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Title: CEMENT WASTE-FORM DEVELOPMENT FOR PuF4
RESIDUES AT THE ROCKY FLATS ENVIRONMENTAL
TECHNOLOGY SITE

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Submitted to: Spectrum 2000

Unclassified/Not UCM

[Signature]
LAW: Class. Group

SEP 24 2000
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CEMENT WASTE-FORM DEVELOPMENT FOR PuF₄ RESIDUES AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE

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ABSTRACT

This report describes the development of a waste form to stabilize Plutonium Tetrafluoride-based residue solids at the Rocky Flats Environmental Technology Site (RFETS). The residue solids stream is composed of a spectrum from almost all PuF₄ to almost all NaF. The work focused on the performance evaluation of several Portland cement/water/residues formulations. Performance standards were chosen to address the Waste Isolation Pilot Plant-Waste Acceptance Criteria (WIPP-WAC), Environmental Protection Agency Resource Conservation and Recovery Act (EPA/RCRA), Transuranic Package Transporter Safety Analysis Report for Packaging (TRUPAC II SARP), and Safeguards Termination Limit (STL). The non-actinide work was performed using NaF and CaF₂ as surrogates for PuF₄. Since soluble fluoride was considered the major interferant to a successful waste form via set retardation, Ca(OH)₂ was used to precipitate the soluble fluoride from the NaF. This would allow one process to address the entire PuF₄/NaF spectrum. Non-actinide containing (cold) studies were first conducted to determine operating boundaries, and the results were verified using actinide-containing residues. The final recommended formulation that passed the performance standards was a cement-to-water ratio of 2 to 1 with 25% stoichiometric Ca(OH)₂ to NaF. This amount of Ca(OH)₂ was shown to produce acceptable waste forms with up to five times the solubility limit of NaF.

INTRODUCTION

The purpose of this project was to 1) develop a cementation formulation for, 2) establish an operating boundary for, and 3) demonstrate cementation as a method for stabilizing RFETS PuF₄ residue solids. The most appropriate technology was identified as Portland cementation by RFETS.

All cold studies were conducted using single shaft/impeller mixing equipment with about 900 ml sample batches. The mixing apparatus used in the study was chosen to produce complete mixing. It is assumed that the mixing apparatus to be used at RFETS will also achieve complete mixing. An objective of the study was to develop a Portland-based process that required minimal processing and use of additives. CaF₂ and NaF were used for the non-actinide testing. Since soluble fluoride was considered the major interferant to a successful waste form via set retardation, Ca(OH)₂ was used to precipitate the soluble fluoride from the NaF. Portland cement already contains Ca(OH)₂, but tests were conducted to investigate the need for additional Ca(OH)₂. The fluoride in the PuF₄ is insoluble and, therefore, considered inert. This would allow one process to address the entire PuF₄/NaF spectrum. The non-actinide testing established a cement/water/residue (C/W/R) ratio that produced a waste form that meets the performance criteria listed below.

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WASTE FORM PERFORMANCE CRITERIA

The performance criteria were set to meet the Waste Isolation Pilot Plant-Waste Acceptation Criteria (WIPP-WAC), Environmental Protection Agency Resource Conservation and Recovery Act (EPA/RCRA), Transuranic Package Transporter Safety Analysis Report for Packaging (TRUPAC II SARP), and Safeguards Termination Limit (STL). The TRUPACT II SARP and STL standards will be met by limiting the Pu content of the waste form. The following were chosen to address the WIPP/WAC and EPA/RCRA standards.

- 1. No free liquid at 24 hours after cementation** The requirement that no free liquid in a waste form being sent to WIPP is derived from the WIPP-WAC Revision 5.² The 24-hour time period was established to maintain a reasonable processing throughput.
- 2. Compressive strength** Compressive strength testing was performed in order to determine the curing strength of the cemented waste forms. Compressive strengths were recorded at 7-, 14- and 28-day intervals. The acceptance criterion was that there should not be a decrease in the compressive strength from previous interval.³ The criterion was derived from previous cementation experiments conducted by G. Veaze³. The compressive strength criterion served as a reasonable indication of a satisfactory cement product.
- 3. Penetration resistance** Penetration resistance is a technique recommended by the American Society for Testing and Materials (ASTM) for determining the initial set of the cement. A penetration resistance of 500 psi is the standard established by ASTM.⁴ The initial set time was established at 24 hours to maintain a reasonable processing throughput.
- 4. Mixability** Mixability is important to ensure that the cement/water/residue/additive paste is mixed to a homogeneous mixture to meet the STL criteria. The viscosity of the mixture must not be above the maximum viscosity at which the mixing equipment can provide thorough mixing. The maximum mixing was attained when the viscosity was such that the center to edge mixing could no longer be maintained.
- 5. Toxicity Characteristic Leaching Procedure (TCLP) for RCRA metals** The TCLP is used to demonstrate compliance to EPA RCRA standards.⁵ RFETS requested that the final waste form pass the TCLP to reduce storage costs. Since additional costs are associated with the storage of mixed waste, it is cost-effective if the waste form pass the RCRA TCLP and be declared a non-hazardous waste form.

