TREATMENT OF LIQUID WASTE AND REGENERATION OF SPENT ION EXCHANGE RESIN USING ELECTROCHEMICAL TECHNIQUES

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ABSTRACT

Liquid waste and spent ion exchange resin are generated during the decontamination, refurbishment and decommissioning of nuclear power reactors and nuclear facilities. The liquid waste and spent resin may contain radionuclides, metals, organic chelating (complexing) agents and inorganic reagents. The liquid waste is treated at high cost, and the dewatered spent resin is transferred to containers and stored in a radioactive waste storage facility. During storage of resin waste, radiolytic and other decomposition processes can occur resulting in gas generation and release of free liquids. Therefore, storage facilities are built to allow continuous monitoring of the resin waste container for at least 50 years. It is therefore ideal to develop methods for the treatment of liquid and resin waste in order to treat the waste as soon as it is generated.

An electrochemical method is being developed at Chalk River Laboratories which has potential to be used for treating liquid waste and for regenerating spent ion exchange resin. A three compartment electrochemical cell has been designed and fabricated; the central compartment contains liquid waste or spent ion exchange resin, while the anode and cathode compartments contain electrolytes. This paper discusses the results of cyclic voltammetry tests performed in simulated spent CAN-DEREM™ reagents to determine the iron redox potential in these electrolytes. CAN-DEREM™ is a dilute regenerative chemical decontamination process developed by Atomic Energy of Canada Limited for use in the primary heat transport system of CANDU®[1] reactors, pressurized water reactors and boiling water reactors. The paper also presents the results of tests to study the current efficiency of iron deposition as a function of solution pH, cathode material and temperature. The influence of three commercial cation exchange membranes on the transport efficiency of iron is also discussed.

The ultimate goal of the project is to force (under an electric field) the migration of metal ions in spent ion exchange resin through a membrane into the cathode compartment where they can be reduced to metal and deposited on the cathode. As a result, the spent ion exchange resin can be regenerated and reused, lowering the volume of ion exchange resin required. The reduced solid metal on the cathode would have a significantly lower volume and be much easier to dispose of.

1. INTRODUCTION

CAN-DEREM™ is a dilute regenerative chemical decontamination process developed by Atomic Energy of Canada Limited (AECL) for use in the heat transport system (HTS) of CANDU® reactors, pressurized water reactors and boiling water reactors. The CAN-DEREM™ reagent consists of ethylenediaminetetraacetic acid (EDTA) and citric acid. The use of ascorbic acid as a reducing agent has shown benefit in lowering corrosion of carbon steel components and

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[1] CANDU® is registered trademark of Atomic Energy of Canada Limited.

increasing reagent regeneration during CAN-DEREM™ applications [1]. The removal of magnetite (Fe_3O_4), the major oxide present in the CANDU HTS, from surfaces in EDTA-based reagents occurs by a combination of direct (Eq. (1)) and reductive dissolution (Eq. (2)), releasing ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions into solution. During dissolution of magnetite, radionuclides entrained by the magnetite are also released into solution.

$$\mathbf{Fe_3O_4 + 8H^+ \rightarrow 2Fe^{3+} + Fe^{2+} + 4H_2O} \qquad (1)$$

$$\mathbf{Fe_3O_4 + 8H^+ + 2e^- \rightarrow 3Fe^{2+} + 4H_2O} \qquad (2)$$

The dissolved iron and radionuclides are removed by ion exchange (IX) resin and the reagent is regenerated and returned into the system. As IX resin have limited capacity for metals and radionuclides, a large volume of spent IX resin may be generated during the application of a chemical decontamination process. Storage of this radioactive spent resin may become an impediment for routine use of the chemical decontamination processes. Therefore, it is important to minimize the volume of spent resin waste. Liquid waste containing radionuclides, metals, organic chelating (complexing) agents and inorganic reagents are also generated during decontamination and decommissioning (D&D) activities and the treatment of the liquid waste is costly.

