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by

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ABSTRACT

The properties of concrete as a matrix for solidification of Savannah River Plant (SRP) high-level radioactive wastes were studied. In an experimental, laboratory-scale program, concrete specimens were prepared and evaluated with both simulated and actual SRP waste sludges. Properties of concrete were found adequate for fixation of SRP wastes. Procedures were developed for preparation of simulated sludges and concrete-sludge castings. Effects of cement type, simulated sludge type, sludge loading, and water content on concrete formulations were tested in a factorial experiment. Compressive strength, leachability of strontium and plutonium, thermal stability, and radiation stability were measured for each formulation. From these studies, high-alumina cement and a portland-pozzolanic cement were selected for additional tests. Incorporation of cesium-loaded zeolite into cement-sludge mixtures had no adverse effects on mechanical or chemical properties of waste forms. Effects of heating concrete-sludge castings were investigated; thermal conductivity and DTA-TGA-EGA data are reported. Formulations of actual SRP waste sludges in concrete were prepared and tested for compressive strength; for leachability of ^{90}Sr, ^{137}Cs, and alpha emitters; and for long-term thermal stability. The radioactive sludges were generally similar in behavior to simulated sludges in concrete.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

EVALUATION OF CONCRETE AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE

INTRODUCTION

Concrete has been used for many years for solidification of low-level and intermediate-level radioactive wastes. Various sites in the United States and Europe have used or tested concrete as a waste form.[1] In recent years, interest has developed in methods for solidification of high-level radioactive waste at the Savannah River Plant (SRP).[2] Concrete is an attractive candidate for solidification of SRP waste because:

- The raw materials are inexpensive
- Elevated temperatures are not required
- Only simple mixing operations are needed
- SRP waste is expected to be compatible with concrete.

Aged SRP high-level waste is alkaline and is diluted by nonradioactive salts. Because of dilution and aging, its heat output is relatively low. It consists of a solid component (sludge) and an aqueous component (supernate). The sludge is primarily composed of hydrous oxides of various metal ions encountered in SRP separations processes.[3] It contains most of the fission products, including ^{90}Sr, which is the principal radioactivity in the aged sludge. The supernate contains various soluble salts, such as sodium nitrate, and most of the ^{137}Cs radioactivity.[4]

A conceptual process[5] has been proposed for fixation of SRP waste. In this process, the sludge and supernate are separated by centrifugation, and the sludge is washed, dried to a powder, and incorporated into a suitable solid waste form. The ^{137}Cs from the supernate is absorbed on zeolite[6] which is then blended with the washed, dried sludge before solidification. Various solid forms, such as concrete, glass, ceramics, minerals, asphalt, and calcine, have been suggested for incorporation of SRP waste.[2,5,7,8,9] An experimental program for evaluating concrete as a matrix for solidification of SRP waste is described in this report.

Much of the laboratory-scale evaluation of concrete was performed with nonradioactive simulated wastes. This approach permitted the best types of cements and formulations to be determined before proceeding to more difficult experimental work with actual SRP wastes. A major part of this program was directed toward incorporating simulated sludge alone into concrete and evaluating the products. Concrete waste forms containing tracer-level ^{239}Pu or ^{137}Cs-loaded zeolite also were prepared. Finally, concrete forms containing actual SRP waste sludges, with and without zeolite, were prepared and evaluated.

Three compositions of simulated sludges were chosen for initial studies. In mole %, these are:

Sludge I: 50% $Fe(OH)_3$, 50% $Al(OH)_3$

Sludge II: 40% $Fe(OH)_3$, 40% $Al(OH)_3$, 20% HgO

Sludge III: 50% $Fe(OH)_3$, 50% MnO_2

Although actual SRP waste sludges are very complex mixtures and are highly variable,[3] these simulated sludge compositions were selected as simple first approximations, with properties that should be representative of the actual sludges.

A factorial experimental design was used to study 162 formulations of cement, simulated sludge, and water. The formulations were systematic combinations of the following factors:

- 6 types of cement
- 3 types of simulated sludge
- 3 levels of sludge content
- 3 levels of water content

In addition, 18 mixtures containing only cement and water were prepared as control specimens. About 1200 cylindrical castings were prepared for evaluation. The principal properties studied were:

- Compressive strength
- Leachability
- Radiation stability
- Thermal stability

The statistical significance of the effects of the various factors and interactions was determined, and from this work two cement types were selected for further studies.

In other work with simulated sludges incorporated in concrete, specimens were prepared with additions of ^{137}Cs-loaded zeolite, then evaluated for compressive strength and cesium leachability. The effects of heating concrete-sludge specimens were determined by measuring the pressure generated in closed containers and the time-to-failure at various temperatures.

Several studies on other aspects of concrete as a matrix for solidification of SRP waste are closely related to the work described in this report. The following additional properties of the cement/simulated sludge/water system were explored: cement bonding mechanisms,[10] set-time control,[11] and incorporation of other cesium sorbents.[12] Other studies with concrete-sludge specimens include: radiolytic gas evolution,[13] a new impact-test method,[14] and compatibility of metal container materials.[15] General studies on incorporation of simulated SRP waste into concrete were conducted by Brookhaven National Laboratory in support of the Savannah River Laboratory (SRL) waste solidification program.[16]

Actual SRP high-level radioactive waste sludges were incorporated into concrete in SRL shielded cell facilities. The washed, dried sludges were used to prepare 108 castings of 18 formulations that were systematic combinations of the following factors:

- 2 types of cement
- 3 types of sludge
- 3 levels of sludge content
- 1 level of water content

These specimens were evaluated principally for compressive strength and for leachability of ^{90}Sr, ^{137}Cs, and alpha emitters, although other tests were performed.

From these studies, an understanding of the properties of concrete incorporating SRP waste has been obtained. The data provide a technical basis for engineering design of a facility to solidify SRP waste in concrete.

SUMMARY

Concrete was studied as a matrix for solidification of SRP high-level radioactive waste. In an experimental, laboratory-scale program, concrete specimens were prepared and evaluated with both simulated and actual SRP sludges. Properties of concrete were found adequate for fixation of SRP waste.

Studies with Simulated Sludges. In nonradioactive studies, procedures were developed for preparation of simulated sludges and concrete-sludge castings. Formulations were prepared and tested in a factorial experiment using 6 types of cement, 3 types of simulated sludge, 3 levels of sludge loading, and 3 levels of water content. The water/cement ratio increased with increasing sludge content, indicating that the sludges were hydrophilic. Compressive strengths of the concrete waste forms decreased from ∿10,000 psi with no sludge to ∿2000 to ∿3000 psi when sludge content was 40% of dry solids. Leachabilities [L_0 initially, L_1 after six weeks leaching, expressed in g/(cm^2)(d)] of natural strontium, including strontium present in the cements, was 10^{-3} to 10^{-2} for L_0, and 10^{-5} to 10^{-3} for L_1. A sludge containing FeOOH and MnO_2 inhibited strontium leaching from concrete. ^{239}Pu, doped into a portion of each formulation, gave $L_0 = 10^{-5}$ and $L_1 = 10^{-8}$. Long-term thermal stability was evaluated by prolonged heating of specimens at 100°C, the expected operating temperature of a waste storage facility; only minor changes in compressive strength were found. Long-term radiation stability was studied by γ-irradiating specimens to 10^{10} rads, simulating a 100-year dose from actual waste; no adverse effects on compressive strength or strontium leachability could be ascribed to radiation. High-alumina cement (HAC) was superior to portland cements in all tests. A portland-pozzolanic cement (I-P) was slightly better than other portland cements. HAC and I-P were selected for additional tests.

Studies with Cesium-Loaded Zeolite. The effects of adding cesium-loaded zeolite to cement-sludge mixtures were studied with two series of formulations containing ^{137}Cs tracer. One series contained 37.5% simulated sludges and 2.5% Cs-zeolite; the second had no sludge but 10, 25, and 40% Cs-zeolite. The first series had compressive strengths similar to those with sludges alone and L_1 ∿ 10^{-3} g/(cm^2)(d) for cesium leachabilities. The second

series was superior to the first, with high compressive strengths like those of neat-cement formulations, and L_1 was $\sim 10^{-5}$. Incorporation of Cs-zeolite into concrete had no adverse effects on mechanical or chemical properties of the waste forms.

Thermal Studies. Effects of heating concrete-sludge castings were investigated. Thermal conductivity and DTA-TGA-EGA data are reported. The principal feature of heating concrete waste forms was massive evolution of water from 100 to 500°C. Heating specimens in a closed container, such as that proposed for waste storage canisters, gave steam-table pressures; for example, the pressure at 240°C was ~450 psig. By heating the specimen prior to sealing it in a container, the pressure was limited to ~50 psig at 240°C. Tests to determine time to failure at various temperatures showed no loss of mechanical integrity of concrete-sludge samples up to 400°C, above which increasingly early failure times at higher temperatures (~10 minutes at 1000°C) were observed.

Studies with Actual SRP Waste Sludges. Actual SRP sludges were incorporated into concrete and tested in shielded cell facilities. The behavior of the radioactive specimens was generally similar to that with simulated sludges. Formulations were prepared with 2 types of cement, 3 types of SRP sludge, and 3 levels of sludge content. Rapid setting was observed in one formulation. Compressive strengths were comparable to those with simulated sludges, except for unusually weak specimens for the rapid-set formulation and two others in which excess water was added to prevent rapid setting. For ^{90}Sr, L_0 was from 10^{-5} to 10^{-3} and L_1 was from 10^{-7} to 10^{-5}. For residual ^{137}Cs, L_0 was 10^{-2} to $\sim 10^{0}$ and L_1 was $\sim 10^{-4}$ to $\sim 10^{-3}$; addition of ^{137}Cs-loaded zeolite to two formulations resulted in markedly reduced ^{137}Cs leachabilities. For alpha emitters, L_0 was $\sim 10^{-5}$ and L_1 was $\sim 10^{-8}$. Sludges from three different SRP waste tanks gave widely different results in all tests. Long-term thermal stability was assessed by heating selected specimens at 400°C for one month and then by measuring leachability; for ^{90}Sr, L_0 and L_1 increased greatly; for ^{137}Cs, L_0 increased with HAC but decreased with I-P, and L_1 was unchanged; for alpha emitters, L_0 decreased and L_1 increased slightly.

INCORPORATION OF SIMULATED WASTE SLUDGES INTO CONCRETE

Preparation of Simulated Sludges

Three nonradioactive simulated waste sludge compositions were defined for waste solidification studies. The nominal compositions, in molar quantities, are: Sludge I, equal amounts of iron and aluminum; Sludge II, equal amounts of iron and aluminum, but with mercury added; Sludge III, equal amounts of iron and manganese. In addition, each sludge was to contain 400 ppm strontium, to simulate the ^{90}Sr content of SRP waste sludge. The sludges are the hydrous oxides formed by caustic precipitation from metal nitrate solutions.

Laboratory methods for preparation of the simulated sludges were developed with a batch size of one mole. Procedures for preparing each simulated sludge on this scale are given below. Because several hundred moles of each sludge were required for waste solidification studies, these procedures were scaled up for preparation of large batches at the SRL semiworks. Single batches of about 30 kg of each simulated sludge were prepared. Use of material from a single batch eliminated possible variations in properties from multiple preparations. Only simulated sludges from the large batches prepared at the semiworks were incorporated into concrete for the studies described in the following sections of this report.

Chemical analyses of the three simulated sludges are given in Table 1. Metal ions were determined by atomic absorption spectrophotometry of HCl solutions; sorbed water and total water were determined by thermogravimetric analyses. Residual oxygen (in the metal oxides after dehydration) was calculated by difference. Table 2 gives the planned and actual mole percents of the metal ions. The mole ratios of the principal metals were as planned, although the final sludges contained substantial amounts of sorbed water, and impurities such as sodium that proved difficult to wash out. The analyses show less water content in the washed, dried sludges than is calculated for $Fe(OH)_3$ and $Al(OH)_3$ species. More detailed calculations indicate that the analytical results can be accounted for by assuming the iron species to be FeOOH in all three simulated sludges. The aluminum stoichiometry in Sludges I and II appears to lie between $Al(OH)_3$ and AlOOH. Also, in Sludge III, the data are consistent with a hydrated form of MnO_2. The actual compounds could not be identified by x-ray diffraction powder patterns because the sludges were amorphous.

TABLE 1

Analytical Data for Simulated Sludges

	Wt %					
	Sludge I		*Sludge II*		*Sludge III*	
	Calc[a]	*Meas*	*Calc*[b]	*Meas*	*Calc*[c]	*Meas*
Fe	30.19	32.86	19.04	20.43	28.80	23.42
Al	14.59	15.20	9.20	9.23		
Hg			34.19	38.23		
Mn			0.00	0.35	28.33	23.56
Sr	0.04	0.04	0.04	0.02	0.04	0.04
Na	0.00	1.08	0.00	0.18	0.00	2.26
K			0.00	0.05	0.00	1.09
NO_3^-	0.00	2.97	0.00	0.00	0.00	0.00
H_2O[d]	29.23	17.90	18.43	8.40	13.94	10.25
H_2O[e]	0.00	2.00	0.00	2.40	0.00	15.45
O[f]	25.96	27.95	19.10	20.71	28.89	23.93

a. For 0.5 $Fe(OH)_3$ + 0.5 $Al(OH)_3$

b. For 0.4 $Fe(OH)_3$ + 0.4 $Al(OH)_3$ + 0.2 HgO

c. For 0.5 $Fe(OH)_3$ + 0.5 MnO_2

d. Crystallization H_2O + hydroxide H_2O

e. Sorbed H_2O

f. Residual oxygen, by difference

TABLE 2

Composition of Simulated Sludges

		Mole %	
Sludge	*Element*	*Calc*	*Meas*
I	Fe	50.0	49.1
	Al	50.0	47.0
	Na	0.0	3.9
II	Fe	40.0	40.0
	Al	40.0	37.4
	Hg	20.0	20.9
	Na	0.0	0.9
	K	0.0	0.1
	Mn	0.0	0.7
III	Fe	50.0	43.0
	Mn	50.0	44.0
	Na	0.0	10.1
	K	0.0	2.9

Each sludge had unique features in its preparation and properties.

Sludge I was prepared by adding NaOH to a solution of aluminum and ferric nitrates until the pH reached 9.5. This pH value was chosen to assure complete precipitation of strontium as $Sr(OH)_2$, without redissolving the $Al(OH)_3$ in excess base to form $NaAlO_2$. No attempt was made to simulate the complex equilibria actually existing in the waste tanks, where aluminum is found in both sludge and supernate with high OH^- concentration. The composition of Sludge I can be approximated as an equimolar mixture of $Fe_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot nH_2O$, with n equal to 2.5.

Special precautions were necessary in the preparation of Sludge II to prevent formation of hazardous mercury vapor. Mercurous ion (Hg_2^{2+}), present as a 0.1 wt % impurity in commercial $Hg(NO_3)_2$ reagent, reacts with caustic to form both HgO and Hg(metal). This undesirable side reaction was eliminated by oxidizing all of the Hg_2^{2+} ions to Hg^{2+} with permanganate before adding caustic to precipitate the sludge. Thus, small amounts of potassium and manganese, from the $KMnO_4$ reagent, as well as sodium and sorbed water are present in Sludge II. The composition with respect to the major elements can be approximated as a 40:40:20 mole ratio mixture of $Fe_2O_3 \cdot H_2O$, $Al_2O_3 \cdot nH_2O$ (with n = 2.0), and HgO.

In Sludge III, MnO_2 was precipitated in the same manner as in the production processes from which plant waste MnO_2 originates:[17] $KMnO_4$ solution was added to a 10% excess of $Mn(NO_3)_2$ solution, forming MnO_2 in situ. Then caustic was added to precipitate hydrous ferric oxide. Sludge III was found to have large sorptive properties for both water and cations. Thus, the washed, dried sludge contained more than 15 wt % sorbed water and significant quantities of sodium and potassium. It also had the desirable property of acting as a scavenger for strontium. Sludge III contained approximately equimolar quantities of $Fe_2O_3 \cdot H_2O$ and $MnO_2 \cdot nH_2O$, with n equal to about 0.85.

The following are procedures for preparation of one mole of each simulated sludge.

Sludge I. 202 g (0.5 mole) of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.085 g (0.0004 mole) of $Sr(NO_3)_2$ were dissolved together in one liter of water, then 313 g (0.5 mole) of 60 wt % $Al(NO_3)_3 \cdot 9H_2O$ solution was added. To this solution about 156 ml (3.0 moles) of 19.2M NaOH was added slowly, with stirring, until the pH reached 9.5. The slurry was diluted to 1800 ml, stirred for 30 minutes, and then centrifuged, with the supernatant liquid being decanted and discarded. The wet sludge was dried at 140°C for 16 hours; after drying, the sludge was washed twice with 1800 ml of water adjusted to pH 9.5 with NaOH. The sludge was centrifuged after each wash and then dried a second time at 140°C for 16 hours. The yield was 66 g of washed, dried Sludge I.

Sludge II. 161.6 g (0.4 mole) of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.085 g (0.0004 mole) of $Sr(NO_3)_2$ were dissolved together in one liter of water, then 250 g (0.4 mole) of 60 wt % $Al(NO_3)_2 \cdot 9H_2O$ solution was added. In this solution with pH approximately 1.5, 64.9 g (0.2 mole) of $Hg(NO_3)_2$ was dissolved. Then, 0.32 g (0.002 mole) of $KMnO_4$ dissolved in about 15 ml of water was added slowly, and the mixture stirred for 30 minutes. To this solution about 146 ml (2.8 moles) of 19.2M NaOH was added slowly, with stirring, until the pH reached 9.5. The slurry was diluted to 1800 ml, stirred for 30 minutes, and then centrifuged, with the supernatant liquid being decanted and discarded. The wet sludge was dried at 140°C for 16 hours; after drying, the sludge was washed twice with 1800 ml of 0.002M $KMnO_4$ solution adjusted to pH 9.5 with NaOH. The sludge was centrifuged after each wash and then dried a second time at 140°C for 16 hours. The yield was 95 g of washed, dried Sludge II.

Sludge III. 118.1 g (0.33 mole) of 50 wt % $Mn(NO_3)_2$ solution was mixed with 500 ml of water, then 31.6 g (0.2 mole) of $KMnO_4$ dissolved in 500 ml of water was added slowly, with stirring. In this slurry, 202 g (0.5 mole) of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.085 g (0.0004 mole) of $Sr(NO_3)_2$ was dissolved. About 102 ml (1.96 moles) of 19.2M NaOH was added slowly, with stirring, until the pH reached 9.5. The slurry was diluted to 1800 ml, stirred for 30 minutes, and then centrifuged, with the supernatant liquid being decanted and discarded. The wet sludge was dried at 140°C for 16 hours. After drying, the sludge was washed twice with 1800 ml of water adjusted to pH 9.5 with NaOH. The sludge was centrifuged after each wash and then dried a second time at 140°C for 16 hours. The yield was 100 g of washed, dried Sludge III.

Preparation of Concrete-Sludge Specimens

Cements

Concrete is the hardened solid product of a mixture of cement, water, and an aggregate.[18] In the construction industry, common aggregates are sand and gravel, but in the present study powdered waste sludges may be considered as aggregate materials incorporated into concrete. Three basic kinds of hydraulic cements are available for making concrete. These are portland cement, portland-pozzolanic cement, and high-alumina cement. The term "hydraulic" indicates cements that react with water to form pastes that subsequently set and harden to concrete.

Cements are composed primarily of various calcium silicates and calcium aluminates.[19,20] In portland cements, the major compounds present are tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). Each of these compounds has a role in defining the properties of portland cement, and by varying the relative amounts of the compounds, the properties of the cement may be altered. Several standard types of portland cements are manufactured, with compositions chosen to emphasize different properties. Portland-pozzolanic cements are mixtures of portland cement with a finely divided silicious material such as fly ash (primarily SiO_2) that enhances the cementitious properties of the cement in the presence of water. High-alumina cement (HAC) differs markedly from the portland cements, in that its composition is chiefly monocalcium aluminate ($CaO \cdot Al_2O_3$).

The chemical reactions involved in the setting and hardening of concrete are the hydration reactions of the cement compounds. Heat is evolved in all these reactions. For portland cements, the reaction products are the cementitious hydrates and calcium hydroxide. $Ca(OH)_2$ does not have cementitious properties and can contribute to the long-term deterioration of concrete. In portland-pozzolanic cements, the pozzolan reacts with $Ca(OH)_2$ to form new compounds that have cementitious properties. High-alumina cement[21] reacts with water to form hydrated calcium aluminates (cementitious) and aluminum hydroxide (noncementitious). $Al(OH)_3$ does not have the undesirable properties of $Ca(OH)_2$.

Five standard types of portland cement have been defined by ASTM.[22]

- Type I is normal, general-purpose portland cement, used when the special properties of the other types are not required.
- Type II is modified portland cement; it has a lower heat of hydration than Type I, generates heat at a slower rate, and has improved resistance to sulfate attack.
- Type III is high early-strength portland cement, which attains a large fraction of its ultimate strength in 3 days, compared with 28 days for Type I; the rate of heat generation is correspondingly greater.
- Type IV (not used in the present study) is low-heat portland cement; the amount and rate of heat generation is very low with this cement.

- Type V is sulfate-resistant portland cement, for use in applications with severe sulfate attack; it develops strength more slowly than Type I.

In addition to the five standard portland cements, other standard cements containing admixtures of various substances have been designated, including:

- Type I-P,[23] a standard portland-pozzolanic cement.

To evaluate the incorporation of simulated sludges into concrete, six cements were used. Portland cements were Type I (Santee Portland Cement Co., Holly Hill, SC), Type II (Southwestern Portland Cement Co., Odessa, TX), Type III (Medusa Cement Co., Cleveland, OH), and Type V (California Portland Cement Co., Los Angeles, CA). A Type I-P portland-pozzolanic cement (Santee Portland Cement Co., Holly Hill, SC) and a high-alumina cement (Universal Atlas Division of U. S. Steel Corp., Pittsburgh, PA) were included. Typical elemental compositions of these types of cement are given in Table 3; the values were calculated from nominal compound compositions,[20] except for HAC where literature values[21] are shown. The elemental compositions of portland cements are very close to one another, even though there may be substantial variation in the relative amounts of the constituent compounds.

TABLE 3

Composition of Cements

Cement Type	*Literature and Calculated Values, wt %*						
	CaO	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MgO*	*SO_3*	*Other*
I	63.1	21.3	5.8	2.6	2.9	1.8	2.5
II	63.3	22.4	4.6	4.3	2.5	1.7	1.2
III	64.8	20.6	6.0	3.0	2.0	2.4	1.2
V	64.3	25.0	3.4	3.0	1.9	1.6	0.8
I-P[a]	50.5	37.0	4.7	2.1	2.3	1.5	1.9
HAC[b]	36.5	8.5	40.5	5.5	1.0	0.2	7.8[c]

a. Assumed 80% Type I + 20% SiO_2.

b. Literature values[21] for high-alumina cement; all others calculated.

c. Includes FeO 5.5, and TiO_2 2.0.

Concrete-Sludge Specimens

To evaluate the solid waste forms prepared from various formulations of cement, simulated sludge, and water, a factorial experimental design suitable for statistical analysis was used.[24] Although other statistical designs[25] are available that require considerably fewer experiments than a factorial design, the thorough characterization of the system obtainable with a factorial design was desired. Four factors were studied: cement type, simulated sludge type, amount of sludge, and amount of water. A 6 x 3 x 3 x 3 factorial design was established, with 6 types of cement, 3 simulated sludges, 3 levels of sludge content, and 3 levels of water content.

Cements used in the factorial experiment were Types I, II, III, V, I-P, and HAC. Simulated Sludges I, II, and III were used at sludge contents of 10, 25, and 40 wt % of the solids. Water contents were adjusted to give pastes with different workabilities that were designated dry, ideal, and wet. Of the 162 combinations of the factors, formulations were prepared of 150. (Only the ideal workability pastes with Types II and V cements with Sludge II were prepared to conserve the supply of the sludge.) In addition, 18 mixtures containing only cement and water were prepared as control specimens.

Six cylindrical castings, with nominal dimensions of 2.5 cm in diameter and 11.5 cm in length, were made from each formulation. An additional casting of each was doped with plutonium. The castings were cured for 28 days in a humid environment and then were removed from their molds and sawed into specimens for various evaluation tests. Representative castings are shown in Figure 1, for concretes containing no sludge, Sludge I, and Sludge III.

The batch size requirement was estimated by assuming that for each formulation, cylinders of total length 76 cm and volume 386 cm^3 were to be prepared. For concrete, with density about 2 g/cm^3, batch sizes of at least 772 g of paste were needed for six castings 11.5 cm long and one casting 6.3 cm long (containing plutonium). A small-scale preparation (10 g of solids) was made for each combination of cement type, sludge type, and sludge content, to determine the approximate amount of water required for ideal workability of the paste. With this information, the formulation was scaled up to give about 772 g of total weight of cement, sludge, and water.

Experimental Procedure. In the general procedure for preparing a formulation, the calculated amounts of cement and simulated sludge were weighed out and blended together dry. Portions of a weighed amount of water were added to the mixt

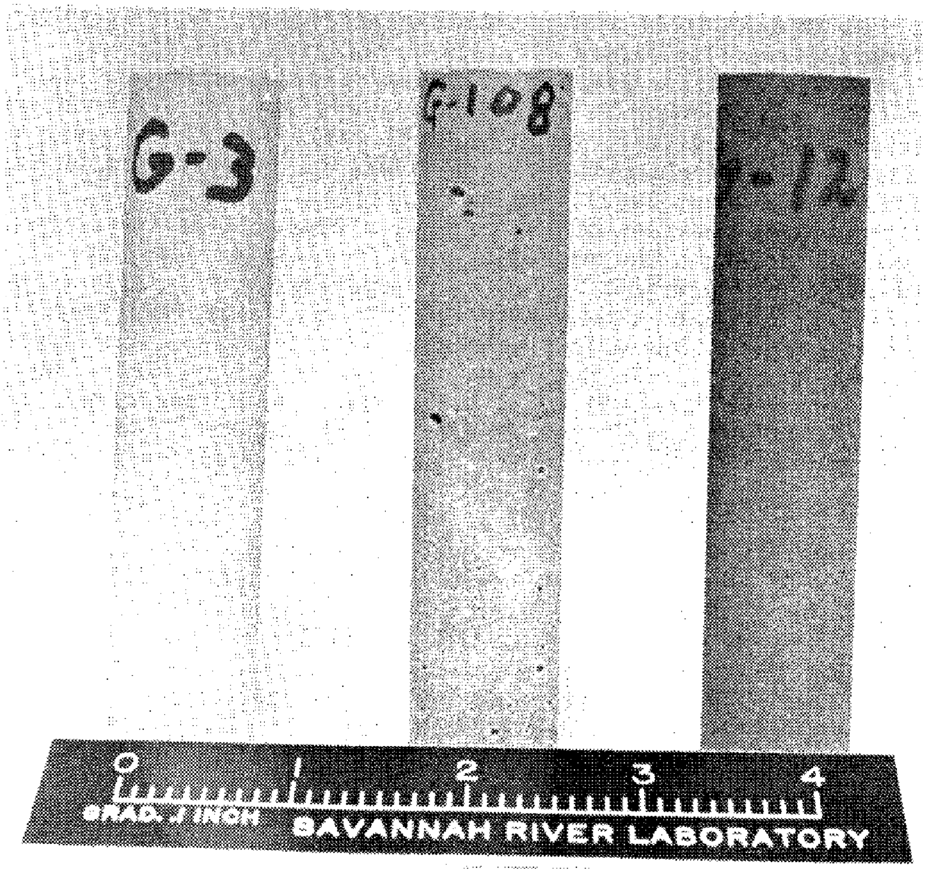

FIGURE 1. Concrete-Sludge Castings

with slow stirring until a paste was obtained. Careful additions of water were continued until the paste attained the proper consistency for best workability.[26] The amount of water used was determined by reweighing the water container. About 30 cm^3 of paste was set aside for plutonium doping, and the remainder was poured immediately with vibration into six plastic molds. A plutonium-containing casting was made by adding 0.1 ml of plutonium tracer solution (10^8 dis/min of ^{239}Pu) to the 30-cm^3 portion of paste, mixing manually, and casting in a plastic mold. The castings were placed in covered cans lined with wet sponges for setting and curing. After determining the water/cement ratio ([illegible]) for ideal workability, formulations with W/C changed by ±0.025 were made for the dry and wet consistencies.

