

**Application of Membrane Technology to Minimize Liquid Waste from Reprocessing Plants  
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**ABSTRACT**

JGC Corporation (JGC) is developing an advanced process for nitrate decomposition and sodium ion recovery. This advanced process called Denitrate and Na Recovery process (DNR process) treats the low level liquid waste from nuclear fuel reprocessing plants. One of the key technologies for Na recovery in the DNR process uses NaSelect® ceramic membrane (Na super ion conductor)-based low temperature electro dialysis developed by Ceramatec Inc.

Electro dialysis properties when adopting the NaSelect® membrane have been evaluated by laboratory scale experiments. The results show that the sodium ion can be recovered at a stable cell voltage of up to 1 M or higher concentration of NaOH in the anolyte. The predicted operation of the ceramic membrane process is longer than one year without the need for replacement of the NaSelect® membrane. Radionuclides such as Sr-85 and Ru-106, but not Cs-137, are blocked from transport through the membrane. A very small amount of Cs-137 permeated through the NaSelect® membrane and the decontamination factor of Cs-137 was greater than 100 in continuous recycle mode operation.

The material balance applying the DNR process has been preliminarily calculated for the liquid waste from the Rokkasho Reprocessing Plant in Japan. Calculation results show a liquid waste volume reduction of 95%.

**INTRODUCTION**

The reduction of radioactive waste volume is an important issue in the management of the nuclear fuel cycle. Liquid waste containing sodium compounds, mainly sodium nitrate, is generated from the reprocessing process. Due to its oxidant property and chemical toxicity, the nitrate ion affects the environment in a permanent geologic repository as well as the behavior of radioisotopes. The presence of sodium ions results in increased waste volume.

JGC Corporation (JGC) is developing a system called the “Denitrate and Na Recovery” process (DNR process).

This concept is shown in Fig. 1. The DNR process comprises nitrate ion decomposition and sodium ion recovery.

In the nitrate ion decomposition process, the nitrate ions are reduced to nitrogen by hydrazine as a reductant and by a catalyst, with sodium nitrate being converted to sodium hydroxide [1 - 4]. In the sodium ion recovery process, the sodium ions are selectively recovered from the waste by electrolysis adopting the NaSelect® (Na super ion conductor) membrane based cell. Electrodialysis by the NaSelect® membrane has been developed for the recovery and recycle of sodium hydroxide from high-salt radioactive tank wastes in the U.S. [5-9].

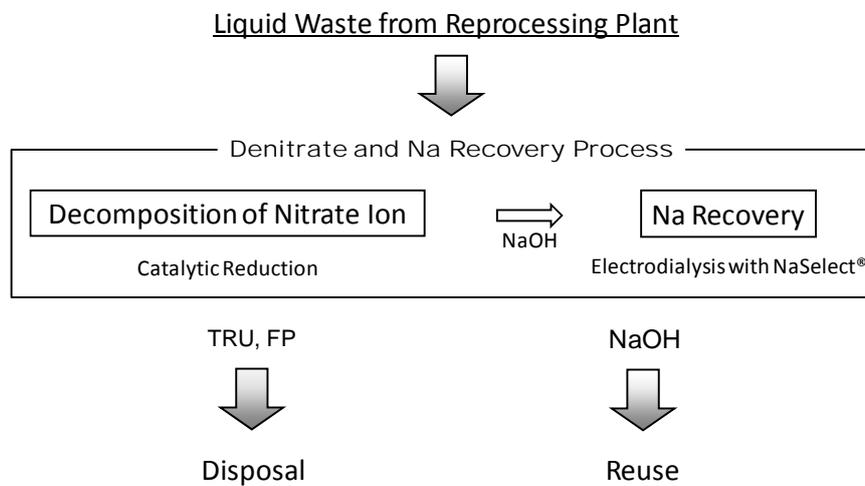


Fig. 1. Concept of DNR Process

The DNR process has a number of advantages as well as possibilities, including:

1. Removal of nitrate ions from the liquid waste
2. Separation of sodium ions from the radioactive waste
3. Reuse of the sodium as alkaline reagent in the reprocessing process
4. Volume reduction

