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Title: Report on the Effectiveness of Flocculation
for Removal of Pu-239 at Concentrations of
1pCi/L and 0.1 pCi/L

RFP Pond Water Characterization and Treatment
(LATO-EG&G-91-022)
Task C Deliverables: 5.1.2 and 5.2.2

Author(s): I. R. Triay
G. K. Bayhurst
A. J. Mitchell
M. R. Cisneros
D. W. Efur
F. R. Roensch
D. J. Rokop
R. D. Aguilar
M. Attrep
H. E. Nuttall

Submitted to: LATO at Rocky Flats

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Principal Investigator: I. R. Triay

Other Investigators:

G. K. Bayhurst

A. J. Mitchell

M. R. Cisneros

D. W. Efur

F. R. Roensch

D. J. Rokop

R. D. Aguilar

M. Attrep

H. E. Nuttall

Handwritten:
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Objective

The objective of this work is to assess the effectiveness of flocculation for the removal of Pu from RFP pond waters spiked with ^{239}Pu at the 1.0 and 0.1 pCi/L level. This report corresponds to deliverables 5.1.2 and 5.2.2 of Task C in the Rocky Flats Pond Water Characterization and Treatment study (No. LATO-EG&G-91-022).

Experimental

Treatment Procedure:

The treatment procedure utilized in these studies is based on flocculation. The procedure consists of:

- 1) adding sorber to a ^{239}Pu solution and stirring,
- 2) adding the flocculant CATFLOC to the sorber-containing Pu solution and stirring,
- 3) sedimenting suspension under gravity and taking aliquots of the treated water as a function of time, and
- 4) determining the Pu concentration of the water before and after treatment by liquid scintillation counting, alpha spectrometry, or mass spectrometry.

^{239}Pu -Solutions Preparation:

Two ^{239}Pu oxidation states were studied. Solutions were prepared by adding an aliquot of a well-characterized Pu(IV) polymer acidic stock to distilled water or to water from the RFP pond C-2. The size of the Pu(IV) polymer in the acidic stock was determined by autocorrelation photon spectroscopy. The Pu(IV) polymers were found to be 7 nm in diameter. Solutions were also prepared by adding an aliquot of a well-characterized soluble Pu(VI) acidic stock to distilled water or to water from the RFP pond C-2.

Sorber Characteristics:

The sorbers tested in the flocculation treatment were: Ca-Montmorillonite, Na-Montmorillonite, kaolinite, illite, illite/smectite, commercially available enhanced clays, neutral alumina, mica, and zeolite NaA. The characteristics of the sorbers utilized are given in Table 1. The mineralogical composition of the sorbers was determined by powder pattern X-ray diffraction. The sorbers' particle size and the zeta potential of the sorbers in RFP pond C-2 water were determined utilizing the procedures and instrumentation described in Appendix D.

Table 1: Sorber Characteristics

Sorber	Type	Designation	XRD Results	Particle Size, μm	Zeta Potential in mV	Expansion	Ion Exchange Capacity (milliequivalents/100g)
Ca-Montmorillonite	Clay	SAz-1	>95% smectite; impurities of quartz and feldspar	0.6	-12	Swelling	80-140
Na-Montmorillonite	Clay	SWy-1	75-85% smectite; impurities of quartz, feldspar, and calcite	0.7	-12	Swelling	80-140
Kaolinite	Clay	KGa-2	90-95% kaolinite; impurities of anatase	1.1	-19	NonSwelling	1-10
Illite	Clay	IMt-1		0.8	-12	NonSwelling	
Illite/Smectite	Mixed Layer Clay	ISMt-2	25-50% smectite ; major impurities of kaolinite, gypsum, and mica	1	-12		
RM-10-ME	Enhanced Montmorillonite			0.7	-11		
RM-10-FR	Enhanced Montmorillonite			0.8	-16		
Na-A	Zeolite		100% Zeolite A				
Synthetic Mica		SYN-1		0.4	-15		

Flocculant:

The polyelectrolyte utilized as a flocculant is a long chain cationic polymer: polydiallyldimethyl ammonium chloride (CATFLOC). The molecular weight of the monomer is 161.5; the molecular weight of the polymer is 10^4 - 10^6 . CATFLOC was dissolved in distilled water and added in the treatment experiments as a solution.

Analytical Procedures for ^{239}Pu Determination:

The concentration of ^{239}Pu in the water before and after treatment was determined by liquid scintillation counting, alpha spectrometry, or mass spectrometry. Liquid scintillation counting consists of counting the ^{239}Pu solution three times for twenty minutes in a Packard Liquid Scintillation Counter with a window setting from 25 to 800 KeV. The liquid scintillation samples consist of an aliquot of the Pu solution and an aliquot of make-up water totaling 6 mls, and 14 mls of Ultima Gold Liquid Scintillation Fluor. The efficiency of the counter was determined by counting an aliquot of the ^{239}Pu standard SRM-949F. The counter was found to be 100% efficient. The procedure utilized for ^{239}Pu determinations by alpha and mass spectrometry is described in Appendix C.

Results and Discussion

The results of the treatment studies for the removal of Pu from C-2 water spiked with ^{239}Pu are given in Appendix A; the results for the removal of Pu from distilled water spiked with ^{239}Pu are given in Appendix B.

