

SALT SPLITTING OF SODIUM-DOMINATED RADIOACTIVE  
WASTE USING CERAMIC MEMBRANES

G. W. Hollenberg  
C. D. Carlson  
A. Virkar<sup>(a)</sup>  
A. Joshi<sup>(b)</sup>

August 1994

Presented at the  
Spectrum '94 Nuclear and Hazardous Waste Management  
International Topical Meeting  
August 14-18, 1994  
Atlanta, Georgia

Prepared for  
the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory  
Richland, Washington 99352

- (a) University of Utah, Salt Lake City, Utah  
(b) Ceramatec, Salt Lake City, Utah

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

# SALT SPLITTING OF SODIUM-DOMINATED RADIOACTIVE WASTE USING CERAMIC MEMBRANES

G. W. Hollenberg and C. D. Carlson  
Pacific Northwest Laboratory  
P.O. Box 999  
Richland, Washington 99352  
(509) 376-5515

Anil Virkar  
University of Utah  
2220 Merrill Eng. Bldg.  
Salt Lake City, Utah 84112  
(801) 581-5396

Ashok Joshi  
Ceramatec  
2425 South 900 West  
Salt Lake City, Utah 84119  
(801) 972-1925

## ABSTRACT

The potential for salt splitting of sodium dominated radioactive wastes by use of a ceramic membrane is reviewed. The technical basis for considering this processing technology is derived from the technology developed for battery and chlor-alkali chemical industry. Specific comparisons are made with the commercial organic membranes which are the standard in nonradioactive salt splitting. Two features of ceramic membranes are expected to be especially attractive: high tolerance to gamma irradiation and high selectivity between sodium and other ions.

## I. INTRODUCTION

Many radioactive waste streams in the DOE complex consist of high concentrations of sodium salts containing environmentally-significant quantities of radioactive impurities. A prime example is the Hanford Tank Waste, (50 million gallons) which consists of large quantities of sodium nitrate as the result of sodium hydroxide neutralization of various acidic waste streams associated with weapons production. The ultimate disposal of the high-level waste constituents (HLW) is in the form of a HLW waste glass for geological burial. Because of the high concentration of sodium in this waste and because of its detrimental effect on leachability of the glass produced, separation of the sodium could provide a HLW glass volume reduction of up to a factor of 200. Removal of sodium will lead to the largest reduction of HLW volume in comparison to other cations.

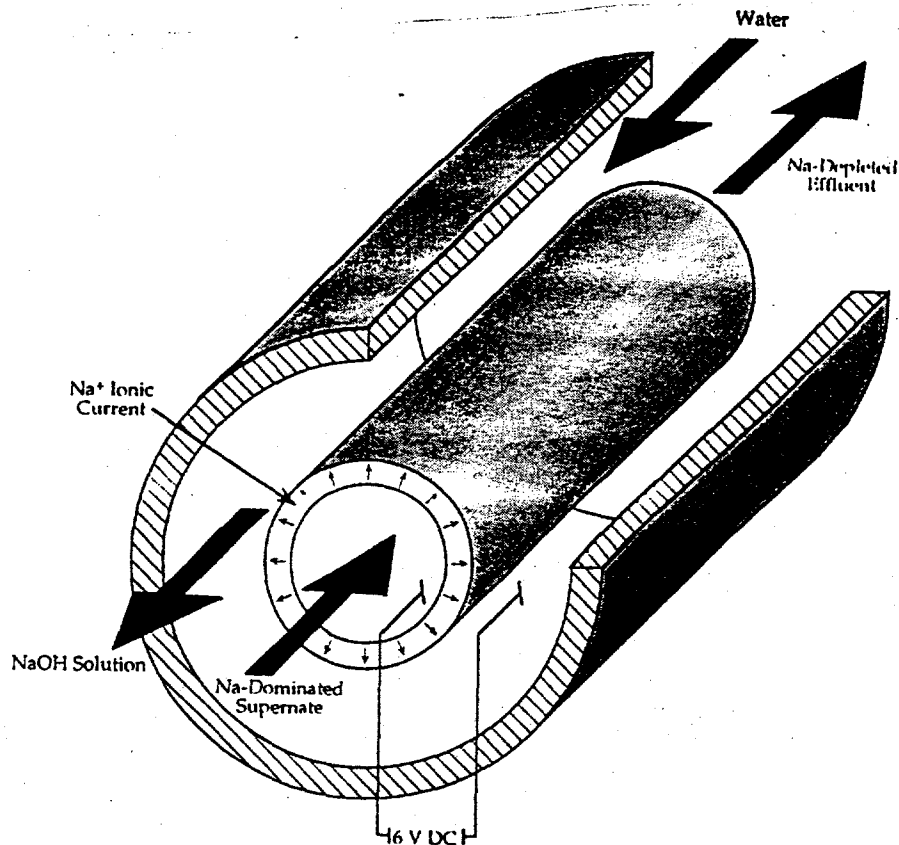
The objective of the salt splitting process is to separate nonradioactive sodium from contaminated sodium salts prior to other pretreatment processes in order to: 1) concentrate the waste in order to reduce the volume of subsequent additives and capacity of equipment,