NON-ACTINIDE EXPERIMENTATION

The non-actinide experiments were conducted to evaluate various combinations of NaF, Ca(OH)₂ and CaF₂. All experiments were conducted using a 2.0 cement to 1.0 water ratio. The experiments were divided into the following four categories:

- 1) CaF₂ used to simulate PuF₄ as an inert material
- 2) NaF at solubility limit with various amounts of Ca(OH)₂
- 3) NaF above the solubility limit with no Ca(OH)₂,
- 4) NaF above the solubility limit with various amounts of Ca(OH)₂

Group 1 - Ca₂

The purpose of Group 1 testing was to determine if an insoluble form of fluoride as in PuF₄ would interfere with the physical characteristics of the cement form through physical obstruction. CaF₂ was chosen as a surrogate for PuF₄ since its fluoride is also insoluble. Only one sample, CT1, was prepared in this group using a mixture of cement, water and CaF₂. The upper limit of CaF₂ was added, based on the amount of Pu²³⁹ (assuming PuF₄ is all Pu²³⁹) that could be added to a waste container and not exceed the wattage limit for a drum (two containers per drum). Any amount of CaF₂ below limit would yield better results.

CT1 was found to pass all the performance criteria (see Table 1). The penetration resistance at 7½ hours was, well over the minimum initial-set penetration resistance of 500psi. The compressive strength increased over the 28-day duration. This indicates the PuF₄ as an inert material has no adverse affects on the setting of the cement, and pure PuF₄ can be cemented up to the amount that it would take to reach the wattage limit for shipment to WIPP.

Table 1 Group 1 - CaF₂

Test #	Amount CaF ₂ (g)	Penetrometer (psi)			Compressive strength (psi)			Remarks
		3-4 hr	5-6 hr	7-8 hr	7-day	14-day	28-day	
CT1	CaF ₂ only			5400	4200	Max*	Max*	

* defined as compressive strength above limits of the readout gauge.

Group 2 - Ca(OH)₂ with NaF at Solubility Limit

The purpose of Group 2 testing was to determine the effectiveness of Ca(OH)₂ in precipitating soluble fluoride from NaF to produce a satisfactory set. NaF was added to all samples at its solubility limit and the amount of Ca(OH)₂ was varied. The data in Table 2 shows that for all samples the initial set was achieved within the 7-8 hour time frame. The compressive strength was not affected by the increasing amounts of Ca(OH)₂, and the maximum compressive strength was reached by the 28th day. Sample CT2g, with 2.3X stoichiometric Ca(OH)₂, performed well on penetration resistance and compressive strength, but free water was not reabsorbed within the 24-hour time frame. Sample CT2A, with 3.4X stoichiometric Ca(OH)₂, had free water at the 5-6 hour time that was poured off. Although the liquid was poured off before the 24-hour time limit, it is assumed, that the free water would not be reabsorbed in the 24-hour time limit. The data in Table 2 shows a satisfactory stabilization is obtained with NaF at the solubility limit with the addition of Ca(OH)₂ from 1.0X to 1.7X stoichiometric. The data also shows that excess Ca(OH)₂ results in free liquid.