As an example of the preparative procedure, the following operations were performed to prepare specimens with HAC and 40 wt % Sludge III. 360.0 g of HAC and 240.0 g of Sludge III were blended together in the 5-quart mixing bowl of a laboratory mortar mixer (Soiltest, Inc., Model CT-345). Distilled water was added in weighed aliquots, with slow mixing, until the paste had ideal consistency; 169.9 g of water had been added for W/C = 0.472. About a 30-cm^3 portion of the paste was removed from the bowl for plutonium doping. The paste was cast in plastic molds with the aid of vibration from a laboratory sieve-shaker; this treatment caused the paste to flow easily from the bowl through a funnel into the molds. The molds were 1-in. OD butyrate plastic tubing (United States Plastic Corp., No. 33566) with polyethylene end caps (Tube-Pak, Type TP1.00). Six molds 11.5 cm long were filled with the paste, capped, and placed in a curing can (Soiltest, Inc., Model CT-205) for 28 days. The plutonium-doped casting was prepared by adding to the 30 cm^3 ($\sim$50 g) of paste, 100 µl of a solution containing 1.2×10^9 dis/(min)(ml) of $^{239}Pu^{4+}$ in 0.36M HNO_3. The plutonium was distributed throughout the paste by manual mixing, and then the paste was cast in a mold 6.3 cm long and stored in a separate curing bucket. Subsequent formulations were made with 364.7 g of HAC, 243.1 g of Sludge III, and 164.1 g of water (W/C = 0.450) for a too-dry paste, and with 356.3 g of HAC, 237.5 g of Sludge III, and 178.2 g of water (W/C = 0.500) for a too-wet paste. After 28 days, the molds were removed from the hardened castings, either by cutting the plastic away, or by melting a seam longitudinally down the mold with an electrically-heated device. 2.5- and 5.0-cm-long specimens for various evaluation tests were cut from the castings with a specially-modified band saw.

TABLE 4

Experimental Water/Cement Ratios[a]

			Water/Cement Ratios (W/C) for Cement Types					
Sludge	*S/(S+C)*	*S/C*	*I*	*II*	*III*	*V*	*I-P*	*HAC*
None	0	0	0.350	0.265	0.293	0.285	0.320	0.258
I	0.10	0.11	0.352	0.339	0.377	0.349	0.383	0.304
	0.25	0.33	0.534	0.506	0.526	0.443	0.491	0.418
	0.40	0.67	0.925	0.785	0.840	0.679	0.743	0.599
II	0.10	0.11	0.335	0.329	0.346	0.325	0.369	0.301
	0.25	0.33	0.440	0.445	0.423	0.395	0.461	0.372
	0.40	0.67	0.586	0.624	0.599	0.541	0.619	0.484
III	0.10	0.11	0.350	0.304	0.338	0.322	0.350	0.281
	0.25	0.33	0.427	0.370	0.417	0.400	0.417	0.342
	0.40	0.67	0.625	0.525	0.575	0.543	0.529	0.472

a. For formulations with best workability.

Water/Cement Ratios

A formulation of cement-sludge-water may be defined by the weight ratio of water to cement (W/C) and by the weight ratio of sludge to cement (S/C). Experimental W/C ratios for pastes with ideal workability are given in Table 4. The values of W/C generally increase with increasing sludge content, indicating that the sludges are hydrophilic.

The data in Table 4 were analyzed to determine the fractions of water required by the cement and by the sludge. With no cement-sludge interaction, the water required, W, is the sum of the water required by the cement, W_C, and by the sludge, W_S:

$$W = W_C + W_S$$

In terms of the measured ratios,

$$W/C = (W_C/C) + (W_S/S)(S/C)$$

where W_C/C = water required per gram of cement

W_S/S = water required per gram of sludge

For this model to represent the data, a plot of W/C vs. S/C for a single sludge should yield a family of straight lines, one for each cement, with identical slopes W_S/S. However, the data generally do not behave in this manner, as shown in Figure 2 for the Sludge I data. Curves through the data points are neither linear nor parallel. Thus, a simple model that neglects cement-sludge interaction is not adequate.

If the cement and sludge interact, the water required by the sludge will vary with the sludge/cement ratio. This can be expressed as

$$W = W_C + W_S\ [1 + a(S/C)]$$

where a = interaction coefficient for each cement-sludge pair.

In this equation, W_C and W_S apply in the limit of $(S/C) \rightarrow 0$. Rearrangement gives the quadratic equation

$$W/C = (W_C/C) + (W_S/S)(S/C) + a(W_S/S)(S/C)^2$$

which contains the same terms as the linear model, plus an interaction term. A least-squares fit of a quadratic equation to the data for each of the 18 cement-sludge pairs (54 adjustable ~ameters) gave an adequate representation of the data.

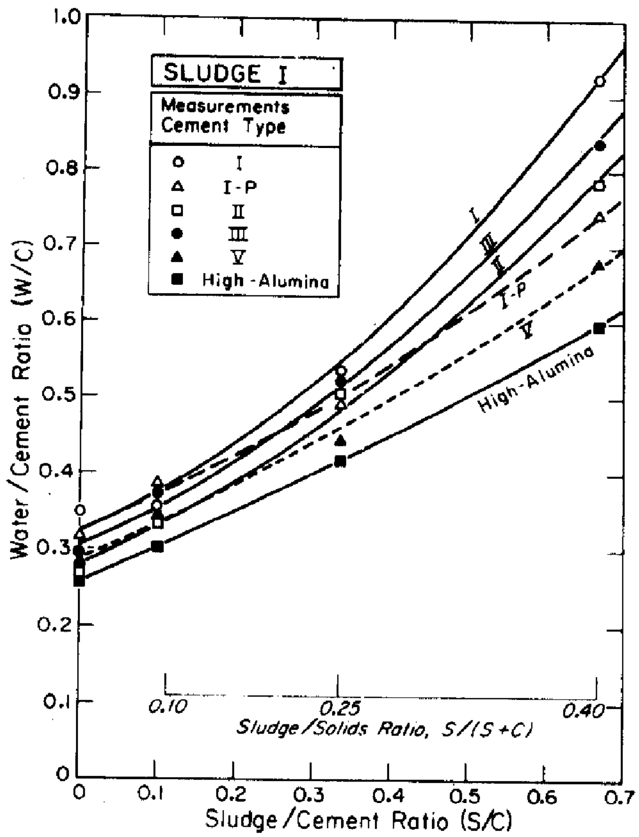

FIGURE 2. Water/Cement Ratios for Formulations with Sludges

However, to be more physically realistic, the model should constrain W_C/C to a constant for each cement type and W_S/S to a constant for each sludge. By introducing these constraints, the least-squares fit is reduced to 27 adjustable parameters, but the full 27 x 27 matrix must be inverted. Results of a computer calculation are given in Table 5 for the least-squares fit of the data with constraints on W_C/C and W_S/S. The best-fit curves from this model are shown in Figure 2 for the Sludge 1 data, where the variation in W/C is most pronounced.

As an example of the use of Table 5, W/C may be calculated for Type I cement with 33.3% Sludge I, which corresponds to S/C = 0.5. With $W_C/C = 0.323$, $W_S/S = 0.449$, and a = 1.49, the equation gives

$$
\begin{aligned}
W/C &= (0.323) + (0.449)(0.5) + (1.49)(0.449)(0.5)^2 \\
&= 0.323 + 0.225 + 0.167 \\
&= 0.715
\end{aligned}
$$

Thus, with this combination of cement and sludge, 71.5 g of water would be required for each 100 g of cement and 50 g of sludge.

The calculated values of W_C/C agree very well with the measured values of W/C for formulations containing no sludge. The calculated values of W_S/S for the sludges are in the order

Sludge I > Sludge II > Sludge III

indicating the relative hydrophilic nature of each sludge composition. The interaction term needed to represent the data suggests that reactions may occur between cement and sludge when water is added. The interaction coefficients given in Table 5 generally are smallest for Sludge II and for high-alumina and Type I-P cements.

TABLE 5

Parameters Calculated from Least-Squares Fit with Constraints

			Simulated Sludge		
			I	*II*	*III*
		W_S/S	0.449	0.341	0.229
Cement Type	W_C/C		*Interaction Coefficient, a*		
I	0.323		1.49	0.22	1.44
II	0.278		1.07	0.82	0.90
III	0.303		1.21	0.43	1.18
V	0.286		0.45	0.16	1.05
I-P	0.323		0.59	0.46	0.53
HAC	0.257		0.22	0.00	0.60

Evaluation of Cement Types

Initial work, in addition to obtaining a general understanding of the properties of concrete waste forms, was aimed at selecting the best type of cement from the group studied. The effects of additional factors could then be investigated using only the cement selected. Thus, the cement-sludge formulations described in the previous section were evaluated by a variety of tests.

Compressive strength and leachability are considered the most important measures of the quality of the concrete-sludge specimens. Compressive strength is a measure of mechanical durability, which is desirable for reducing the probability of waste forms breaking into smaller pieces. Leachability is a measure of ~~ility of the waste form to retain chemical species when con- with water. Strontium and plutonium leachabilities are described in this section. Long-term thermal and radiation stabilities of the waste forms also are discussed. To study thermal stability, specimens were held at 100°C for several months, then measured for weight loss and compressive strength. Radiation stability was tested by gamma-irradiating the castings and then measuring compressive strength and strontium leachability. Other tests, including cesium leachability and thermal effects, are described in later sections.

The data were analyzed to determine the statistical significance of the various factor effects and interactions.[24] For most of the evaluation tests, the data formed a 6 x 3 x 3 x 3 factorial design. The 95% confidence intervals (error bars) on each data point also were obtained from the statistical analysis. From the large amount of data generated in these experiments, representative results and the more significant conclusions are presented.

Compressive Strength

Typical results of compressive strength measurements are shown in Figure 3. The sludge content was the predominant factor affecting the compressive strength of concretes containing simulated sludges. For most of the sludges and cement types studied, the compressive strength decreased from about 10,000 psi with no sludge to about 3000 psi with 40% sludge. The range from 2000 to 5000 psi is considered satisfactory for most commercial applications of concrete.[27] Of the six cements used, high-alumina cement specimens consistently gave higher compressive strengths than did portland cement specimens.

Experimental Procedure. For measuring compressive strengths of the concrete-sludge specimens, a casting was sawed into duplicate specimens about 5 cm long. Specimens never included the bottom 0.3 cm or top 1.0 cm of the casting; these portions were sawed off and discarded. The ends of each specimen were ground flat and parallel; then the piece was measured and weighed. A typical specimen was 2.39 cm in diameter, 5.02 cm in length, and 41.32 g in weight. Densities ranged from about 2.1 g/cm^3 with no sludge to about 1.7 g/cm^3 with 40% sludge. Compressive strengths were measured with a specially constructed press designed for specimens of this size. The compressive strength was calculated from the cross-sectional area and the loading force required to break the specimen. Each test was performed at least 90 days after the formulation was cast, so that the results would approximate the ultimate strength.

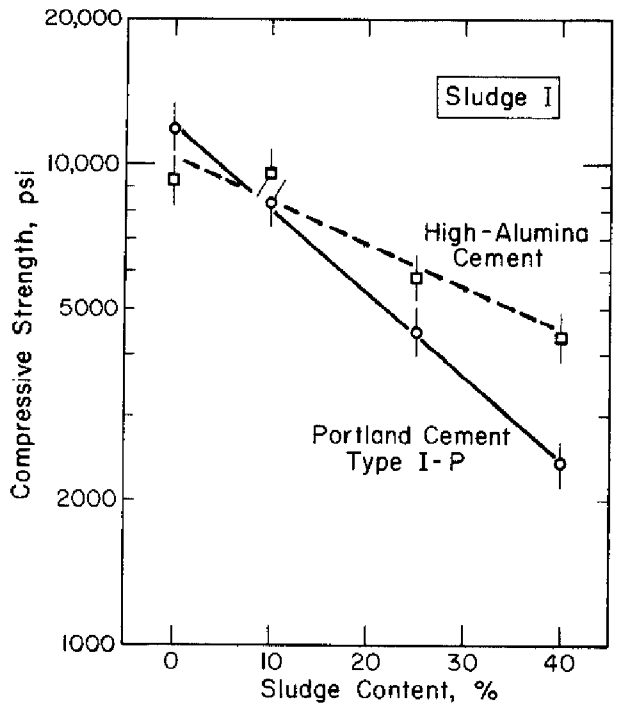

FIGURE 3. Compressive Strength of Concrete-Sludge Specimens

Results. The statistical treatment of the 336 measurements of compressive strength was an analysis of variance, separately for each sludge type. Because constant percent errors were expected, the data were transformed logarithmically; consequently, averages from the statistical treatment were geometric means. The results indicated that the data should be averaged over the three water contents as well as over the two duplicate specimens, for each combination of cement type, sludge type, and sludge content. Table 6 gives the compressive strengths of the concrete waste forms, where each entry is the average of six data points. For all three sludges, the effect of sludge content has overwhelmingly the greatest statistical significance, the effect of cement type has high significance, but the effect of water content has only minor significance. An interaction between sludge content and cement type also is significant.

An examination of the data for the effect of sludge type shows that the sludges at the 10% level had no significant differences. At the 25% level, Sludge II gave higher compressive strengths than the others. At the 40% level, significant differences exist between the sludges, and the compressive strengths for the portland cements are in the order of Sludge II > ;e III > Sludge I; for high-alumina cement, the order is e II > Sludge I > Sludge III.

Compressive strength decreased monotonically with increasing sludge content for every combination of sludge and cement type. The decrease is believed due to lack of strength in the sludge particles. The cement provides nearly all of the strength of the concrete, and as the concentration of sludge particles increases, the load-bearing area of hydrated cement particles decreases.

The presence in the data of a statistical interaction between sludge content and cement type means that the ordering of compressive strength with respect to cement type may be different for each sludge content. Also, because of the size of the error bars on the data points, there are no statistical differences between some of the cement types for many of the sludge type and content combinations. However, high-alumina cement clearly has superior compressive strength as sludge content increases, for all of the simulated sludges. Beyond this, an overall ordering of cement types from the compressive strength data is difficult to define. One overall ordering, based upon the number of combinations for which a cement type is within two standard deviations of the largest compressive strength, is

$$HAC > III > V > I \approx II > I\text{-}P$$

TABLE 6

Compressive Strength of Concrete Waste Forms

Sludge		*Compressive Strength, psi, for Cement Types*[a]					
Type	*Content, %*	*I*	*II*	*III*	*V*	*I-P*	*HAC*
None[b]	0	10,824	11,284	13,478	11,898	11,916	9,311
I[b]	10	8,402	8,243	8,694	8,829	8,296	9,574
	25	4,588	4,630	6,180	5,620	4,472	5,792
	40	464	1,259	1,546	3,054	2,380	4,364
II[b]	10	8,973	9,045	9,321	11,159	7,692	9,624
	25	5,779	6,412	7,230	7,158	5,855	7,158
	40	3,932	3,352	4,736	4,234	3,311	5,884
III[b]	10	9,313	7,557	7,603	8,490	7,761	8,465
	25	5,171	4,627	5,817	4,732	4,930	6,658
	40	2,388	2,884	3,317	2,700	3,088	3,371

a. Each entry is the average of six measurements.

b. Error factor ε (95% confidence), where upper limit is $x \cdot \varepsilon$, and lower limit is x/ε: No sludge, $\varepsilon = 1.15$; Sludge I, $\varepsilon = 1.12$; Sludge II, $\varepsilon = 1.15$; Sludge III, $\varepsilon = 1.08$.

Other orderings are possible, but, as shown in Table 6, HAC has the best compressive strength, and the other cement types differ very little.

The small effect of water content is somewhat surprising because water content is an extremely important factor in producing high-quality commercial concrete.[18] In the cement-sludge formulations, the range of water content investigated was rather narrow, even though the variations used gave substantial differences in workability of the paste. Undoubtedly, much weaker forms, and thus a greater statistical significance, could have been obtained by using higher water contents (lower water contents would have resulted in moist solids, rather than a paste). However, the water contents used defined a range over which the best compressive strength can be obtained for a cement-sludge formulation.

Strontium Leachability

Leachability was investigated as a function of time over a six-week leaching period. Thus, in addition to the factors of cement type, sludge type, sludge content, and water content, the effect of cumulative time of leaching was also studied. Results of a typical strontium leach test are shown in Figure 4. Both the strontium leachability and the fraction leached from the solid may be obtained from leach data. Leachability was found to be a strong function of time, decreasing by factors of 10 to 200 over the six-week leach period. The principal conclusions from strontium leach data are:

- Leachabilities range from 10^{-5} to 10^{-2} g/(cm^2)(d).
- Sludge III is less leachable than Sludge I or Sludge II.
- Leachability decreases as Sludge III content increases; the opposite effect occurs with Sludge I and Sludge II.
- High-alumina cement is less leachable than portland cements at high sludge contents and long leach times.
- Water/cement ratio has little effect on strontium leachability.

Leachability is defined by the equation

$$L = \frac{1}{F\ A}\ \frac{\Delta m}{\Delta t}$$

where F = weight fraction of strontium in the leach specimen

A = surface area of the leach specimen

Δm = mass of strontium leached during time Δt

= (concentration of strontium in leach water) x (volume of leach water)

Δt = time interval between changes of leach water

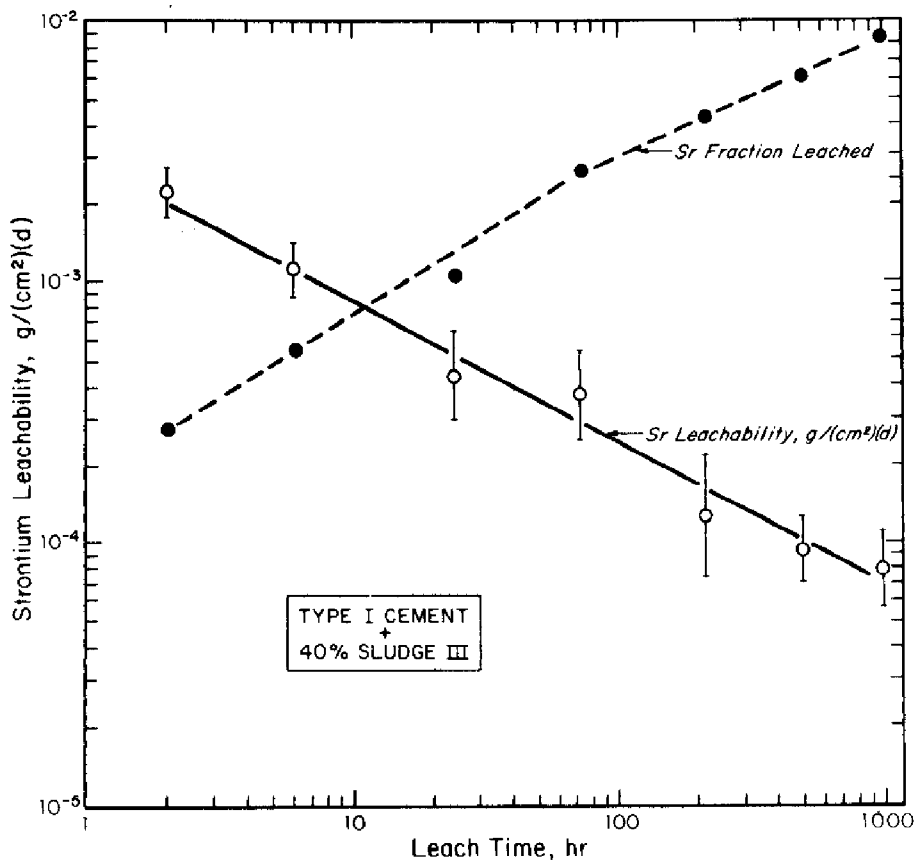

FIGURE 4. Typical Leach Test Results

Experimental Procedure. For leach tests, a casting was sawed into duplicate specimens about 2.5 cm long. The specimens were always sawed from the lower half of the castings, after removing the bottom 0.3 cm. The leach specimens were measured and weighed, with a typical specimen having a 2.38-cm diameter, 2.52-cm length, and 20.90-g weight. Surface areas were about 28 cm^2. Each leach specimen was suspended with a 0.64-mm stainless steel wire into a 16-oz wide-mouth polyethylene bottle containing 268 ml of unstirred distilled water. Samples were taken periodically by completely changing the leach water. For strontium, the leachant was changed after 2 hours, 6 hours, 1 day, 3 days, 9 days, 21 days, and 42 days, so that Δt increased logarithmically. About 2500 leach water samples were generated in the tests, and each was analyzed for strontium by copper-spark emission spectroscopy. Strontium concentrations ranged from 0.01 to 2 ppm. Blank leach tests, without concrete specimens, were run in parallel with the actual tests; no strontium (<0.01 ppm) was detected in any blank sample.

The sampling schedule was chosen to give an adequate description of the time behavior of strontium leachability without creating a prohibitively large number of samples to be analyzed. Δt was increased in a manner to give strontium concentrations that would be approximately constant and within the range of sensitivity of the copper-spark method. This method is particularly well suited to determining strontium in a large number of leach-water samples; it is rapid and sensitive, with precision of ±50% for a single determination by visual estimation. The experimental procedures differ from those of a proposed standard leach test for radioactive waste forms,[28] principally in the fewer and less frequent samples taken in the present leach tests. The proposed standard test was judged to be impractical for a large factorial experiment such as described in this section. The procedures used gave an internally consistent set of leach data, from which the major features of the leaching behavior could be obtained, even with the ±50% precision expected for each data point. Because the main features, such as time behavior, were expected to change by factors of 10 or more, the low precision was acceptable. More complete information about the other factors could be extracted from the data by a statistical analysis.

Natural strontium was present in the concrete leach specimens in concentrations that approximated those expected for radioactive ^{90}Sr in SRP waste incorporated into concrete. Strontium was added in the preparation of the simulated sludges and was present in similar amounts in the cements used. Accurate and precise analyses of the strontium fraction in each type of cement, f_C, and sludge, f_S, were obtained by atomic absorption spectrophotometry. These strontium fractions, given in Table 7, were used to calculate F for each leach specimen, from the following equation:

$$F = \frac{f_C + (S/C)\ f_S}{(W/C) + (S/C) + 1}$$

Values of F obtained in this way were used in all calculations of strontium leachability. As a check on obtaining F by calculation, F was measured for selected concrete castings by x-ray fluorescence spectrometry, with an accuracy of about ±20%. Measured and calculated strontium fractions are compared in Table 7 for some typical formulations; the agreement was adequate. The leach tests could not distinguish differences in behavior between strontium from sludge or from cement. The assumption was made that strontium from both sources behaved the same way once the formulation was contacted with water and mixed into a paste.

TABLE 7

Strontium Content of Cements, Simulated Sludges, and Typical Concrete Waste Forms

Cements and Sludges	*Sr, ppm Meas*[b]
Cements	
Type I	908
Type II	749
Type III	692
Type V	1348
Type I-P	742
HAC	201
Sludges	
Sludge I	437
Sludge II	155
Sludge III	398

Concretes[a]				*Sr, ppm*	
Cement	*Sludge*	*S/C*	*W/C*	*Calc*	*Meas*[c]
I	III	0.67	0.625	512	460
II	III	0.67	0.525	463	410
III	III	0.67	0.575	427	410
V	III	0.67	0.543	730	655
I-P	III	0.67	0.529	459	390
HAC	III	0.67	0.472	218	175
I-P	I	0.67	0.743	429	530
I-P	I	0.33	0.491	487	552
I-P	I	0.11	0.383	529	625
I-P	–	0	0.320	362	695
HAC	–	0	0.258	160	130

a. Water contents for best workability.

b. By atomic absorption spectrophotometry.

c. By x-ray fluorescence spectrometry.

Results. For the 2352 measurements of strontium leachability, an analysis of variance was performed separately for each sludge type and time period. This statistical treatment showed that water content was not a significant factor in the data; thus, the data were averaged over the three water contents as well as over the two duplicate specimens. Some examples of strontium leachabilities are given in Table 8, where each entry is the average of six data points. Leachability decreased monotonically with time for all combinations of sludge type, sludge content, and cement type. The effect of sludge content increased in statistical significance with time for Sludge I and Sludge II, ranging from insignificant at early times to highly significant at later times. For sludge III, the effect of sludge content was high and relatively constant at all time periods. The effect of cement type was statistically significant for nearly all time periods and sludge types. For Sludge I and Sludge III, an interaction of minor significance also was found between cement type and sludge content.

TABLE 8

Typical Strontium Leachabilities for Concrete Waste Forms

Time, hr	*Sludge*[a] *Content, %*	*Sr Leachability,*[b] 10^{-3} *g/(cm²)(d), for Cement Types* *I*	*II*	*III*	*V*	*I-P*	*HAC*
2[c]	0	2.7	12.0	5.0	3.4	3.6	9.1
	10	2.5	7.6	4.7	2.4	2.7	6.6
	25	3.3	4.6	2.5	2.7	2.1	5.8
	40	2.2	2.8	2.7	1.6	2.5	5.3
72[c]	0	1.5	1.2	1.4	1.4	1.5	1.5
	10	0.73	1.1	1.2	1.2	0.79	1.0
	25	0.63	0.83	0.72	1.1	0.53	0.48
	40	0.37	0.82	0.56	0.52	0.24	0.22
1008[c]	0	0.25	0.24	0.14	0.18	0.16	0.23
	10	0.16	0.22	0.13	0.17	0.13	0.13
	25	0.13	0.11	0.15	0.11	0.093	0.041
	40	0.079	0.098	0.11	0.13	0.054	0.024

a. Sludge III.

b. Each entry is the average of six measurements.

c. Error factor ε (95% confidence): at 2 hr, ε = 1.24; at 72 hr, ε = 1.49; at 1008 hr, ε = 1.40.

The effects of sludge content, sludge type, and cement type may be considered individually.

Some of the data for Sludge III given in Table 8 is illustrated in Figure 5, which shows the time behavior of strontium leachability for specimens containing different amounts of Sludge III. An unusual effect was observed: leachability decreased as the sludge content increased. The effect was especially pronounced with high-alumina cement specimens, as shown in Figure 5. After leaching for six weeks, the strontium leachability for specimens containing 40% Sludge III was a factor of 10 lower than for specimens containing no sludge. Similar behavior with Sludge III was observed for each type of cement (Table 8). The opposite behavior was observed with Sludge I and Sludge II; with increasing sludge content, the strontium leachabilities generally showed little change or increased.

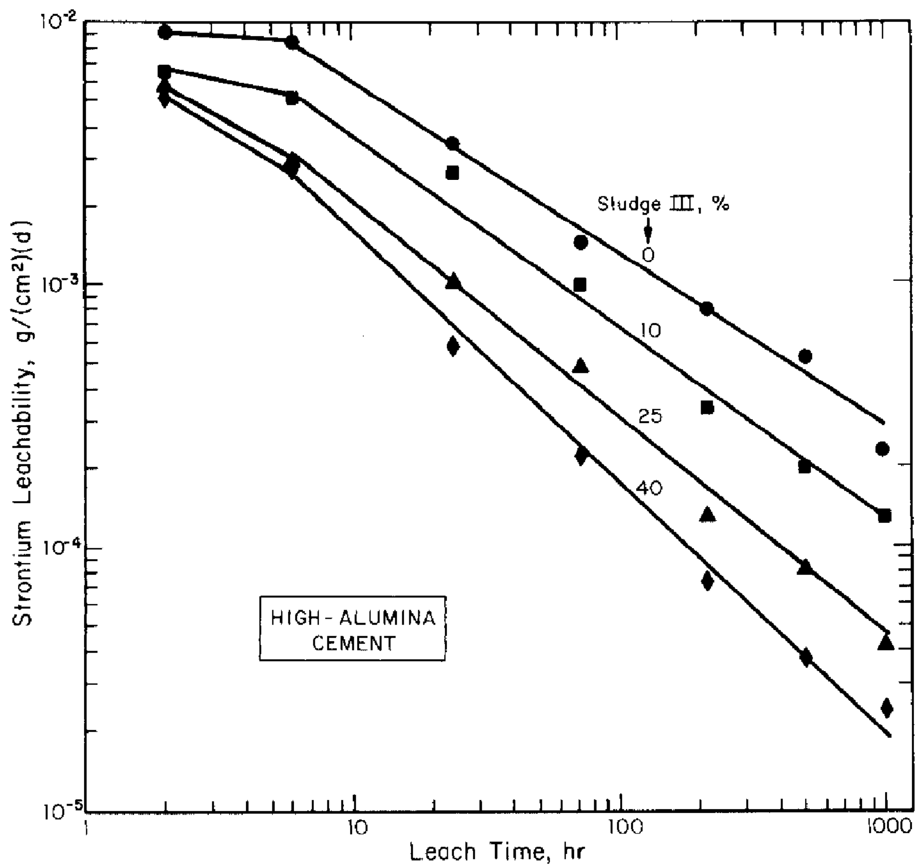

FIGURE 5. Effect of Sludge III Content on Strontium Leachability

This difference in behavior of the different sludge types is illustrated further in Figure 6. The variation of strontium leachability with sludge content is shown for the three sludge types and two typical cement types, after leaching for six weeks (1008 hours). Similar, but less pronounced, variation was observed at each of the earlier time periods. Clearly, the strontium leachabilities of Sludge I and Sludge II increase with sludge content, while that of Sludge III decreases. The difference is attributed in Sludge III to the presence of MnO_2, which apparently can act as a scavenger for strontium in concrete, thus retarding its leachability.

