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ELEVATED TEMPERATURES AND PRESSURES
(FUELTAP CONCRETES) ***

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For presentation at the Symposium on the Scientific Basis for
Nuclear Waste Management, Boston, Mass., November 16-19, 1981

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* Research sponsored by the Office of Waste Operations and Technology, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

CEMENTITIOUS RADIOACTIVE WASTE HOSTS FORMED UNDER ELEVATED TEMPERATURES AND PRESSURES (FUETAP CONCRETES)*

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ABSTRACT

Concretes formed under elevated temperatures and pressures (FUETAP concretes) are effective hosts for trans-uranic (TRU) and high-level defense and commercial wastes.

INTRODUCTION

Concretes formed under elevated temperatures and pressures (FUETAP concretes) are effective hosts for TRU and high-level defense and commercial radioactive wastes [1-8]. These tailored concretes, developed at Oak Ridge National Laboratory (ORNL), are prepared from common Portland cements, fly ash, sand clays, and waste products by accelerated curing under mild autoclave conditions (100°C, 1 atm gage). These solids are subsequently dewatered at 250°C for 24 h, producing strong (40-100 MPa compressive strength), leach resistant ($Pu\ 10^{-11}$ g/cm²·d), and radiolytically stable monolithic waste forms.

Figure 1 illustrates one of the proposed flow sheets for a FUETAP concrete developed for the Savannah River Plant (SRP) high-level defense waste [9].

Specimens are cast in sizes from 1 cm³ to 75 L for the evaluations of leaching, tensile and compressive strengths, thermal conductivity, porosity, permeability, density, and dewatering kinetics. Only pourable mixes requiring light vibration to fill the molds uniformly and to remove entrained air are selected for study.

This paper discusses briefly the processing, MCC-1 Static leach tests, α -radiolysis, phase characterization, and thermal expansion of FUETAP concretes and will summarize their status as a host for radioactive wastes.

PROCESSING: MIXING AND SET TIME

An advantage of FUETAP as a radioactive waste disposal alternative is its ease of processing. For example, one FUETAP flow sheet for the SRP defense high-level waste requires 2 h to add 2 t of dry solids to a full charge of water and set-retarder in a ribbon mixer.

To assess the consequences of possible accidents affecting this step, such as a broken blender shaft or a frozen transfer boom, investigations were made of the minimum solids required for setting the phase separation, and the set time (Table I).

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These results show that this process step needs no auxiliary agitation and no back-up transfer system or extraordinary operational procedures to deal with these abnormal events in a hot cell operation.

STATIC LEACH TEST

Our results show that the Materials Characterization Center (MCC)-1 static leach tests [10] give negatively biased results for cementitious waste forms and give no insight into the long-term leaching behavior [11,12] because an initial wash-out dominates the 28 d results.

Leach testing of two FUEATAP formulation series, MIX:MCC1 and MIX:MCC6, evaluated:

1. the effect of substituting slag and Fondu cements for Portland type I cement (Table II);
2. the effect of adding sodium bentonite and Indian red pottery clay (Table III);
3. the effects of MCC standard brines and of temperature on cesium, strontium, uranium, cerium, and neodymium from a FUEATAP MIX:MCC6, with a simulated SRP waste (Table IV).

Data in Table II show that the FUEATAP process produces acceptable products with three readily available commercial cements.

Table III demonstrates that clay additives reduce the initial cesium wash-out by about a factor of two.

Figure 2 illustrates the initial leaching data for strontium with MCC-1 concrete at 90°C. In such cases, the short-term leach rate data, reported as specified in the MCC-1 testing procedure manual, is biased against concretes.

Using a revised, simulated SRP reference waste and the same FUEATAP formula, the FUEATAP MIX:MCC6 series was leached to determine the effects of the three standard MCC-1 leachants at 40°C and 90°C (Table IV).

The MIX:MCC6 data in Table IV shows that only strontium leaching in silica water has a statistically significant difference between leach rates at 40°C and 90°C. The cesium leached from MIX:MCC6 was 4-5 times higher than from MIX:MCC1 (Table III). The revised SRP simulated waste used in MIX:MCC6 had a higher water/cement (W/C) ratio than the previous reference waste and, therefore, had a 50% greater porosity (~40%).

The MCC-1 numbers for all transuranics in Table IV do not reflect leach rates but initial wash-out divided by 28 d. The concentrations of uranium, cerium, and neodymium in the leachates were constant throughout the 3-, 7-, 14-, and 28-d MCC-1 leach tests.

