Design Description for the Seeded Ultrafiltration Plant at Sudbury. SNO-STR-95-003

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Introduction

This is the first (and probably not the last) revision of the design description of the seeded ultrafiltration plant to be based at Sudbury. The previous document, dated September 27th, 1994 [1], gave an outline of the components and the modes of operation of the SUF plant. Whilst the philosophy of operation, outlined in the design criteria document [2], is essentially unchanged, a number of major changes are proposed to the design of the SUF plant. Some of the major changes proposed are:

- Physical separation of the D_2O filtration and the H_2O elution circuit.
- Automation of the membrane elution, washing and priming procedures.
- Provision for membrane integrity testing and backflushing.

At the simplest level, the revised filtration plant consists of two identical and independent SUF rigs which may be run in series or parallel. The purpose of these SUF rigs will be to clean and to assay the D_2O. Periodically, it will be necessary to assay the activity captured by the HTiO coating on the membrane or simply to clean a membrane. Membranes will be removed from the filtration system and placed in the elution system. This will be done by first isolating the SUF rig from the D_2O supply and draining the residual D_2O to the high isotopic waste tank. The spongy structure of ultrafiltration membranes has a significant hold-up volume, N_2 at 10 psi can be applied to the permeate side of the membrane in order to maximise the drainage. The membrane is then disconnected from the filtration rig and placed in the separate elution rig. This separation will avoid the possibility of major degradation of the D_2O.

The two filtration rigs, each containing two removable 4ft ultrafiltration membranes, are shown in drawing N2-93-93(v5). The D_2O inlets and outlets are connected to the D_2O system via the manifold. This allows the rigs to be used separately or together in series or in parallel. This manifold may be connected to D_2O pump

(200 l/min at 60 psi) to run the two rigs in series. It can also be used for running a rig in a small volume closed D_2O loop on its own, which may be useful for full procedural blanks.

The internal components of the elution rig are shown in flow sheet N2-93-92(3). The elution rig will be required, with the exception of D_2O filtering, to perform all the other basic functions of the seeded ultrafiltration process: acid elutions of the membrane, alkali washes of the membrane, HTiO priming and deuteration. It is proposed that most of these repetitious washes of the membrane be performed automatically, with a microprocessor controlling the pump and pneumatic valves.

Components of the D_2O Filtration System

- **UF Membranes:** Each rig will house two 4ft Amicon cartridges (connected in parallel), either H53P30-20 cartridges (10 nm pore) or H26MP01-43 cartridges (0.1 micron pore), which should deliver, respectively, 100 and 200 l/min D_2O flow at 10°C and 60 psi trans-membrane pressure. Either set of two cartridges has a hold-up volume of about 1.4 litres when drained by gravity, and about 0.7 litres when drained by gravity with the assistance of 10 psi gas pressure on the permeate side and a flushing flow of gas on the concentrate side.

- **D_2O Plumbing:** 2" and 1.5" plumbing will be used for delivering D_2O to the concentrate side of the UF membrane and back from the permeate side respectively (the inlet pressure of 60 psi giving a flow of up to 200 l/min is generated by D_2O pumps which are external to the rig). This plumbing is optimised for minimal flow impedance so that as little as possible of the 60 psi inlet pressure is wasted in getting the D_2O to and away from the membrane. For this reason connections are made to the top and bottom ports of both the concentrate and permeate sides of the membrane, which is consequently used used as a dead-end filter. There are 6 D_2O valves in the rig with additional valves further along the D_2O inlet pipes and also on the D_2O manifold which may be used to isolate the membrane from the D_2O system. Because of the requirement to insert and remove UF membranes from the rigs there should be enough "give" ($\sim$ mm) in the polypropylene inlet pipes to flex them away from each other.

- **Compressed N_2 supply:** An N_2 cylinder will deliver gas at both 5 and 10. In both cases the maximum flow of N_2 is restricted by a throttle to $\sim$ 10 l/min.

