



TREATMENT OF LIQUID WASTE CONTAINING ALPHA NUCLIDES BY ADSORPTION

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Abstract

In this paper, experimental investigations on the removal of actinides from a decontaminating waste stream by using adsorption technique following the cementation of a resultant absorbent sludge are described. One kind of apatites was selected as an actinide absorbent from a number of indigenous materials by batch equilibrium tests. The influence of contact time, temperature, particle size and pH variables on the adsorption of actinides is given. The removal of total alpha activity is higher than 97% by absorbent precipitation process when the absorbent addition percentage of the liquid waste is more than 3.25 wt%, making alpha-activity level of the primary waste stream below 3.7×10^3 Bq/L, which can meet the acceptance requirements of the Low Level Radwaste Treatment Plant. The studies on the cementation of the absorbent sludge included the selection of cements used for solidification, formulation and characterization of the selected cemented waste forms. The results obtained have shown that both 525 type Portland cement and 325 type Portland pozzolana cement were compatible with the absorbent sludge. The selected cemented waste forms meet the requirements of the Chinese National Standard (GB 14569.1-93): Characteristic Requirements for Solidified Waste of Low and Intermediate Level Radioactive Waste—Cement Solidified Waste.

1. INTRODUCTION

In the China Institute of Atomic Energy (CIAE), about 70 m³ of liquid waste containing ^{239,240}Pu, ²⁴¹Am, etc. generated from cleaning a glove-box and other laboratory equipment have been stored in an A-01/2 stainless steel tank for about 20 years. The waste is not suitable for treatment in the Low Level Radwaste Treatment Plant (LLRTP) because its alpha-activity level exceeds 3.7×10^3 Bq/L, the acceptance limit of the LLRTP. This waste should be safely treated in coming years according to the schedule of the CIAE Waste Management Programme. A conceptual treatment process for this specific liquid waste was proposed, which includes: (1) The liquid waste will be pretreated by adsorption, making its alpha-activity levels below 3.7×10^3 Bq/L prior to transfer the waste to the LLRTP; (2) The absorbent sludge will be immobilized with cement. The purpose of the present study is to demonstrate the feasibility of the conceptual treatment process on a laboratory scale.

2. REMOVAL OF ACTINIDES FROM THE DECONTAMINATING WASTE

There are many approaches to the removal of actinides from radioactive liquid wastes. Treatment of alpha bearing wastes has been reviewed in IAEA Technical Reports Series No.287 in 1988 [1]. A study of treatment of plutonium- and americium-bearing waste, performed in our laboratory by Mr. Xianhua Fan et al. [2], have shown that P301 material, a kind of apatites, was suitable for treating these wastes because of their high affinity for Pu(Am). *K_d* value of Pu(Am) is in the range 10^3 - 10^4 mL/g at pH1-3. Owing to this reason the P301 material is considered as a prospective absorbent.

P301 absorbent was obtained from the Guizhou Kaiyang Phosphorus Mineral Prospecting Bureau. Seven kinds of phosphorus ore from different mining areas were collected for the present study. Two other kinds of phosphorus ore from Sichuan and Jiangsu province were also collected for comparison.

2.1. EXPERIMENTAL ARRANGEMENTS

2.1.1. Preparation of absorbing materials

At first, nine samples of phosphorus ore collected for the test were given their code number, and then crushed and sieved. The particles in the range of 30-60, 60-120 and 120-200 mesh were selected for the test.

2.1.2. Sampling and analysis of the liquid decontaminating waste

Sampling of the liquid decontaminating waste stored in a stainless steel tank was carried out by means of a suction pump system. The chemical composition of the liquid waste was analyzed using a weight method, titrimetry, chromatography of ions and ICP-AES method. The concentration of radionuclides was determined by HPGe gamma-spectroscopy for gamma-emitters, by radiochemical analysis for ^{90}Sr - ^{90}Y , and by alpha-spectroscopy for alpha-emitters.

2.1.3. Determination of an adsorption ratio

The amount of 0.25 g of each granulated material (generally 60-120 mesh) was added to 5.0 mL of the liquid waste in a polyethylene vials (15 mL) or centrifuge tubes (10 mL). These samples were mixed either by electromagnetic stirring for 5 minutes, or by shaking. The contact time was 24 hours, phases separation was usually performed by high speed centrifugation at 18000 rpm for 30 minutes. The supernatant liquid was analyzed for gross alpha-activity, appropriate aliquots of each test solution were affixed to stainless steel planchets and measured by a low background alpha-measurement apparatus (Model FJ-332, made in China).

The adsorption ratio R_d (mL/g) was calculated from the following equation:

$$R_d = \frac{C_o - C_t}{C_t} \cdot \frac{V}{W} \quad (1)$$

where

C_o is the initial alpha-activity per mL of the liquid waste (cpm),
 C_t is the alpha-activity per mL in the supernatant liquid after the contact time t (cpm),
 V is the volume of liquid phase (mL), and
 W is the weight of the absorbent used (g).

