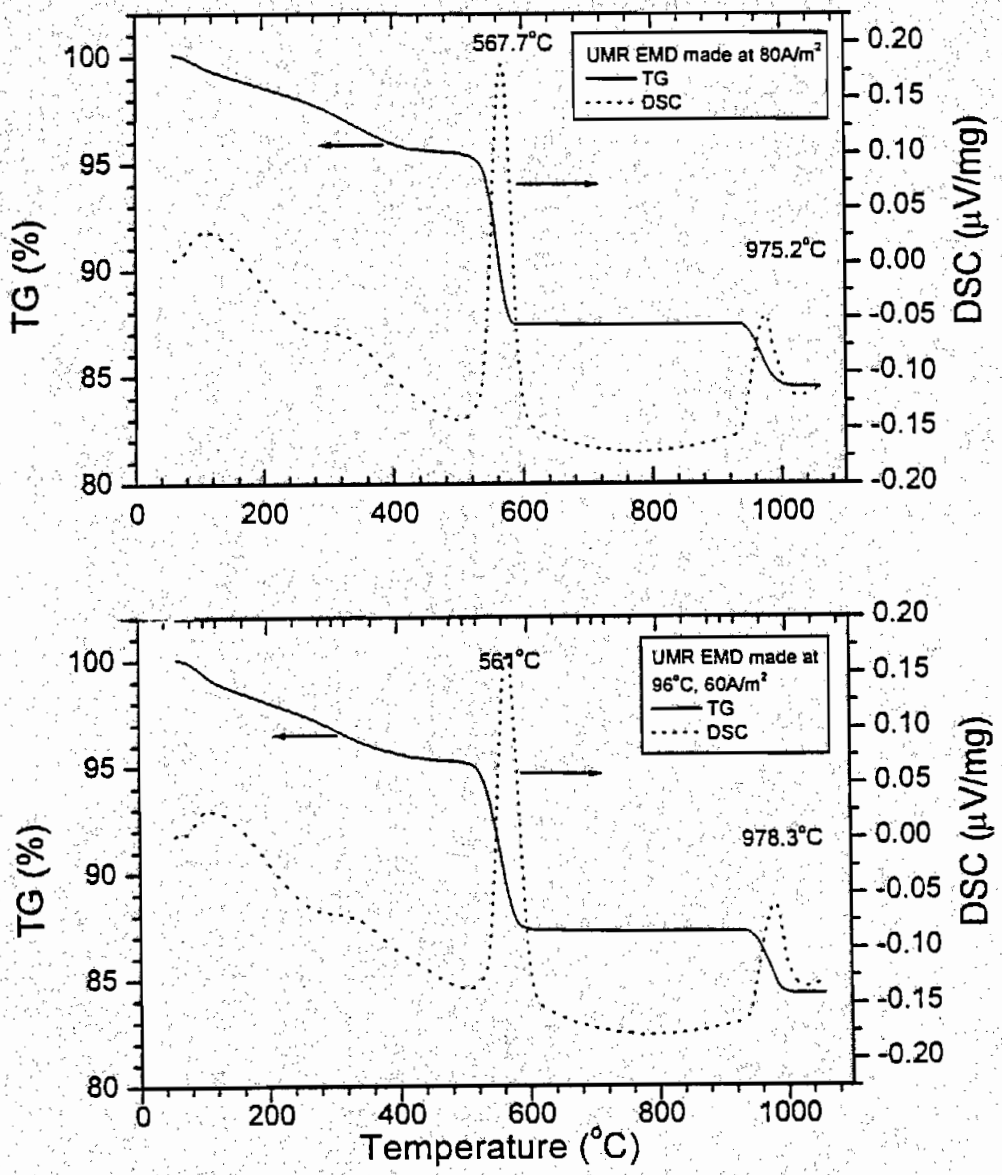

UMR EMD made at 96°C, 60A/m²
UMR EMD made at 60 A/m², starting [HCl] 0g/L
UMR EMD made at 60 A/m², starting [HCl] 18g/L
UMR EMD made at 60 A/m², starting [Mn²⁺] 40g/L
CPS
2θ (degree)

