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Interim Report
Chancellor Water Colloids:
Characterization and Radionuclide Association

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I.   Experimental Methodology

Ultra-filtration: Without any stirring or agitation, water from near top of the Chancellor water drum was pumped into a 2-gallon Nalgene jug using a peristaltic pump. The tubing and the container were pre-cleaned before the operation. About 1.5 liters of the extracted sample were filtered through a 100,000 NMWL ultra-filtration membrane followed by an inline 0.02 μm syringe filter. The filtration was carried out in multiple steps in an ultra-filtration cell (350 ml) operated under pressure (~15-20 psi). The same membrane was retained for the entire filtration routine but the 0.02 μm syringe filtered was changed every ~ 500 ml. The above filtration procedure was repeated after the contents of the 55-gallon drum were stirred vigorously with a long nylon rod to scrape the bottom and stir up and re-suspend settled or deposited colloids. Water was extracted using a peristaltic pump 2 hours after the sample was stirred which allowed any large, non-colloidal fragments to settle.

Liquid Scintillation Counting (LSC): 5ml aliquots of filtered and unfiltered samples from the stirred and unstirred water samples were pipetted into plastic LSC vials. The first step in determining the activity of the radionuclides was to construct a quench curve to distinguish the alpha-emitting radionuclides from gamma-emitters. 1ml mixtures of varying proportions (1:10 to 10:1) of unfiltered Chancellor water samples and deionized water was transferred into LSC vials with 19 ml of Ultima Gold AB Scintillation cocktail and shaken vigorously prior to analysis. Filtered J-13 water was used as background to be subtracted from the LSC spectra.

Particle Size and Counts: Particle size distribution and count analysis was performed using a laser particle spectrometer (Particle Measuring Systems, Inc.). Samples were collected in 8ml aliquots in clean glass tubes. For the unfiltered water samples, 8ml aliquots from the stirred and unstirred drum were analyzed. Ultrafiltered samples were collected downstream of the 100,000 NMWL membrane and prior to the 0.02-μm syringe filter change and two more 8ml aliquots (stirred and unstirred samples) were collected after filtration through the membrane and the 0.02 μm syringe filter. All samples were diluted about 200 times and analyzed for particle size and counts. Deionized water was used for dilution, which was also analyzed a priori to account for background colloids.

Surface Charge Measurements (Zeta (ζ) Potential): The surface charge measurements were performed on 2 ml aliquots of different samples using a Malvern Zetasizer. Zeta potential (mV) was measured twice with each measurement consisting of an average of 5 sub-runs spaced 1 minute apart. Another longer duration measurement was carried out on each of the samples with 100 sub-runs spaced 1 minute apart.

Suspension Stability:
The coagulation kinetics of the Chancellor water colloid suspension was measured at different ionic strength and pH values using the Malvern Zetasizer instrument. The early-stage coagulation rate (doublet formation rate) was determined as the slope of the size Z-

average versus time plot in the first few minutes. The ionic strength and pH at which high coagulation rates were observed were determined by comparing the experimental rate to that estimated under barrier-less coagulation conditions. The stability ratio (W) = (barrier-less coagulation rate)/(experimental coagulation rate); and the attachment efficiency = $1/W$.

Table 1. Sample numbering scheme implemented in the experiments.

Sample ID	Description
7011-08-170	Drum Sample, not stirred
7011-08-171	Unfiltered Drum Sample, not stirred; ~1L in marinelli beaker for gamma counting
7011-08-172	Unfiltered Drum Sample, not stirred; 8mL for PMS analysis
7011-08-173	Unfiltered Drum Sample, not stirred; 5mL for LSC counting
7011-08-174	Unfiltered Drum Sample, not stirred; 5mL for alpha counting on Pt disk
7011-08-175	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and 0.02 mm syringe filter, ~1L in marinelli beakers for gamma counting
7011-08-175.1	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and prior to 1st syringe filter change, 8 mL for PMS
7011-08-175.2	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and prior to 2nd syringe filter change, 8 mL for PMS
7011-08-176	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 8 mL in glass tube for PMS
7011-08-177	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 5mL in LSC plastic vial for LSC counting
7011-08-178	Filtered Drum Sample, not stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 5mL in LSC plastic vial alpha counting on Pt disk
7011-08-179	100,000 NMWL membrane used in ultrafiltration cell, for SEM/EDS identification
7011-08-179.1	SEM/EDS sample prepared by rubbing/smearing pin mount sample holder against the membrane
7011-08-179.2	Resuspended colloids from membranes using few mL of filtered (membrane & syringe filter) chancellor sample water
7011-08-179.3	SEM/EDS samples prepared by evaporating 50mL of resuspended colloids deposited on the pin mount

