

Performance of Liqui-Cel Extra-Flow Membrane Contractor in a Pure Water and in
a 0.2% Sodium Chloride Solution
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Introduction

After completion of SNO's first phase measurement of the neutrino charge current, two tons of salt were added into the SNO heavy water to increase the sensitivity of the neutral current measurement (Phase II). Liqui-Cel Extra-Flow Membrane Contactors (simply called Liqui-Cel) are used in the SNO heavy-water circulating system to remove the dissolved gases, such as oxygen, nitrogen, radon, and water vapor from the liquid water. One possible scenario with phase II operation is that the salt may leak through the Liqui-Cel Membrane and come in contact with the vacuum pumps and other metal components of the Heavy-Water Vapor Recovery System. In this scenario, corrosion will damage these components, especially the vacuum pump (Pfeiffer UniDry Pump with cast iron interior), and increase the operational difficulties.

A series of tests for the behavior of the Liqui-Cel System in pure water and in salt systems was conducted at the Brookhaven National Laboratory in order to measure the transfer of (a) water vapor and (b) salt, if there is any, through the membrane. Initially a 10-inch by 28-inch Liqui-Cel unit, identical to those used in the SNO heavy-water circulating system, was obtained from SNO site. However, extensive analysis showed that the membrane in this unit was defective; a replacement membrane would cost several thousand dollars. Instead, a smaller, 2.5-inch \times 8-inch Liqui-Cel, obtained from Dr. Richard Helmers of the University of British Columbia, was used in this experiment. A comparison of the present experiment with the SNO heavy-water system is done with theoretical calculations. The results are discussed in the following sections.

Membrane Contactor Integrity Test

Three conditions can cause the contactor to leak. These are membrane wet-out, fibers break, and leaking O-rings. An integrity test can verify the possibility of leaking, particularly caused by broken fibers or faulty O-rings, which normally lead to significant liquid passage into the vacuum stream (the "lumenside") of the contactor. This test pressurizes the contactor with water in the "shellside" and measures its drip rate through the lumenside port.¹ Before the test, the contactor was cleaned with distilled water in accordance with the Liqui-Cel *Cleaning Guidelines* procedures. The streams lumenside and shellside were dried by blowing nitrogen gas at 40 psig pressure through them. The contactor was filled with distilled water, the shellside lower outlet valve was closed, and 60 psig pressure was slowly applied at the shellside outlet valve. The lower lumenside port was then opened to measure the drip rate through the

top shellside outlet valve. The lower lumenside port was then opened to measure the drip rate for 1 hour. The results indicated that there was no noticeable leaking of liquid water through the contactor.

Gas Transfer Efficiency Test

An experimental scheme for the vapor-trapping system is shown in Figure 1. The water flow rate on the shellside was controlled at 1.5 gallons per minute (5.7 liters/min). Vacuum on the lumenside was maintained at < 25.4 mm Hg by a mechanical roughing pump. The ice and acid traps were used to collect water vapor that passed through the membrane. A water trap (~100 ml of distilled water) at the end of the series served to prevent acid fumes from entering the vacuum pump. After passing the water through the shellside, the top and lower lumenside ports were connected to the first trap, where a vacuum flask was immersed in a dry-ice, acetone bath (-79.5°C) to freeze the water vapor. Any residual vapor, if not completely caught in the cold trap, was then collected in the second trap filled with conc. H₂SO₄. Concentrated sulfuric acid is a valuable desiccating agent. It acts so vigorously in this respect that it removes water from almost any surface and thus becomes a very efficient absorber for water vapor.

A preliminary test was done by pressurizing an air stream through 100 ml of conc. H₂SO₄ solution. After 16 hours of continuous operation, more than 300 ml of water vapor from the air were caught in this sulfuric acid bath.

a). With Distilled Water

In the initial measurement with the Liqui-Cel, distilled water was used to evaluate the capability of catching water vapor with Trap I being kept either at room temperature or at -79° C. The data are presented in Table 1.