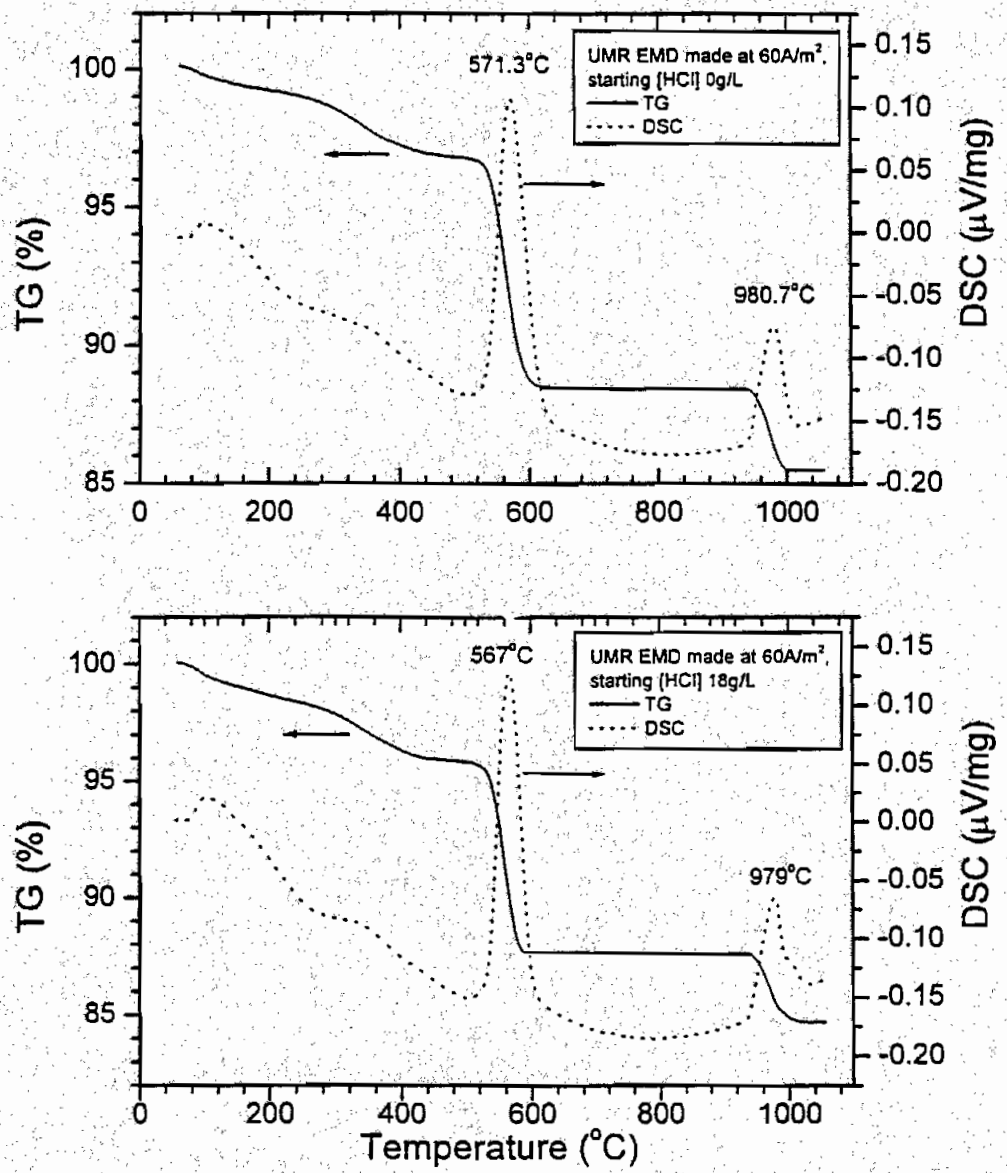
Appendix IV-B

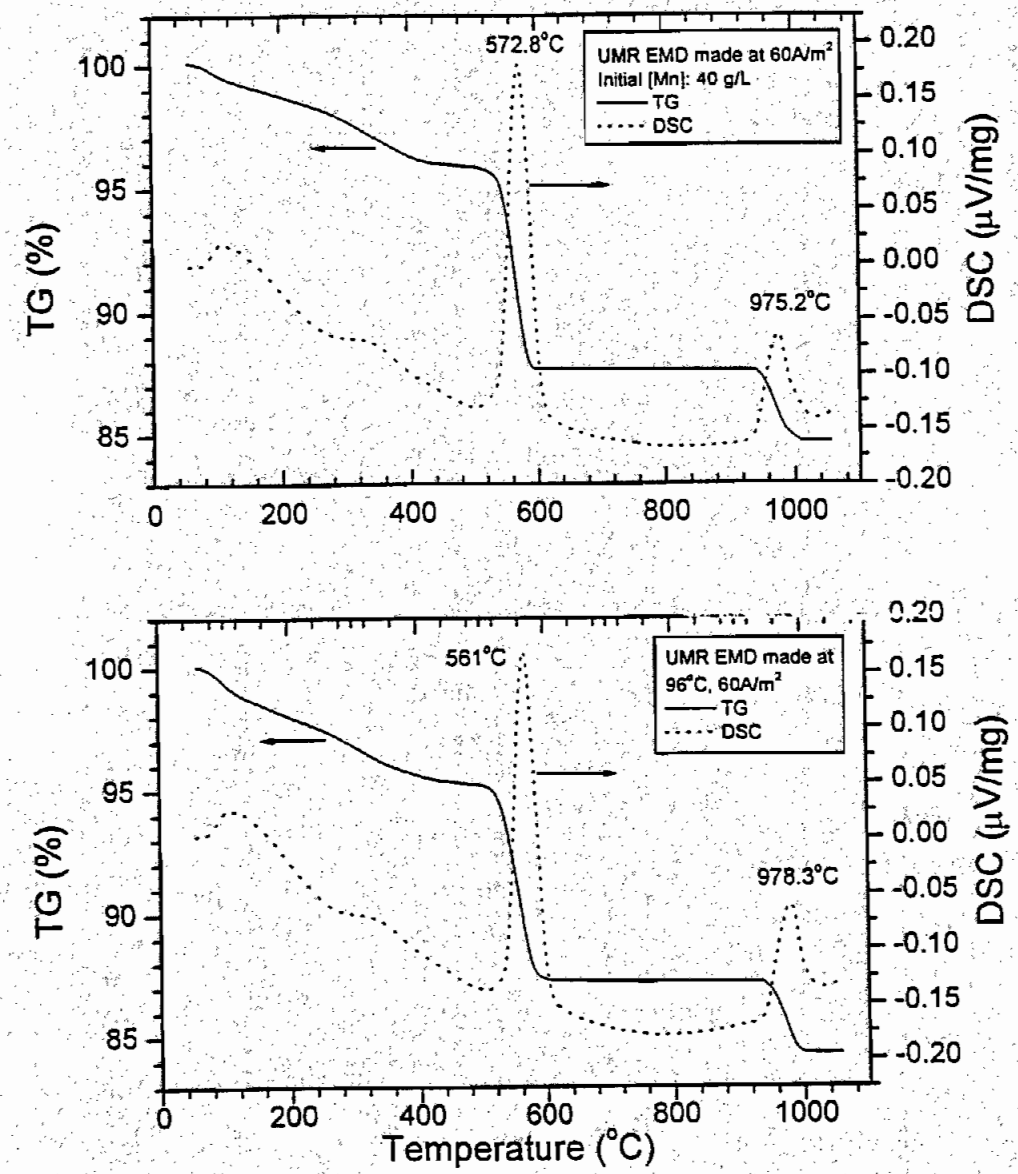
DTA Curves




565.6°C
UMR EMD made at 96°C
TG
DSC
979.7°C
TG (%)
DSC (μV/mg)
561°C
UMR EMD made at 93°C
978.3°C
Temperature (°C)


567.7°C
UMR EMD made at 80A/m²
TG
DSC
975.2°C
TG (%)
DSC (μV/mg)
100
95
90
85
80
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
0
200
400
600
800
1000
561°C
UMR EMD made at
96°C, 60A/m²
TG
DSC
978.3°C
Temperature (°C)


UMR EMD made at 60A/m², starting [HCl] 0g/L
TG
DSC
571.3°C
980.7°C
TG (%)
DSC (μV/mg)
UMR EMD made at 60A/m², starting [HCl] 18g/L
TG
DSC
567°C
979°C
TG (%)
DSC (μV/mg)
Temperature (°C)