7011-08-180	Drum Sample, Stirred
7011-08-181	Unfiltered Drum Sample, stirred;~1L in marinelli beaker for gamma counting
7011-08-182	Unfiltered Drum Sample, stirred; 8mL for PMS analysis
7011-08-183	Unfiltered Drum Sample, stirred; 5mL for LSC counting
7011-08-184	Unfiltered Drum Sample, stirred; 5mL for alpha counting on Pt disk
7011-08-185	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and 0.02 mm syringe filter, ~1L in marinelli beakers for gamma counting
7011-08-185.1	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and prior to 1st syringe filter change, 8 mL for PMS
7011-08-185.2	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and prior to 2nd syringe filter change, 8 mL for PMS
7011-08-186	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 8 mL in glass tube for PMS
7011-08-187	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 5mL in LSC plastic vial for LSC counting
7011-08-188	Filtered Drum Sample, stirred; Filtered through 100,000 NMWL membrane and 0.02 μm syringe filter, 5mL in LSC plastic vial alpha counting on Pt disk
7011-08-189	100,000 NMWl membrane used in ultrafiltration cell, for SEM/EDS identification
7011-08-189.1	SEM/EDS sample prepared by rubbing/smearing pin mount sample holder against the membrane
7011-08-189.2	Resuspended colloids from membranes using few mL of filtered (membrane & syringe filter) chancellor sample water
7011-08-189.3	SEM/EDS samples prepared by evaporating 50mL of resuspended colloids deposited on the pin mount

II. Results

1- Size distribution and surface charge (zeta-potential)

Figure 1 summarizes the measured size distribution and number concentration for 4 samples: unstirred unfiltered, stirred unfiltered, unstirred filtered, and stirred filtered. As the Figure indicates, stirring did not notably change the colloid concentration and size distribution of in both filtered and unfiltered samples. Ultrafiltration reduced the number concentration of particles between 50 and 120-nm, indicating the presence of nano-colloidal species in the Chancellor water with sizes essentially between < 120-nm in size. The insignificant difference between the stirred and unstirred samples clearly indicates highly stable colloids in the Chancellor water, thus high potential of transport in a porous or fractured medium saturated with water having similar chemistry as the Chancellor water.

Separate experiments using classical drying and weighing of the unfiltered stirred samples gave a mass concentration of the colloidal species of 0.12 g/l.
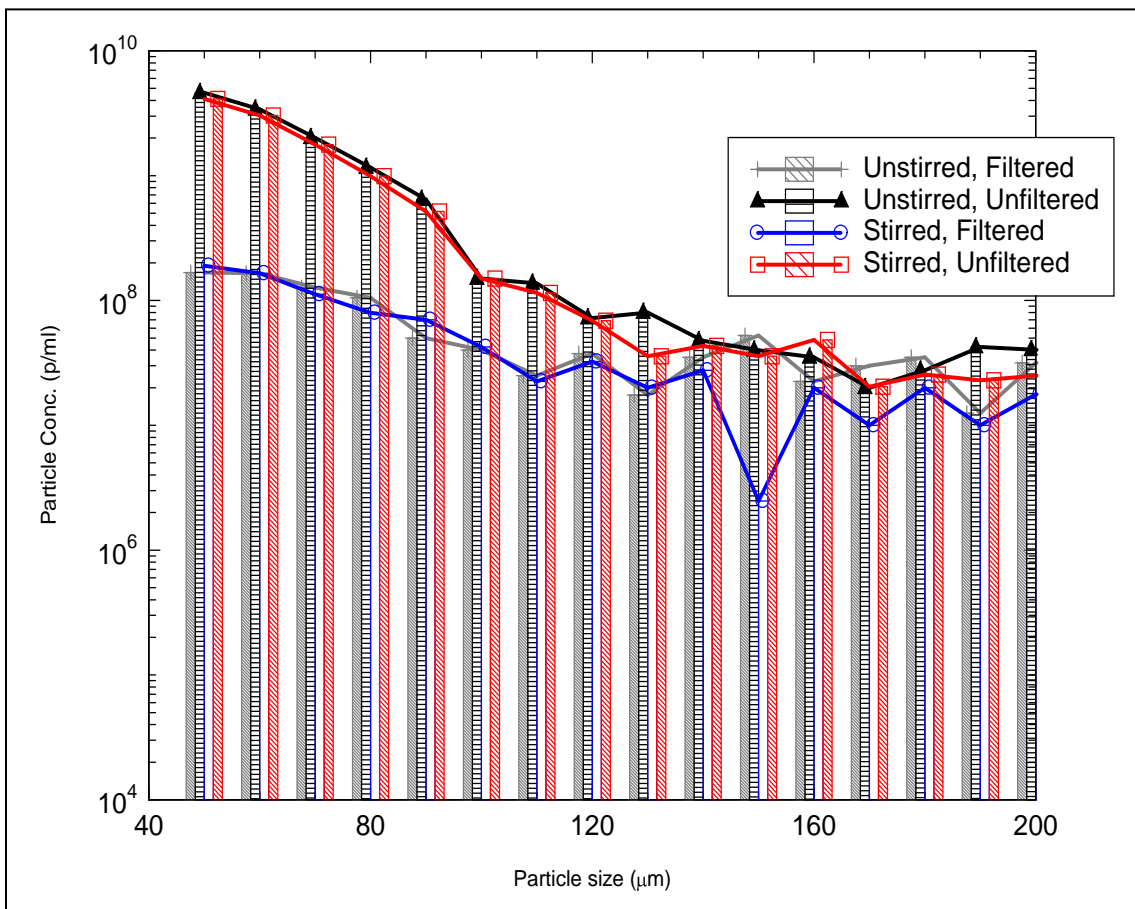