Table 1. Vapor Collected from Pure Water

	System I (Without ice bath)	System II (With ice bath)
Trap I (ml/min)	0.05	0.24
Trap II (ml/min)	0.24	0.14
Trap III (ml/min)	-0.06	-0.07

The data represent that, in total, 0.29 ml/min of water was accumulated without an ice bath in the system, while 0.38 ml/min water was collected with the ice bath. The latter system shows a better efficiency in trapping water vapor. Without the dry-ice bath, more than 80% of the water vapor was trapped in the Trap II, conc. H₂SO₄ solution, and only a few ml of water vapor resided in Trap I due to condensation. In contrast, in the system with ice bath, 63% of water vapor was trapped by the dry ice, while 37% was collected in the H₂SO₄. It should be noted that, in this test, the ice bath only covered about 2/3 of the collector. This might explain why some water vapor can escape from Trap I and be eventually stopped in Trap II. The small reduction of water in the water-filled Trap III was caused by water vapor being swept out by the vacuum pump. This will be discussed in the *Water Pressure* section.

b). *With Salt Solution*

The 0.2% NaCl solution was prepared by dissolving 20.25g of pure NaCl in 10 liters of distilled water. The corresponding concentration of Na⁺ ion in this solution is 786 ppm. The salt solution was circulated through the shellside ports for 24.5 hours and the water vapor was collected from the lumenside ports as indicated in Figure 1. Trap I was set up so that the dry-ice/acetone mixture covered ~95% of the trapping area. The solutions collected from the three traps were assayed in the BNL Chemistry Department for Na⁺ ions by atomic absorption (AA, Na⁺ sensitivity~ tenths ppm). The data are shown in Table 2.

Table 2. Vapor collected from 0.2% NaCl Solution and Measurement of Na⁺ ion

	System II (w/ ice bath)	
	Collected Solution	Na ⁺ (ppm)
Trap I (ml/min)	0.31	0.65
Trap II (ml/min)	0.00014	0
Trap III (ml/min)	-0.08	0

From Table 2, note that the salt solution has less total water collected than that from pure distilled water, which is attributed by the fact that the vapor pressure of salt solution is expected to be slightly smaller than that of pure water. In Trap I, 0.65 ppm of Na⁺ were found in 452 ml of collected solution, as compared to using pure water as the blank during the AA measurement. No Na⁺ ions were found in the other traps. By converting the concentration of Na⁺ ions in the collected solution into its total weight and comparing with the total weight of Na⁺ ions in the original salt solution (786 ppm in 10 liters), we find that 0.0037% of the original salt solution was leaked through to the shellside.

Since the NaCl cannot be vaporized under the experimental conditions, it is clear that this very small quantity of NaCl accumulated in Trap I was not from water vapor, but from other pathways, such as membrane wet-out, broken fiber, or leaking O-rings. Among them, membrane wet-out might be the main cause due to the following reasons: 1) Either broken fibers or leaking O-rings will cause a large quantity of water break through (as was observed in the previous tests with the 10 × 28 contactor). In our results, 0.0037% of Na⁺ ions only correspond to 0.37 ml collected in 24.5 hours, or 2.5 × 10⁻⁴ ml/min of NaCl, from the 10 liters of original salt solution. Recall also that the initial *Integrity Test* showed no signs of significant leaking. 2) Membrane wet-out has been reported in the literature for solutions such as surfactants and proteins. In our case of long-term operation, the possibility of membrane wet-out is highly suspect.

Another cause might be the migration of Na⁺ and Cl⁻ ions penetrating through the membrane. The effective pore size of the membrane (0.03 micron) is bigger than the atomic radius of Na⁺ (99 pm) and Cl⁻ (181 pm), respectively. Although the structure between the shellside and lumenside of the contactor has

several layers of membranes, it is possible, but not highly likely, that the ions may find a way through those layers to reach the lumenside, and thus be washed out.

Water Pressure Test

Le Châtelier's Principle explains the phenomenon of water reduction in Trap III. In a simple system, $A \rightarrow B$, as more of B (water vapor in our case) is removed, more of A (liquid water) is converted to vapor. A test was performed to determine the transitional rate between water liquid and vapor under the vacuum condition of the system. An amount of 200 ml of distilled water was placed in a flask under the vacuum for 16 hours and the reducing rate of water due to the phase transition was found to be 0.07 ml/min, which is similar to the previous observations in either pure distilled water test or salt solution test.

