

Salt Splitting with Ceramic Membranes

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EM Focus Area: high-level waste tank remediation

Task Description

The purpose of this task is to develop ceramic membrane technologies for salt splitting of radioactively contaminated sodium salt solutions. This technology has the potential to reduce the low-level waste (LLW) disposal volume, the pH and sodium hydroxide content for subsequent processing steps, the sodium content of interstitial liquid in high-level waste (HLW) sludges, and provide sodium hydroxide free of aluminum for recycle within processing plants at the DOE complex. Potential deployment sites include Hanford, Savannah River, and Idaho National Engineering Laboratory (INEL). The technical approach consists of electrochemical separation of sodium ions from the salt solution using sodium (Na) Super Ion Conductors (NaSICON). As the name implies, sodium ions are transported rapidly through these ceramic crystals even at room temperatures.

Technology Needs

Many radioactive aqueous wastes in the DOE complex have high concentrations of sodium, which negatively affects waste treatment and disposal operations. Sodium can decrease the durability of waste forms such as glass and contributes to large disposal volumes. Waste treatment processes such as calcination, cesium ion exchange, and sludge washing are made less efficient and more expensive because of the high sodium concentrations. Some disposal strategies^{1,2} call for adding more sodium to the wastes as they are prepared for conversion to final waste forms. Separation

and recycle of sodium from radioactive wastes can potentially reduce costs by reducing waste disposal volumes, improving the efficiency of waste treatment processes, and avoiding the procurement of additional chemicals.

Scientific Background

The technology being developed involves using an electrochemical salt-splitting process based on inorganic ceramic membranes, as shown in Figure 1. In this process, the waste is added to the anode compartment of the electrochemical cell, and an electrical potential is applied to the cell, subsequently driving sodium ions through the membrane while most other cations (e.g., K^+ , Cs^+) are rejected by the membrane. The charge balance in the cell is maintained by the electrolysis of water. The accumulation of potentially flammable gas mixtures can be prevented by providing adequate volumes of a sweep gas or by using oxygen and a gas diffusion electrode. As H^+ is generated in the anode compartment, the pH drops while the production of OH^- in the cathode compartment results in a rise in pH as sodium hydroxide is produced.

The ceramic membranes are from a family of materials known in the electrical battery industry as sodium (Na), super fast ionic conductors (NaSICON). The unique characteristic of NaSICON ceramics is that they possess channels within the crystal structure for fast sodium ion conduction. Silica tetrahedra "rings" and sodium and heavy metal ions form the structure around these channels, which are filled with highly mobile sodium ions. The primary NaSICON compo-

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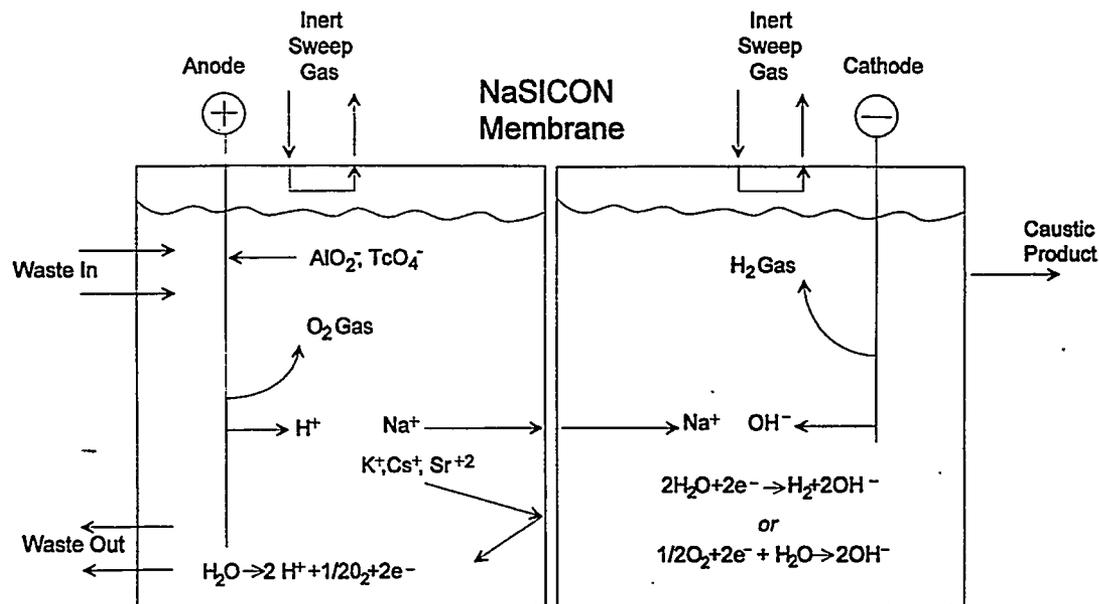