In the DNR process the sodium ion recovery process is especially important from the standpoint of achieving waste volume reduction. Fig. 2 shows the sodium ion recovery process by electrodialysis adopting the NaSelect® membrane. Radioactive liquid waste, in which  $\text{NaNO}_3$  is converted to  $\text{NaOH}$  in the nitrate ion decomposition process, is supplied to the anode compartment. Non-radioactive  $\text{NaOH}$  is supplied to the cathode compartment. When electrical potential is applied to the cell, the NaSelect® membrane allows the selective transport of sodium ions to the cathode compartment. Other cations ( $\text{TRU}$ ,  $\text{Sr}^+$ ,  $\text{Cs}^+$ , etc.) and anions remain in the anode compartment where the radioactivity remains.

The charge balances in the anode and cathode compartments are maintained by generating  $H^+$  and  $OH^-$  from the electrolysis of water, respectively. Water is generated by the neutralization reaction between  $OH^-$  from NaOH and generated  $H^+$  in the anode compartment, and NaOH by the reaction between  $Na^+$  transported from the anode compartment and generated  $OH^-$  in the cathode compartment. The concentrated NaOH is recovered from the cathode compartment.

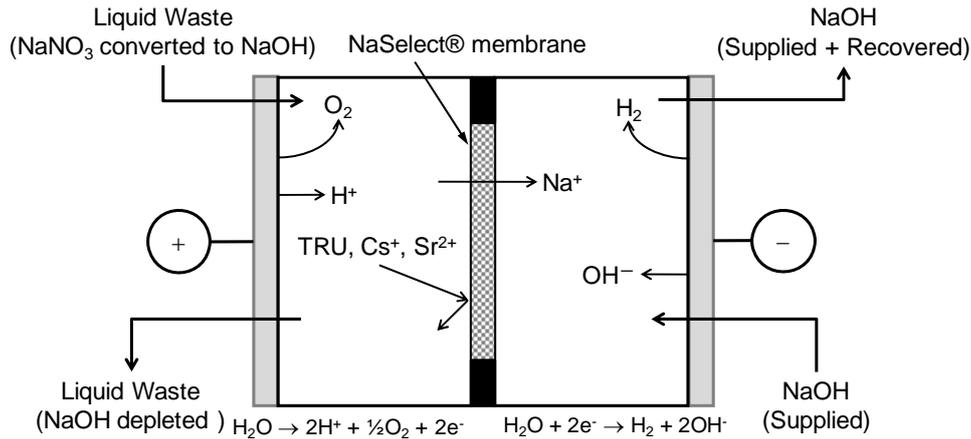


Fig. 2. Na Recovery Process

Key issues in the sodium ion recovery process are as follows:

1. Sodium concentration region for the recovery process
2. Long-term operation of the NaSelect® membrane used in the electro dialysis for NaOH solution
3. Separation efficiencies of radionuclides from the liquid waste

Laboratory scale experiments were conducted for the key issues. Based on the results, the material balance has been determined for liquid waste from the actual reprocessing plant.

#### PROPERTIES OF ELECTRODIALYSIS BY NaSelect® MEMBRANE FOR SODIUM SEPARATION

Fig. 3 is a schematic of the electro dialysis setup for NaOH solution. Separate flow loops were provided for the anolyte and catholyte solutions. Each loop consisted of a solution storage tank, pump, pressure gauge and flow-control meter. Each tank was supplied with an Ar purge line to prevent the built-up of gases, namely,  $H_2$  and  $O_2$ , from the decomposition of water by electrolysis. Temperature was maintained by a heater and temperature controller. Power was supplied by a DC power supply unit and cell voltage was measured by a galvanometer. All experiments were conducted at a constant current.

The electro dialysis cell was manufactured by Ceramatec Inc. The cell consisted of an anode (platinized titanium and Kovar), cathode (nickel), flow promoter (PP: Polypropylene), gasket (EPDM: Ethylene Propylene

Diene Monomer) and scaffold (HDPE: High Density Polyethylene) with a NaSelect® membrane having a thickness of 1.4 mm and a diameter of 7.6 cm. The membrane disk was sealed at the edge and the surface area of the membrane was 44 cm<sup>2</sup>.