572.8°C
UMR EMD made at 60A/m²
Initial [Mn]: 40 g/L
TG
DSC
975.2°C
TG (%)
DSC (μV/mg)
561°C
UMR EMD made at 96°C, 60A/m²
978.3°C
Temperature (°C)

13

EXECUTIVE SUMMARY

of

CALENERGY PROJECTS:

EMD Production. LR 5640-001

Calcium Scrubbing from QL Organic: LR 10088-001

Iron Removal from $MnCl_2$ Liquors: LR 10138-001

Progress Report No. 1 LR Project: 10088-002

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February 5, 2002

INTRODUCTION

Lakefield Research performed experimental testwork for CalEnergy Operating Company from mid 2000 until early 2001. Results have been submitted to George Furmanski and John Featherstone of CalEnergy and Kevin Anthony of Martech Consulting Pty.

The testwork performed by Lakefield Research focussed on investigating aspects of a proposed flowsheet for the recovery of manganese as electrolytic manganese dioxide (EMD) from a geothermal brine solution. Three distinct areas for experimental testwork were identified and investigated. The first project dealt with the electrowinning of EMD from a chloride solution, which would be produced as a solvent extraction strip liquor. The second project dealt with the removal of iron from two process streams by means of crystallisation, and the third project in this phase of process development dealt with removing calcium from a manganese loaded solvent extraction organic phase. These investigations were assigned Lakefield Research Project numbers 5640-001, 10138-001 and 10088-001, respectively.

CalEnergy has requested Lakefield Research to prepare an executive summary that combines and incorporates the results and recommendations of the aforementioned projects. This report addresses that request.

Niels Verbaan, M.Eng. Ron Molnar, Ph.D. Chris Fleming, Ph.D.

Executive Summary

1. Process overview

A conceptual flowsheet was developed by CalEnergy to treat the Zn IX raffinate, to recover manganese as electrolytic manganese dioxide. In addition three other flowsheets were discussed and evaluated briefly by Lakefield/CalEnergy personnel. The alternative flowsheets considered the technical viability of handling iron in the brine solution by loading it onto the organic phase during manganese solvent extraction, and then selectively scrubbing or stripping the iron separately from the manganese strip solution/EMD cell feed. Preliminary testwork showed that this was not possible. Iron loaded onto the organic phase with approximately the same efficiency as manganese, and it was not possible to separate the two metals by solvent extraction.

Ultimately the testwork focussed on a flowsheet that was based on Lakefield Flowsheet #1, as detailed in Lakefield's original proposal. The solvent extraction part of the flowsheet consisted of QL loading, QL scrubbing and QL stripping with spend electrolyte from EMD EW. In the initial test work, iron was loaded onto the organic and then co-stripped with manganese. It was then removed from the strip liquor prior to EMD EW, by oxidation and precipitation. During the course of the test program, this flowsheet was modified to incorporate the iron removal step for before the QL loading, which would increase the loading capacity of the QL organic for manganese. Figure 1 presents the modified Lakefield Flowsheet (1).

