A Ceramic Membrane to Recycle Caustic in Low-Activity Waste Stream Processing

The Office of Waste Processing is sponsoring an R&D project with Ceramatec, Inc. to develop a ceramic membrane capable of separating sodium from the Hanford Low Activity Waste (LAW) stream. The Hanford High-Level Waste (HLW) tanks must be maintained in a caustic environment to inhibit corrosion. Consequently, they contain large quantities of NaOH. Ultimately the HLW will be retrieved, separated into HLW and LAW streams, with both streams being vitrified at the Waste Treatment Plant (WTP). Prior to processing, additional NaOH will be added to the LAW stream to solubilize the alumina, preventing alumina precipitation, but further increasing the NaOH quantity. This project's goal is to separate the sodium from the LAW stream prior to vitrification which will allow the NaOH to be recycled and further reduce the amount of vitrified waste product for disposal.

Ceramatec is developing a ceramic membrane based on a family of sodium phosphate ceramic materials referred to as sodium (**Na**) **S**uper **I**on **Con**ductors (NaSICON). Unlike polymer membranes, the NaSICON membrane does not foul in the presence of solids or complex elements. In addition, the membrane provides near zero transport of water and no back diffusion or transport of anions which allows high ionic specificity to sodium over other elements present in the LAW stream. The membranes are chemically stable to corrosive chemicals, operate in a wide pH range, and are thermally stable up to 1,200 ^{o}C.

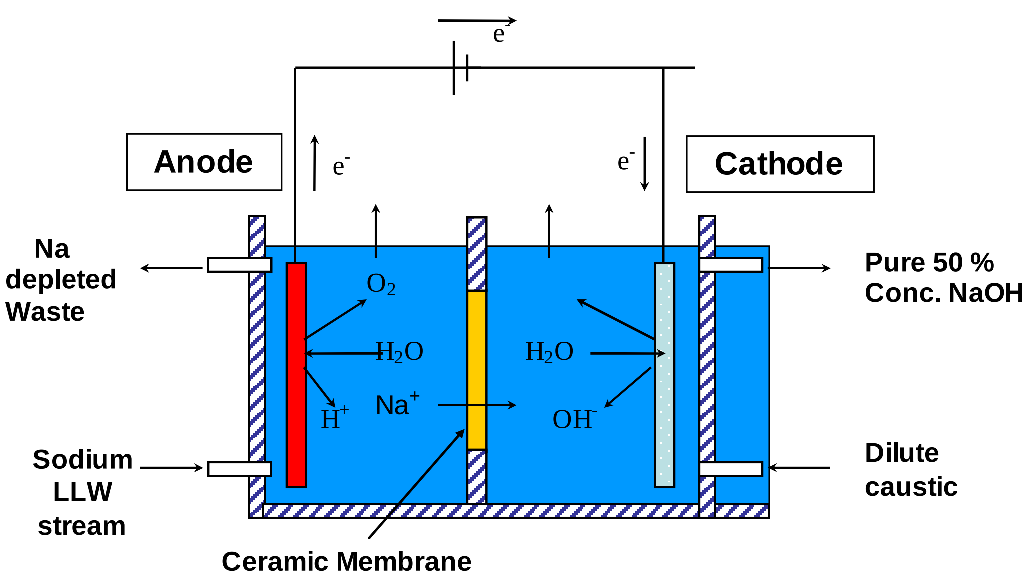

Figure 1: Schematic of a Two Compartment Electrochemical Process Using the NaSICON Membrane

Figure 1 illustrates the two compartment cell configuration. The waste solution is pumped to the anode compartment, and an electrical potential is applied to the cell. The sodium ions permeate through the membrane to the catholyte solution where caustic is concentrated. The membrane rejects most other monovalent cations (e.g., K^+, Cs^+) because of their large size and other multivalent ions due to electro-neutrality constraints. The charge balance in the anode compartment is maintained by electrolyzing water to oxygen gas and protons (H^+). The charge balance is balanced in the catholyte by electrolyzing water to hydrogen gas and hydroxyl ions (OH^-). As protons are generated in the anode compartment, the pH drops and the waste stream becomes less alkaline. Production of hydroxyl ions in the cathode compartment results in a rise in pH as the NaOH product is recovered.

Results to date have been highly encouraging:

- Sodium transport efficiencies averaged 93% for testing with non-radioactive waste simulants and 99% for test with actual radioactive tank waste.

- Experiments produced Na transport rates in good agreement with theoretical Na transport rates based on applied current. Average Na separation rates of 9.6 kg/day/m^2, 10.3 kg/day/m^2, and 10.3 kg/day/m^2 were observed.

- The NaSICON membrane is highly selective to sodium. No transport of any cations or anions was detected except for Na and ^{137}Cs. Decontamination factors on the order of 2000 were observed with respect to ^{137}Cs.

- The electrochemical cell system successfully produced a 19 M NaOH (50 weight %) solution with no observable membrane performance loss.

The project is currently focusing on:

- Establishing the performance reliability of the electrolytic cells to make 50 weight % caustic from Low Activity Waste (LAW) simulant and establish the impact of the process operating conditions on the stability of the NaSICON membranes and other cell components.

- Determining the practical amount of sodium that can be recovered from the LAW stream based upon the sodium flow sheet requirements as developed by PNNL.

- Determining the radiation and chemical stability of the NaSICON membrane and the other cell components.

- Scaling-up the process to fabricate planar and tubular NaSICON ceramics;

- Developing low cost electrodes and non hydrogen evolving air cathodes;

- Evaluating the technology benefits of tubular and planar membrane design configuration based on process-flow requirements at the Site, robustness and device reliability for application at WTP;

- Developing and testing a bench scale unit (electrolytic ceramic device) for caustic recycling demonstration at Hanford. Figure 2 illustrates a pilot-scale membrane module.

Figure 2: Pilot Scale Electrochemical Reactor Module

The three-inch diameter ceramic membrane is planned to be assembled in plastic scaffolds (membrane housing plates). Up to 48 membranes, assembled in a scaffold, are mounted in a plate and frame support. As illustrated in Figure 2, up to 40 repeat scaffold/electrode units may be configured into a production cell. Each production cell can process up to 1.4 kg/scaffold-day of sodium in the feed LAW stream. For full-scale operations, the WTP will require approximately 48 production cell modules.

The Pacific Northwest National Laboratory (PNNL) conducted an economic analysis of NaOH recycle using the Ceramatec membrane and concluded that the concept may provide a significant return on investment. Although considerable developmental work yet remains, the Ceramatec NaSICON membrane may appreciably diminish the amount of Hanford tank waste requiring vitrification, and, hence, greatly reduce the WTP life-cycle cost.

The current technology development and demonstration phase commenced August 2008. Completing this phase of development and bench-scale demonstration of the NaSICON membrane testing should be concluded by December 2009.