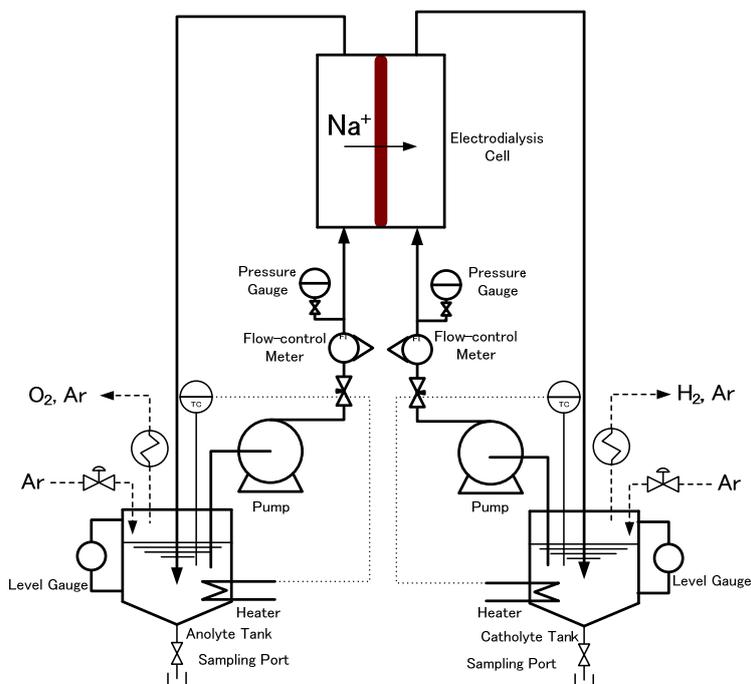


Fig. 3. Setup Schematic

The operation mode was set to batch or continuous recycle mode. The batch recycle mode was operated from charged concentration up to a given level of NaOH in the anolyte. After the first batch recycle mode operation, the anolyte and catholyte were drained and new electrolyte recharged to duplicate the test. The continuous recycle mode was conducted by depleting sodium from the initial NaOH anolyte until reaching a certain NaOH concentration, before recharging to the starting NaOH concentration. The catholyte NaOH concentration in both modes was increased from the initial concentration. The continuous recycle mode was conducted on the assumption that sodium concentration in the anolyte is maintained by concentrating the sodium-depleted waste and recharging.

#### Sodium Concentration Region for Recovery Process

To estimate the lowest sodium concentration in the anolyte during electrodesalination at stable cell voltage, tests were carried out at current densities of 50, 75, 100 mA/cm<sup>2</sup> using the setup shown in Fig. 3.

The setup was operated on a batch recycle mode and flow rate was 2 L/min. The initial anolyte was 4.5 M or 2 M NaOH solution with initial catholyte of 2 M NaOH. The initial volume of each solution was 1L. During

operation, each solution was maintained at 40°C. Samples of solution and gas were collected from the anode and cathode sides once hourly. Solution samples were analyzed using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) to determine the sodium ion concentration. Gas samples were measured using a gas chromatograph to determine the hydrogen and oxygen concentrations. Changes in the anolyte and catholyte volumes were measured by the level gauge. Gas volume generated during the operation was measured by a gas meter.

Cell voltage changes during each operation are shown in Fig. 4. The cell was operated in two concentration regions: one with a high concentration of NaOH of around 4.5 M and the other with a low concentration of NaOH of less than 2 M. In the test results shown in Fig. 4, the cell voltage was mathematically determined between high and low concentrations.

