Using Molecular Sieve

July 18   H Lee   DRAFT

Molecular sieve (a compound of silicon oxide, aluminum oxide and sodium) has been proposed for use in the recovery of D_2O vapor from the SNO vacuum degassers. Molecular sieve is very efficient at recovering D_2O and is also an energy efficient recovery process. There are four problems which have to be examined to determine its impact on the SNO heavy water system design :

(a) Hot nitrogen gas will carry molecular sieve dust into the vapor recovery system. The alleviation of this problem will require filtering to sub-micron sizes.

(b) The tank nitrogen gas should be radon-free. This can be achieved using cooled activated-charcoal.

(c) There will be a buildup of radon gas in the circulating hot nitrogen gas used for sieve regeneration. The nitrogen gas will have to be periodically purged and new nitrogen gas used for makeup.

(d) ^{222}Rn emanation from sieve material (due to its radium content) will add radon to the recovered liquid D_2O.

In the following we look at the problem of ^{222}Rn emanation from the molecular sieve. A measurement at Queen's on Union Carbide 13X molecular sieve gives a radon emanation rate into vacuum of about 1200 radon atoms per liter of sieve per hour at room temperature. Guelph has measured an emanation rate of 3200 radon per liter of sieve. Additionally Guelph has counted the 13X molecular sieve and finds a level of

$0.59\pm0.04 \times 10^{-6}$ gram ^{238}U per gram of sieve (based on ^{226}Ra)
$1.19\pm0.40 \times 10^{-6}$ gram ^{238}U per gram sieve (based on ^{238}U)
$2.10\pm0.11 \times 10^{-6}$ gram ^{232}Th per gram sieve
$0.203\pm0.006\%$ potassium

(Note the U and Th levels in the molecular sieve are much higher than is typically found in stainless steel, plastics and some pure aluminum).

In the proposed SNO D_2O vapor recovery system there is about 1000 liters of molecular sieve in each of the three recovery units. One unit is to operate for 8 hours recovering 30 ℓ/hr of D_2O vapor. The second unit is in series with the first to recover vapor that gets past the first unit. The third unit spends 8 hours with hot nitrogen gas blowing through it to regenerate the sieve.

The molecular sieve does not adsorb any of the degassed radon as its pore size is optimal for water vapor only. The degassed radon is pumped away into the gas header.

A condenser of about 100 liter gas volume will be used to condense the D_2O. There will be about 50 liters of liquid D_2O lying on the bottom at all times. The liquid is drained off continuously using a gravity controlled bleed valve.

We do not know how the radon emanation rate from molecular sieve is affected by the D_2O vapor it captures or the effect of the hot nitrogen gas on the emanation rate. If we assume the above measured Rn emanation rate, then there will be

$$1200 \times 1000\ell \times 8hr = 9.6 \times 10^6$$

radon emanated in the unit undergoing regeneration.

The volume of the nitrogen recirculation loop is around 2500 ℓ. Hence the partial pressure of the radon from the molecular sieve in the nitrogen flow loop is at most 2.3×10^{-19} atm. We apply Henry's Law to the recovered D_2O liquid to find how much radon dissolves into it:

$$\frac{n_{Rn}}{n_{D_2O}} = \frac{P}{k}$$

where k is Henry's constant for radon
  n_{Rn} is the number of moles of radon in the liquid D_2O
  n_{D_2O} is the number of moles of liquid D_2O
  P is the partial pressure of radon

At 90°C, k is about 10^4 atm [reference]. Hence

$$\frac{n_{Rn}}{n_{D_2O}} = \frac{10^{-19}}{10^4} = 10^{-23}$$

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or

$$\frac{N_{Rn}}{\ell D_2 O} = \frac{n_{Rn}}{n_{D_2 O}} \times \frac{N_A}{18 g/mole} \times 1000 g/\ell = 334 Rn/\ell$$

where N_A is Avogadro's number.

The recovered D_2O (liquid) will not be more than a couple of weeks in the D_2O holding tank before it is put back into the D_2O recirculation loop. Rocovered D_2O containing radon from the molecular sieve is continuously entering the tank and mixing completely, hence there is a factor of only about 3 reduction in the radon. The recovered D_2O then will go through one degassing at 99% efficiency in the D_2O recirculation thus picking up a factor of $1/(1-.99)$ = 100 reduction of radon. In total, this leaves $334/(3 \times 100) = 1.1$ molecular sieve Rn/ℓ.

D_2O at 1×10^{-14} gU/gH$_2$O contains 0.06 [222]Rn per liter. If we require no more than a 10% contribution then the radon from the molecular sieve is a factor of $1.1/(0.06/10) = 180$ too high.

The physical reason why we require low radioactivity sieve is because the D_2O is at the 10^{-14} level whereas the molecular sieve is at the the ppm level or, at best, probably the ppb level. Passing ultrapure D_2O through a material with much higher radioactivity requires that a very small amount of the material radioactivity can be allowed to exchange into the D_2O.