Table 2 Group 2 - Ca(OH)₂ with NaF at Solubility Limit

Test #	Stoichiometric amount Ca(OH) ₂	Penetrometer (psi)			Compressive strength (psi)			Remarks
		3-4 hr	5-6 hr	7-8 hr	7-day	14-day	28-day	
CT2c	1.0X		1760	Max*	4250	5825	Max*	
CT2f	1.7X		340	2810	4225	5450	Max*	
CT2g	2.3X		200	2100	4000	5750	Max*	Free water next day
CT2A	3.4X	24	352	5480	5200	6000	Max*	Poured bleed water off Above mix limit

Group 3 - NaF and No Ca(OH)₂

The third set of tests was performed to determine if satisfactory results could be attained without Ca(OH)₂ added to precipitate soluble fluoride since Portland cement already contains Ca(OH)₂. The results are reported in Table 3. All samples reached the initial set point of 500psi within the 7-8 hour time frame. All samples had a compressive strength well above the compressive strength performance criterion, however, they were generally lower than the samples with Ca(OH)₂ reported in Table 2. The compressive strength for samples CT2b, through CT2m increased over the 28-days. The compressive strength for CT2h increased ~26.6% from the 7th day to 14th day but increased only 6.1% from 14th day to 28th day. Sample CT2j, at 4X the NaF solubility limit, did not completely set within 24 hours and the compressive strength decreased from 14th day to 28th day.

It is noted that there is not much difference in the 14-day compressive strength between CT2b in Table 3 and CT2c in Table 2.⁶ This indicates that at NaF saturation, there is already enough Ca(OH)₂ in the Portland cement to precipitate the NaF without additional Ca(OH)₂. When comparing the rest of the (NaF only) samples to CT2b, there is a considerable difference in the compressive strength. This gives an indication that NaF above the solubility limit has an effect on the set of the cement, and Ca(OH)₂ is needed to precipitate the soluble NaF.

A comparison between the data in table 2 and table 3 indicate that the relatively soluble NaF is slowly reacting with the calcium silicate hydrates and reducing compressive strength.⁷ If this is the case, in about six months the reaction would be complete and the compressive strength reduced.⁶ The data here shows that NaF at the solubility limit didn't need Ca(OH)₂ above the Ca(OH)₂ in the cement, and that NaF can be cemented up to 3.5X the solubility limit without Ca(OH)₂. Even though the sample hardens without Ca(OH)₂, there is a reduction in compressive strength when the NaF is above the solubility limit. These adverse effect on compressive strength strongly indicates Ca(OH)₂ is necessary for long-term durability of the waste form.

Table 3 Group 3 with NaF only (no Ca(OH)₂)

Test #	Solubility limit NaF	Penetrometer (psi)			Compressive strength (psi)			Remarks
		3-4 hr	5-6 hr	7-8 hr	7-day	14-day	28-day	
CT2b	1.0 X			1133 (avg.)	4875	5500	Max*	
CT2d	2.0 X		5240	7720	2400	3400	4300	
CT2h	3.0 X	2080	5240	Max*	2250	2850	3025	
CT2m	3.5 X	800	2920	4480	2500	3000	3550	
CT2j	4 X	360	820	1200	2150	2750	2400	Did not set over night

Group 4 - NaF above solubility limit with varying amounts of Ca(OH)₂

The unfavorable effect seen in the no-Ca(OH)₂ Group 3 at higher NaF concentrations showed that some amount of Ca(OH)₂ is needed to precipitate above-solubility NaF in order to assure a long-term durable product. The starting point for testing in this group was established in CT2e where 2X the solubility limit of NaF was added with a stoichiometric amount of Ca(OH)₂. The sample exceeded the 500psi initial set point in 5-6 hours, and had a continuous increase in compressive strength from the 7th day to the 28th day. This sample, however, was above the mixability limit, and therefore, could not be considered a satisfactory mixture.

Table 4 NaF above solubility limit with various amounts of Ca(OH)₂

Test #	Solubility limit NaF	Stoichiometric amount Ca(OH) ₂	Penetrometer (psi)			Compressive strength (psi)			Remarks
			3-4 hr	5-6 hr	7-8 hr	7-day	14-day	28-day	
CT2e	2X	1.0X stoic		Max*		3000	3175	4600	Above mixing limit
CT2i	2X	.75X stoic	6240	Max*		3800	3600	3925	
CT2k	3X	.75X stoic	Max			3250	3250	4250	High temp. during set
CT2l	3X	.50X stoic	Max			3100	3875	5650	High temp. during set
CT2n	3X	.25X stoic	7040	Max*		2900	3650	3875	
CT2o	3.5X	.25X stoic	7040	Max*		2425	2825	3675	
CT2p	4X	.25X stoic	5280	6800	6550	2250	2650	3550	
CT2q	5X	.25X stoic	1260	4160	5040	1825	2450	2925	

For sample CT2i, the Ca(OH)₂ concentration was reduced to 0.75X stoichiometric, with the solubility limit maintained at 2X the NaF solubility. The compressive strength decreased from the 7th day to the 14th day and therefore failed the criterion for the compressive strength. Sample CT2k, at 3X the solubility limit of NaF with .75 stoichiometric Ca(OH)₂, reached the 500psi initial set point in about 1-2 hours. During the initial set time, there was a large increase in the heat being generated to the point at which the can could no longer be handled without insulated gloves. This appears to indicate a point had been reached at which the Ca(OH)₂ was acting as a set accelerator.⁶ Due to high temperature safety concern, this sample was not considered satisfactory. Sample CT2l was prepared with 3X the solubility limit of NaF and .50 stoichiometric Ca(OH)₂. Elevated heat was also generated as in CT2l, prompting this sample to be considered unsatisfactory.