The treatment technique designed employs sorbers to adsorb plutonium; flocculation is utilized to remove the sorber particles (carrying the contaminants) from the water. In the flocculation scheme designed, a cationic long-chain polymer is utilized to remove the sorber particles from suspension after the adsorption of actinide contaminants by the sorber particles is effected. The mechanisms responsible for flocculation by polyelectrolytes are charge neutralization and polymer bridging. Particles in aqueous suspensions are stabilized by their surface charge due to the electrical double layer repulsion that prevents particle contact. Since the sorber particles have a negative surface charge in water (see Table 1), using a cationic polyelectrolyte may partly or completely neutralize the sorber particles, thus reducing or eliminating the electrical repulsion and destabilizing the particles. Long-chain polymers link or "bridge" the suspended particles together by attachment of different segments of a single polymer to different particles to form a cluster. These clusters may rapidly grow to a larger size and settle by gravity. Since the long polymers must attach themselves to a free surface, optimal flocculation occurs at very low surface coverage and thus low polymer concentration as compared to the sorber concentration.

The kinetics of polymer flocculation are well understood. The number of collisions between particles and polymer molecules in a suspension in unit time per volume,

J_{12} , is given by eq. 1, where N_1 is the number of particles per unit volume, N_2 is the number of polymer molecules per unit volume, and k_{12} is the rate constant.

$$J_{12} = k_{12}N_1N_2 \quad (1)$$

In our studies, flocculation was carried out with agitation; consequently, particle collisions resulted from fluid motion. In this case the rate constant is given by eq. 2, where a_1 and a_2 are the radii of the particles and the polymer molecules, respectively, and G is the velocity gradient or shear rate (in s^{-1}).

$$k_{12} = 4/3 G (a_1 + a_2) \quad (2)$$

Kinetic considerations are responsible for the addition of a sorber as an actinide adsorbent in the first step of the treatment technique. If actinide flocculation is effected without prior addition of sorber, the time required for the flocculation of the actinide species would be given by a second-order reaction. The time required for flocculation of a fraction of the actinide particles originally in suspension would be dependent on the original concentration of actinides. Since the remediation technique is intended for removal of actinides at trace levels, the time required for successful removal of a large fraction of actinides would be too large to be practical. Addition of large amounts of polymer to change the flocculation reaction to pseudo first order is not possible because the polymer needs to be in the appropriate concentrations to be fully extended in aqueous suspension and be effective in bridging together the particles.

Addition of a sorber as a first step in the flocculation technique corresponds to a pseudo first order reaction because the concentration of sorber added is extremely large as compared to the concentration of actinides in the contaminated waters. The time required (t_f) for a fraction (f) of the actinide contaminant to be adsorbed onto the sorber is given by eq. 3, where $[\text{sorber}]_0$ is the initial concentration of sorber, and k is the rate of the adsorption reaction.

$$t_f = -\ln(f) / (k [\text{sorber}]_0) \quad (3)$$

Equation 3 is independent of the initial concentration of actinide contaminants. The rate and rate constant of the flocculation of the sorber particles by polymer addition is then given by eqs. 1 and 2, respectively. Inspection of the results in Appendices A and B indicates that the percent removal of plutonium as a result of treatment is independent of initial ^{239}Pu concentration. For instance, Table 1 (in Appendix A) indicates that addition of Ca-montmorillonite followed by CATFLOC removes from 93-97% of the $^{239}\text{Pu(IV)}$ polymer originally present in C-2 water at concentrations ranging from 0.3 to 10^5 pCi/L.

The results presented in Appendices A and B indicate that sedimentation alone of the plutonium-containing solution does not remove a significant amount of plutonium from the water. Addition of finely-divided clay particles followed by sedimentation does not remove the plutonium from water in a timely manner (see for example Table 1 in Appendix A). Addition of CATFLOC alone is not effective in the removal of plutonium from water due to kinetic considerations.

The collisions of the CATFLOC with plutonium follow second order kinetics; since plutonium is present in such small quantities, the time required for flocculation and sedimentation is extremely long (see for example Table 1 in Appendix A). However, addition of clay particles followed by CATFLOC is very effective for the removal of Pu.

Treatment with the enhanced montmorillonites (RM-10-ME and RM-10-FR) does not require addition of a flocculant (see for example Tables 3 and 4 in Appendix A). These two montmorillonite samples are commercially available and already have an organic polymer intercalated into the clay structure. Consequently, the addition of flocculant is not necessary for water treatment.

Cationic sorbers (Ca- Montmorillonite, kaolinite, RM-10-ME, RM-10-FR, and Na-A) proved to be very effective for flocculation treatment of pond C-2 water spiked with $^{239}\text{Pu(IV)}$ polymer (see Tables 1-5, in Appendix A). Treatment with these sorbers resulted in 93%-99% removal of $^{239}\text{Pu(IV)}$ polymer from C-2 water after only 15 minutes of sedimentation time.

Utilization of kaolinite and alumina in the flocculation treatment resulted in 77%-85% removal of Pu from C-2 water, spiked with $^{239}\text{Pu(VI)}$, after 15 minutes of sedimentation (see Tables 9, 13, and 14 in Appendix A). The Pu percent removal determined for C-2 water spiked with Pu polymer was not obtained for Pu(VI) until 72 hours of sedimentation time had elapsed. Utilization of cationic sorbers (Ca-montmorillonite, kaolinite, RM-10-ME, RM-10-FR) and alumina in the flocculation treatment resulted in 91%-99% removal of Pu from C-2 water, spiked with $^{239}\text{Pu(VI)}$, after 72 hours of sedimentation (see Tables 8-11 and 13 in Appendix A). One possible explanation for these observations is that Pu(VI) is not stable at near-neutral pH conditions. However, oxidation states interconversions have been reported to be slow. It may take a significant amount of time for the Pu(VI) to convert to Pu(IV) and start acting as the Pu polymer.

Comparison of the results in Table 7 (of Appendix A) with the results in Tables 1-3 (of Appendix A) indicates a discrepancy. The Pu percent removals in Table 7 are lower than the ones reported in Tables 1-3. The reason for this apparent discrepancy is that the age of the flocculant solution for the treatment experiments reported in Tables 7 and 14 was over 21 days. After the flocculant solution ages it becomes ineffective. Consequently, flocculant solutions that are at most one day old are now being utilized for treatment. The results in Tables 7 and 14 are too low and will only be utilized for comparison among sorbers and not for reporting absolute effectiveness of the treatment technique.