In CANDU® reactors, between 75 to 80% of the deposits reside inside the steam generators (SGs); mechanical decontamination of the SGs prior to a chemical decontamination of the HTS will remove the majority of the deposit loading, resulting in a reduced volume of spent IX resin [2] during chemical decontamination. However, even with the use of mechanical decontamination, the volume of spent resin generated can be significant.

An electrochemical method has been developed which has been shown to be effective for reducing the volume of spent IX resin by removing the metals and radionuclides from the spent resin under the influence of an electric field [3]. A similar approach is being investigated at AECL. A three compartment electrochemical cell was designed and fabricated; the central compartment contains liquid waste or spent IX resin, while the anode and cathode compartments contain electrolytes. The ultimate goal of the project is to force (under an electric field) the migration of metal ions in spent IX resin through a membrane into the cathode compartment where they can be reduced to metal and deposited on the cathode. As a result, the spent IX resin can be regenerated and reused, lowering the volume of IX resin required. The reduced form of the metal on the cathode would have a significantly lower volume and be much easier to dispose of.

This paper presents the results of cyclic voltammetry (CV) tests performed in simulated spent CAN-DEREM™ reagents to determine the iron redox potentials. Next, the results of iron deposition tests performed in simulated spent CAN-DEREM™ solution to study the current efficiency of iron deposition as a function of pH, cathode material, potential and temperature are presented. In the absence of a membrane, the potential determined from CV tests was sufficient to deposit ~ 40 weight% of the iron on the cathode (working electrode). When a membrane was used, a higher applied potential was required to remove iron from the liquid waste. The tests with a membrane were conducted first using liquid waste to optimize the test conditions before testing the method on spent IX resin. The results of tests using three commercial cation exchange membranes to study transport efficiency of iron through these membranes are also discussed in this paper.

2. EXPERIMENTAL

An electrochemical cell made of polycarbonate (Figure 1) was designed and used for CV and iron deposition tests. The cell can be divided into three compartments by inserting two membranes into the slots (not shown in the figure). The cell included a working electrode (WE, cathode), a counter electrode (CE, anode), and a reference electrode (RE). A computer controlled PAR 263A Potentiostat with the software PowerCORR® Version 2.48 was used to record the cyclic voltammograms at scan rates ranging from 25 to 200 mV/s. For iron deposition tests, a solution loop consisting of a flow meter, a Micropump, and a round bottom flask was connected to the cell using Tygon tubing. Argon gas was used to purge the solution.

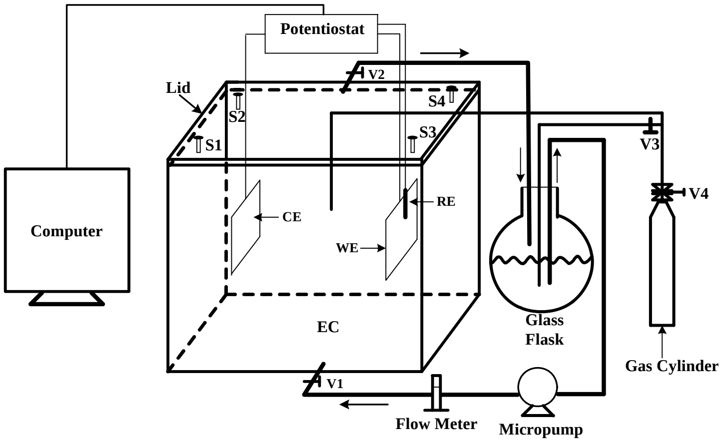

Figure 1. Schematic diagram of the electrochemical cell used for cyclic voltammetry and iron deposition tests.

The CV tests were carried out in solutions containing ferric citrate, ferric EDTA, or ferric formate at several pH values and at room temperature. Platinum (Pt) foil was used as the anode, while the cathode was made of either 304 stainless steel (304SS) or Pt foil. The reference electrode was Ag/AgCl (4 M KCl). The iron deposition tests were carried out at constant potential, which was selected based on the result of the CV tests. The cathode was either 304SS or copper (Cu), while the anode was Pt foil. The test solution was a simulated spent CAN-DEREM™ solution containing 600 mg/L EDTA, 200 mg/L ferric ions (as ferric citrate) and 880 mg/L of ascorbic acid used as a reducing agent [1]. The effects of solution pH, cathode material, temperature and potential on the current efficiency of iron deposition were investigated.