The Performances of 2.5×8 Liqui-Cel and 10×28 Liqui-Cel Liqui-Cel Degassing Systems

The hydrophobic polypropylene membrane in the Liqui-Cel contactor allows the gas and liquid phases to be brought in contact with each other in order to transfer mass between the phases. The performance factor, defined as the ratio of outlet dissolved-gas concentration (c_o) to inlet dissolved-gas concentration (c_i), of the contactor was given by Reed et. al.² as a function of mass-transfer coefficient (k), effective fiber area per volume (a), effective fiber length (L), and interfacial velocity (v):

$$performance = \frac{c_o}{c_i} = e^{-k a L / v} \quad \text{Eq. (1)}$$

and

$$v = \frac{4v_o}{\pi d^2 n} \quad \text{Eq. (2)}$$

where v_o is the water flow rate, d is the fiber diameter, and n is the number of fibers in the membrane. The gas stripping efficiency (ε , percentage of gas removal) with which a contactor can remove dissolved gas from water is typically described by the contactor's performance and is defined through Eq. (3):

$$\varepsilon = \frac{c_i - c_o}{c_i} \times 100 \quad \text{Eq. (3)}$$

For a gas molecule (vapor) to be collected in the lumenside of the Liqui-Cel, it has first to diffuse through the liquid water to reach a pore in the membrane, and then diffuse through the gas molecules inside the pore to the other side of the membrane. Yang and Cussler³ verified that the liquid water phase is the dominant resistance to mass transfer, and that the gas-phase and membrane resistances are negligible. The mass-transfer coefficient (k) was later formulated by Reed et. al.²:

$$k(d/D) = 1.62 \times \left(d^2 v / LD \right)^{1/3} \quad \text{Eq. (4)}$$

where D is the diffusion coefficient of gas in the liquid.

To compare the present experiments conducted at BNL with the operating conditions at SNO, the performance factors for both systems were calculated. Their operational parameters are listed in Table 3.

Table 3. Operational Parameters of individual *Liqui-Cel* Contactor.

Parameters	2.5×8 <i>Liqui-Cel</i>	10×28 <i>Liqui-Cel</i>
Effective Fiber Length ¹ (L , cm)	17.78	68.58
Interfacial Velocity ² (v , cm.s ⁻¹)	22.12	93.78
Number of Fibers ¹ (n)	10000	235000
Internal Fiber Diameter ¹ (d , cm)	0.024	0.022
Effective Area per Volume ³ (a , cm ⁻¹)	167	182
Water Flow Rate ⁴ (v_w , cm.s ⁻¹)	100	2666

¹Liqui-Cel Web site; ²Calculated from Eq (2); ³ $a = 4/d$ from Ref. 2; ⁴Experimental conditions at BNL and SNO, respectively.

Using the diffusion coefficient of water vapor¹, $D = 2.39 \times 10^{-5}$ cm².s⁻¹, the mass-transfer coefficients for 2.5×8 and 10×28 *Liqui-Cels* were calculated as 5.01×10^{-3} and 5.32×10^{-3} cm.s⁻¹ from Eq. (4). By applying these k values to Eq. (1), the performance factors for the 2.5×8 *Liqui-Cel* and 10×28 *Liqui-Cel* were determined as 0.511 and 0.523, respectively. Subsequently, through Eq. (3), the gas-stripping efficiencies for the 2.5×8 *Liqui-Cel* and the 10×28 *Liqui-Cel* were calculated as 48.9% and 47.7%.

Henry's law states that the amount of vapor in contact with the water at equilibrium is proportional to its partial pressure, which is a function of temperature and the concentration of dissolved gas in water. Thus the amount of dissolved gas is proportional to the quantity of water flowing through the contactor. The amount of vapor collected from the *Liqui-Cel* degassing system can then be correlated to the gas-stripping efficiency (ϵ) and water flow rate (v_w):

$$\text{vapor collection rate} = \Omega \times \epsilon \times v_w \quad \text{Eq. (5)}$$

where Ω is the percentage of vapor in the water, which is a function of temperature, dissolved gas, vacuum, and other operational conditions relating to the emanation and production of vapor.

