

## K Leaching From MnO<sub>2</sub> Preparations

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The acceptable accumulation of K (potasium) in SNO is 2 ppb, ie 2 gm in the 1000 tons water in the lifetime of the experiment. The isotopic abundance of <sup>40</sup>K is .012% and the half life is  $\tau_{1/2}=1.28 \times 10^9$  yrs which would give rise to a  $\beta^-$  and  $\gamma$  activity of  $\sim 60$  cps with  $E_{max} \approx 1.3$  MeV.

The principal MnO<sub>2</sub> preparations under consideration have been examined for the amount of K that they will contribute to SNO from use in the water monitoring and purification system. The preparation denoted 'CRPP' is made from XAD-7 'macroreticular' acrylic beads that swell with water uptake. The preparations denoted 'Diakon' or 'Elvacite' are made from solid acrylic beads that do not swell. Test sample availability of the Elvacite was limited and the bead size distribution extended to small sizes making it a minor option. The coating was made from either NaMnO<sub>4</sub>·H<sub>2</sub>O denoted 'Na' or KMnO<sub>4</sub> denoted 'K'. The K content of these coatings was analysed and found to be .4% and 25% respectively. On the Diakon preparations there were thicker coatings looking black to the eye and denoted 'Bl', and thinner coatings looking brown and denoted 'Br' or 'MnO<sub>x</sub>'

Two techniques for determining the leached levels of K have been employed: 1. coating analysis and 2. leaching tests which simulate the projected use in SNO of the MnO<sub>2</sub>.

### Coating Analysis

In the first technique the K content of the MnO<sub>2</sub> coating was examined by dissolving the MnO<sub>2</sub> of the finished product and submitting the solutions to commercial flame atomic absorption analysis (FAA). The limit of detection (LOD) was .01 ppm. The results for different MnO<sub>2</sub> preparations are summarized in table 1. They show a reduction of up to a factor of 30 of the incorporated K for a) solid bead preparations where the total coating is reduced (MnO<sub>x</sub>) and b) for preparations from 'Na' instead of 'K'.

### Leaching Test

The second method was to wash the MnO<sub>2</sub> final products with UPW and to analyse samples of the wash water for K by FAA. About 190 liters of wash water was used for each test. It was recycled through the MnO<sub>2</sub> at 20 lpm, ie 40 bvm for up to 80 hrs. The results are shown in figure 1. The ordinate indicates [K] logarithmically. The abscissa indicates the integrated flow past the MnO<sub>2</sub> column, ie the time of washing at 20 lpm. The initial UPW [K] value is indicated at tons=-10. In the last measurement, the Diakon.Bl.(Na), the point at tons=-5 is a measurement of the first few liters in that run which were directed to drain. The rest of the wash was recycled as for the other samples.

The curves all show final levels that are many orders of magnitude lower than the solubility limits for possible K salts in the system. The different plateau levels alone may be interpreted as an equilibrium process with different equilibrium constants for the different MnO<sub>2</sub> preparations and possibly different forms of K in the H<sub>2</sub>O. However, the curves also show that most of the K comes off early in the wash. This strong plateauing of

some of the curves indicates that there was sometimes a well defined removable K fraction. The high [K] of the initial wash water only of the run Diakon.Bl.(Na) also indicates that a loose K fraction was being washed away in a nonequilibrium process.

The [K] from the CRPP sample continued to rise for the longest times indicating either a larger slowly removed fraction or a continued (perhaps mechanical) production of K. The latter possibility correlates with the continuous production of fines seen elsewhere (see SNO-STR-94-045, Large scale Extraction, Emanation, and Fines using  $MnO_2$ ). This particular sample was washed and dried 3 times. The second cycle produced less released K, but the third cycle did not produce a clear change, possibly due to the continuous mechanical action, and possibly due to systematic problems in the procedure. The Diakon preparations did much better as could be anticipated from the coating analysis above. The [K] reached a well defined plateau, lower and earlier, indicating a smaller, more easily removed fraction, and perhaps a stable remainder. The initial wash to drain for the Diakon.Bl.(Na) sample had high [K] but contained little total K and would not have affected the final [K] had it been returned to the tank as in previous runs. Thus, the final level for this sample can be compared to the other runs and is seen to show the lowest amounts of K released.

