V' . '

DP-MS-77-108

CONF-780545--1

MASTER

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

by

J. A. Stone

E. I. du Pont de Nemours and Co.
Savannah River Laboratory
Aiken, South Carolina 29801

A paper to be presented at the
Annual Meeting of the American Ceramic Society
Detroit, Michigan
May 6-11, 1978

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

DISCLAIMER

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

by

J. A. Stone

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29801

INTRODUCTION

The Savannah River Plant (SRP) has stored in underground tanks large quantities of highly radioactive waste from reactor fuel processing. Solidification of this waste is desirable for safe, long-term storage. A variety of solid matrices have been suggested for fixation of SRP high-level waste.[1] These include concrete, glass, ceramics, minerals, asphalt, and calcine.

Concrete has been evaluated as a candidate for fixation of SRP waste because of its simplicity for a process operated at ambient temperature. However, glass is now being investigated as a reference process for future solidification of SRP waste, on the potential basis of comparable cost and superior product characteristics. Nevertheless, in studies to be described in this paper, concrete was found adequate for fixation of wastes of this general type.

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

In laboratory-scale studies, concrete was evaluated thoroughly as a matrix for solidification of SRP waste.[2] Results of tests with simulated waste in nonradioactive and tracer-level concrete specimens were reported earlier.[3] The major results and conclusions from experiments with fully radioactive specimens containing actual SRP waste are summarized here.

DESCRIPTION OF SRP HIGH-LEVEL WASTE

As shown in SLIDE 1, SRP high-level waste consists of two phases: an aqueous supernate (some of which has been evaporated to a salt cake) and a gelatinous sludge.

About 20 million gallons of supernate and salt cake are stored in the waste tanks. The supernate is an alkaline aqueous solution of various process chemicals, primarily sodium nitrate. Hydroxide, nitrite, aluminate, sulfate, carbonate, and other anions also are present in significant quantities.[4] The supernate contains nearly all of the ^{137}Cs in the waste.

About 2 million gallons of sludge are in the waste tanks. The sludge is composed of hydrous oxides of various metal ions encountered in fuel processing, principally iron, manganese, and aluminum. Appreciable amounts of uranium, entrained sodium, and more than 30 other elements also are found in the sludge.[5] Except for most of the ^{137}Cs in the supernate, all of the radionuclides in the waste are in the sludge; the principal radionuclides in aged sludge are ^{90}Sr and alpha emitters such as ^{239}Pu.

In a conceptual process for solidification of SRP waste, essentially all of the radionuclides in the waste would be fixed in the concrete. Only washed, dried sludge and ^{137}Cs separated on zeolite from the supernate would be incorporated into concrete.

EXPERIMENTAL PROCEDURE

Concrete formulations were prepared with 2 types of cement, 3 types of sludge, and 3 levels of sludge content, as shown in SLIDE 2.

High-alumina cement (HAC) and Type I-P portland-pozzolanic cement were selected as the best of six cement types in earlier studies with simulated sludges.[3]

Washed, dried sludges from three waste tanks were representative of the chemical difference expected of wastes generated at different times from diverse processes.[5] Tank 5 sludge contains principally iron and manganese (40 and 16 mol %, respectively). Tank 13 sludge is similar but also contains 21 mol % aluminum. Tank 15 sludge is very high in aluminum (86 mol %).

Sludge contents of 10, 25, and 40 wt % of solids were used. Formulations without sludge also were prepared as experimental controls.

Two of the 18 formulations with sludges also incorporated a small amount of zeolite loaded with cesium from SRP supernate.

SLIDE 3 shows mixing and casting of the cement-sludge paste in a shielded cell. These operations were performed remotely with master-slave manipulators.

Water content for each formulation was adjusted to give best workability of the paste. Water/cement ratios for best workability increased with increasing sludge content, and ranged from 0.23 to 0.66 with HAC, and 0.33 to 0.77 with Type I-P cement.

In one preparation with HAC and 40% sludge, the mixture set rapidly. In two subsequent formulations with HAC and 40% sludge, excess water was added to prevent rapid setting. In other formulations with either HAC or Type I-P cement, the correct amount of water was used, and no rapid setting was observed. Later studies showed that an organic set retarder was effective in preventing rapid set of cement-sludge pastes.[6]

The concrete-waste castings were cured, sawed into test specimens, and evaluated by compressive strength measurements, leach tests, and long-term heating tests. These tests also were made in shielded cells.

RESULTS AND DISCUSSION

Compressive Strength

Typical results of compressive strength measurements are shown in SLIDE 4, where strength is plotted as a function of sludge content.