- **Cover Gas System:** The same as that used by the rest of the D_2O systems. The cover gas piping at the top of the rig needs to be transparent or at least translucent and the inlets should be at the highest respective points in the pipework. To ensure that all the N_2 is expelled from the rig and no bubbles remain prior to filtration, a small transparent bulb or sight pipe is required on the cover gas inlets to the membrane. An air release valve, which will not allow D_2O through, will be fitted above the sight pipes as insurance against D_2O entering the cover gas system through operator error.

- **D_2O Manifold:** This 2" piping system receives D_2O from either the D_2O recirculation system or the initial fill system, and, after routeing it through the SUF rig(s), returns it to the appropriate line. It is assumed that the input flow of D_2O is driven by pumps external to the SUF plant which deliver D_2O at 60 psi pressure and at a variable flow between 100 and 200 l/min. When the two rigs are being used in series a the D_2O pump which is part of the SUF plant is used to boost the pressure between the two rigs back to 60 psi.

- **1 Tonne Tank:** A problem with all the D_2O filtering systems is the emanation of radon from radium captured on the membranes. The ^{222}Rn, with a 4 day half-life, can only be removed by the vacuum degasser. However, at a flow rate of 200 l/min, the D_2O will have a residence time of 5 minutes in a 1 tonne tank placed between the two SUF rigs. This will ensure that more than 95% of the ^{220}Rn emanated will have decayed to ^{212}Pb which can be captured for assay when the membranes are run in series. Baffles will be needed in the tank to ensure that a mean residence time of 5 minutes is achieved. Whilst the final decision on the type of membranes to be used has yet to be made, it is possible that SUF Rig 2 will contain finer membranes than Rig 1. If this is so, the permeate rate of Rig 2 will be lower and hence there will be an increase in pressure. To circumvent this, the 1 tonne tank will need an overflow pipe which will take excess D_2O back to the pump supplying the D_2O to the SUF system. A problem also arises if the D_2O pump for series operation runs too fast and the tank begins to empty, resulting in N_2 entering the D_2O system. A float switch will therefore be required in the tank to control the pump. Should the SUF rigs be run in parallel, the 1 tonne tank will be bypassed, but this will mean ^{220}Rn and therefore ^{212}Pb re-entering the acrylic vessel.

- **High Isotopic D_2O Drain Tank:** This 100 litre tank is used to drain the pure D_2O in the rig at the end of a filtration run. This D_2O may be contaminated with trace amounts of HTiO. It must therefore be passed through a fine filter before re-introduction into the bulk of the D_2O. The tank will be demountable and connected to the cover gas.

Components of the Membrane Elution and Priming System

- **H_2O Recirculation Plumbing:** 1/2" pipe will be employed for all of the following chemistry operations: HTiO priming, acid elutions, alkali washes and deuteration. This plumbing has been optimised to minimise the pipe volumes whilst still allowing flows of up to 100 l/min. It allows recirculation of the concentrate stream in either direction (up or down the inside of the hollow fibres) and also recirculation of the permeate stream. The will require 11 valves and a pressure gauge (up to 80 psi).

- **Recirculation Pump:** Must deliver at least 80 l/min H_2O at 80 psi output pressure and must be speed controlled. The dead-volume of the pump after draining in the forward direction must be less than 100 ml. Because it is always separated off from the 1,000 tonne D_2O solution, its radon requirement

is not as severe as for other pumps in the D_2O system, but some care must still be taken to prevent contamination of the assay. As the pump will be required to circulate hydrochloric acid, which attacks stainless steel, it would be preferable if it were lined with PTFE. At present a pump has not been chosen. A possible candidate is an air driven double diaphragm pump sold by CP Instruments.

- **Stock Tanks:** removable 12 litre tanks to hold the following chemicals: 5M HCl, 1M HNO_3, 2,500 ppm HTiO and 10M NaOH. Additionally, a 30 litre D_2O stock tank will be required for 3x10 litre deuteration washes of the membranes. The HTiO stock must be vigorously stirred before dispensing to the HTiO mixer tank. It is possible that gas scrubbers will be needed on the cover gas pipes from the acid tanks. Scrubbers can take the form of traps containing water or, preferably, an alkali solution, e.g. NaOH. In addition to the reagent stock tanks a 30 litre D_2O header tank is required for the deuteration of the membranes. The tank will be manually filled prior to elution of the membranes and be completely emptied when used to rinse the membranes three times with 10 litres. The rinse water will be drained to the low isotopic waste tank. The pipework connecting the stock tanks to the dosing pump should be as short as possible.

