^{6}Li Neutron Poison for SNO

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Abstract

The physics motivation for introducing a neutron poison into the D_2O is briefly reviewed and R&D on the purification, introduction and removal of ^{6}Li reported. One new aspect of this physics motivation is that the NC background from radioactivity in the NCDs can be measured, in-situ, by adding a poison to the D_2O with the NCD array in place. The proposed poison is 300 kgs of $LiNO_3$ (95% ^{6}Li enriched). The RO separation of $LiNO_3$ has been measured as a function of $LiNO_3$ concentration and is found to be very close to that of $MgCl_2$ and NaCl. Based on these results, the removal of the $LiNO_3$ from the D_2O would take about 19 days. Purification methods have been tested with ^{6}Li enriched sample material from Oak Ridge and the results indicate that it should be relatively straight forward to produce 300 kgs of purified $LiNO_3$. The cost is estimated at $60,000 and the production time of order one year.

1 Introduction and Physics Motivation

There are two independent possible signatures of neutrino oscillations in SNO: i) a NC/CC ratio greater than unity, and ii) a distortion of the ^{8}B CC spectrum. If oscillations are occurring it is most probable that both of these signatures will manifest themselves. However, there are some scenarios where only one of the signatures is present, e.g. in the case of oscillations into 'sterile' neutrinos the NC/CC ratio will be unity, whereas CC distortions should still occur.

The motivation for introducing ^{6}Li into the heavy water is primarily to enhance the detector's ability to measure CC distortions. For the theoretically favoured 'non-adiabatic' MSW solution [1] these distortions correspond to a suppression in the 5-7 MeV part of the spectrum, where complications will arise from neutron capture on deuterium (Q=6.25 MeV). To remove this complication, and measure a clean CC spectrum, it is proposed to introduce 300 kg of $LiNO_3$ salt (95% ^{6}Li) into the D_2O. The ^{6}Li will absorb the neutrons and reduce the capture efficiency on deuterium down to 1%, as compared to the 31% capture efficiency in pure D_2O, (see Table 1).

It has already been shown [2] that the complication arising from the deuterium n-capture gamma peak in pure D_2O reduces the significance of the non-adiabatic MSW CC distortion to a negligible level (a 1 sigma effect in one year's data). In contrast, by adding a poison such as ^{6}Li, the statistical significance of the CC distortion is greatly enhanced and one can exclude the null hypothesis (no distortion) at the 99.9% confidence level with one year's data.

Other reasons for considering a poison include the following:

- The combination of ^{6}Li and pure D_2O data sets would be another way of measuring the NC/CC ratio, with 10% error [3], providing that the background wall is at 5 MeV or lower. The attractive feature of this method is that the NC detection occurs in pure D_2O, when the photodisintegration backgrounds are likely to be smaller (and easier to measure) than with either of the other NC detection methods ($MgCl_2$ or NCDs).

- Adding ^{6}Li to the D_2O, with the NCDs in place, provides a way of measuring, in-situ, the NCD backgrounds, see Section 2.

- There is a 10-20% systematic error in the NC/CC ratio from the analysis of salt and pure D_2O data [2]. This is caused by not knowing a priori the CC shape. This error would be considerably reduced with ^{6}Li data. Moreover, there may be other systematic errors in the NC/CC ratio from unknown low energy backgrounds which would be easier to control with ^{6}Li data.

- In the unfortunate condition where the D_2O is swamped by a photodisintegration background which is large compared with the NC signal, using ^{6}Li may be our only chance of measuring CC distortions.

- The main difficulty in the calibration of the algorithms for NC/CC separation (in salt data) using event topology is obtaining a data set of single electron events. Although it is expected that the ^{8}Li calibration source will provide these events, the effect on the hit pattern from the shadowing by the source is a complication which does not arise if one were to use the CC events from a ^{6}Li run.

It has been suggested [4] that a simultaneous analysis of one year's salt data and one year's pure D_2O data should remove some of the ambiguities pertaining to the deuterium gamma peak. Another alternative [5] is to use the information from neutron captures on ^{3}He to account for the residual 12% capture efficiency on deuterium when the NCD array is in the D_2O. It is easy to show that using ^{6}Li is qualitatively better than either of these methods (salt + pure D_2O

or NCDs). However, a quantitative evaluation of the sensitivity to MSW distortions, for all of these schemes, requires a careful analysis where numerous systematic effects are studied. This analysis is in progress and results are expected within the next six months.

^{6}Li enriched lithium nitrate (300 kilograms) has been chosen as the most suitable chemical form for introducing a neutron poison into the heavy water because it is chemically very similar to the magnesium chloride salt (2 tons) which has been developed, over many years, as a neutral current additive. Thus, the reverse osmosis technology (already purchased by SNO) for removing magnesium chloride from the D_2O can also be used for removing lithium nitrate. This has been demonstrated, in small scale laboratory tests, by A. Kumar and K. Lamb [9] of NRC Canada at LBL's request, (see Section 3 and Appendix 1).

^{6}Li is supplied by Oak Ridge National Lab. in the chemical form of $LiOH.H_2O$. A 1 kg sample has been purchased and analysed for chemical and radioactive contamination, (see Appendices 2 and 3). A chemical procedure has been established for converting the $LiOH.H_2O$ into $LiNO_3$ and, at the same time, removing the Th and U chain contamination as well as chemical contaminants, (see Section 4). This procedure has been successfully carried out at the 1 kg scale using the sample material from Oak Ridge.