Figure 1. Size distribution and number concentration of colloidal particles in the Chancellor water.

Figure 2 shows the time variation of Zeta potential of different samples (see legend). Notably, the filtered samples have slightly positive zeta potential (+1 to +2.5 mV); these values at the current pH 7.9-8.1 are similar to those measured for Pu(IV) PuO_2 intrinsic colloids, but are also typical for colloid-free water. Also, there is a significant difference in the zeta potential of unfiltered stirred versus unstirred samples: zeta potential of the unfiltered stirred (7011-08-182) sample is much higher than that of the unfiltered unstirred sample (7011-08-172). This distinguishable difference in the zeta potential values between the stirred and unstirred samples can be explained by: 1) enhanced desorption of potential determining counter-ions from the colloids' surfaces, leaving behind more negative surfaces, or 2) enhanced dissociation in the aqueous phase leading to more negative charges (co-ions) in the electric double layers around the colloids.

The zeta potential values at the pH of the Chancellor water are identical to those obtained for smectite clay colloids in the ATC 19D1water.
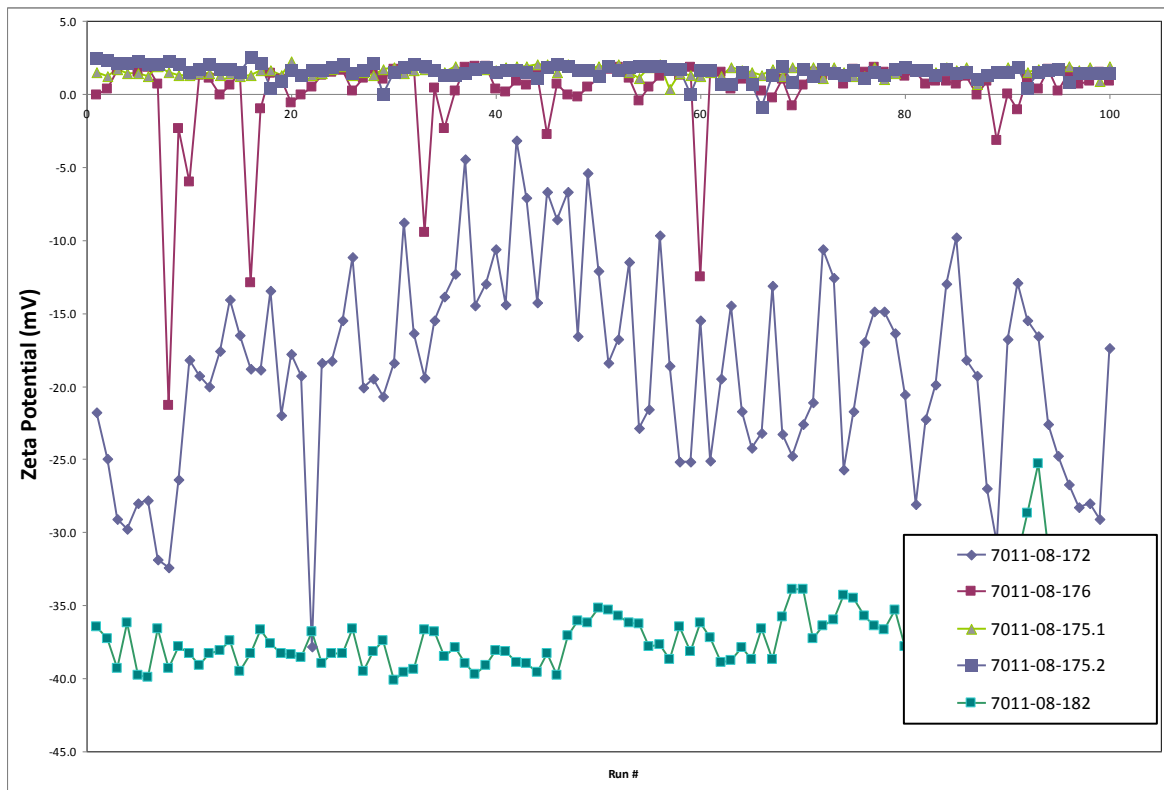

Figure 2. Zeta potential of colloidal particles in the Chancellor water measured over time.