2.1.4. Experimental procedure for absorbent precipitation

Each 100 mL portion of the liquid waste was taken out into 150 mL Erlenmeyer flasks. pH value of samples was adjusted to 2.0 by the addition of 4 mol/L of NaOH solution. The samples were then heated to a desirable temperature on a constant temperature magnetic stirrer. Various amounts of absorbent were added into flasks. Phase mixing was carried out by magnetic stirring for 15 minutes. The flasks were made to stand overnight at a given temperature. The supernatant was then filtered through the 0.2 μm micropore filter film. The filter liquor was measured for gross alpha activity and pH. Percentage of the alpha activity removal was calculated.

2.2. RESULTS AND DISCUSSION

2.2.1. Characteristics of the liquid decontaminating waste

The chemical composition and radionuclide concentration of the liquid waste are listed in Table I and Table II, respectively. It can be seen that the composition of the liquid waste is rather complex, consisting of many non-radioactive components such as sodium nitrate and significant amounts of polyvalent metal ions, including hydrolyzable ions such as iron, aluminum and manganese. Fission products are primarily ^{90}Sr , ^{90}Y and ^{137}Cs , actinides are ^{241}Am and $^{239,240}\text{Pu}$.

TABLE I. CHEMICAL COMPOSITION OF THE LIQUID WASTE

Constituent	Content (mg/L)	Constituent	Content (mg/L)
K	<15	F ⁻	6.3
Na	907	Cl ⁻	58
Al	88	PO ₄ ³⁻	<15
Ca	1000	NO ₃ ⁻	15600
Ce	<0.03	SO ₄ ²⁻	240
Cr	2.5	C ₂ O ₄ ²⁻	<50
Fe	580		
Mg	190	Acidity	0.119 (mol/L)
Mn	28	Specific density	1.03 (g/mL)
Ni	0.65	Total residue (dried at 180°C for 2 hours)	6700
Sr	1.0		
Ti	0.58		

TABLE II. RADIONUCLIDE CONCENTRATION OF THE LIQUID WASTE

Radionuclides	Concentration (Bq/L)	Analytical method
^{137}Cs	6.3×10^5	
^{155}Eu	8.9×10^3	
^{154}Eu	8.9×10^3	HPGe-Spectroscopy
^{60}Co	3.0×10^4	
^{90}Sr - ^{90}Y	2.1×10^6	Radiochemical Analysis
^{241}Am	4.70×10^4	HPGe-Spectroscopy
$^{239+240}\text{Pu}$	4.33×10^4	α -Spectroscopy
^{241}Pu	1.30×10^4	

2.2.2. Selection of absorbent materials

The adsorption ratios of actinides for the liquid waste and nine kinds of phosphorus ores are shown in Table III. It can be seen that not all of phosphorus ores have a high adsorption capacity for actinides. Both colophane from Jiangsu and svanbergite from Sichuan are not comparable with apatite from kaiyang of Guizhou with regard to actinide adsorption. Of apatites only P301 and absorbent D sorb well when pH value of the liquid waste is adjusted to 2.0, adsorption ratios are 676 and 808, respectively. Absorbent D was used in the subsequent experiments. Its chemical composition is given in Table IV.

TABLE IV. CHEMICAL COMPOSITION OF THE ABSORBENT D

Constituent	Content (wt%)	Constituent	Content (wt%)
SiO ₂	3.54	P ₂ O ₅	31.48
Al ₂ O ₃	1.16	CO ₂	1.74
TFe ₂ O ₃	2.32	F	2.05
CaO	50.98	Loss on ignition	3.51
MgO	0.30		

TABLE III. RESULTS OF THE DETERMINATION OF AN ADSORPTION RATIO

Material	Origin	Code name	Initial pH	Final pH	Rd (mL/g)
Apatite	Guizhou	P301	1.09	2.44	41
			2.00	5.61	676
		A	1.09	2.59	58
			2.00	5.05	90
		B	1.09	1.89	66
			2.00	3.58	109
		C	1.09	1.92	66
			2.00	3.53	197
		D	1.09	1.89	57
			2.00	3.49	808
		E	1.09	1.84	70
			2.00	3.38	280
F	1.09	1.92	72		
	2.00	3.82	159		
Collophane	Jiangsu	G	1.09	---	---
			2.00	4.84	62
Svanbergite	Sichuan	H	1.09	1.28	6
			2.00	2.72	130

2.2.3. Influence of several variables on the adsorption ratio

The influence of temperature on the adsorption ratios is illustrated in Table V. These data show that Rd increases when the temperature of the liquid is increasing. When temperature reaches 38°C, Rd value of the order of 10³ could be obtained. In the subsequent experiments the temperature was selected as 38°C.