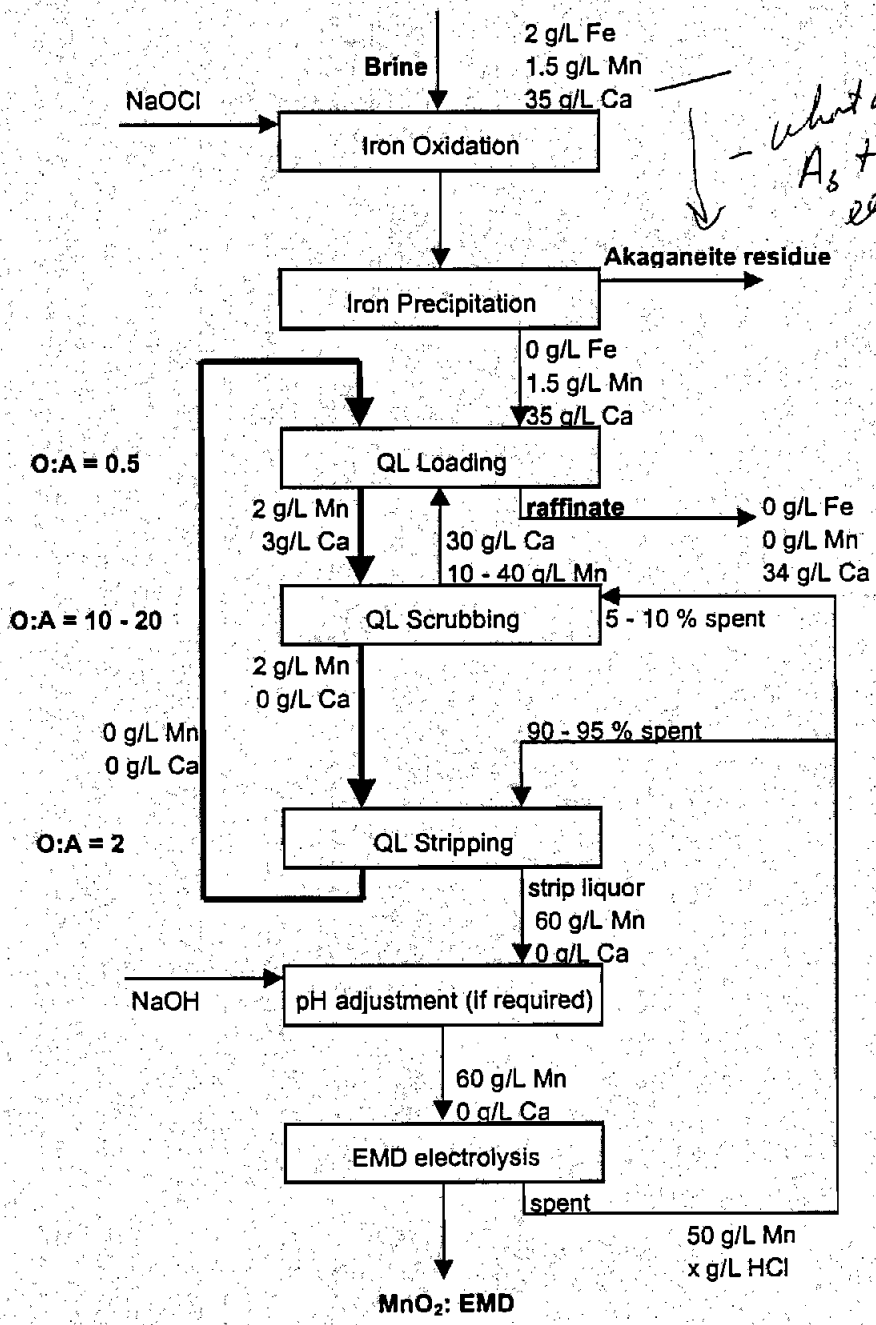

Figure 1 Modified Lakefield Flowsheet # 1

2. *Iron Removal (Project 10138-001)*

Iron removal from chloride liquors was evaluated by ferrous oxidation (with sodium hypochlorite) and precipitation of akaganeite ($Fe_8(O,OH)_{16}Cl_{1.3}$).

There was some question about where to place this unit operation in the flowsheet. This project evaluated (a) removing iron from a manganese strip liquor, since iron will follow the manganese in the SX circuit, or (b) removing iron from the brine solution prior to SX, as this would reduce the organic inventory requirement. Both options were tested on a bench scale basis.

In an atmospheric precipitation process, the thermodynamically-favoured crystalline compound for iron removal from chloride liquors is akaganeite ($Fe_8(O,OH)_{16}Cl_{1.3}$), which is a ferric oxy-hydroxide compound. Seed material for these tests was synthetically produced from a ferric chloride solution. In a continuous process seed material would be generated by internal recycling of solids.

Experiments were performed to establish the effect of pH on Fe precipitation, as well as to determine the induction pH as a function of dissolved iron. Based on these results, operating pH values were determined for the oxidation/precipitation experiments. It was found that a three-stage process operating around pH 1.7 to 1.8 in the first stage and pH 2.3 to 2.4 in the second stage, followed by a polishing stage operating at pH 3.4, was optimum for iron precipitation as akaganeite, as well as producing an iron-free liquor. The operating pH range is defined as the range between solubility pH and induction pH.

Six oxidation experiments were carried out to investigate the influence of the addition of stoichiometric excess of oxidant on (a) the residual iron concentration, (b) the uptake of manganese in akaganeite and (c) the crystal properties. Initial attempts to oxidise ferrous iron involved the use of hydrogen peroxide, but these failed in this particular chloride system. Sodium hypochlorite, however, proved to be a very efficient oxidant, reacting with 99% efficiency relative to stoichiometry. Though the manganese concentration decreased somewhat as the iron was oxidised by sodium hypochlorite, the uptake of manganese in the solids was minimal. Less

than 1.5 % of the total manganese reported to the akaganeite solids in each of the tests. A detailed summary of these results is presented in Table 1.

Table 1 Summary of oxidation test work

	Hypochlorite (NaClO)		Ferrous iron			Fe_T (mg/L)	Manganese		Residue, assays		
Test id.	stoich add.	efficiency	Feed, mg/L	Fe^{2+}, pH 1.8	% oxidised	polish, pH 3.4	Feed, mg/L	Recovery	Fe, %	Mn, %	Cl, %
Test 1-1	97.8%	101.9%	7400	19	99.7%	<0.5	6090	99.6%	58.4	0.10	5.24
Test 1-2	146.8%	68.0%	7400	10	99.9%	<0.5	6090	99.6%	58.5	0.12	4.59
Test 1-3	78.3%	97.4%	7400	1760	76.2%	1040	6090	99.6%	59.5	< 0.05	7.37
Test 2-1	120.5%	82.5%	6010	39	99.4%	<0.3	55600	98.8%	54.6	2.54	9.02
Test 2-2	180.7%	55.1%	6010	28	99.5%	<0.5	55600	98.6%	54.2	2.05	7.36
Test 2-3	78.3%	121.0%	6010	316	94.7%	203	55600	99.9%	59.9	0.13	5.78

XRD analysis of the solids confirmed the formation of akaganeite as the major phase in all the oxidation tests, along with traces of lepidocrocite, hematite and magnetite. SEM imaging showed akaganeite as compact anhedral aggregates. Individual crystals were sub-micron in size.

Qualitative filtration testwork indicated that akaganeite that had been precipitated from strip liquors with lower ionic strength, i.e. low manganese concentration, filtered more easily than akaganeite that had been precipitated from concentrated Mn solution. Although filtration was quite slow, it was assumed that crystals will grow larger in a continuous operation (with internal recycling) , and have improved filtration properties.

3. *Calcium Scrubbing (Project 10088-001)*

The QL loading stage is quite selective against calcium co-extraction with manganese. However, due to the high calcium concentration in the brine going to extraction (20 times greater than Mn) the ultimate loadings of Ca and Mn in the QL organic were similar (2-3 g/L each). Bench testwork and three continuous scrubbing runs were undertaken to investigate the removal of calcium from the loaded organic, by scrubbing with a simulated bleed of spent electrolyte from electrolytic manganese dioxide (EMD) production. The bench testwork and the continuous testwork were performed with organic (QL) prepared according to CalEnergy's instructions. The scrub feed (aqueous phase) was taken from the spent electrolyte of the EMD electrowinning work. Variables that were tested during the continuous piloting runs included O/A ratio (10 to

20) and the acidity of the scrub feed (7.4 to 20 g/L HCl). For the continuous runs, a mini- pilot plant was constructed of materials that were suitable for the high temperature and corrosive nature of the chloride liquor. Figure 2 is a photograph of this setup. A summary of the operating conditions and chemical results of the three runs is presented in Table 2. The major findings of this part of the project were the following:

- Continuous scrubbing of calcium with an acidic $MnCl_2$ solution was successful. In all three runs more than 99.5% of the calcium was removed;
- Calcium appears to be removed by displacement of the calcium cations by both manganese and hydrogen ions. The relative proportions of Mn and hydrogen ion loading onto the QL organic phase vary with the O/A ratio and the acid/metal ratio in the scrub feed;
- No manganese is stripped from the organic during scrubbing of Ca with the acidic scrub feed solution. In fact, there was a net loading of manganese onto the organic phase during PP1 and PP2;
- Calcium removal from the QL organic phase appears to be a flexible, robust process, as it was able to handle different spent electrolyte compositions (7.4 g/L HCl and 20 g/L HCl) as well as different O/A ratios, with no detrimental effect on calcium removal efficiency;
- At the maximum O/A ratio tested of 20, the residual calcium concentration on the loaded organic was 13 mg/L, versus a conc. of <2 mg/L in PP1 where the O/A ratio was 10;
- Iron scrubbing from the loaded QL organic by contacting it with a bleed stream from the spent electrolyte from EMD production was found to be not feasible. No iron was removed from the organic phase during Ca scrubbing, under any of the conditions tested.
- The aqueous scrub solution (after scrubbing) contained 10-40 g/L Mn and ~30 g/L Ca in the various continuous tests. This solution would be recycled to the feed to SX in the overall flowsheet. At the highest scrubbing O/A ratio of 20 tested in the project, this would constitute an internal Mn recycle of ~25%.

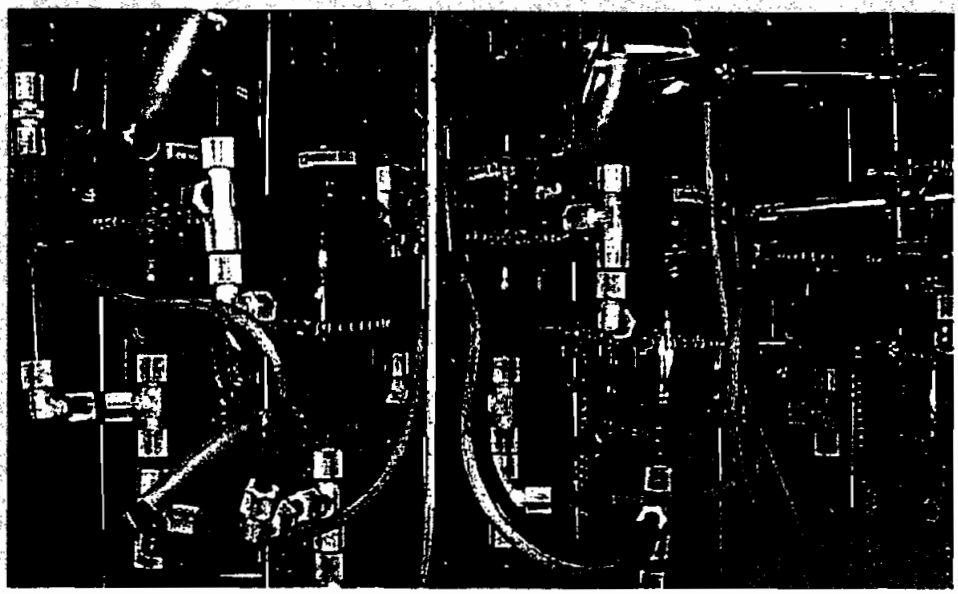

Figure 2 Calcium Scrubbing SX Pilot Plant Overview

Table 2 Summary Calcium Scrubbing Runs PP1 to PP3

Pilot Plant Conditions:		PP1		PP2		PP3	
Overall O/A		10		20		10	
Mixer O/A		1		1		1	
Total Operating time (h)		24		15.5		15.5	
Mixer retention time (min)		4.6		2.3		2.3	
Mixer temperature (°C)		85		85		85	
Aq. feed acid (g/L HCl)		7.4		7.4		20	
Average Assays:		Ca	Mn	Ca	Mn	Ca	Mn
Feed	ORG↓	2110	1180	2580	1620	1800	1350
B1	ORG	243	2700	845	2523	114	2703
	AQ	23833	29405	33773	8273	15525	48364
B2	ORG	9	2563	157	2930	17	2687
	AQ	2673	56485	14160	35007	2420	61252
B3	ORG	2	2178	13	2792	3	1610
	AQ	99	56062	3323	55714	417	63720
Feed	AQ↑	17.5	56000	18	54850	33.8	53700
% calcium scrubbed		99.9		99.5		99.8	

4. *EMD Electrowinning (Project 5640-001)*

4.1. Experimental Setup and Test Program

In the investigation at Lakefield Research of the electrowinning of electrolytic manganese dioxide (EMD) from a chloride feed solution, a series of 7 test runs was carried out under different specific operating conditions. These were laid out by Dr. Kevin Anthony, consultant to CalEnergy, in the form of a partial factorial experimental design. The test conditions were chosen to investigate three operating parameters; electrolyte manganese concentration, electrolyte acidity and anode current density. One additional run looked at the effect of a lower operating temperature.

It was necessary to produce 1000 L of clean stock solution of manganese chloride as a feed to the electrowinning tests. Manganese chloride of sufficient purity could not be obtained commercially. To produce an ultra pure feed solution, manganese carbonate was initially reacted with hydrochloric acid. The solution was further treated with hydrogen peroxide to dissolve colloidal MnO_2, and Mn metal was finally added to adjust the Mn concentration. The pH of the stock solution was then adjusted to 3.7 using precipitated manganese hydroxide. All tests were performed with this stock solution.

The electrowinning apparatus is shown schematically in Figure 3. The test program required the construction of a sealed PVDF test cell, fitted with ancillary equipment that was compatible with the high temperatures and chloride concentration. In addition, the cell temperature had to be controlled within tight limits.

To heat the cell, it was positioned in an oil bath in which the oil was heated and circulated. The oil bath was situated atop two magnetic stirrers that were able to provide circulation inside the cell by driving magnetic stir bars located in the bottom of the cell. The oil bath, heaters and oil bath stirrer are not indicated in Figure 3. Fresh electrolyte was preheated through a glass coil submerged in the oil bath before entering the cell. Off-gas produced at the two graphite cathodes was collected and drawn through a reflux condenser (to minimise loss of water due to evaporation), and then through a two-stage scrubber train to capture co-evolved chlorine. This was monitored by means of a Chloride Ion Sensitive Electrode (CL-ISE). The

electrode data were used to determine when the scrubber solution needed to be changed, and the ISE traces also gave an indication of the rate of chloride production.

