



Durability testing for the recovery of sodium hydroxide from alkaline waste solutions

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Received 24 July 1998; accepted in revised form 7 July 1999

Key words: alkaline waste, durability testing, sodium hydroxide

Abstract

Testing successfully demonstrated the operation of an electrochemical flow cell for more than 1000 h to recover 13–14 wt% sodium hydroxide from an alkaline waste solution. The nickel cathode, platinized-titanium anode and cationic membrane exhibited no visible signs of attack upon inspection after testing. The membrane experienced a slow, but steady decline in current efficiency, from a high of greater than 95% down to approximately 90% after 1079 h. We attribute the loss in current efficiency to the accumulation of silicon and aluminium within the membrane structure.

1. Introduction

High-level radioactive wastes (HLW) stored at the Department of Energy's Hanford, Oak Ridge and Savannah River (SRS) sites contain large amounts of sodium salts that can, in principle, be recovered as sodium hydroxide (caustic) for recycling. A possible separation process for the recovery of caustic uses electrochemical salt splitting with a two-compartment cell. When the electrolyser is switched on, hydroxide forms at the cathode by the reduction of water, and oxidizes at the anode to produce oxygen and water. Sodium ions migrate from the anode compartment to the cathode compartment across the cationic membrane. Anionic species such as nitrate, nitrite, aluminate, and sulfate do not pass through the membrane, and remain in the anode compartment or feed stream of the cell. As a result, the caustic strength in the catholyte increases while the anolyte depletes of sodium hydroxide.

A number of ion-selective membranes exist for industrial electrochemical processes including the manufacture of inorganic and organic chemicals, the recovery of metals, water purification and effluent treatment [1]. Organic-based membranes, such as the commercially available perfluorinated membranes, have been used extensively in the chlor-alkali industry and increasingly in salt splitting applications such as the production of sodium hydroxide and sulfuric acid from sodium sulfate solutions [2]. These membranes exhibit excellent chemical stability over a wide range of pH values.

Previous testing successfully demonstrated caustic recovery from simulated and radioactive SRS waste solutions in a two-compartment cell using Nafion[®]

type 324 and 350 membranes [3]. These membranes typically operate at about 85% current efficiency for the production of 15–20% caustic in the chlor-alkali type processing and generally prove less sensitive to the influence of impurities than other perfluorinated membranes [4].

To assess the process viability, longer-term testing is desirable to investigate the durability of cell components (e.g., membrane, anode and cathode). This paper details the results of two tests conducted with a two-compartment flow cell for the recovery of caustic from an alkaline solution simulating the SRS Decontaminated Salt Solution. The first test operated for 143 h using a nickel cathode, a nickel anode, and a Nafion[®] 350 membrane. The second test operated for 1155 h using a nickel cathode, a platinized-titanium anode and a new piece of Nafion[®] 350 membrane.

2. Experimental details

Figure 1 shows a diagram of the testing apparatus which included the following major components: an ICI FM01 electrochemical flow cell equipped with polytetrafluoroethylene (PTFE) spacers and gaskets, flat-plate nickel electrodes and Nafion[®] 350 membrane (active surface area 0.0064 m²), anolyte and catholyte reservoirs, pumps for circulating liquids, d.c. power supply and data acquisition system. After 143 h of operation, the nickel anode in the electrochemical cell was replaced with a platinized-titanium flat-plate anode. The membrane was pretreated by soaking in 3.5 M NaOH for several days. PTFE turbulence promoters were placed

