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Completion of R & D for the Seeded Ultrafiltration System

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Introduction

This R & D note is in effect a supplement to the Design Criteria (August 9th), Design Description (September 9th) and HTiO Progress Report (August 30th). It is intended to correct and complete the existing papers, enumerate the tests which are required, and draw attention to questions yet to be addressed. It is not intended to attempt to finalize the design as we are still awaiting comments, but that finalization cannot be pushed too far into the future.

Practically all our attention has been directed towards the SNO operation with 0.2% $MgCl_2$. This is both the most difficult and most important measurement and we can be confident that if the background for the $MgCl_2$ solution can be adequately controlled then we shall not have trouble with pure D_2O .

The operational tests of seeded ultrafiltration are executed with a small 1 ft filter with an area and throughput of 1% of the equivalent 4 ft filter. The actual filtration material, the hollow fibres, is the same in both cases and the differences are the number and length of the fibres. It is proposed to use the filters fed from both ends without a recirculated cross-flow and it is unlikely that the length of the filter will exert a serious influence on the operation. Tests are carried out with H_2O at $20^\circ C$ which has about half the viscosity D_2O at $10^\circ C$; the permeate rate is fixed at the value planned for D_2O at $10^\circ C$ which implies that the transmembrane pressure for tests is half that expected for the $D_2O/10^\circ C$ operation.

The question of potassium, both in the $MgCl_2$ and in the D_2O , does not have the same level of priority as thorium but some progress has been made. It is claimed that the Atomic Absorption Spectrometer, Hitachi Z-8200, can detect potassium down to the level of ~ 0.1 ppb in water and ~ 0.1 ppm in $MgCl$, and indeed these sensitivities have been demonstrated.

It is an impressive device which could analyse the chemical impurities in the D_2O at the level at which there can be interference with Th absorption by HTiO (see below). In a number of favourable cases, e.g. Cd, the sensitivity is 10 ppt which may be worth considering as the basis for determining the flow pattern in the D_2O by chemical tracer. We do not have access to such a spectrometer and are unlikely to obtain the necessary £50K without external contributions and a cooperative deal with other potential users.

gel electrophoresis

Fines

There is very convincing evidence that the grain size of HTiO is in the region of tens of microns and that there is $\ll 1\%$ at or below one micron. Huge numbers of tenth micron filters have been used for secondary concentration without any losses, and as we know from work with MnO_2 many years ago it is the fines that have all the surface area and carry all the activity.

The one reservation for HTiO is that most of the above information comes from circumstances of significant ion density. In high purity water, peptization can occur as in the case of MnO_2 . Measurements are in progress to determine whether a large quantity of pure water will release fines from HTiO on a 0.1μ filter. If so then tests will be pursued with a 0.01μ filter.

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Saturation of HTiO

The several grams of Ti deposited as HTiO on the filter membranes has been shown to have a capacity for Ba, and presumably Th, of tenths of a gram, $\sim 10^5$ times the $1 \mu\text{g}$ of Th acceptable in the D_2O . The radio-active chemical species cannot saturate the HTiO but other species certainly can. The few tenths of a gram in say 100 tons of D_2O constitutes a few ppb, detectable by good atomic absorption spectroscopy but few if any other chemical techniques. It will be important to measure the chemical impurities of the D_2O at the ppb level, and remove if necessary.

It is proposed to demonstrate the performance of HTiO seeded U/F for a large total throughput per unit membrane area by using a 1 ft filter cartridge fed with high purity water which is dosed with ^{228}Th and daughters immediately prior to filtration. For a 1 ft, 0.1μ filter, a ton of $\text{H}_2\text{O}/20^\circ\text{C}$ at 1l/min and 30 psi corresponds to 200 tons of $\text{D}_2\text{O}/10^\circ\text{C}$ at 200l/min and 60 psi on the full scale system. Dosing at 10 Bq per litre would allow the $\beta - \alpha$ counting of 10 ml permeate samples without further concentration for a decontamination factor of 100.

The existing clean water supply (softener, R.O., mixed ion bed) may not be good enough and analysis techniques of sufficient sensitivity are not available. An additional clean up stage will be added, either a HTiO seeded U/F filter of the 4 ft size or a high quality ion exchange cartridge, probably the former.

The growth/decay curve of the $\beta - \alpha$ counting of the 10 ml samples can be analysed in terms of three lifetimes 10.6hr ^{212}Pb , 3.65d ^{224}Ra , and 1.9y ^{228}Th , and interpreted in terms of the initial mix of activities in that permeate sample. The mix in a permeate sample will depend on the activity already absorbed on the filter which will release some if not all of the 55 sec. ^{220}Rn into the permeate stream and will give the impression of a decreasing absorption of ^{212}Pb . It is expected that the initial $\beta - \alpha$ count rate in the permeate samples will increase linearly with flow time.

At the completion of the 1 ton throughput dosed with ^{228}Th the 1 ft filter is expected to have accumulated the best part of 10 kBq of activity which can be readily counted without elution. A further ton of water will be passed through the filter without any ^{228}Th dosing to determine whether the deposited thorium washes out.

If the question of escape of fines has not been fully resolved a second 1 ft filter with a 30 ID pore size (about 0.01μ) will be added in series with the HTiO coated 0.1μ filter to collect the fines.

The time scale for completion of this work is probably a few months.