TABLE V. INFLUENCE OF TEMPERATURE ON THE ADSORPTION RATIO (particle size 60-120 mesh; initial pH2.0)

No.	Temperature (°C)	Rd (mL/g)
1	17	1.6×10 ²
2	28	8.1×10 ²
3	38	1.1×10 ³

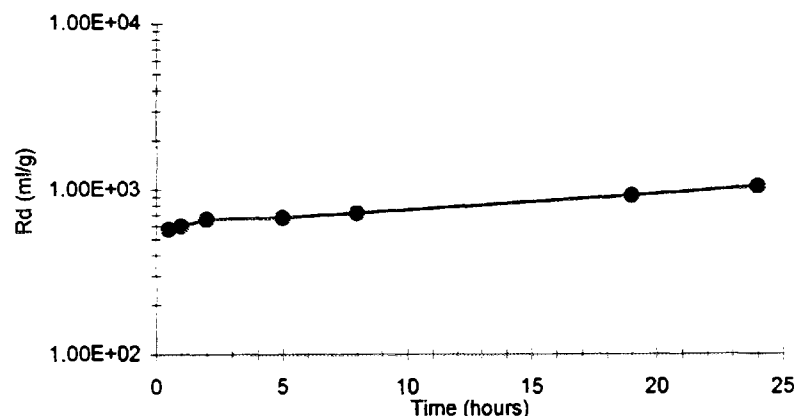


Fig.1 Rd of actinides as a function of contact time

Figure 1 illustrates Rd of actinides as a function of the contact time. It shows that Rd rises steeply initially and then gradually. However, equilibrium could not be reached before 24 hours. It indicates that sorption kinetics of the apatite absorbent behaves not very well. In the subsequent experiments the contact time of 24 hours was used.

TABLE VI. INFLUENCE OF A PARTICLE SIZE ON THE ADSORPTION RATIO (initial pH2.0)

No.	Range of particle size (mesh)	Rd (mL/g)
1	30 — 60	7.2×10^2
2	60 — 120	1.1×10^3
3	120 — 200	3.8×10^3

Table VI summarizes the results of the influence of a particle size on the adsorption ratio. It can be seen that Rd increases when a particle size is decreasing. This indicates that adsorption processes occur mainly on the surface of the absorbent. The larger specific surface is, the higher adsorption ratio is.

An influence of pH on the adsorption ratio can be studied as follows. Take out each 100 mL of the liquid waste into 150 mL Erlenmeyer flask, raise pH of the liquid to desirable pH by addition of 4 mol/L NaOH solution, stand the flask over night, and then filter the liquid through 0.2 μm micropore filter film. The filtrate was used for these experiments.

The results of the influence of pH on the adsorption ratio are shown in Table VII. It can be seen that Rd value increases with the increasing pH value. Two kinds of a mechanism may exist: (1) competitive adsorption from H^+ decreases while pH value increasing; (2) absorbent dissolves partially resulting in a rise in pH due to H^+ consumption, hydrolyzable metal ions form precipitates which carry actinides.

TABLE VII. INFLUENCE OF pH on Rd VALUES

No.	Initial pH	Final pH	Rd (mL/g)
1	1.09	1.94	8.1×10^2
2	1.52	2.70	1.0×10^3
3	2.00	3.44	1.1×10^3
4	2.50	4.02	2.4×10^3

2.2.4. Removal of actinides by absorbent precipitation

The results of the actinide removal by absorbent precipitation are shown in Table VIII. It is clear that the removal of gross alpha activity increases with increasing of the amount of the absorbent.

TABLE VIII. RESULTS OF ABSORBENT PRECIPITATION EXPERIMENTS

No.	Liquid waste (mL)	Addition of absorbent (g)	Initial pH	Final pH	Removal of gross alpha-activity (%)
1	100	1.50	2.0	3.62	95.8
2	100	3.25	2.0	4.01	97.6
3	100	5.00	2.0	4.24	98.7

When the absorbent addition percentage of the liquid waste was higher than 3.25wt%, the removal of gross alpha-activity was above 97%. In this case, the gross alpha-activity of the liquid waste was below 3.7×10^3 Bq/L that meets the acceptance requirements of the LLRTP.

3. CEMENTATION OF THE ALPHA BEARING ABSORBENT SLUDGE

The alpha bearing absorbent sludge produced from the treatment process needs to be immobilized to meet the requirements for interim storage, transport and shallow land disposal according to the Waste Management Programme. Inorganic cements are considered attractive matrices for waste solidification as they satisfy a number of process and waste form requirements [3]. Cementation is considered to be suitable for this purpose because cements are inexpensive, tolerant to wet materials and durable in the natural environment [4]. Moreover we had an experience in immobilization of the intermediate level wastes from reprocessing plants by cementation[5]. Therefore, we have decided to adopt this technique.