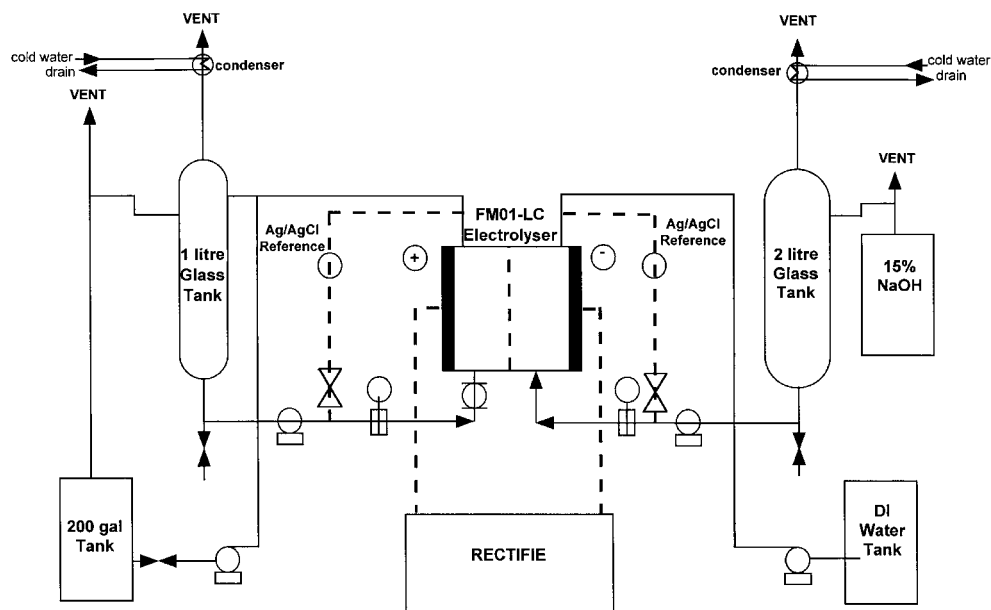


Fig. 1. Schematic diagram of testing equipment.

on either side of the membrane for support and to prevent it from touching the electrodes.

Anolyte and catholyte temperatures were monitored using an Omega CN310 temperature controller coupled with a type 'J' thermocouple mounted in a glass thermowell in the solution reservoir. A glass condenser was mounted on top of each reservoir to remove water vapor from the gases exiting the reservoir. Non-condensable gases were vented to the atmosphere. Power was supplied using a Sorenson DCS 20-50 d.c. power supply.

The anolyte loop consisted of a one litre glass reservoir and a March MDK-MT3 circulating pump with a Kynar[®] head. The flow rate was monitored using a Signet Scientific 3-2507.100-6V Kynar[®] magnetic paddle wheel flow sensor coupled with an Omega DPF75 flow controller. Synthetic SRS solution was circulated continuously from the bulk (800 dm³) reservoir to the glass reservoir at approximately 3.6 dm³ h⁻¹. The catholyte loop consisted of a two litre glass reservoir and a magnetically coupled gear pump (Cole Parmer Instrument H07144-91 motor, H07001-40 SS head) for circulation. The flow rate was monitored using a Signet Scientific 3-2507.100-6V Kynar[®] magnetic paddle wheel flow sensor coupled with an Omega DPF78A flow controller. Deionized water was fed continually to the catholyte reservoir to maintain the caustic strength and the product caustic overflowed to a separate collection vessel. Solution samples were also taken frequently and analysed for caustic strength. Anode and cathode potentials were monitored continually using an Ag/AgCl reference electrode mounted in separate circulation loops and connected to Luggin probes placed at each electrode.

Selected data (cell voltage, electrode potentials, membrane voltage drop, solution temperatures) were monitored and recorded continually using a computer data

acquisition system. All other data were recorded manually. All major electrical components of the system were connected to a Sola model 510 uninterruptible power supply to ensure continued operation. A safety interlock system, allowing unattended operation at night and weekends, was installed to shut down the testing apparatus in the event an unsafe condition occurred. Potential unsafe conditions included low anolyte and catholyte flowrates, low and high anolyte and catholyte temperatures, liquid spills and high cell voltage.

A waste solution simulating the SRS decontaminated salt solution was prepared by dissolving the appropriate reagent grade sodium salt in deionized, distilled water to produce 610 dm³ of solution. Table 1 provides a list of solution components. The initial catholyte solution was a 3.5 M NaOH solution prepared from reagent grade sodium hydroxide and deionized distilled water.