Due to the accelerated sets at .75X and .50X stoichiometric Ca(OH)₂, the Ca(OH)₂ was reduced to 0.25X stoichiometric on samples CT2n, o, p and q, with 3X, 3.5X, 4X and 5X the solubility limit of NaF, respectively. The compressive strength for the four samples with .25X stoichiometric amounts Ca(OH)₂ are plotted below in Figure 1. The initial set point was reached within the 3-4 hour time frame for all samples. This set of tests showed that all samples, continued to increase in a progressive matter for 28 days. All of these samples had an increased in compressive strength greater than 30% from the 7th day to the 28th day. None of the samples with the .25X stoichiometric amounts of Ca(OH)₂ exceeded the mixability limit or liberated excessive heat. The data shows that if the amount of Ca(OH)₂ was maintained at .25X stoichiometric, an acceptable product could be produced when the NaF concentration is 2-5 times its solubility limits.

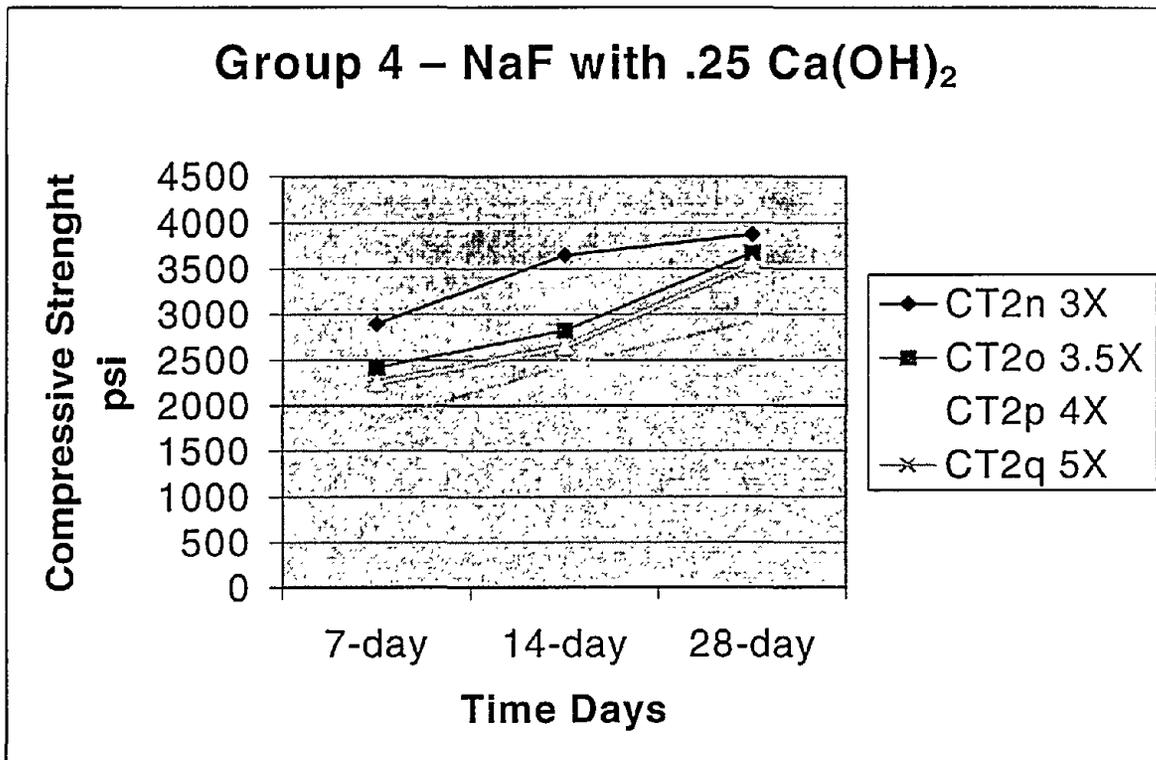


Figure 1 Group 4 – NaF with .25 Ca(OH)₂

TCLP Results for RCRA Metals

Four samples were prepared for the TCLP. A sample was made from each of Groups 1-4 and spiked with Cr₂O₃ to simulate the elevated Cr typically found in the RFETS PuF₄. The samples were chosen based on the performance within the group. All samples were mixed with a 2.0 cement to 1.0 water ratio.