2) decrease the pH of the waste in preparation for further processing, and 3) provide sodium with very low radioactivity levels for caustic washing of sludge or low level and mixed waste vitrification.

## II. APPROACH

The proposed technical approach consists of electrochemical separation of sodium ions from the salt solution, commonly referred to as the supernate, immediately after removal from storage or at least with minimal chemical processing. As schematically shown in Figure 1, the sodium-dominated supernate would flow through a dense ceramic tube composed of a sodium ion conductor which essentially clean water flowed across its exterior. Because the membrane is fabricated from a ceramic, a tubular configuration is normally adopted rather than the plate type configuration common to organic membranes. Application of a small DC voltage across the tube wall causes splitting of the  $\text{NaNO}_3$  or other salts with subsequent sodium ion transport through the ceramic tube. This process concentrates the nitrate (and nitrite) ions and radioactive elements in the original process stream since the ceramic is not permeable to these substances.

Salt splitting has been successfully used in many nonradioactive applications in the past, primarily with the use of fluorinated hydrocarbon membranes. In many commercial applications, salt splitting permits recycling of the resultant base and acid streams. A classical industrial example is the production of caustic soda, i.e., sodium hydroxide, in the chlorine-alkaline industry. A perfluorinated membrane, such as Nafion (du Pont de Nemours, U.S.A.), have been used to replace the mercury-cell, Krebs technology for production of caustic soda. Some plants produce hundreds of metric tons per day. Ceramic, Sodium fast ion conductors, such as



**Figure 1.** Schematic of sodium fast ion conductor being used to separate sodium from a sodium-dominated supernate.

NASICON, have also been considered for such applications. It is projected that these ceramic membranes will possess better performance in terms of: 1) ion selectivity, and 2) irradiation stability.

### III. ION SELECTIVITY

NASICON,  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ , is a class of material compositions with a particular crystal structure that permits very rapid diffusion of  $\text{Na}^+$  ions through the matrix from specific lattice sites. The  $\text{Na}^+$  ions are thought to move along a path created by a rigid oxide framework via small bottlenecks in the structure. Since the early work of Hong and Goodenough<sup>1,2</sup>, a large number of researchers have not only measured the high sodium ionic conductivity of these materials at low temperatures, but have also focused on the ionic selectivity of this crystalline transport. The natural crystallographic restrictions on these sites provides a high degree of selectivity which limits both the ability of other ions to replace  $\text{Na}^+$  in these lattice positions and also their mobility once in the sites. Cations which possess excessive charge, i.e.,  $\text{Pu}^{4+}$ ,  $\text{Al}^{3+}$ , etc. are thermodynamically unstable in these sites from an electrostatic standpoint. Cations which are much larger (or smaller) than  $\text{Na}^+$ , i.e.,  $\text{Cs}^+$ , do not fit well and are far less mobile. This

characteristic of ion selectivity has led to consideration of NASICON as an ion-selective electrode for potential measurements in bio-medical and other applications<sup>3</sup>.