### **Best Measurement**

The Diakon.Bl.(Na) produced the lowest K level measured. It shows .06 mg/l K at the end of the wash from which .03 mg/l was in the UPW water to start. A total of 5.7 mg dissolved K leached from the .5 l sample into the 190 liters UPW (which was recirculated about 250 times, ie  $\approx$  50 tons pumped through). (The 5.7 mg represents only 10% of the contaminant K expected to be in the preparation.) Thus, using the indication that the recycled UPW is equivalent to fresh UPW, and the best of the present measurements, 350 Ra assays using .5 l  $MnO_2$  preparations would produce the 2 gm K in SNO .

### **Remaining Measurements**

The lowest K containing coating, Diakon.Br.(Na) has not yet been examined in the leaching test. Furthermore, the effect of successive washing for the Diakon samples has not yet been completely studied. The recommended procedure would be to circulate 200l through a sample,  $\sim$ 100 times, measure [K], then change the water and repeat. After establishing a nonchanging level of K, the water velocity should be increased and [K] measured again. These tests would distinguish between a (mechanical) 'washing' process that can be controlled and a chemical 'solution' process that would continue.

### **Outlook**

The present results indicate that the Diakon will be significantly cleaned by a small rinse. The cleanest level achievable from washing and choice of  $MnO_2$  preparation is still to be determined. As well, there are further measures to be taken to further reduce the leached K: eg.  $MgCl_2$  leaching of a  $MnO_2$  preparation would substitute Mg for the remaining K in the preparation. A reduction of the determined [K] by a factor of 3 to the LOD of the FAA analysis projects about 1000 Ra assays/2gm/1000tons water or about 2 assays per week using .5 liters/assay in SNO. More sensitive K assay techniques are being investigated.

resin	g beads/ cc solution	K ppm in solution	K content mg	K (% weight of beads)
Diakon <sub>S</sub> (K)	2/100	25±1	2.5±0.1	0.12 ± 0.05
Diakon <sub>E</sub> (K)	2/100	26 ± 1	2.6 ± 0.1	0.13 ± 0.05
Elvacite <sub>E</sub> (K)	2/100	20 ± 1	2.0±0.1	0.10 ± 0.05
CRPP <sub>E</sub> (K)	2/250	249 ± 9	62.3 ± 2.3	3.11 ± 0.12
Diakon <sub>A</sub> (K) (MnO <sub>x</sub> )	5/50	18.8 ± 0.4	0.94 ± 0.02	0.019 ± 0.001
Diakon <sub>S</sub> (Na)	2/60	5.5 ± 0.5	0.33 ± 0.03	0.017 ± 0.002
CRPP <sub>S</sub> (Na)	2/60	40.5 ± 0.5	2.43 ± 0.03	0.122 ± 0.002
Diakon <sub>A</sub> (Na) (MnO <sub>x</sub> )	2/80	0.6 ± 0.1	0.05 ± 0.01	0.003 ± 0.001

K contents in the Mn Oxide coating of solid and CRPP beads

Except when designated MnO<sub>x</sub>, resins are MnO<sub>2</sub> coated.

Coating was removed by Radiacwash ('S') EDTA-Na<sub>4</sub> ('E') or nitric acid ('A') solutions

(K) and (Na) refer to the use of KMnO<sub>4</sub> and NaMnO<sub>4</sub>(H<sub>2</sub>O)

respectively as coating agents

K content is 25 weight% in KMnO<sub>4</sub> and 0.4 weight% in NaMnO<sub>4</sub>(H<sub>2</sub>O)

### K Leaching Measurements

