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WASTE SALT RECOVERY, RECYCLE, AND DESTRUCTION*

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Introduction

Starting in 1943 and continuing into the 1970s, radioactive wastes resulting from plutonium processing at Hanford were stored underground in 149 single shell tanks. Of these tanks, 66 are known or believed to be leaking, and over a period are believed to have leaked about 750,000 gal into the surrounding soil. The bulk of the aqueous solution has been removed and transferred to double shell tanks, none of which are leaking.

The waste consists of 37 million gallons of salt cake and sludge. Most of the salt cake is sodium nitrate and other sodium salts. A substantial fraction of the sludge is sodium nitrate. Small amounts of the radionuclides are present in the sludge as oxides or hydroxides. In addition, some of the tanks contain organic compounds and ferrocyanide complexes, many of which have undergone radiolytic induced chemical changes during the years of storage.

As part of the Hanford site remediation effort, the tank wastes must be removed, treated, and the residuals must be immobilized and disposed of in an environmentally acceptable manner. Removal methods of the waste from the tanks fall generally into three approaches: dry removal, slurry removal, and solution removed. The latter two methods are likely to result in some additional leakage to the surrounding soil, but that may be acceptable if the tank can be emptied and remediated before the leaked material permeates deeply into the soil. This effort includes three parts: salt splitting, acid separation, and destruction, with initial emphasis on salt splitting.

Technical Background

For a long time it has been possible to do salt splitting with just one or two ion permeable membranes and two electrodes. This process is inherently inefficient from the standpoint of energy consumption because for every equivalent of salt split, one or more

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equivalents of both H_2 and O_2 are produced. In the one-membrane process, in particular, further coulombic inefficiencies are present because some unwanted ion from an electrode reaction will permeate the membrane in parallel with the desired permeable ion.

This project has focused on the use of bipolar membranes that, when used in conjunction with anion and cation permeable membranes (as in electrodialysis), can be combined into cells of 3 membranes each and hundreds of cells can be put into a stack with only a single pair of electrodes. This avoids most of the previously mentioned inefficiencies and the technology is finding rapid commercial application for recycling and waste minimization. Because most metal hydroxides are not soluble in basic solution except for those in Group I of the periodic table, all heavy metal ions must be removed by preprocessing. The underlying reason is that within a cell stack, cations permeate through one type of membrane into a solution that is basic. In fact, it can be two molar in hydroxide ion and the heavy metal ions that permeate into this stream will precipitate on the exit face of the membrane, thus fouling the membrane and rendering the entire cell stack inoperable.

The key development in this process was the bipolar membrane that allows stacking. Such a membrane is capable of causing dissociation of water molecules into hydrogen and hydroxide ions at electric potentials across the membrane as low as 0.6 V, although this is the reversible voltage and 0.8 V is usually needed to pass useful current. The bipolar membrane can be an intimately bonded laminate of an anion and cation permeable membrane or it may be an unlaminated membrane in which different ionic functional groups have been added to either side so as to accomplish the same effect. Water enters either side of the membrane and permeates to the charge discontinuity plane in the center where the water is dissociated in a locally high electric field.

Brine is circulated in some compartments, with product acid and base being withdrawn from the two adjacent compartments, which also may be recirculating. As already mentioned, hundreds of cells can be incorporated into a stack so the relative amount of hydrogen and oxygen produced is 1% or less that of a simple one of two-membrane cell. Furthermore, oxidation and reduction reactions associated with water electrolysis requires 2.3 V. Stacking the 3 membrane cells where the bipolar membrane requires only 0.6 V to create the desired hydrogen and hydroxide ions provides an important 1.7 V saving per cell. This advantage is obtained at the same time the relative volume of both hydrogen and oxygen produced is decreased in proportion to the number of cells in the stack. Many safety analysts find any hydrogen source a threat that must be addressed. In the case of a cell stack for salt splitting, an oxygen depolarized cathode may be used. In such an arrangement, the oxygen produced at the anode is routed to the

outside face of a porous cathode. The cathode contains a catalyst that causes the oxygen gas to react with the hydrogen ion as it is discharged, forming water. Therefore, no hydrogen gas is evolved.