An important consideration for any poison is plating-out on the acrylic vessel. The solubility of $LiNO_3$ is 100 g per 100 g of H_2O which is larger than the proposed operating concentration of 300 ppm by a factor of 3,000. Nevertheless, the question of plating-out or diffusing into the acrylic vessel should be addressed, through tests, well before introducing any poison into SNO.

2 NCDs with $LiNO_3$ or $MgCl_2$ in the D_2O

A new way of measuring, in-situ, the NC background from radioactivity in the NCDs is proposed. It relies on the fact that the capture efficiency on ^{3}He is different for neutrons born near the NCDs ('NCD β-γ' neutrons) than for neutrons born uniformly in the D_2O ('NC' neutrons), see Table 1. On its own, this fact is not sufficient to decouple these two kinds of neutrons. However, by adding ^{6}Li (or $MgCl_2$ [6]) to the D_2O, with the NCDs still in place, one can enhance the difference in ^{3}He capture efficiencies between the two kinds of neutrons. Let us assume, for example, that SNO was run for 1 year with NCDs in pure D_2O and 1 year with NCDs in D_2O + $LiNO_3$ then the number of ^{3}He captures in the two years, M_1 and M_2 respectively, would be given by the following matrix equation:

$$\begin{pmatrix} M_1 \\ M_2 \end{pmatrix} = \begin{pmatrix} E_{\mathrm{NC},1} & E_{\mathrm{NCD},1} \\ E_{\mathrm{NC},2} & E_{\mathrm{NCD},2} \end{pmatrix} \begin{pmatrix} N_{\mathrm{NC}} \\ N_{\mathrm{NCD}} \end{pmatrix} \qquad (1)$$

where N_{NC} is the number of 'NC' neutrons (from neutrinos + radioactivity in the water), N_{NCD} is the number of 'NCD β-γ' neutrons, and the E matrix represents the ^{3}He capture efficiencies for the different neutron types in the different years.

Assuming that these capture efficiencies are given by Table 1 (they can be calibrated), and that the statistical errors in M_1 an M_2 are, respectively, $\sqrt{1.5 M_1}$ and $\sqrt{1.5 M_2}$, one can use Eq. (1) to find $N_{\rm NC}$ and $N_{\rm NCD}$ and their errors. (The choice of using $\sqrt{1.5 M_1}$ for the error is a reasonable guess given that half the ^{3}He neutron captures fall in the 'background-free' region whilst the other half appear in a peak above an alpha continuum [7]). In the case of a full SSM flux of neutrinos, negligible water background, and a 20% SSM NCD background the measured values would be $N_{\rm NC} = 5000 \pm 570$ and $N_{\rm NCD} = 1000 \pm 430$. If one were to use 2 tons of $MgCl_2$ or only 100 kg of $LiNO_3$ instead of the 300 kg of $LiNO_3$ then, for the same scenario, the measured values would be $N_{\rm NC} = 5000 \pm 850$ and $N_{\rm NCD} = 1000 \pm 660$.

There are, of course, a number of implicit assumptions in the above treatment: a very low or constant water background, a very small NCD 'counting' background (e.g. from electronics) and small uncertainties in the calibration of ^{3}He capture efficiencies. The uncertainty in the 'NC' rate after two years of data taking $N_{\rm NC} = 5000 \pm 570$ is certainly not as good as the 2% statistical error in M_1 (which does not take into account any uncertainty from NCD backgrounds). Nevertheless, in the case of non-adiabatic MSW oscillations the NC/CC ratio would still be many standard deviations away from unity, even with this relatively high error.

Other methods for measuring, in-situ, the NC background from the NCDs include a variety of coincidence measurements and the analysis of low energy signals. In all these cases, the measured rate (of coincidences or low-energy signals in some energy range) is a strong function of the location (within the NCDs) of the radioactivity. This is *not* the case for the method proposed above, and this is its principal attraction. For this reason, it is especially important to model the dead-zone for neutron detection which occurs at the join between two NCD segments, to see what effect this has on the ^{3}He neutron capture efficiency for neutrons from radioactivity in these dead-zones.

It would be very useful to bring together all the methods for measuring the NC background from the NCDs into one coherent analysis, where they could be quantitatively compared under a variety of scenarios for the amounts and locations of Th and U backgrounds.

3 Introduction and Removal of $LiNO_3$ from the D_2O

Three hundred kilograms of $LiNO_3$ in 1,000 tonnes of D_2O corresponds to a 300 ppm solution. This solution has a density about 300 ppm greater than pure D_2O at the same temperature. At the 10°C operating temperature of the detector the density of D_2O is close to its maximum and changes very slowly with temperature: 10 ppm per °C. Thus it should be easy to establish stratification with a 300 ppm $LiNO_3$ solution, as is planned for the 2,000 ppm $MgCl_2$ solution [8]. By pumping 300 ppm $LiNO_3$ solution into the bottom of the acrylic vessel (AV) and