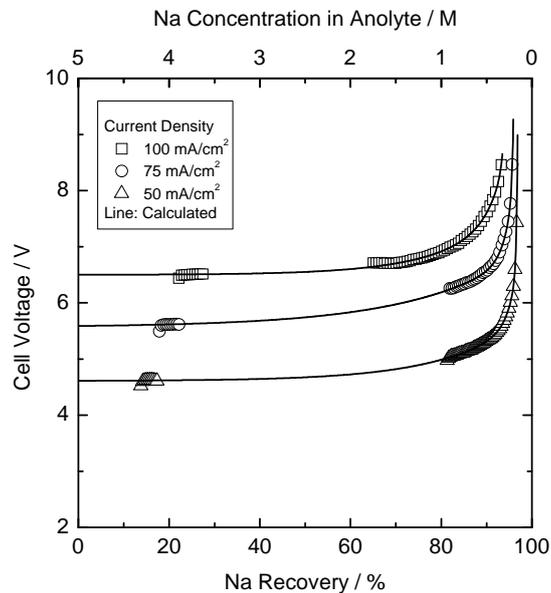


Fig. 4. Cell Voltage Change during Each Operation

Stable cell voltage is required during operation. The cell voltage increases drastically when the Na concentration in the anolyte decreases below 1 M in the case of electrodialysis at current densities of 50-100 mA/cm<sup>2</sup> as shown in Fig. 4. The lowest concentration of sodium ion in the anolyte will therefore be ~1 M for this process. The lowest concentration in the anolyte suggests that 80% of the sodium from the waste can be recovered in the case of 5 M NaOH in the waste in the batch recycle mode.

Current efficiency is calculated based on the following equation:

$$\text{Current Efficiency [\%]} = \frac{\text{Actual Na}^+ \text{ Transport Rate [mol/h]}}{\text{Theoretical Na}^+ \text{ Transport Rate [mol/h]}} \times 100$$

here

$$\text{Theoretical Na}^+ \text{ Transport Rate [mol/h]} = \frac{\text{Membrane Area [cm}^2\text{]} \times \text{Current Density [A/cm}^2\text{]}}{\text{Faraday constant [A h/mol]}}$$

Fig. 5 shows the change of sodium ion concentration in the anolyte and catholyte during the tests at 50 mA/cm<sup>2</sup> as well as actual transport rates.

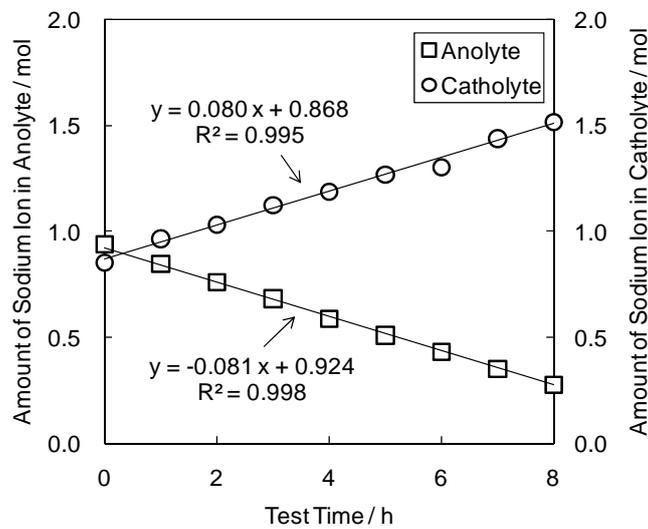


Fig. 5. Sodium Ion Transport Rate during Test

The theoretical sodium ion transport rate at 50 mA/cm<sup>2</sup> is determined to be 0.082 mol/h. The sodium transfer current efficiencies determined from the actual transport rate of the anolyte and catholyte were 98.8% and 97.6%, respectively, and the average current efficiency was 98.2%. The results of other tests at 75 mA/cm<sup>2</sup> and 100 mA/cm<sup>2</sup> gave almost the same current efficiencies. The sodium recovery process by electrodialysis adopting the NaSelect® membrane operates at about 100% current efficiency.

### Long Term Operation of NaSelect® membrane

From a long term operation standpoint, the lifetime of the NaSelect® membrane was estimated based on the results of tests using a multi-membrane cell for a total test period of three months.

Fig. 6 shows the setup which is similar to that shown in Fig. 3. The setup consisted of 210 L plastic polypropylene containers as tanks of electrolyte and a large size cell with three scaffolds fitted with six membranes per scaffold. One of the three scaffolds was removed each month and the strength of the post-tested

membrane was measured. Strength measurements of the membranes were conducted using a standard pressure burst test for individual membranes.