Catholyte and anolyte samples were taken daily and analysed for caustic strength by titration with acid using phenolphthalein as the indicator. The carbonate content was also determined by titration using a bromocresol green indicator. Water transport across the membrane was calculated based on the volume of dilution water fed to the caustic reservoir, and the volume, density, and concentration of caustic collected. For example, Figure 2 provides a plot of the dilution water addition rate (dm³ h⁻¹) and Figure 3 provides a plot of the caustic production rate (mol h⁻¹) over the course of the second test with the platinized-titanium anode. Periodically, both solutions were analysed for anions (NO₂⁻, NO₃⁻, F⁻, Cl⁻, PO₄³⁻, SO₄²⁻) using a Dionex DX 500 ion chromatograph equipped with an IonPac AS4A-SC analytical column, AG4A-SC guard column, CD-20 conductivity detector, GP-40 gradient pump, and controlled using the Peaknet[™] software system.

Table 1. Initial and final analyte compositions

Element	Initial concentration (nickel anode run)/M	Final concentration (nickel anode run)*/M	Final concentration (platinized-Ti anode run)/M
NO ₂ ⁻	0.57	0.59	0.081
NO ₃ ⁻	2.10	2.30	2.89
F ⁻	0.017	0.017	bdl
Cl ⁻	0.024	0.024	0.022
PO ₄ ³⁻	0.006	0.0072	0.006
SO ₄ ²⁻	0.14	0.15	0.148
CO ₃ ²⁻	0.17	0.12	0.098
OH ⁻	1.55	1.34	0.69
Si	3.96 × 10 ⁻³	4.27 × 10 ⁻³	2.40 × 10 ⁻³
Al	0.146	0.149	0.179
Cr	2.6 × 10 ⁻³	3.1 × 10 ⁻³	4.3 × 10 ⁻³
Ni	<8.4 × 10 ⁻⁶	9.7 × 10 ⁻⁵	<8.4 × 10 ⁻⁶
Na	5.2	5.2	4.3

* Final solution from Ni anode run used as the initial feed solution for the test equipped with Pt/Ti anode bdl below detection limit

The analyte off gas flow rate was measured using a simple burette/soap solution bubble meter. Qualitative analysis of the analyte off gas utilized a GowMac gas chromatograph equipped with a series 550 thermal conductivity detector and a Hewlett Packard 3396A integrator. Oxygen was detected on a molecular sieve 60/80 6 ft column using helium as carrier gas.

3. Results and discussion

3.1. Nickel anode/cathode configuration

Figure 4 shows the voltage versus elapsed time for the individual cell components as well as the overall cell voltage measured throughout the test. The cell operated for 143 h with a Ni anode before terminating due a high voltage and the presence of an increasing amount of solids in the analyte causing difficulties with maintaining a consistent flow rate. The results show that the overall cell voltage stayed constant near 5.5–5.6 V for the first 60 h before it began to rise, reaching a high of 7.3 V before terminating the test. The increase coincided with a similar increase in the membrane voltage drop. Anode

and cathode potentials remained relatively constant near +1.6 and -1.6 V vs Ag/AgCl, respectively. Measurements of the analyte offgas flow rate and composition indicated oxygen-producing reactions consumed greater than 95% of the current. Therefore, nitrite oxidation consumed less than 5% of the current. This agrees with previous results that demonstrated nickel anodes as very inefficient for the oxidation of nitrite in strongly alkaline solutions [5].

Examination of the cell components at the end of this test showed the anode suffered severe corrosion and had lost a significant amount of mass (approximately 7 g). Solution analyses indicated a significant increase in the nickel content (from <0.4 ppm to 4.6 ppm) in the analyte (s Table 1). We speculate that attack occurs as the result of hydroxide depletion in the boundary layer immediately adjacent to the anode (due to insufficient mixing and the very high current density) allowing corrosive ions such as sulfate and nitrate to react with the nickel surface. A white precipitate covered the anode side of the membrane and appeared to have penetrated into the membrane structure.