A much greater wealth of data on ion selectivity for sodium ion conductors is available for the original sodium fast ion conductor,  $\beta$  alumina, which should provide insight into the degree of selectivity of NASICON.  $\beta$ -alumina is used at higher temperatures in the sodium sulfur batteries, sodium winning and sodium refining technologies. Early work by Yu Yao and Kummer, on diffusion of alkali ions in  $\beta$ -alumina provide a systematic evaluation. In Figure 2, their data on ionic diffusion of several monovalent ions demonstrates that as ionic size increases<sup>5</sup> that the measured diffusion coefficients decrease dramatically. Rasmussen<sup>6</sup> actually used  $\beta$ -alumina to produce pure sodium from an  $\text{NaCl-AlCl}_3$  eutectic composition. As would be expected no aluminum ions were in the product. In the later studies potassium was transported at a rate approximately 1/20th that of sodium which is consistent with the earlier diffusional studies of Yu Yao in Figure 2. Yu Yao was working with radioactive tracers, but did not measure any diffusion of cesium in the  $\beta$ -alumina body.

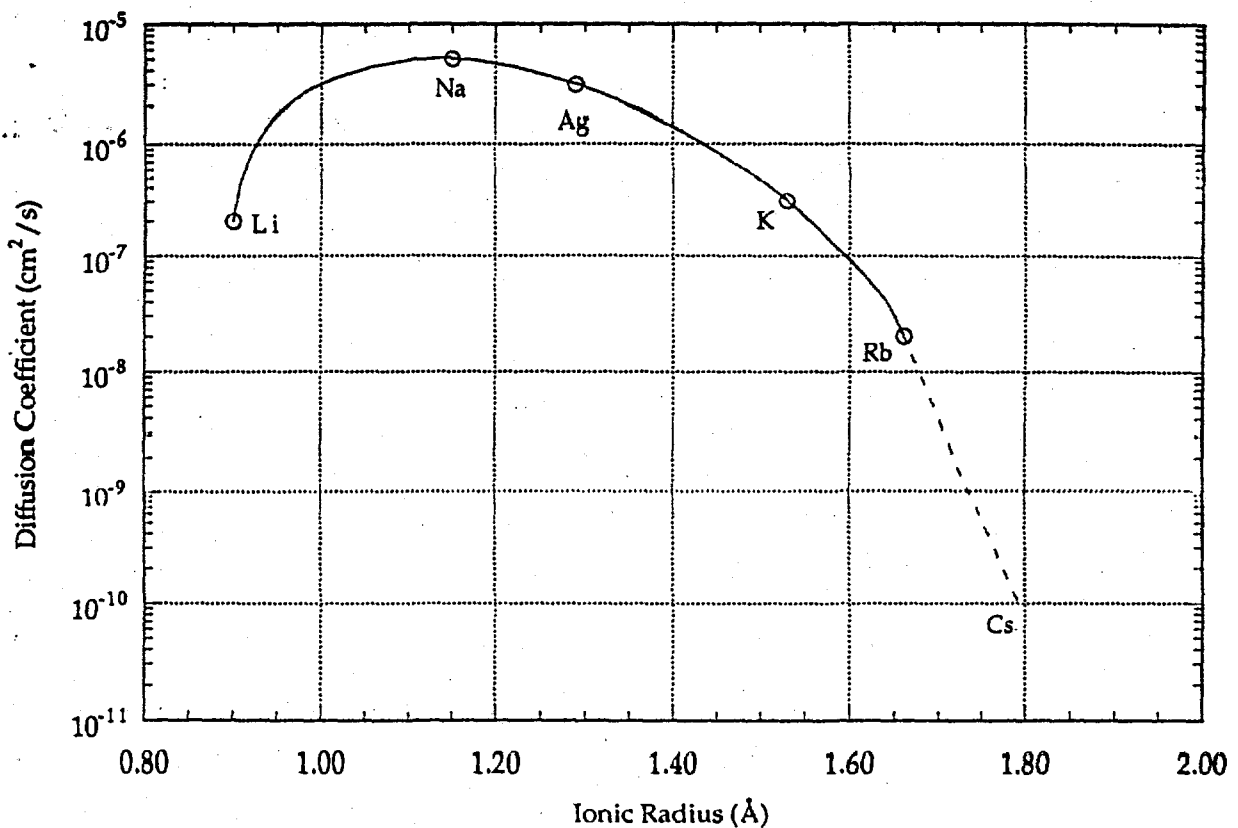


Figure 2. Extrapolated diffusion rates of Li, Na, Ag, K and Rb at 500K measured in sodium  $\beta$ -alumina measured by Yu Yao and Kummer. The diffusional transport of cesium was not measured.

