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SIZE AND DENSITY OF A ^{242}Pu COLLOID

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ABSTRACT

The size and density of a ^{242}Pu colloid has been measured by autocorrelation photon spectrometry. The density of the colloid was determined by ultraspeed centrifugation. From the concentration profiles of ^{242}Pu in the centrifuged test tubes, a standard sedimentation formula was used to calculate the density; the size of the colloid was known from the light scattering experiments. The determined density of the ^{242}Pu colloid was unexpectedly low compared to the density of crystalline PuO_2.

INTRODUCTION

Transport of radionuclides, either as radiocolloids or more probably as pseudo-colloids, is one possible mechanism for the release of actinides from an underground repository for high-level radioactive waste[1]. The transport of colloids may not be retarded by adsorption on mineral surfaces.

In addition to transport considerations there is the possibility of misinterpreting sorption measurements. For example, if a low-density, low-molecular-weight colloid specie is formed, then when centrifugation is performed to separate phases for a sorption measurement part of the colloidal suspension will be sedimented with the crushed rock. If the scientists performing the measurements are exceedingly careful, the centrifugation procedure would give a reproducible ratio of activity in the solid and aqueous phases. This ratio would be independent of concentration and would mimic a linear isotherm exactly, even if no adsorption had actually taken place.

Two of the problems impeding the study of colloidal transport are the small number and small size of colloids present in deep groundwaters; these factors mean that conventional methods for analyzing colloids can not be used[2]. Autocorrelation photon spectroscopy, APS, has the advantage of high sensitivity and it is nondestructive.

In this study, the size of a ^{242}Pu colloid has been measured by APS, and the density of the colloid was subsequently calculated from ultracentrifugation experiments.

EXPERIMENTAL

Preparation of the colloid

The colloid was prepared by increasing the pH in an acid solution containing ^{242}Pu. The colloid was formed at a pH around 2-3, and the ^{242}Pu concentration in the solution was $1 \cdot 10^{-4}$ M. Two samples were prepared, one with a cation column cleanup to remove any residual cation species of plutonium. It was thought that the cation resin may contribute particulates to the suspension. No significant difference

was observed in the APS analysis of the two samples, so the purified colloid was used exclusively in this study.

Size determination

The size of the colloid was measured by autocorrelator photon spectroscopy. The APS system, run be INC-Division at LANL, consists of a SpectraPhysics Model 165 2 watt Argon Ion laser (tuned to the 514.5 nm line), a Brookhaven Instruments Corp. BI-200 automatic goniometer, which has a temperature-controlled sample cell holder, and a Brookhaven Instruments Corp. BI-2030 autocorrelator[3].

The apparatus is a light scattering system where laser light is directed on the sample vial, and scattered light is detected by a photomultiplier through a telescope mounted on the goniometer arm. The light pulses are autocorrelated in real time by the autocorrelation circuit and accumulated. As the particles make a random walk through the solution they can position themselves so that light scattered from two particles will constructively interfere. The resulting increase in light intensity will decay in time as the particles diffuse. The autocorrelation function will exhibit an exponential decay where the decay constant is proportional to the diffusivity. The hydrodynamic diameter can be determined from the diffusivity using the Stokes-Einstein equation. The correlation function is in fact a continuous sum of exponential decays because in general the colloid is not monodisperse. The autocorrelation spectrum is therefore a function of the size distribution and can be described by the following equation,

$$g(\tau) = \int_0^\infty \exp(-\Gamma\tau) f(\Gamma)\, d\Gamma, \qquad (1)$$

where,

- g the autocorrelation function,
- τ time,
- Γ the decay constant.

The ^{242}Pu colloid size distribution measurements were determined at a 90 degree scattering angle. The average size and the second moment(if the distribution is gaussian the second moment is the standard deviation) were determined by the cumulant method.[4]

Density determination

The density of the colloid was determined by ultra-speed centrifugation. A centrifuge with a swinging bucket rotor capable of a maximum speed of 65,000 rpm was used in the experiments. The centrifuge speed was varied from 3000 rpm for 5 minutes up to 40,000 rpm for two hours. Samples of solution of 4.5 mℓ volume were centrifuged and "layers" of solution (typically 0.5 mℓ) were carefully pipetted from the top of the centrifuge tubes yielding concentration profiles of ^{242}Pu in the tubes. From the concentration profiles, with the colloid size determined known from the light scattering experiments, the density of the colloid was calculated using Eqn. (2)[5].

$$\ln\left(\frac{R_2}{R_1}\right) = \frac{2r^2\omega^2(d_p - d)}{9\eta}(t_2 - t_1), \qquad (2)$$

where,

R_1 = radial position at time t_1,
R_2 = radial position at time t_2,
r = hydrodynamic radius of the particle,
ω = angular velocity of rotor,
d_p = particle density,
d = density of solution,
η = dynamic viscosity (the rotor temperature was kept at 4 °C).

RESULTS

The size of the colloid was measured to be 29 nm with a second moment of 10 nm. The second moment does not represent an actual width of the particle size distribution because the deconvolution methods used for autocorrelation data yields a broader distribution when the data contains error. Therefore the second moment should be considered a maximum width for the particle size distribution. The results of the centrifugation experiments are given in Table 1. The density of the colloid was calculated using Eqn. (1) using the point at which the concentration was one half the starting concentration(33000 cpm/mℓ to be the radial position of an average particle starting from the top of the centrifuge tube(6.41 cm from the center of the rotor). The density was found to be 1.07 to 1.08 g/cm^3, which is surprisingly low, i.e., close to that of pure water. This could indicate that attached water is the major part of the colloid.

Table 1. Concentration profiles of ^{242}Pu in centrifuge tubes (1 = top of the tube, 7 = bottom).

20,000 rpm for 2 hours					40,000 rpm for 2 hours				
Sample	mℓ	top (mm)	cpm/mℓ	cpm/mm	Sample	mℓ	top (mm)	cpm/mℓ	cpm/mm
1	0.495	0	13100	1030	1	0.485	0	2420	189
2	"	6.3	30800	2420	2	"	6.2	2780	217
3	"	12.6	33100	2600	3	"	12.4	4310	337
4	"	18.9	32200	2530	4	"	18.6	11300	886
5	"	25.2	31300	2460	5	"	24.8	23400	1830
6	"	31.5	32400	2550	6	"	31.0	26800	2100
7	0.52	37.8	71800	4060	7	0.58	37.2	153000	9060

The stability of a Pu colloid prepared by the same method used for the experiment described in this paper was determined in another experiment where the size of a ^{239}Pu colloid was measured repeatedly over a time period of 2 years with a reproducible size of 180nm and a stable concentration. A ^{239}Pu colloid was prepared at the same time as the ^{242}Pu colloid but the size was an order of magnitude larger. The difference in the size of the two colloids is not clear, but possible reasons could be alpha-radiolysis, time and/or the rate of increase in pH when the two colloids were prepared. REFERENCES

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