The cathodic current efficiency remained at >95%, producing 13–14% caustic for the entire test. The

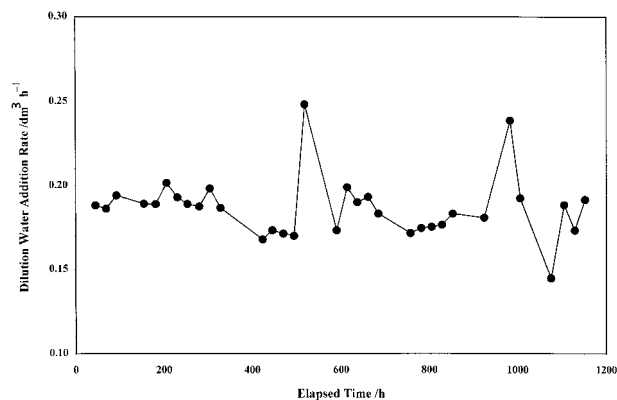


Fig. 2. Plot of the dilution water addition rate during test with platinized-titanium anode.

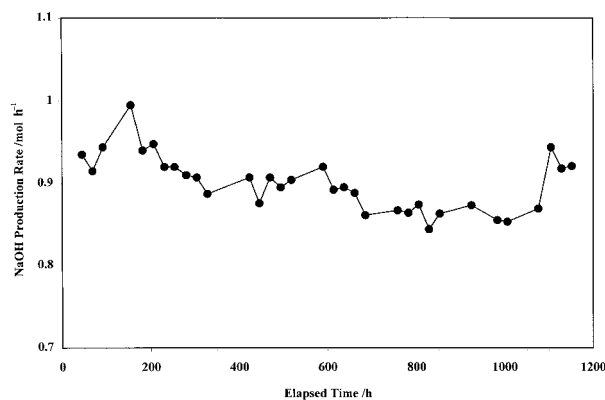


Fig. 3. Plot of the NaOH production rate during test with platinized-titanium anode.

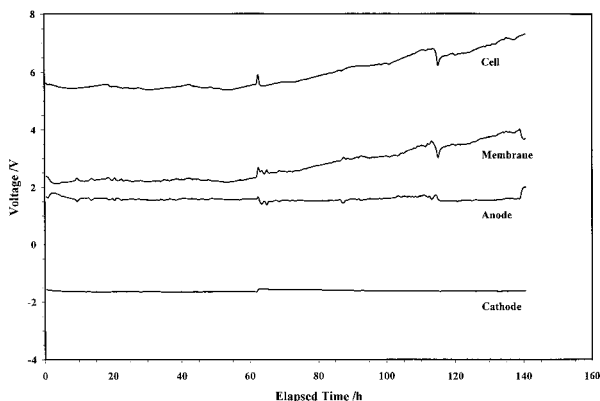


Fig. 4. Plot of individual and combined cell potentials during test with nickel anode.

current efficiency significantly exceeds that typically achieved for this type of membrane in chlor-alkali service (85%) [6]. The high current efficiency may result from the high salt concentration in the anolyte, which would tend to dehydrate the membrane and reduce the back migration of hydroxide species from the catholyte compartment. The high current efficiency does not result from the elevated temperature, which averaged 40 ± 5 °C. This temperature range falls well within that previously studied, which showed no temperature influence on caustic recovery efficiency with simulated waste solutions [2]. Water transport varied between 2.3–2.6 mol per mol Na^+ during the test. This result is slightly lower than values reported previously for chlor-alkali applications [7].

3.2. Platinized-titanium anode/nickel cathode configuration

Due to the premature failure of the Ni anode, a second long-term test was conducted with a platinized-titanium anode. This test used the anolyte solution from the end of the first test with the nickel anode (see Table 1). The test operated for a total of 1155 h. The test included several actions taken to ensure continued operation of the experiment. Table 2 provides a list of these actions.

Figure 5 provides a plot of the individual and combined cell potentials measured during the experiment. The cell voltage started near 6.4 V and remained stable for roughly 150 h before beginning to increase, reaching a high of 7.1 V after 258 h when the cell was shut down (event 1). The higher cell voltage results from the higher anode potential with a Pt-Ti anode (2.4–2.5 V) as compared to a Ni anode (1.6 V). The anode and cathode potentials remained fairly constant during this period. The membrane voltage, however, closely mirrored that of the cell, remaining relatively flat for 150 h before rising significantly.