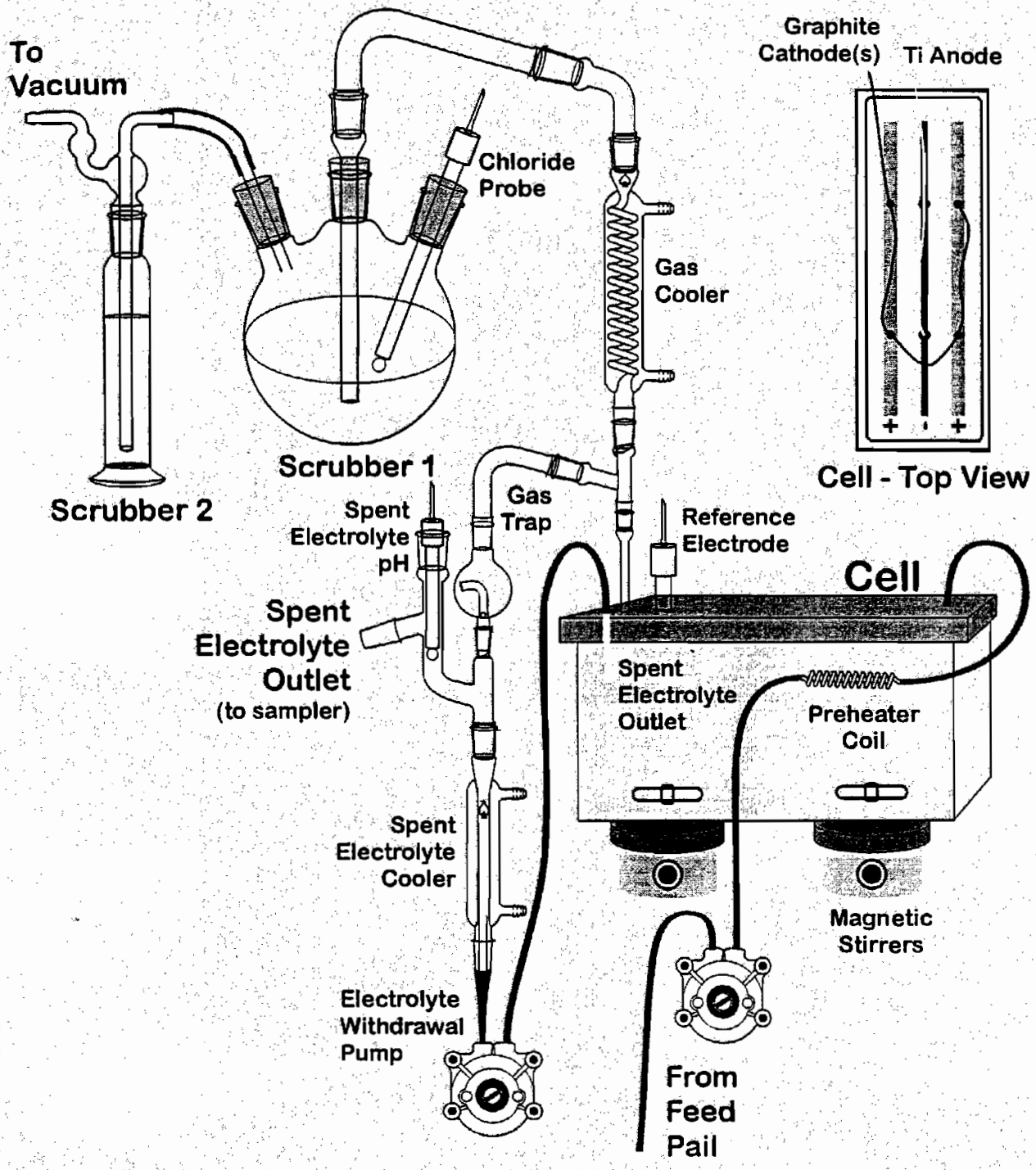

Figure 3 Schematic of the EMD Electrowinning Apparatus

Current was supplied to the cell by a constant current DC power. Manganese dioxide was produced at both sides of a grade 2 titanium plate anode. Spent electrolyte was continuously drawn from the top of the cell by means of a peristaltic pump. Cell voltage and current were recorded continuously by a Bailey process control system. In addition, the pH of the spent electrolyte stream and the reading generated by the CL-ISE were constantly recorded. The process control system also monitored the cell, oil bath and scrubber temperatures, and controlled the heaters in the oil bath to give the desired temperature in the cell. The potential of each electrode was periodically measured against a standard Ag|AgCl reference electrode that was located in the cell.

The spent electrolyte stream was sampled continuously using a sampling pump. The sampling sub-stream was in turn split into aliquots spanning a fixed time interval, typically 90 minutes, using an auto-sampler. A sub-set of the sample fractions collected by the auto-sampler was submitted for analysis to determine free acidity and manganese contents.

After each run, the EMD was harvested from the cell. A portion of this material was ground to the desired target fineness. The ground material was then washed in a multi-stage procedure to remove any residual chloride, and then with a final neutralising wash to neutralise any residual acidity. Upon completion of the testwork, both unground and unwashed raw deposit and the processed materials were returned to CalEnergy for further characterisation.

Once it had been demonstrated that the cell apparatus was operating as required, a series of seven tests was carried out in random order, to examine the effects of the three main variables.

In addition, the pulverized samples were analyzed by X-ray Diffraction and the patterns produced in these scans were submitted to Dr. Anthony for interpretation.

4.2. EMD Operating Results and Discussion

Table 3 presents a detailed summary of the results obtained in this test program, showing test conditions, operating results and the physical and chemical characteristics of the deposits.