The performances for the TCLP are shown in Table 5. The leach resistance value demonstrates the ability of the cement to retain RCRA metals and can be defined as the percentage of the total metal concentration that remains in the waste form after the TCLP.³ Leach resistance is calculated assuming a 50g sample and 1L leach solution.

The leach resistance shows that barium and chromium are the two major RCRA metals in the cemented waste form and that the waste form is able to retain >95% of the metals. All of the samples passed the TCLP.

Table 5
TCLP Leach Resistance

Sample #2114735 TCLP 1 (CaF ₂ only)				
Constituent	Totals (mg/Kg)	TCLP (mg/L)	Leach Resistance (%)	Remarks
Barium	193	0.4	95.85	
Cadmium	3	ND		
Chromium	118	0.05	99.15	
Lead	10	ND		
Mercury	0.06	ND		

Sample #2144737 TCLP 2 (NaF at solubility limit w/ 1.7X stoichiometric Ca(OH) ₂)				
Constituent	Totals (mg/Kg)	TCLP (mg/L)	Leach Resistance (%)	Remarks
Barium	185	0.3	96.76	
Cadmium	2.82	ND		
Chromium	55.1	0.06	97.82	
Lead	10	ND		
Mercury	ND	ND		

Sample #2145305 TCLP 3 (3.5X NaF solubility limit)				
Constituent	Totals (mg/Kg)	TCLP (mg/L)	Leach Resistance (%)	Remarks
Barium	175	0.3	96.57	
Cadmium	ND	ND		
Chromium	197	0.09	99.09	
Lead	11.8	ND		
Mercury	ND	ND		

Sample #2144736 TCLP 4 (3.5X NaF solubility limit w/ 0.25 stoichiometric Ca(OH) ₂)				
Constituent	Totals (mg/Kg)	TCLP (mg/L)	Leach Resistance (%)	Remarks
Barium	167	0.1	98.80	* result = ND, value = detection limit
Cadmium	3.44	ND		
Chromium	147	0.02	99.73	* result = ND, value = detection limit
Lead	8.3	ND		
Mercury	ND	ND		

ACTINIDE-BASED (HOT) EXPERIMENTATION

The hot experiments were conducted to confirm the recommended formulations of the non-actinide experimentation using an actinide-containing residue. The hot samples were prepared using material from LANL. The HT2 and HT3 samples were spiked with NaF at the 1.0X and 5X the NaF solubility limit to demonstrate the cement formulations for the range of materials at RFETS. All samples were mixed using a 2 to 1 cement-to-liquid ratio. The data is shown in

Table 6 below. The hot tests confirm the data from the non-actinide experiments, showing that the PuF₄ can be stabilized in cement and that the soluble F is effectively precipitated with .25X stoichiometric Ca(OH)₂ added to the mixture.

Table 6 Actinide-based (Hot) Experimentation

Test #	Amount PuF ₄ (G)	Solubility Limit NaF	Stoichiometric Amount Ca(OH) ₂	Compressive Strength (psi)		
				7-day	14-day	28-day
HT1	8.56	None	None	4325	5150	Max*
HT2	8.56	1X	0.25X	4175	3950 ⁺	5275
HT3	7.18	5X	0.25X	1775	2100	2750

* Decrease in the psi is due to improper technique when operating the hydraulic jack.

CONCLUSIONS/RECOMMENDATIONS

The above work has identified that the PuF₄ at the RFETS can be immobilized in Portland cement to meet the performance requirements indicated in this report. The cement-to-liquid ratio on all the tested samples was 2 to 1, and for full-scale production should be maintained. Group 1, Group 2, and Group 3 all showed indications that failed the waste form performance criteria. Group 4 indicates that the optimum ratio of Ca(OH)₂ to NaF is a Ca(OH)₂ addition of .25X the stoichiometric amount of NaF, and an acceptable product could be produced when the NaF concentration is between 1X and 5X the solubility limits. This would be the recommended ratio of Ca(OH)₂ to NaF.

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