	'NC' neutrons			'NCD β-γ' neutrons		
Fill	^{2}H	Cl or ^{6}Li	^{3}He	^{2}H	Cl or ^{6}Li	^{3}He
D_2O	31.4±0.6					
D_2O + 0.3 kg $LiNO_3$	29.8±0.6	2.4±0.2				
D_2O + 300 kg $LiNO_3$	1.1±0.1	90.7±1.0				
D_2O + 2 tons $MgCl_2$	2.8±0.2	82.8±0.9				
NCD	12.5±0.4		47.3±0.7	13.1±0.8		56.1±1.7
NCD + 0.3 kg $LiNO_3$	12.2±0.3	1.0±0.1	46.4±0.7	13.0±0.8	0.9±0.2	55.5±1.7
NCD + 300 kg $LiNO_3$	1.1±0.1	85.7±0.9	4.8±0.2	1.1±0.2	83.8±2.0	11.2±0.7
NCD + 2 tons $MgCl_2$	2.4±0.2	73.8±0.9	9.8±0.3	2.8±0.4	72.6±1.9	16.8±0.9

Table 1: Neutron capture efficiencies (in %) on ^{2}H, ^{35}Cl, ^{6}Li and ^{3}He from Monte-Carlo simulations using SNOMAN 2_09 (development release). In each case, 10,000 NC neutrons were generated and, where applicable, 1,000,000 β-γ's in the outer volume of the NCDs. The errors are purely statistical.

removing pure D_2O from the top of the AV, the full 300 kg of $LiNO_3$ would be introduced in 4 days, the turn-over time of the 1,000 tonnes of D_2O. In practice, just after the 4 day fill, there may be some small non-uniformities in $LiNO_3$ concentration as a function of position in the D_2O but these would be quickly damped out over a time scale of one or two weeks (by adjusting the $LiNO_3$ concentration in the D_2O recirculation flow).

Removal of the $LiNO_3$ proceeds in the reverse direction: 300 ppm solution is pumped out of the bottom of the AV, passed through a reverse osmosis (RO) plant and returned to the top of the vessel at a lower concentration. If there is sufficient density difference between the 300 ppm solution and the return D_2O solution then stratification occurs and in 4 days the $LiNO_3$ concentration has been reduced by a factor $1/(1-\varepsilon_{\rm RO})$ where $\varepsilon_{\rm RO}$ is the RO separation [8]. This process, of reduction in concentration by a factor $1/(1-\varepsilon_{\rm RO})$ every 4 days, will repeat itself until the concentration of $LiNO_3$ is too small to sustain stratification ($\sim$ a few ppm). At this point convective mixing may occur in the vessel (or be forced to occur, if necessary). In this case the concentration falls like an exponential with a time constant $\tau = 4/\varepsilon_{\rm RO}$ in units of days [8].

An investigation [9] of $\varepsilon_{\rm RO}$ as a function of $LiNO_3$ concentration has been carried out, at LBL's request, by A. Kumar and K. Lamb of the Process Technology Division, Institute for Environmental Research and Technology, NRC Canada. For this investigation, Seprotech, the company that has supplied the D_2O RO plant, donated samples of the same membrane type as in the D_2O plant. The method and results of the investigation can be found in Appendix 1 of this report.

In summary, $LiNO_3$ exhibits very similar RO separation to NaCl and $MgCl_2$. At 300 ppm,

$\varepsilon_{\mathrm{RO}} = 97 \pm 1\%$, so that one can reasonably expect the $LiNO_3$ concentration to drop by a factor of about 30, down to 10 ppm, after the first four days of removal. At this lower concentration the data suggest that $\varepsilon_{\mathrm{RO}}$ drops to $90 \pm 1\%$, although A. Kumar indicates in his report that this is probably an artifact of using conductivity to measure $LiNO_3$ concentration (this is not an accurate method at such low concentrations). In any case, even assuming $\varepsilon_{\mathrm{RO}} = 90\%$, the exponential time constant for removing $LiNO_3$, when mixing is occurring in the vessel, is $4/\varepsilon_{\mathrm{RO}} = 4.5$ days. Using this decay time (i.e. assuming no stratification at concentrations of 10 ppm and lower) it would take a further 15 days to reduce the $LiNO_3$ concentration from 10 ppm down to 0.3 ppm, the point at which it has practically no effect on neutron capture efficiencies, (see Table 1). Thus, the total time for removal is 19 days. An even more conservative estimate can be derived by assuming mixing (no stratification) throughout the removal process in which case it would take 30 days.

One of the advantages of using ^6Li as a poison is that the whole process of introducing and removing the poison from the D_2O can be tested with ^7Li enriched $LiNO_3$ at no risk to the NC capabilities of the detector. Alternatively, $MgCl_2$ can be used as a representative test case since it has practically identical RO separation ($\varepsilon_{\mathrm{RO}}$) to $LiNO_3$.

In terms of capital equipment, the only significant addition to the D_2O system needed to accommodate the ^6Li option would be a brine holding tank of about 7.5 tons capacity. This volume has been chosen to store the 300 kg of $LiNO_3$ at 4% concentration. The maximum concentration that can be achieved by RO separation at the system's working pressure of 1000 psi is 6% [10].

4 Preparation and Purification

Oak Ridge supplies 95% enriched ^6Li in the chemical form of $LiOH.H_2O$, and this has to be converted into $LiNO_3$ before introduction into the D_2O. A chemical procedure has been established for performing this task and, at the same time, removing chemical and radioactive contamination by using exactly the same techniques that have been developed for the purification of $MgCl_2$.