By taking account of the average amount of water vapor collected from the Liqui-Cel column in the present experiment (0.33 ml/min at $v_{in} = 5.7$ liters/min) and at SNO (0.44 ml/min at $v_{in} = 160$ liters/min), the average percentage of vapor equilibrated with water during the period of operational time for each system can be calculated from Eq. (5).

$$\Omega_{BNL}, \% = \frac{0.33}{5.7 \times 0.489} \times 100 = 11.6\%$$

$$\Omega_{SNO}, \% = \frac{0.44}{160 \times 0.477} \times 100 = 0.58\%$$

with the assumption of 100% collection of water vapor in each condensation system (cold trap plus H₂SO₄ trap at BNL, heat exchanger/condenser at SNO). The difference of vapor pressure between heavy and light water is negligible.

Conclusions

(a). What can We do about the Salt?

In this study, a small quantity of NaCl (0.0037% w/w of original solution) was found to leak into the vacuum system either by the membrane wet-out or by the penetration of Na⁺ or Cl⁻ ions through the membranes. This result implies that in Phase II of SNO operations, salt ions will eventually reach the inside of the vacuum pump in the SNO heavy-water degassing system. This may damage the vacuum pump and then cause operational problems. Thus a careful evaluation for the rusting resistance of Pfeiffer Pump used at SNO heavy water system should be done.

Another aspect for consideration is to remove the salt ions before they reach the vacuum pump. Since the NaCl can only travel with the condensation water collected from the vapor, two possible ways are: 1) To place a simple filtration system (a horizontal column half filled with charcoal) in between the contactor and the vacuum pump to remove any break-through ions from the water; or 2) To add an accumulating tank in front of vacuum pump to serve as a reservoir to collect any liquids in the vacuum system before they entering the pump. The size of the tank depends on the amount of solution collected in the system, and an outlet valve in the bottom of the tank can be set up to release the accumulating liquid. This can be a very simple design and will not interfere with the system.

(b). A Comparison of SNO heavy-water system with Present Setup

The performance of the Liqui-Cel degassing system is an operationally defined method, which is very sensitive to the experimental conditions in each system. As can be seen from Eqs. (1), (2) and (4), the performance of the contactor can be correlated to the velocity through the fiber, the effective area of the fiber, the diameter of the fiber, and the diffusivity of the gas in the water. For a given contactor design, its performance is then simplified to a function of the water flow rate only. Accordingly, through the

theoretical discussion in our study, the gas-stripping efficiency decreases with increasing water flow rate for a specific degassing system.

The mass-transfer coefficients (k), a term that describes how quickly a mass can move through a medium, were calculated to be 5.01×10^{-3} and 5.32×10^{-3} cm.s^{-1} for the 2.5×8 Liqui-Cel (BNL) and the 10×28 Liqui-Cel (SNO), respectively, by using the known parameters of each operating system. The data also suggested that the 2.5×8 Liqui-Cel (48.9%) has a slightly better gas stripping ability than that of the 10×28 Liqui-Cel (47.7%) by a factor of 1.02. It should be noted that it is not proper to apply the performance factor of one specific system to another system, such as going from the 2.5×8 Liqui-Cel at BNL to the 10×28 Liqui-Cel at SNO, due to their different operating conditions, different water-collection systems, and particularly the differences in reaching liquid-vapor equilibrium in each system.

It is not surprising that the average percentage of vapor equilibrated with the heavy water (Ω) at the SNO degassing system (0.58%) is a factor of ~20 times smaller than that of present setup at BNL (11.6%). This discrepancy can be a result of several factors that differ between the two systems; among these are differences in their vapor collection methods, their water temperatures, and particularly, their water circulation pathways. At BNL, the circulating water flowing through the 2.5×8 Liqui-Cel contactor comes from an open reservoir, which is in contact with the room air during the operation. The gas content of the water can be recompensed by reestablishing equilibrium with the contacting air within a short time. On the other hands, the SNO heavy-water degassing system is designed to remove the gas in a closed system. Thus, the equilibrium between the liquid and vapor phases in the SNO degassing system cannot be really achieved. During long-term operation, the amount of water vapor at SNO decreases with increasing operating time, which is in contrast with the present BNL study, where the water vapor amount remains essentially constant at all times.