Sludge content had the greatest effect on strength, which decreased as the sludge content increased. The effects of cement type and sludge type on compressive strength were relatively minor.

All of the specimens with HAC and 40% sludge were exceptionally weak, because of rapid set or excess water. Specimens with Type I-P cement, for which no set-time problems were encountered, gave strengths with a regular trend up to 40% sludge content.

Cesium-loaded zeolite, added to two formulations, had no discernible effect on compressive strength.

Compressive strengths were 2000 to 3000 psi for many of the formulations with 40% sludge content. Strengths in this range are considered adequate to ensure a low probability of breaking into smaller pieces.

Leachability

The principal features of leaching radionuclides from concrete-waste specimens are shown in SLIDE 5. Leachability in $g/(cm^2)(d)$ is plotted as a function of time over a six-week leaching period (1008 hours). Leachabilities are shown for residual free ^{137}Cs (not bound to zeolite), ^{90}Sr, and alpha emitters, for one of the best formulations.

Leachabilities decreased with time, often over several orders of magnitude in six weeks.

Effect of Radionuclide

For all the formulations, the relative order of leachabilities was:

$^{137}Cs >> ^{90}Sr >$ alpha emitters

Typical leachabilities were:

- ^{137}Cs 10^{-1} to 10^{-3} g/(cm^2)(d)
- ^{90}Sr 10^{-4} to 10^{-6} g/(cm^2)(d)
- alpha emitters 10^{-5} to 10^{-8} g/(cm^2)(d)

The leachability of free ^{137}Cs from concrete is unsatisfactorily large. Up to 75% of ^{137}Cs in small test specimens was leached in six weeks. However, formulations with zeolite added had ^{137}Cs leachabilities 10 to 30 times lower than without zeolite. Subsequent studies by Plodinec have shown that adequately low ^{137}Cs leachability from concrete may be attained by incorporation of zeolite or other sorbents.[7]

^{90}Sr is retained very well in concrete. Less than 1%, and in some cases less than 0.01% of ^{90}Sr in small test specimens, was leached in six weeks.

Concrete retains alpha emitters extremely well, with less than 10^{-3}% leached after six weeks. This compares favorably with the leachability of alpha emitters from glass.

Effect of Cement Type

SLIDE 6 compares the ^{90}Sr leachability of HAC and Type I-P cement for a typical case. HAC specimens generally were less leachable than specimens made with Type I-P cement. The differences were statistically significant, but were not very large.

Similarly, the ^{137}Cs leachability with HAC generally was less than with Type I-P cement. For alpha-emitter leachability, no difference between the cement types was detected.

Effect of Sludge Type

SLIDE 7 compares ^{90}Sr leachability of the three sludge types for a typical case. In every case, the ^{90}Sr leachability was in the following order:

Tank 5 < Tank 13 < Tank 15

The same ordering of sludge types was found for ^{137}Cs leachability, compressive strength, and water/cement ratios. The good correlation of these properties with aluminum content in the sludges is a likely explanation for the differences in behavior of the three sludges.

For alpha-emitter leachability, only minor differences between the sludge types were detected.

Effect of Sludge Content

In SLIDE 8, ^{90}Sr leachability is plotted as a function of sludge content, for a typical leach time. The behavior shown is consistent with the chemical compositions of the sludges. Tank 5 sludge has high manganese and low aluminum contents, and its ^{90}Sr leachability decreases with increasing sludge content. Tank 15 sludge has low manganese and high aluminum contents, and its behavior is opposite that of Tank 5 sludge. Tank 13 sludge, in which both aluminum and manganese are fairly high, is intermediate in behavior.

For ^{137}Cs, the effect of sludge content was somewhat different. Increasing sludge content generally increased the ^{137}Cs leachability. For alpha-emitter leachability, only minor differences between sludge contents were detected.

Thermal Stability

Specimens of selected concrete formulations containing actual SRP waste were heated at 400°C for one month and then measured for leachability. Examples of changes in leachability after heating are shown in SLIDE 9.

These tests were made to determine 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.[2]

As shown in SLIDE 9, the ^{137}Cs leachability of Type I-P specimens after heating decreased by factors up to 20; however, for HAC specimens, it increased by factors up to 6. The ^{90}Sr leachability increased by factors up to 500. Alpha-emitter leachability decreased slightly. The changes in leachability after heating are presumably due to chemical effects and not to any change in effective surface area, because each radionuclide behaved differently.