During iron deposition tests, current data as a function of time were recorded. The iron concentrations of the test solution before and after the test were determined using an UV-visible method. After the tests, the surface morphology and (semi-quantitative) elemental composition of the deposit were studied using Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS). The current efficiency (CE) of iron deposition can be calculated using Eq. (3).

$$CE = \frac{\{([Fe]_{initial} \times V_1 - [Fe]_{final} \times V_2)/M_{Fe}\}}{\{Q/(Z \times F)\}} \times 100\% \qquad (3)$$

In Eq. (3), $[Fe]_{initial}$ and $[Fe]_{final}$ are the initial and final concentrations of iron (g/L), respectively, V_1 and V_2 are the initial and final volumes of the solution (L), M_{Fe} is the atomic weight of iron (g/mol), Q is the total charge (Coulomb, C) consumed during the period of iron deposition, Z is the number of electrons transferred in the overall metal reduction reaction, and F is the Faraday constant (96,485 C/mol). The total charge was obtained by integrating the current curve during the test.

The tests for membrane efficiency for transporting iron ions were carried out in a new electrochemical cell constructed using thicker polycarbonate material for higher mechanical strength. This second cell (Figure 2) consisted of three compartments: an anode compartment, a cathode compartment and a central compartment; the compartments are separated by cation exchange membranes. The central compartment was used to contain either spent solution or spent IX resin. Each compartment had an independent recirculation system that circulated the solution between the compartment and the reservoir (Figure 2). The reservoirs were heated using heating tape and insulated to maintain temperature in each compartment, and were connected to each compartment using stainless steel braided Teflon hoses.

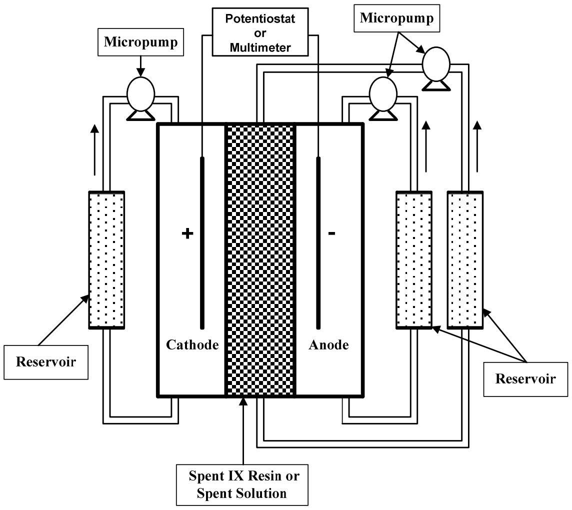

Figure 2. Schematic diagram of the electrochemical regeneration system used for testing membranes.

Tests using three commercial cation exchange membranes (Neosepta CMX, NAFION® Membrane N424 and N324) are underway using simulated spent CAN-DEREM™ solutions to determine the extent of iron transfer through the membranes. Neosepta CMX is manufactured by ASTOM Corporation, and N424 and N324 are manufactured by Ion Power Inc. A DC power supply model HR40-5B, made by TRYGON Electronics was used to apply an external voltage in the range 0 to 40 V. In these tests, the effects of cathode materials, current, time and ion valence on the amount of iron removed by the membrane were investigated.

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry Tests

The CV tests were performed in ferric citrate, ferric EDTA and ferric formate solutions at pH values ranging from 2.2 to 5.5. The CV scans were initiated at -1.1 V, reversed at 1.2 V, and ended at the initial potential. Figure 3 shows CVs for ferric citrate solution at pH 5.0 using either Pt foil or 304SS as the cathode material at different scan rates. During the cathodic scan at a scan rate of 200 mV/s, a cathodic peak (denoted CC1 in Figure 3, left figure) at -0.06 V was observed. This peak was attributed to the reduction of dimeric ferric hydroxo citrate to ferrous citrate (Eq. (4)) [4], where L represents the citrate ligand.