Upon opening the cell, the membrane was found to have a white precipitate on its surface as well as within its structure. The anode was also coated with a whitish-yellow thin film. Analysis of the acid washings from the

Table 2. List of actions taken during test with platinized-titanium anode

Event	Elapsed time/h	Description
1	258	Cell opened, acid washed anode and membrane 1.0 M HCl, Membrane soaked in 4.0 M NaOH over weekend
2	426	Cell opened, acid washed anode and membrane 1.0 M HCl, Membrane soaked in 4.0 M NaOH for 1 h
3	594	<i>In situ</i> acid wash with 1.0 M HCl
4	640	<i>In situ</i> acid wash with 1.0 M HNO_3 , Added NaOH soln to bulk anolyte
5	808	<i>In situ</i> acid wash with 1.0 M HNO_3 , Added NaOH pellets to bulk anolyte, Washings analysed
6	934	<i>In situ</i> acid wash with 1.0 M HNO_3 , Washings analysed
7	1009	Cell opened, new platinized-titanium anode inserted, Added NaOH soln to bulk anolyte
8	1079	Cell opened, new membrane inserted, Added NaOH soln to bulk anolyte

membrane and anode indicated elevated levels of silicon and aluminium species as well as some calcium. The cell was reassembled and the test resumed. Thereafter, the cell was washed five more times with dilute acid solution (events 2 to 6) primarily due to increased membrane voltage. For event 2, the cell was washed to clear the plugged Luggin probe on the anode side. Each washing appeared to return the membrane voltage drop back to its original value. Analysis of the acid washings from events 5 and 6 indicated elevated levels of aluminium and silicon.

Bissot reported that silica species in the anolyte can transport into the membrane where it may combine synergistically with Ca and Al species to form precipitates, permanently damaging the membrane structure [8]. This movement is likely facilitated by the water transport occurring with the Na^+ ions and ultimately results in a reduction of the membrane lifetime [9]. Established silica maxima as low as 10 ppm as SiO_2 have been reported in chlor-alkali applications [10].

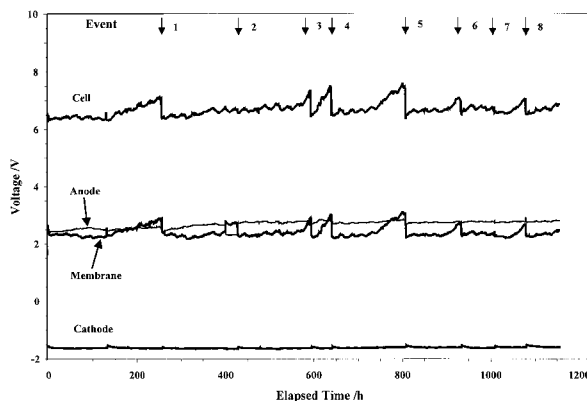


Fig. 5. Plot of individual and combined cell potentials during test with platinized-titanium anode.

(Note that these levels have been established for the bilayer membranes containing carboxylate polymer. These membrane structures show greater sensitivity to impurities than the 300 series membranes, which do not contain the carboxylated-polymer layer.)

Over the course of the test, the anode potential increased slowly but consistently from 2.4 to 2.7 V. This increase likely results from the changing nature of the reactions occurring at the anode. Figure 6 provides the anode gas production rate over the course of the test. The results show that for the first 650 h, 40% or less of the current is consumed by oxygen evolving reactions, with the remaining current used in oxidization of nitrite. Oxygen was the only gaseous product identified in the anode offgas. Analysis of the bulk anolyte (s Figure 7) during the test showed a steady decrease in the nitrite content and a corresponding increase in the nitrate content. Thereafter, the offgas production rate increases until the end of the experiment when the oxygen producing reaction consumed 75% of the current. The almost instantaneous increases in offgas flow rates observed after events 4, 5 and 7 likely result from the caustic added at those times, making conditions more favorable for oxygen evolution.

Sodium hydroxide was added to the bulk anolyte on several occasions to prevent precipitation of aluminium and silicon solids. Precipitation was initially observed after approximately 594 h when the caustic content dropped to 0.54 M NaOH. This caused a rapid increase in cell voltage and necessitated an acid wash (event 4) shortly after the previous one. Subsequently, the hydroxide concentration was maintained above 0.6 M in NaOH throughout the remainder of the test.