Figure 1. Schematic of an electrochemical process using the NaSICON membrane. Anolyte Composition: Hanford Simulant: 1.5 M NaNO_3 , 0.2 M $\text{Al}(\text{NO}_3)_3$, 1 M NaOH . Catholyte Composition: 1 M NaOH . Temperature: 70°C. Applied Potential: 8-10V.

sitions that have been investigated are based on rare earth (RE) ions (i.e., $\text{Na}_3\text{RESi}_4\text{O}_{12}$).

In contrast to conventional organic-based bipolar or ion exchange membranes used in salt splitting, ceramic-based membranes are much more resistant to gamma/beta radiation and are highly selective for sodium ions. This high selectivity is useful for minimizing the transport of fission products (e.g., ^{137}Cs) and nonradioactive components (e.g., K^+), parasitic hydronium conduction, and reducing membrane fouling by multivalent metal ions (e.g., Ca^{+2} , $\text{Fe}^{+2,3}$, Al^{+3}). Radiation effects on the organic membranes could lead to rapid failure and high maintenance costs.

Technical Approach

Initial investigations were directed at selecting and modifying membrane compositions compatible with the expected chemical and radioactive environment. FY 1996 work consists of completing a preconceptual design of a ceramic membrane-based salt splitting process for sodium separation and caustic recycle, manufacture and nonradioactive demonstration testing

of a unit cell of this design, preparing for radioactive testing, and an applications study. The preconceptual design is primarily to distinguish critical issues for testing and provide a vision for potential users. Work in FY 1997 is expected to include one or more bench-scale demonstrations with actual wastes and nonradioactive testing of the process at the pilot-scale.

Accomplishments

Rare earth-based NaSICON (RE-NaSICON) membranes were fabricated, tested, and evaluated against an initial set of criteria developed on the basis of potential applications. These tests confirmed the high selectivity of RE-NaSICON for sodium ions relative to hydronium, cesium, aluminum, and strontium ions in alkaline waste and slightly acidic solutions. Testing of membrane samples irradiated with a ^{60}Co gamma source indicated an initial decrease in conductivity that recovered after current was passed. Ionic conductivities and current densities achieved in dysprosium-based NaSICON were comparable to those of bipolar

or cationic organic membranes. Excellent compatibility with basic or even slightly acidic solutions was observed with dysprosium-based NaSICON; however, mass loss and surface cracks were observed in strong acids. Acid-resistant ceramic compositions are being developed under another DOE program.

Recirculating cell experiments with an advanced RE-NaSICON membrane were conducted at Ceramatec Inc. to demonstrate sodium removal from a Hanford tank waste simulant. The anolyte pH decreased from 12.6 to ~7 as 60 g of sodium ions were transported through the advanced RE-NaSICON membrane. (Figure 2). As pH levels decreased to <9, precipitation of aluminum-hydroxide (or salts) occurred. However, the throughput of the cell appeared to fall only slightly.

Benefits

Potential applications have been identified at Hanford, INEL, and Savannah River and include 1) caustic recycle, 2) pH adjustment and reduction of competing cations for enhancement of cesium ion exchange

processes, 3) sodium reduction in high-level waste sludges, and 4) sodium removal from acidic wastes to facilitate calcining.

Hanford and Savannah River sites have large inventories of radioactively contaminated wastes that consist primarily of sodium salts. Separation and recycle of the caustic from the tank wastes could reduce the waste disposal volume and avoid the cost of purchasing fresh caustic. Potential uses for the caustic include sludge leaching, regeneration of ion exchange resins, corrosion inhibition in carbon steel storage tanks, and tank waste retrieval.