From this information, one would expect that cesium transport through this fast ion conductor would be a factor of more than  $10^4$  slower than sodium. Similar expectations are anticipated for NASICON, but this type of transport testing is yet to be accomplished. Buehler et. al.<sup>7</sup> conducted electro dialysis work with NAFION membranes in order to evaluate the separation of  $\text{Na}^+$  from  $\text{Cs}^+$ . Their and our focus on cesium is caused by the less challenging concept of separating  $\text{Na}^+$  from multivalent ions. In Buehler's experiments with Nafion they were able to achieve a transport rate of  $\text{Cs}^+$  which was a factor of 2 or 3 faster than sodium. Note that in an organic membrane cesium is more mobile than sodium but in the ceramic membrane the larger cesium ion (1.8 Angstrom) is less mobile than sodium ion (1.16 Angstrom). In organic membranes transport is still in the aqueous phase, hence the sodium ion with several water molecules (1.8 to 2.9 Angstroms) attached is actually larger than the cesium ion. As Buehler points out salt splitting and sodium/cesium separation using Nafion would require numerous cascading cells. Because of the low concentration of cesium in comparison to sodium in Hanford Tank Waste, many Nafion-based cells would be required to separate cesium from sodium. Whereas the ceramic membrane would transport sodium, the

dominant species, away from the low concentration species.

In many cases, fouling by non-alkali cations occurs because of the imposed pH gradient through the organic membrane. However, in the NASICON membrane, these ions are excluded from the crystal structure and hence can not contribute to fouling. However, in the ceramic membrane alkali ions which are near the size of sodium can enter the lattice sites. When potassium ions enter the ceramic, they expand the lattice and secondly, their lower diffusional rates can potentially block the rapid transport of sodium<sup>6</sup>. In the worst case scenario, at high current densities, these effects could lead to failure of the ceramic.

#### IV. RADIATION STABILITY

The physical stability of most ceramics is expected to be excellent in gamma fields<sup>8</sup>. In high gamma fields, it is anticipated that electronic conductivity could be increased, perhaps by several orders of magnitude. Radiation induced conductivity (RIC) is anticipated to be a parasitic loss in the use of NASICON for separation of highly radioactive waste since the normal electronic conductivity is expected to be many orders of magnitude less than the ionic conductivity.

In contrast, the base material for Nafion, i.e., a perfluorinated hydrocarbon, is expected to be rapidly degraded by irradiation with the evolution of fluorine. Physical stability is expected to be impacted at slightly over 20,000 R and it is not recommended for use<sup>9</sup>. Hobbs<sup>10</sup>, however, has exposed Nafion 417 to a field that could be as high as 50,000 R/hr (cobalt 60) for up to 8 hours and then measured some performance parameters. He did not determine significant degradation of electrochemical performance. The radioactivity in Hanford tank wastes will vary from tank to tank and with recovery techniques. Measurements in tank SY101 indicate a potential dose of 200 R/hr. A perfluorinated hydrocarbon membrane might be expected to possess operating lifetimes as low as 100 hours or more than 3 months with the uncertainty in existing data. Shielding, dilution, etc. can help reduce the dose rate, but in order to be effective in salt splitting near the beginning of pretreatment, the membrane must be directly exposed to the cesium and other constituents in the waste.

## V. OPERATIONAL CONSIDERATIONS

The use of salt splitting in the processing is presently under consideration and requires a specific chemical flow diagram that interfaces with other requirements. One of the most interesting facets of salt splitting in general during such deliberations is the ability to reduce the pH of supernate without the addition of acid or other chemicals, hence minimizing secondary waste or other processes. Low pH levels are more compatible with many of the processing steps, for example solvent extraction and ion exchange. The Minimum Additive Waste Stabilization (MAWS) concept pursues exactly this type of processing on a more global basis. When salt splitting is conducted early in the waste processing the total quantity of cations being processed can be dramatically reduced since sodium dominates the waste stream. Consequently, the volume of chemicals and equipment capacity can be reduced substantially; perhaps not by a factor of 200 but reductions of up to 90% seem achievable. Alternatively, the NASICON membrane might find more valuable utilization in separation of caustic solutions from other processes where cesium, aluminum and sodium salts are recovered by washing. Caustic washing would require the introduction of even additional soda to the already voluminous quantities. Simple soda separation from

the other constituents provides a manner to recycle the existing material in the Hanford tanks.