After 1009 h (event 7) the anode was reversed so as to expose the unused side to the solution. The cell operated a further 146 h with this anode surface to establish a new baseline with the changed anolyte composition. The potential profile for the new anode surface was almost identical to that of the used surface, indicating no apparent damage to the anode over the initial 1009 h.

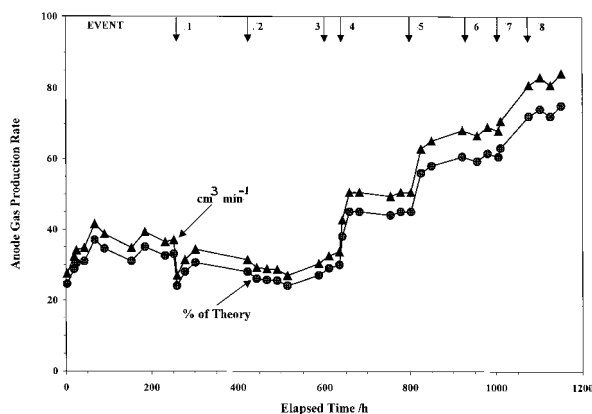


Fig. 6. Plot of anode gas production rates during test with platinumized-titanium anode.

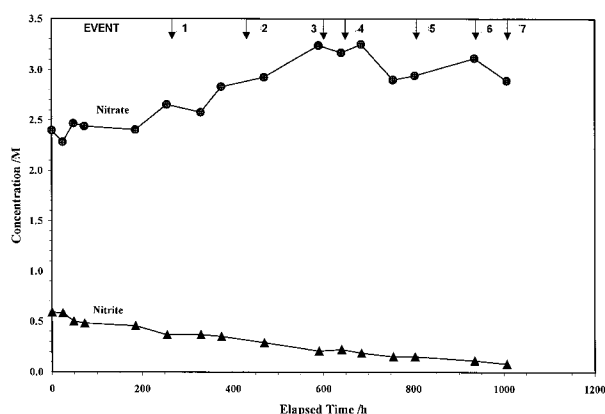


Fig. 7. Plot of nitrate and nitrite concentrations during test with platinumized-titanium anode.

Figures 8 and 9 show the catholyte hydroxide concentration and current efficiency, respectively, over the course of the test. The results indicate quite high current efficiencies for roughly the first 200 h, producing approximately 14% NaOH at an efficiency of greater than 95%. However, the efficiency declined slowly, finally averaging around 90%. After 1079 h, the Nafion® 350 membrane was replaced to determine the effect on current efficiency (event 8). The replacement resulted in an immediate and sustained increase in the current efficiencies back to >95%, as measured initially.

Samples of the used and unused membrane were analyzed by scanning electron microscopy. Comparison of the micrographs revealed no evidence of physical damage (e.g., blistering) to the membrane after 1079 h of testing. X-ray dispersion analysis indicated the presence of slightly elevated levels of silicon and aluminium. Apparently, the accumulation of silicon and aluminium has not reached the level necessary to produce visible physical damage in the membrane. However, the reduced current efficiency (Figure 9) suggests that the level of silicon and aluminium has resulted in a slight decrease in the performance of the

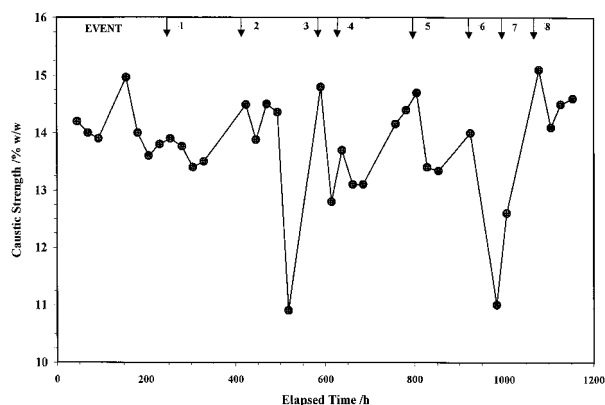


Fig. 8. Plot of catholyte caustic strength during test with platinumized-titanium anode.