$$\frac{1}{2}Fe(III)_2L_2OH_2^{2-} + H^+ + e^- \rightarrow Fe(II)L^- + H_2O \tag{4}$$

The second cathodic peak, CC2, at –0.59 V corresponded to the reduction reaction of monomeric ferric hydroxo citrate to ferrous citrate (Eq. (5)).

$$Fe(III)LOH^- + H^+ + e^- \rightarrow Fe(II)L^- + H_2O \tag{5}$$

During the cathodic scan and when the potential was below –0.8 V, the cathodic current density rapidly decreased, but the iron reduction peak (Eq. (6)) could not be defined due to the simultaneous hydrogen evolution (Eq. (7)). Ferrous citrate accumulated in the layer adjacent to the cathode was reduced to metallic iron by the following reaction (6).

$$Fe(II)L^- + 3H^+ + 2e^- \rightarrow Fe + H_3L \tag{6}$$

Hydrogen evolution occurred according to (Eq. (7)).

$$2H^+ + 2e^- \rightarrow H_2 \tag{7}$$

During the anodic scan, a peak CA3 at –0.74 V was observed, corresponding to iron dissolution according to (Eq. (8)).

$$Fe + H_3L \rightarrow Fe(II)L^- + 3H^+ + 2e^- \tag{8}$$

Another anodic peak, CA2 at –0.35 V, corresponded to the oxidation of ferrous citrate to monomeric ferric hydroxo citrate (Eq. (9)).

$$Fe(II)L^- + H_2O \rightarrow Fe(III)LOH^- + e^- + H^+ \tag{9}$$

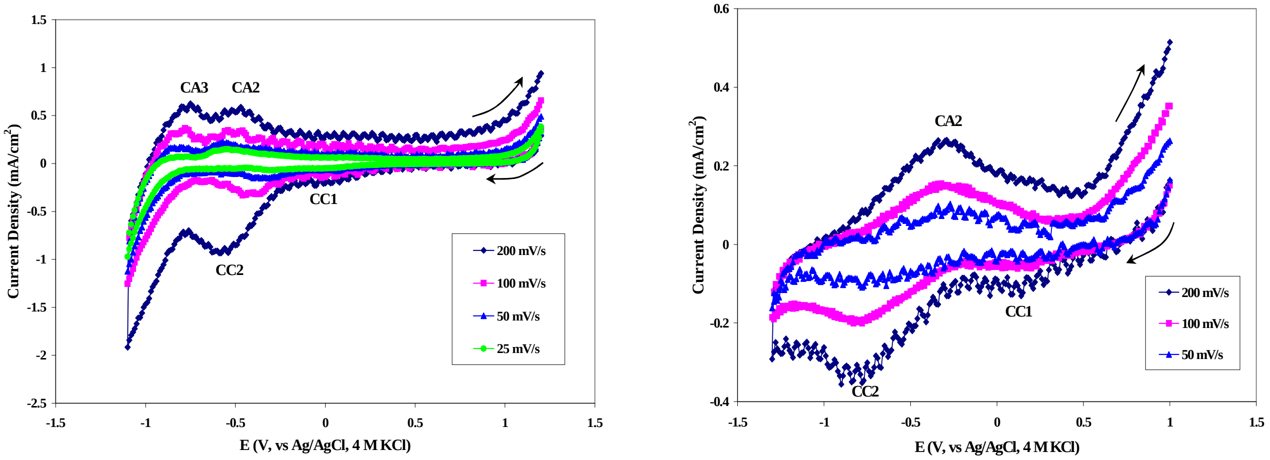

Figure 3. Cyclic voltammograms of ferric citrate solution containing 100 mg/L Fe3+ at pH 5.0 with platinum foil (left figure) and with 304SS (right figure) as the cathode. Arrows indicate the scan direction.