Other effects of elevated temperatures on concrete waste forms include gas generation, which could cause high pressure in closed containers. Water is evolved from the concrete above 100°C, and the pressure in a closed container was found experimentally to follow steam-table pressures.

Radiolytic gas production was not considered in this study, but has been investigated by Bibler. Beta-gamma radiolysis gave a relatively low equilibrium pressure of hydrogen, but alpha radiolysis did not reach a steady-state pressure.[8]

CONCLUSIONS

Some of the favorable and unfavorable characteristics of concrete as a matrix for solidification of SRP waste, as found in this study, are listed in SLIDE 10.

As noted earlier, compressive strength and leachability of ^{90}Sr and alpha emitters are very good. The waste forms have reasonable long-term thermal stability up to 400°C, although water is evolved above 100°C. Long-term radiation stability of the solid, as measured by strength and leachability, is excellent.

For the unfavorable characteristics, methods are available to overcome any problems these properties might cause. ^{137}Cs leachability can be reduced by additives such as zeolite. Steam generation can be reduced by an initial degassing step; however, radiolytic gassing may require further study. Set times can be retarded with additives. These are areas where additional development would be useful.

In conclusion, the fundamental characteristics of concrete forms containing SRP waste have been defined. This study provides a starting point in efforts to create improved waste forms with concrete.

REFERENCES

1. R. M. Wallace, H. L. Hull, and R. F. Bradley. *Solid Forms for Savannah River Plant High-Level Waste*. USAEC Report DP-1335, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1973).
2. J. A. Stone. *Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste*. ERDA Report DP-1448, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1977).
3. J. A. Stone. "Incorporation of Savannah River Plant Radioactive Waste into Concrete." *Am. Ceramic Soc. Bull. 54*, 463 (1975).
4. R. S. Ondrejcin. *Chemical Compositions of Supernates Stored in SRP High-Level Waste Tanks*. USAEC Report DP-1347, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1974).
5. J. A. Stone, J. A. Kelley, and T. S. McMillan. *Sampling and Analyses of SRP High-Level Waste Sludges*. ERDA Report DP-1399, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1976).
6. J. A. Stone and P. D. d'Entremont. *Measurement and Control of Cement Set Times in Waste Solidification*. ERDA Report DP-1404, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1976).

7. M. J. Plodinec. *Evaluation of ^{137}Cs Sorbents for Fixation in Concrete*. ERDA Report DP-1444, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1977).

8. N. E. Bibler. *Radiolytic Gas Production from Concrete Containing Savannah River Plant Waste*. DOE Report DP-1464, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, SC (1978).

Slide 1

SRP HIGH-LEVEL WASTE

Supernate ~20 Million Gallons

- Aqueous Solution and Salt Cake
- Primarily $NaNO_3$
- Also: OH^-, NO_2^-, AlO_2^-, SO_4^{2-}, CO_3^{2-}
- Radionuclides: ^{137}Cs

Sludge ~2 Million Gallons

- Gelatinous Precipitate - Hydrous Oxides
- Bulk Chemicals: Fe, Mn, Al, U, Na, etc.
- Radionuclides: ^{90}Sr, α-Emitters

Slide 2

CONCRETE FORMULATIONS WITH SRP WASTE SLUDGES

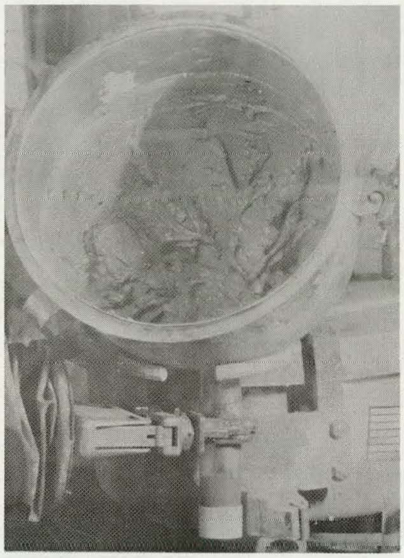
Cement Types — High-Alumina Cement (HAC)
Portland-Pozzolanic (I-P)