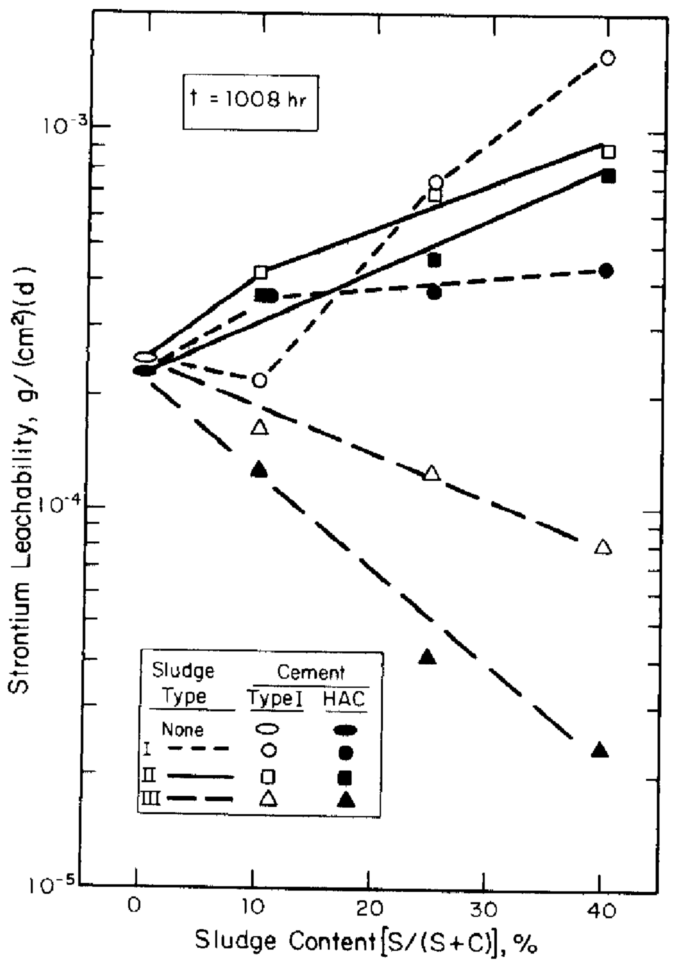

FIGURE 6. Effect of Sludge Type on Strontium Leachability

The differences among the cement types, although statistically significant, are not so pronounced as are the effects of time, sludge type, and sludge content on strontium leachability. Figure 7 shows the time behavior of strontium leachability for several cement types, all with 40% Sludge I. This case has some of the widest differences between cement types that were found.

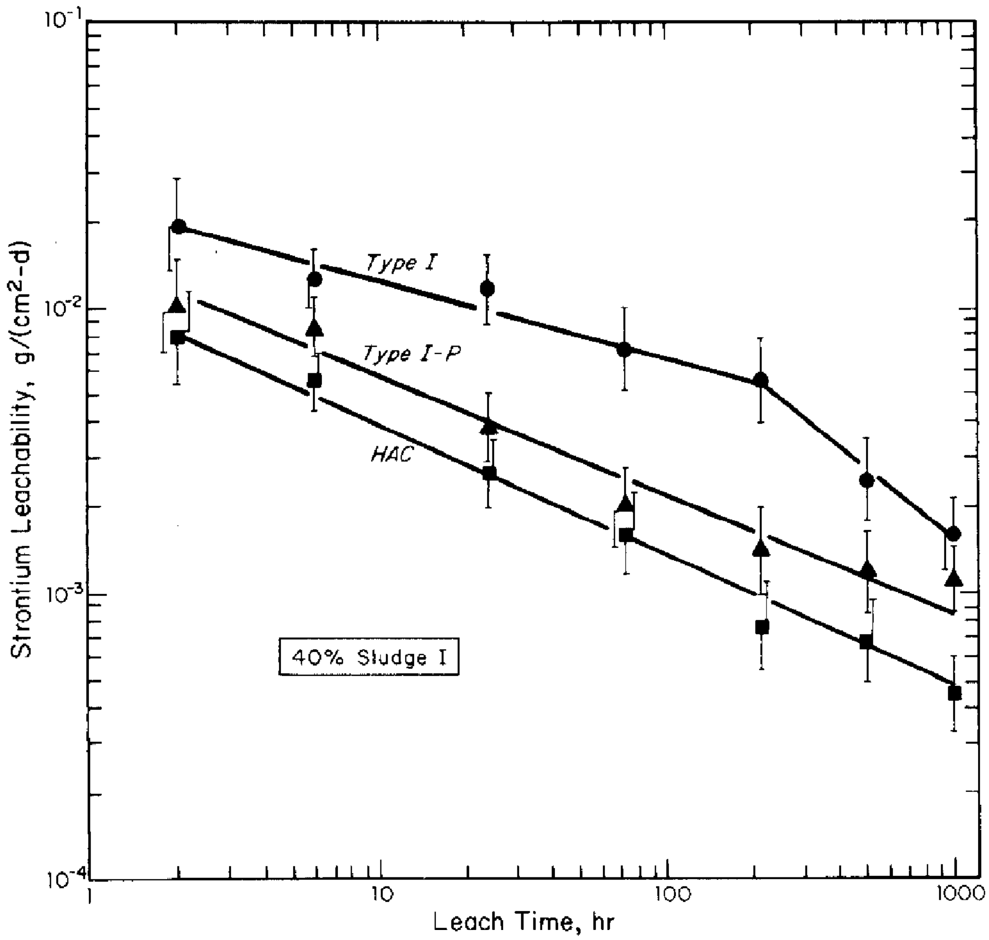

FIGURE 7. Effect of Cement Type on Strontium Leachability

For this combination of sludge type and content, there is a factor of about 4 between the strontium leachabilities of the best cement (HAC) and the worst (Type I), with intermediate values for the other cement types. Other combinations of sludge type and content gave data for the different cement types that spanned narrower ranges, had different orderings of the cement types, and showed crossovers with time.

No single ordering of cement types can be specified for all combinations and time periods. Some general statements can be made about some of the cement types. For example, Types I and II portland cements show significantly poorer behavior (higher leachability) that the other cements for most of the combinations. High-alumina cement gave lower strontium leachabilities than did the portland cements, especially at the higher sludge contents and later time periods. Types III, V, and I-P cements generally showed intermediate behavior, although each was best in a few combinations and worst in others. The lower leachability of HAC is attributed to chemical effects: portland cements react with water to precipitate $Ca(OH)_2$, which would be expected to carry strontium; however, high-alumina cement reacts with water to precipitate $Al(OH)_3$, which has less affinity for strontium. $Ca(OH)_2$ and $Al(OH)_3$ are easily leached from hardened concrete. Thus, in the leaching process, strontium should follow $Ca(OH)_2$ to a greater extent than it would follow $Al(OH)_3$.

Because the effect of cement types was considerably smaller than the effects of sludge types and sludge content and because the statistical interaction of cement type and sludge content was of only minor significance, a reasonable display of all the strontium leach data can be obtained by averaging over the cement types (in addition to the average over duplicate specimens and different water contents). The data treated in this way are shown in Table 9, where each entry is the average of 36 measurements.

TABLE 9

Strontium Leachabilities Averaged Over Cement Types

Sludge		*Sr Leachability, 10^{-3} g/(cm²)(d), for Hours Leached*[a,b]						
Type	*Content, %*	*2*	*6*	*24*	*72*	*216*	*504*	*1008*
None	0	5.2	4.7	2.7	1.4	0.82	0.35	0.20
I	10	11	6.7	3.4	1.6	0.88	0.37	0.24
	25	11	6.1	3.3	1.9	1.1	0.76	0.43
	40	11	8.1	4.9	3.0	1.9	1.5	1.0
II	10	6.6	4.8	2.5	1.4	0.57	0.41	0.32
	25	6.6	4.6	2.7	1.6	0.82	0.49	0.45
	40	7.3	5.2	3.2	1.8	0.89	0.64	0.74
III	10	3.9	3.0	1.8	0.98	0.48	0.26	0.15
	25	3.3	2.3	1.2	0.69	0.31	0.18	0.098
	40	2.7	1.6	0.65	0.41	0.15	0.093	0.071

a. Each entry is the average of 36 measurements.

b. Error factor ε (95% confidence) varies from 1.09 to 1.25, depending on the sludge type and time period.

The trend of sludge types, for all time periods, is easily seen to be

Sludge I > Sludge II > Sludge III

where Sludge III has the lowest strontium leachability. This order of sludge types holds for all sludge contents, except for the later time periods with 10% sludge content, where the order of Sludge I and Sludge II is reversed.

Other information derived from the experimental data includes cumulative fractions leached and power laws of time behavior.

The incremental fraction Δf and the cumulative fraction f of strontium leached from each specimen were calculated from the experimental data by

$$\Delta f = \Delta m/FM \text{ and } f = \Sigma(\Delta f)$$

where M = mass of the leach specimen. The minimum detectable value of f after six weeks leaching ranged from 0.001 with Type V cement to 0.005 with HAC. Measured values of f after six weeks were typically 0.05 to 0.10 for specimens with Sludge I, 0.03 to 0.06 with Sludge II, and 0.02 to 0.05 with Sludge III. Some notable exceptions included specimens with HAC and Type I cement, with 40% Sludge III, which had $f \approx 0.005$, and a few specimens with Type I cement and 40% Sludge I, which had $f \approx 0.4$. From tabular L and Δt data such as in Table 9, f can be determined from the relationship:

$$\Delta f = (A/M)(L\Delta t)$$

Leachability L is independent of the size of the object leached, but the fraction leached depends upon the ratio of surface area to volume. Thus, the fraction leached from a plant-size concrete waste form (2-ft diameter x 10-ft height) would be about 3% of that from the laboratory leach specimens.

Most of the experimental data may be represented by a power law for the time behavior. Thus, L was found to be proportional to t^{-n}, where values of n from 0.3 to 1.0 were found for individual specimens. Much of the data is adequately represented with $n = 0.5$. Mathematical models which predict the time dependence of L are available.[29] A variety of theoretical expressions have been derived using different assumptions for the leaching mechanisms, including diffusion, dissolution, and others. Models usually have simple limiting equations for the asymptotic behavior at short and long times. For example, with leaching by diffusion only, L is proportional to $t^{-\frac{1}{2}}$, and this model appears to be applicable to most of the strontium leach data up to six weeks leaching. Some models predict that at long times L will become constant and independent of time; such behavior was not observed in the present experiments. Although qualitative comparisons of the data with models were made, extensive fitting of the data with theoretical expressions was beyond the scope of the study.

Plutonium Leachability

Leach tests for plutonium were similar to those for strontium, although more limited in scope. The factors studied were leach time, cement type, sludge type, and sludge content. Specimens from the pastes with ideal workability only were used, so that water content was not a factor. Results of the leach tests indicate that concrete has very low plutonium leachability. The principal conclusions from the plutonium leach data are:

- Plutonium leachabilities are about 1000 times lower than strontium leachabilities.
- Plutonium leachabilities range from 10^{-5} g/(cm^2)(d) after 2 hr to 10^{-8} g/(cm^2)(d) after 12 weeks leaching.
- Plutonium leachabilities are strong functions of time, but cement type, sludge type, and sludge content had little effect.

Experimental Procedure. The experimental arrangement for the plutonium leach tests was the same as for strontium leach tests, except that all operations were conducted in a radioactive hood. Each leach specimen was about 2.5 cm long and contained 5×10^7 dis/min of ^{239}Pu. Plutonium in leach water samples was determined by alpha counting. A preliminary experiment using the same sampling schedule as for the strontium leach tests gave leach water samples containing plutonium too low to measure. Therefore, a modified sampling schedule, with leach water changes at 2 hours, 42 days, and 84 days was used for the plutonium leach tests. About 150 leach-water samples were generated, containing from 0.1 to 10 dis/(min)(ml) plutonium, with most samples <1 dis/(min)(ml). For radioactive specimens the leachability is calculated from

$$L = \frac{M}{CA} \frac{\Delta C}{\Delta t}$$

where ΔC = activity of plutonium leached during time Δt

= [dis/(min)(ml) of plutonium in leach water] x (volume of leach water)

C = activity of plutonium in leach specimen

Incremental and cumulative fractions leached are given by

$$\Delta f = \Delta C/C \quad \text{and} \quad f = \Sigma(\Delta f)$$

Results. Special problems were encountered with the leach-water samples taken at 42 days (1008 hours). Most of the soluble species in the concrete specimens, such as $Ca(OH)_2$, were leached during this time period, so that aliquots that were evaporated for alpha counting left sizable amounts of solids on the counting plates. The sensitivity and accuracy of the analyses were limited by the solids content. For all the leach-water samples at 1008 hours, only an upper limit of 1 dis/(min)(ml) could be obtained. This corresponds to $L < 1 \times 10^{-7}$ g/(cm^2)(d) and $\Delta f < 5$ ppm (5×10^{-4}%). Only minor amounts of solids were found in the leach-water samples taken at 2 hours and 84 days (2016 hours).

For the remaining 108 measurements of plutonium leachability, an analysis of variance was performed separately for the 2- and 2016-hour time periods. Considering the factors of cement type, sludge content, and sludge type, the statistical treatment was for a 6 x 3 x 3 factorial experiment, not replicated. The statistical analysis showed that sludge content and sludge type were not significant factors in the data at either time period; thus, the data for these factors were averaged. Table 10 gives the plutonium leachabilities, where each entry is the average of nine data points. Mean leachabilities, averaged over 54 data points, also are given for each time period.

TABLE 10

Plutonium Leachabilities for Concrete Waste Forms

Cement Type	*Pu Leachability, 10^{-7} g/(cm^2)(d)*[a]			*Fraction Leached, ppm*
	at 2 hr[b]	*at 1008 hr*	*at 2016 hr*[c]	*at 2016 hr*
I	200	<0.1	0.97	<19
II	160	<1.1	0.59	<12
III	130	<1.0	0.56	<11
V	220	<1.0	0.33	<10
I-P	180	<0.9	0.55	<11
HAC	780	<1.1	0.33	<17
Average[d]	220	<1.0	0.52	<13

a. Each entry is the average of 9 measurements for cement types and 54 measurements for averages.

b. Error factor ε (95% confidence): for cement types, $\varepsilon = 1.59$; for average, $\varepsilon = 1.21$.

c. For cement types, $\varepsilon = 1.81$; for average, $\varepsilon = 1.27$.

d. Geometric mean.

The plutonium leachability decreased monotonically with time. The leachability after 2016 hr was about 400 times less than that after 2 hr. Time of leaching was the only highly significant factor in the data. Of the other factors, cement type was of minor significance at 2 hr, but not at 2016 hr. Plutonium leachability at 2 hr for high-alumina cement was about 4 times greater than for the portland cements; this difference did not occur in the data at 2016 hr. The difference between the various portland cements were not significant at either time period.

Also shown in Table 10 are cumulative fractions of plutonium leached after 2016 hr. The average fraction leached is <13 ppm (<1.3 x 10^{-3}%), and since the contribution to f at 1008 hr is <5 ppm, then 8 < f < 13 ppm. The amount of plutonium leached was extremely small in all cases, which shows that concrete retains plutonium very effectively.

Thermal Stability

Long-term thermal stability was assessed by measuring the compressive strength of concrete-sludge specimens that had been held at 100°C for several months. The normal operating temperature of a waste storage facility is expected to be ∿100°C. Prolonged heating at this temperature causes slow evaporation of capillary water from the concrete, resulting in weight losses of 6 to 16%. Compressive strengths declined slightly for most of the specimens, but were unchanged or were greater than the strength of the unheated specimens in some cases. Typically, the strength of a specimen heated 3 months was 25% less than that of an unheated specimen of the same formulation. The principal features of the compressive strength data for unheated specimens, such as strong dependence on sludge content, also were present in the data for heated specimens. Relatively greater reductions in strength were found for formulations that had unusually high strengths in unheated specimens, for example, high-alumina cement or Sludge II specimens. However, these formulations were superior to others even after heating.

Experimental Procedure. One casting of each concrete-sludge formulation was sawed into two 5-cm long specimens that were distinguished as originating from the top half or the bottom half of the casting. The weighed specimens were placed in a forced-draft laboratory oven at 100°C for prolonged heating. After 1 month, all top-half specimens were removed from the oven for testing, and after 3 months all bottom-half specimens were removed. Each specimen was cooled, weighed, and measured for compressive strength by the same method as with the unheated specimens.

Results. The compressive strength data were treated by an analysis of variance separately for each heating period and sludge type. Thus, each analysis was for a 6 x 3 x 3 factorial experiment, not replicated; as before, the factors were cement type, sludge content, and water content. Results of the statistical treatment were similar to those for unheated specimens. Sludge content was of major significance in every case, cement type was of lesser significance, and water content was not significant. The data showed significant interaction between the cement type and sludge content factors. For comparison with compressive strengths of unheated specimens, the data were averaged over the three water contents. The change in compressive strength after heating for 1 month is given in Table 11, and after 3 months in Table 12. Changes of less than about 20% were not statistically significant.

TABLE 11

Thermal Stability of Concrete Waste Forms
Heated 1 Month at 100°C

Sludge		*% Change[a] in Compressive Strength, for Cement Types*						
Type	*Content, %*	*I*	*II*	*III*	*V*	*I-P*	*HAC*	*Mean[b]*
None	0	- 24	+19	-23	-11	-18	+ 8	-10
I	10	+ 4	+23	-16	- 2	- 1	-13	- 2
	25	+ 13	-14	-15	+10	+ 4	-41	- 9
	40	+144	+ 6	+45	- 2	-22	-44	+ 8
II	10	- 5	-44	-19	-17	- 8	-27	-21
	25	- 26	-34	-19	+ 2	-23	-28	-22
	40	- 38	-36	-36	-26	-33	-26	-32
III	10	- 39	+31	- 9	+ 7	+22	+ 6	0
	25	- 13	+ 7	-21	- 4	-10	- 8	- 8
	40	- 32	-19	-16	- 2	-15	-16	-17

a. Underlined values are statistically significant differences between specimens heated 1 month and unheated specimens.

b. Geometric mean.

TABLE 12

Thermal Stability of Concrete Waste Forms
Heated 3 Months at 100°C

Sludge		*% Change[a] in Compressive Strength, for Cement Types*						
Type	*Content, %*	*I*	*II*	*III*	*V*	*I-P*	*HAC*	*Mean[b]*
None	0	- 15	+ 9	-25	+ 1	-20	+ 3	- 9
I	10	- 24	-13[c]	-24	-13	-41[c]	-10	-22
	25	- 10	- 1	-27	+ 2	-24	-28	-16
	40	+141	+47[d]	+71	+16	-17	-24	+28
II	10	- 24[c]	0[d]	-28	-42[c]	-25	-34	-27
	25	- 26	-16[d]	-23	- 2	-17	-36	-21
	40	- 28	-21[d]	-29	-42[c]	-16[d]	-33	-30
III	10	- 34	+ 8	-22	-23[c]	-12[c]	-12	-12
	25	- 21	+ 2	-27	0	-22	-30	-17
	40	- 14	-28	-12	+ 5	-18	-24	-16

a. Underlined values are statistically significant differences between specimens heated 3 months and unheated specimens.

b. Geometric mean.

c. 3-month value less than 1-month value; statistically significant.

d. 3-month value greater than 1-month value; statistically significant.

The compressive strengths of the heated specimens were generally less than those of unheated specimens. The principal exception was with formulations containing 40% Sludge I, where the unheated specimens were unusually weak. For comparison of sludge types, the data were averaged over cement types, and these mean values also are shown in Tables 11 and 12. With both the 1- and 3-month heating periods, the strength changes are in the order

Sludge II > Sludge III > Sludge I

Among the cement types, the strength of HAC declined most, but its reduced strength was still larger than that of many of the portland cements.

As indicated in Table 12, there are few time trends apparent in the data. In most cases, the strength after 3-months heating was nearly the same as after 1-month heating. In a few cases, the specimens heated 3 months were significantly weaker than those heated 1 month, but in other cases the opposite was found, indicating an increase in strength after an initial loss. The behavior of compressive strength appears to be correlated with the behavior of weight changes; in all of the specimens, most of the weight loss occurred in the first month of heating.

Some examples of compressive strengths and weight losses after heating are given in Table 13, for high-alumina and Type I-P cements, all of which contain 40% sludge. The behavior of Type I-P cement is typical of the portland cements. At 40% sludge content the strength of HAC specimens is comparable to or better than that of unheated Type I-P specimens. Even after considerable reduction in strength because of heating, HAC formulations are superior to those with portland cements. Loss of strength of HAC concretes under hot, wet conditions is a well known phenomenon, believed to be caused by slow conversion of calcium aluminate hydrates to different crystalline forms.[21]

TABLE 13

Typical Properties of Concrete Waste Forms[a] Heated at 100°C

Cement Type	*Heating Time, months*	*Compressive Strength, psi*			*Weight Loss, %*		
		Sludge I	*Sludge II*	*Sludge III*	*Sludge I*	*Sludge II*	*Sludge III*
HAC	0	4364	5884	3371	-	-	-
	1	2433	4359	2838	11.6	6.9	6.3
	3	3313	3948	2546	13.5	7.4	7.8
I-P	0	2380	3311	3088	-	-	-
	1	1865	2228	2639	14.5	6.4	10.6
	3	1980	2779	2534	16.1	7.1	12.1

a. With 40% sludge content.

Typical weight losses on heating were 6 to 14% in the first month, then an additional 1 to 2% loss in the next two months. Largest weight losses were with Sludge I specimens, which also required the largest amounts of water in the formulations. Smallest weight losses were with Sludge II specimens, even though about the same amount of water was required in Sludge II and III formulations; the small weight loss suggests that negligible mercury was lost by decomposition of HgO. Specimens made with high-alumina cement also had significantly smaller weight losses than specimens made with portland cements.

Radiation Stability

A concrete-sludge casting from each formulation was gamma-irradiated to 10^{10} rads, to simulate the total radiation dose expected from self-irradiation by SRP waste over a 100-year storage period. During irradiation, the samples were heated to temperatures up to 95°C by gamma ray absorption. Compressive strength measurements after gamma irradiation gave results that were not significantly different from those for samples exposed only to heat (in thermal stability tests discussed in the previous section). Although the effects of radiation and heat were intermingled, no evidence was found for any effect of radiation on the strength of concrete-sludge specimens.

As a final check on strontium leachability under conditions of high sludge content, heat, and gamma radiation, a small factorial experiment was performed with only sludge type and cement type as factors. Specimens with 40% sludge content and ideal water content were gamma-irradiated and then measured for strontium leachability. In every case, the strontium leachability after six-weeks leaching was markedly lower for irradiated than for unirradiated specimens by factors ranging from 2 to 20. The largest reduction in leachability was exhibited by specimens containing Sludge I, as shown in Figure 8. Again, no adverse effects could be ascribed to radiation.

Experimental Procedure. Castings were gamma-irradiated in a ^{60}Co facility at a dose rate of 3.5×10^7 rads/hr. Figure 9 shows concrete-sludge castings in an irradiation rack designed to hold 76 pieces. The sample-loaded rack was sealed in a special vessel, shown in Figure 10, for placement inside the irradiation facility. Three separate irradiations were made, each about 300 hr for total dose of 10^{10} rads. Because the irradiation facility was not continuously available, each irradiation required about three weeks. With forced-air cooling, the irradiation temperatures were 65 to 95°C. One casting from each of 168 formulations was irradiated for compressive strength tests. An additional casting of 24 formulations (6 with no sludge and 6 with each simulated sludge at 40% loading) was irradiated for subsequent measurements of strontium leachability. Experimental methods for both tests were the same as described previously.

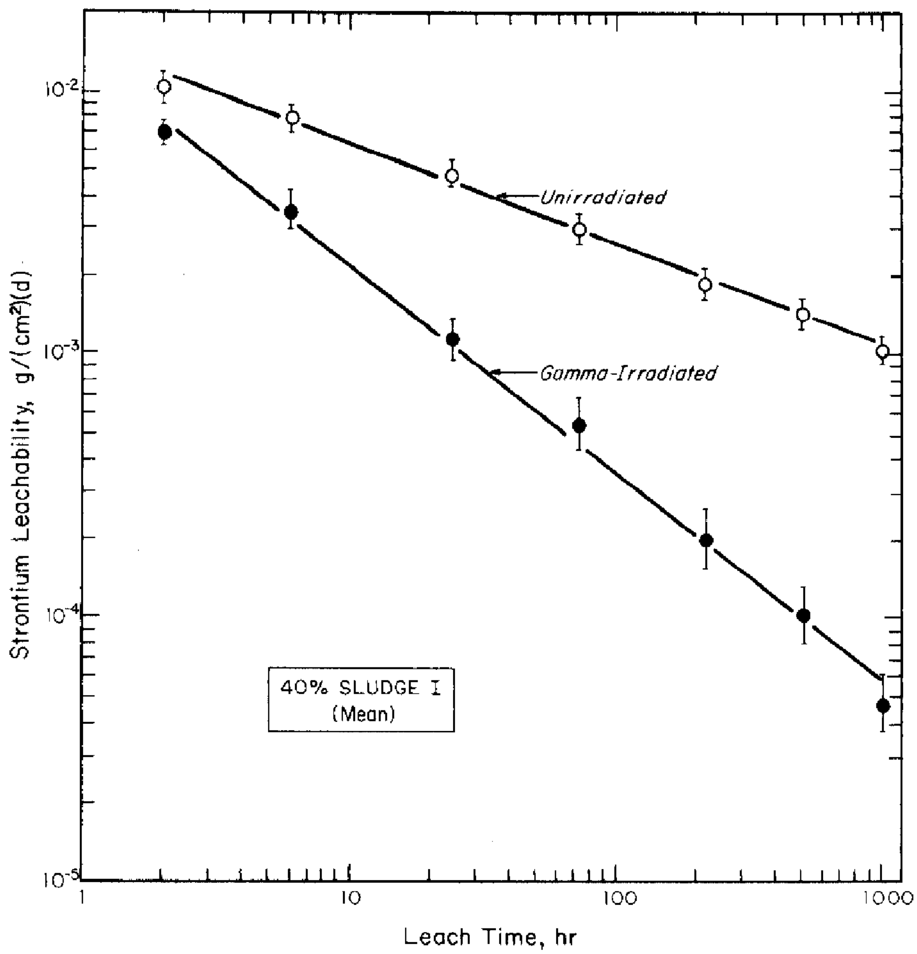

FIGURE 8. Effect of Gamma Irradiation on Strontium Leachability

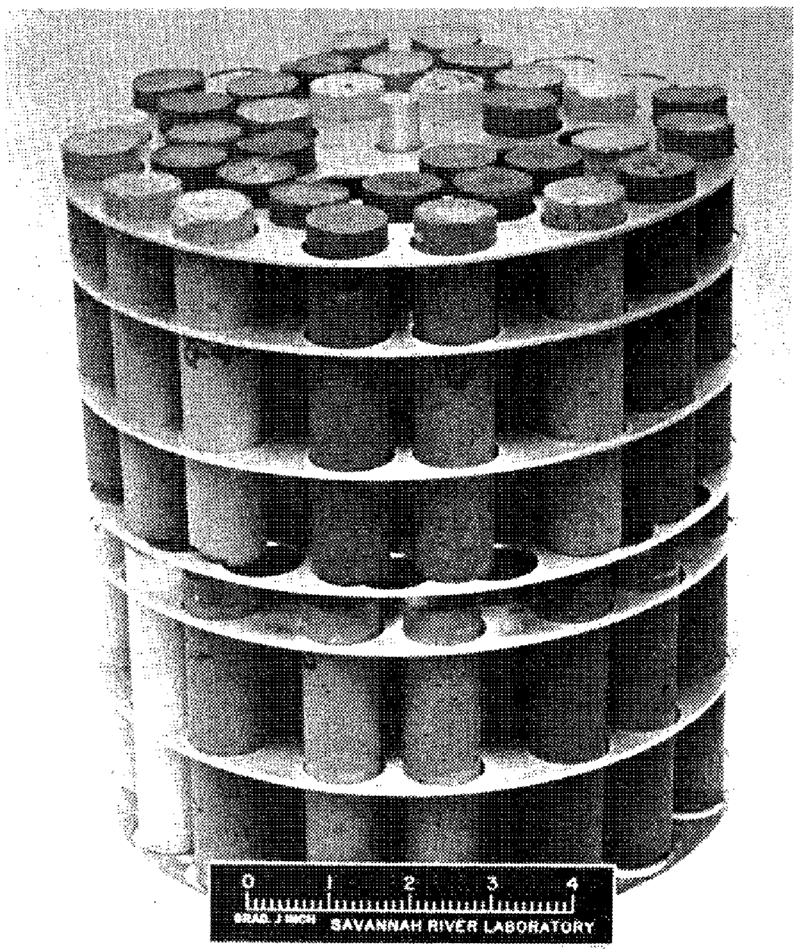

FIGURE 9. Irradiation Rack for Concrete-Sludge Castings

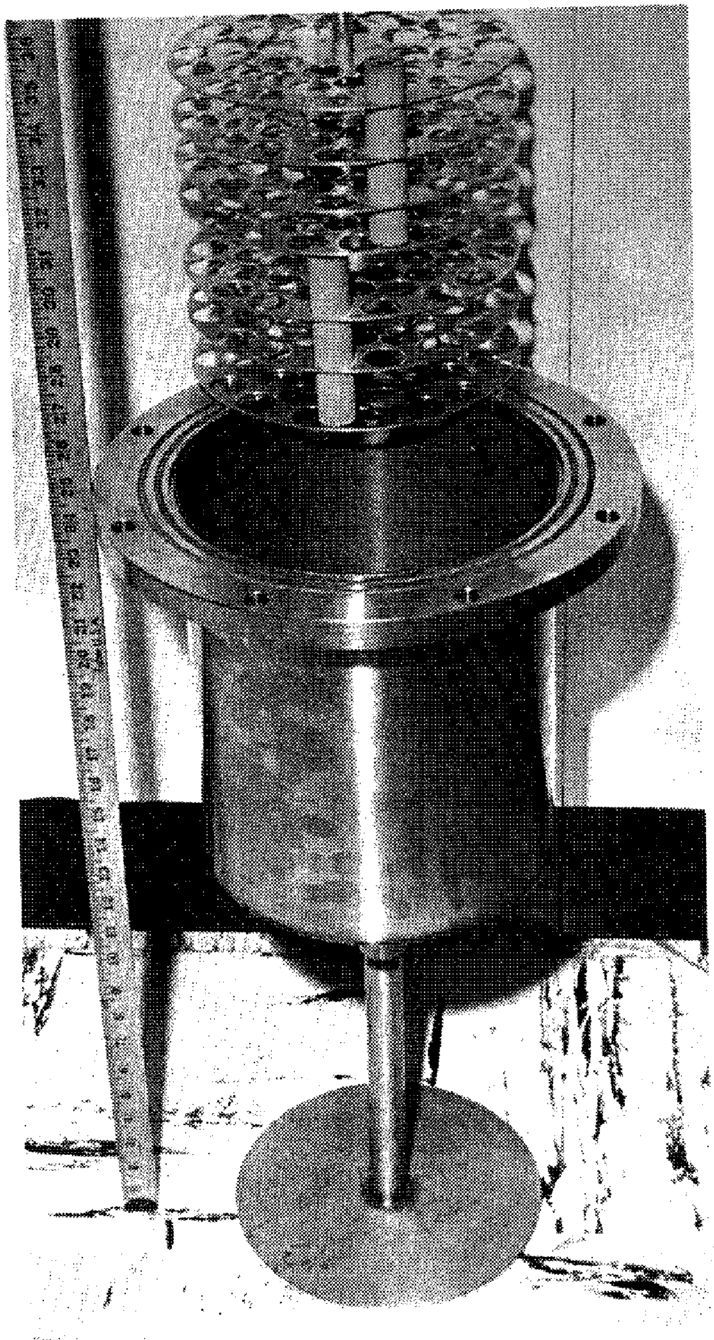

FIGURE 10. Vessel for Gamma Irradiations

Results. The compressive strength data were treated statistically with an analysis of variance for each sludge type separately. Each statistical analysis was for a 6 x 3 x 3 factorial experiment with duplicate samples, the factors being cement type, sludge content, and water content. The principal features of compressive strength behavior of concrete-sludge specimens again were found with the gamma-irradiated specimens: sludge content was of predominant significance, cement type was less significant, and water content was not statistically significant. The data were averaged over water contents and duplicate specimens to give compressive strengths that are the average of six data points.