Comparison of Table 1 with Table 2, and Table 8 with Table 9 (of Appendix A) yields evidence to conclude that kaolinite is more effective than Ca-montmorillonite for the removal of Pu by flocculation treatment. The reason for this is not clear. Chemically, there is no reason for a larger adsorption of Pu onto kaolinite than onto montmorillonite. One potential explanation for larger Pu removals with kaolinite could be the kinetics of agglomeration. According to equation 2, the rate of agglomeration is dependent on the size of the particles being flocculated. The mean particle size of kaolinite is larger than the mean particle size

of Ca-montmorillonite by a factor of two. The fact that the Pu removals for treatment with kaolinite and montmorillonite after 72 hours of sedimentation are the same substantiates the hypothesis that Pu chemical sorption is not larger for kaolinite than montmorillonite.

The effect of potential changes in water chemistry and their effect on the flocculation treatment was studied by utilizing distilled water as well as C-2 water for our studies. Comparison of the results obtained for C-2 water (Tables 1 and 8 of Appendix A) with the results obtained for distilled water (Tables 15-16 of Appendix B) does not indicate any major differences in the effectiveness of the flocculation treatment as a function of water chemistry. This is an important conclusion because one of the potential water poisons for the flocculation treatment is the existence of organics (such as fulvics or humics) which may preferentially bind the actinides in the pond water.

Inspection of tables in Appendix A (for instance Tables 12-13) indicates that the Pu solutions prepared in C-2 water are not always stable over a long time period. This is probably due to the suspended solids in the RFP pond waters which cause Pu losses as the solids sediment, scavenging the Pu. Preliminary results from Task B of this study indicate that approximately 80% of the Pu in the pond waters is associated with particles larger than 0.45 μm . Consequently, our future treatment studies will be performed after the Pu-spiked pond water is filtered through a 0.45 μm filter.

Summary

- 1) The flocculation technique designed requires the addition of a sorber to the Pu-containing water to adsorb Pu. This step is followed by addition of a flocculant to agglomerate the sorber particles, and removal of the sorber particles (carrying the Pu contaminant) by sedimentation.
- 2) Utilization of commercially-available enhanced montmorillonite as the sorber does not require the addition of flocculant for water treatment. The enhanced montmorillonite already has an organic polymer intercalated in the clay structure and addition of another flocculant is not necessary.
- 3) The cationic exchangers (Ca-montmorillonite, kaolinite, enhanced montmorillonite, and zeolite NaA) utilized for water treatment, with a 15 minute sedimentation time, yielded 93%-99% removal of Pu from C-2 water spiked with $^{239}\text{Pu}(\text{IV})$ polymer at concentrations from 0.3 to 10^5 pCi/L.
- 4) Based on 15-minute sedimentation time in the treatment technique, the effectiveness of the sorbers for the removal of Pu from pond water spiked with $^{239}\text{Pu}(\text{IV})$ polymer is: kaolinite > Ca-montmorillonite ~ enhanced montmorillonite ~ zeolite Na-A > illite > Na-montmorillonite > mixed layer clay > mica > neutral alumina.

- 5) The utilization of kaolinite and neutral alumina in the water treatment, with a 15-minute sedimentation time, resulted in 77%-85% removal of Pu from C-2 water spiked with $^{239}\text{Pu}(\text{VI})$ at concentrations from 0.08 to 10^5 pCi/L.
- 6) Based on 15-minute sedimentation time in the treatment technique, the effectiveness of the sorbers for the removal of Pu from pond water spiked with $^{239}\text{Pu}(\text{VI})$ is: neutral alumina > kaolinite > enhanced montmorillonite > Ca-montmorillonite ~ Na-montmorillonite ~ zeolite Na-A > mica.
- 7) The differences in the behavior of Pu(VI) vs. the behavior of Pu(IV) polymer are probably due to kinetics of speciation in the pond water. Pu(VI) is probably not stable in the pond water and its interconversion to Pu(IV) or Pu(V) is slow.
- 8) CATFLOC solutions utilized for water treatment lose their effectiveness as they age. CATFLOC solutions that are at most one day old are now being used for water treatment.
- 9) The flocculation treatment designed does not appear to be very sensitive to water chemistry ranging from distilled water to C-2 pond water.
- 10) The Pu solutions prepared in C-2 water are not always stable over a long time period. This is probably due to the suspended solids in the RFP pond waters which cause Pu losses as the solids sediment. Preliminary results from Task B of this study indicate that approximately 80% of the Pu in the pond waters is associated with particles larger than $0.45\text{ }\mu\text{m}$. Consequently, our future treatment studies will be performed after the Pu-spiked pond water is filtered through a $0.45\text{ }\mu\text{m}$ filter.