$\beta - \alpha$ Coincidence Counters

It is proposed to modify the design for the 2 in. counters as less than satisfactory features have emerged. The present photomultipliers are not overcapped and two tubes have been broken. The price that must be paid is a reduction of the copper shielding which is not really serious.

A design for a 5 in counter, 5 in photomultiplier and 2l. scintillator vessel has been prepared, and we shall manufacture this counter complete with shielding if there is a demand.

Mechanical Strength of U/F Cartridges

The rig for testing big filter cartridges to the point of mechanical failure is now complete. The hollow fibres will be taken to 100 psi internal pressure and the case to 150 psi.

Radio-active Background of Membranes

Arrangements have been made with Amicon for the manufacture of fibres in the high cleanliness part of the plant, and the installation with polyurethane rather than epoxy.

Samples of fibres can now be assayed for radio-activity by soaking in acid, squeezing to dryness in a press and collecting the acid. After neutralization it can be concentrated and $\beta - \alpha$ counted in the usual way.

The Bubble Test

Testing of hollow fibre cartridges for broken fibres or other failures of integrity is normally done by some form of bubble test. Suppliers' literature (Amicon, Netto, Millipore, etc.) gives further details, and an example is given below. The pressure p required to force gas through the pores of a wet hydrophillic membrane is related to the pore diameter $2R$ by the well-known formula $p = 2T/R$ where for water $T = 70 \times 10^{-3} \text{ Nm}^{-1}$.

Method 1:

1. Place unit in vertical position.
2. Close off lower permeate port.
3. Fill cartridge housing half way with distilled water.
4. Close off upper recirculation exit.
5. Apply about 2 psi (0.18 kg/cm²) gas pressure (clean air or nitrogen) to the lower recirculation exit.
6. Steady bubbling in the cartridge housing indicates a broken fibre.
7. Reverse cartridge position and repeat procedure.

Method 2:

1. Place unit in vertical position.
2. Close off lower recirculation exit.
3. Close off upper permeate port.
4. Partially fill upper recirculation exit with water (H5 and H10 type cartridges).
5. Apply about 2 psi (0.18 kg/cm²) gas pressure (clean air or nitrogen) to the lower recirculation exit.
6. Steady bubbling at the upper recirculation unit (H5 or H10 cartridges) or in the beaker of water (H1 cartridges) indicates a broken fibre.

These techniques have certain limitations. If, for example, an area of the fibre bundle is not thoroughly wetted, a small amount of bubbling may be observed. Also, diffusion of the gas through the membrane may cause small bubbles to appear. Damaged fibres can usually be recognized by a prolonged, rapid, steady stream of bubbles.

From n.tanner1@physics.oxford.ac.uk Mon Sep 26 12:58 EDT 1994
Received: from mail.physics.ox.ac.uk by mips2.Phy.QueensU.CA (5.61/4.7)
id AA05451; Mon, 26 Sep 94 12:58:28 -0400
Received: from av1.physics.ox.ac.uk by mail.physics.ox.ac.uk with SMTP
(5.65c+/IDA-1.4.4-UK-t for <bonvin@mips2.phy.QueensU.ca>)
id AA08762; Mon, 26 Sep 1994 17:52:46 +0100
Date: Mon, 26 Sep 1994 17:57:27 +0100 (BST)
From: n.tanner1@physics.oxford.ac.uk
To: bonvin@mips2.phy.QueensU.ca
Cc: TANNER@v1.ph.ox.ac.uk
Message-Id: <940926175727.20409620@v1.ph.ox.ac.uk>
Subject: Addition to earlier list
Status: RO

Note to be added to "Completion of R&D etc".

Extraction of Thorium.

It is well established that HTiO can most effectively decontaminate water spiked with an acid solution of Th228 and neutralised with alkali. There are however two uncertainties which must be addressed, viz., (i) it is not known in what chemical form the thorium will be present in the D2O and the D2O/MgCl2 solution, and (ii) at pH 7, and indeed well below pH 7, the equilibrium of a thorium nitrate solution is strongly in favour of the thorium "plating out", i.e. depositing on the walls of the vessel.

In a strongly acid solution thorium is likely to be in an ionic form, but otherwise there is a tendency to form complexes and colloids. The latter can be filtered out but the complexes may remain in solution and may pass through the U/F filter membranes coated with HTiO. Probably the only practical solution to this problem is to store the permeate from a seeded UF analysis for a week during which Th228 (if any) decays to Ra224, with very different chemistry, and re-analyse the permeate via seeded UF. For storing the permeate it will be necessary to make use of the 60 ton tanks.

The "plating" of thorium, and similarly lead and to a lesser extent radium, raises questions. It can confound the calibration of the thorium assay, even if we are bold enough to introduce a spike: it is not at all obvious that a thorium spike would be in the same chemical as the thorium contamination of the D2O. One can be more confident of the chemistry of Ra224 which can be used as a spike as it is short-lived and can be separated from parent Th228.

The other plating question is whether it will occur and if so where? The surface area of the acrylic vessel and the pipework are similar, but about 100 times less than the micro-surface of the membrane of a large UF module. Furthermore, diffusion is a very slow process and, unless there is an unexpected degree of mixing, plating on the acrylic vessel and polypropylene pipework will take a very long time indeed. In all probability the plating will primarily occur on the surface of the UF membrane which would be highly advantageous. The decay of Th228 via Ra224 releases 55 sec. Rn220 which lives quite long enough to escape from the membrane and just about get to the acrylic vessel where it will appear as Pb212.