The compressive strengths of irradiated and unirradiated specimens are compared in Table 14, which gives the percent difference in strength after irradiation. Changes less than about 20% were not statistically significant. The data are very similar to those for thermal stability (Tables 11 and 12), even though the experimental conditions were quite different. Most of the compressive strengths for gamma-irradiated specimens were not statistically different from those of specimens heated for thermal stability tests. Exceptions are for specimens containing 40% Sludge II and specimens containing Type I-P cement, all of which are significantly stronger than the heated samples. Because the irradiated specimens also were heated, the effects of radiation and heat are intermingled. Many of the reductions in strength can be attributed to heat alone, but none to radiation alone.

Strontium leachabilities of other irradiated specimens were measured.

Specimens of castings irradiated for strontium leachability tests formed a 6 x 3 factorial experiment with duplicate samples. The factors were the six cement types and the three sludge types, each combination having 40% sludge content and ideal water content. In addition, specimens with each cement type and no sludge were irradiated and leached. As before, the strontium leach tests were performed at seven time periods, from 2 to 1008 hours. An analysis of variance was made for each time period separately. The effect of sludge type was highly significant at all time periods. The effect of cement type was not statistically significant, except for the first and last time periods. The data were averaged over cement types and duplicate specimens to give strontium leachabilities that are the average of 12 data points.

TABLE 14

Radiation Stability of Concrete Waste Forms Gamma Irradiated to 10^{10} rads

Sludge		% Change[a] in Compressive Strength, for Cement Types						
Type	*Content, %*	*I*	*II*	*III*	*V*	*I-P*	*HAC*	*Mean*[b]
None	0	- 12	+ 3	-10	-16	+10	+ 3	- 4
I	10	- 27	-20	-28	-29	- 6	-20	-22
	25	- 17	- 6	-34	-11	+ 1	+ 2	-12
	40	+134	-17	+ 9	- 7	-17	-15	+ 6
II	10	- 23	-38	-12	-23	+ 9	-28	-20
	25	- 14	-15	+ 4	-15	+ 4	-23	-10
	40	+ 3	+21	+ 7	+ 3	+11	-13	+ 5
III	10	- 34	- 9	-23	-23	-12	+ 4	-17
	25	- 25	-19	-35	- 6	+ 3	- 7	-16
	40	- 19	-13	-25	+ 1	- 7	+19	- 8

a. Underlined values are statistically significant differences between irradiated and unirradiated specimens.

b. Geometric mean.

Table 15 shows the time behavior of strontium leachability for each sludge type. These data also are compared with similarly averaged values for unirradiated specimens as percent differences in leachability after irradiation. Changes less than about 30% were not statistically significant. Strontium leachability of the irradiated specimens also decreased monotonically with time, as shown in Figure 8. For every sludge type, the strontium leachability was generally lower for the irradiated than for the unirradiated specimens. The differences were particularly striking after 1008-hr leaching; the leachability for Sludge I specimens was lower by a factor of ∿20 (Figure 8), and was lower for Sludge III specimens which approach 1×10^{-5} g/(cm^2)(d). For irradiated specimens the strontium leachability decreased in the order

Sludge II > Sludge I > Sludge III

For 40% sludge content, this ordering reverses the positions of Sludges I and II from that for unirradiated specimens.

Neither the strontium leachability nor the compressive strength measurements showed large differences among the cement types for irradiated specimens. In the leach tests, no significant differences were found, except at 2 hr and at 1008 hr. In both cases, the strontium leachabilities of HAC specimens did not decrease as much as those of portland cement specimens. At these two times, the average value for HAC was about a factor of two larger than those for the other cements. At 40% sludge content, the compressive strengths of HAC specimens were significantly larger than those of the other cements, with average values of 3723, 5095, and 4003 psi for Sludges I, II, and III, respectively. The corresponding values for Type I-P cement specimens were 1983, 3684, and 2868 psi.

TABLE 15

Strontium Leachability of Selected Concrete Waste Forms Gamma Irradiated to 10^{10} rads

Time, hr	*Sr Leachability,[a,b,c] 10^{-3} g/(cm^2)(d), and % Change, for Sludge Types*							
	No Sludge		*40% Sludge I*		*40% Sludge II*		*40% Sludge III*	
2	7.7	(+48%)	7.1	(-33%)	6.5	(-12%)	2.8	(+ 4%)
6	4.2	(-10%)	3.6	(-56%)	4.4	(-15%)	1.6	(+ 2%)
24	2.3	(-14%)	1.2	(-77%)	1.8	(-42%)	0.43	(-34%)
72	1.3	(-11%)	0.55	(-82%)	1.4	(-25%)	0.17	(-59%)
216	0.47	(-43%)	0.20	(-89%)	0.65	(-27%)	0.047	(-69%)
504	0.32	(- 9%)	0.10	(-93%)	0.41	(-36%)	0.022	(-76%)
1008	0.092	(-53%)	0.048	(-95%)	0.28	(-62%)	0.011	(-84%)

a. % change given in parentheses; underlined values are statistically significant differences between irradiated and unirradiated specimens.

b. Each leachability value is the average of 12 data points.

c. Error factors ε (95% confidence) range from 1.10 to 1.30.

Selection of Optimum Cement Types

The principal conclusions with regard to cement selection are:

- High-alumina cement was superior to all the portland cements.
- Type I-P cement was slightly better than other portland cements.

On the basis of the compressive strength and strontium leachability tests, HAC was clearly superior. In the thermal and radiation stability tests, HAC specimens underwent larger changes than portland cements but still had as good or better properties. The portland cements were quite similar to each other in all properties measured, and all were poorer than HAC. Of the portland cements, Type I-P had the best all-around properties, especially at 40% sludge content.

In further studies with concrete-sludge waste forms, only HAC and Type I-P cement were used. The portland-pozzolanic cement was carried into the next phase of the evaluation in case any severely undesirable property were found later for HAC. With simulated sludges, HAC and Type I-P cement formulations were used to investigate the effects of adding cesium-loaded zeolite and of heating concrete-sludge beyond 100°C. These studies are described in the following sections. Finally, HAC and Type I-P cement were used in formulations with actual SRP waste sludges, described in the latter portion of this report (page 71).

Effects of Adding Cesium-Loaded Zeolite

Two series of concrete formulations were prepared containing cesium-loaded zeolite that was tagged with ^{137}Cs tracer. One of the series contained simulated sludges at 40% sludge content but with 1/16 of the sludge replaced by cesium-loaded zeolite. This mixture has been proposed as a means of equally distributing the heat from decay of SRP ^{137}Cs waste among the solid waste forms. The other series contained cesium-loaded zeolite at contents up to 40%, but with no sludge. The formulations were evaluated by measuring their compressive strengths and cesium leachabilities. Specimens with only cesium-loaded zeolite were superior to those with the sludge-zeolite mixture. For example, a formulation with HAC and 40% cesium-loaded zeolite had $\sim$11,000 psi compressive strength and $\sim 10^{-5}$ g/(cm^2)(d) cesium leachability after six weeks leaching; the corresponding values with 37.5% Sludge III and 2.5% zeolite were $\sim$3,000 psi and $\sim 10^{-3}$ g/(cm^2)(d). However, either set of specimens provided adequate durability and fair retention of cesium. The results of these studies indicate that additions of cesium-loaded zeolite have no adverse effect on concrete waste forms.

Preparation of Specimens

A solution of $CsNO_3$ containing ^{137}Cs tracer was prepared by dissolving 3.90 g (0.02 mole) of $CsNO_3$ in 500 ml water and then adding ~350 µl of ^{137}Cs tracer [nominally 2.15×10^{10} dis/(min)(ml)]. This solution was quantitatively sorbed on wet zeolite to form the starting material for incorporation into concrete. The sorbed cesium solution contained 8.50×10^9 dis/min of ^{137}Cs, or 3.20×10^9 dis/(min)(g) of cesium.

The zeolite used was a chabazite, 20-50 mesh *Linde* AW-500*, known to have a high capacity for sorbing cesium ions. 1000 g of the dry zeolite was equilibrated with water, drained, and then equilibrated with the ^{137}Cs tracer solution described above. The cesium-loaded zeolite was filtered to remove supernatant liquid and rinsed with 20 ml of water. The filtrate and rinsings contained negligible cesium (~0.03% of the original amount). The product, 1634 g of wet cesium-loaded zeolite, was used as stock material for incorporation into various concrete formulations. For convenience, the wet weight was employed for defining the formulations.

As shown in Table 16, six formulations were prepared with 37.5% simulated sludge and 2.5% zeolite, and six other formulations were prepared with no sludge and up to 40% zeolite. Each series formed a 2 x 3 factorial experiment with the factors cement type and sludge type in the first series, and cement type and zeolite content in the second. The cement types were HAC and Type I-P. In Table 16, the water/cement ratio is given for the amount of water actually added for ideal workability and also for an amount calculated by including water from the wet zeolite. The W/C values for total water agree fairly well with those in Table 4.

The formulations were prepared with the same mixing equipment as used previously for preparing nonradioactive formulations, except that the work was done in a radioactive hood. The procedure was essentially the same; each formulation contained 600 g of solids plus sufficient water for ideal workability. Six castings of each formulation were made, cured for 28 days, and then sawed into specimens for compressive strength and leach tests. These

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measurements were made by the same methods as those described for specimens without cesium-loaded zeolite, except that additional precautions in handling and radiation shielding were employed (see pages 26 and 31).

TABLE 16

Formulations Containing Cesium-Loaded Zeolite

Sludge Type	*Sludge Content,*[a] *wt %*	*Zeolite Content,*[a] *wt %*	*Water/Cement Ratio, for Cement Types*			
			HAC		*Type I-P*	
			Added	*Total*[b]	*Added*	*Total*[b]
I	37.5	2.5	0.576	0.592	0.708	0.724
II	37.5	2.5	0.478	0.494	0.572	0.588
III	37.5	2.5	0.475	0.491	0.534	0.550
None	0	10	0.247	0.290	0.330	0.373
None	0	25	0.231	0.360	0.342	0.471
None	0	40	0.214	0.473	0.287	0.546

a. % of total solids (sludge + cement + wet zeolite).

b. Including water in the wet cesium-loaded zeolite (39 wt %).

Compressive Strength

Specimens containing cesium-loaded zeolite had compressive strengths equal to or greater than specimens with sludge only. This comparison is shown in Figure 11 for HAC specimens and in Figure 12 for Type I-P cement specimens. In these figures, the data for sludge-containing specimens were averaged over the three sludge types. Also shown are the averaged data for the formulations with 37.5% sludge and 2.5% cesium-loaded zeolite. The compressive strengths of these specimens were similar to those with 40% sludge. In the tests with cesium-loaded zeolite, the strengths with HAC were generally greater than with Type I-P cement.

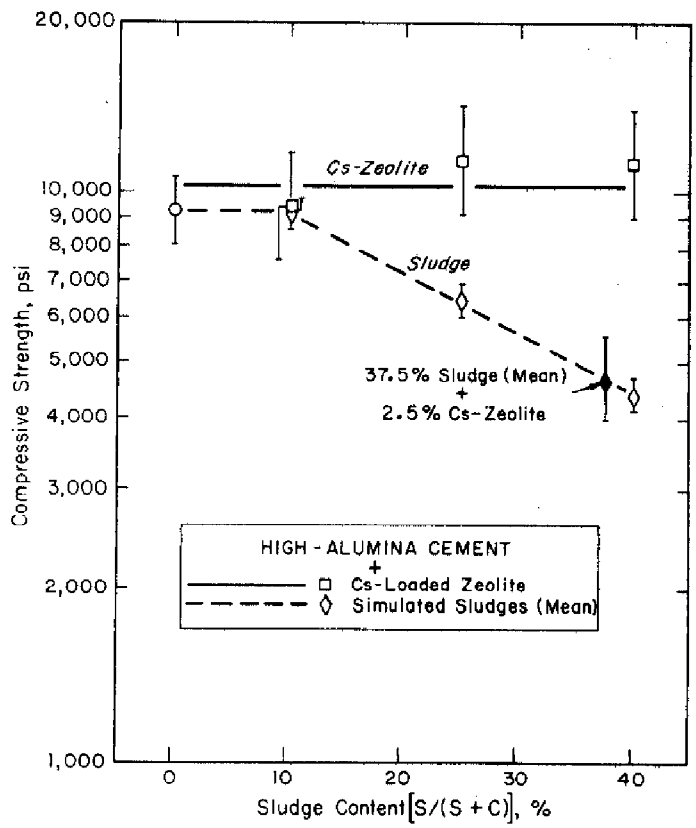

FIGURE 11. Compressive Strength of High-Alumina Cement Waste Forms Containing Cs-Zeolite

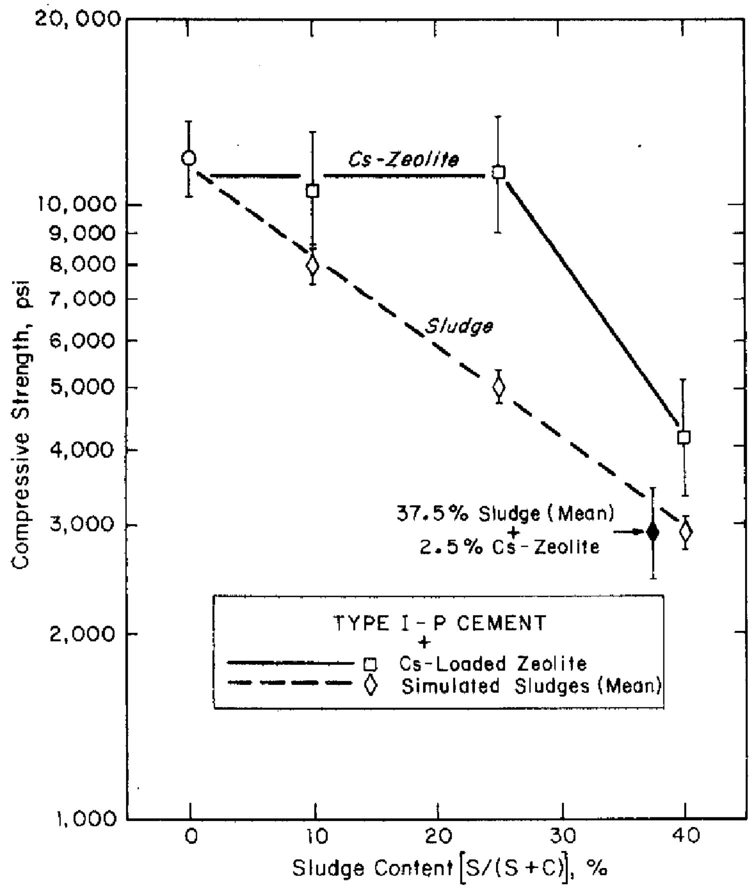

FIGURE 12. Compressive Strength of Type I-P Cement Waste Forms Containing Cs-Zeolite

Experimental Procedure. For the compressive strength measurements, the cesium-loaded zeolite/concrete castings were sawed, measured, and tested in a shielded cell facility. Except for provisions for remote handling with master-slave manipulators, the experimental equipment and procedure were identical to those used for nonradioactive specimens. Duplicate specimens of each formulation were tested.

Results. Compressive strengths for both series of concrete formulations are given in Table 17, averaged over the duplicate specimens. The data were treated by an analysis of variance for each series separately. For the series with sludge-zeolite mixtures, both the factors cement type and sludge type were statistically significant, but the interaction between them was not significant. For the series with zeolite only, both the factors cement type and zeolite content and their interaction were significant. Also shown in Table 17 is a comparison of the data with compressive strengths of counterpart specimens with sludge only, expressed as percent difference. Differences of less than about 25% were not statistically significant.

TABLE 17

Compressive Strength of Concrete Waste Forms Containing Cesium-Loaded Zeolite

Sludge Type	*Sludge Content, wt %*	*Zeolite Content, wt %*	*Compressive Strength,[a,b] psi, for Cement Types* HAC	Type I-P
I[c]	37.5	2.5	5,055(+ 16%)	2,880(+ 21%)
II[c]	37.5	2.5	6,892(+ 17%)	3,864(+ 17%)
III[c]	37.5	2.5	3,020(- 10%)	2,194(<u>- 29%</u>)
None	0	0	9,311[e]	11,916[e]
None	0	10[d]	9,452(+ 3%)	10,546(<u>+ 33%</u>)
None	0	25[d]	11,481(<u>+ 76%</u>)	11,279(<u>+123%</u>)
None	0	40[d]	11,344(<u>+156%</u>)	4,141(<u>+ 43%</u>)

a. % change from compressive strength with sludge instead of cesium-loaded zeolite, given in parentheses; underlined values are statistically significant differences.

b. Each entry is the average of 2 data points.

c. Error factor (95% confidence): $\varepsilon = 1.35$.

d. Error factor (95% confidence): $\varepsilon = 1.25$.

e. From Table 6.

The formulations with 37.5% sludge and 2.5% zeolite had compressive strengths that were not significantly different from those for formulations with 40% sludge; one exception was for Type I-P cement with Sludge III, for which the specimens containing zeolite were significantly weaker. The order of cement types, for all the sludge types, was HAC > I-P, the same as for formulations with sludge only. The order of sludge types, for both cement types, was Sludge II > Sludge I > Sludge III. This ordering is the same as for 40% sludge formulations with HAC, but reverses the order of Sludges I and III with Type I-P cement. As shown in Figures 11 and 12, specimens containing the sludge-zeolite mixtures or sludge alone are considerably weaker than specimens containing no sludge or zeolite alone.

The formulations with zeolite alone had compressive strengths that were independent of both cement type and zeolite content, up to 40% zeolite with HAC, and up to 25% zeolite with Type I-P cement. Within experimental error, these strengths were the same as for the formulations with no sludge. At 40% zeolite with Type I-P cement, the strength dropped off but was still significantly stronger than for 40% sludge with Type I-P cement. The behavior of zeolite in concrete is unusual because other additions, such as gravel in commercial concrete, normally reduce the strength.

Cesium Leachability

The magnitudes of cesium leachability values for concrete waste forms containing cesium-loaded zeolite were comparable to those of strontium leachability from concrete containing sludge. The cesium leachability ranged from 10^{-6} to 10^{-1} g/(cm^2)(d), depending on the formulation and the time of leaching. The data were strongly time dependent, approximately following a $t^{-1/2}$ law, as shown in Figure 13. Typical cesium leachabilities for the two series of formulations also are compared in Figure 13. The leachability for specimens containing zeolite only was 10 to 400 times lower than for specimens containing the sludge-zeolite mixture. The leachability decreased with increasing zeolite content. HAC specimens were generally less leachable than Type I-P cement specimens, with one notable exception, shown in Figure 13.

Experimental Procedure. For the leachability measurements the cesium-loaded zeolite/concrete castings were sawed, measured, and tested. A total of 25 leach tests (duplicate specimens of 12 formulations and a blank) were conducted, using the experimental procedure described previously. Leach-water samples (175) were analyzed for ^{137}Cs by measuring gamma activity; from 1 to 570 dis/(min)(ml) were found from the concrete specimens and <1 dis/(min)(ml) from the blank.

Results. Data for the series with sludge-zeolite mixtures are given in Table 18 and for the series with zeolite only in Table 19. The cesium leachabilities shown are averages over the duplicate specimens. The data were treated by an analysis of variance for each series and time period, separately. For the sludge-zeolite series, the factors cement type and sludge type were both statistically significant at all time periods, and their interaction was significant at all time periods except 2 hr. For the series with zeolite only, the factor cement type was significant only at 72, 216, and 504 hr, but zeolite content was highly significant at all time periods. Surprisingly, their interaction was significant at all time periods.

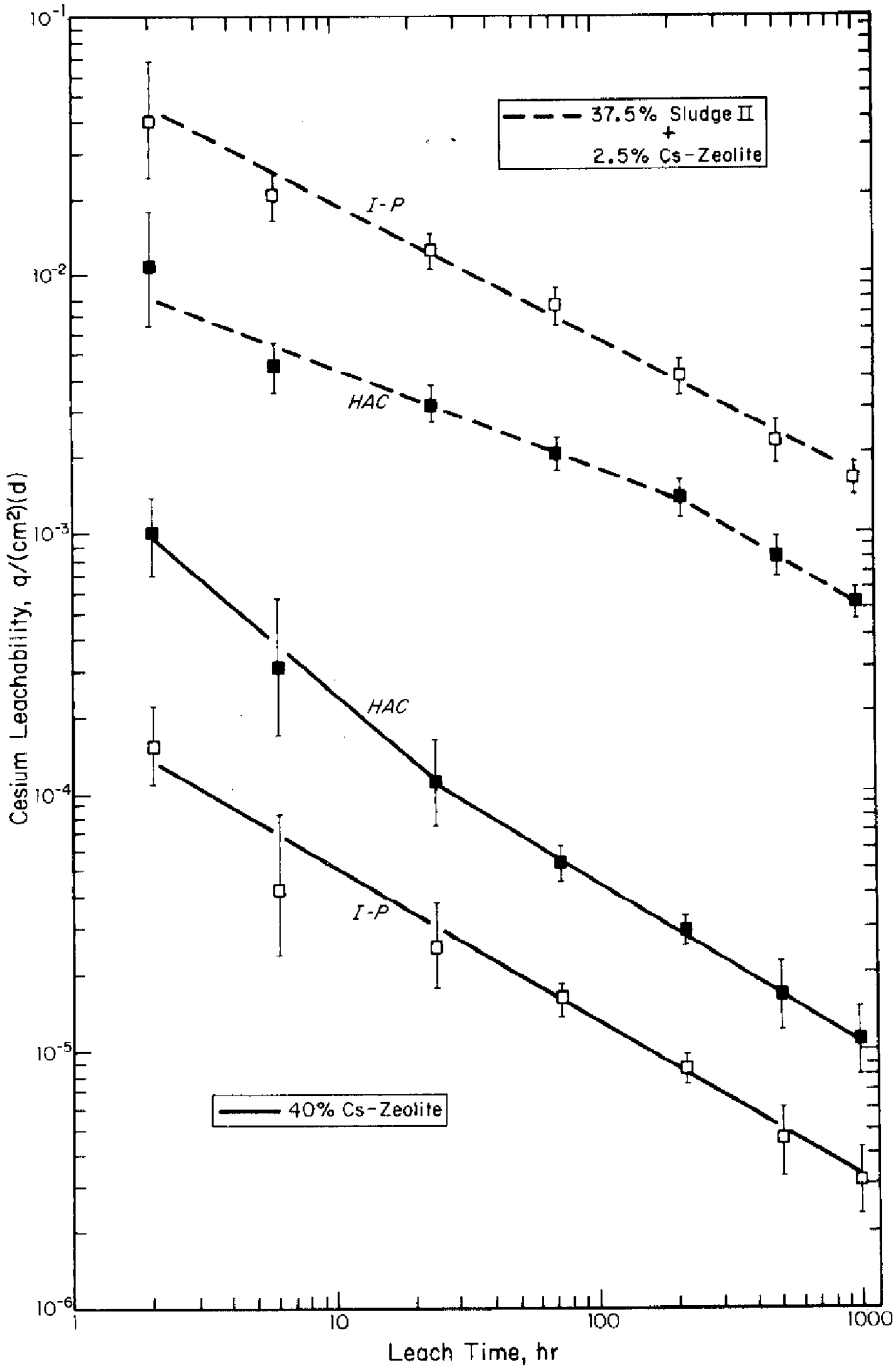

FIGURE 13. Cesium Leachability of Concrete Waste Forms Containing Cs-Zeolite

TABLE 18

Cesium Leachability of Concrete Waste Forms Containing 37.5% Simulated Sludge and 2.5% Cesium-Loaded Zeolite

Cement Type	*Sludge Type*	*Cs Leachability,*[a,b] 10^{-3} *g/(cm²)(d), for Leach Time* 2 hr	6 hr	24 hr	72 hr	216 hr	504 hr	1008 hr	*% Cesium*[a] *Leached at 1008 hr*
HAC	I	26	12	7.6	4.2	1.9	0.79	0.44	6.4
	II	11	4.5	3.2	2.0	1.4	0.81	0.53	4.3
	III	42	25	13	7.0	3.5	1.8	1.1	13.1
I-P	I	54	27	14	7.5	3.5	1.7	1.1	14.0
	II	40	20	13	7.6	4.1	2.3	1.6	14.7
	III	67	45	20	10	5.2	2.6	1.5	20.5

a. Each entry is the average of 2 data points.

b. Error factors ε (95% confidence) range from 1.13 to 1.69.

TABLE 19

Cesium Leachability of Concrete Waste Forms Containing Only Cesium-Loaded Zeolite

Cement Type	*Zeolite Content, wt %*	*Cs Leachability,*[a,b] 10^{-3} *g/(cm²)(d), for Leach Time* 2 hr	6 hr	24 hr	72 hr	216 hr	504 hr	1008 hr	*% Cesium*[a] *Leached at 1008 hr*
HAC	10	1.8	0.74	0.41	0.18	0.10	0.045	0.051	0.39
	25	1.4	0.61	0.20	0.11	0.054	0.032	0.023	0.22
	40	1.0	0.31	0.11	0.054	0.029	0.016	0.011	0.12
I-P	10	6.2	2.4	1.3	0.81	0.46	0.24	0.17	1.63
	25	1.9	0.94	0.50	0.30	0.16	0.090	0.059	0.62
	40	0.15	0.044	0.026	0.016	0.0085	0.0046	0.0031	0.03

a. Each entry is the average of 2 data points.

b. Error factors ε (95% confidence) range from 1.14 to 1.85.