In applying salt splitting to tank wastes there are two special concerns that must be resolved before the technology can be recommended for use. They both relate to membrane longevity. Specifically, membrane life time must be determined at operating conditions that will include exposure to a mixed acid product that will probably be 0.5 M or greater and possibly to ionizing radiation. It is desirable to remove as much of the radionuclides as possible before the salt solution is introduced into the stack. Of greatest concern are Cs and Sr, although the hydroxide of Sr is only slightly soluble and would be removed regardless. Nevertheless, membrane materials, e.g., fluorocarbons that show a high degree of resistance to degradation by oxidizing acids, are quickly degraded by moderate doses of ionizing radiation. The reciprocal situation also prevails for commercial membranes: good radiation resistance implies poorer chemical resistance.

The expected method for separating the mixed acid product is multistage fractionation. This is a well-known industrial technology and is probably the best developed and most robust separation technology used. It is based on the difference of relative vapor pressures of different liquids as functions of temperature, concentration, and total pressure. Many reference and text books are available on this technology and further description here is not warranted.

Experimental Work on Membranes

It was decided to work with a limited number of membranes that represented a typical offering from a U.S. vendor. For this purpose, Riapore[®] membranes were selected. Three kinds of materials were selected for both cation permeable and anion permeable membranes. The three materials were polytetrafluoroethylene (PTFE), another fluorocarbon polymer with ether cross linking bonds (FEP), and polypropylene (PP). Another well known product line is Nafion[®] by Dupont. Most other suppliers are in other countries. The six membranes selected are far from the entire product line but are representative of the materials available. Bipolar membranes were not included in this test series because only one domestic supplier was known at the beginning of the project and resources for materials testing were very limited.

Complete evaluation of the membranes was not possible. It would have required a large number of specimens to be tested prior to chemical exposure, a large matrix of chemical concentrations and temperatures during exposure, and then a very large number of post exposure tests for the relevant physical properties. Then it would have been

possible to determine quantitatively if changes had occurred, if so by how much, and the degree of confidence in the results on a statistical basis, could be reported. Instead, we chose to expose the cation permeable membranes to 1 M NaOH, the anion permeable membranes to 1 M HNO₃, and all at room temperature for 100 days. No changes were expected for the membranes exposed to NaOH because the conditions were milder than those normally used industrially. They, therefore, might be thought of as a control group. In the case of HNO₃ exposure, the expected outcome was far less certain. These membranes are not usually exposed to oxidizing acids, although the fluorocarbon polymer membranes were expected to show little change because the full density polymers are very resistant. All the tests performed on the membranes were performed in accordance with Method A as outlined in ASTM D 882-88, "Standard Test Method for Tensile Properties of Thin Plastic Sheeting."

Membrane Test Results and Comments

All the materials were tested at two different crosshead rates, 0.1, and 10 inches/minute. ASTM D 882-88 recommended using the two different crosshead rates. The slower one, 0.1 inches/minute, was used to determine the modulus of elasticity, and yield strengths. The faster crosshead rate was used to determine the ultimate and breaking strengths. The gage length for calculating the strain for all tests equaled 0.63 inches. In addition, the test sample's dry thickness was used to calculate the stress and ultimate strength.

For those specimens that did not break within the gage length, the specimen was slipping in one or both of the grips. While data was obtained, it is not of the same validity as the rest and cannot be used with confidence. Only the specimens that did break in the gage length should be used. Their rather small number and the amount of scatter in the data for identical samples is such that on a statistical basis with reasonable confidence, one cannot assert that the chemical exposure degraded the membranes. The qualitative observation based on specimen appearance and the numerical data is that no significant change occurred, which is very encouraging.

Experimental Work on Salt Splitting

Like the membrane testing, the salt splitting work was limited in scope and is to be considered as proof-of-principle for sodium nitrate based systems as contrasted with a detailed evaluation of the technology for the treatment of tank wastes. Data acquisition, storage, and display were done by computer in addition to control of some of the flows and current supplied to the cell stack. Salt was slowly added and the product streams

were recirculating to provide the desired concentrations with small bleed streams of each being removed to the product storage tanks.