The efficiency and chemical stability of some cesium ion exchange materials is decreased at high pH levels. For example, the distribution coefficient (K_d) for a powder form of crystalline silicotitanate (TAM-5-11) was reported to increase from about 150 mL/g at pH 14.1 to about 1600 at pH 12 in a Hanford simulant.³ This difference would result in a tenfold reduction in the required amount of exchanger. This reduction in pH would also permit the use of granular

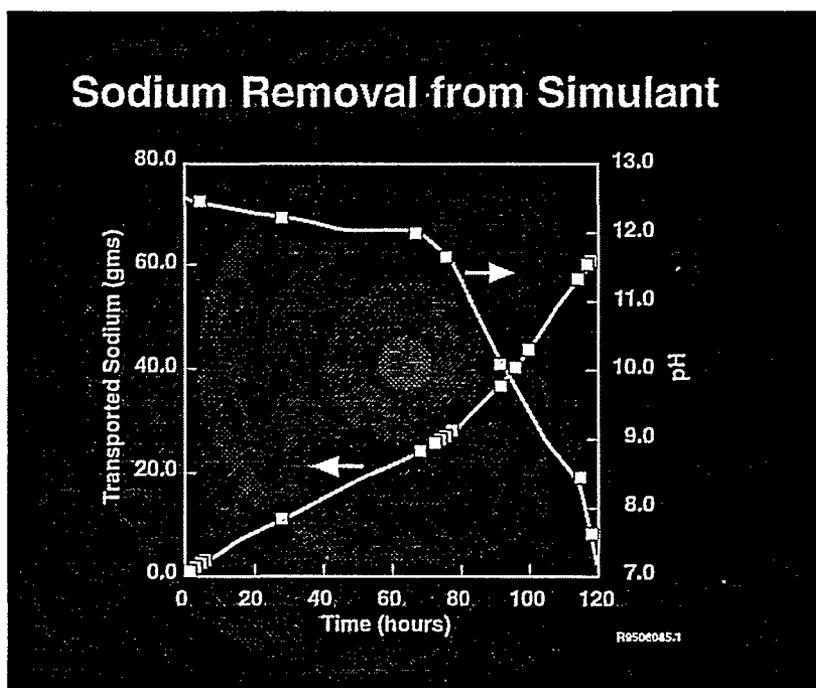


Figure 2. Bench-scale process demonstration with Hanford waste simulant.

potassium cobalt hexacyanoferrate(II). This material has extremely high cesium K_d 's but hasn't been considered for application at Hanford because it is unstable in solutions having a pH >13.

Many of the sludges at Hanford and Savannah River will possess interstitial liquid containing sodium concentrations as high as 5 M. Current plans are to remove the sodium by dilution of the interstitial liquid with 0.01 M sodium hydroxide and sodium nitrite with subsequent solid/liquid separation. Electrochemical sodium separation offers the potential for directly removing sodium from the sludge, thereby reducing water usage and radionuclide carryover during solid/liquid separation.

Sodium removal is also considered beneficial for treating 5.7 million gallons of sodium-bearing waste at the Idaho Chemical Processing Plant (ICPP). Calcination at high temperatures is an established process at the ICPP used to convert nonsodium bearing liquid waste into a granular solid. Sodium tends to cause bed agglomeration, anion volatilization, and alpha aluminum formation. Current mitigation strategies include chemical additions or calciner equipment modifications. These strategies slow processing rates and increase waste volume and costs. Removing the sodium before calcining would allow direct calcination of the waste and provide caustic for recycle.

Technology Transfer/Collaborations

Collaborations are under way with Westinghouse Savannah River Company in the design of electrochemical cells for radioactive waste processing and assessment of caustic recycle applications for alkaline supernates and sludge leaching/washing solutions. A sodium-bearing waste simulant will be provided for an initial nonradioactive test at INEL. WHC will participate in design reviews of the preconceptual design, applications studies and process demonstrations on Hanford supernate if applicable.

Ceramatec Inc. (Salt Lake City, Utah) is being aided by Pacific Northwest National Laboratory to adapt nonradioactive electrochemical waste treatment technology to a radioactive environment. Ceramatec Inc. is refining the manufacturing process to produce unit electrochemical cells incorporating the RE-NaSICON membrane. The unit cells are expected to include bench, pilot, and full scale testing. A production run will be completed followed by electrical and mechanical testing to identify and resolve production issues. Initial testing of the unit cells with simulants will be conducted at Ceramatec.

Ceramatec Inc. is funded by DOE's Office of Energy Efficiency and Renewable Energy under a separate program to provide technology that would permit the salt splitting of pulp/paper mill waste into a sodium hydroxide stream and a sulfuric acid product. The primary milestone in this program is development of a NaSICON-type product that is compatible with strong acids. This program is being monitored because some applications require or may benefit from an acidic processing environment.

Anil Virkar and Jan-Fong Jue, University of Utah, participated in this task in FY 1995 and continue membrane development. Materials and Systems Research is funded under the Small Business and Innovative Research program to examine new types of NaSICON membranes.

Keywords

NaSICON, salt splitting, caustic, sodium hydroxide, separation, recycle

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