The right figure in Figure 3 shows CVs for the test carried out using 304SS as the cathode material. When a scan rate of 200 mV/s was used, the first cathodic peak (CC1, at 0.14 V) corresponded to the reaction shown in (Eq. (4)). The second cathodic peak (CC2, at –0.78 V) corresponded to the reaction shown in (Eq. (5)). At potentials down to –1.3 V, hydrogen evolution was not obvious. Hydrogen evolution at the Pt electrode was much more significant than that at the 304SS electrode as expected since the exchange current density for hydrogen evolution on Pt is about four orders of magnitude higher than that on 304SS [5]. The anodic peak CA2 corresponded to the reaction shown by (Eq. (9)).

3.2 Iron Deposition Tests

Iron deposition tests were conducted in simulated spent CAN-DEREM™ solutions at constant potentials determined from the CV tests to investigate the effects of test conditions on the current efficiency for iron deposition. At room temperature, the current efficiency for iron deposition on a Cu electrode (cathode) was higher than that on a 304SS cathode and more iron was removed from the solution when Cu electrode was used. The measured current at each potential was the sum of contributions from reduction of ferrous ions (Eq. (6)) and hydrogen evolution (Eq. (7)). The relatively low current efficiency for the 304SS electrode was expected because the exchange current density for hydrogen evolution on 304SS is one order of magnitude higher than that on Cu [6]. This is consistent with the observation that more hydrogen bubbles were produced when a 304SS electrode was used compared to a Cu electrode.

Since the purification system during the application of the CAN-DEREM™ process is operated at 60ºC, iron deposition tests were performed at 60ºC. When 304SS was used the iron removal increased with increasing cathodic potential (Figure 4); the highest amount of iron removed was ~ 40 weight% at an applied potential of -1.5 V. Current efficiencies for iron deposition at both 304SS and Cu electrodes were quite low, indicating that the hydrogen evolution dominated the cathodic reaction.

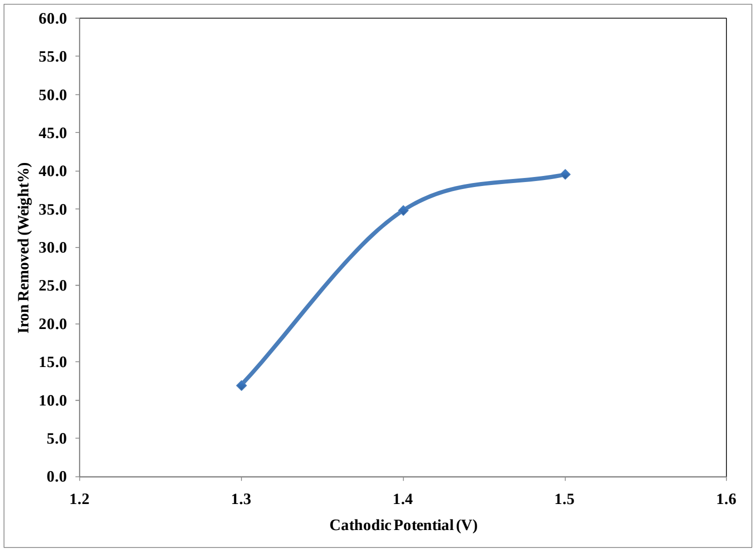

Figure 4. Iron removed (weight%) as a function of applied cathodic potential.

The data in Table 1 show that the current efficiency of iron deposition and the iron removal on the 304SS electrode were generally higher than those on the Cu electrode. It can be concluded that 304SS is more suitable as an electrode for iron deposition in the spent CAN-DEREM™

solution than Cu at 60ºC. The current efficiencies for iron deposition on 304SS and Cu decreased with increasing temperature from 25ºC to 60ºC; however, the amount of iron removed increased with increasing temperature. Increasing the temperature decreases the activation overpotentials of both iron deposition and hydrogen evolution reactions; however, the effect of temperature on hydrogen evolution may be more significant than its effect on iron reduction [7].

The data in Table 1 also show that the current efficiency for iron deposition increased with increasing pH at 60ºC. Increasing the pH of spent CAN-DEREM™ solution increased the degree of dissociation of the iron complex, leading to a reduction in the activation overpotential of iron deposition, and increasing the current efficiency [7]. The current efficiency on 304SS showed a maximum value of 4.9% at an applied potential of -1.4 V.