Tests at the 100 g and 1 kg scale (mass of $LiNO_3$) have been performed using both technical grade natural $LiOH.H_2O$ and a sample of the ^6Li enriched $LiOH.H_2O$ from Oak Ridge. The procedure was as follows:

1. Dissolve $LiOH.H_2O$ in deionised H_2O to make a volume x of 3.75 M LiOH.
2. Filter the LiOH solution to remove particulates.
3. Prepare a volume (slightly less than $x/2$) of 7.5 M HNO_3 with a 1,000 ppm concentration of dissolved Ti^{4+} ions.

			purification factor			
Raw material	mass of $LiNO_3$	# of HTiO stages	Ra	Th	U	K
natural $LiOH.H_2O$	1.5 kg	1	≥ 20	≥ 20	-	-
95% ^{6}Li $LiOH.H_2O$	1.1 kg	2	-	≥ 50	≥ 140	1.5

Table 2: Purification factors, measured by gamma counting, for two tests of the procedure for converting $LiOH.H_2O$ into $LiNO_3$. In the case of natural $LiOH.H_2O$ only one stage of HTiO purification was used, i.e. steps 6 and 7 of the procedure were omitted. The Ra and Th purification factors were established using gamma lines corresponding to ^{226}Ra and ^{228}Th (and their short-lived daughters). In the case of the 95% enriched ^{6}Li, these gamma lines were too weak to give meaningful results and instead the lines corresponding to ^{235}U and ^{234}Th were used, (see Appendix 2).

4. Mix the HNO_3 acid with the LiOH alkali to neutralize (most of) the alkali into $LiNO_3$ and precipitate the Ti^{4+} (300 ppm) into an suspension of hydrous titanium oxide (HTiO) that absorbs Th, U, Ra and other contaminants. The final pH should be between 10-11 to maximize the effectiveness of the HTiO.
5. Allow the solution to settle and filter the supernate to remove the HTiO.
6. Add a small volume of HNO_3 with a high concentration of Ti^{4+} ions to the $LiNO_3$ + LiOH solution to make the Ti^{4+} (300 ppm) precipitate into HTiO giving a second chance for absorbing contaminants. The final pH should still be in the range 10-11 for maximum effectiveness of the HTiO.
7. Repeat step 5.
8. Adjust pH to 7 by adding a small amount of HNO_3. The solution is now 15% $LiNO_3$.
9. Evaporate solution to dryness by heating. Above 70°C the $LiNO_3$ looses all its waters of hydration.

In all of the tests carries out so far, the gamma count of the final purified material showed an activity level consistent with zero, at the sensitivity limit of the counter. The detailed results for the 1 kg test with enriched ^{6}Li are shown in Appendix 2. In table 2 we summarize these results by taking a conservative view of using 4 sigma limits to calculate the minimum purification factor obtained, where the purification factor is defined as the specific activity (per gram of Li) before purification divided by the specific activity after purification.

The overall conclusion is that the HTiO purification works well and is not influenced by the quite large amounts of chemical contamination in the ^{6}Li enriched $LiOH.H_2O$, (see Appendix 3). Unfortunately, gamma counting is not sufficiently sensitive to determine whether the required levels of 10 ppt Th chain and 100 ppt U chain have been reached (10% SSM NC background).

30 kg ^{6}Li (205 kg of LiOH.H_2O)	$41,525
Five 55 gallon polypropylene tanks	$1,500
Peristaltic pump + accessories	$1,250
Chemicals	$2,725
Teflon coated immersion heaters	$1,500
9 cubic ft. convection oven	$3,500
Filters (coarse and ultra-filters)	$3,000
Mechanical mixer	$1,000
400 hours of student labour	$4,000
Total	$60,000

Table 3: Estimated cost of producing 300 kg of $LiNO_3$ (95% enriched ^{6}Li).

Nevertheless, it seems likely that the purity of the final product is not too far from these targets since the raw material starts at a few ppb contamination (see Appendix 2) and the purification factor per HTiO stage is at least 20.

Curiously, there is about 1 ppm of ^{238}U and ^{235}U (equivalent) contamination in the Oak Ridge material. This does not represent any danger with respect to a photodisintegration background, since the U chain is broken by the 1,600 year half-life of ^{226}Ra. Nevertheless, it would be preferable to reduce this contamination down to the 100 ppt level so that there are no dramatic disequilibria in the Th and U chains which might affect our ability to distinguish U and Th in the D_2O by spectral analysis of low energy signals [13]. The results in Appendix 2 suggest that 3 stages of HTiO purification would be sufficient to reach the 100 ppt level.

HTiO is not expected to remove K, and so the purification factor of only 1.5 (see Table 2), after two stages of HTiO purification, is not surprising. A technique for K purification in $MgCl_2$ solutions, using sodium tetraphenylboron (TBP) and ammonium, has been developed by W. Locke at Oxford. This technique is expected to work equally well in $LiNO_3$ solutions. Small scale tests have been carried out by W. Locke with natural $LiNO_3$ and the preliminary results indicate a purification factor in excess of 300. A report will be available soon. It seems very likely that this technique will be able to purify the ^{6}Li enriched $LiNO_3$ by the required factor of ten to bring the K level down to 2 ppm.

The remaining R&D tasks with regards to the preparation and purification of the $LiNO_3$ are as follows: i) determine the exact number of HTiO stages (2, 3 or 4) required to reach the Th and U chain purity goals (by using more sensitive assay techniques which have been developed by the water group), ii) test the TBP potassium purification technique on ^{6}Li enriched $LiNO_3$, and iii) measure the chemical purity, optical transmission in the wavelength range 300-500 nm, and residual hydrogen content of purified and dried $LiNO_3$.