3.1. EXPERIMENTAL ARRANGEMENTS

3.1.1. Preparation of a simulated alpha bearing absorbent sludge

A simulated decontaminating feed prepared for this study was composed of the main chemical constituents listed in Table I. Certain amounts of chemical reagents were dissolved in distilled water and poured into a 20 L polyethylene container, subsequently adjusting pH of feed with HNO_3 up to 1.07 that is the same as the pH of the actual decontaminating waste. This feed was used for the preparation of the absorbent sludge.

The absorbent sludge was prepared precipitation. To 10 L simulated decontaminating feed preadjusted to pH2.0 with 4 mol/L of NaOH solution was added 500 g of apatite absorbent-D (particle size 60-120 mesh). Phase mixture was carried out by electric power stirring for 15 minutes, the mixture was allowed to stand overnight and then the supernatant was decanted. The residue as dilute simulated alpha bearing absorbent sludge was conserved for further tests.

The diluted simulated alpha-bearing absorbent sludge needs to be dewatered in order to improve the loading of a solidified waste form. Two dewatering technologies including vacuum filtration and centrifugation were adopted on a laboratory scale. Vacuum filtration was performed by transferring absorbent sludge to a 150 mm diameter Buchner funnel; centrifugation was carried out by using a centrifuge with 4000 rpm for 30 min.

The water content of the absorbent sludge was determined by a weight method. The absorbent sludge was fully mixed by manual stirring and sampled into weighed bottles. Samples were dried in an oven at 105°C and weighed up to a constant weight. The water content of the absorbent sludge sample was calculated, and an average value of the water content was reported.

3.1.2. Preparation of a specimen of the cemented absorbent sludge

A general procedure for the solidification of the absorbent sludge with cement can be as follows:

Weigh a calculated amount of the fully mixed absorbent sludge and put into a plastic beaker (if necessary, add a calculated amount of supernatant), add some amount of weighed cement, mix manually for 5 minutes, fill the mixture into cylindrical plastic molds (diameter and height are equal to 40 mm) to make an individual form. The molds should be mechanically vibrated for 2 minutes before cure. Two replicated specimens for each condition were prepared.

After aging in a curing box with the relative humidity above 95% at 25°C for 1 day, the specimens were demoulded, and cured in the same curing box for an extended cure period of 7 days. Testing of compressive strength was then conducted on the specimens.

3.1.3. Characterization of the cemented waste forms

Various characteristics of the cemented waste forms were determined according to the the Chinese Standard [6].

Compressive strength

Mechanical stability of waste forms is an important parameter for safe disposal of waste. The compressive strength of the cemented absorbent sludge waste forms was tested using a compression tester (home made) with a loading rate of 4900 N/S in order to examine the effects of water/cement and solid/cement ratios, pH, range of a size of absorbent, immersion, radiation damage etc. on mechanical stability.

Impact resistance

The specimens prepared as described in Section 3.1.2 were used for an impact test. From a height of 9 m, specimens were made to fall freely upon the concrete floor to examine whether they would break into pieces.

Leach resistance

Leach testing was performed in accordance with the Chinese Standard GB 7023-86 [7].

Immersion resistance

After specimens were immersed in tap water for a period of 90 days, compressive strength was measured.

Freeze-thaw resistance

Freeze-thaw cycle tests were carried out as follows:

The specimens sealed in a plastic bag were immersed into a 15-20°C cold water bath for 4 hours, then taken out and placed in a refrigerator at a temperature of -20°C for a period of over 2 hours. After that the specimens were removed from the refrigerator and placed into a plastic bag, sealed, and immediately placed into a 15-20°C cold water bath to thaw out for above 4 hours. Thus far, the first freeze-thaw cycle was finished. The second freeze-thaw cycle was started in the above manner. After 25 freeze-thaw cycles, compressive strength of specimens was measured.

- *Radiation stability*

The specimens were gamma-irradiated in an annular Co-60 facility at a dose rate of 10 kGy/h. Six specimens sealed in a plastic bag were annularly emplaced in the center of the facility to make each specimen situated nearly in the same irradiation field condition. After the dose of 1000 kGy the compressive strength of specimens was measured.

3.1.4. Long term leach testing of the solidified actual radioactive waste forms

- *Preparation of specimens*

Alpha bearing absorbent sludge produced from absorbent precipitation of the actual liquid waste was mixed with cement manually. The cement-waste mixture was filled into a cylindrical polyethylene container of 40 mm diameter and treated for the elimination of air bubbles by vibrating during 15 minutes. The mixture was cured in a water-vapour saturated atmosphere for 28 days, and then the cement block was withdrawn from the container. The upper and lower surface of the cylindrical block was polished with 200 grit paper and cleaned from dust particles with cotton. All specimens were measured and weighed before leach testing.