RADIOLYSIS

Long-term α -radiolysis experiments (>500 d) at 25-30°C used 10-cm³ steel capsules containing FUEATAP concrete specimens (8.2 g) which were spiked with 4.5 mg (in tests 1, 2, and 3), 0.5 mg (in tests 4 and 5), and 1.5 mg (in test 6) of ²⁴⁴Cm. Each test day is the equivalent to 300, 30, and 100 years, respectively, in the life of a real waste drum (based on an estimated α -dose of 6 rad/h for Savannah River Plant waste).

Table V summarizes the data for α -radiolysis gas generation. These conservative total gas values were averages of the steeper initial linear pressure increases, and are 20-30% lower than Bibler's values [13].

These data also show that the first 1000 equivalent-years of accelerated dose to a FUEATAP concrete results in only a 1-bar-gage drum pressure in the samples that are not dewatered and negligible pressures in the dewatered samples. Nitrogen was the predominant species (96-98 vol %) in Tests 2 and 3 with the FUEATAP concrete that was not dewatered. This substantiates the conclusions of Katz [14], who showed that FUEATAP concretes are very active hydrogen-oxygen recombination catalysts, suggesting that these radiolysis products could not accumulate there. Shorter tests (200 h) by Kazanjian and Killion [15] produced nitrogen as a major radiolysis product from nitrate-containing, dewatered, Rocky Flats 774 sludge.

PHASE CHARACTERIZATION

A scanning electron microscope (SEM), using backscatter electrons with an energy-dispersive x-ray analyzer (EDX), revealed the presence of calcium, silicon, and aluminium evenly distributed over the sample surface, along with large sand grains (SiO_2) and small, scattered iron oxide phases.

Numerous phases were observed under an optical microscope using polarized light. The largest phase (500-1000 μm) was the included sand, and small red phases (50-300 μm), probably Fe_2O_3 , were scattered throughout the field of view. Microprobe analysis confirmed the presence of a few metallic inclusions (50-150 μm).

Using the SEM with the EDX counting system, nine or ten phases were found. Figure 3 shows a SEM photograph of one sample; its EDX analysis is found in Table VI. It has been found that cesium is located either in the zeolite or in a cement phase high in silicon and aluminium; strontium has been found only with manganese.

THERMAL EXPANSION

The thermal expansion coefficient for FUEATAP concrete is ~ 0.5 that of hard rolled steel and of most high-level waste glasses.

To determine this thermal expansion coefficient, the FUEATAP concrete sample was heated at a rate of $4^\circ\text{C}/\text{min}$ to 800°C , held constant for ~ 5 min, then returned to room temperature at a rate of $4^\circ\text{C}/\text{min}$.

Figure 4 shows a typical expansion curve for the MCC-1 FUEATAP formula. The length increased almost linearly to $\sim 0.2\%$ at 400°C . The length increased more rapidly until 580°C , due to the transition from low to high quartz, remained constant between 600°C and 700°C , and then began shrinking rapidly. At 800°C , the sample's expansion was approximately -0.7% .

Using the expansion curve in Fig. 4, an average thermal expansion coefficient of $4.7 \times 10^{-6}/^\circ\text{C}$ can be derived between 20°C and 400°C .

SUMMARY AND CONCLUSIONS

As a radioactive waste form, the FUEATAP concretes show dynamic leach rates of transuranics below detectable limits ($0.01 \text{ g}_i/\text{m}^2\cdot\text{d}$). Cesium and strontium leachabilities compare with those for glass, but the initial wash-out is higher.

Radiolytic decomposition of these low-water ($<2\%$) FUEATAP concretes is negligible over accelerated time tests to $>10^5 \text{ y}$. They are thermally stable to 900°C [1-5] with less thermal expansion than steel.

1

The FUEETAP concretes are high strength concretes (40-100 MPa, compressive strength) and produce less than 0.4 wt % respirable fines upon impact of $\sim 10 \text{ J/m}^2$. The porosities and permeabilities are directly proportional [1,4,5], while the thermal conductivities and densities are inversely proportional to the formula's W/C ratio. This W/C ratio depends on the rheological limits and the water demand of the specific process waste stream. The FUEETAP concrete must be formulated as an engineering buffer between the specific waste stream and the disposal environment.

Since concretes are the principal hosts for low- and intermediate-level wastes, and since accelerated curing is a common industry practice, no innovation is required for implementation of the FUEETAP process. Other advantages of the process include its use of inexpensive and readily available materials, at low temperatures, and its application to a broad range of waste streams and cementitious materials.

The cementitious and radioactive waste phases are complex mixtures, and the identification and location of their specific nuclides has just begun. However, FUEETAP concretes have already been shown to work as durable, tenacious hosts for most of the major defense and reprocessing radioactive waste streams.

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Fig. 1. Flow sheet for FUETAP concrete developed for the Savannah River Plant high-level defense wastes.