In the data for formulations with 37.5% sludge and 2.5% cesium-loaded zeolite, time has the greatest effect on cesium leachability. The leachabilities are from $\sim 10^{-1}$ g/(cm^2)(d) at 2 hr to $\sim 10^{-3}$ g/(cm^2)(d) at 1008 hr. The order of cement types, for all sludge types and time periods, is HAC < I-P; this is consistent with the compressive strength results and shows that HAC formulations have superior properties. The order of sludge types changes with time and differs for HAC and Type I-P cement formulations. With HAC, Sludge II is less leachable than Sludge III for all time periods. With HAC, Sludge I at 2 hr is about as leachable as Sludge III and then is intermediate between the other two sludges until 504 hr when it is about the same as Sludge II. With Type I-P cement, Sludge I is less leachable than Sludge III after 6 hr; with Type I-P cement, Sludge II is about as leachable as Sludge I until 504 hr when it is about as leachable as Sludge III. These orderings of sludge types are generally consistent with the compressive strength results. As shown in Figure 13, specimens containing the sludge-zeolite mixture have considerably larger cesium leachability than have specimens containing zeolite alone.

For the formulations with zeolite alone, at each time period the mean (averaged over all the zeolite contents) for HAC is nearly equal to the mean for Type I-P cement. However, for individual zeolite contents, the time curves for HAC and Type I-P cement are widely separated (Figure 13). This fortuitous behavior accounts for the rather minor significance of cement type in the analysis of variance and for the strong cement type - zeolite content interaction. Actually, highly significant differences exist between cement types at all time periods and zeolite contents: HAC < I-P at 10 and 25% zeolite, but at 40% zeolite, I-P < HAC. The remarkably low cesium leachability in the latter case [$\sim 10^{-4}$ g/(cm^2)(d) at 2 hr, to $\sim 10^{-6}$ g/(cm^2)(d) at 1008 hr] is not consistent with other properties of Type I-P cement formulations, and is unexplained. The cesium leachability decreased monotonically with increasing zeolite content for both cement types at all time periods. This is illustrated in Figure 14 for the data at 1008 hr.

The decrease in cesium leachability with increasing zeolite content is also correlated with decreasing cement content. This suggests that cesium ions and ions produced during hydration of the cement compete for sites on the zeolite. Large numbers of calcium and/or aluminum ions are generated in the course of the reaction between cement and water. To the extent that some of these ions displace cesium on the zeolite, the cesium leachability will be increased. With less cement, fewer calcium and aluminum ions will form, and thus, the cesium leachability will decrease. All of the data, including those for the sludge-zeolite mixtures, are qualitatively consistent with this model. Quantitatively, the situation is more complex because changes in cesium leachability are not proportional to changes in the cement/zeolite ratio. For the formulations with simulated sludges, an additional factor is present. Each of the sludges contains a small amount of sodium (Table 2), and sodium ions also can compete with cesium ions for sites on the zeolite. The order of sludges for sodium content is Sludge III > Sludge I > Sludge II, and interestingly, this is identical to the ordering of the sludges for cesium leachability from the sludge-zeolite mixtures at early time periods.

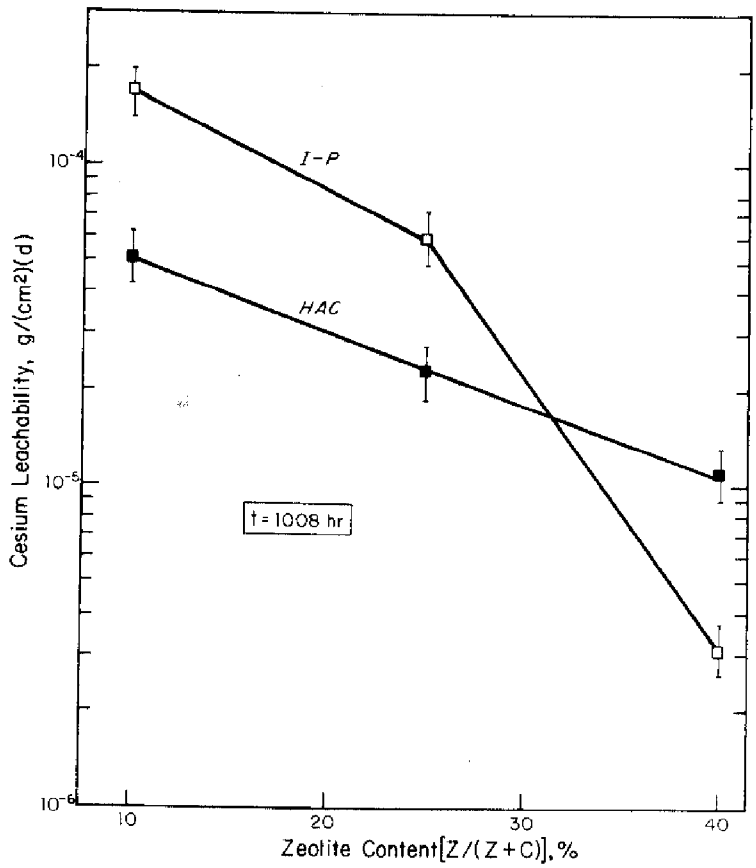

FIGURE 14. Effect of Zeolite Content on Cesium Leachability

Also shown in Tables 18 and 19 are the cumulative fractions of cesium leached from each formulation after 1008 hr, expressed as percent of the cesium originally present in the solid. Since the activity of ^{137}Cs tracer (C) was directly proportional to the cesium content, C was used in calculations of fraction leached and cesium leachability. C for a leach specimen was taken as 1/27 (the approximate volume ratio) of the total ^{137}Cs activity added to the formulation as cesium-loaded zeolite; for example, for specimens containing 2.5% zeolite, C = 2.89 x 10^6 dis/min. The cumulative fraction f of cesium leached from specimens containing sludge-zeolite mixtures was not negligible, ranging from 10 to 20%. However, as pointed out earlier, f is a function of the specimen size; f = 10% for laboratory specimens corresponds to f = 0.3% for plant-size monoliths. Values of f for specimens containing zeolite only are quite small, even for laboratory-size specimens.

Effects of Heating Concrete-Sludge Specimens

In current proposals for long-term management of SRP wastes, solid waste forms would be stored in a retrievable surface storage facility for about 100 years. Heat would be produced in the solid forms from radioactive decay of nuclides in the waste, principally ^{90}Sr and ^{137}Cs. Cooling by natural convection would give an ambient temperature of $\sim$100°C in the storage facility. The solid waste forms would be encased in sealed metal containers. Detailed information is required on the thermal properties of the waste forms, not only at the ambient temperature but also under postulated conditions of abnormally high temperatures.

For concrete waste forms, several studies of thermal effects were made in addition to the thermal and radiation stability measurements described earlier. Thermal analyses included measurements of thermal conductivity, weight change, heat evolved, and gases evolved, as a function of temperature. Pressures generated by heating concrete waste forms in a closed container were measured. The times required for concrete waste forms held at temperatures up to 1000°C to show signs of mechanical failure were determined. These studies are described in the following sections.

Thermal Analyses

Two types of thermal analyses were made. Thermal conductivity values, required for engineering calculations of temperatures in concrete waste forms, were measured at 100 and 200°C for selected concrete specimens containing simulated sludges. The thermal conductivities ranged from 0.2 to 0.7 (Btu)(ft)/(hr)(ft^2)(°F) and were similar to values for ordinary concrete.[18] Differential thermal analyses (DTA), thermogravimetric analyses (TGA), and effluent-gas analyses (EGA) were made as a function of temperature up to 1000°C. These analyses were useful in characterizing the various chemical changes that occurred in sludges and concretes when heated. The principal feature of heating concrete waste forms was massive evolution of water from 100 to 500°C.

Thermal Conductivity. Specimens of eleven SRL concrete-sludge formulations were supplied to Brookhaven National Laboratory (BNL) for thermal conductivity measurements. In the procedure reported by BNL, thermal conductivity measurements were made at 100, 200, and again at 100°C, after equilibrating the samples for 30 minutes at each temperature. As confirmed by weight changes, the samples contained substantial free water during the initial measurement at 100°C, but were in a dried condition for the 200°C and second 100°C measurement. Samples containing Sludge II were heated to 200°C before testing to remove any residual mercury, so that all three measurements were for the dried condition with these samples. Results of the thermal conductivity measurements are given in Table 20.

TABLE 20

Thermal Conductivity of Selected Concrete Waste Forms

Cement Type	*Sludge Type*	*Sludge Content, wt %*	*K, (Btu)(ft)/(hr)(ft²)(°F)* 100°C (Not Dry)	100°C (Dry)	200°C (Dry)
HAC	None	0	0.70	0.49	0.63
	III	10	0.53	0.44	0.62
	III	25	0.51	0.37	0.59
	I	40	0.53	0.30	0.58
	II	40	0.33[a]	0.36	0.51
I-P	None	0	0.51	0.37	0.56
	III	10	0.50	0.35	0.56
	III	25	0.45	0.29	0.42
	III	40	0.41	0.24	0.36
	I	40	0.42	0.25	0.46
	II	40	0.20[a]	0.24	0.34

a. Dried condition because of preheating to 200°C.

Several trends are apparent in the data for thermal conductivity, K. At 100°C, samples containing free water have larger K than the dried samples. For dried samples, values of K at 200°C are larger than at 100°C. K is larger for HAC samples than for the corresponding samples with Type I-P cement. K decreases with increasing sludge content. No trends are evident among the sludge types. The thermal conductivity of concrete-sludge samples compares favorably with that of commercial concrete, for which a typical value of K is 0.5 (Btu)(ft)/(hr)(ft^2)(°F).

DTA-TGA-EGA. These analyses were made in SRL facilities. TGA and EGA were performed simultaneously by heating the sample, measuring the weight loss, and determining gases evolved with a mass spectrometer. On a separate DTA instrument, heat absorbed or evolved was measured as a function of temperature. The three analyses taken together characterize many of the thermal properties of a material and assist in identifying the reactions that occur. An example of DTA-TGA-EGA data is shown in Figure 15 for a typical portland-cement concrete.

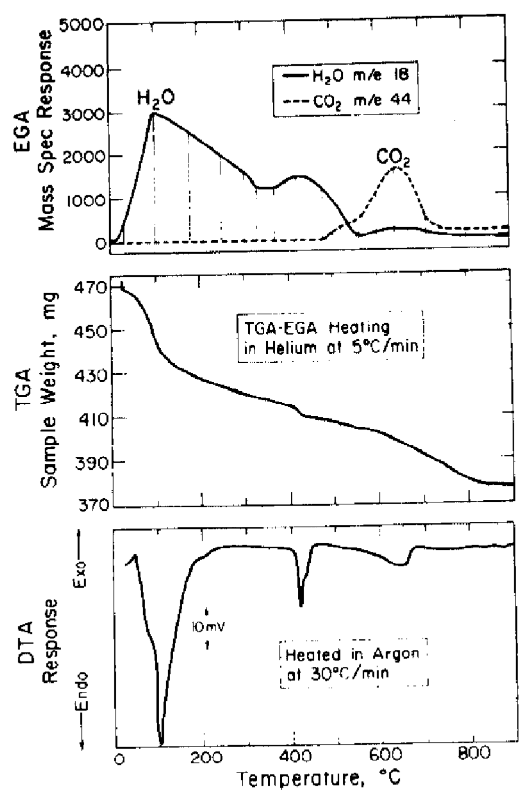

FIGURE 15. Typical DTA-TGA-EGA Data for Concrete

Samples of concrete-sludge specimens, of concrete alone, of simulated sludges alone, and of individual sludge components were investigated by DTA-TGA-EGA. Results are summarized in Table 21, which gives the temperature ranges over which reactions, principally dehydrations, occur in typical concrete-sludge samples. The behavior of each simulated sludge was essentially a superposition of the individual components. Similarly, concrete-sludge samples gave a superposition of the individual behavior of the concrete and the sludge. The largest effect of heating a concrete-sludge specimen occurs near 100°C, where copious amounts of water are evolved from dehydration reactions in the concrete and in some of the sludge components. At somewhat higher temperatures, the sludge components dehydroxylate and HgO decomposes. MnO_2 converts to lower oxides, with evolution of oxygen, at temperatures below 900°C. The thermal behavior of $Ca(OH)_2$ and $CaCO_3$, present in portland-cement concrete, is given in Table 21, although these compounds are not present in concretes made with HAC and Type I-P cement.

TABLE 21

Reactions in Heated Concrete Waste Forms[a]

Temperature Range, °C	*Reactant*	*Solid Product*	*Gaseous Product*	*Remarks*
25-200	Concrete	Dry Concrete	H_2O	Sorbed, capillary, and crystallization water
	$Al_2O_3 \cdot xH_2O$	$Al(OH)_3$	H_2O	In HAC; Sludge I; Sludge II
	$MnO_2 \cdot xH_2O$	MnO_2	H_2O	Continues up to 500°C
200-250	$Fe_2O_3 \cdot xH_2O$	Fe_2O_3	H_2O	
350-450	$Al(OH)_3$	γ-Al_2O_3	H_2O	In HAC; Sludge I; Sludge II
	HgO	--	Hg, O_2	
	$Ca(OH)_2$	CaO	H_2O	In portland-cement concretes
500-550	MnO_2	Mn_2O_3	O_2	
500-800	$CaCO_3$	CaO	CO_2	From $Ca(OH)_2$ + CO_2 in air
800-900	Mn_2O_3	Mn_3O_4	O_2	

a. From DTA-TGA-EGA data.

Pressure Generated in Closed Containers

In the proposed process for solidification of SRP waste, concrete waste forms would be stored in closed metal containers and cooled by natural convection to ∿100°C. Pressure effects were evaluated to ensure that steam buildup from heating would not lead to rupture of the storage containers. Tests were performed to define the consequences of postulated loss of cooling or external heatup during storage of the concrete waste forms. Heating test specimens in a closed chamber created pressures of 450 to 500 psig at 240°C, which closely approximates the vapor pressure of water. However, by preheating at 150°C prior to sealing, the pressure can be limited to ∿50 psig at 240°C.

Experimental Procedure. The test chamber for pressure measurements is shown in Figure 16. The apparatus was designed to contain one of the 2.5 x 11.5-cm cylindrical concrete castings and have nominally 63% void volume. The chamber was heated in a laboratory oven to a maximum temperature of 240°C. The test volume was connected to a pressure transducer via a short length of tubing outside the heated zone; this line contained water as a fluid for transmitting the pressure. Thermocouples measured the temperature inside the chamber, at its outer surface, and in the oven volume. The thermocouples and pressure transducer were connected to a strip-chart recorder for continuously recording measurements.

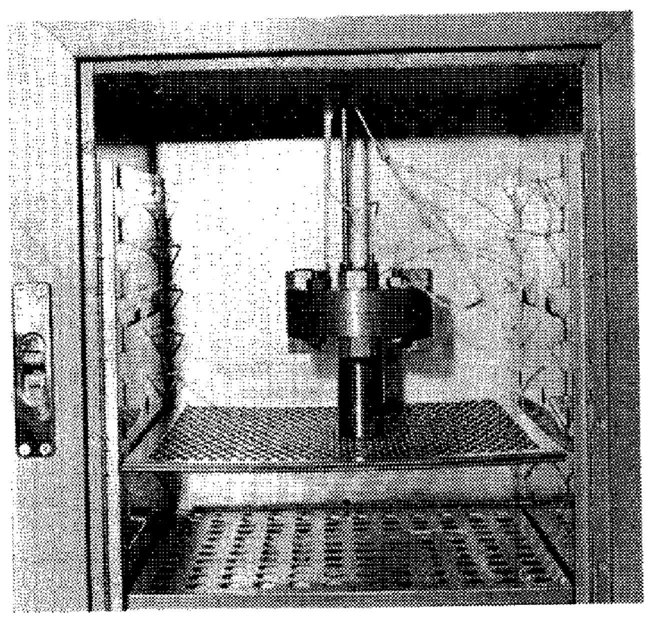

FIGURE 16. Pressure Measurement Chamber for Concrete Waste Forms

The experimental procedure consisted of sealing a concrete casting in the chamber, evacuating it at ambient temperature, and then increasing the oven temperature in steps while monitoring the pressure. The system was allowed to reach equilibrium, generally in 1 to 2 hr, at 100, 150, and 200°C; then was held at the maximum oven temperature, ~240°C, for 24 to 48 hr; and finally, the system was cooled to ambient temperature in one step. Several well-cured concrete waste forms representing a variety of cement types, sludge types, and sludge contents were studied. The pressures generated by heating the castings were independent of these factors.

Results. Data for a typical test are shown in Figure 17. The observed pressures agree closely with those predicted from steam tables.[30] Final pressures of 450 to 500 psig were observed at 240°C. When the temperature was lowered to ambient, the concrete reabsorbed all the water, and the pressure returned to its initial value. This behavior suggests that no gases other than water vapor were formed during heating and agrees with the thermal analysis results (Table 21). The reversible release of capillary water and some of the chemically bound water, both as steam, accounts for the experimental data of Figure 17.

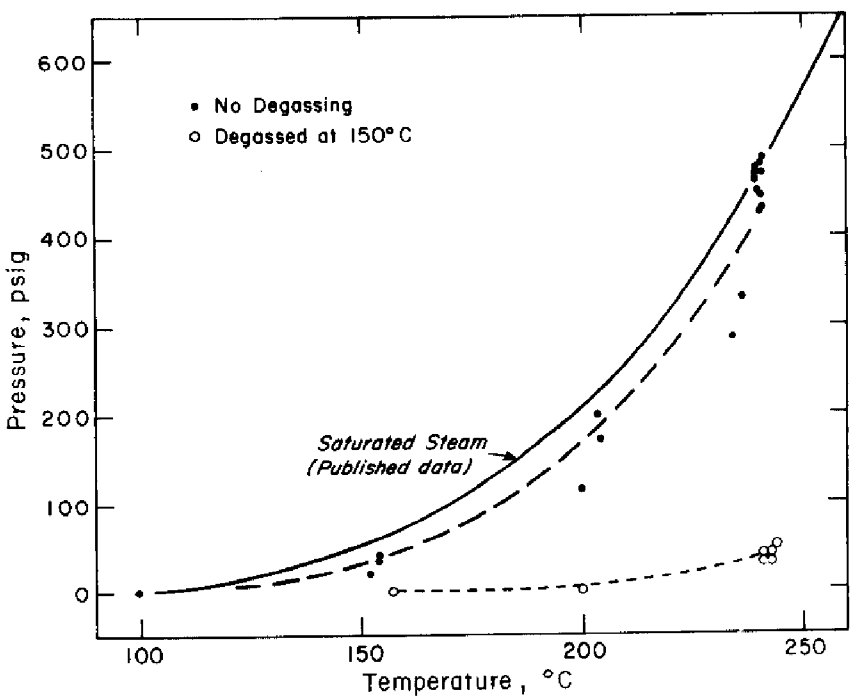

FIGURE 17. Pressures from Heating Concrete Waste Forms

For plant-size concrete-waste cylinders, these data indicate that high pressures could develop if cooling were interrupted in the storage facility or during postulated external heatup. Thus, the cylinder canisters must be designed to withstand steam pressures at the highest temperature that might occur. Alternatively, a method of reducing maximum pressures might be developed. Two methods of pressure reduction were studied: use of a desiccant that might reduce the pressure in the test chamber by absorbing water liberated from the concrete, or a preliminary degassing step before sealing the chamber. In laboratory tests, neither dry cements nor soda lime reduced the final pressure in the test chamber.

To determine the effect of a preliminary degassing step, samples of cured concrete were heated for 5 to 6 hr at 150°C to expel capillary water, then sealed in the test chamber, and heated to 240°C. As shown in Figure 17, the final pressures were typically ~50 psig instead of ~500 psig. This technique may be useful for reducing steam pressures in plant-size concrete cylinders, although the larger forms may require longer preheating times at higher temperatures.

Time to Failure at Various Temperatures

Prolonged heating at temperatures up to 1000°C causes concrete to lose its structural integrity. Several tests were made to determine how long concrete-sludge specimens could withstand elevated temperatures before giving evidence of mechanical failure. Specimens held at 200 and 400°C for 150 days did not fail, but at 1000°C, some of the specimens failed after only 10 minutes. Behavior at 600 and 800°C was between these extremes. At the higher temperatures, specimens made with HAC withstood heating considerably better than specimens made with Type I-P cement.

Experimental Procedure. Castings of six formulations were sawed into wafers ~1.2 cm high for the time-to-failure tests. Five wafer specimens of each formulation were required, one for each of five temperatures to be investigated. Specimens were placed in open crucibles in laboratory muffle furnaces operated at 200, 400, 600, 800, and 1000°C. Six specimens of the different concrete-sludge types were heated at the same time in one of the furnaces. The specimens were tested for mechanical failure periodically by removing the crucibles from the furnace, lifting the wafer with tongs, and gently squeezing the wafer. At failure the specimens would break, crumble, or disintegrate. Although very qualitative, this simple test was quite effective; the possibility that repeated applications of the test could contribute to premature failure was recognized. The specimens were checked with decreasing frequency as the heating time progressed. Time intervals ranged from five minutes initially to two weeks after several months heating. Number of failure tests per specimen ranged from 2 for specimens that failed at 10 minutes to 40 for specimens that did not fail after 150 days.

Results. Data from the time-to-failure tests are given in Table 22. At 200 and 400°C, the tests were discontinued after 150 days (3600 hr) each, with all of the specimens intact. Heating of four specimens at 600°C was discontinued at 100 days; two specimens containing Type I-P cement with simulated sludges failed earlier. At 800°C, two specimens containing HAC were heated for ~28 days without failure before the tests were discontinued; the other four specimens failed much earlier. These same four types of specimens failed almost immediately at 1000°C, and a specimen with HAC and Sludge I failed after 1 day; however, an HAC specimen without sludge was heated at 1000°C for ~14 days without failure.

TABLE 22

Time to Failure of Heated Concrete Waste Forms

Cement Type	*Sludge Type*	*Sludge Content, wt %*	*Heating Time Before Failure,[a] hr*				
			200°C	*400°C*	*600°C*	*800°C*	*1000°C*
HAC	None	0	>3600	>3600	>2400	>665	>334
	I	40	>3600	>3600	>2400	>649	24
	III	40	>3600	>3600	>2400	30	0.25
I-P	None	0	>3600	>3600	>2400	2	0.17
	I	40	>3600	>3600	428	1.5	0.17
	III	40	>3600	>3600	212	2	0.17

a. > indicates time a test was discontinued without failure.

The results give the order of magnitude of time available for corrective action should abnormally high temperatures occur in a waste storage facility; months up to 400°C, weeks at 600°C, only a few hours at 800°C, and minutes at 1000°C. The specimens with sludge failed earlier in most cases than specimens without sludge; this is consistent with the lower compressive strength of specimens containing sludge. At 600°C and above, the HAC specimens were appreciably better than those with Type I-P cement. HAC concrete is well known as a refractory[21] (used as a mortar with firebrick, for example), and although additions of sludge tend to accelerate time of failure, the HAC-sludge concretes have excellent heat resistance.

INCORPORATION OF ACTUAL SRP WASTE SLUDGES INTO CONCRETE

Treatment of Radioactive Sludges

For use in waste solidification studies, nine batches of sludge from three SRP tanks were processed in shielded cells. A total of 4.3 kg of washed, dried sludge was prepared. Details of the sludge collection, processing, and analyses are given in another report.[3] The treatment of the radioactive sludges was similar to that given to freshly precipitated simulated sludges, described earlier. The principal difference in the procedures was that for the radioactive sludges the solid and liquid phases were separated by settling, decantation, and filtration, rather than by centrifugation. Small amounts of sodium, sulfate, and ^{137}Cs remained in the sludges after thorough washing. The sludge products were complex mixtures of more than 30 elements, principally in the form of hydrous oxides. The major elements found in the product sludges from SRP Tanks 5, 13, and 15 are shown in Table 23. The specific activities of principal radionuclides in the product sludges are given in Table 24.

TABLE 23

Chemical Composition of Washed, Dried SRP Waste Sludges

Element[a]	*Wt % (mol %)*[b] *in Sludges from SRP Tanks*		
	Tank 5	*Tank 13*	*Tank 15*
Fe	27.5 (39.6)	27.9 (39.9)	3.1 (3.9)
Mn	10.8 (15.9)	8.8 (12.8)	2.3 (2.9)
Al	1.5 (4.6)	7.1 (21.0)	33.5 (86.2)
U	15.4 (5.2)	4.0 (1.3)	0.9 (0.3)
Na	6.1 (21.6)	3.1 (10.7)	1.2 (3.6)
Ca	0.6 (1.3)	2.3 (4.7)	0.2 (0.4)
Hg	0.1 (-)	2.1 (0.8)	0.9 (0.3)
Ni	5.1 (7.1)	0.5 (0.7)	0.5 (0.6)

a. Major elements only.

b. Calculated from sum of elements without O, N, or C.

TABLE 24

Major Radionuclides in Washed, Dried SRP Waste Sludges

Radionuclide	*Specific Activity of Sludges, mCi/g*		
	Tank 5	*Tank 13*	*Tank 15*
^{90}Sr	74.7	15.5	25.6
^{144}Ce	4.8	2.0	16.9
^{106}Ru	2.7	0.4	1.7
^{125}Sb	0.4	0.1	1.3
^{154}Eu	0.5	0.3	1.2
^{137}Cs	1.3	0.3	0.1
Gross α	0.1	0.3	0.1

The following procedure was used for processing Tank 13 sludge; similar operations were performed on sludges from Tanks 5 and 15. Each of four 3-liter batches of sludge collected from Tank 13 was allowed to settle, the supernate decanted, and the sludge dried in an oven at ∿140°C. The dried sludge was washed with ∿4 liters of water, allowed to settle and then decanted. Each batch was washed again and then redried. For further washing, the four batches were combined and washed with ∿12 liters of water on a stainless steel filter frit. Filtration was not practical for earlier washes because the sludge was gelatinous before the bulk of soluble salts was removed. A final drying and pulverization yielded 1375 g of powdered sludge product for incorporation into concrete waste forms.

The composition of Tank 5 sludge is believed to be representative of sludges from Purex process wastes. As expected, iron and manganese were the principal components. The uranium content was higher than for the other sludges, but was consistent with other data for Tank 5. This sludge was more difficult to wash than the others and had a higher content of sodium and residual anions. These usually soluble components appeared to be fixed in the sludge because very little could be removed by vigorous leaching.

Sludges from Tank 13 and Tank 15 were expected to be representative of combined Purex and HM process wastes. Tank 13 sludge contained principally iron, aluminum, and manganese, as expected. Tank 15 sludge was anomalously high in aluminum. Mercury was expected in larger quantities than was found in either the Tank 13 or the Tank 15 sludges. Thus, the samples obtained may not be representative of material deeper in the sludge layers.

Specific activities of all the major fission products were determined (except ^{147}Pm, which was not determined because lengthy separation procedures would have been required). Total radioactivities in the washed, dried sludges were ∿85 mCi/g for Tank 5 sludge, ∿20 mCi/g for Tank 13 sludge, and ∿50 mCi/g for Tank 15 sludge. ^{90}Sr was the principal radionuclide in each of the sludges. Most of the ^{137}Cs in the original sludges was washed out, but a residual quantity of 3 to 12% appeared to be fixed in the product sludges. The highest ^{137}Cs content was found in washed Tank 5 sludge, which also had high residual sodium. The alpha radioactivity was low in each of the sludges, and consisted only of ^{238}Pu, ^{239}Pu, and ^{244}Cm in detectable amounts.

Preparation of Radioactive Concrete-Sludge Specimens

Concrete castings containing actual SRP waste sludges were prepared in shielded cells by methods similar to those used for the nonradioactive castings. The waste forms were evaluated with a 2 x 3 x 3 factorial experiment for 2 types of cement (HAC and Type I-P), 3 types of sludge (from Tanks 5, 13, and 15), and 3 levels of sludge content (10, 25, and 40%). From these 18 cement-sludge formulations, 108 castings were made for evaluation. In one formulation, a rapid set time was observed, which led to further studies described in a later section of this report. Two formulations also incorporated a small amount of zeolite loaded with cesium from SRP waste supernate. Water/cement ratios for best workability were determined, and these data were fit with the mathematical model described earlier.

The radioactive formulations were prepared with the same or duplicate equipment as used for the nonradioactive formulations. The equipment was modified for remote operation with master-slave manipulators. An in-cell mixing operation is shown in Figure 18. The mixing bowl was provided with an outlet for transferring a paste directly into molds, when coupled to a vibrator as shown in Figure 19. About 800 g of each cement-sludge-water formulation was prepared, from which six castings were made. A series of freshly poured castings is shown in Figure 20.

In one preparation, with a formulation of HAC and 40% sludge from Tank 13, the mixture set in about 5 minutes, which was insufficient time to make castings. Additional water was added to the set material, primarily to remove it from the bowl before hardening, and castings were made of this mixture. In two subsequent formulations with HAC and 40% sludge from Tanks 5 or 15, excess water (about 20% more than required for ideal workability) was added to prevent rapid setting. In the other formulations with either HAC or Type I-P cement, the correct amount of water was used, and no rapid setting was observed.