- *Leach testing*

The cylindrical polyethylene bottles of 90 mm in diameter were used as leachant containers. The bottles were thoroughly cleaned with deionized water prior to use. The specimens (diameter to height ratio is about equal) were suspended in containers filled with 900 mL of deionized water. After certain intervals (as specified in the standard [7]), the specimens were withdrawn from the containers and immediately transferred to the next leachant container filled with a fresh leachant. The used leachant containers containing all leached material were closed and allowed to stand for analysis.

- *Analysis of the leachant solution*

Both $^{239,240}\text{Pu}$ and ^{241}Am in the leachant solution were determined by using a low background large area gridded ionization chamber [8]. The technological process of preparing 1400 cm² α -spectrometric source and method of determination of α -nuclides in a sample is described in Ref. [9].

After determination of pH and conductivity, the leachant solution was acidified with HNO₃ to about pH1. An aliquot containing about 100 mg of solids in the leachant solution was taken into a beaker and evaporated to dryness, the residue was dissolved in a suitable amount of deionized water. The beaker was placed in a supersonic breaker to grind non-soluble solids in the sample and then the sample was stuck on aluminized polyester film in a vacuum drying oven.

Both the leachant solution sample and the blank solution sample that resulted from leaching of a blank cemented waste form were measured in an ionization chamber. Usually, a measured time was 30 hours and then α -spectrum was plotted. The activities of $^{239,240}\text{Pu}$ and ^{241}Am were calculated from the following equation:

$$C = \frac{N}{60W\eta Pf} \quad (2)$$

where

- C is the specific activity of sample (Bq/g or Bq/L),
- N is the net counting rate (cpm),
- W is the amount of sample (g or L),
- η is the counting efficiency of the ionization chamber (48%),
- P is the branching ratio of nuclide, and
- f is the chemical recovery.

- *Expression of the leach testing results*

The results are expressed for each constituent by plots of leaching rates, R_n^i , and cumulative leaching fractions, P_t^i , as a function of time, t , of leaching:

$$R_n^i = \frac{a_n^i / A_0^i}{(F/V)t_n} \quad (3)$$

where

R_n^i is the leaching rate for the i -th constituent in the n -th leaching period ($\text{cm}\cdot\text{d}^{-1}$),
 a_n^i is the activity for the i -th constituent leaching in the n -th leaching period (Bq),
 A_0^i is the initial activity for the i -th constituent in the specimen of leach test (Bq),

$$P_t^i = \frac{\sum a_n^i / A_0^i}{F/V} \quad (4)$$

where

F is the geometric surface area of the specimen in contact with leachant (cm^2),
 V is the volume of the specimen (cm^3),
 t_n is the duration of the n -th leaching period (d);
 P_t^i is the cumulative leaching fraction of the i -th constituent when the time equal t (cm), and
 t is the cumulative leaching time (d). $t = \sum t_n$.

3.2. RESULTS AND DISCUSSION

3.2.1. Preparation of the simulated alpha bearing absorbent sludge

Simulated decontaminating feed used for the tests was prepared with non-radioactive chemical agents so that experiments can be carried out in a non-radioactive chemical laboratory. The chemical composition of the simulated decontaminating feed was about the same as the actual decontaminating liquid waste (See Table I). The range of pH value of supernatant produced from a series of absorbent precipitation processes using simulated decontaminating feed was 3-4, which was similar to that from the same process using the actual decontaminating liquid waste. This suggested that properties of both the simulated feed and the actual waste liquid were approaching each other. The water content of the dilute absorbent sludge was about 80%, which could be dropped to about 40% by means of vacuum filtration or centrifugation (see Table IX).

TABLE IX. DEWATERING OF SIMULATED ABSORBENT SLUDGE

Dewatering	water content of the absorbent sludge (%)					average
	1	2	3	4	5	
Centrifugation	42.1	38.0	40.2	35.2	36.7	38.4
vacuum filtration	44.2	44.6	44.2			44.3

3.2.2. Selection of cements for the solidification of the absorbent sludge

Cement has been used for many years for solidification of a wide variety of low and intermediate level radioactive wastes. However, immobilization of apatite absorbent sludge with cement has not been reported. Therefore, compatibility of the absorbent sludge with different types of cements needs to be investigated. Seven types of home-made cements, including Portland cement, Portland-pozzolana cement and moderate heat Portland cement were used for tests, and selection criteria were defined as follows:

When water/cement ratio of the solidified waste form was 0.5-0.55, depending on the mixing workability, loading of the absorbent sludge in the solidified waste form was about 30%, which makes the solidified waste form to have an α -activity less than 4 kBq/g suitable for near surface disposal. The compressive strength of the specimens should be greater than 5 MPa after curing for 7 days. The results of the experiments are shown in Table X.