Table 1. Effect of test conditions on current efficiency for iron deposition and iron removed in spent CAN-DEREM™ solutions.

Test Variables				Current Efficiency (%)	Iron Removed (Weight%)
Cathode Material	**Applied Potential (V)**	**Temperature (ºC)**	**Initial pH**		
304SS	-1.4	25	4.0	5.7	5.6
Cu	-1.4	25	4.0	6.2	8.5
304SS	-1.4	60	2.9	3.3	13.5
Cu	-1.4	60	3.0	2.8	15.2
304SS	-1.5	60	3.0	2.5	13.8
304SS	-1.3	60	3.8	3.9	12.0
304SS	-1.4	60	3.9	4.9	34.9
304SS	-1.5	60	3.9	4.3	39.6
Cu	-1.3	60	3.8	1.2	2.7
Cu	-1.4	60	3.6	4.2	27.6

Figure 5 compares the surface morphology of the iron deposit on the 304SS and Cu electrodes. The deposit on the 304SS plate was silver-grey and loose, and when the electrode was lifted out of the solution at the end of tests, part of the deposit fell off. The deposit on the Cu electrode, on the other hand, was black and strongly adherent to the electrode surface.

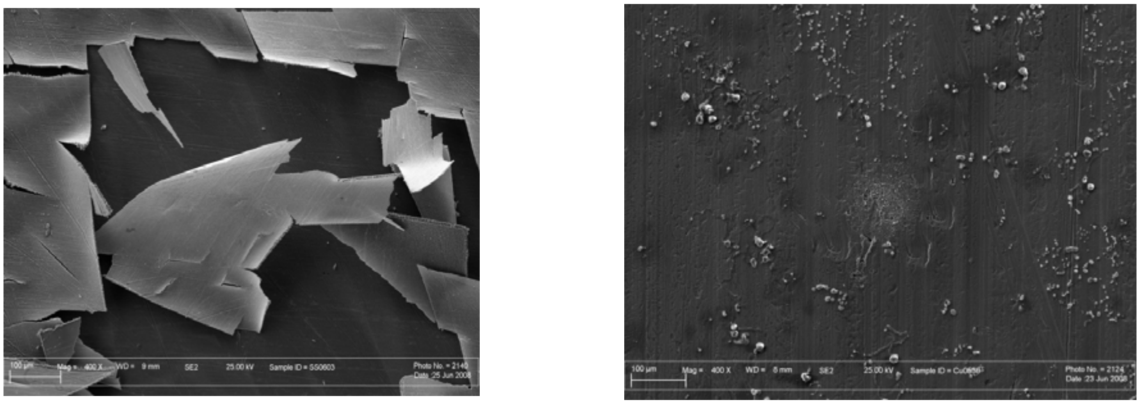

Figure 5. SEM images (X400 magnification) showing the surface morphology of the deposited layers on a 304SS plate (left image) and on a copper plate (right image).

EDS analysis of the deposit revealed that the Fe-rich deposit contained a trace amount of carbon and oxygen. The carbon contamination in the deposit may have originated from the CAN-DEREM™ reagents, which could be adsorbed at the cathode; however, carbon is also a ubiquitous contamination on most surfaces.

3.3 Cation Exchange Membrane Tests

Three types of membrane (Neosepta CMX, N424, and N324) were tested for their ability to transport iron. All three membranes are strongly acidic cation membranes containing sulphonic acid ($-SO_3^-H^+$)[2] functional groups in the polymeric matrix. The fixed negative charge in the matrix excludes mobile anions and permits transfer of mobile cations. The transport of ions not only depends on the composition and the structure of the membrane, but also depends on the chemical potential gradient, pH gradient and the mobility of ions [8].

Tests were conducted under various conditions to determine the effects of current, potential, electrolyte in cathode and anode compartments, cathode material, presence of ascorbic acid (reducing agent) and changes in pH of the spent solution and test duration on the amount of iron removed by the Neosepta CMX, N324 and N424 membranes. The solution in the middle compartment consisted of CAN-DEREM™ solution, 200 mg/L iron as ferric citrate and 880 mg/L ascorbic acid. During the tests, copious amounts of bubbles were generated at both the cathode and anode, indicative of hydrogen evolution on the cathode and oxygen evolution on the anode. At the end of the tests, black stains were noted on the cathode surface, due to the formation of metallic iron from reduction of ferric and ferrous ions.