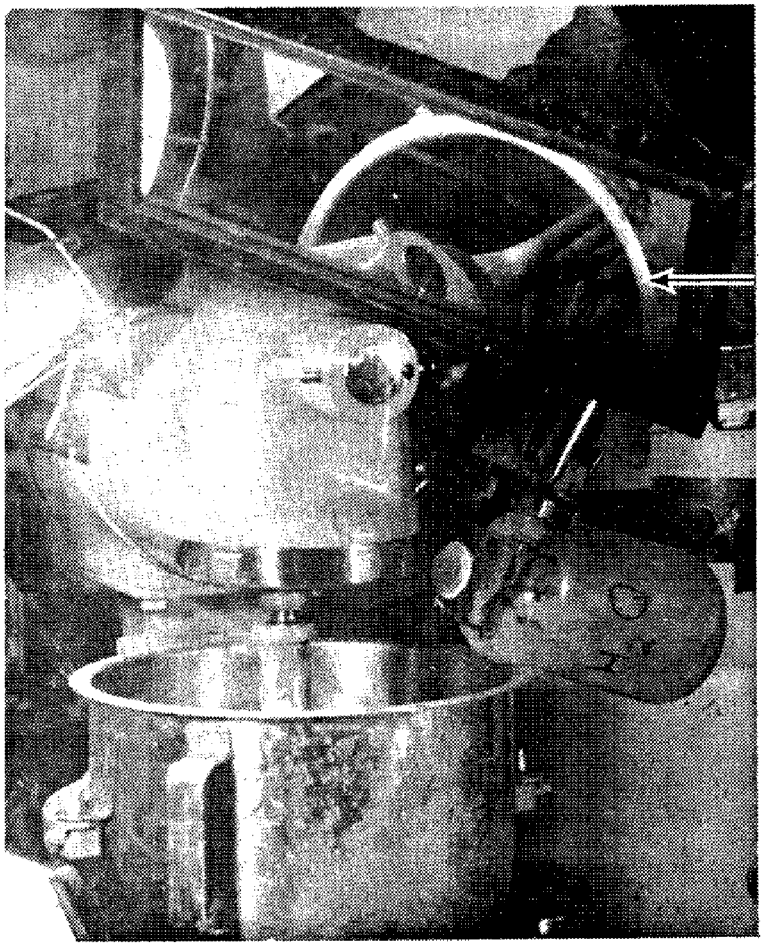

FIGURE 18. In-Cell Mixing of Cement Paste with Actual SRP Sludge

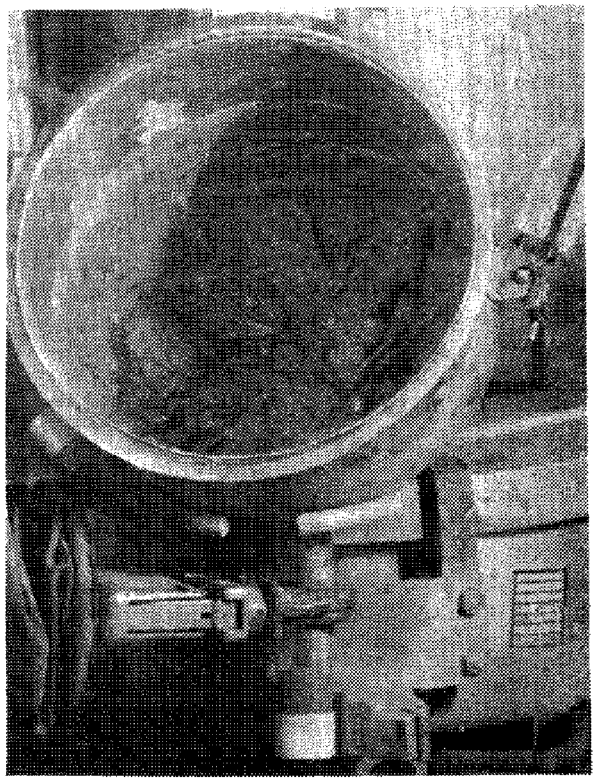

FIGURE 19. Transfer of Radioactive Cement-Sludge Paste to Mold

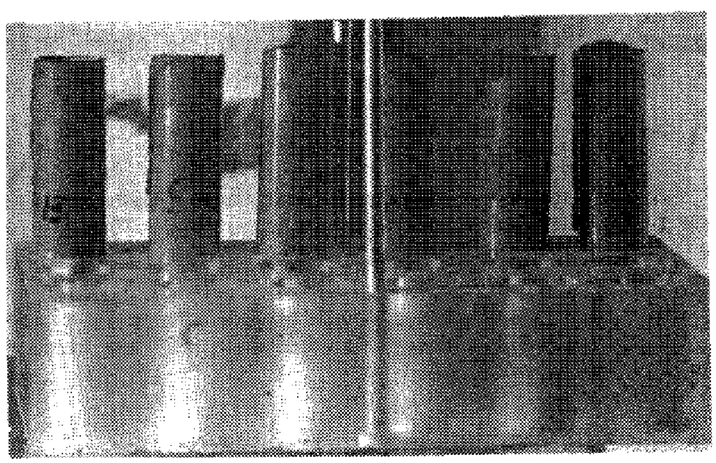

FIGURE 20. Freshly Poured Castings of Concrete with Actual SRP Sludge

A small amount of zeolite loaded with cesium from actual SRP supernate was available from another investigation which is reported separately.[6] To evaluate the effects of zeolite additions to radioactive sludge in concrete, this zeolite material was incorporated with sludge into two of the formulations. 43.0 g of dry cesium-loaded zeolite was washed twice with water to give 73.5 g of wet zeolite, which contained 1.22×10^{11} dis/(min)(g) of ^{137}Cs (wet). Formulations containing 37.5% sludge from Tank 15 and 2.5% of the zeolite (dry equivalent weight) were prepared with HAC and with Type I-P cement. In both formulations, 360 g of cement, 225 g of sludge, and 25.6 g of wet cesium-loaded zeolite (equivalent to 15 g of dry zeolite) were mixed with the appropriate amount of water.

Twelve castings of two additional formulations containing only cement and water were prepared, for a total of 120 castings. After curing for 28 days, the castings were removed from their molds, sawed into specimens, and evaluated by leach tests and compressive strength measurements. Some of the castings were heated at 400°C for one month and then measured for leachability to determine effects of postulated abnormal storage temperatures.

Water/Cement Ratios

Table 25 gives the water/cement (W/C) ratios used in the formulations with actual SRP waste sludge. Like the simulated sludges, the actual sludges were hydrophilic, as shown by the increase in W/C values with increasing sludge content. The orders of W/C for cement and sludge types are generally HAC < I-P, and Tank 5 < Tank 13 < Tank 15.

As described earlier, the W/C data can be represented by an equation of the form

$$W/C = (W_C/C) + (W_S/S)(S/C) + a(W_S/S)(S/C)^2$$

with W_C/C constrained to a constant for each cement type and W_S/S constrained to a constant for each sludge type. This gives 11 adjustable parameters, and a least-squares fit of the data can be obtained by inverting an 11 x 11 matrix. There are 20 data points, including those for no sludge, but some of the points should be excluded from the least-squares fit because of the known differences in method of preparation.

TABLE 25

Water/Cement Ratios for Formulations Containing Actual SRP Sludges

Cement Type	Sludge Waste Tank	Water/Cement Ratios[a] for Sludge Contents[b] of		
		10%	*25%*	*40%*
HAC	5	0.254	0.382	0.610[c]
	13	0.304	0.424	0.663[d]
	15	0.289	0.513	0.794[c,e]
I-P	5	0.362	0.481	0.605
	13	0.378	0.513	0.751
	15	0.412	0.590	0.767[e]

a. For control formulations (no sludge): HAC, 0.234; Type I-P, 0.332.

b. Expressed as Sludge/(Sludge + Cement).

c. Contains excess water to prevent rapid setting.

d. This formulation had a rapid set time; additional water was added after setting to give a water/cement ratio of 0.818.

e. 37.5% sludge + 2.5% Cs-loaded zeolite, from SRP waste supernate.

The least-squares calculation was performed for four cases: with 14 data points, excluding all points for 40% sludge; with 16 data points, excluding the rapid set-time, excess water, and zeolite points; with 18 data points, excluding only the zeolite points; and with all 20 data points. As expected, both the 14- and 20-data point cases gave distorted results; the 16- and 18-data point cases gave practically identical results, with reasonable values for the adjustable parameters. Table 26 gives the parameters calculated by excluding only the zeolite data points.

The best-fit curves for the 18 data points are shown in Figure 21. The calculated values of W_C/C agree very well with the measured values of W/C for the control formulations. The relative hydrophilic nature of each sludge is given by the order of W_S/S, as

Tank 5 < Tank 13 < Tank 15

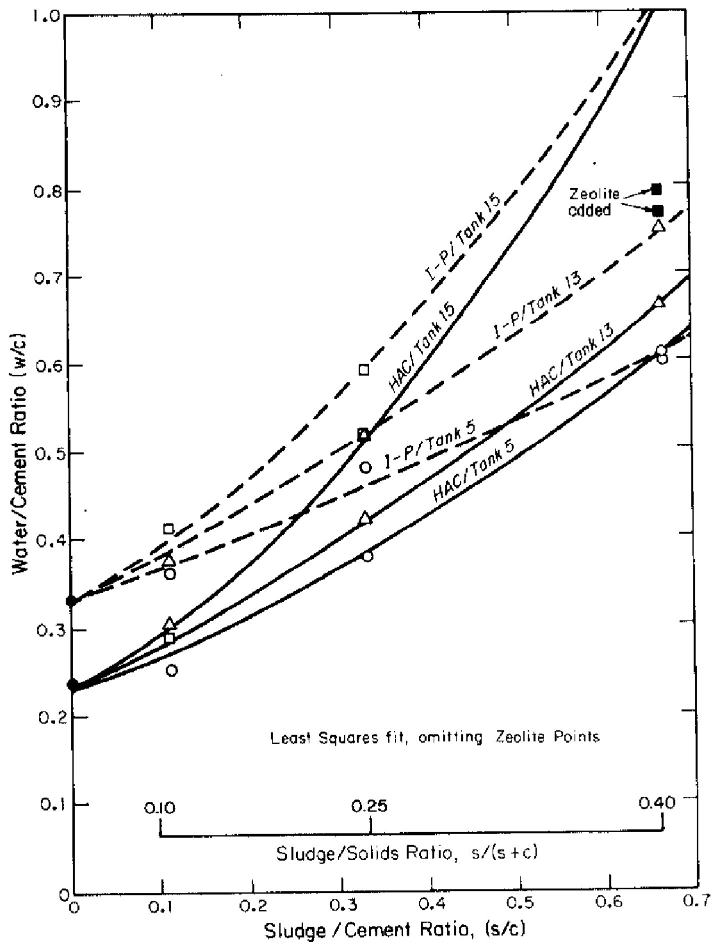

FIGURE 21. Water/Cement Ratios for Formulations with Actual SRP Sludges

TABLE 26

Parameters Calculated for Formulations Containing Actual SRP Sludges from Least Squares Fit[a] with Constraints

			Sludge Type		
			Tank 5	*Tank 13*	*Tank 15*
		W_S/S	0.361	0.496	0.537
Cement Type	W_C/C		*Interaction Coefficient, α*		
HAC	0.226		0.86	0.47	1.73
I-P	0.332		0.23	0.39	1.35

a. Excluding two data points for 40% (sludge + zeolite).

This is also the order of decreasing manganese and sodium content, and increasing aluminum content (Table 23). Results for the simulated sludges showed similar correlations (Tables 2 and 5); W_S/S for the sludges from Tank 13 and Tank 15 are larger than those for any of the simulated sludges. The interaction coefficients between the two cements and the radioactive sludges are similar to those for the simulated sludges, except for the Tank 15 sludge where the coefficients are larger.

Evaluation of Radioactive Concrete-Sludge Specimens

By determining the properties of a small set of concrete specimens containing actual SRP waste sludges, an understanding of the system could be obtained and related to the more extensive data with simulated sludges. The results of evaluation tests on the radioactive concrete-sludge specimens were very similar to those with simulated sludges. This similarity gives confidence that most of the important properties of concrete forms containing SRP wastes can be inferred from experiments with simulated waste forms. In addition, the effects of three quite different SRP sludges could be determined. Details of the evaluation tests are given in the following sections.

The only problem encountered in preparing the radioactive specimens was the short set time of some of the formulations with high sludge contents. A brief description is given of a method developed to increase the set times of sludge-cement pastes. As with the simulated sludges, the principal evaluation tests for the radioactive concrete-sludge specimens were compressive strength and leachability. Results of measurements of compressive strength, ^{90}Sr leachability, ^{137}Cs leachability, and alpha-emitter leachability are described. Finally, results are given for a thermal stability test somewhat different than those with the simulated sludges.

Separate leach tests for ^{90}Sr, ^{137}Cs, and alpha emitters were not performed, but rather, these three constituents were determined in the leach waters from a single set of leach tests. A comparison of the three leachabilities is shown in Figure 22 for one formulation. The relative order of leachabilities,

$$^{137}Cs \gg {}^{90}Sr > \text{alpha emitters}$$

held for all the formulations, at all time periods. The example shown for 40% Tank 5 sludge and HAC was somewhat less leachable for all three components than were other formulations. The results of statistical analyses to determine effects of cement type, sludge type, and sludge content are discussed for each of the three species leached.

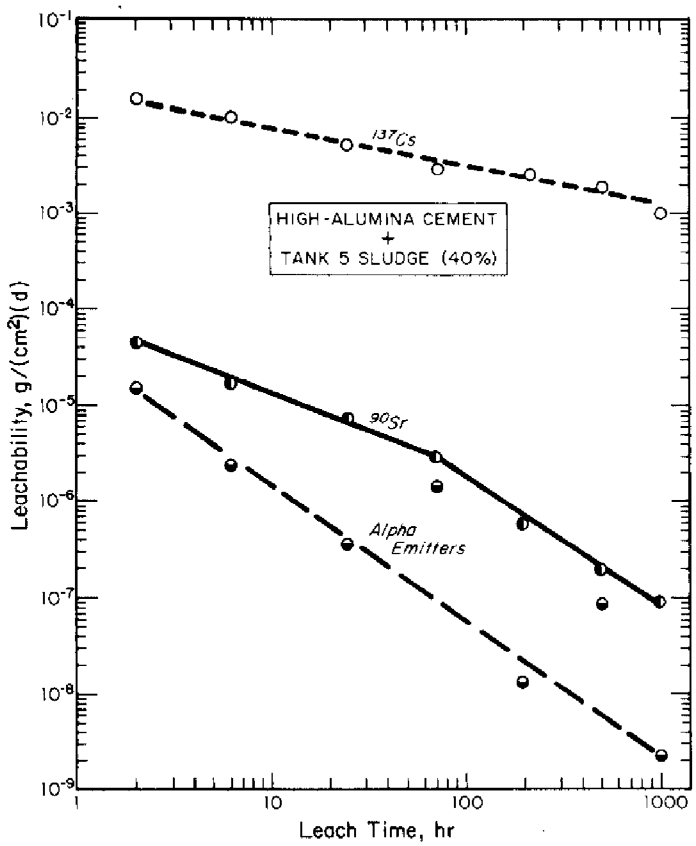

FIGURE 22. Typical Leachabilities of Radioactive Concrete Waste Forms

Set Times

Formulations in addition to those given in Table 25 were prepared to test the effect of an organic set-time retarder. Pastes were made with and without the retarder, and set times were measured by a standard method.[31] Under the test conditions, set times shown in Table 27 were found. The retarder increased the set times to more than 4 hours, which would be adequate for making castings in a large-scale process.

TABLE 27

Effect of Set Retarder on High-Alumina Cement Formulations with Actual SRP Sludges

Sludge Waste Tank	*Set Time, minutes* Without Retarder	With 1.5 wt % Retarder
5[a]	32	280
13[a]	30	240
15[b]	30	290

a. 40% Sludge, 60% HAC

b. 37.5% sludge, 2.5% Cs-loaded zeolite, 60% HAC

Initial investigation of set-time effects was made with simulated sludges with compositions based on the actual compositions shown in Table 23. Details of this work are given in a separate report.[11] Set times were found to be effectively increased by adding 1.5 wt % (of dry solids) of a commercial organic set retarder (Pozzolith 122-R, Master Builders, Cleveland, Ohio) to formulations with HAC. These results were confirmed in the tests with actual sludges. Formulations with 40% actual sludges and HAC had shown rapid set times in the specimen preparations described earlier; in pastes prepared specifically for set-time measurements, the set times were about 30 minutes without retarder, but were greater than 240 minutes with the retarder. The three sludge types behaved in about the same way.

Compressive Strength

The results of compressive strength tests on concrete specimens containing actual SRP waste sludges were very similar to those with simulated sludges. As in the tests described earlier, sludge content had the greatest effect on strength, with the strength decreasing as the sludge content increased. This behavior is shown in Figure 23 for specimens with Tank 5 sludge, in Figure 24 with Tank 13 sludge, and in Figure 25 with Tank 15 sludge. All of the specimens with HAC and 40% sludge were exceptionally weak; this is attributed to the fast set in the case of the Tank 13 formulation and to the large amount of excess water added to prevent a fast set in the others. Specimens with Type I-P cement, for which no set-time problems were encountered, gave compressive strengths with a regular trend up to 40% sludge content. Cesium-loaded zeolite, added to two formulations, had no discernible effect on compressive strength.

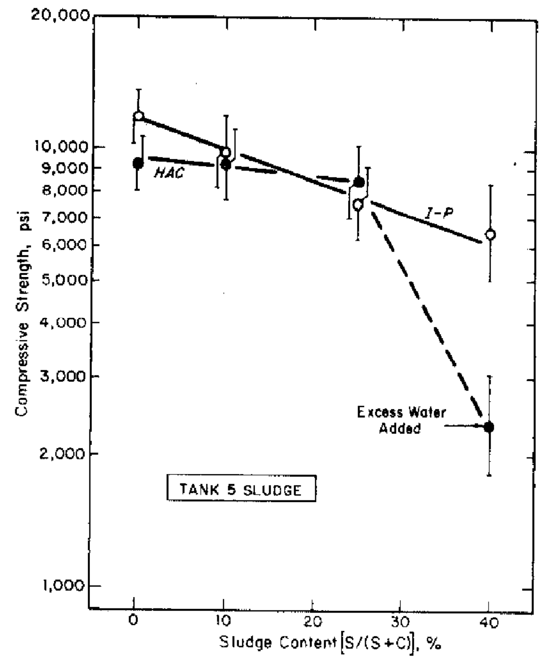

FIGURE 23. Compressive Strength of Concrete with SRP Sludge (Tank 5)

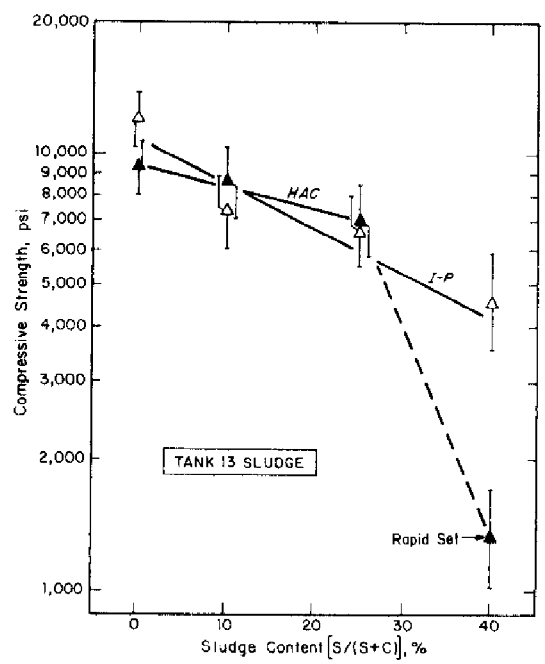

FIGURE 24. Compressive Strength of Concrete with SRP Sludge (Tank 13)

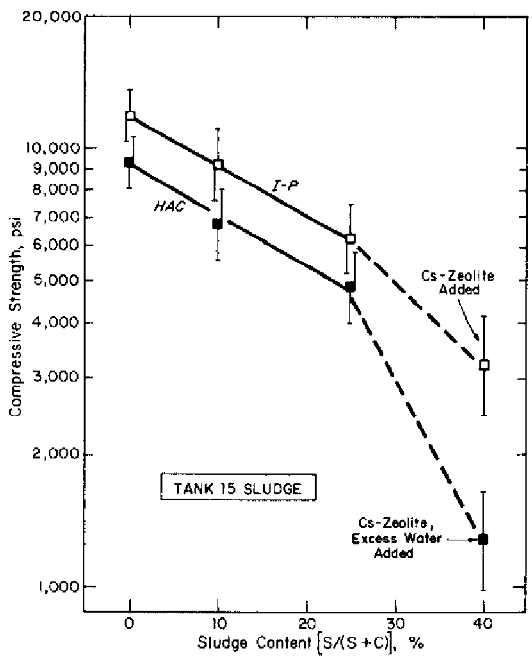

FIGURE 25. Compressive Strength of Concrete with SRP Sludge (Tank 15)

Experimental Procedure. The measurements were made in a shielded cell facility, with the same equipment as described for the tracer-level cesium-loaded zeolite specimens. The procedure was essentially the same as for tests on specimens with the nonradioactive simulated sludges. Most of the castings with actual sludges contained one or more large voids; sections containing a void were sawed off and discarded as unsuitable for testing. Thus, most of the "duplicate" compressive strength test specimens came from different castings of a formulation. As with previous tests, two measurements were made for each formulation, but these gave generally poor reproducibility. Subsequently, a third specimen of each formulation was tested, and the triplicate measurements were treated statistically.

Results. Table 28 gives the compressive strengths of the concrete waste forms with actual SRP sludges, where each entry is the average of the three replicate specimens. The data were treated in two ways, first as the full 2 x 3 x 3 factorial experiment, then as a 2 x 2 x 3 factorial experiment by excluding all of the points with 40% sludge content. The latter case is a pure factorial experiment, whereas four of the six additional formulations of the first case were altered in significant ways (Table 25). The effects of the alterations can be estimated by a comparison of analyses of variance for the two cases. The factors were the two cement types, the two or three sludge contents, and the three sludge types, all with triplicate samples.

TABLE 28

Compressive Strength of Concrete Waste Forms Containing Actual SRP Sludges

Cement Type	*Sludge Waste Tank*	*Compressive Strength,[a] psi, for Sludge Contents of*		
		10%[b]	*25%[b]*	*40%[c]*
HAC	5	9252	8496	2349[d]
	13	8601	7053	1316[e]
	15	6702	4816	1279[d,f]
I-P	5	9911	7559	6505
	13	7337	6667	4564
	15	9188	6235	3199[f]

a. Each entry is the average of 3 measurements.

b. Error factor (95% confidence): $\varepsilon = 1.21$.

c. Error factor (95% confidence): $\varepsilon = 1.30$.

d. Formulation contained excess water to prevent rapid setting.

e. Formulation set before castings were made.

f. 37.5% sludge + 2.5% cesium-loaded zeolite.

The effect of cement type was statistically significant with all three sludge contents considered, but was not significant if only the 10 and 25% sludge contents were included in the analysis of variance. This means that only at 40% sludge content are the differences between cement types significant. The compressive strengths are in the order I-P >> HAC for each sludge type at the 40% level. Of course, the HAC specimens were weakened by known mechanisms, either by casting after initial set had occurred or by the excess water added to prevent fast set. Based on the work with simulated sludges, HAC specimens with 40% sludge would be expected to be stronger if the set were retarded and the correct amount of water were used. If these conditions had been present, the differences between cement types might not have been significant or the ordering might have been reversed. Type I-P cement behaved well with the actual sludges; in most cases, the specimens were stronger than with the simulated sludges. Similarly, HAC behaved well at 10 and 25% sludge contents, but its potential behavior at the 40% level is unknown.

The effect of sludge content was statistically significant for both types of analysis of variance. The degree of significance was less pronounced if only the 10 and 25% sludge contents were considered, but the effect was still much greater than for any of the other factors. As with the simulated sludges, there was a monotonic decrease in strength with increasing sludge content, regardless of cement type or sludge type. Thus, the compressive strengths are in the order 10% > 25% > 40%.

Statistically significant differences between the three sludge types were also found in both types of analysis of variance. The compressive strengths are in the order Tank 5 > Tank 13 $\sim$ Tank 15. Most of the data points for Tank 13 are greater than for Tank 15, but the differences are not large enough to be significant. As shown in Figure 23, the specimens with Tank 5 sludge were especially strong (except for the point with excess water). With Tank 15 sludge, specimens made with HAC were noticeably weaker than specimens with the other sludges; this may be due to the high aluminum content of the Tank 15 sludge.

The only significant statistical interaction in the data was between cement type and sludge content when all three sludge contents were included in the analysis of variance. This is another manifestation of the poor behavior of the compressive strengths of specimens with HAC and 40% sludge content.

The effect of replacing 1/16 of the sludge with cesium-loaded zeolite can be assessed from the data. Two formulations containing Tank 15 sludge with nominally 40% sludge content were chosen for zeolite additions. The compressive strength measurements are shown in Figure 25. With Type I-P cement, the zeolite data point follows the trend of the data for lower sludge contents. Points with 40% Tank 5 and Tank 13 sludges and with no zeolite follow the same kind of trends with Type I-P cement. Thus, there is no evidence of an effect on strength from addition of zeolite to Type I-P cement. With HAC, the specimen containing zeolite was very weak; however, the formulation also contained excess water to prevent fast set. As shown in Figure 23 with Tank 5 sludge and no zeolite, the low strength at 40% sludge content can be attributed entirely to the excess water. Again, there is no evidence of any effect on strength from addition of zeolite to HAC. This behavior is consistent with the behavior described earlier for simulated sludges with additions of cesium-loaded zeolite.

Strontium Leachability

In leach tests on concrete specimens containing actual SRP sludges, the effects of leach time, cement type, sludge type, and sludge content were determined for ^{90}Sr leachability. The leaching behavior for ^{90}Sr was generally similar to that for natural strontium in specimens with simulated sludges. The chief differences were in the magnitudes of the leachabilities; the ^{90}Sr values were factors of 10 to 100 lower than those for natural strontium. The principal conclusions from the ^{90}Sr leach data are:

- Initial leachabilities are 10^{-5} to 10^{-3} g/(cm^2)(d).
- Leachabilities after six weeks are 10^{-7} to 10^{-5} g/(cm^2)(d).
- Sludges from three tanks differ widely in ^{90}Sr leachability.
- High-alumina cement specimens are less leachable than specimens made with Type I-P cement.
- Increasing sludge content decreases the leachability with one sludge type, but increases it with another.
- Neither fast set, excess water, nor zeolite addition have any significant effect on ^{90}Sr leachability under the conditions investigated.

Experimental Procedure. Forty-one leach tests were performed in a shielded cell on duplicate specimens of the 18 formulations containing sludges and 2 containing no sludge; a blank leach test (with no concrete specimen) was made in parallel with the others. The general method and sampling schedule were the same as for nonradioactive leach tests described earlier. Some modifications in technique were made to minimize handling and ensure a low level of cross-contamination in the leach waters. In the most important modification, separate leach bottles were used for each time period, so that leach waters were never transferred between containers inside the cell. For each time period, 268 ml of process water was placed in each of 41 clean leach bottles outside the cell, and the the capped bottles were passed into the cell. The caps were removed inside the cell, with care taken not to contaminate the inner surface. To change leach water at the end of a time period, each specimen, suspended by a wire from a bottle cap, was lifted out of the old bottle and inserted into the new bottle while touching only the outer surface of the cap. A cap, formerly on the new bottle, was placed on the old bottle, which then became the storage container for the used leach water. Subsequently, the entire bottle was removed from the cell and submitted for analysis.

To evaluate the success of these precautions, three leach tests were performed in a relatively uncontaminated hood. Two tests were with radioactive specimens removed from the shielded cell, and the third was blank. Shielded by a lead-brick fort, the leach water was changed manually, by the same procedure as in the cell. Results of the leach tests on the two radioactive specimens were essentially the same as for tests on similar specimens inside the cell. The blank test showed negligible contamination in the hood. Thus, the hood tests confirmed the validity of the in-cell leach tests.

The 308 bottles of leach water produced by the tests were analyzed radiochemically for ^{90}Sr. The leach water from specimens with the radioactive sludges contained from 10^4 to 10^6 dis/(min)(ml) of ^{90}Sr. The concrete specimens contained from 5×10^{10} to 1×10^{12} dis/min of ^{90}Sr, depending on sludge type and content. Leach waters from the in-cell blank showed 10^3 dis/(min)(ml) or less of ^{90}Sr, and typically had less than 1% of the ^{90}Sr found from radioactive specimens leached at the same time. The amount of surface contamination introduced on the concrete specimens during handling and sawing could be assessed from the leach tests on the concrete specimens containing no sludge. The ^{90}Sr content in these leach waters ranged from about 3×10^3 dis/(min)(ml) at 2 hr, to about 3×10^2 dis/(min)(ml) after 1008 hr. In nearly all cases, these values were negligible compared to the amount of ^{90}Sr leached from specimens containing sludge.