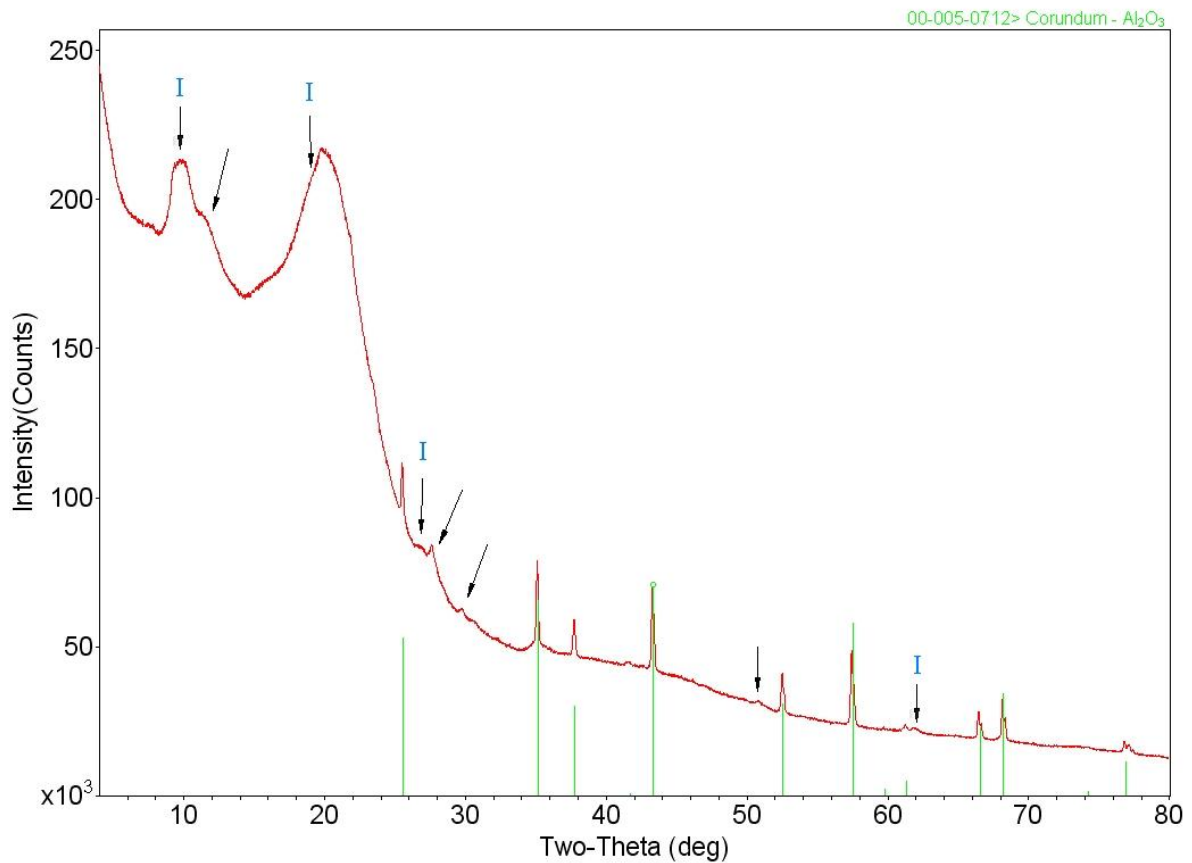## 2-   XRD analysis of the Chancellor water colloids

Figure 3. XRD analysis results of Chancellor water colloids.

The XRD data in Figure 3 indicates broad peaks at lower angles (marked with an "I") and are possibly Illite. The broad peaks are possibly due to intrastratification of different clays that is causing a peak shift, implying the presence of other clays, e.g., smectite, consistent with the electrokinetic data. The sharper peaks at higher angels are probably zeolite, but no good match exists with any of the more common zeolite phases. The strongest peak at $2\theta = 27.6°$ matches several zeolite phases (Mordenite, Phillipsite, analcime), but remaining peaks don't. It also agrees with anorthite (feldspar), but again remaining peaks don't. No quartz phases were detected.