The effect of pH on the amount of iron removed using membranes N324 and N424, at applied potentials of 15 V and 20 V are shown in Figure 6. The amount of iron removed increased with increasing pH at an applied potential of 15 V. Figure 6 shows that at an applied potential of 20 V using N324, the iron removed had its highest value, 44.4 weight%, at pH 3.0 and then decreased with increasing pH. This can be attributed to the formation of iron hydroxide precipitates on the membrane at pH higher than 3.0 and at 20 V, which retarded the transfer of iron ions [9].

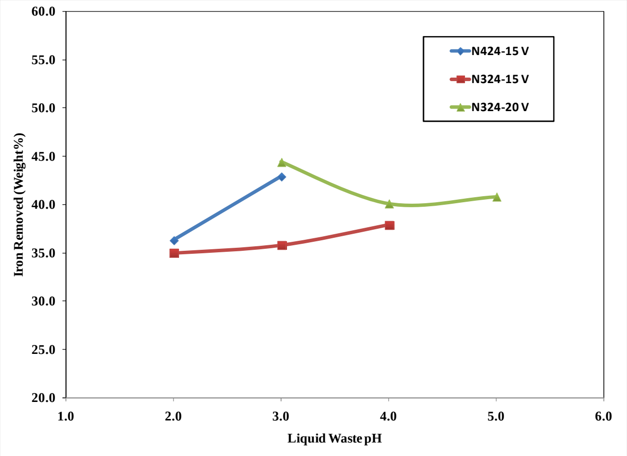

Figure 6. Effect of pH of test solution on the amount (weight%) of iron removed using N424 and N324 membranes.

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[2] Neosepta CMX is in sodium (Na^+) form.

The effect of test duration on the iron removed using Neosepta CMX and N324 membranes are shown in Figure 7. Both the cathode and anode solutions were CAN-DEREM™ plus 880 mg/L ascorbic acid at pH 4.0 when the Neosepta CMX membrane was tested. The catholyte was CAN-DEREM™ plus 880 mg/L ascorbic acid at pH 3.0 and the anolyte was 400 mg/L citric acid at pH 3 when N324 was tested. The cathode was a 304SS plate and the anode was Pt foil. The test results in Figure 7 show that the amount of iron removed using the Neosepta CMX and N324 membranes increased with increasing test duration. Up to 52.5 weight% of iron was removed after six hours using a N324 membrane.

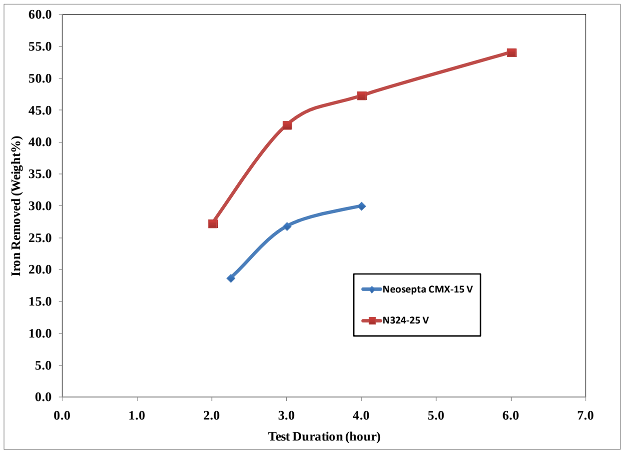

Figure 7. Effect of time on the amount (weight%) of iron removed using Neosepta CMX and N324 membranes.

The effect of applied potential on the amount of iron removed using a N324 membrane is shown in Figure 8. For this series of test the catholyte was CAN-DEREM™ solution plus 880 mg/L ascorbic acid, and the anolyte was 400 mg/L citric acid, both at pH 3. The cathode was 304SS and the anode was Pt foil, and the test duration was three hours at 60ºC. The test results in Figure 8 show that the amount of iron removed increased with increasing potential applied; at an applied potential of 35 V, 46 weight% of iron was removed.