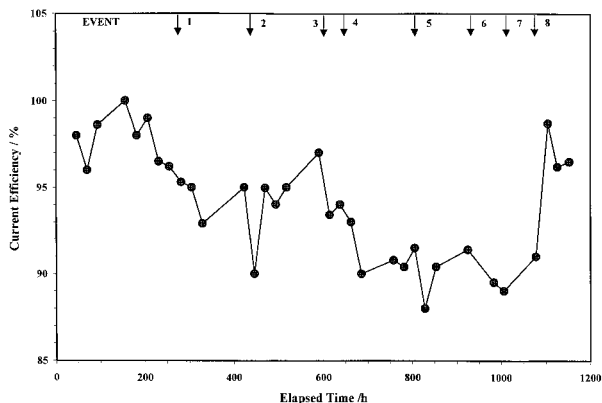


Fig. 9. Plot of caustic current efficiency during test with platinumized-titanium anode.

membrane. Based on these findings, we estimate an operational lifetime of greater than 5000 h for the membrane in this application.

Examination of the platinumized-titanium anode after the testing revealed a slight surface discoloration, but no evidence of corrosion or erosion. The cathode surface had a dark discoloration, easily removable by washing with dilute acid. The cathode exhibited no signs of corrosion or erosion. Based on the physical condition and the performance of the electrodes, we estimate the operational lifetimes for the electrodes at much greater than 5000 h in this application.

Figure 10 provides a plot of the water migration (mol H₂O/mol Na⁺) over the course of the latter test. For the majority of time, the water transport ranged between 2–3 mol/mol Na⁺, as reported in the initial test with the nickel anode. Over the course of the latter test, nitrate was the only impurity detected in the caustic product, averaging 0.4 mM with a high of 0.6 mM. These levels compare reasonably well with chloride levels reported in the caustic product of chlor-alkali membrane cells [11]. From this result, we calculate a maximum diffusion coefficient of nitrate at $3.6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, which is quite low compared to reported diffusion rates of other anions through perfluorosulfonic acid-type membranes

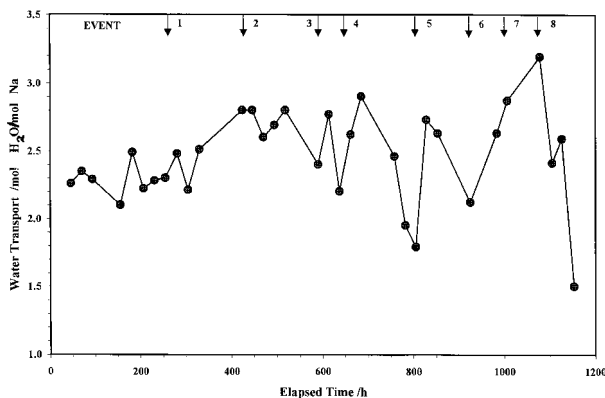


Fig. 10. Plot of the water transport during test with platinumized-titanium anode.

[12]. The low apparent diffusion coefficient reflects the retardation of nitrate migration due to the applied electrical field.

4. Conclusions

Long term performance of key cell components in a two-compartment membrane cell has been determined for the recovery of caustic from alkaline salt solutions. At a current density of 4000 A m^{-2} and temperature of $40 \pm 4^\circ \text{C}$, the cell consistently produced an average of 13.8 wt% NaOH solution of high purity. Comparison of the used membrane performance with that of a new piece indicates some damage. This damage likely results from the precipitation of aluminium and silicon species, which could form complex precipitates within the membrane structure. Based on examination and observed performance, we estimate an operational lifetime of the membrane in this application at greater than 5000 hours. A nickel cathode and platinumized-titanium anode exhibited excellent performance and durability. In contrast, a nickel anode exhibited significant corrosion at the high current density and, therefore, is not recommended for this application if the cell is operated at 4000 A m^{-2} .

Acknowledgements

The Department of Energy funded this work through a grant awarded to the Westinghouse Savannah River Company by the Office of Science and Technology through the Tanks Focus Area Program. David Hobbs thanks the Savannah River Technology Center for a mini-sabbatical and Augusta State University (Augusta, GA) for assistance in preparing this manuscript. The authors thank Dr Louis Burton (E. I. duPont de Nemours and Company) for invaluable discussions and assistance in membrane characterization.

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