Two sets of cell stack performance runs were performed with slightly (2.5%) different concentrations of sodium nitrate feed. The main parameters being evaluated were temperature and current density so that cell (not the stack) performance at full scale operating conditions could be estimated. From these data, one can extrapolate upwards in temperature (which reduces the cell voltage) and current density (which increases the cell voltage) to arrive at an estimate of 2.54 V/cell at the anticipated operating conditions. This voltage is considered economical in commercial applications. Significant changes in concentration of products and/or feeds would cause additional shifts, but sodium nitrate splitting seems quite feasible on the basis of energy costs.

The cell stack consisted of three recirculating loops with feed to and bleed from each in order to maintain uniform concentrations during a run. There were four cells in the stack. Membranes used were CMV (cation permeable) and AAV (anion permeable), both manufactured by Asahi Glass. The bipolar membrane was produced by WSI Inc., the supplier of the cell stack and ancillary hardware. With spacers in place, each cell is 0.6 cm thick. The active area of each cell is 94 cm² and four cells in parallel were used, although the stack can be expanded to accommodate eight.

A short investigation was made on the influence of product nitric acid concentration on coulombic efficiency. While current and cell voltage give a good measure of power consumption, the power is a poor figure of merit for energy per unit of feed processed. The cell voltage is known to be relatively insensitive to the sodium hydroxide product concentration, but the influence of product nitric acid concentration was not known. Three runs at differing HNO₃ product concentrations were run with the NaNO₃ feed and NaOH product concentrations held constant at 2M. Current efficiency increases substantially as nitric acid product concentration is dropped. The current efficiency at 0.5M HNO₃ is 88%, about the same as that for NaOH production. Coincidentally, it has been found that 0.5M HNO₃ is an excellent first stage leaching agent for the radionuclides found in the Hanford tank sludges.

One final experiment was run to see if any anomalous effects would be present if the feed was a mixture of salts. The salts chosen were sodium nitrate and sodium sulfate in the concentration ratio typical of Hanford salt cake. Nothing unexpected was observed. One would expect, however, that the sulfate ion mobility through the membrane would be different than the nitrate due to twice the ionic charge and a larger size.

Fractionation of Mixed Acids

The mixed acids will be more corrosive than if they were pure. Therefore, the fractionation column, including the boiler and condenser are made of glass. Ceramic packing is used, and fully assembled the system is 26 ft. tall, providing approximately ten theoretical stages of separation. The system is equipped with vacuum capability so a substantial amount of separation can be achieved at low temperatures. In addition, vacuum conditions allow certain azeotropes that form at ambient pressure to be broken. As presently configured, three product streams can be produced from the column: the overhead, the liquid at mid column, and the still bottoms. Experimental work is deferred pending funding decisions.

Summary and Conclusions

On the basis of work performed to date, salt splitting of the Hanford salt cake and brines appears feasible. The product sodium hydroxide is partially recycled. The balance can be converted to soda-lime glass for use in windows or else cast as logs for disposal. The product acids can be separated using multistage fractionation for reuse. Surplus nitric acid can be converted to air and released, while surplus hydrochloric acid can be immobilized. Salt splitting technology itself has proved to be an economical solution for a number of industries and in at least one instance, an actual money maker, when radioactivity was not a factor.

There is no other known work on sodium nitrate salt splitting. Nitric acid is expected to be more damaging to the anion exchange and bipolar membranes than nonoxidizing mineral acids. Long-term performance at operating conditions is still to be determined, but improvements in the membranes available can also be expected in the future. More extensive testing of currently available membranes is clearly in order.

Based on recent commercial acceptance of the process, its advantages cannot be ignored. These include high energy efficiency, minimization of waste, no noxious gaseous effluents, inherently safe operating conditions near ambient temperature and pressure, and an industrial base from which to draw.