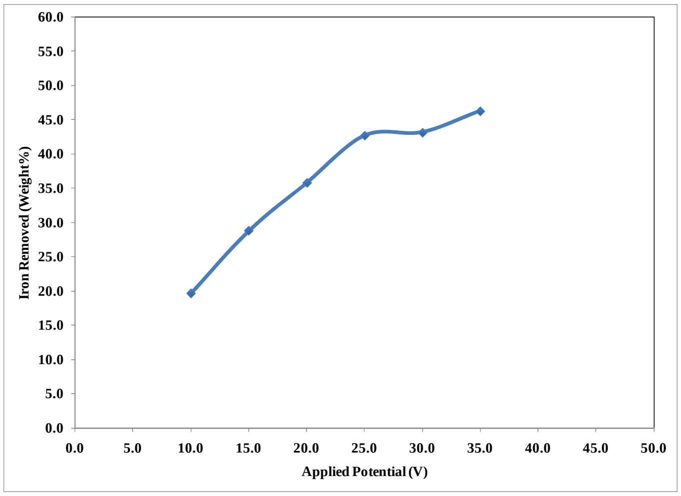

Figure 8. Effect of applied potential on the amount (weight%) of iron removed using a N324 membrane.

A limited number of tests on the removal of iron from spent IX resin with a N424 membrane were also conducted. IRN77, a strong acid cation resin and a solution of either ferrous sulphate or simulated spent CAN-DEREM™ was used to prepare the spent IX resin. The amount of iron removed using the N424 membrane from spent IX resin increased with decreasing conductivity of the middle compartment solution, with increasing applied potential, and with increasing time. However, the overall amount of iron removed from spent resin was always less than 10 % of the initial iron concentration on the spent resin.

4. CONCLUSIONS

An electrochemical method is being developed at AECL for the regeneration of liquid waste or spent IX resin generated during the application of CAN-DEREM™ or other decontamination processes. Cyclic voltammetry tests were conducted to determine the potential for the conversion of ferric ions to ferrous ions and to metallic iron. In the absence of a membrane and the potential determined from CV tests approximately 40 weight% of the iron was deposited on the cathode. When a membrane was used, higher applied potentials were required to remove iron from the liquid waste. The tests using membranes were conducted first using liquid waste to optimize the test conditions before testing the method on the spent IX resin. Based on tests performed to date, the following preliminary conclusions can be made.

- The current efficiency for iron deposition on a Cu electrode was higher than that on a 304SS electrode at room temperature. The current efficiency for iron deposition on 304SS and Cu electrodes decreased with increasing temperature from 25ºC to 60ºC. However, the amount of iron removed increased with increasing temperature. The current efficiency for iron deposition increased with increasing pH from 3 to 4 at 60ºC.
- The iron deposit on the 304SS electrode was silver-grey and loose, while the deposit on the Cu electrode was black and strongly adherent to the electrode surface.
- The amount of iron removed by the Neosepta CMX and N324 membranes from the spent CAN-DEREM™ solution increased with increasing potential from 15 V to 35 V, and with increased test time from 2.25 hours to 6.0 hours. The material of construction of the cathode (304SS or Cu) did not have a significant effect on the amount of iron removed under these conditions.
- Addition of ascorbic acid as a reducing agent to spent CAN-DEREM™ solution significantly enhanced the iron transport through membranes. This is due to conversion of ferric ions to ferrous ions which are easier to transport through the membranes.
- The amount of iron removed by the N324 and N424 membranes increased with increasing pH from 2.0 to 4.0 at an applied potential of 15 V. However, when the applied potential was 20 V, the iron removed decreased with increasing pH from 3.0 to 5.0.

The electrochemical method is proved to be promising and suitable for the treatment of liquid waste. However, further studies of other types of membranes and optimization of the parameters for the removal of metals from spent IX resin are required.

5. ACKNOWLEDGEMENT

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