From Table X, it can be seen that 325 type Portland cement, 425 type Portland blast furnace-slag cement and ordinary Portland cement seem to be unsuitable for solidification of the absorbent sludge from the point of view of mechanical stability. The solidified forms possess low compressive strength; whereas 525 type Portland cement and moderate heat Portland cement appear to be compatible with the absorbent sludge. Their solidified forms possess high compressive strength. 325 type Portland pozzolana cemented waste forms have also higher compressive strength and meet the selecting criteria. In the present study, the Qinghai 525 type moderate heat Portland cement was the first choice for further formulation study. Its chemical composition is shown in Table XI.

TABLE X. COMPRESSIVE TESTS OF THE CEMENTED ABSORBENT SLUDGE

Test No.	Type of cement	Water/cement ratio	Loading %	Compressive strength (MPa)
1	Liulihe 425 type Portland blast furnace-slag cement	0.5	29.6	2.4*
2	Zhoukoudian 325 type Portland pozzolana cement	0.55	31.4	5.8
3	Taiyuan 325 type Portland cement	0.5	35.4	1.7
4	Shanxi 425 type ordinary Portland cement	0.5	33.2	2.0
5	Qinghai 425 type ordinary Portland cement	0.5	37.9	1.0
6	Qinghai 525 type moderate heat Portland cement	0.5	33.9	18.3
7	Lasa 525 type Portland cement	0.5	36.5	16.7

* data measured after curing for 15 days.

TABLE XI. CHEMICAL COMPOSITION OF 525 TYPE MODERATE HEAT PORTLAND CEMENT (MHPC) AND 325 TYPE PORTLAND POZZOLANA CEMENT (PPC)

Constituent	Content (wt%)		Constituent	Content (wt%)	
	MHPC	PPC		MHPC	PPC
SiO ₂	20.55	33.33	P ₂ O ₅	0.32	0.08
Al ₂ O ₃	5.17	8.14	TiO ₂	0.26	0.52
CaO	61.86	40.05	MnO	0.07	0.08
MgO	1.50	3.35	TFe ₂ O ₃	5.10	2.59
K ₂ O	0.98	1.38	SO ₃	2.68	1.92
Na ₂ O	0.26	0.53	Loss on ignition	1.92	7.61

3.2.3. Formulation of the cemented waste form

Performance of the cemented waste forms depends on many factors, such as a water/cement ratio, waste loading, grain size of waste, pH of liquid waste, etc. A number of formulations for the solidified waste forms with above variables were investigated by testing the compressive strength of the specimens. The data obtained are given in Table XII.

The results indicated that the compressive strength of the specimens of solidified waste forms increased as the water/cement ratio increased, the loading decreased, and pH value of the liquid waste increased. The effect of the grain size of the absorbent on the compressive strength of a specimen of the solidified form was clearly understood.

TABLE XII. COMPRESSIVE STRENGTH TESTS OF THE CEMENTED WASTE FORMS OF DIFFERENT FORMULATIONS

Test No.	Water/cement ratio	Loading %	Grain size of absorbent, mesh	Initial pH of absorbent sludge	Compressive strength (MPa)
1	0.5	30.0	60-120	4	19.1
2	0.5	33.9	60-120	4	18.3
3	0.5	39.0	60-120	4	13.1
4	0.5	30.0	120-200	4.5	20.7
5	0.5	30.0	30-60	4	24.2
6	0.55	30.0	60-120	4	16.4
7	0.5	30.0	60-120	8	30.0

To sum up, the compressive strength of all the specimens prepared for the formulation tests met the criteria.

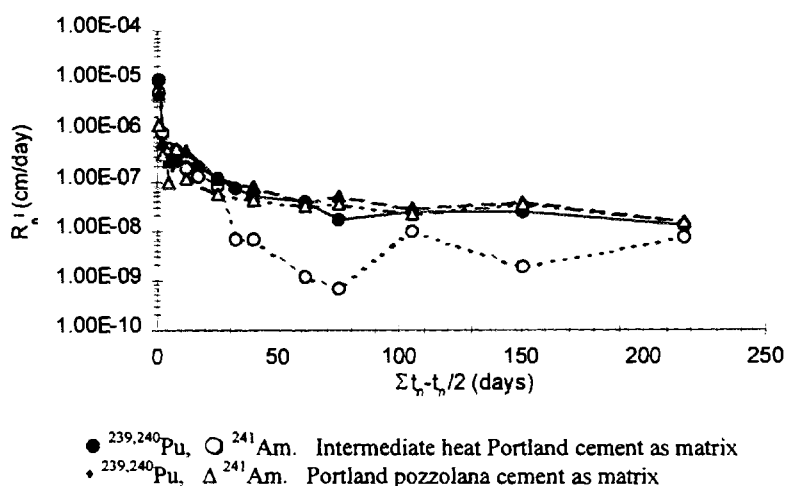


Fig.2 Leaching rate of ^{239,240}Pu and ²⁴¹Am in both cement-silidified waste forms