An estimate of the cost of making 300 kg of $LiNO_3$, using a procedure with 3 HTiO and 1 TBP (potassium) purification stages, is given in Table 3. It is estimated that it would take three months to set-up a production facility and three months to produce the $LiNO_3$ in ten batches of 30 kg. This does not include the lead time in ordering of components, e.g. the Oak Ridge ^6Li enriched $LiOH.H_2O$ takes 4-6 months for delivery.

5 Conclusion and Recommendation

Adding a neutron poison to the D_2O is an important running option for measuring CC distortions, the NC/CC ratio with pure D_2O and NCD photodisintegration backgrounds, (see Sections 1 and 2). Although there are several other ways of configuring the detector, each with its own advantages, it seems clear that we will learn the most by running the detector in as many ways as is practical over the five years or so that SNO will take data. This is one of the strengths of SNO with respect to other experiments in the field of solar neutrinos.

Over the course of the last year, about four man-months of SNO R&D effort have revealed the following: i) RO separation of $LiNO_3$ is very similar to that of $MgCl_2$ and hence the RO system for removing $MgCl_2$ from the D_2O should also be able to remove $LiNO_3$, ii) Th, Ra and U purification using HTiO works well for $LiNO_3$ solutions and there should be no difficulty reaching the required purity goals, and iii) K purification using TBP works well for $LiNO_3$ solutions and there should be no difficulty reaching the required purity goal. In addition, it is estimated that it would take one year and $60,000 to produce three hundred kilograms of purified $LiNO_3$ (95% ^6Li enriched).

Since it is likely that the earliest time at which ^6Li would be added to the D_2O is at least two years from now, it is not necessary, at present, to reach a decision about the use of ^6Li. We propose to continue investing a small amount of effort to pursue the remaining R&D tasks discussed in Section 4. In addition, the detailed question of the sensitivity to MSW distortions for the various running options (^6Li, NCDs and salt + pure D_2O) will be investigated and it is hoped that these studies will clarify the case for a poison.

The objective is to assemble, over the next year, all the relevant information to enable the collaboration to make a decision about the desirability of the ^6Li option. This time scale has been chosen to leave enough time for production of 300 kgs of $LiNO_3$, should the collaboration decide to go ahead with the ^6Li option.

References

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Appendix 1

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Process Technology
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Lithium Nitrate Separation Data for a Commercial Membrane

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For: Lawrence Berkeley Laboratory

NRC No. ER-1356-95S
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Canada

Lithium Nitrate Separation Data for a Commercial Membrane

Objective:

Performance evaluation of a commercial membrane for separation of lithium nitrate from aqueous solutions of varying concentrations at a constant trans-membrane pressure.

Experimental:

Laboratory RO water (mean conductivities of 1.18±0.11 μS) was used for permeation tests and for preparing lithium nitrate solutions of different concentrations. Temperature of pure water and the lithium nitrate solutions was maintained at 23±1 °C in all experiments. These experiments were performed at a trans-membrane pressure of 920 psi (6.3 MPa).

Standard NRC test cells, with a membrane test area of 10.5 cm^2 were used. A schematic diagram of the experimental set-up is given in Figure 1. A more detailed description of this set-up is given elsewhere (1).

Six membrane coupons of proper size were cut from the sample of the commercial membrane supplied by Seprotech and placed in tests cells. These coupons were rinsed with fresh water to remove the preservatives and other chemicals. Permeation rates for these coupons were determined after permeation of test solutions (RO water, sodium chloride or lithium nitrate solutions) for 2 h. A combined feed flow rate of 22.8 kg/h for the six cells was maintained. Lithium nitrate separations were primarily based on conductivity measurements.

Results:

Preliminary Tests:

Samples of the pure water permeate from all six coupons were collected after the stabilization. Similar data were collected for permeation and separations of a 5,000 ppm sodium chloride solution. Data for individual membrane coupons, mean and standard deviation values are listed in Table 1:

Table 1: Separation of sodium chloride and permeation rates for sodium chloride and pure water.

Membrane Coupon #	1	2	3	4	5	6
Pure Water						
Initial permeation rate, kg/m^2.d	4,544	4,219	4,387	4,047	4,291	4,008
Final permeation rate, kg/m^2.d	3,438	3,175	3,347	3,061	3,265	3,114
Sodium Chloride, 5,000 ppm						
Initial permeation rate, kg/m^2.d	4,109	3,459	3,569	3,339	3,553	3,289
Mean, standard deviation	3,553±294					
Final permeation rate, kg/m^2.d	2,869	2,659	2,793	2,559	2,730	2,585
Mean, standard deviation	2,699±121					
Initial separation, %	98.9	99.0	98.7	99.0	98.9	99.0
Mean, Standard Deviation	98.9±0.1					
Final separation, %	98.9	99.2	99.0	99.3	99.2	99.2
Mean, Standard Deviation	99.1±0.1					

Experiments with Lithium Nitrate Solutions:

Lithium nitrate solutions of various concentrations (10-3000 ppm) were prepared using RO water and analytical grade lithium nitrate. Permeation rates and separation were calculated for six membrane coupons. A combined feed flow of 22.8 L/h was maintained. The permeate rate was about 4% of the combined feed flow rate. It should be noted that in the case of a spiral wound element the permeate rate is usually about 10% of the feed flow rate of such dilute solutions. Mean values of permeation rate and separations of these six membrane coupons for feeds of varying lithium nitrate concentrations are listed in Table 2.