Fig. 6. Three-Month Test Setup at Ceramatec Inc

Operation was conducted by batch and continuous recycle modes at current densities of  $75 \text{ mA/cm}^2$  and  $100 \text{ mA/cm}^2$ , respectively. The initial anolyte was a 5 M NaOH solution and the initial catholyte 3.5 M NaOH. The batch recycle mode was operated for up to 1.5 M of final concentration of NaOH in the anolyte and was duplicated several times per month. The catholyte in the test was recharged to 3.5 M at the end of each batch. Continuous recycle mode was conducted by depleting sodium from 5 M NaOH anolyte until reaching a final concentration of  $\sim 4 \text{ M NaOH}$  before recharging to the starting level of 5 M NaOH concentration. The catholyte concentration in the test was increased from the initial concentration of 3.5 M NaOH to a final concentration of  $\sim 19 \text{ M}$ . The electrolyte was maintained at  $40^\circ\text{C}$  during operation.

Data resulting from the batch recycle mode test are shown in Fig. 7. The cell operated for 2160 hours at stable voltage for the duration of the test, other than on two occasions when the anolyte concentration was allowed to drop below 1 M NaOH. This reproduced the result from Fig. 4. The cell voltage which had been increased in the region of 1 M NaOH returned to the original level after recharging. Current efficiency remained close to 100% for the entire test.

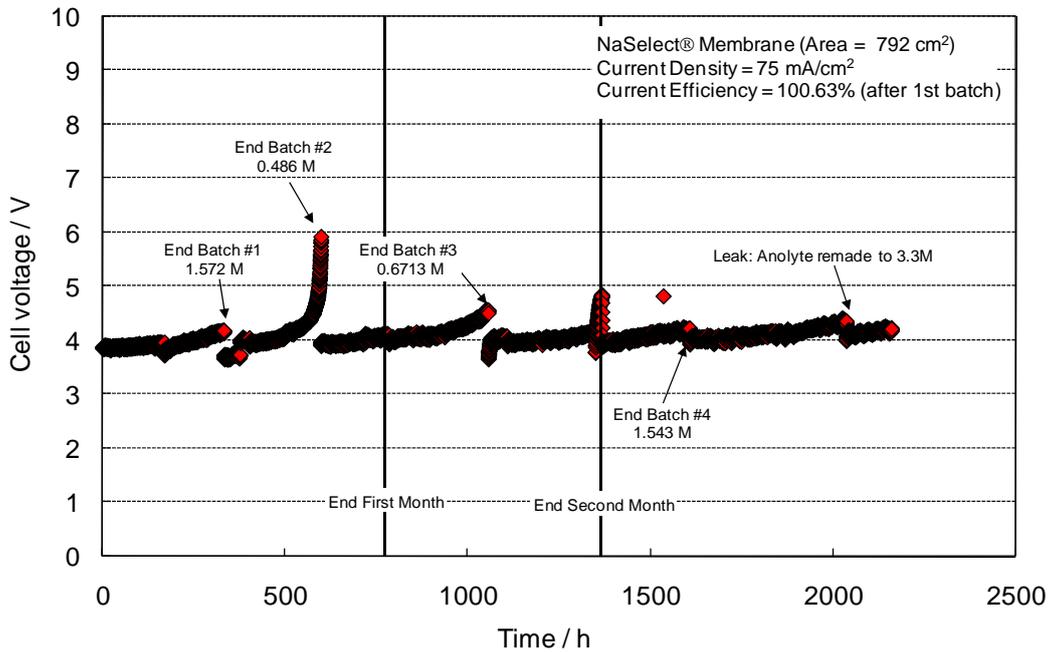


Fig.7. Cell Voltage Change during Three-Month Batch Recycle Mode Test

The cell was operated for a total of 2160 hours in the continuous recycle mode test, with cell voltage stable for the duration of the test.

After the batch and continuous recycle mode tests, all of the membranes were removed from the cell and confirmed to be intact. The post test leak analysis showed all scaffolds to be leak tight.