APPENDIX A

Table 1						
Radionuclide	Pu-239					
Initial Oxidation State	IV					
Physical Form	Polymer					
Pond Water	C-2					
I.D. of Water	SW60193WC					
Sorber	Ca-Montmorillonite					
Flocculant	CATFLOC					
pH of Contaminated Solution	7.7-8.0					
Temperature	20-25 degrees Celsius					
Initial Concentration of Contaminated Solution (pCi/L)	% Removal after Sedimentation Time T1	T1 (in min)	% Removal after 24 hours	Grams of Sorber Added per Liter of Contaminated Solution	Milligrams of Flocculant Added per Liter of Contaminated Solution	
1.2E+05	97	15	99	2.5	3.75	
1.2E+05	97	15	99	2.5	3.75	
1.2E+05	46	15	88	2.5	0	
1.2E+05	46	15	83	2.5	0	
1.2E+05	5	15	75	0	3.75	
1.2E+05	8	15	76	0	3.75	
1.2E+05	8	15	18	0	0	
1.2E+05	8	15	20	0	0	
2.8E+04	99	15		2.5	3.75	
2.8E+04	98	15		2.5	0.75	
2.8E+04	5	15		0	3.75	
3.5E+02	97	15		2.5	0.75	
1.9E+02	98	15		2.5	0.75	
7.5E-01	98	65		2.5	0.75	
3.2E-01	93	15		2.5	0.75	

APPENDIX A

Table 2							
Radionuclide	Pu-239						
Initial Oxidation State	IV						
Physical Form	Polymer						
Pond Water	C-2						
I.D. of Water	SW60193WC						
Sorber	Kaolinite						
Flocculant	CATFLOC						
pH of Contaminated Solution	7.7-8.0						
Temperature	20-25 degrees Celsius						
Initial Concentration of Contaminated Solution (pCi/L)	% Removal after Sedimentation Time T1	T1 (in min)	% Removal after 24 hours	Grams of Sorber Added per Liter of Contaminated Solution	Milligrams of Flocculant Added per Liter of Contaminated Solution		
1.2E+05	99	15		2.5	3.75		
1.2E+05	99	15	99	2.5	3.75		
1.2E+05	95	15	99	2.5	0		
1.2E+05	95	15	99	2.5	0		
1.2E+05	5	15	75	0	3.75		
1.2E+05	8	15	76	0	3.75		
1.2E+05	8	15	18	0	0		
1.2E+05	8	15	20	0	0		
3.5E+02	98	20		2.5	0.75		
1.9E+02	98	20		2.5	0.75		
3.4E-01	96	80		2.5	0.75		
3.1E-01	94	80		2.5	0.75		

APPENDIX A

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Table 5

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APPENDIX A

Table 7									
Radionuclide		Pu-239							
Initial Oxidation State		IV							
Physical Form		Polymer							
Pond Water		C-2							
I.D. of Water		SW60193WC							
Flocculant		CATFLOC							
Initial Concentration of Contaminated Solution (pCi/L)	% Removal after 15 min	% Removal after 24 hours	Sorber	Grams of Sorber Added per Liter of Contaminated Solution	Milligrams of Flocculant Added per Liter of Contaminated Solution				
1.0E+04	73	84	Ca-Montmorillonite	2.5	0.75				
1.0E+04	74	84	Ca-Montmorillonite	2.5	0.75				
3.0E+03	74	91	Ca-Montmorillonite	2.5	0.75				
3.0E+03	71	93	Ca-Montmorillonite	2.5	0.75				
3.0E+03	71	90	RM-10-ME	2.5	0.75				
3.0E+03	76	95	RM-10-ME	2.5	0.75				
3.0E+03	72	95	RM-10-ME	2.5	0.75				
1.0E+04	63	73	Na-Montmorillonite	2.5	0.75				
1.0E+04	66	74	Na-Montmorillonite	2.5	0.75				
1.0E+04	84	90	Kaolinite	2.5	0.75				
1.0E+04	82	90	Kaolinite	2.5	0.75				
1.0E+04	59	69	Synthetic Mica	2.5	0.75				
1.0E+04	59	65	Synthetic Mica	2.5	0.75				
1.0E+04	69	85	Illite	2.5	0.75				
1.0E+04	72	78	Illite	2.5	0.75				

APPENDIX A

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APPENDIX A

Table 8		Radionuclide		Initial Oxidation State		Pond Water		I.D. of Water		Sorber		Flocculant		pH of Contaminated Solution		Temperature		Initial Concentration of Contaminated Solution (pCi/L)		% Removal after Sedimentation Time T1		T1 (in min)		% Removal after 72 hours		Grams of Sorber Added per Liter of Contaminated Solution		Milligrams of Flocculant Added per Liter of Contaminated Solution	
Pu-239		VI		C-2		SW60193WC		Ca-Montmorillonite		CATFLOC		7.6-8.1		20-25 degrees Celsius															
1.8E+05		45		15		91		2.5		3.75																			
1.8E+05		42		15		91		2.5		3.75																			
1.8E+05		26		15		94		2.5		0																			
1.8E+05		27		15		93		2.5		0																			
1.8E+05		12		15		62		0		3.75																			
1.8E+05		13		15		56		0		3.75																			
1.8E+05		7		15		18		0		0																			
1.8E+05		7		15		19		0		0																			
1.6E+05		58		15				2.5		3.75																			
1.6E+05		47		15				2.5		0.75																			
1.6E+05		6		15				0		3.75																			
1.9E+03		35		15				2.5		0.75																			
1.0E+03		41		15				2.5		0.75																			
6.8E+00		79		65				2.5		0.75																			
3.0E+00		70		60				2.5		0.75																			
8.0E-01		77		15				2.5		0.75																			
7.8E-02		82		15				2.5		0.75																			

APPENDIX A

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APPENDIX B

Table 15				
Radionuclide	Pu-239			
Initial Oxidation State	IV			
Physical Form	Polymer			
Type of Water	Distilled			
Sorber	Ca-Montmorillonite			
Flocculant	CATFLOC			
pH of Contaminated Solution	6.9-7.0			
Initial Concentration of Contaminated Solution (pCi/L)	% Removal after 15 min	Grams of Sorber Added per Liter of Contaminated Solution	Milligrams of Flocculant Added per Liter of Contaminated Solution	
7.8E+04	95	2.5	0.75	
7.8E+04	95	2.5	0.75	
7.8E+04	24	2.5	0	
7.8E+04	26	2.5	0	
7.8E+04	26	0	0.75	
7.8E+04	25	0	0.75	
7.8E+04	23	0	0	
7.8E+04	22	0	0	
7.3E+04	98	2.5	0.75	
7.3E+04	97	2.5	0.75	
7.3E+04	9	2.5	0	
7.3E+04	8	2.5	0	
7.3E+04	12	0	0.75	
7.3E+04	12	0	0.75	
7.3E+04	9	0	0	
7.3E+04	7	0	0	
8.9E+03	97	2.5	0.75	
8.9E+03	8	2.5	0	
8.9E+03	5	2.5	0	
8.9E+03	13	0	0.75	
8.9E+03	8	0	0.75	
8.9E+03	8	0	0	
8.9E+03	10	0	0	