Table 2: Permeation rates and separation of lithium nitrate solutions

Concentration of lithium nitrate in feed, ppm	Permeation rate, standard deviation, $kg/m^2.d$	Separation, standard deviation, %
10	3,580±126	90.5±0.8
30	3,730±142	90.2±2.3
300	3,121±107	96.9±1.1
500	3,326±174	97.0±0.7
1,500	3,095±149	98.0±0.3
3,000	2,859±93	98.3±0.3

It is clear from the data in Table 2 , that separations are increasing with increase in lithium nitrate concentrations. It is mainly due to the errors associated with measuring conductivities of very dilute solutions. Additional experiments were performed to determine the separations for dilute sodium chloride solutions which showed similar trends. For example separations of 98.9±0.0 and 94.2±0 % were observed for 3,000 and 30 ppm sodium chloride solutions, respectively.
In order to clarify this point further, separations were calculated based on lithium analysis by atomic absorption spectroscopy for 500 and 1,500 ppm lithium nitrate solutions. These data are listed in Table 3.

Table 3: Separations of lithium nitrate determined by conductivity and atomic absorption methods.

Concentration of lithium nitrate in feed, ppm	Mean separations, standard deviations, %	
	conductivity	atomic absorption
500	97.0±0.7	97.6±0.9
1,500	98.0±0.3	98.4±0.4

It is evident from the data in Table 3 that separation values determined by conductivity measurement and atomic absorption analysis were comparable.

Reference:

1. J. D. Hazlett, O. Kutowy and T. A. Tweddle, "Commercial Ultrafiltration Membrane Performance Evaluation", M. H. Baird and S. Vijayan, Eds. 1989, Proceedings of 2nd International Conference on Separations Science and Technology, Canadian Society for Chemical Engineering, Ottawa, ON, pp 65-74.

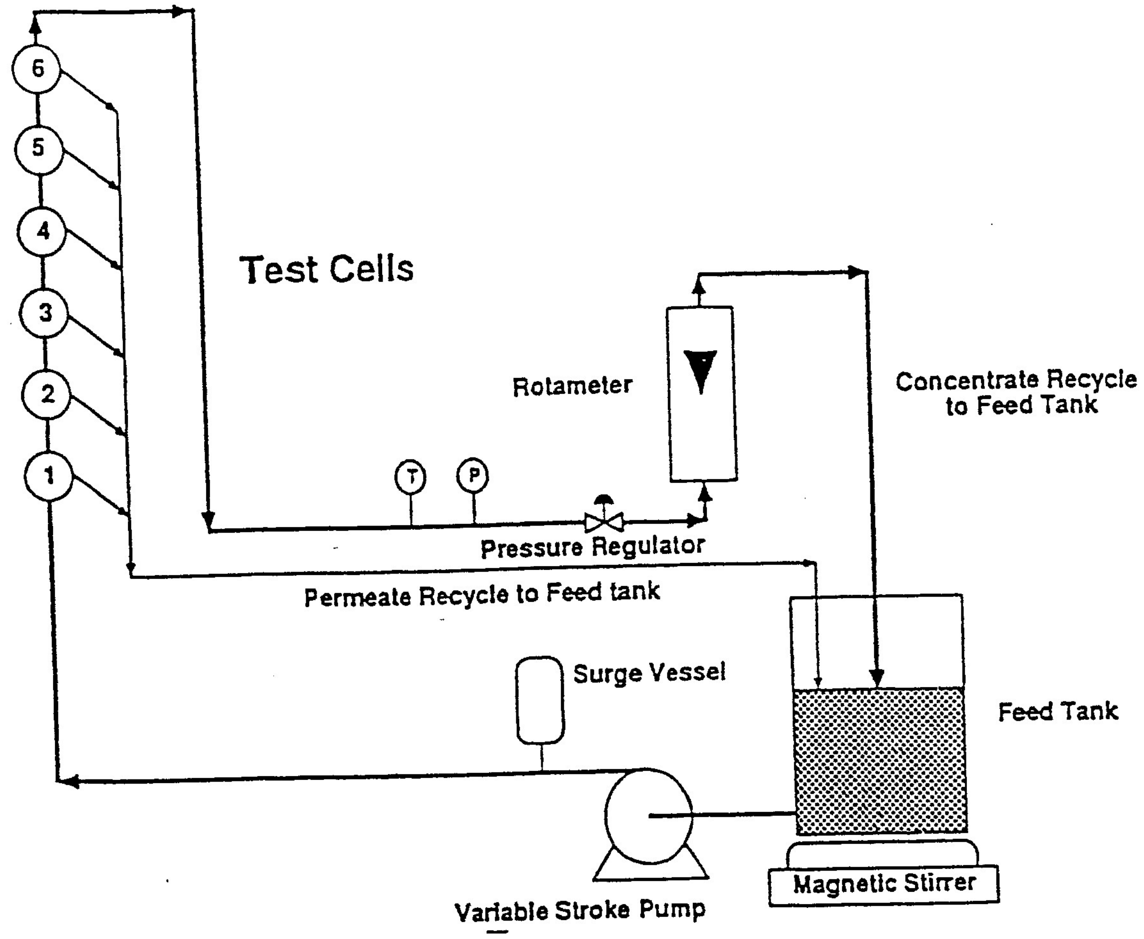

Figure 1: Schematic diagram of RO/NF test system.