In order to predict the useful operational lifetime of the NaSelect® membrane, an extrapolation was made based on the four data points recorded (i.e. pre-tested, one, two, and three months later). The acceptable engineering strength of the membrane was 50% of the pre-tested membrane strength data. It was assumed that the aging trend could be represented by a linear extrapolation. The expected life of the membrane resulting from analysis will be more than one year for the batch recycle mode case and approximately one year for the continuous recycle mode case, respectively. The predicted lifetimes suggest that the sodium recovery process can be operated for one year without membrane replacement.

### Separation Efficiencies of Radionuclides from Liquid Waste

Laboratory scale experiments using the NaSelect® membrane were conducted for Ce-139, Sr-85, Ru-106, Cs-137 and TRU (Am-241 and Np-237 mixture) for simulated wastes to determine Decontamination Factor (DF) and selectivity. The DF is defined as follows:

$$DF = \frac{\text{Initial Amount of Nuclide in Anolyte [Bq]}}{\text{Final Amount of Nuclide (Transferred Amount) in Catholyte [Bq]}}$$

The selectivity is represented as follows:

$$\text{Selectivity} = \frac{\text{Transferred Amount of Na [mol]} / \text{Initial Amount of Na [mol]}}{1 / DF}$$

Fig. 8 shows the setup to be almost identical to that in Fig.3. Operation was conducted in the batch recycle mode to determine the DF for Ce-139, Sr-85, Ru-106 and TRU at a current density of 100 mA/cm<sup>2</sup> for 30 hours based on 7 hours of operation daily. The initial anolyte was 5 M NaOH solution and the initial catholyte 4.4 M NaOH. For tests with Cs-137, the setup was operated with an initial anolyte of 2.5 M and 5 M NaOH and initial catholyte of 4.4 M NaOH at current densities of 50 and 100 mA/cm<sup>2</sup> for 30 hours continuously, respectively. The electrolyte was maintained at 40°C during operation. Samples from the anolyte and catholyte were taken every hour and analyzed by the ion chromatograph for Na ion concentration and by the Ge semiconductor detector for the concentration of radioisotopes.



Fig. 8. DF Test Setup at JGC

Because the concentrations were below the detection limits of the detector, no permeation of Ce-139, Sr-85, Ru-106 and TRU was observed in the catholyte. The DF and selectivity of these nuclides are shown in Table I. Nuclides other than Cs-137 are minimum values determined from the detection limits of the Ge semiconductor detector.

Table I. Decontamination Factor and Selectivity

Nuclide	DF	Selectivity
Sr-85	> 42000	> 30000
Ru-106	> 1000	> 700
Ce-139	> 15000	> 11000
Cs-137 (at 50% Na recovery)	300	200
TRU (Np-237 + Am-241)	> 20000	> 23000

Limited permeation of Cs-137 through the membrane occurred during the tests. Data were reproduced from the duplicate tests conducted by JGC and the results obtained from the DOE [6-9]. The DFs obtained from the tests by JGC and the DOE-conducted tests are shown in Fig. 9. The DF from the DOE experiments showed a high value. The DF from the test by JGC, however, decreased from ~10000 to around 100 with an increased Cs-137 ratio in the analyte.

It was assumed that DF depends on current density, which determines cell voltage. The DF from the test at a current density of 50 mA/cm<sup>2</sup> is higher than that of 100 mA/cm<sup>2</sup>. Therefore, the amount of Cs-137 transferred at 100 mA/cm<sup>2</sup> was larger than that at 50 mA/cm<sup>2</sup>. It is believed that cell voltage determines the amount of Cs-137 transferred.