- **Dosing Pump:** this must be microprocessor controlled and able to deliver precise volumes to the circulation reservoir. A Masterflex peristaltic pump, with the correct tubing, can deliver 38-2300 ml/min with $\pm$ 0.1% precision. Peristaltic pumps have a number of advantages over other pump types. There is no concern over pump or fluid cleanliness, as the pump itself does not come into contact with the liquids; the fluid is confined to replaceable tubing. Peristaltic pumps also do not allow any fluid through when switched off. When in use, the pump will be gravity fed by the stock tanks on the mezzanine level. The volumes delivered may be pre-set (e.g. water rinses) or, alternatively, may be controlled by the pH of the circulation reservoir. After the required volume of acids or NaOH has been delivered, residues remaining in the pipework and pump may be flushed with water to the glove box waste tank. Periodically the silicone tubing contained in the glove box will need to be replaced. The tubing has a lifetime in excess of 50 hours of use, depending on the normal operating speed. The pump will normally be used for *ca.* 2 hours per elution procedure.

- **Circulation Reservoir.:** The circulation reservoir will be required to perform a number of functions. It will be used as a mixing tank for making the following 15 litre dilute solutions: 0.5M HCl, 0.03M HNO_3, 250-500 ppm HTiO (3-6g HTiO), and 0.1M NaOH. All of these solutions must be thoroughly stirred before introduction into the recirculation plumbing. The circulation reservoir will be used to neutralise acid eluates before draining to the elution tanks. The reservoir tank will need to have a number of features not found in the stock tanks: a pH electrode, a float switch, a thermometer and a conical bottom with the drain at the lowest point. The float switch, the thermometer and the

pH electrode will be connected to the microprocessor. Optical float switches are available which do not need contact with the liquid.

- **Elution Drain Tanks:** These two 12 liter tanks, located below the recirculation plumbing are used to store the 0.5M HCl and 0.03M HNO_3 acid eluates. They need to be stirred and will have to be connected to the cover gas system. They are also connected by 5mm bore flexible piping to peristaltic pumps in the glove box.

- **Low Isotopic H_2O Drain tank:** A 100 litre tank for collecting the H_2O solutions which are used to clean the UF membrane, i.e. NaOH and HCl solutions as well as H_2O rinses. It is demountable and connected to the cover gas.

- **Cover Gas:** The cover gas for this system comes into contact with low isotopic D_2O, H_2O and various acid and alkali solutions such as 0.5M HCl and 0.1M NaOH. It is possible that the cover gas systems needed for the filtering and elution plants will need to be separate.

- **Glove Box:** This contains the SUF rig for secondary concentration of the neutralised acid elutions: peristaltic pumps, small UF membranes (150-700 cm^2 area), acid bottles (filled from the stock tanks). The resulting acid eluates from these secondary SUF rigs are mixed with liquid scintillator in a counting jar which is sealed before removing from the glove box via a side-port with air interlock. Connected to the cover gas.

- **Glove Box Waste Tank:** A couple of tundishes also feed this tank from the glove box, so that waste solutions from the glove box can be disposed. It is connected via an air return line to the glove box, to facilitate draining from the tundishes. Demountable.

Modes of Operation

The sole function of the SUF plant shown in drawing N2-93-93(v.5) will be to filter the D_2O. However, the elution rig, shown in drawing N2-93-92(v.3), will be run in a repeating cycle of six operations:

1. De-deuteration of filters
2. Acid elution of filters
3. Secondary concentration of the eluate
4. Alkali washes of filters
5. HTiO priming
6. Deuteration

Other operations will also be required periodically for routine membrane maintenance:

7. Integrity testing

8. Backflushing

With the exception of integrity testing and backflushing, all the operations performed on the elution rig will be automated. We will attempt to describe these operations in a separately, so that as many different permutations as necessary are allowed.