APPENDIX B

Table 16		Pu-239			
Radionuclide		Pu-239			
Initial Oxidation State		VI			
Type of Water		Distilled			
Sorber		Ca-Montmorillonite			
Flocculant		CATFLOC			
pH of Contaminated Solution		6.9-7.5			
Initial Concentration of Contaminated Solution (pCi/L)	% Removal after 15 min	Grams of Sorber Added per Liter of Contaminated Solution	Milligrams of Flocculant Added per Liter of Contaminated Solution		
6.1E+04	41	2.5	0.75		
6.1E+04	43	2.5	0.75		
6.1E+04	31	2.5	0		
6.1E+04	34	2.5	0		
6.1E+04	8	0	0.75		
6.1E+04	6	0	0.75		
6.1E+04	7	0	0		
6.1E+04	9	0	0		
5.6E+04	29	2.5	0.75		
5.6E+04	32	2.5	0.75		
5.6E+04	27	2.5	0		
5.6E+04	29	2.5	0		
5.6E+04	2	0	0.75		
5.6E+04	4	0	0.75		
5.6E+04	3	0	0		
5.6E+04	4	0	0		
6.8E+03	43	2.5	0.75		
6.8E+03	38	2.5	0.75		
6.8E+03	36	2.5	0		
6.8E+03	38	2.5	0		
6.8E+03	6	0	0.75		
6.8E+03	7	0	0.75		
6.8E+03	5	0	0		
6.8E+03	4	0	0		

APPENDIX C

Analytical Procedure for Preparation and Analysis of Environmental Flocculation Samples for Determination of Plutonium by Mass Spectrometric Analysis and/or Alpha Spectrometry

1.0 Overview

- 1.1.** This document describes the chemical procedure for the separation and purification of samples for quantitatively determining plutonium by means of mass spectrometric analysis (MS) and/or alpha spectrometry (α -spec). The levels of detection of plutonium for each method (MS or α -spec) in each sample are dependent upon the corresponding analytical blank for each sample instrumental detection. The procedure described here is performed in clean room facilities (Class 100). Samples are dissolved using conventional methods (strong mineral acids). Following dissolution the plutonium is co-precipitated with LaF_3 and the plutonium cleanup is performed by three anion exchange column steps. The sample is prepared for instrumental analysis. By doing all the analyses in a clean room environment, using all clean, new glassware/labware, and using ultra pure reagents, the reagent blank for the samples is lower and consequently the detection limit for plutonium is lower.

1.2 Principle of Method

- 1.2.1.** Environmental samples are wet ashed, the plutonium is isolated by a combination of co-precipitation and ion exchange separation techniques, and the plutonium is submitted for mass spectrometric analysis or prepared for alpha counting.
- 1.2.2.** All samples are traced prior to dissolution with standardized ^{242}Pu for MS analysis or with ^{236}Pu for α -spec analysis.
- 1.2.3.** Chemical dissolution, separation, purification, counting preparation and mass spectrometric analyses are conducted under clean room protocol. All these steps are performed in Class 100 room facilities and follow clean room protocol.

2.0 Application

- 2.1.** The chemical separation method described here is appropriate for the quantitative isotopic analysis of plutonium by mass spectrometry or quantitative analysis in water samples and related solids associated with flocculation experiments. It is also adaptable to a variety of samples: soil, geological, water, air filters, and biological samples with minor modifications in sample treatment prior to analysis.

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3.0 Sensitivity

- 3.1. Approximately 0.01 pCi/sample (0.01 pCi approximately equals 7×10^8 atoms of Pu-239) of any isotope may be detected by mass spectrometric methods based on work reported in Attrep, et al. 1992.
- 3.2. The methods described here are designed to detect levels of $\sim 8 \times 10^8$ atoms plutonium using mass spectrometric analysis as compared to work performed on plutonium in uranium ores (see Attrep et al. 1992). However, the limit of detection is established by the values obtained in the analytical blanks (ab). The limit of detection for plutonium in these samples is set as the arithmetic mean of the analytical blank (M_{ab}) plus 3 times the standard deviation (s): $M_{ab} + 3s$. This value will differ from sample type to sample type because of the differences in processing, dissolution, and chemistry. It is anticipated that the detection limit should become lower when analytical separation methods are employed which differ from that described in the reference.
- 3.3. The size of the water samples is usually 10 L or less. Sample size is typically 500 ml. For samples greater than 10 L particular attention should be paid to the accompanying reagent blank with reference to greater blank values. If greater reagent blank values are obtained, this should be considered in the evaluation and calculation of plutonium in the sample.

4.0 Interferences

- 4.1. Mass Spectrometric Analysis. Two actinides which present problems with the plutonium analysis are uranium and thorium. Both can cause problems when the samples are being analyzed by a thermal ionization mass spectrometer. If uranium is present, the mass 238 may glow and interfere with that of the 239 (plutonium) peak. Thorium in the microgram quantities, if present, can effectively poison the source and hence produce "poor" runs. Organics from the flocculation process may produce mass spectrometric signals in the mass region 239.
- 4.2. α -Spectrometric Analysis. The procedure used in this analysis is specific to remove most of the interfering alpha emitters (uranium and decay chain products and thorium and decay chain products). Particular care must be exercised to eliminate airborne α -emitting radionuclides and their daughters, especially radon-222.