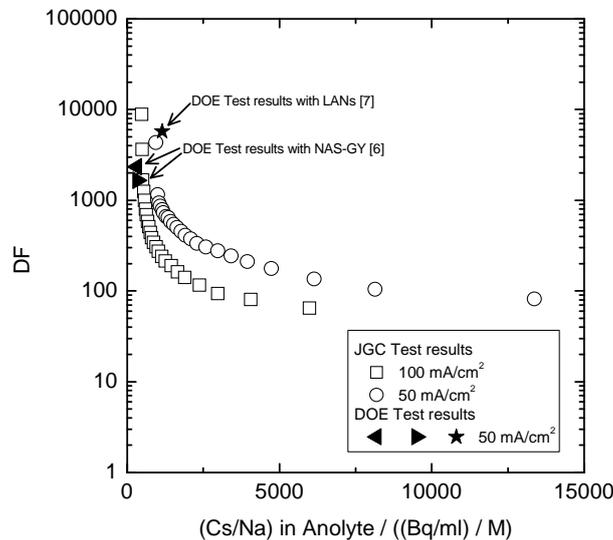


Fig. 9. DF of Cs-137 from Test

Fig. 10 shows the DF obtained from the test with Cs-137 conducted by JGC. In the batch recycle mode, the Na

recovery rate is limited up to 1 M (i.e. 80% in the case of initial concentration of 5 M) to achieve a DF of more than 100. In the less than 1 M NaOH region (i.e. more than 80% recovery), the tendency of DF change increased, and cell voltage also increased as shown in Fig. 4. This result suggested also that the DF depends on cell voltage; namely, a higher cell voltage will induce lower DF.

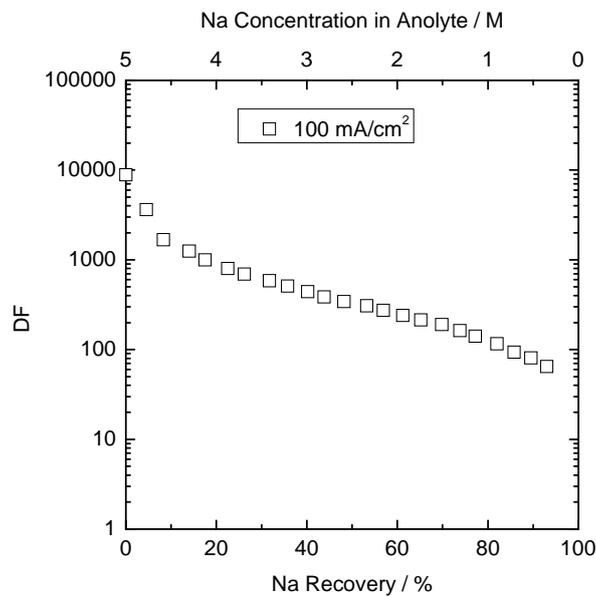


Fig. 10. Na Recovery vs DF of Cs-137 Resulting from Test at 100 mA/cm<sup>2</sup>

### FEASIBILITY STUDY FOR ACTUAL REPROCESSING PLANT

The tests described in the above served to determine the following operational requirements to ensure stable cell voltage, long term operation and DF of Cs-137 of more than 100:

1. Anolyte concentration: more than 1 M NaOH
2. Current density (maximum): 100 mA/cm<sup>2</sup>

In the batch recycle mode, recovery of up to 1 M NaOH achieves stable cell voltage and a DF for Cs-137 of more than 100. On the other hand, the continuous recycle mode recovers sodium in given amounts to maintain more than 1 M NaOH before recharging to the starting NaOH concentration. Therefore, the continuous recycle mode is adopted in the feasibility study for the actual reprocessing plant, the Rokkasho Reprocessing Plant (RRP) in Japan.

Operational conditions (Nos. 3 to 5) are added to operational requirements (Nos. 1 and 2 above) in order to estimate the material balance in the RRP applying the DNR process, as follows:

3. Almost 50% recovery to maintain more than 1 M NaOH in the anolyte before recharging
4. Overall sodium recovery from the Low-level Liquid Waste (LLW): 90%

5. DF as shown in Table I (DF for  $\beta \gamma$  radiation is averaged from the results in Table I other than Cs-137.)

The material balance was calculated for application of the DNR process to the LLW treatment at the RRP. The composition and feed condition of the LLW is shown in Table II [10].