D_2O Filtration Rig

D_2O Filtering: It is assumed that before this operation is begun the membrane has already been primed with HTiO and deuterated in the elution rig. One of the overriding concerns in many of the steps described below is to disturb as little as possible the deposited layer of HTiO. Sudden rushes of water, especially from the permeate to the retentate side of the membrane, might remove some of the HTiO, which might then find its way into the D_2O drain tanks. Nevertheless, this is not a serious problem, as these drain tanks will be filtered (by fine UF or maybe even RO) before re-introducing the D_2O into the 1,000 tonne solution. The most likely way in which HTiO is disturbed from the membranes is when the rigs are initially filled with D_2O. The D_2O is supplied to the the SUF rigs at a rate of 200 L/min, which makes the task of slowly introducing D_2O by the opening of valve Din (drawing N2-93-93(v.5) and also N2-93-98, Figure A) a rather delicate operation. This problem can be alleviated by the use of a short section of 0.5" which by-passes valve Din. This bypass will allow the rig to slowly fill with D_2O. In order to avoid the problem of joining 0.5" to 2" pipework, the bypass pipe can be be constructed by machining a 0.5" hole through a length of solid 2" polypropylene. The more serious problem of allowing HTiO into the permeate stream (and hence into the 1,000 tonne solution) does not occur except if HTiO goes through the membrane. As a consequence of transferring the membranes between rigs, another concern is maintaining cleanliness with respect to dust. The chance of contamination can be reduced in a number of ways. Obviously, the simplest solution is to reduce the time to a minimum that the membranes and the rigs are open to the atmosphere. Additionally, whilst a membrane is being transferred between rigs, a small positive N_2 pressure should be applied within the rigs to all the unconnected inlet and permeate pipes. This should prevent any dust getting into the pipework before the ends are capped. The operation proceeds in a number of steps:

1. Open and close valves on the D_2O manifold according to how the rigs are to be used (drawing N2-93-93(5), i.e. only one rig or both in series or in parallel. It will now be assumed that there is enough pressure on the D_2O inlet line (of the relevant SUF rig) to push D_2O to the top of the rig (just below the mezzanine floor).

2. Fully open the following four D_2O valves: Dconctop, Dconcbot, Dpermtop, Dpermbot, and Cgasconc (Figure A).

3. Slowly open the D_2O inlet valve Dinfill, to the point where a small flow of D_2O enters the rig. Wait until all the trapped gas has been expelled from the concentrate side of the membrane and D_2O enters the sight pipe. At this point Cgasconc is shut.

4. Open the N_2 valve Gasperm so that D_2O slowly fills the permeate side of the membrane. When the permeate side of the membrane is full, Cgasperm is firmly shut.

5. Fully open the D_2O valves Din and Dout and, if the other SUF rig is being used in this run, then repeat all of the above steps with the other rig. The rig is now ready to filter D_2O and the D_2O pumps can be switched on.

6. During the D_2O filtration run it may happen that gas from elsewhere in the D_2O system comes down the line and is trapped on the concentrate side of the membrane. If sufficient gas is trapped, then the flow rate will drop and step 3 should be repeated to remove the gas.

7. After the required volume of D_2O has been filtered, the D_2O pumps are switched off, and valve Din is closed. The membrane is then drained. This can be done by opening valves Cgasperm, Pgasconc and the Drain. Opening Pgasconc will allow gas (from the cylinder) at 5 psi into the rig. This will only work if there is minimal back pressure on the D_2O outlet line. After draining, close valves Cgasperm, Pgasconc and Dout .

8. Drain the D_2O on the concentrate side of the membrane to the high isotopic tank.

9. Open valve Pgasperm to further drain the membrane by squeezing a bit of D_2O out of the walls of the membrane and into the concentrate side.