Appendix 2

LBL/LBF
11/26/95

A.R. Smith
D.L. Hurley
R.J. McDonald

RADIOACTIVITY IN Li-6 ENRICHED LITHIUM NITRATE: PURIFIED FILTRATE AND RAW MATERIAL

We summarize results of gamma-spectrometric measurement on the residual radioactivity in one sample of purified lithium nitrate that is enriched in Li-6 (ORNL-supplied material). Filtration and chemical purification were done by Martin Moorhead on a 1000-gram amount of the compound. The resulting solution was evaporated to a volume of about 2000 ml, almost all of which was transferred into a "standard" counting container: a 6-in diameter Marinelli Beaker. The following analysis is based on a lithium nitrate quantity of 1000 grams.

This sample was counted at our Oroville Facility with the "Morgen" Ge-detector system (30% rated efficiency) for a period of about 13 days (two weeks minus an initial "cooling off" interval to allow for decay of Rn-222 and Rn-220 daughters). The observed peak count rates were BKG-corrected and then converted into radionuclide concentrations by comparison to a same-geometry "standard" containing known quantities of these same activities.

The "standard" material used for this comparison is an expanded volcanic ash, called "PERLITE". It is a material with major element composition and specific gravity similar to the previously used VERMICULITE, but has an important advantage of significantly higher uranium and thorium content, which permits use of shorter counting times for calibration runs (a two-fold reduction).

Element & (KeV)	BKG c/min	Net c/min	Concentration	
U (93)	0.0222+-.0019	0.0043+-.0026	4.1+-2.5	ppb
U (186)	0.0137+-.0017	0.0047+-.0021	3.5+-1.6	ppb
U (295)	0.0092+-.0012	0.0032+-.0018	1.1+-0.6	ppb
U (352)	0.0203+-.0014	-0.0009+-.0020	-0.2+-0.4	ppb
U (609)	0.0134+-.0010	0.0067+-.0016	1.7+-0.4	ppb
U (1120)	0.0028+-.0005	0.0011+-.0008	1.2+-0.9	ppb
U (1764)	0.0025+-.0004	0.0002+-.0006	0.3+-1.0	ppb
****** Weighted average (5)			0.8+-0.2	ppb
Th (238)	0.0298+-.0020	0.0012+-.0025	0.4+-0.9	ppb
Th (583)	0.0077+-.0008	-0.0001+-.0011	-0.1+-1.4	ppb
Th (911)	0.0053+-.0006	-0.0015+-.0008	-2.5+-1.3	ppb
Th (2614)	0.0041+-.0005	-0.0002+-.0007	-0.6+-2.2	ppb
****** Weighted average (4)			-0.5+-0.6	ppb
K (1461)	0.0039+-.0005	0.0385+-.0015	25. +-1.	ppm

Available BKG data is only of statistical quality comparable to the sample data. BKG data from a much longer count time could reduce the standard deviations on the above results by a factor of 1.4 at most. However, really important improvement in statistical quality of results would require use of the MERLIN system and larger sample size.

A sample of the lithium nitrate raw material (as received from ORNL) had previously been analysed at our Berkeley Facility with the "NGEM" detector system (about 30% rated efficiency). The sample consisted of the entire contents of "Can #2", a 1564 gram quantity of granular material, which was divided equally into 4 plastic bags and packed around the detector. A counting time of 4060 minutes produced the results summarized below:

U (63,93,1001)	0.74 +-0.02	ppm
U (186)	1.41 +-0.02	ppm
U (295,352,609,1120,1764)	-0.004+-0.001	ppm
Th (238,338,583,911,2614)	0.006+-0.003	ppm
K (1461)	54. +-4.	ppm

These results indicate that if the Th-series is present in this sample of raw material, it is at about the lower limit of detection for the NGEM system - - a few ppb concentration. There is clearly measurable potassium, at the 50 ppm level.

Results for the U-series are more complex, and are presently understood as follows. The third entry for U indicates there is no measurable Ra-226: all 5 of the listed gamma-rays are radium descendants, and they are not detectable at the 1 ppb level. The second entry for U is derived from the 186 KeV line alone, which in an equilibrium situation originates from both U-235 and Ra-226; however, in our raw material it must be due only to the presence of U-235 since we have already determined Ra-226 is absent. The first entry for U indicates the amount of U-238 present in the sample, based on gamma-rays from Th-234 and Pa-234m.

There is clearly a discrepancy between the concentrations of U indicated by early members of the of U-238 and U-235 decay series. The sense of this discrepancy is in the direction of enrichment of the material in U-235. An earlier analysis of a smaller quantity of lithium nitrate from this SAME can indicates the same situation with respect to these parent isotopes.

NOTE: THIS WAS A DIFFERENT CAN OF MATERIAL THAN THAT USED IN THE PURIFICATION PROCESS.

We have now analysed samples of the residues obtained from processing that produced the purified filtrate - - filter papers and precipitates. Please note: from results presented above, there is no measurable excess of U-235 (with respect to U-238) in the purified filtrate. Analysis of these items provides more details regarding this situation, as discussed below.