TABLE XIII.CHARACTERISTICS OF THE SELECTED CEMENTED WASTE FORMS

Stability Criteria	Acceptance criteria for cemented waste forms as specified in the Chinese Standard	Waste form with moderate heat Portland cement matrix	Waste form with Portland pozzolana cement matrix
Compression impact resistance	CS \geq 7MPa No breaking into pieces	CS: 54.3 MPa No breaking into pieces (CS: 34.4 MPa)	28.1 MPa No breaking into pieces (CS: 17.8 MPa)
Leachability	R_{α}^i for each nuclides, ^{239}Pu , ^{241}Am and other actinides (42th day) $\leq 1 \times 10^{-5}$ cm/d.	R_{α}^i of $^{239,241}\text{Pu}$ and ^{241}Am are 5.1×10^{-8} and 7.0×10^{-9} cm/d (42th day), respectively	R_{α}^i of $^{239,241}\text{Pu}$ and ^{241}Am are 8.3×10^{-8} and 4.1×10^{-8} cm/d (42th day), respectively
Immersion resistance	CS: \geq 5.25 MPa with reduction in strength < 15%	CS: 51.7 MPa Reduction in strength 4.8%	CS: 25.9 MPa Reduction in strength 7.8%
Freeze-thaw resistance	CS > 7 MPa with reduction in strength < 15%	CS: 48.0 MPa Reduction in strength 11.6%	CS: 24.8 MPa Reduction in strength 11.7%
Radiation stability	No requirements	CS: 47.9 MPa Reduction in strength 11.8%	CS: 26.0 MPa Reduction in strength 7.5%

Note: CS refers to compression strength.

TABLE XIV. RESULTS OF Pu AND Am LEACHING.

Sample No.	pH	Conductivity (ms/m)	Specific activity (Bq/L)	
			$^{239,240}\text{Pu}$	^{241}Am
1-1	8.43	48	4.3×10^{-1}	2.8×10^{-1}
1-2	8.43	58	7.6×10^{-2}	9.2×10^{-2}
1-3	8.55	52	5.5×10^{-2}	9.0×10^{-2}
1-4	8.33	37	3.5×10^{-2}	5.7×10^{-2}
1-5	8.39	38	3.6×10^{-2}	3.5×10^{-2}
1-6	8.41	38	5.7×10^{-2}	4.3×10^{-2}
1-7	8.42	35	3.8×10^{-2}	2.9×10^{-2}
1-8	8.39	33	2.4×10^{-2}	2.4×10^{-2}
1-9	8.34	28	1.4×10^{-2}	2.0×10^{-2}
1-10	8.35	33	2.9×10^{-2}	1.0×10^{-2}
1-11	8.46	34	2.4×10^{-2}	1.0×10^{-2}
1-12	8.56	28	3.2×10^{-2}	1.4×10^{-2}
1-13	9.69	45	6.8×10^{-2}	5.3×10^{-2}
2-1	8.65	80	2.1×10^{-1}	5.8×10^{-2}
2-2	8.55	55	4.4×10^{-2}	2.9×10^{-2}
2-3	8.56	62	3.9×10^{-2}	1.7×10^{-2}
2-4	8.40	43	4.5×10^{-2}	5.9×10^{-2}
2-5	8.40	42	6.4×10^{-2}	2.0×10^{-2}
2-6	8.43	43	5.3×10^{-2}	2.0×10^{-2}
2-7	8.43	37	4.1×10^{-2}	1.9×10^{-2}
2-8	8.39	37	3.1×10^{-2}	1.5×10^{-2}
2-9	8.30	34	2.0×10^{-2}	1.1×10^{-2}
2-10	8.40	43	2.7×10^{-2}	2.3×10^{-2}
2-11	8.39	43	6.4×10^{-2}	5.0×10^{-2}
2-12	8.36	30	3.6×10^{-2}	3.0×10^{-2}
2-13	8.59	30	9.7×10^{-2}	9.2×10^{-2}
leachant (deionized water)	6.25	0.15		