Sludge Types — Tank 5, Tank 13, or Tank 15

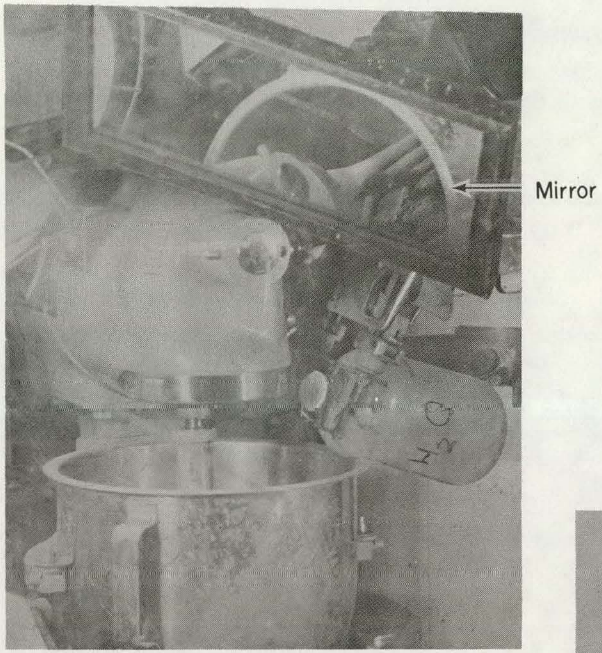
Sludge Contents — 10%, 25%, or 40%

Slide 3

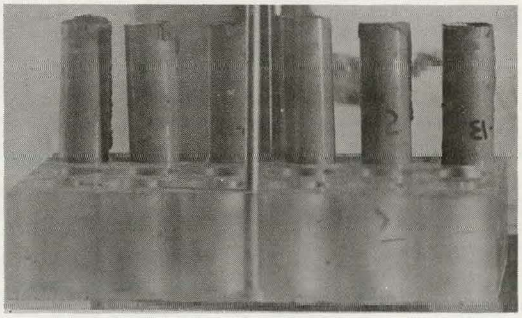
TRANSFER



MIXING

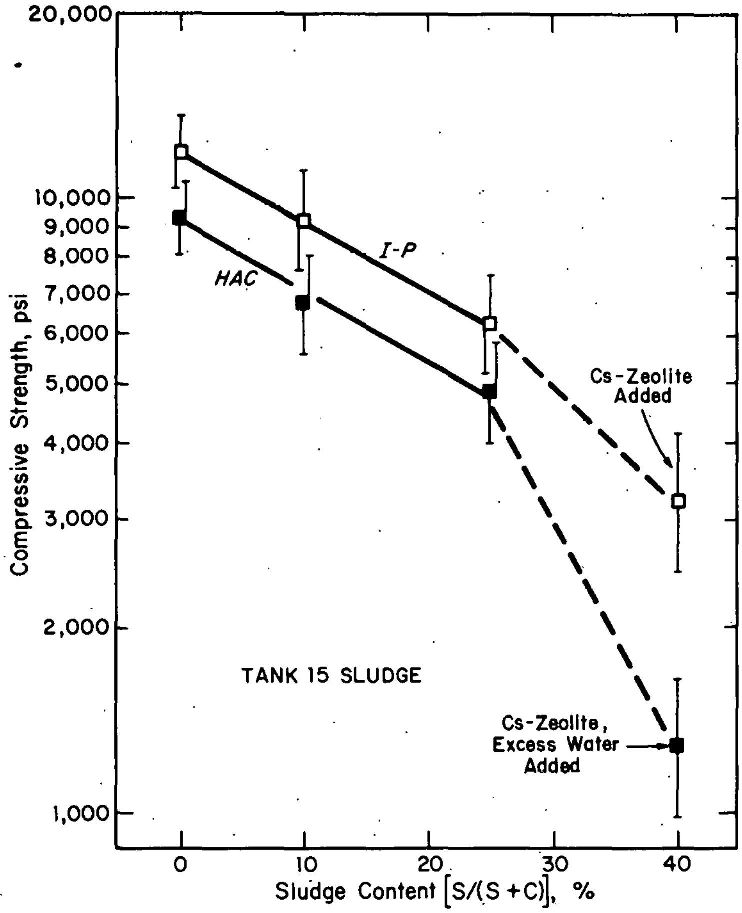