Table 3 Data Summary for EMD Production Tests

		Run	1	2	3	4	5	6	7
Plating Time		h:mm	120:00	125:00	123:00	121:00	101:45	120:20	123:10
Temperature	Average	°C	97.0	96.9	97.2[c]	97.0	97.0	97.0	92.0
	Standard Deviation	°C	0.7	0.6	0.6[c]	0.3	0.2	0.1	0.3
Anode Current Density		A/m^2	59.9	99.8	60.5	59.8	99.9	100.1	99.5
Rich electrolyte	Acid	g/L	1.0	1.0	0.7	1.1	1.1	0.8	0.9
	Mn	g/L	64.5	64.5	46.8	71.5	71.5	46.7	46.6
Spent	Average Acid[a]	g/L	11.1	10.2	9.9	17.4	17.4	10.2	9.6
	Standard Deviation		0.8	0.2	0.3	0.4	0.4	0.1	0.3
	Average Mn[a]	g/L	60.8	58.5	37.0	58.0	60.1	41.4	33.3
	Standard Deviation		3.4	1.5	2.5	1.9	1.2	1.2	1.3
sg	Rich Electrolyte	g/mL	1.115	1.115	1.083	1.126	1.126	1.082	1.074
	Spent Electrolyte	g/mL	1.110	1.108	1.076	1.110	1.112	1.074	1.066
emf (Ag|AgCl)	Rich Electrolyte	mV	613	613	n/a	n/a	n/a	610	620
	Spent Electrolyte	mV	930	1000	964	1040	1045	938	934
Mn Deposited		g	993	1714	1028	890	1267	1686	1683
		moles	11.4	19.7	11.8	10.2	14.6	19.4	19.4
Current Efficiency (MnO_2)		%	102	101	100	90	91	102	100
Cl in Scrubbers		g	0.13	4.3	1.0	10.8	19.0	8.3	6.6
		moles	0.00	0.12	0.03	0.31	0.54	0.24	0.19
Cl Production Rate[d]		g/min	<0.1	0.8	0.8[b]	3.5	7.4	2.8	1.8
Current	Average	A	5.08	8.47	5.13	5.07	8.47	8.49	8.44
	Standard Deviation	A	0.01	0.02	0.09	0.01	0.03	0.02	0.02
Cell Voltage[e]	Maximum	V	2.40	2.74	3.37	2.25	3.06	2.96	3.27
	Minimum	V	1.89	2.05	1.91	1.94	2.06	2.15	2.15
	Time Weighted Average	V	2.20	2.40	2.12	2.16	2.79	2.70	2.97
Anode Voltage[e]	Maximum Measured	V	1.71	1.81	2.40	1.54	2.35	2.18	2.09
	Minimum Measured	V	1.43	1.34	1.26	1.36	1.43	1.43	1.78
Cathode Voltage[e]	Maximum Measured	V	-0.42	-0.67	-0.62	-0.63	-0.57	-0.58	-0.71
	Minimum Measured	V	-0.80	-0.91	-0.80	-0.68	-0.75	-0.77	-1.08
Anode/Cathode	Average		2.63	2.10	1.99	2.25	3.17	2.83	2.10
	Standard Deviation		0.57	0.21	Data S	0.10	0.50	0.42	0.22
Power		kWh	1.33	2.50	1.34	1.32	2.40	2.76	3.09
Power/kg EMD		kWh/kg	1.34	1.46	1.30	1.49	1.90	1.64	1.84
LOI at 105°C			0.10%	0.40%	0.35%	0.45%	0.50%	0.30%	0.20%
Combined Water (LOI @ 400°C)			1.8%	3.2%	2.7%	2.7%	3.4%	3.6%	3.3%
Mn_T			61.59	61.17	61.79	61.30	60.37	61.07	61.65
Mn(IV)			62.87	60.50	61.87	62.07	61.24	60.75	60.95
x for MnO_x			2.02	1.99	2.00	2.01	2.01	1.99	1.99
Chloride		g/t	< 10	50	30	30	60	50	70
Fineness	K80 (80% passing)	µm	106	104	110	113	113	116	109
	K20 (20% passing)	µm	13	13	17	18	10	13	18

[a] average of samples 10 to the end of the run, except Run 1 where averages are samples 35 to end.

[b] last 13 hours of run only; <0.1 for the rest of the run.

[c] In Run 3, there was one temperature excursion of 9 h duration which bottomed out at 47°C. This period is not included in the temperature average and standard deviation calculations. Highest voltage also occurred during this excursion.

[d] Average slope of linear portion of ISE plots of Cl in scrubber 1 vs time. Intercepts are not shown because they are somewhat arbitrary, depending on where the zero point of the linear portion of the period for a particular scrubber batch was taken to be.

[e] Cell voltage measured continuously by Bailey controller. Anode and cathode voltages only measured periodically by hand (DVM).

Each electrowinning test lasted 5 days (120 h) of continuous operation. Depending on the test conditions, up to ~1.7 kg of EMD was deposited on the anode, which had a plating surface of 20 cm width by 21 cm height on each side of the anode blank. To strip the deposits, the anode was heated to 100°C in an oven and then plunged into cold de-ionized water. The deposit generally broke up into chunks and could be readily removed from the titanium sheet using this procedure.

Two examples of EMD deposits are shown in Figure 4. The deposits, which were up to 1 cm thick, generally exhibited smooth surfaces with rough patches, as seen in the figure. The run 6 deposit was heavier than that from run 3 and it shows more of the rough areas. Generally, the deposits, were hard and dense, except for regions where a flake or a large bubble appeared to have lifted the deposit off from the rest of the mass. Even these bubble or flake regions were quite solid and competent and there was minimal loose flaking or spalling.