5.0 Lower Limit of Detection or Analytical Detection Limit

- 5.1. The analytical limits of detection (ALD) for the instrumental method of detection above are set by the ability of the procedure to distinguish between plutonium in the analytical blank and that of a sample. Thus the analytical limit of detection is defined as the smallest concentration of plutonium that can be detected that has a 99% probability of being validly

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detected. This is an experimental detection limit and is based on the compilation of reagent blanks for each sample type where the analysis conditions and steps are unique to that analysis.

- 5.2. Analytical blanks are run with each set of samples. A plutonium spike of known quantity is processed through the analysis in its entirety duplicating every step of the analysis and in the identical environment.

6.0 Shipment and Storage of Sample and Sample Stability

- 6.1. Instructions concerning collection of the samples are given to the requester prior to obtaining the sample. Generally, the following is to be followed: If experiments prohibit acidification of the sample then this is to be noted on the sample analysis and container. The samples are to be stored in cleaned plastic bottles or other vessels, sealed and stored until dissolution. Samples are to be preserved by refrigeration, freezing, or freeze drying if required until dissolution and analysis takes place. For samples requiring acidification, water samples must be acidified immediately upon collection at the rate of 6-10 ml per liter of water sample. The samples are to be stored in cleaned plastic bottles or other vessels, sealed and stored until dissolution, plastic is preferred. The sample is then spiked with the ^{242}Pu (usually ~ 1 ng) or ^{236}Pu (activity depending upon estimated sample size) tracer.
NOTE: If the samples are to be filtered, preferably this is done first.

7.0 Reagents

- 7.1. Water: MilliQTM
- 7.2. Hydrochloric acid, concentrated (Seastar Brand, Double subboiling distilled in quartz); 4M; 3M; 6M
- 7.3. Hydrobromic acid, 47%
- 7.4. Nitric Acid, concentrated (Seastar Brand, Double subboiling distilled in quartz); 4M; 8M
- 7.5. Perchloric Acid, concentrated (Seastar Brand, Double subboiling distilled in quartz)
- 7.6. Hydrofluoric Acid, concentrated (Seastar Brand)
- 7.7. Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$): 35% (w/v) in water
- 7.8. Lanthanum carrier: 5.34 mg/ml 1.666 gm $\text{La}(\text{NO}_3)/100\text{ml}$ water

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- 7.9. Quartz wool. The quartz wool is soaked in 4 M HNO_3 overnight, removed and rinsed 7 times with deionized water, air dried, and stored in sealed plastic bags until used.
- 7.10. AGMP-1, 50-100 mesh macroporous anion exchange resin. The resin is pretreated by stirring overnight in a 6 M HCl solution. The acid is decanted and the resin is washed at least 20 times with deionized water and stored in a plastic bottle as a water slurry.
- 7.11. Ion exchange columns: All columns are prepared using disposable automatic pipette tips, approximately 7 cm long and approximately 5 mm i. d. A plug of prewashed quartz wool is placed in the tip of the pipetter tip and resin is added with a plastic delivery pipette to a depth of approximately 2 cm. The resin is then pre-treated with the acids as indicated in each step.
- 7.12. $\text{HCl-H}_2\text{O}_2$ - 10 ml of concentrated HCl + 2 drop 30% H_2O_2 (prepared immediately before use).
- 7.13. HCl-HI solution: Mixture 1:9 by volume of 48% HI and conc HCl (prepared immediately before use)
- 7.14. Soln # 1 (5 ml conc HCl - 1 drop HNO_3) (prepared immediately before use)
- 7.15. Ethanol, absolute
- 7.16. Ammonium Chloride crystals reagent grade
- 7.17. Methyl Red indicator
- 7.18. Ammonium Hydroxide

8.0 Apparatus and Equipment

- 8.1. Mass spectrometer
- 8.2. Alpha Spectrometers
- 8.3. Class 100 clean room facilities
- 8.4. Hot plates (Corning PC-351 or PC-300, 5" x 7")
- 8.5. Quartz test tubes 13 mm x 100 mm, Ace Glass Inc. (Cat. No. 18683-08)
- 8.6. Centrifuge Tubes, 40 ml: Pyrex # 8120 and # 8320
- 8.7. 50 ml Oakridge style centrifuge tubes (PC)

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- 8.8. Aluminum Block: Width = 3", L = 3 13/16", H = 3 5/8 " drilled to hold 6 quartz tubes described in 9.4.
- 8.9. Aluminum Block: Width = 3", L = 3 13/16", H = 4 3/8 ", drilled to hold four 40 ml centrifuge tubes
- 8.10. Teflon Beaker, 100, 250, 600 ml (PTFE)
- 8.11. Teflon Beaker, 1000 ml, PFA Heatable Beaker
- 8.12. Samco® Sterile Plastic Transfer Pipettes Style #222-20S Saint-Amand Mfg. Co., Inc.
- 8.13. Chromatographic column: Blue Eppendorpf disposable pipette tips 7 cm x 0.5 cm i.d.
- 8.14. Beakers, glass, Pyrex or Kimax 150 ml
- 8.15. Parafilm™
- 8.16. Graduated cylinder: plastic and glass, variable sizes up to 1000 ml
- 8.17. Electroplating apparatus
- 8.18. Electroplating cell: (Brass base with a 1" Pt disc on the base, a plastic gasket is placed on the disc and a thin walled chimney is placed on the disc and secured to the base with the use of springs).