Results. The ^{90}Sr leachabilities from tests with specimens containing actual SRP waste sludges are given in Table 29 for several time periods. The data were treated statistically by analyses of variance, separately for each time period. The factors were cement type, sludge type, and sludge content. As with the compressive strength data, the analysis of variance was done in two ways, first with all of the data points and then excluding the points for 40% sludge content. In the case of ^{90}Sr leachability, the same factor effects and interactions were significant in both methods of analysis. Thus, the alterations in some of the formulations with 40% sludge content appear to have had little effect on ^{90}Sr leachability.

As with specimens with simulated sludges, the leachability decreased monotonically with time, and this is the most pronounced effect in the data (Table 29). The statistical analyses showed that all of the other factors had significant effects. The differences between sludge types were highly significant at all time periods, and these differences were nearly as pronounced as the time effect. The difference between cement types was significant, but not at all time periods; at the intermediate times, from 6 to 216 hr, the effect was significant. The effect of sludge content had minor significance at all time periods. In addition, a statistical interaction between sludge type and sludge content was significant at all time periods.

TABLE 29

Typical ^{90}Sr Leachabilities for Concrete Waste Forms

		^{90}Sr *Leachability,*[a,b] 10^{-5} *g/(cm²)(d)*					
		High-Alumina Cement			*Type I-P Cement*		
Time, hr	*Sludge Content, %*	*Tank 5*	*Tank 13*	*Tank 15*	*Tank 5*	*Tank 13*	*Tank 15*
2	10	23	63	110	16	61	78
	25	10	39	76	7.0	25	150
	40	4.4[c]	25[d]	122[c,e]	3.2	18	150[e]
72	10	1.2	4.2	9.6	2.9	16	24
	25	0.87	4.4	16	2.5	16	43
	40	0.30[c]	4.6[d]	7.8[c,e]	0.65	12	57[e]
1008	10	0.15	0.87	1.5	0.17	0.71	1.1
	25	0.022	0.19	2.4	0.055	0.68	1.3
	40	0.0091[c]	0.50[d]	2.0[c,e]	0.014	0.069	3.2[e]

a. Each entry is the average of two measurements.

b. Error factor ε (95% confidence) varies from 1.27 to 1.63, depending on the sludge content and time period.

c. Formulation contained excess water to prevent rapid setting.

d. Formulation set before castings were made.

e. 37.5% sludge + 2.5% cesium-loaded zeolite.

The ^{90}Sr leachability for the different sludge types was in the order

Tank 5 << Tank 13 << Tank 15

for all time periods, cement types, and sludge contents. These differences are illustrated in Figure 26 for specimens with HAC and 25% sludge contents; other combinations have similar sets of time curves. The same ordering of sludge types was observed with compressive strength data and water/cement ratios. Chemically, high MnO_2 content is associated with low strontium leachability, as shown by the results with simulated sludges. However, the manganese contents of sludges from Tanks 5 and 13 are not widely different and, thus, are not a probable reason for the differences in ^{90}Sr leachability. There is a good correlation of ^{90}Sr leachability with aluminum content in the sludges (Table 23), which reflects a likely explanation for the differences in behavior of the three sludges.

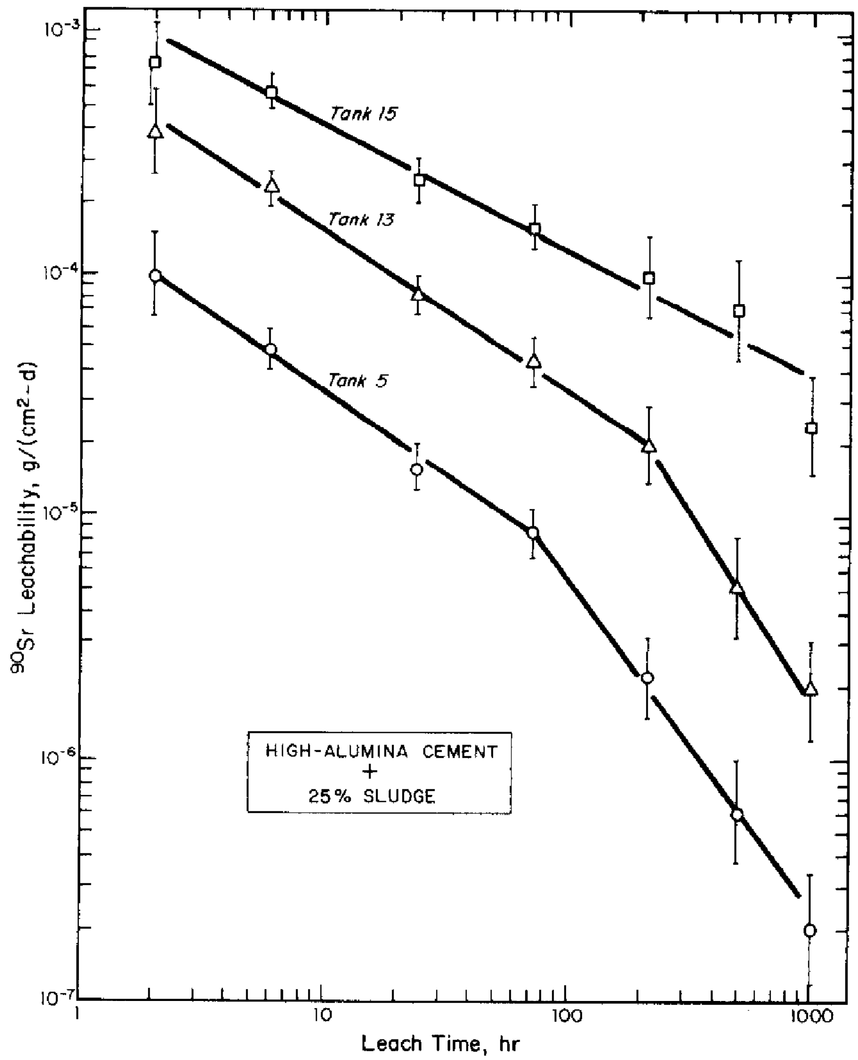

FIGURE 26. Effect of Sludge Type on ^{90}Sr Leachability

The behavior of ^{90}Sr leachability for the two cement types is shown in Figure 27 for specimens containing 40% Tank 15 sludge, a typical case. Over most of the time range the order of cement types was

HAC < I-P

for all sludge types and sludge contents. Initially, the two cements were not significantly different, but the ^{90}Sr leachability for HAC decreased more rapidly than for Type I-P cement.

At later times, the ^{90}Sr leachability for Type I-P cement decreased more rapidly than for HAC, so that for most combinations at 504 and 1008 hr, the data for the two cements again were not significantly different. Similar behavior was found with various cements and simulated sludges. The data for simulated and actual sludges were consistent in showing that HAC has generally lower strontium leachability than other cements.

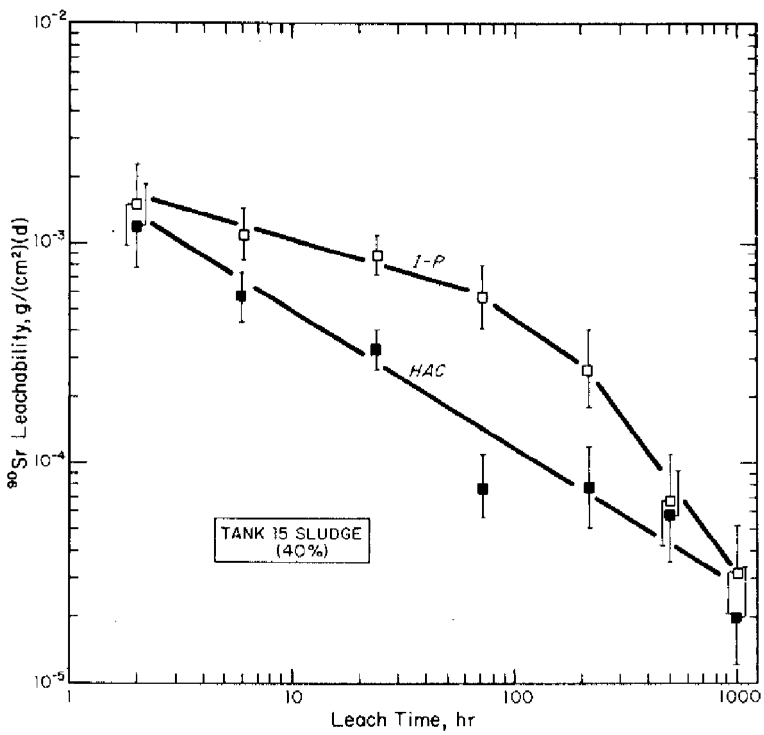

FIGURE 27. Effect of Cement Type on ^{90}Sr Leachability

Figure 28 shows typical behavior of ^{90}Sr leachability as a function of sludge content for different sludge types. The data shown for HAC at the 24-hr time period were generally similar to those for either cement at any time period. The statistical interaction in the data between sludge type and sludge content is clear. For Tank 5 sludge, the order of ^{90}Sr leachability was 40% < 25% < 10% at all time periods. For Tank 13 sludge, there was little variation with sludge content (with a few exceptions). For Tank 15 sludge, the order was 10% < 25% < 40% for most cases, except at long times when in some cases the leachabilities became nearly equal for the different sludge contents. Similar behavior was observed with simulated sludges (Figure 6), with Tank 5 sludge behaving like simulated Sludge III and with Tank 15 sludge behaving like simulated Sludge I. Again, this behavior is consistent with the chemical compositions of the sludges. Tank 5 sludge has high manganese and low aluminum contents like Sludge III, and Tank 15 sludge has high aluminum and low manganese contents like Sludge I. Tank 13 sludge, in which both aluminum and manganese contents are fairly high, is intermediate in behavior.

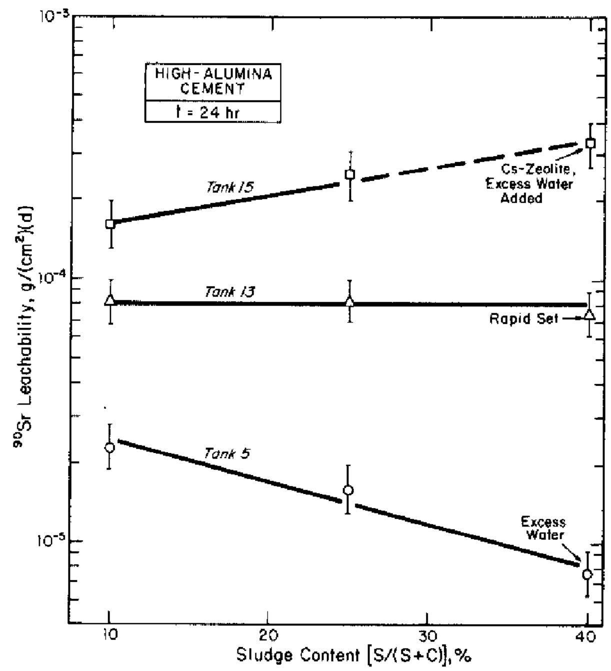

FIGURE 28. Effect of Sludge Content on ^{90}Sr Leachability

No effects on ^{90}Sr leachability were found that could be attributed to the fast set, excess water, and/or zeolite additions in some of the 40% sludge-content formulations. This was shown in the similar results of analyses of variance with and without the 40% sludge-content data. The ^{90}Sr leachabilities for these formulations behaved in a fairly regular manner, as the examples in Figures 27 and 28 and Table 29 show.

Because the magnitudes of ^{90}Sr leachabilities from concretes containing actual sludges were smaller than for natural strontium from simulated sludges, the fractions leached from actual sludges were much smaller. Table 30 gives the cumulative fractions, expressed as percent, after 1008 hr of leaching. The effects of sludge type, cement type, and sludge content are also evident in these data. The fractions of ^{90}Sr leached range from 0.004 to 0.9% compared with 5 to 10% typically found with the simulated sludges.

This difference may be explained partially as due to strontium in the cements (Table 7) that was leached from the concrete waste forms. The method of leach-water analysis with simulated sludges would detect all of the cement strontium, but none of it would be detected in the radiochemical analysis for ^{90}Sr with actual sludges. Since ^{90}Sr is the only isotope of strontium whose leachability is of interest in evaluating concrete as a waste form, the data with actual sludges more accurately represent the magnitudes to be considered.

TABLE 30

^{90}Sr Fraction Leached from Concrete Waste Forms

Cement Type	*Sludge Content, %*	*Cumulative Fraction,[a] %, of ^{90}Sr Leached after 1008 hr*		
		Tank 5	*Tank 13*	*Tank 15*
HAC	10	0.019	0.090	0.188
	25	0.009	0.055	0.364
	40	0.004[b]	0.081[c]	0.342[b,d]
I-P	10	0.033	0.174	0.304
	25	0.018	0.148	0.544
	40	0.009	0.096	0.869[d]

a. Each entry is the average of 2 measurements.

b. Formulation contained excess water to prevent rapid setting.

c. Formulation set before castings were made.

d. 37.5% sludge + 2.5% cesium-loaded zeolite.

Cesium Leachability

A residual amount of ^{137}Cs remained on all of the actual SRP sludges after washing. This may be considered free cesium, in contrast to cesium bound to zeolite. The leach tests on concrete specimens containing actual SRP sludges gave the first opportunity in this study to measure the leachability of free ^{137}Cs. The results showed that concrete retains free ^{137}Cs very poorly, with 50 to 75% leached out in some cases. The addition of ^{137}Cs-loaded zeolite to two of the formulations gave marked improvement in ^{137}Cs leachability. For these specimens, the results agreed with the previous work with simulated sludges and tracer-level ^{137}Cs-zeolite in concrete. Principal conclusions from the ^{137}Cs leach data are:

- Initial leachabilities are $\sim 10^{-2}$ to $\sim 10^{0}$ g/(cm^2)(d).
- Leachabilities after six weeks are $\sim 10^{-4}$ to $\sim 10^{-3}$ g/(cm^2)(d).
- ^{137}Cs-zeolite is less leachable than free cesium in concrete.
- Sludges from three tanks differ widely in ^{137}Cs leachability.
- The ^{137}Cs leachability of high-alumina cement specimens is less than or equal to that of specimens made with Type I-P cement.
- Increasing sludge content generally increases the ^{137}Cs leachability.

Experimental Procedure. The same leach waters described for ^{90}Sr leachability measurements also were analyzed for ^{137}Cs by high-resolution gamma ray spectrometry. Leach waters from duplicate tests gave excellent reproducibility for ^{137}Cs content, at all time periods except 504 hr. Some scatter in the data led to larger error bars on points at 504 hr than for the other time periods. The leach waters from specimens with the radioactive sludges contained from 1×10^4 to 5×10^6 dis/(min)(ml) of ^{137}Cs. The concrete specimens without zeolite contained from 2×10^8 to 2×10^{10} dis/min of ^{137}Cs, depending on sludge type and content; specimens with zeolite contained 7×10^{10} dis/min of ^{137}Cs. The ^{137}Cs leachability from tests done in a relatively uncontaminated hood agreed well with results from similar tests in the shielded cell. The in-cell blank test gave $<4 \times 10^2$ dis/(min)(ml) of ^{137}Cs at all time periods; this was negligible compared to amounts leached from actual specimens. Leach waters from specimens without sludge contained $<4 \times 10^3$ dis/(min)(ml) of ^{137}Cs, and typically contained less than 1% of the ^{137}Cs found from specimens with sludge.

Results. Data from the ^{137}Cs leach tests with specimens containing actual SRP waste sludges are given in Table 31 for several time periods. Separate analyses of variance were made for each time period with the factors cement type, sludge type, and sludge content. As with the compressive strength and ^{90}Sr

leachability data, the analysis of variance was done in two ways, first with all the data points and then excluding the points for 40% sludge content. The statistical treatment gave complex results, with all the possible factor effects and interactions found to be significant at some or all the time periods. Without the 40% sludge-content data points, one major interaction disappeared or was greatly reduced, and a minor interaction also disappeared. Thus, the alterations in some of the formulations with 40% sludge content had significant effects on ^{137}Cs leachability.

TABLE 31

Typical ^{137}Cs Leachabilities for Concrete Waste Forms

		^{137}Cs *Leachability,*[a] 10^{-3} *g/(cm²)(d)*					
	Sludge	*High-Alumina Cement*			*Type I-P Cement*		
Time, hr	*Content, %*	*Tank 5*	*Tank 13*	*Tank 15*	*Tank 5*	*Tank 13*	*Tank 15*
2[b]	10	10	52	270	110	240	360
	25	8.3	53	320	160	380	580
	40	16[c]	160[d]	9.0[c,e]	130	510	52[e]
72[b]	10	1.5	9.6	21	8.3	13	26
	25	2.0	11	51	9.7	20	41
	40	2.9[c]	26[d]	1.9[c,e]	12	30	4.7[e]
1008[b]	10	0.65	3.0	4.1	0.48	0.96	1.6
	25	0.82	5.0	2.2	0.56	1.9	1.9
	40	1.0[c]	1.6[d]	0.33[c,e]	0.63	1.8	0.56[e]

a. Each entry is the average of two measurements.

b. Error factor ε (95% confidence): at 2 hr, $\varepsilon = 1.20$; at 72 hr, $\varepsilon = 1.15$; at 1008 hr, $\varepsilon = 1.21$.

c. Formulation contained excess water to prevent rapid setting.

d. Formulation set before castings were made.

e. 37.5% sludge + 2.5% cesium-loaded zeolite.

With respect to time behavior and the main effects of the factors cement type, sludge type, and sludge content, ^{137}Cs leachability was similar to that of ^{90}Sr.

The ^{137}Cs leachability decreased monotonically with time (Table 31). All of the other factors were significant; sludge type was the most important, followed by cement type, and then by sludge content. For the statistical analyses with all data points, the interaction between sludge type and sludge content was largest; a large interaction between sludge type and cement type was found, along with a minor three-way interaction. At 2 and 1008 hr, the interaction between cement type and sludge content also was significant. At 504 hr, with large variance, only the effects of sludge type, sludge content, and the interaction between them were significant. For the statistical analyses without the 40% sludge-content data, the same effects and interactions were found, except that the interaction between sludge type and sludge content was eliminated or greatly reduced, and the three-way interaction was eliminated. Other major differences were found: at 504 hr, the effect of sludge content was not significant, and at 1008 hr, the interaction between cement type and sludge content was not significant.

The ^{137}Cs leachability for the different sludge types generally was in the order

Tank 5 < Tank 13 < Tank 15

for specimens without zeolite. The differences between sludge types are shown in Figure 29 for specimens with HAC and 25% sludge contents. Other combinations with HAC have similar sets of time curves; the differences between sludge types with Type I-P cement are not as pronounced. At the later time periods, the ^{137}Cs leachability for Tank 15 sludge became equal to or less than that for Tank 13 sludge, as shown in Figure 29. Data at 1008 hr were particularly noteworthy because a number of relationships that held at earlier times changed. The ordering of sludge types for ^{137}Cs leachability is the same as for ^{90}Sr leachability, compressive strength, and water/cement ratios. For the specimens with zeolite (Tank 15 sludge with nominally 40% sludge content), the order changed to Tank 15 < Tank 5 < Tank 13 with HAC, and Tank 15 $\sim$ Tank 5 with Type I-P cement. The change in ordering with zeolite reflects the large decrease in ^{137}Cs leachability caused by the addition of zeolite.

The differences in ^{137}Cs leachability between the two cement types varied with sludge type, sludge content, and time period. For most combinations, the order of cement types was

HAC < I-P

but for some combinations, HAC $\sim$ I-P, and for a few, I-P < HAC.

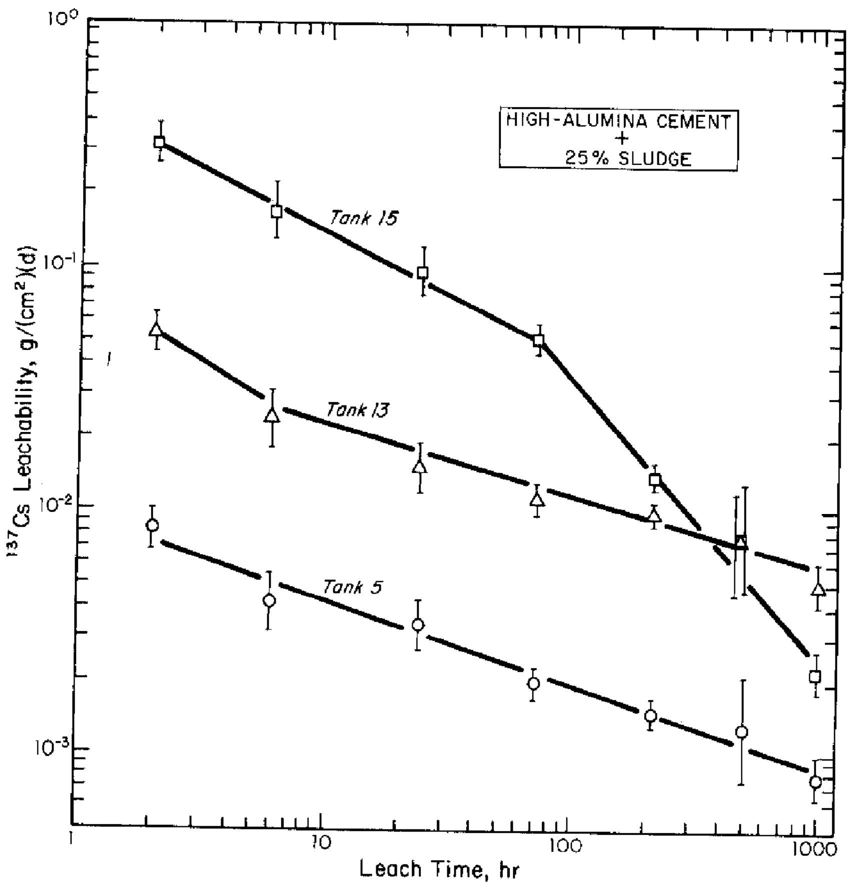

FIGURE 29. Effect of Sludge Type on ^{137}Cs Leachability

This somewhat complex behavior is summarized in Table 32. An example of the differences in ^{137}Cs leachability for the two cements is shown in Figure 30, for specimens containing 10% Tank 5 sludge. This case had particularly large differences between the cements, but the curves converged with time, until the differences between cements disappeared at 1008 hr. With Tank 5 sludge, HAC had lower ^{137}Cs leachability at all sludge contents through 216 hr of leaching. With Tank 13 sludge at 10 and 25%, HAC had lower ^{137}Cs leachability through 72 hr of leaching; at 40%, there was little difference between the cements, which could possibly be associated with the rapid setting of the HAC formulation, leading to an abnormally high ^{137}Cs leachability for the HAC specimens. With Tank 15 sludge at 10 and 25%, no significant differences between the cements were found at most of the time periods; at 40%, with zeolite, HAC had lower ^{137}Cs leachability by factors of 2 to 3, consistent with the data for simulated sludges (Table 18). The differences in behavior of the cement types for the various sludge types account for the statistical interaction between cement type and sludge type, and for the three-way interaction when the 40% sludge-content data is included.

TABLE 32

Effect of Cement Type on ^{137}Cs Leachability of Concrete Waste Forms

Sludge Waste Tank	*Sludge Content, %*	*Cement with Lower ^{137}Cs Leachability, for Leach Time, hr*						
		2	*6*	*24*	*72*	*216*	*504*[b]	*1008*
5	10	HAC	HAC	HAC	HAC	HAC	*a*	*a*
	25	HAC	HAC	HAC	HAC	HAC	*a*	I-P
	40[c]	HAC	HAC	HAC	HAC	HAC	*a*	I-P
13	10	HAC	HAC	HAC	HAC	*a*	*a*	I-P
	25	HAC	HAC	HAC	HAC	*a*	*a*	I-P
	40[d]	HAC	*a*	*a*	*a*	I-P	*a*	*a*
15	10	*a*	*a*	*a*	*a*	*a*	*a*	I-P
	25	HAC	*a*	*a*	*a*	*a*	*a*	*a*
	40[c,e]	HAC	HAC	HAC	HAC	HAC	*a*	HAC

a. Difference not statistically significant.

b. Large error factor at 504 hr (ε = 1.63).

c. HAC formulation contained excess water to prevent rapid setting.

d. HAC formulation set before castings were made.

e. 37.5% sludge + 2.5% cesium-loaded zeolite.

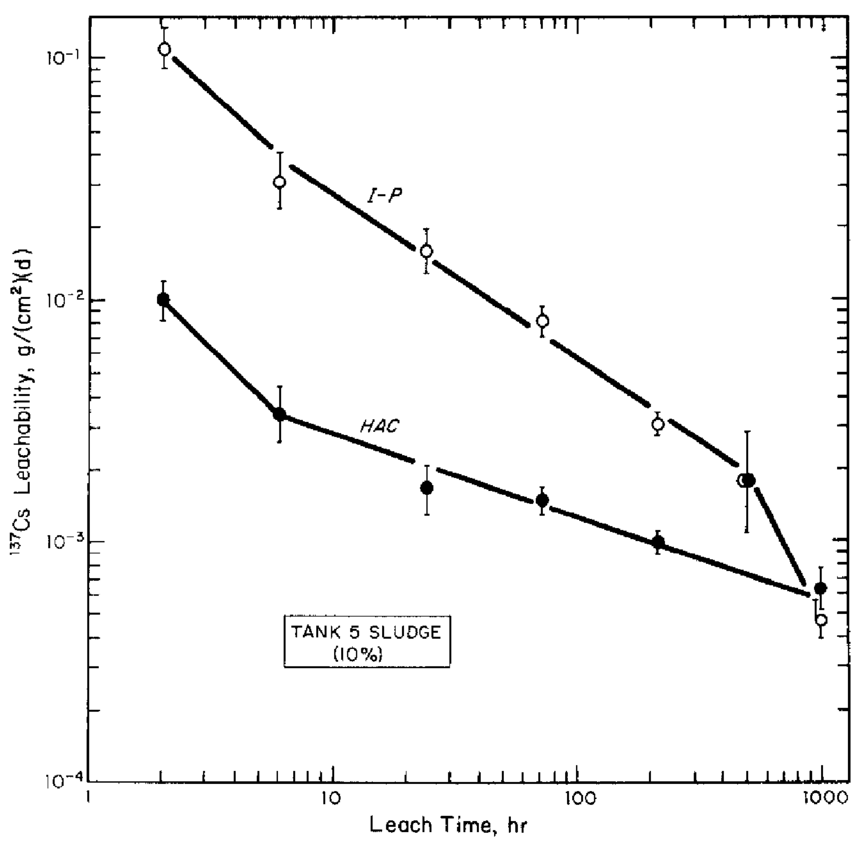

FIGURE 30. Effect of Cement Type on ^{137}Cs Leachability

Figure 31 shows typical behavior of ^{137}Cs leachability as a function of sludge content for different sludge types. The data shown for HAC at the 24-hr time period were generally similar to those for either cement at any time period (except 1008 hr). Where differences between sludge contents were present in the data, the order of sludge contents for ^{137}Cs leachability was

$10\% < 25\% < 40\%$

for specimens without zeolite. The data contain numerous instances of 10% $\sim$ 25% and 25% $\sim$ 40%, but only at 1008 hr are there a few cases with 25% < 10% and 40% < 25%. The general behavior of increasing ^{137}Cs leachability with increasing sludge content shows that the sludges have no chemical properties that would help retain free cesium. For the specimens with zeolite (Tank 15 sludge with nominally 40% sludge content), the order changed to

$40\% < 10\% < 25\%$

for both cement types. The presence of zeolite greatly decreased the ^{137}Cs leachability for these specimens and caused the statistical interaction between sludge type and sludge content.

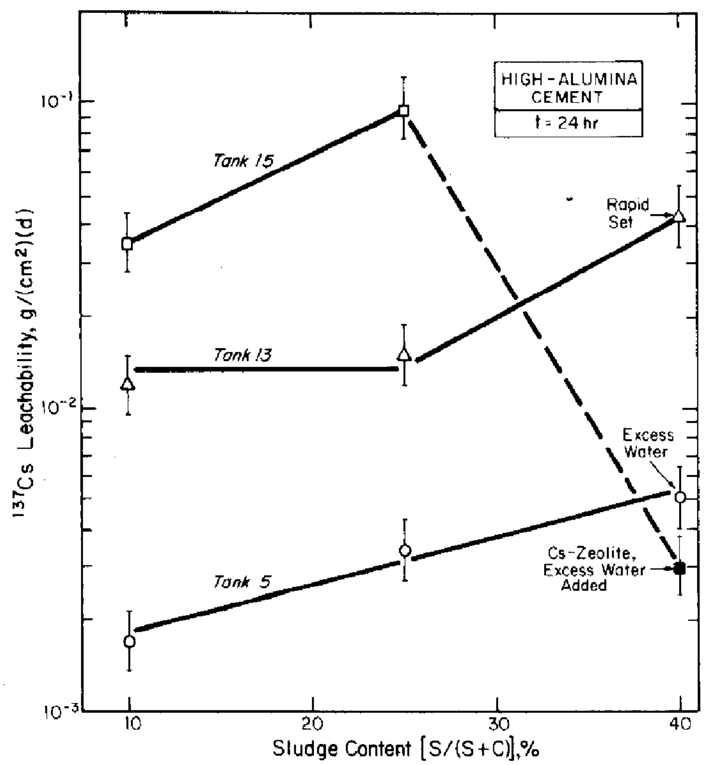

FIGURE 31. Effect of Sludge Content on ^{137}Cs Leachability

Effects of the alterations to some of the 40% sludge-content formulations are evident in the data. The addition of zeolite to two of the formulations had the largest effect on ^{137}Cs leachability, as expected. The ^{137}Cs leachability of specimens containing zeolite and actual SRP sludge was slightly less than that of similar specimens containing simulated sludges (Table 18). Specimens containing free cesium and no zeolite had ^{137}Cs leachabilities 10 to 30 times higher. There is some evidence for an adverse effect of fast set on ^{137}Cs leachability. As shown in Table 32 and Figure 31, the formulation with fast set (HAC with 40% Tank 13 sludge) has a higher leachability than might be predicted by extrapolating the data at 10 and 25% sludge contents. At most, the ^{137}Cs leachability of the fast set formulation is a factor of 3 higher. No effects on ^{137}Cs leachability were found that could be attributed to the excess water in two formulations (HAC with 40% Tank 5 sludge or 40% Tank 15 sludge).