10. Open valve Pgasconc which will also further drain the membrane, by pushing D_2O down the inside of the hollow fibres. After a couple of minutes, close Pgasconc, Pgasperm. The membrane is now fully drained and will contain about 800 ml of D_2O.

11. Open the valves to the cover gas (Cgasconc, Cgasperm) and uncouple the top 3" sanitary fitting. Spring the flanges apart and insert plastic covers for both the cartridge flange and the pipework flange. Repeat for the two 1.5" permeate fittings.

12. Remove the cartridge and fit to the elution rig by the reverse procedure.

Elution Rig

As mentioned previously, with the exception of membrane maintenance, all operations performed by the elution rig will be automated. The elution rig has been designed so that the two D_2O membranes are held in parallel.

De-deuteration:

To recover the 800 ml of D_2O contained in each membrane, 15 litres of H_2O will be introduced into the circulation reservoir and the pump is then started to recirculate the water at about 10 l/min with 5 psi backpressure for 10 minutes (see Drawing N2-93-98, Figure B). This will mix the 15 litres of H_2O and 0.8 litres of D_2O inside the walls of the membrane. The pump is then stopped and the drain valve opened to allow the 6% D_2O solution to pass into the low isotopic D_2O tank. Valve Gasconc will then be open to facilitate draining. Once completed, valves Gasperm, Gasconc and the drain valve will close. This de-deuteration step recovers 750 of the 800 ml of D_2O, leaving behind 50 ml in the membrane, which is the accepted loss per D_2O filtration run with a SUF rig. The rig is now ready for the H_2O chemical operations, which usually start with acid elutions.

Acid Elutions:

In order to elute the radioactive deposits from the membrane, two acid elutions, 0.03 M HNO_3 and 0.5M HCl, will be performed in quick succession. However sometimes two elutions with acid of the same strength will be carried out in succession to check the elution efficiencies measured using the ratio of counts in the two elutions. In terms of circulation flow there are two ways of eluting the membrane. The first, standard method, shown in Figure B, is better understood and relies on recirculating acid through the membrane and also along the inside of the hollow fibres, with enough back pressure to approximately equalise the permeate and retentate flows. In this way excellent contact is achieved between the acid and the HTiO (deposited on the membrane surface). An alternative method, which has not yet been investigated, would be to only recirculate inside, but not through, the hollow fibres. This is expected to be just as efficient and has the advantage of less acid being required (perhaps 3-4 litres less). We will first describe the former, understood standard method:

1. The correct volumes of acid stock and water required will be dispensed by the dosing pump into the circulation reservoir to prepare 15 litres of the required acid.

2. Valves are opened to give the flow pattern in Figure B, with Permbot open. The recirculation pump is then switched on and is adjusted, along with the throttle valve, so that the concentrate flow is roughly equal to the permeate flow (10-20 l/min). After the relevant elution time (5 minutes for 0.5 M HCl and 10-15 minutes for HNO_3) the recirculation pump is switched-off.

3. The valves Gasperm and Gasconc are opened and the acid is allowed to drain into one of the elution drain tanks.

4. Valves Gasperm, Gasconc and the drain valve are then shut.

At this point the system is ready for another acid elution, starting at step (1). The alternative elution method differs as follows:

1. 15 litres of acid is prepared in the reservoir.

2. Open valve Gasperm whilst valve Permbot remains shut. The pump is then switched on and the acid is recirculated at 10-20 l/min. There should be no back pressure so the throttle should remain fully open.

3. Gasconc and Drain valves are then opened and the acid is collected nto one of the elution drain tanks.

4. The valves Gasconc and Drain are then shut.

After the first two elutions, it is customary to perform two more washes with 0.5M HCl for one hour each, using the standard elution method and draining to the H_2O waste tank. These are used to dissolve the HTiO which is impaired by the first acid elutions and cannot be re-used. After the two acid washes the rig is rinsed three times with 15 litres of water.