9.0 Procedure

- 9.1. Glassware is cleaned in the following manner before use. Each piece is soaked in a solution of (1 part HCl, 1 Part HNO₃, 2 parts water) for 20-24 hours, rinsed with distilled water and air dried. The pieces are then stored in sealed plastic containers. All glassware and plastic ware is treated as described above unless otherwise noted.
 - 9.1.1. To the acidified water sample or the solid flocculation solid material add tracer (which had been weighed on an analytical balance to the nearest 0.1 mg) of ²⁴²Pu or ²³⁶Pu tracer. Transfer the sample (which has been weighed to the nearest gram) to a appropriate size Teflon beaker. To the sample add 10 ml of conc HNO₃, 5 ml of conc HClO₄ and 10 ml of conc HF. Place Teflon beaker on a hot plate and heat (250° C) to HClO₄ fumes. Remove and cool.
 - 9.1.2. Add 10 ml of conc HNO₃, and an additional (no more than 3 ml) of HClO₄ if necessary. Repeat digestion on hot plate, heat to dryness. Remove and cool.

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- 9.1.3. To the residue add 20-30 ml 3 M HCl (all the sample should be dissolved), add 5 mg La^{+3} carrier. Add 5 ml of 35% hydroxylamine hydrochloride and 5 ml of conc HF, wait at least 1 hour. Centrifuge and discard the supernate.
- 9.1.4. Transfer the precipitate (LaF_3) with 20 ml concentrated HClO_4 into a small Teflon beaker. Place on hot plate at 200-225° C until the perchloric acid fumes, and take to dryness. Remove and cool.
- 9.1.5. Add 5 ml of conc HCl with a drop of conc HNO_3 (Soln #1) and transfer to an anion exchange column that has been previously treated as follows: three 1 ml washes with deionized water and two 1 ml washes with Soln #1. Rinse the beaker with 2 ml of Soln #1 and add the rinse to the column. Discard all eluents from the loading and washings.
- 9.1.6. Rewash the beaker which contained the sample with three 1 ml washings of conc HCl, add each wash to the column, discard the run thru. Add a few small $\text{NH}_2\text{OH}\cdot\text{HCl}$ crystals to the top of the resin, add 2 ml of conc HCl and discard the run thru.
- 9.1.7. Place a clean 40 ml centrifuge tube under the column to collect the plutonium. Add four successive additions of approximately 0.5 ml of the HCl-HI solution (Pu is converted to the III state.) and collect the eluted plutonium.
- 9.1.8. Place the centrifuge tube containing the Pu sample in a heat block at a hot plate setting of 3 and evaporate to dryness. Add 6 drops of concentrated HNO_3 (to remove iodine) and evaporate to dryness again. Add 6 drops of concentrated HCl and evaporate to dryness. Dissolve the plutonium in 1 ml of the $\text{H}_2\text{O}_2\text{-HCl}$ solution (note it may be necessary to place samples into a heat block each time to avoid losing the sample).
- 9.1.9. Pretreat an anion exchange column by passing 2 ml of the $\text{H}_2\text{O}_2\text{-HCl}$ solution through the column. Load above sample onto the column with a plastic transfer pipette. Rinse the centrifuge tube with 1 ml of the $\text{H}_2\text{O}_2\text{-HCl}$ solution and pass the rinse through the column. Wash the column with approximately 2 ml of 8 M HNO_3 using a disposable plastic pipetter. Wash the tip of the column with a stream of deionized water from a wash bottle and discard all eluents and washes. Place a 40 ml centrifuge tube under the column and elute the plutonium with three 1 ml portions of concentrated HBr. Allow each solution addition to drain completely before adding the next portion of HBr.
- 9.1.10. Evaporate the HBr solution to dryness in an aluminum heat block. Add 4 drops of HNO_3 and 4 drops of HClO_4 and heat at 130° C for one hour. Evaporate at > 180° C to dryness.

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- 9.1.11. Pretreat an anion exchange column by passing 2 ml of conc HBr through the column. Dissolve the plutonium in 1 ml of concentrated HBr and load onto the column with a plastic transfer pipette. Collect the eluent in a 40 ml centrifuge tube (8320). Rinse the centrifuge tube with 1 ml of conc HBr and pass through the column adding it to the previous collected HBr. Repeat the wash of the centrifuge tube with HBr and collect the HBr with the other two portions.
- 9.1.12. Place centrifuge tube in the heat block. Evaporate the HBr solution to dryness. (The HBr will splatter if the sample is heated too rapidly. It is best to place the sample in the cold block and allow a gradual heating). Destroy the traces of HBr and organic matter remaining by adding 4 drops of concentrated HNO₃ and 4 drops of HClO₄ and heating at 130° C for 1 hour. The sample is evaporated to dryness by heating at 180° C.
- 9.1.13A. If sample is to go to mass spectrometer elute sample into a quartz tube (13 mm x 100 mm), dry the sample in a block that accepts the 100 mm size tubes with setting at 6.5, remove the tube, cool, cap, label and submit for mass spectrometric analysis,
- OR
- 9.1.13B. Remove the tube, cool and prepare for electroplating as follows:
- 9.1.14. Preparation of the sample for alpha spectrometry. Evaporate all the solution to dryness. Add 4 drops of conc HNO₃ and heat in a heating block to dryness. Add 0.5 ml of HCl and take to dryness. Repeat the HCl treatment using 4 drops conc HCl four times. Take up the residue in 0.5 ml of conc HCl and transfer to an electroplating cell that is equipped with a 1-inch platinum or stainless steel plating disc, a thin-walled chimney, and a plastic gasket. Wash the centrifuge tube with two 0.5 ml portions of distilled water, and transfer the washings to the plating cell (~1.5 ml volume). Add two small spatulas of NH₄Cl and 1 drop of methyl red indicator solution. Make the solution alkaline by adding dropwise conc NH₄OH and then add 1 M HCl dropwise until the solution is barely acidic. Electroplate at 1 A and ~6.8 V for 15 min while stirring the solution with a Pt rod. Just before the plating is completed, add 0.5 ml of conc NH₄OH. Immediately turn off the stirrer and the current and pour the plating liquid back into the centrifuge tube. Remove the chimney and wash the Pt or stainless steel disc with water and then with ethanol. Flame the plate and count on an alpha counter.