Stategies for reducing radon

A. Sieve with less radioactive contaminants

The manufacture of molecular sieve involves the making of the sieve crystals followed by mixing into natural clay binder and final shaping into beads or rods. It is believed that the large portion of the radioactive contaminants comes from the clay.

Another type of molecular sieve (Union Carbide 4A) has been gamma counted at Guelph. They found

U 0.94 ± 0.08 ppm

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Th 2.64 ± 0.05 ppm
K 0.281 ± 0.003 %

which is not significantly different from the 13X type sieve above.

We are consulting with the manufacturers to determine if there are alternative binders with low-radioactivity.

B. Removing the radon from the nitrogen-D_2O vapor mixture

In this stategy one would try to remove the radon from the nitrogen-D_2O vapor gas mixture before the D_2O is condensed. Alternatively one might try to first freeze out the D_2O (and hope that not much radon gets entrained in the ice) and then remove the radon with activated charcoal.

C. Decay tanks

In an eight hour shift there is at most 240 kg of recovered D_2O. The present holding tanks have a capacity of 0.5 and 4.2 tonnes. Assuming only one eight hour shift every day, this gives a maximum holding time of about 17 days for the first bit of recovered D_2O before it is returned to the recirculation loop. Because the incoming D_2O mixes completely, only a factor 3 reduction in radon occurs during the filling time of the holding tank.

A ten tonne holding tank would give a maximum holding time of 41 days. Because of mixing, there is only a factor of about 8 reduction in radon.

D. Purging the N_2 gas and Degassing the recovered D_2O

There is going to be a time interval where the D_2O saturated molecular sieve will be sitting before regeneration. Just before the hot N_2 gas is turned on, the sieve should be purged with cool clean N_2 to blow away emanated radon.

The recovered D_2O could be degassed once. This would bring down the radon content by a factor of 100. The D_2O vapor would then be recovered with sieve and go through the hot N_2 gas sieve regeneration cycle.

After awhile the radon level will build up in the hot N_2 gas. A periodic purge with new N_2 gas will be required.

Comment on the use of Molecular Sieve
Note of July 18
A.B. McDonald, July 22

On page 2 it is assumed that the number of radon produced which will eventually be absorbed in the water are those which are produced in eight hours ie 9.6×10^6. Unless the nitrogen is replaced after each extraction the amount will instead be the amount which is produced in an equilibrium time which is on the order of 5 days. Therefore the equilibrium number of radon in the nitrogen will be about 150×10^6. Therefore, the number of radon per litre in the water would be about 15 X 300 Rn/l or 4500 Rn/l.

On page 3 a comparison is made between the residual numbers of radon atoms per litre in the D_2O from the holding tank and the number of radon per litre in D_2O in the 1000 tonnes of the main tank. It would seem that the appropriate comparison to make is the number of atoms of radon added in an equilibrium situation in comparison to the total number of atoms of radon in the 1000 tonnes, in an equilibrium situation there. At 0.06 radon atoms per litre, the total number of radon atoms in the 1000 tonnes of D_2O would be 6×10^4.

For a 10 tonne holding tank which would take 41 days to fill, there would be about a factor of 7 reduction in the radon content due to decay and a factor of 100 reduction due to a single degassing. This would result in about 6 radon per litre in the tank or about 6 X 1000 X 10 or 6×10^4 added every 40 days. This would result in a 100% increase in the radon content of the D_2O for a level of 1×10^{-14} grams of uranium per gram of D_2O. However, if bled in steadily, it would be equivalent to about 150 per day versus 1100 per day generated by the uranium decay chain at 1×10^{-14}.

This level is still high. Moreover, one would like to work at a level well below 1×10^{-15} grams of uranium per gram of D_2O. If two 10 tonne holding tanks were used instead of one, so that one tank is able to decay for an additional 40 days while the other is being filled, then there would be an additional factor of $(0.5)^{11}$ or a factor of 2000 reduction in radon level in the water being returned to the D_2O vessel. This would certainly be an adequate level of reduction as one would add only 3 Rn atoms every 40 days

Using two 5 tonne holding tanks in the method described (one is allowed to decay while the other is being filled) one would have a factor of three reduction in radon due to decay during filling and a factor of 0.5^5 or a factor of 32 for decay during the filling of the other tank. This would still result in only 384 atoms of radon to be added to the D_2O every 20 days (19 per day) compared to the steady state number of 600 (110 per day) at 1×10^{-15} grams of uranium per gram of D_2O. This would be a barely acceptable level of additional background.

Therefore it is possible to conclude that two 10 tonne holding tanks would enable molecular sieve to be used even with the present levels of radioactivity. It is suggested that this be seriously considered unless a more suitable approach is developed or a lower radioactivity molecular sieve is discovered in which case, the extra holding tank may not be necessary.