Secondary Concentration:

Usually, the first two elutions of the SUF rig will be drained to the acid elution drain tanks for secondary concentration. This can occur whilst the membranes are being washed free of any remaining HTiO. In most SUF runs the first elution will be 0.03M HNO_3 for eluting Ra and the second elution will be 0.5M HCl for eluting ^{212}Pb and ^{228}Th. Because of the 10.6 hour half-life of ^{212}Pb it is important to process the 0.5M HCl elution as quickly as possible. Hence, there are two acid elution drain tanks, so that the 0.03M HNO_3 elution can be stored whilst the 0.5M HCl elution goes through the secondary concentration process first.

At present there are two possible techniques for secondary concentration of the ^{212}Pb and ^{228}Th in the 0.5M HCl. These are either successive filtration and elution stages with HTiO or, alternatively, a solvent extraction technique. The number of concentration stages needed for each of these techniques is dependent on the size of the β-α scintillation counters available. The scintillation jars currently used have a capacity of 12 ml for an aqueous sample. Whilst there are problems associated with scaling up such equipment, larger, 2 litre counters, counters would be desirable but have as yet to get past the design stage.

Each elution of HTiO with 0.5M HCl results in approximately 25% of the HTiO dissolving whilst 80% of the ^{212}Pb and ^{228}Th is eluted. The size of the membranes and the number of elution stages required to reduce the volume to 12 ml is dictated by the amount of HTiO used during D_2O filtration and also by the amount of HTiO that can be deposited on a membrane.

Therefore, with the current β-α counters and assuming that 2.5g of HTiO is used on each D_2O membrane, concentration of the eluate by means of successive filtration\elution may be carried out by the following two (optimistically) stages:

1. Neutralise the 10-15l of 0.5M HCl eluate to pH 8-9 with NaOH.

2. Filter half (5-7l) of the neutralised solution with a secondary UF membrane of area 1 m^2.

3. Elute the secondary filter with 3l of 0.5M HCl and neutralise the eluate with NaOH.

4. Filter the solution through a 0.3 m^2 membrane and elute with 1l of 0.5M HCl. Neutralise with NaOH.

5. Filter the solution through a Mediakap 10 Filter and elute with 12 ml of 0.5M HCl

6. Mix the eluate with 40 ml of liquid scintillator in a counting jar. Seal the jar and remove it from the glove box.

7. Repeat steps (2)-(6) for the remaining 6-7l of eluate.

8. Count the β-α coincidences for two weeks.

The above concentration technique, whilst possible, is both tedious, time consuming and is only 40-50% efficient. A promising alternative, to be documented in a forthcoming SNO-STR, involves the use of a solvent extraction technique to concentrate the ^{212}Pb and ^{232}Th in the 0.5M HCl.

Concentration of the ^{224}Ra contained in the 0.03M HNO_3 primary acid eluates is a simpler operation as ^{224}Ra is almost quantitatively eluted with only 5% of the HTiO dissolving. The procedure is as follows:

1. Neutralise the 10-15l of 0.03M HNO_3 to pH 8-9 with NaOH.

2. Filter half of the neutralised solution with a Mediakap 10 filter.

3. Elute the filter with 12 ml of 0.5M HCl.

4. Mix the eluate with 40 ml of liquid scintillator in a counting jar. Seal the jar and remove it from the glove box.

5. Repeat steps (2)-(6) for the remaining 5-7l of eluate.

6. Count the β-α coincidences for two weeks.

Alkali Recirculation cleaning:

These are used to recondition the membrane. A 0.1M NaOH is an very effective cleaning agent for membranes and restores permeate rate to high values. Almost invariably these alkali washes will occur after the acid elutions and the water rinses. The technique that will be used is a high flow recirculation cleaning with the permeate valves shut and the cartridges full on both sides of the membrane. A first wash will be performed with the concentrate flow in the upward direction, which will result in partial cleaning of the cartridge (Drawing N2-93-98, Figure C). More complete cleaning can be obtained by reversing the flow in the downward direction (Figure D). In this way the whole length of the hollow fibres are effectively washed. Once the membranes have been washed with 0.1M NaOH the membranes are rinsed by repeating the process (in both directions) twice, for 10 minutes, with water.