Table II. LLW Composition and Feed Conditions

Flow Rate	113 t / y
NaNO <sub>3</sub>	28.9 t / y
Concentration of NaNO <sub>3</sub>	3.0 kmol / t
Total $\alpha$ radiation	$1.7 \times 10^{10}$ Bq / t
Total $\beta, \gamma$ radiation	$2.6 \times 10^7$ Bq / t
Cs-137	$4.2 \times 10^6$ Bq / t

The cell for electro dialysis by NaSelect® in the DNR process was designed by Ceramatec Inc. The specification is shown in Table III.

Table III. Design Specification of the Electro dialysis Cell

Current Density	100 mA/cm <sup>2</sup>
Total active NaSelect® area	1.9 m <sup>2</sup>
Active area per NaSelect® membrane	44 cm <sup>2</sup>
Total number of NaSelect® membranes	431
Number of NaSelect® membranes per scaffold	6
Total number of scaffolds	72
Number of scaffolds per module	21
Number of modules	4

Fig. 11 shows the DNR process and the material balance based on the operational requirements and conditions described above. The NaNO<sub>3</sub> of 29 t/y in the LLW is reduced to NaOH of 1.4 t/y in the concentrated LLW. Volume reduction of LLW is therefore 95%. The recovered NaOH is decontaminated and disposed of in a shallow ground repository or reused as alkaline reagent in the RRP.

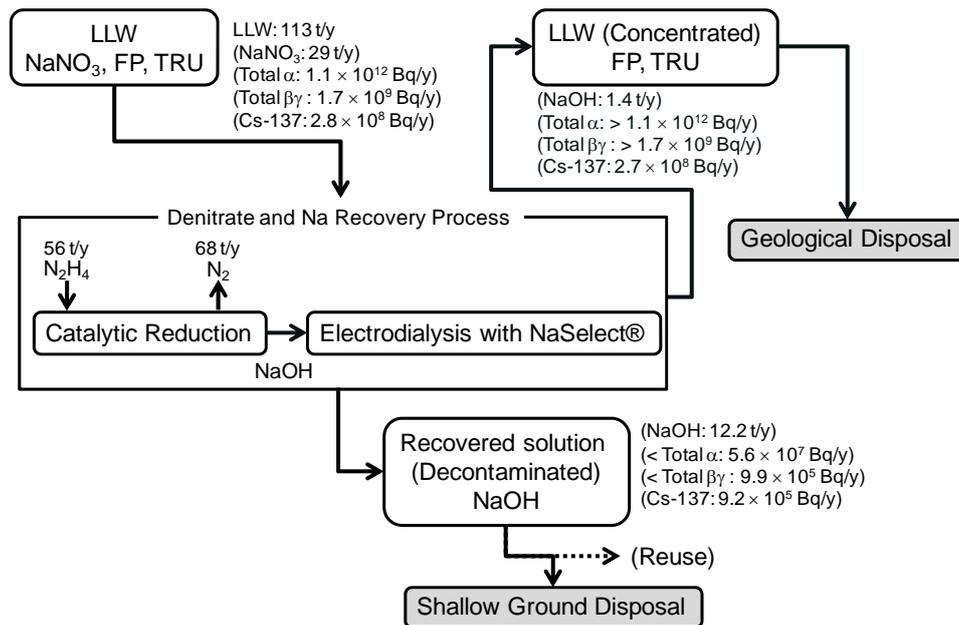


Fig. 11. Material Balance by the DNR process

## CONCLUSION

A series of experiments was conducted to study sodium recovery in the DNR process. Properties of electro dialysis using the NaSelect® membrane were clarified as follows:

1. Lowest concentration of 1 M NaOH for stable cell voltage during operation
2. Sodium ion recovery current efficiency of ~100% in NaOH solution
3. Lifetime of membrane of more than one year at  $75 \text{ mA/cm}^2$  and  $100 \text{ mA/cm}^2$
4. No permeation of radionuclides through membrane other than Cs-137
5. DF of Cs-137 greater than 100 obtained in the concentration region of more than 1 M NaOH in the anolyte.

The DNR process was applied for the estimation of material balance in LLW based on the operational requirements. The material balance indicated a volume reduction of 95%. Therefore, the material balance shows that the DNR process is suitable for the treatment and reduction of LLW volume.

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