Design studies for a processing facility for Hanford tank waste using ceramic membrane salt-splitting have not been conducted. However, a cost analysis for a 100,000 ton (Cl<sub>2</sub>)-per-year, chlor-alkali plant has been made<sup>11</sup>. A comparison was made between a NASICON-based plant and the present standard a Nafion type of plant for production of caustic soda. Accepting the uncertainties of the author, his conclusion is that NASICON is competitive with the organic polymer if the conductivity of the NASICON is greater than 2 KA/m<sub>2</sub> for a 40% NaOH product. The operating and depreciated cost would be approximately 3 million dollars for both membranes.

Recent experimental activities with NASICON at Ceramatec have been directed at the salt splitting of Na<sub>2</sub>SO<sub>4</sub>, an effluent at some paper mills which is coming under environmental controls. The recovery of sodium hydroxide by salt splitting would permit recycle of these waste products. A NASICON cell was operated at 4.8 volts and 70°C in order to separate a 40% sodium hydroxide stream from a 3M H<sub>2</sub>SO<sub>4</sub> stream. The current efficiency was 95%. A current density of 3.5KA/m<sub>2</sub> was achieved which is much higher than needed to satisfy the economic criteria of Kjaer in competing with Nafion for a non-radioactive application. The primary difficulty in these experiments was poor corrosion resistance in the 3M H<sub>2</sub>SO<sub>4</sub> which was produced. Of course, there is no necessity in the processing of tank wastes to achieve such a strong acid.

## VI. CONCLUSIONS

The use of salt splitting to pretreat sodium-dominated tank wastes offers several unique advantages: pH reduction without chemical additions; removal of nitrate salts from further processing steps; etc.

The use of a ceramic membrane such as NASICON in the salt splitting pretreatment is expected to 1) reduce HLW volume by separation of sodium from radioactive constituents; 2) provide extended life over organic membranes through greater irradiation tolerance; and 3) concentrate the process stream so that subsequent activities will be smaller and require fewer additives.

Although extensive research has been conducted on NASICON throughout the world, no commercial production facility exists today. Consequently, scale up activities will be required in order to construct a major separation facility. NASICON is a ceramic with all the associated issues associated with low fracture toughness.

#### ACKNOWLEDGEMENTS

This research has been funded by the U.S. Department of Energy through Battelle, Pacific Northwest Laboratories and also Ceramatec Inc.

#### REFERENCES

1. H. Y. P. Hon. Mat. Res. Bull. 11 (1976) 173
2. J. B. Goodenough, H. Y. P. Hong and J. A. Kafalas, "Fast Na<sup>+</sup>-Ion Transport in Skeleton Structures," Mat. Res. Bull. 11 203-220 (1976)
3. E. Siebert, A. Caneiro, P. Fabry and M. Levy, "Na<sup>+</sup> Exchange at the Nasicon/Water Interface," J. Electroanal. Chem. 286 (1990) 245-251
4. Y. F. Yu Yao and J. T. Kummer, "Ion Exchange Properties of and Rates of Ionic Diffusion in Beta-Alumina," J. Inorg. Nucl. Chem. 29, 2453-2475 (1967)
5. Shannon, R. D. "Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," Acta Cryst A32 (1976) 751
6. J. R. Rasmussen, G. R. Miller and R. S. Gordon, Proceedings of the Meeting of Electrochemical Society, May 9-14, 1982, Montreal, Canada
7. M. F. Buehler, W. E. Lawrence, and J. D. Norton, PNL-9022, "Evaluation of Aqueous Na<sup>+</sup>/Ca Separation by Electrodialysis," Dec 1993.
8. F. W. Clinard, "Ceramics for Fusion Devices" J. Mat for Energy Sys. 6 100-106 (1993)
9. K. Abe, C. M. Logan, K. Saneyoshi, and F. W. Clinard, Special Tech Publication 956, ASTM, Philadelphia, PA.
10. D. Hobbs, J. D. Gender, and D. Hartsough, "Electrochemical Treatment of Liquid Nuclear Waste," 185th Electrochemical Society Meeting, May 23, 1994, San Francisco, CA
11. J. Kjaer, NEI-DK--354 "Evaluation of the Economic Aspects of Utilization of NASICON in the Chlor-alkali Industry," Energilaboratoriet, Odense, Denmark. 1987