The large fractions of ^{137}Cs leached lead to consideration of a correction to the leachability data.

The relatively large values of ^{137}Cs leachability given in Table 31 led to substantial portions of the cesium being leached from the test specimens. Table 33 gives the cumulative fractions, expressed as percent, leached after 1008 hr. The effects of sludge type, cement type, sludge content, and zeolite addition may be seen in these data.

TABLE 33

^{137}Cs Fraction Leached from Concrete Waste Forms

Cement Type	*Sludge Content, %*	*Cumulative Fraction,[a] %, of ^{137}Cs Leached after 1008 hr*		
		Tank 5	*Tank 13*	*Tank 15*
HAC	10	5.6	26.6	51.9
	25	5.8	36.3	62.2
	40	9.5[b]	52.2[c]	4.3[b,d]
I-P	10	11.5	21.5	44.7
	25	13.5	33.3	75.8
	40	15.7	46.3	9.2[d]

a. Each entry is the average of two measurements.

b. Formulation contained excess water to prevent rapid setting.

c. Formulation set before castings were made.

d. 37.5% sludge + 2.5% cesium-loaded zeolite.

When large fractions ($f > 0.1$) of a species are leached out, a correction to the calculated leachability is required. In this study, leachabilities of radioactive species were calculated with the equation

$$L = \frac{M}{C_0 A} \frac{\Delta C}{\Delta t}$$

where C_0 is the original amount of the species in the test specimen, expressed in radioactivity units. To a good approximation, C may be considered a constant, C_0, when less than 10% has been leached out. However, the approximation introduces significant error when more than 10% has been leached. A correction may be made by noting that $C = (1-f)C_0$, where $1-f$ is the fraction remaining in the solid. The corrected leachability is given by

$$L' = L/(1-f)$$

When applied to ^{137}Cs leachability data, the correction increased the value of L by significant amounts, especially at the later time periods. However, the correction was not large enough to change any of the conclusions previously stated. Data shown in Tables 31 and 32 and Figures 29, 30, and 31, are uncorrected. In Figure 32, corrected and uncorrected ^{137}Cs leachabilities are compared for the worst case studied, a formulation of Type I-P cement with 25% Tank 15 sludge. In this case, the correction increased the ^{137}Cs leachability by as much as a factor of 4 at long times. Generally, all of the time curves were shifted in the same manner by the correction, so that relative changes were small. One beneficial effect of the correction was in removing some of the anomalous behavior previously noted at 1008 hr.

Alpha-Emitter Leachability

Leachability of alpha radioactivity from concrete waste forms containing actual SRP sludges was very small and near the limit of detection. Results of the leach tests for alpha emitters agree well with data for plutonium leachability with simulated sludges. Alpha leachability was a strong function of time, but scatter in the data was so large that effects of other factors could not be determined with certainty. Principal conclusions from the alpha-emitter leach data are:

- Alpha-emitter leachabilities are typically lower than ^{90}Sr leachabilities by a factor of 10^2 and lower than ^{137}Cs leachabilities by a factor of 10^4.
- Initial leachabilities are $\sim 10^{-5}$ g/(cm²)(d).
- Leachabilities after six weeks are $\sim 10^{-8}$ g/(cm²)(d).
- The fraction leached after six weeks is less than 10^{-3}%.

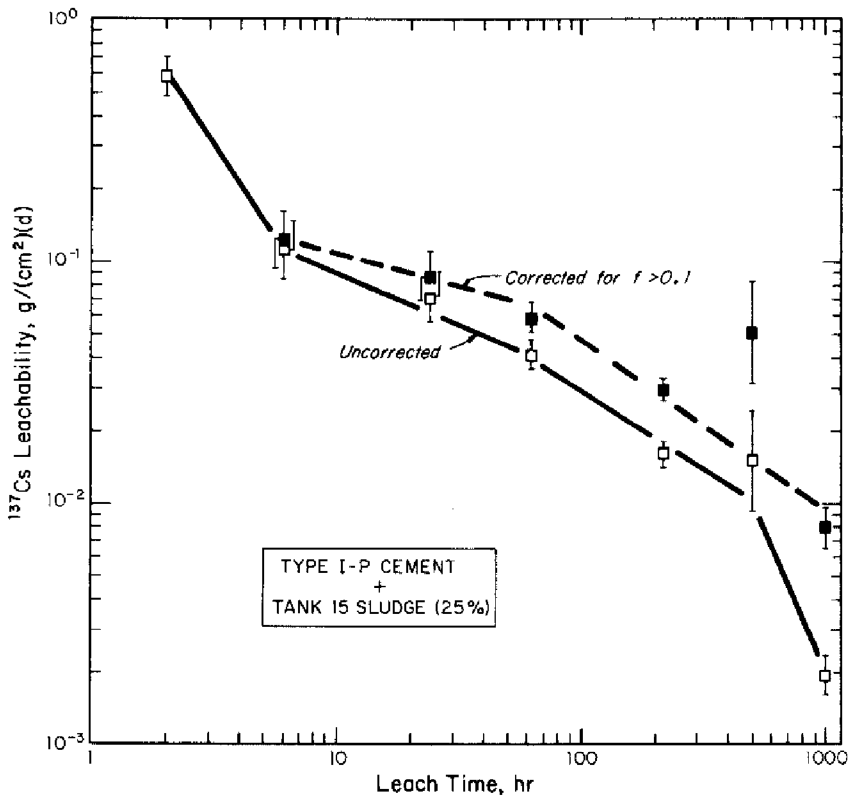

FIGURE 32. Correction for Large ^{137}Cs Fraction Leached

Experimental Procedure. The same leach waters described for ^{90}Sr leachability measurements were analyzed also for alpha emitters by gross alpha counting. Alpha activities were too low to determine isotopic composition of the alpha emitters by pulse-height analysis; analyses of the original sludges suggest that the alpha emitters in the leach waters are largely ^{239}Pu. The leach waters from specimens with the radioactive sludges contained from 0.2 to 268 dis/(min)(ml) alpha activity, with many typically in the range 1 to 10 dis/(min)(ml). Many of the data were reported as 0 dis/(min)(ml), and these "zero points" were taken as <0.2 dis/(min)(ml) for calculational purposes. Reproducibility of the data between duplicate specimens was very poor, with a factor of 10 difference in many cases. The concrete specimens contained from 4×10^8 to 3×10^9 dis/min of alpha emitters, depending on sludge type and content. Results of tests performed in a relatively uncontaminated hood agreed fairly well with those of tests in a shielded cell. Gross alpha activity found in leach waters from blank tests and tests with concrete specimens with no sludge was the same order of magnitude as that found for the actual sludges. Although the experimental uncertainties in the comparison tests were quite large, the results suggest that much of the alpha activity in the leach waters could be from surface contamination. Thus, the actual alpha emitter leachabilities could be much lower than those calculated from the data, which should be regarded as upper limits.

Results. A statistical treatment of the data indicated that averaging all 36 points at each time period would give an appropriate display of the data. Table 34 gives the results of the alpha emitter leach tests. An analysis of variance was performed for each time period separately, for the factors cement type, sludge type, and sludge content. For this purpose, each zero point was assumed to be equal to its upper bound [0.2 dis/(min)(ml)]. This procedure gave the minimum possible variance for the data, so that effects not significant in this treatment would also not be significant if lower values were assumed for the zero points. The statistical analysis showed that none of the factor effects or interactions were significant at any time period, with a few minor exceptions. The variances were so large that any possible effects of individual factors were masked. Thus, the data for each time period were averaged to give the time behavior shown in Figure 33. For the data at 2 hr, the only time period with no zero points, an analysis of variance was performed excluding the 40% sludge-content points, but the results were not significantly different from the analysis including these points.

Some effects of minor significance were found at some, but not all, of the time periods. Because of the manner of data treatment, the importance of these effects could not be assessed. The effect of sludge type was significant at 72, 504, and 1008 hr. At each of these times, the order of alpha emitter leachability was Tank 13 $\sim$ Tank 15 < Tank 5. At 2 hr, the effect of sludge content was significant, with the order 25% < 40% $\sim$ 10%. The effect of cement type was significant at 1008 hr, with HAC < I-P; also at 1008 hr a minor interaction between cement type and sludge type was found.

TABLE 34

Alpha-Emitter Leachability of Concrete Waste Forms Containing Actual SRP Sludges

Time, hr	*Zero Points*[a]	*Error Factor,* ε	*Alpha Leachability,*[b] 10^{-7} *g/(cm²)(d)*	*Cumulative Fraction Leached,*[b] *ppm*
2	0	1.37	240	2.6
6	7	1.53	<14	<3.5
24	14	1.60	<1.8	<4.2
72	8	1.76	<1.7	<6.6
216	13	2.11	<0.39	<9.1
504	18	1.74	<0.12	<10.1
1008	10	1.41	<0.088	<11.0

a. Each zero point was set at its upper bound [0.2 dis/(min)(ml)] to calculate upper limits on alpha leachability and fraction leached.

b. Each entry is the geometric mean of 36 measurements.

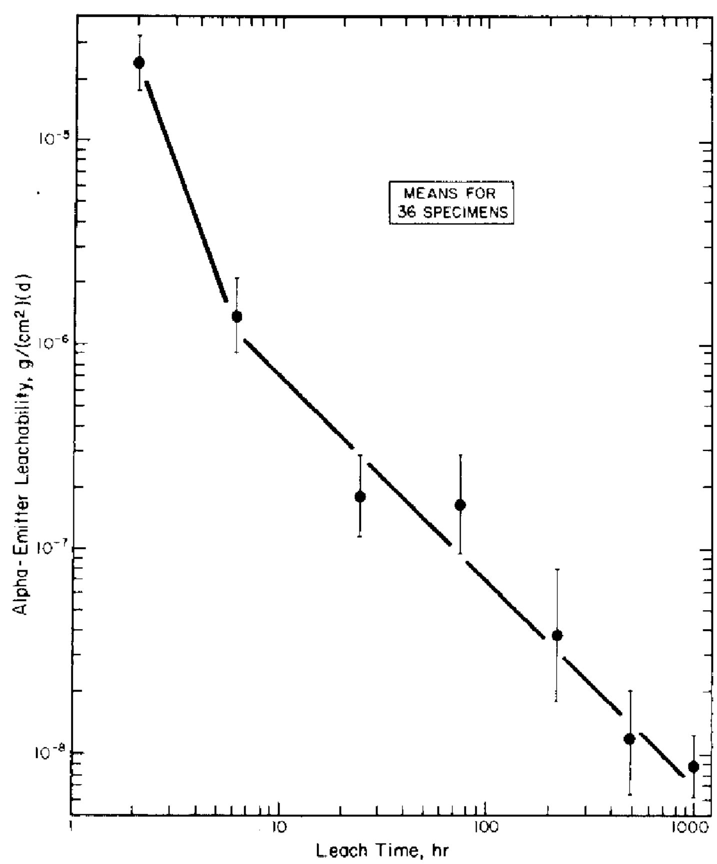

FIGURE 33. Alpha-Emitter Leachability of Concrete Waste Forms

Table 34 shows both the average leachability and the average cumulative fraction leached for alpha emitters from the concrete specimens containing actual SRP sludges. These may be compared with plutonium leachabilities from concrete waste forms containing simulated sludges (Table 10). The results agreed very well for both leachability and fraction leached. The fraction leached with actual SRP sludges is less than 11 ppm, or about 10^{-3}%. Other notable features of the data include the time behavior of the alpha emitter leachability; as shown in Figure 33, the data from 6 to 1008 hr is approximately proportional to t^{-1}. This indicates that a mechanism other than diffusion (which would be proportional to $t^{-1/2}$) controlled the leaching of alpha emitters.

Thermal Stability

Specimens of selected concrete formulations containing actual SRP sludges were heated at 400°C for one month and then measured for leachability and dimensional changes. These tests were made to gain additional information on the effects of a prolonged abnormally high storage temperature on concrete waste forms. Earlier work with simulated sludges showed that concrete specimens maintained mechanical integrity up to 400°C and that prolonged heating at 100°C had only slight effects on compressive strength. However, no leach tests were made with heated specimens containing simulated sludges; these could be done more efficiently with actual sludges. The principal conclusions from the tests with heated specimens are:

- ^{90}Sr leachability increased by factors up to 500.
- ^{137}Cs leachability of HAC specimens increased by factors up to 6.
- ^{137}Cs leachability of I-P specimens decreased by factors up to 20.
- Alpha-emitter leachability decreased slightly.
- Weight losses up to 33% and dimension reductions up to 7% were found.

Experimental Procedure. Castings of 8 representative formulations with actual SRP sludges and 1 without sludge were selected for the thermal stability tests. A single specimen, of leach-test size, was cut from each of the 9 castings. The specimens were measured and weighed prior to heating. Typically, the diameters were about 2.4 cm, the lengths were about 2.5 cm, and the weights were about 20 g. The specimens were placed in a 3 x 3 array in a vertical tube furnace inside a shielded cell, and held at 400°C continuously for one month. At the end of the heating period, the furnace was turned off, and the specimens were cooled and stored in the furnace for 17 days. Then they were removed from the furnace, measured, weighed, and prepared for leach tests. Changes in dimensions and weights are given in Table 35.

TABLE 35

Dimensional Changes in Concrete Waste Forms
Heated 1 Month at 400°C

Cement Type	*Sludge Waste Tank*	*Sludge Content,[a] %*	*Water Fraction,[b] %*	*% Change, After Heating*		
				Weight	*Length*	*Diameter*
HAC	None	0	19.0	-16	-5.5	-1.5
	13	10	21.5	-18	-2.0	-2.6
	13	25	24.1	-20	-2.5	-3.0
	13	40	32.9[d]	-32	-4.6	-5.8
HAC	5	40	26.8[c]	-22	-3.9	-6.7
	13	40	32.9[d]	-32	-4.6	-5.8
	15	40[e]	33.1[c]	-30	-4.3	-6.9
I-P	5	40	26.6	-20	-2.3	-2.6
	13	40	31.1	-28	-2.0	-3.4
	15	40[e]	32.3	-32	-5.1	-7.2

a. Expressed as Sludge/(Sludge + Cement).

b. Expressed as Water/(Sludge + Cement + Water).

c. Formulation contained excess water to prevent rapid setting.

d. Formulation set before castings were made; excess water added after set.

e. 37.5% sludge + 2.5% cesium-loaded zeolite.

Leach tests on the 9 heated specimens and a blank were performed in a shielded cell by the same procedures as for the unheated specimens. Leach waters were changed at 7 time periods up to six weeks (1008 hr), and analyzed for ^{90}Sr, ^{137}Cs, and gross alpha activity, as before. ^{90}Sr and ^{137}Cs measured in the blank were negligible, and in the test with a specimen containing no sludge were less than 10%, and typically 1% of the activity found for the specimens with sludges. As with the unheated specimens, the gross alpha activity was very low, ranging from 0 to 10 dis/(min)(ml), and somewhat higher for the last two time periods; alpha activity of the blank was of the same order of magnitude. However, leach waters from the specimen with no sludge contained 0 dis/(min)(ml) for the first five time periods, and an anomalously high value of 140 dis/(min)(ml) at 1008 hr.

Results. The leach tests revealed leachabilities that decreased with time in much the same way as for unheated specimens. Most of the leachabilities of the heated specimens were greater than those of unheated specimens, although in a few cases the reverse was found. Table 36 gives some of the ^{90}Sr leach data for the heated specimens, and compares those with data for unheated specimens, expressed as percent change after heating. The initial leachabilities (at 2 hr) are given, together with the cumulative fractions leached after 1008 hr. Similar data for ^{137}Cs are shown in Table 37. The alpha emitter leachabilities showed considerable scatter, but were similar to those of unheated specimens. For the 8 tests, the mean alpha emitter leachability at 2 hr was 4.9×10^{-6} g/(cm^2)(d), a change of -80% from the mean for the unheated specimens, and the mean cumulative fraction leached after 1008 hr was <6.4 ppm (-42%). In Figure 34 are shown the mean alpha emitter leachabilities and examples of ^{90}Sr and ^{137}Cs leachabilities for heated and unheated specimens. The ^{90}Sr and ^{137}Cs examples shown represent extremes, rather than typical behavior.

TABLE 36

^{90}Sr Leachability of Concrete Waste Forms Heated 1 Month at 400°C

Cement Type	*Sludge Waste Tank*	*Sludge Content, %*	*^{90}Sr Leachability,[a] 10^{-3} g/(cm^2)(d), at 2 hr*	*Cumulative Fraction, of ^{90}Sr Leached,[a] %, after 1008 hr*
HAC	13	10	2.2 (+ 260%)	0.85 (+ 840%)
	13	25	1.7 (+ 330%)	0.80 (+ 1,400%)
	13	40[c]	2.4 (+ 860%)	1.19 (+ 1,400%)
HAC	5	40[b]	1.3 (+2,900%)	0.54 (+13,500%)
	13	40[c]	2.4 (+ 860%)	1.19 (+ 1,400%)
	15	40[b,d]	3.0 (+ 150%)	1.55 (+ 350%)
I-P	5	40	0.42 (+1,200%)	0.13 (+ 1,300%)
	13	40	0.83 (+ 350%)	0.14 (+ 45%)
	15	40[d]	1.8 (+ 21%)	0.81 (- 7%)

a. % change given in parentheses; underlined values are statistically significant differences between heated and unheated specimens.

b. Formulation contained excess water to prevent rapid setting.

c. Formulation set before castings were made.

d. 37.5% sludge + 2.5% cesium-loaded zeolite.

TABLE 37

^{137}Cs Leachability of Concrete Waste Forms Heated 1 Month at 400°C

Cement Type	*Sludge Waste Tank*	*Sludge Content, %*	*^{137}Cs Leachability,[a] 10^{-3} g/(cm^2)(d), at 2 hr*	*Cumulative Fraction of ^{137}Cs Leached,[a] %, after 1008 hr*
HAC	13	10	240 (+370%)	36.3 (+37%)
	13	25	320 (+510%)	40.2 (+12%)
	13	40[c]	300 (+ 88%)	38.5 (-26%)
HAC	5	40[b]	82 (+430%)	12.2 (+28%)
	13	40[c]	300 (+ 88%)	38.5 (-26%)
	15	40[b,d]	13 (+ 49%)	6.4 (+49%)
I-P	5	40	30 (- 77%)	15.0 (- 4%)
	13	40	25 (- 95%)	25.9 (-44%)
	15	40[d]	8 (- 84%)	13.2 (+42%)

a. % change given in parentheses; underlined values are statistically significant differences between heated and unheated specimens.

b. Formulation contained excess water to prevent rapid setting.

c. Formulation set before castings were made.

d. 37.5% sludge + 2.5% cesium-loaded zeolite.

The ^{90}Sr leachability of heated specimens initially was greater than that of unheated specimens by factors up to 30. For most of the specimens, the time curves of heated and unheated specimens diverged, so that after 1008 hr, the ^{90}Sr leachabilities differed by factors up to 500. The cumulative fraction leached was 136 times greater for the heated specimen in one case, but up to only 15 times greater for the others. All of the HAC specimens had large increases in ^{90}Sr leachability after heating, but two of the specimens made with Type I-P cement had relatively small changes. After heating, the order of cement types for ^{90}Sr leachability was I-P < HAC, the reverse of the order before heating. The order of sludge types was Tank 5 < Tank 13 < Tank 15, both before and after heating. For Tank 13 sludge, the order for sludge contents was 10% ∿ 25% ∿ 40%, both before and after heating. The cumulative fractions of ^{90}Sr leached after heating were no more than 1.5%, which, although larger than before heating, are nevertheless quite small. In Figure 34, HAC with 40% Tank 5 sludge, the example shown for ^{90}Sr leachability, had much greater differences between heated and unheated specimens than any other formulation. In this case, heating changed the ^{90}Sr leachability from exceptionally good to average.

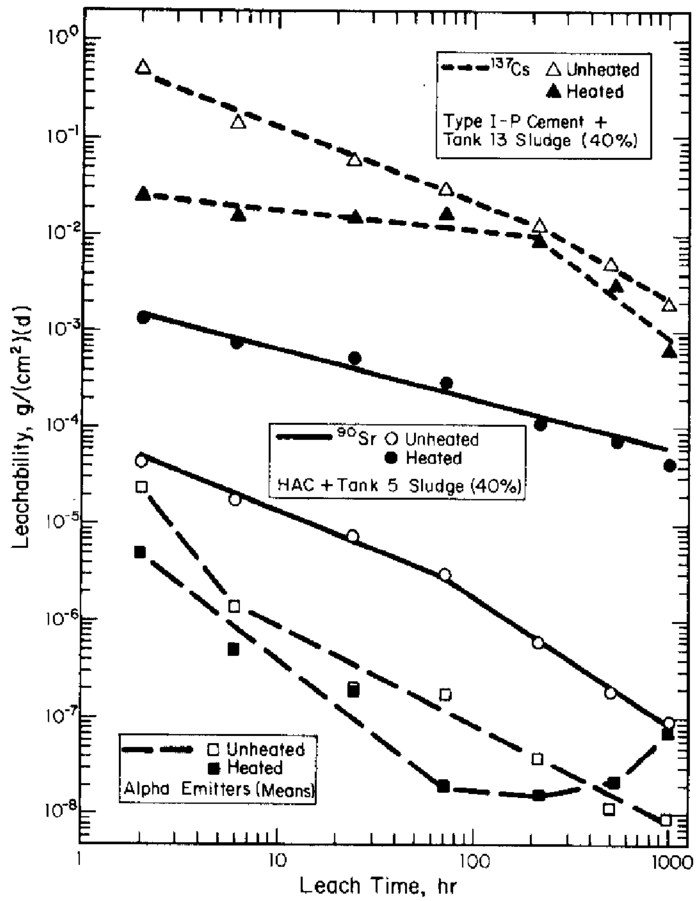

FIGURE 34. Effect of Prolonged Heating at 400°C on Leachability

The behavior of ^{137}Cs leachability at early times for the heated specimens differed for the two cement types. With HAC, the ^{137}Cs leachability of the heated specimens initially was greater than that of unheated specimens by factors up to 6; with Type I-P cement the unheated specimens had greater initial ^{137}Cs leachabilities by factors up to 20. With both cement types, the time curves of heated and unheated specimens converged, and in some cases crossed at later times. Generally at 1008 hr, there was little difference between the ^{137}Cs leachabilities of the heated and unheated specimens. This is shown in Figure 34 for the formulation with Type I-P cement and 40% Tank 13 sludge, the best case found. The order of cement types at early times was I-P < HAC for ^{137}Cs leachability, and at later times HAC < I-P for the heated specimens; the orders are reversed from those found with the unheated specimens. For the specimens heated, the order of sludge types was Tank 15 < Tank 5 < Tank 13 (Tank 5 ∿ Tank 13 with Type I-P cement) for ^{137}Cs leachability, the same order as for unheated specimens; at later times, the leachabilities for the different sludge types converged. For Tank 13 sludge, the heated specimens had the order of sludge contents as 10% ∿ 25% ∿ 40% for ^{137}Cs leachabilities, instead of increasing with sludge content as with the unheated specimens. The cumulative fractions of ^{137}Cs leached after 1008 hr are quite high for both the heated and unheated specimens. However, the addition of zeolite continued to be effective for retaining cesium, even after heating at 400°C for a month.

As shown in Figure 34, the alpha emitter leachability of heated specimens is slightly less than that for unheated specimens, although with large scatter in both sets of data, the differences may be within the uncertainties of the measurements. The unusual upturn in the alpha emitter leachability curve for heated specimens at the later time periods may be associated with an increase in background, as suggested by the blank and no-sludge tests. The alpha emitter leachability and cumulative fraction leached continued to be very small after heating, and apparently were not adversely affected by the heat treatment.

The heat treatment at 400°C caused the specimens to shrink slightly and lose up to 1/3 of their weight (Table 35). From previous studies by thermogravimetric and effluent gas analysis (Table 21), the weight losses were shown to be almost entirely from evolution of water. The small amounts of mercury in the specimens contributed less than 0.5% to the weight losses. The water fractions of the specimens before heating, calculated from the formulations, may be compared in Table 35 to the weight losses after heating; nearly all of the available water, typically 90%, was evolved. Apparently a small part of the available water remained chemically bound in the concrete specimens at 400°C, perhaps contributing to the mechanical integrity at this temperature. The weight losses were more than double those found from prolonged heating at 100°C (Table 13), reflecting the dehydroxylation reactions that occur at the higher temperature. The shrinkage of the specimens is associated with loss of water in two ways: first, the pore spaces lose capillary water to become voids and thus tend to contract; second, loss of water of crystallization and subsequent dehydroxylation change crystal structures to give smaller unit cells. At temperatures higher than 400°C, these processes lead to complete loss of cementitious properties and mechanical integrity.

The changes in leachability found after heating do not appear to be associated with mechanical changes in the specimens. For example, any change in effective surface area should affect the leachability of all species in the same way. However, leachability of alpha emitters decreased, ^{137}Cs leachability increased in some specimens and decreased in others, and ^{90}Sr leachability increased greatly. Thus, the changes in leachability after heating concrete specimens at 400°C for one month are presumed to be due to predominantly chemical effects.

CONCLUSIONS AND FUTURE WORK

These studies have given experimental demonstration of the properties of concrete for solidification of SRP high-level radioactive waste. Formulations of cement and washed, dried sludge powders are easy to prepare, and the waste is chemically compatible with concrete. Sludge loadings up to 40 wt % give waste forms with generally excellent properties.

Among the properties of concrete waste forms measured and found to be adequate are:

- Compressive strengths of 2000 to 3000 psi for many formulations with 40% sludge content, and greater compressive strengths if the sludge content is reduced.
- ^{90}Sr leachabilities typically 10^{-6} to 10^{-4} g/(cm^2)(d).
- Alpha emitter leachabilities typically 10^{-8} to 10^{-5} g/(cm^2)(d).
- Reasonable long-term thermal stability up to 400°C, although water is evolved above 100°C.
- Excellent long-term radiation stability of the solid waste form, as manifested by strength and leachability; radiolytic gassing was not considered in this study.

Other properties were measured, and some were found to be inherently poor, but methods are available to overcome any problems these properties might cause. These include:

- ^{137}Cs leachabilities typically 10^{-3} to 10^{-1} g/(cm^2)(d); the high cesium leachability from concrete may require exceptionally thorough washing of sludges to remove free cesium and/or incorporation of quantities of zeolite into the concrete to retain cesium.
- High pressures (of steam) generated when concrete forms are heated in closed containers; a degassing step can reduce final pressures, and containers can be designed to accommodate pressures resulting from an abnormally high temperature.

- Set times of cement-sludge pastes can be rapid in some cases, but can be retarded with additives.

Optimum formulations of cement, waste, and water have been defined. Simulated sludges in concrete behave like actual SRP sludges in all properties measured; therefore, large-scale engineering development with simulated sludges should give valid results. Actual sludges were found to be highly variable, both in composition and in behavior when incorporated into concrete. However, concrete can accommodate all types of sludges encountered so far.

High-alumina cement is superior to portland cements for preparing waste forms with SRP sludges. The various types of portland cements are alike in properties with simulated sludges; a portland-pozzolanic cement was found to be slightly better than others in this group.

A number of possibilities for future studies exist, including:

- Long-term radiation stability of castings with actual sludges.
- Thermal effects and other properties with large-scale castings.
- Evaluation of additional sludge types in concrete.
- Different sorbents and formulations for better cesium retention.
- Evaluation of additional methods for set retardation.

Extra castings of concrete with actual SRP sludges have been stored for future study. Long-term radiation stability of the castings can be evaluated by repeating the series of compressive strength and leachability tests on aged specimens. Several of the castings have been sealed in containers with pressure gauges to monitor the effects of radiolytic gassing over a long period (perhaps years).

All of the measurements described in this report have been directed at determining the fundamental characteristics of concrete forms containing SRP wastes. Thus, a basis case has been defined, which may be used as a starting point in efforts to create improved waste forms with concrete.

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