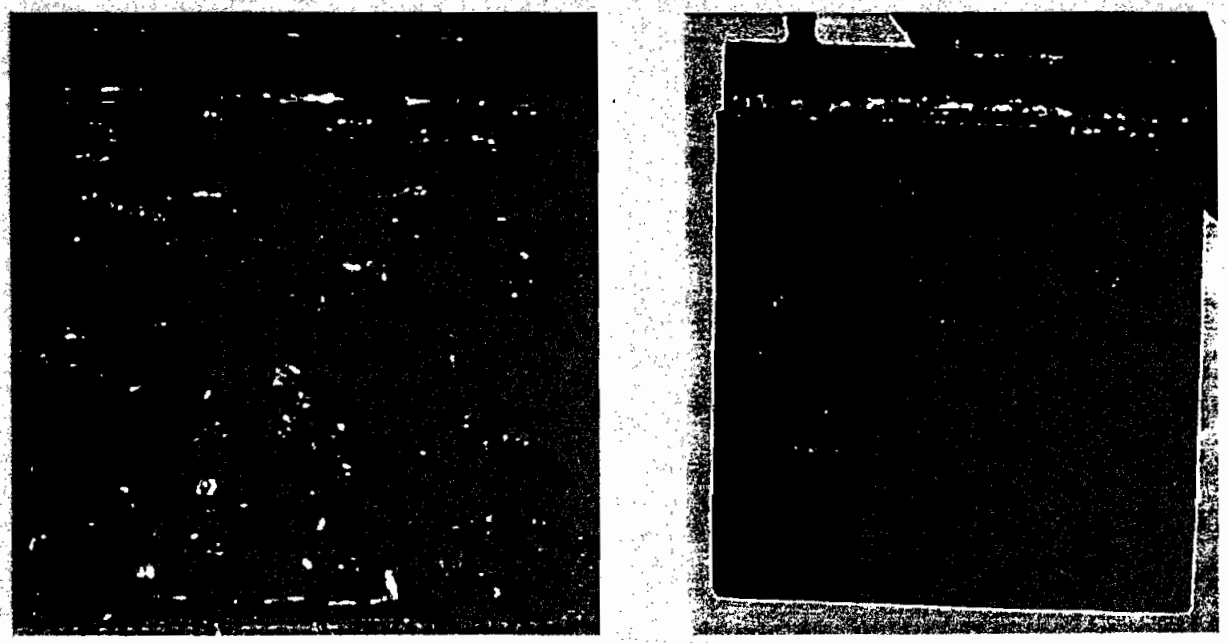

Figure 4 EMD Deposits (run 6 at left, run 3 at right)

As seen in the data in Table 3, the temperature was quite tightly controlled over the whole experimental period. The targeted current densities were 60 A/m^2 and 100 A/m^2 and these were attained to within 0.5 A/m^2. The experiments were designed to achieve a targeted final

acidity in the spent electrolyte. Without knowing the current efficiency under a specific set of conditions, the feed acidity required to produce the particular target spent electrolyte acidity was only a first estimate. Nevertheless, all the tests fell into two fairly narrow ranges of final acidity, either 10 g/L or 17 g/L.

The data showed that spent electrolyte acidity was the key variable affecting performance as measured by anodic current efficiency. Increasing the final acidity from 10 to 17g/L HCl decreased the current efficiency from 100% to 90%. Increasing the concentration of Mn in the feed electrolyte from 30-40 g/L to 60 g/L did not appear to have any significant effect on current efficiency. The same was true of changes to current density from 60 A/m^2 to 100 A/m^2. Decreasing the operating temperature from 97°C from 92°C also had no discernible effect on current efficiency.

Scrubbers containing ferrous sulphate solution were used to capture chlorine gas that was evolved at the anodes. Chlorine is produced at the anodes in competition with EMD, and any chlorine produced represents a loss in current efficiency for EMD production. The high acid runs were the ones that produced the highest levels of chlorine in the scrubber and the lowest current efficiencies. The drop in current efficiency is therefore taken to be, in part, due to increased production of chlorine at the anode at these higher electrolyte acidities.

Cathode voltage was largely constant through the range of conditions studied. Anodic voltage did change somewhat from run to run. However, there was insufficient data to establish a correlation between anodic voltage and the other key operating parameters of temperature, Mn or acid concentrations in the cell and anodic current density. There was only a slight indication that higher Mn levels lead to lower anodic voltages. The power to the cell is also reported in the table as both total power input and as power per unit of plated EMD (specific power). Again, the data were examined to identify any correlations between the specific power requirement. The only apparent correlation was between the power required and the current density. Higher current density resulted in higher power consumption per unit of EMD produced, presumably as more power was going into ohmic losses in the cell, generating heat. Although the operating anodic voltages appeared to be somewhat higher at lower Mn concentrations, the actual specific power requirements did not show the same trend.

As noted, a portion of each deposit was stage-pulverized to a K_{80} of 100 µm. The amount of material passing 20 µm is shown in Table 3. The pulverized material was washed initially with de-ionized water, and a final wash was performed with a mild solution of NaOH to neutralise any residual acidity. The material was dried at 105°C and then heated to 400°C to determine moisture and loss on ignition, respectively. These results are tabulated in Table 3.

As the EMD was produced from synthetic solutions, no chemical analyses were carried out other than a determination of Mn content. These values are also shown in Table 3. The concentrations were used to calculate a value of "x" where it is assumed that the deposit is MnO_x as it is known that EMD is not completely stoichiometric. For example, "x' for stoichiometric MnO_2 would be 2.

Chloride contents in the pulverized and washed EMD product are shown in Table 3. These values, generally in the 30 to 70 mg/L range, need to be compared with the required specifications. An examination of the data reveals that the three samples that washed best (to the lowest chloride levels of 30 mg/L or less) were the ones corresponding to the runs at the lower current density. It is possible that the EMD produced at higher current densities is denser and more difficult to wash. The only other correlation noted between operating conditions and residual chloride levels was the observation that the highest Cl level was seen in the test at the low temperature. As there was only one data point at the low operating temperature, this inference has to be viewed as somewhat tentative.

All further interpretation of the X-ray crystallographic data were carried out by Dr. Kevin Anthony, consulting to CalEnergy.

5. *Recommendations for further testwork*

5.1. Iron Removal

The iron removal project has only been evaluated in batch tests. It is very important to test this continuously in a pilot study. This would allow the impact of crystal recycling and seeding on settling filtration characterisation to be assessed, and would also produce enough

The product characterization done to date appears to indicate that the EMD produced under all the operating conditions would be suitable for battery applications.

What still needs to be done is to confirm that the proposed process flowsheet is capable of producing a feed electrolyte that can in turn yield battery-grade EMD deposits. That is, the upstream flowsheet steps need to be operated to produce sufficient feed electrolyte to allow the cell to be operated. This EMD product will then need to be thoroughly characterized with respect to physical properties and chemical purity.

5.4 Integrated Pilot Plant

Once the individual unit operations (iron removal, calcium scrubbing and EMD production) have been optimized, the process should be modelled using software such as MetSim or Aspen Plus, to ensure there would be no fatal flaws in the integrated process. The overall process should then be piloted (or mini-piloted) with all the unit operations fully integrated (including recycle of the spent scrub solution). The integrated pilot plant should be run for several weeks to ensure all process flows and solution compositions have reached steady state. The objective would be to ensure no impurities that may be detrimental to the process build up at any point in the circuit, and that there is no gradual deterioration in the physical or chemical properties of the final EMD product. The process model would be refined during piloting, and would serve as the model for future full-scale operations.