Fig. 2. FUETAP with Type 1 Portland cement and SFP-4 simulated waste (MCC-1 strontium leach results at 90°C in deionized water).

Fig. 3. Polished-surface SEM photograph of an MCC-1 type concrete sample containing simulated Savannah River Plant waste solids. (See Table VI for identification of labeled items A-G.)

Fig. 4. Typical expansion curve for FUETAP concrete.

TABLE I

Minimum solids requirements, phase separation, and set time for MCC-1 FUETAP with simulated Savannah River Plant defense high-level waste

Total solids added (%)	Set time (h)	Phase separation (%)	Liquid volume (cm ³)	Solids volume (cm ³)
25	No set	43	117.0	155.0
37.5	No set	31	91.0	200.0
50	No set	14	56.0	340.0
62.5	No set	<1	3.0	365.0
75	<10 h	0		399.0
87.5	4-10 h	0		412.0

TABLE II

Effects of cement type on the leach rates of various elements from FUEAP concrete (MCC-1) in deionized water

Cement type	28-d leach rates ^{a)} for MCC-1 concrete at 90°C			
	Al	Fe	Mn	Sr
Type I Portland	3.31	0.0041	0.00096	0.43
Type I-S Slag	1.57	0.0020	0.0234	0.39
Fondu (high alumina)	5.67	0.0091	0.0152	0.83
50% Type I + 50% Fondu	4.10	0.0159	0.0268	0.11

a) Leach rates are found by: $g_i/m^3 \cdot d$, where g_i = reduced grams = g of i th element/mass fraction of i th element.

TABLE III

Effects of clay additives on the leach rates of cesium from FUEBTAP (MCC-1) concrete

Leach time (d)	MCC-1 concrete leach rates ^{a)} at 90°C			
	DIW ^{b)} leachate		SIW ^{c)} leachate	
	Clays ^{d)} added	None added	Clays ^{d)} added	None added
3	97.0	150.0	63.0	99.0
7	53.0	81.0	30.0	52.0
14	35.0	44.0	19.0	35.0
28		29.0		16.0

a) Leach rates are determined by: $g_i/m^2 \cdot d$, where g_i = reduced grams = g of i th element/mass fraction of i th element.

b) DIW = Quartz distilled water.

c) SIW = Materials Characterization Center silica water.

d) 3.5% Indian Red plus 3.5% Bentonite added.

TABLE IV

Results of 28-d leach tests of FUEIAP concrete MCC-6 with Savannah River Plant (SRP) simulated waste formula^{a)}

Leachant	Temperature (°C)	Cs	Sr	U	Ce	Nd
Distilled water (DIW)	90	48 ± 7	.27 ± .02	.035 ± .008	.11 ± .02	<.1
Silica water (SIW)	40	46 ± 3	1.3 ± .1	.007 ± .003	.02 ± .02	<.1
	90	37 ± 3	.30 ± .01	.02 ± .01	.02 ± .01	<.1
Salt brine (BRI)	40	59 ± 12	17 ± 6	.06 ± .01	<.1	1.0 ± .5
	90	53 ± 5	23 ± 5	.06 ± .01	<.1	.6 ± .5

^{a)} SRP6A with Indian red pottery clay ($g_i/m^2 \cdot d$).

TABLE V

Summary of FUETAP α -radiolysis tests with ^{244}Cm

Test No.	Dewatered, 250°C, 24-h	Dose rate (rad/h)	Total gas ^{a)} (molecules/100 eV)	Average range (equivalent dose years) ^{b)}
1	No	5.6×10^5	$.095 \pm .005$	300-15,000
2	Yes	5.6×10^5	$.006 \pm .002$	2,000-50,000
3	Yes	5.6×10^5	$.005 \pm .002$	300-50,000
4	Yes	6.3×10^4	$.001 \pm$	7,500
5	Yes	6.3×10^4	$.002 \pm .001$	1,500-7,500
6	Yes	1.9×10^5	$.008 \pm .005$	2,700-10,000

a) Taken from the initial linear portion of the pressure rise with time.

b) Based on an estimated α -dose of 6 rad/h for Savannah River Plant (SRP) FUETAP formulas.

TABLE VI
EDX^{a)} elemental analysis of MCC-1 concrete containing SRP-4 waste

Phase	Major elements	Minor elements
A	Cs, Si, Al	K, Ca, Ce, Fe
B	Ca, Fe, Gd	Cr, Fe, Si, Al, S
C	Fe	Ca, Si, Al, S
D	Al, Ca, Fe	S
E	Al, Si, Ca, Fe	S, K, Ti, Na
F	Si, Al, S, Fe	Ca, K, Cs, Na
G	Si	

^{a)} EDX = energy-dispersive x-ray analyzer.