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References

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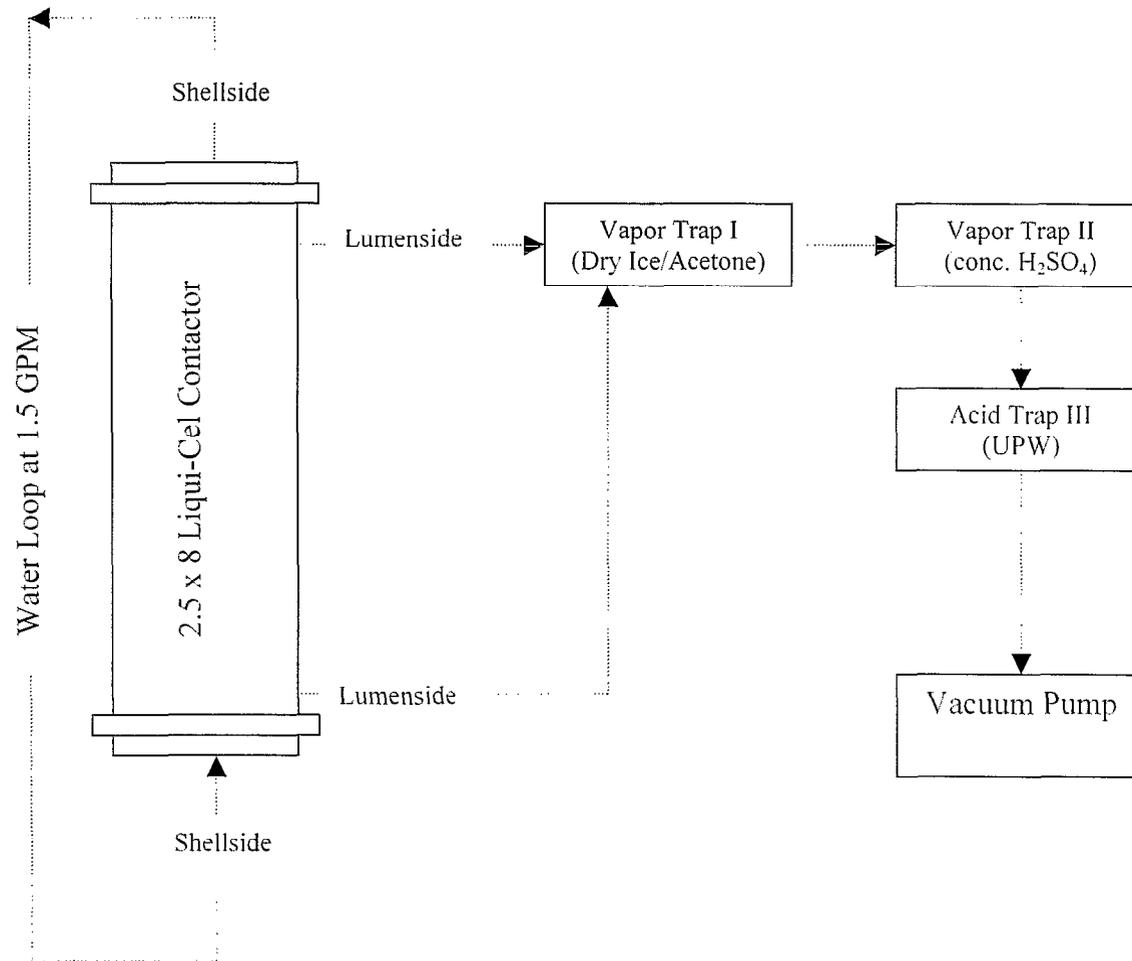


Figure 1. Flow configuration of Liqui-Cel membrane contactor.