3-   Association of radionuclides with the Chancellor water colloids

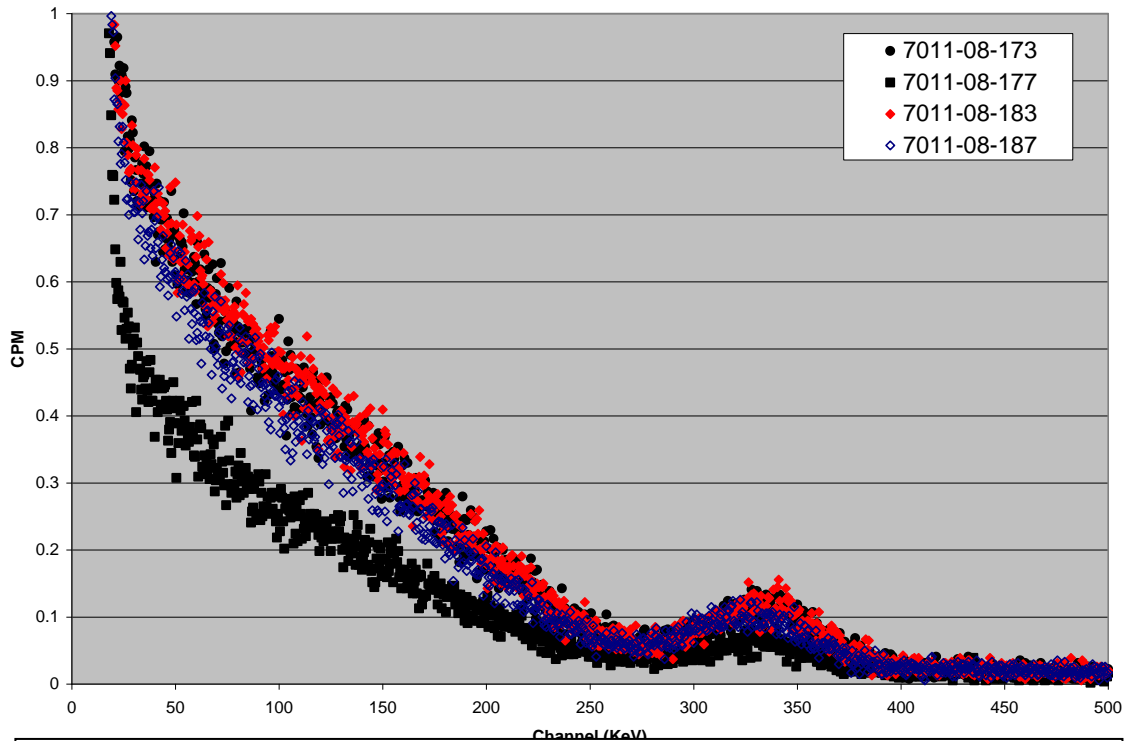#### a) *Ultrafiltration Tests*

Figure 4. Total activity in filtered stirred and unstirred and unfiltered stirred and unstirred samples.

As Figure 4 indicates, ultrafiltration reduced the activity in the unstirred samples (7011-08-173 and 177) much more than it did with stirred samples (7011-08-183 and 187). This implies the disappearance of colloids (e.g., by dissolution) as a result of stirring, which is inconsistent with the particle concentration and size distribution data in Figure 1. Nevertheless, there are always slightly higher alpha and beta activities in the stirred drum sample compared to the unstirred drum samples and that there are measurable alpha and beta activities in the ultrafiltered samples.