10.0 Calculations

- 10.1. All data storage and data reduction is accomplished with the use of Microsoft Excel[®] spreadsheet package.

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11.0 Standardization/Preparation of Tracers

PREPARATION OF RF-TR- ^{236}Pu - A SOLN

- 11.1. Take desired aliquot of your stock and the sample to a soft dryness. Pick up the solution in 2 ml of soln #1 and go directly to the anion column.
- 11.2. ANION COLUMN
 - 11.2.1. Take a blue plastic pipet tip and plug the tip with quartz wool. Add ~3 cm. of AGMP-1 anion exchange resin.
 - 11.2.2. Pretreat the resin with 3 ml of soln #1, and discard run thru into waste container.
 - 11.2.3. Add sample to column. (Pu should stick), and discard run thru into waste container.
 - 11.2.4. Wash tube which contained sample, with 1 ml of soln #1, add wash to column, and discard run thru into waste container.
 - 11.2.5. Rewash tube which contained sample with 3 ml of conc HCl, add wash to column, and discard run thru into waste container.
 - 11.2.6. Elute column with 3 to 5 ml of HI-HCl mixture, collect run thru (HI-HCl = 1 ml of conc HI + 9 ml of conc HCl).
 - 11.2.7. Carefully take sample dry (Note: you may dry over a flame if you wish but please be careful).
 - 11.2.8. Add 0.5 ml of conc HClO_4 and 0.5 ml conc HNO_3 and dry again (see note step #7).
 - 11.2.9. Put sample into solution with 3 ml of conc HBr, (sample is now ready for HBr column).
- 11.3. HBr COLUMN
 - 11.3.1. Prepare column as in step 1 above (anion column prep.).
 - 11.3.2. Pretreat column with 4 ml of conc HBr.
 - 11.3.3. Take sample from step 9 above and add sample to the column, collect run thru.
 - 11.3.4. Wash column with two 1 ml aliquots of conc HBr and combine run thru with previous run thru.

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- 11.3.5. Take run thru from the column, dry (see note on step #7 of anion column).
- 11.3.6. Add 0.5 ml of conc HClO_4 and 0.5 ml conc HNO_3 and dry again (see note on step #7).
- 11.3.7. Add ~ 1 ml of conc HCl and take to near dryness, see note on step #7.
- 11.3.8. Bring sample up to desired volume with 3M HCl , volume will depend on desired specific activity.
- 11.3.9. Take a small aliquot and count for gross alpha on counters 51 and 56 located in TA-48, building RC-1 at LANL.
- 11.3.10. You may also want to have the above samples counted on counters 80 or 81 located in TA-48, building RC-1 at LANL to verify no ^{238}Pu is present.
- 11.4. STANDARDIZATION OF TRACER BY WEIGHT
 - 11.4.1. Very accurately weigh two 500 lambda aliquots onto two one inch platinum discs, dry each disc under a heat lamp, once samples are dry, flame each disc.
 - 11.4.2. Count each sample on counters 51 and 56 located in TA-48, building RC-1 at LANL until 2×500 min. or until at least 100,000 counts have registered.
 - 11.4.3. A dilution can be made from the above sample if need be.

12.0 Quality Control

- 12.1. Notebook. All record of samples, quantitative data, sample identification, etc. will be recorded in a laboratory notebook. Each entry will be dated and signed by the analyst.

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Characterization of Sorbers Using Coulter Multisizer, N4MD, and Coulter Delsa 440

Sample Preparation

Goal:

Sorbers were analyzed as follows for zeta potential and particle size.

Each sorber, in the form of a fine powder, was suspended in pond C-2 water and its electrophoretic mobility measured. The goal was to suspend the sorber particles in an environment that approaches as closely as possible, the original particle environment.

Concentration:

Ten mg of each sorber were weighed into a clean polypropylene container and 20 ml of pond C-2 water were added. The mixture was thoroughly shaken and then sonicated for one minute. This ensures a concentration of less than 10,000 ppm which is suitable for measurement using the Coulter Delsa 440. At this stage immediate flocculation of the sorber was observed. The flocculation was observed with the pond C-2 water as well as distilled and deionized water.

For measurement of particle size, each sample was prepared using the same procedure as above except that distilled and deionized water was used instead of pond C-2 water. This ensures true representation of the sample avoiding colloids present in the pond C-2 water.

Equilibration:

Each sample was kept for at least 24 hours before any measurement was attempted to allow the surface potential to equilibrate to its final value.

pH Measurement:

The pH of the prepared samples needed to be measured for input to the Delsa 440. The measured pH at 25°C was 8.25.

Sonication:

The particles deflocculate to a limited extent on sonication and then flocculate again. The sorber was sonicated for two minutes and then allowed to settle for one minute before sampling so that the larger flocs settle out.

For particle size characterization, the samples prepared in water were sonicated for two minutes and then allowed to sediment for 10 minutes. Two ml of the supernatant fluid was added to 150 ml of electrolyte (ISOTONE II diluent) for measurement in the Coulter Multisizer. The Multisizer results

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indicated particle sizes in the sub-micron range. For measurements in the N4MD sub-micron particle size analyzer, the supernatant fluid after one hour of sedimentation was used without any dilution.

Cleanliness:

Care was taken to avoid dust and contaminants as much as possible. The sample chamber assembly was rinsed with distilled water several times before use. Similarly all containers (flasks, bottles, plastic disposables, syringes) were washed and rinsed with distilled water prior to use.

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