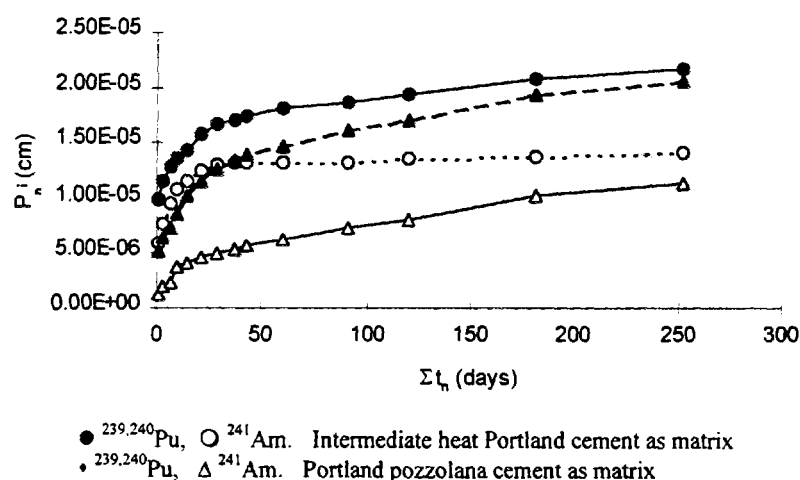


Fig.3 Cumulative leaching fraction of ^{239,240}Pu and ²⁴¹Am in cement solidified waste forms

3.2.4. Characterization of the selected cemented waste forms

The specimens composed of 0.5 (or 0.55 for 325 type Portland pozzolana cement) of the water/cement ratio, 30% loading, 60-120 mesh grain size of absorbent, initial pH8, were used for the characterization. These specimens were prepared by using a simulated absorbent sludge mixed with the moderate heat Portland cement (or Portland pozzolana cement) except that the specimens used for leach tests were prepared by using actual waste sludge produced from the absorbent precipitation process. Several tests that included the determination of compressive strength, impact resistance, immersion resistance, freeze-thaw resistance, radiation stability, have been completed. The results are shown in Table XIII. For comparison with the Chinese Standard [4], the acceptance criteria are listed in the same Table. From Table XIII, it can be seen that the selected cemented waste forms meet the acceptance criteria.

3.2.5. Leach testing

Analytical data obtained for leaching of ^{239,240}Pu and ²⁴¹Am are given in Table XIV. Two kinds of leaching curves for ^{239,240}Pu and ²⁴¹Am, where the leaching rate R is plotted against a time function $\sum t_n - t_n/2$, and the cumulative leaching fraction P is plotted against the total time of leaching $\sum t_n$, are shown in Fig. 2 and Fig. 3, respectively. From the examination of these curves it can be concluded that the leaching of ^{239,240}Pu and ²⁴¹Am from the cemented radioactive waste is low, the leaching rates of them are of the order of magnitude of 10^{-8} cm·d⁻¹ and the cumulative leaching fraction of them are of the order of magnitude of 10^{-5} after 100 days.

4. CONCLUSIONS

The main conclusions which can be drawn from the experiments are the following:

- (1) Experiments of batch equilibrium with actual liquid waste show that the apatite (code name D at the present experiments) from Guizhou Kaiyang Phosphorous Mineral Prospecting Bureau possesses higher adsorption capacity for actinides. The Rd of actinides increases with increasing of temperature, pH value and contact time, and decreasing of the range of particle size. At a temperature of 38°C, initial pH2, contact time 24 hours, and the range of particle size 60-120 mesh, Rd of 1.1×10^3 mL/g can be achieved. Therefore, it can be used as an inorganic absorbent for actinide

- removal from the liquid decontaminating waste stream. The removal of gross alpha-activity was above 97% when the adsorbent addition percentage of liquid waste was more than 3.25 wt%. The gross alpha-activity level of the liquid decontaminating waste stream dropped to below 3.7×10^3 Bq/L which can meet the acceptance requirements of LLRTP.
- (2) Dewatering of the absorbent sludge can be achieved by centrifugation or vacuum filtration. In laboratory tests, the water content of the sludge decreased from 80% to 40%, which is suitable for the formulation of cemented waste forms.
 - (3) From the point of view of mechanical stability, three types of cement, which include 525 type moderate heat Portland cement, 525 type Portland cement and 325 type Portland pozzolana cement are compatible with the absorbent sludge and possible to be used for its immobilization.
 - (4) Formulation tests show that specimens prepared with 525 type moderate heat Portland cement have good mechanical properties when water/cement ratio is 0.50-0.55, loading of absorbent sludge in solidified form 30-39%, grain size of absorbent 60-120 mesh and pH of absorbent sludge 4-8. Compressive strength of these specimens are above 13 MPa that exceeds the minimum criterion (7MPa) in the Chinese Standard.
 - (5) The selected cemented waste forms meet the requirements for solidified waste forms as specified in the Chinese Standard. Therefore, cementation of absorbent sludge with either 525 type moderate heat Portland cement or 325 type Portland pozzolana cement is feasible.
 - (6) Leaching of $^{239,240}\text{Pu}$ and ^{241}Am is low for the cemented radioactive waste forms. As far as its leachability is concerned, both the cemented waste formulations are suitable for the solidification of the alpha-bearing absorbent sludge resulted from absorbent precipitation of the liquid decontaminating waste stream.

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