b) *Ultracentrifugation Tests*

The data in Figure 5 is used to calculate the gross distribution coefficient (k_d) of different radinuclides in the Chancellor water by subtracting the activity in the supernatant from that in the un-centrifuged sample and using the following input:
Colloid mass concentration = 120 mg/L (based on separation by ultracentrifugation and drying)
Volume of LSC counted samples = 5 mL
Using these values, we calculated a $\underline{k_d}$ $\underline{of \sim 8.22x10^3 \ mL/g \ for \ both \ the \ alpha \ emitters}$ $\underline{(narrow \ peak) \ and \sim 7.79x10^3 \ mL/g \ for \ the \ beta \ emitters \ (wide \ peak).}$
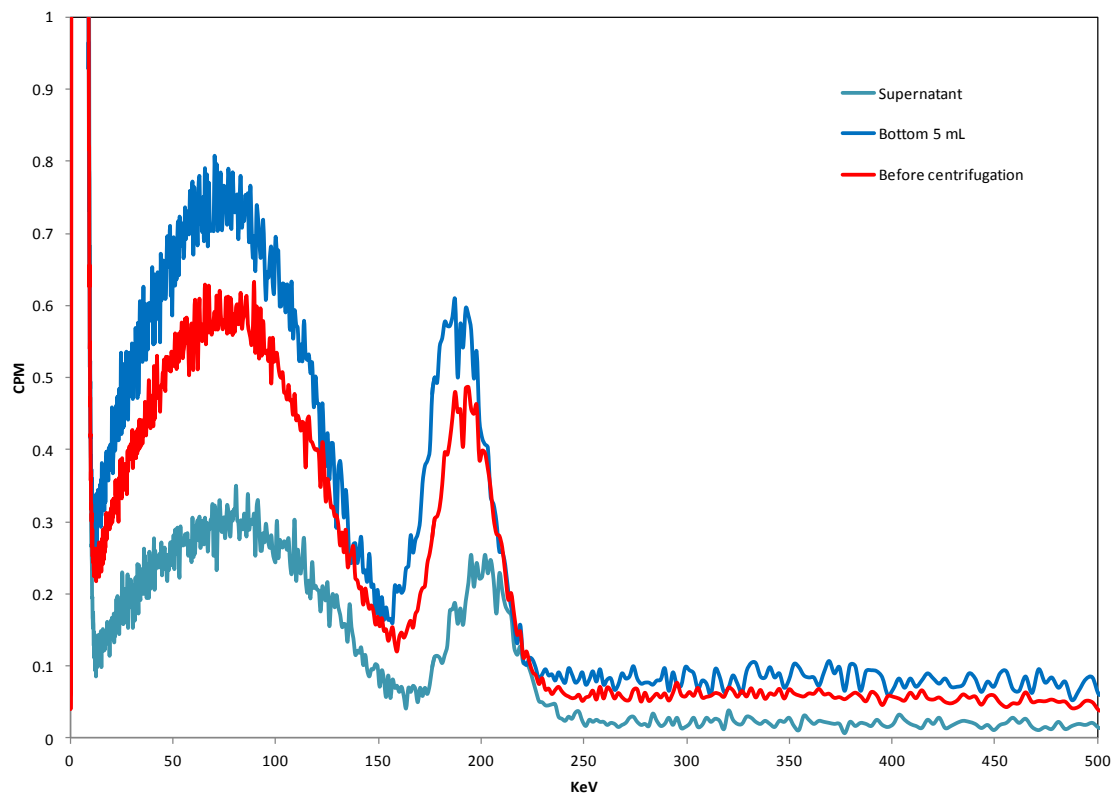
Figure 5. Total activity in stirred samples before and after centrifugation at 55K rpm for 1 hour. Activities are per 5 g of water sample. Bottom 5 mL refers to a sample taken from the bottom half of the sample tube after centrifugation.

The k_d of Pu-239 was also calculated from alpha spectroscopy data obtained using an alpha spectrometer fitted with 450 mm Passivated Implanted Planar Silicon (PIPS) detectors (Ortec Inc.) A volume of 97 ml of the stirred Chancellor water was evaporated to dryness on hot plate and the residues were dissolved in 8.0 M nitric acid. An aliquot of this solution was directly stippled onto a 5/8's inch electro-deposition disk and was counted for 24-50 hours to determine the total activity. To measure the total Pu activity on the colloids, 500 mL of the stirred Chancellor water was first subjected to ultracentrifugation at 55,000 rpm for 1.5 hours. The supernatant was then completely evaporated and dissolved in 8.0 M nitric acid and an aliquot of the solution stippled onto a 5/8's inch electro-deposition disk and was counted for 24-50 hours. The total activity measured for Pu-239 was found to be 46 dpm/L in the un-centrifuged stirred water and 23.5 DPM/L in the supernatant of the ultracentrifuged sample.

Using these values, the k_d for Pu-239 in the Chancellor water was calculated to be ~ 7.98×10^3 mL/g, in a striking agreement with the LSC analysis. This value of kd is also consistent with our previous measurements of the sorption of Pu-239 in the (V) state onto natural smectite colloids in the ATC 19D1 water.