The purification process was carried out as follows. The raw material (Li-6 enriched lithium nitrate from ORNL) was first dissolved in water and filtered, to produce 6 filters with precipitates on them: the F1 Filters. This solution (about 6 liters) was then treated with a reagant whose purpose is to scavange thorium at high efficiency, to produce 3 filters with precipitates on them: the F2 Filters. The same treatment was repeated, to produce 2 filters with a relatively large quantity of precipitate: the F3 Filters. Results from these three samples are summarized here:

F1 FILTERS:

U (63,93,1001)	0.38 +-0.01 ppm
U (186)	0.22 +-0.01 ppm
U (295,352,609,1120,1764)	0.004+-0.001 ppm
Th (238,338,583,911,2614)	0.002+-0.002 ppm
K (1461)	1. +-2. ppm

F2 FILTERS:

U (63,93,1001)	0.19 +-0.01 ppm
U (186)	0.18 +-0.01 ppm
U (295,352,609,1120,1764)	0.002+-0.001 ppm
Th (238,338,583,911,2614)	0.001+-0.002 ppm
K (1461)	0.2 +-2.1 ppm

F3 FILTERS:

U (63,93)	0.028+-0.003 ppm
U (186)	0.028+-0.003 ppm
U (295,352,609,1120,1764)	0.003+-0.001 ppm
Th (238,338,583,911,2614)	0.000+-0.002 ppm
K (1461)	2. +-1. ppm

The analysed samples do not constitute a complete set with which to take a material balance that can be compared with the raw material. No attempt has been made to measure the consequences of plate-out and/or precipitation of the radionuclides on glassware and plasticware used in the purification steps. Hence, comparisons of "filter" contents with either the raw material or the purified filtrate are not easily "quantitative".

The most useful quantitative results are found in comparisons between the raw mateial and the purified filtrate. The quantity labelled "U(63,93,1001)" is a measure of U-238 obtained from measurement of 24-day halflife Th-234 (plus short-lived Pa-234m). The quantity labelled "U(186)" is a measure of U-235 alone when there is NO Ra-226 in the sample (as noted above). Large factors of purification are demonstrated with respect to U-238 and U-235, which actually means we have demonstrated these same purification factors apply to the chemical elements uranium and thorium.

MARTIN MARIETTA

MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX 2009
OAK RIDGE, TENNESSEE 37831

Appendix 3

Date:	August 1, 1995
To:	R. L. Cline
c:	J. R. Brewster, L. A. Headrick(RC), P. C. Jones, C. A. Livengood, J. E. Rausin, Y. H. Tracy
From:	BJ Brown B. J. Brown, 9204-2, MS-8132, 6-2928
Subject:	**SW 81817 - Lithium-6 Hydroxide Monohydrate - (Y-12 WR 1486)**

Two cans of lithium-6 hydroxide monohydrate (~~1000~~ 1002 grams lithium wt.) are ready for shipment to:

Lawrence Berkeley Laboratory
For the U.S. Department of Energy
1 Cylotron Road, MS 69-201
Berkeley, CA 94720
Attn: Maureen Cowger
Ref: P.O. 48-0162 S.W. 81817
Process #'s 358271A3P4 and 358271A3P5

This material is authorized by Request for Special Work No. 7102 from Batch 0426-90-0001. Waybill Numbers 1513-0846 and 1513-0847.

The results of analytical tests may be seen on page 2.

Please charge all costs to 3647-0265.

	Can 1	Can 2	Total
Gross Wt. grams	3262	3300	6562
Tare Wt. grams	336	326	362
Net Wt. grams	2926	2974	5900
Lithium Wt. grams	~~496~~ 497	~~504~~ 505	~~1000~~ 1002

BJB:LAH:kld

SW 81817 - Lithium-6 Hydroxide Monohydrate

Batch No.	0426-90-0001
Laboratory Requisition No.	902316
Isotopic Analysis	
Atom % Lithium-6	95.560
Wt. % Lithium-6	94.860
Chemical Analysis	
g/g Li	.169879
ppm Ca (Metal basis)	580
ppm K (m.b.)	338
ppm Na (m.b.)	179

Spectrographic Analysis, ppm:

Al	1	In	<.500	Sc	<.200	F	.800
As	<.300	Ir	<.400	Se	<.800	I	<.500
Au	<.800	Mg	1	Si	3	Ce	<.200
B	.900	Mn	3	Sn	2	Dy	1
Ba	9	Mo	2	Sr	2	Er	<.600
Be	1	Nb	2	Ta	< 9	Eu	<.400
Bi	.300	Ni	37	Te	28	Gd	4
Br	<.600	Os	<.600	Th	.300	Ho	<.600
Cd	< 3	P	<.200	Ti	<.080	La	<.200
Co	<.080	Pb	6	Ti	< 1	Lu	<.200
Cr	10	Pd	2	U	1	Nd	3
Cs	<.500	Pt	< 2	V	<.070	Pr	<.200
Cu	4	Rb	< 1	W	10	Sm	.800
Fe	33	Re	< 1	Y	<.400	Tb	<.200
Ga	<.400	Rh	<.100	Zn	30	Tm	<.200
Ge	<.300	Ru	<.400	Zr	.800	Yb	<.700
Hg	< 1	S	1	Cl	9		
Hg	< 6	Sb	3				