Figure 6 shows the total activity in three 5ml triplicate aliquots sampled from a stirred drum after different period of gravitational settling (time 0 indicates the initial sample immediately after stirring).
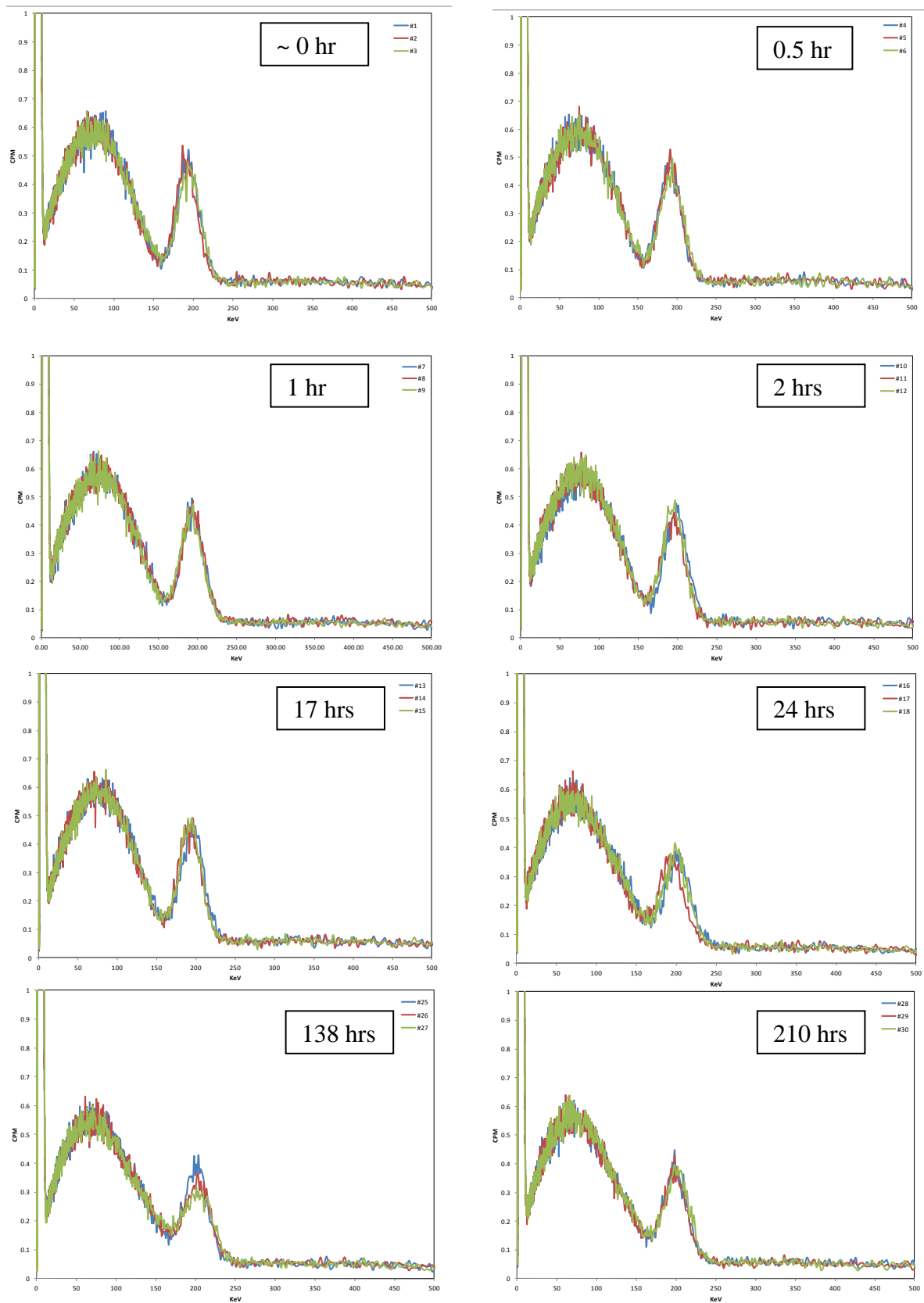
Figure 6. Total activity in samples extracted directly from an initially stirred drum after allowing the drum contents to settle by gravity for the indicated periods of time. Activities are per 5 g of water sample.

As Figure 6 indicates, there is no difference in the total activity in the triplicate aliquots taken at the same time, indicating a highly homogeneous colloid dispersion. If the colloids in the Chancellor water were intrinsic colloids, they would exist at extremely low number concentrations as suggested by the low measured alpha and beta activities. This would in turn likely to result in different concentrations, thus different activities in the triplicate aliquots. Therefore, it can be argued that the colloids in the Chancellor water are less likely to be intrinsic.
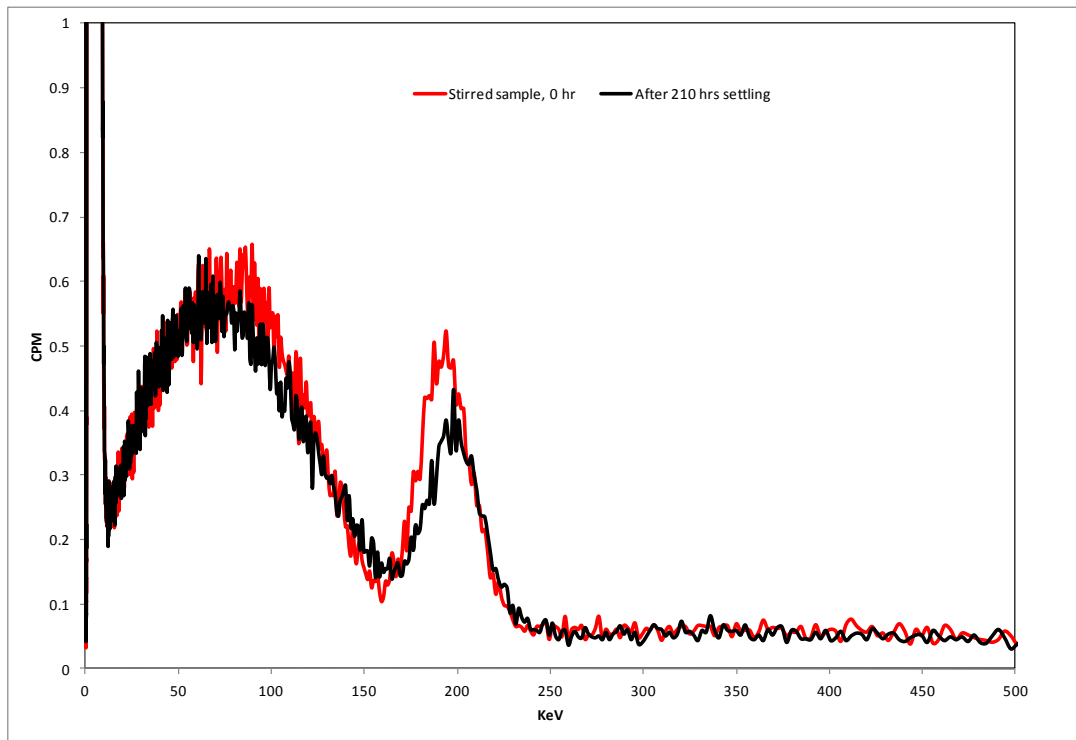

Figure 7. Total activity in sample extracted directly from an initially stirred drum at time 0 and in sample taken after allowing 210 hours of gravitational settling. Activities are per 5 g of water sample.

Figure 7 compares the total activity in the Chancellor water immediately after stirring the drum (time 0) to that after allowing 210 hours of gravitational settling. The settling behavior is consistent with the presence of a colloidal phase. The change in the Pu (narrow peaks) and beta emitters (wide peaks) activities during settling is slightly different. The total activity reduction (difference in the sum of activities under each peak) for Pu was 2.22 CPM and that for the beta emitters was ~ 1.77 CMP, indicating that the beta emitters are associated with colloidal particles smaller than those that the Pu is associated with.

4-   Stability of the Chancellor water colloids
Preliminary analysis of the dependence of the Chancellor colloid stability on both pH and ionic strength indicates the following:
   a) The pH has no significant effect on the stability of the colloids. Increasing the pH caused the zeta potential slightly more negative, which ranged from ~ -39 mV at pH 3.5 to ~ -46 mV at pH 8.3.

b) Increasing ionic strength from its natural value (~ 0.01M) to 0.2 M had no effect on the stability of the colloids (early stage coagulation rate ~ 0). Increasing the ionic strength above 0.2 induced noticeable coagulation, and at ~ 0.75 M, coagulation was very significant and the early stage coagulation rate remaind almost constant. This indicates a critical coagulation concentration (ccc) between 0.7 and 0.8 M. Note, ionic strength was adjusted using 1:1 NaCl electrolyte.
c) The change of ionic strength induced noticeable change in the zeta potential of the colloids, with the lowest values at ionic strengths between 0.7 and 0.8, consistent with the stability data above.

III.   Concluding Remarks

1) Gravitational settling, zeta potential, and ultrafiltration data indicate the existence of a colloidal phase of both the alpha and beta emitters in the Chancellor water.
2) The low activity combined with high dispersion homogeneity of the Chancellor water indicate that both alpha and beta emitters are not intrinsic colloids.
3) Radionuclides in the Chancellor water, particularly Pu, coexist as dissolved aqueous and sorbed phases. In other words the radionuclides are partitioned between the aqueous phase and the colloidal phase.
4) The presence of Pu as a dissolved species in the aqueous phase, suggests the possibility of Pu in the (V) oxidation state. This conclusion is supported by the similarity of the k_d value of Pu determined in the current study to that determined for Pu(V) sorbed onto smectite colloids, and the similar electrokinetic behavior of the Chancellor water colloids to smectite colloids.
5) About 50% of the Pu(V) is in the aqueous phase and 50% is sorbed on colloids (mass concentration of colloids in the Chancellor water is 0.12 g/L).
6) The k_d of the Pu and the beta emitters (fission products) between aqueous and colloidal phases in the Chancellor water is ~ 8.0×10^3 mL/g using two different activity measurement techniques (LSC and alpha spectroscopy).
7) The gravitational settling and size distributions of the association colloids indicate that the properties (at least the physical ones) of the colloids to which the alpha emitters are associated with seem to be different that the properties of the colloids to which the beta emitters are associated with. The beta emitters are associated with very small particles (~ 50 - 120 nm), while the alpha emitters are associated with relatively larger particles.
8) The Chancellor water colloids are extremely stable under the natural pH and ionic strength conditions, indicating high potential for transport in the subsurface.

IV.   Research Needs:

(1) Carful extraction experiments to determine the oxidation state of Pu in the Chancellor water
(2) Transport behavior of the Chancellor water colloids and associated radionuclides in a representative porous medium compared to that of the aqueous phase radionuclides need to be characterized.
(3) Ability of the porous medium to remove radionuclides from the colloids.