CASTINGS



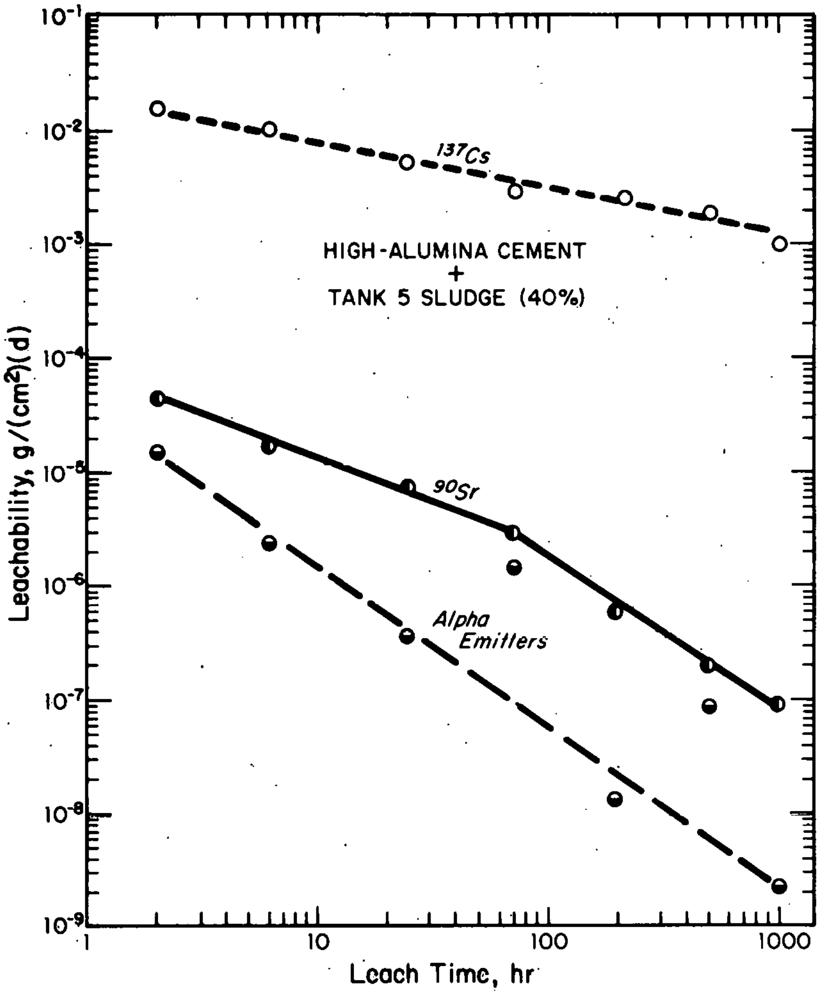
Slide 4

COMPRESSIVE STRENGTH OF CONCRETE WITH SRP SLUDGE

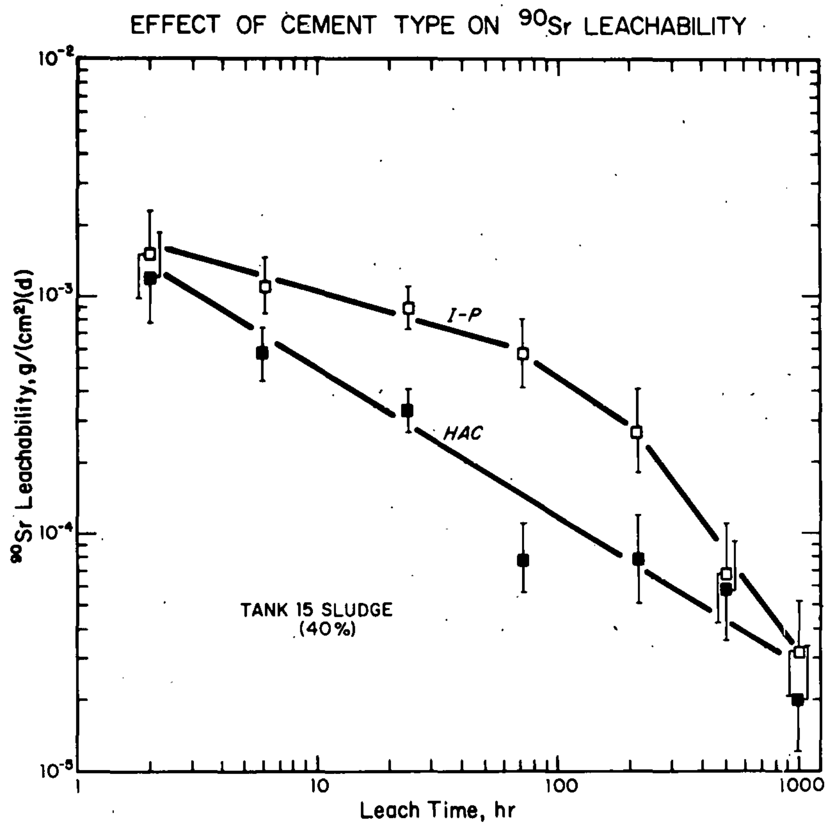


Slide 5

TYPICAL LEACHABILITIES OF RADIOACTIVE CONCRETE WASTE FORMS

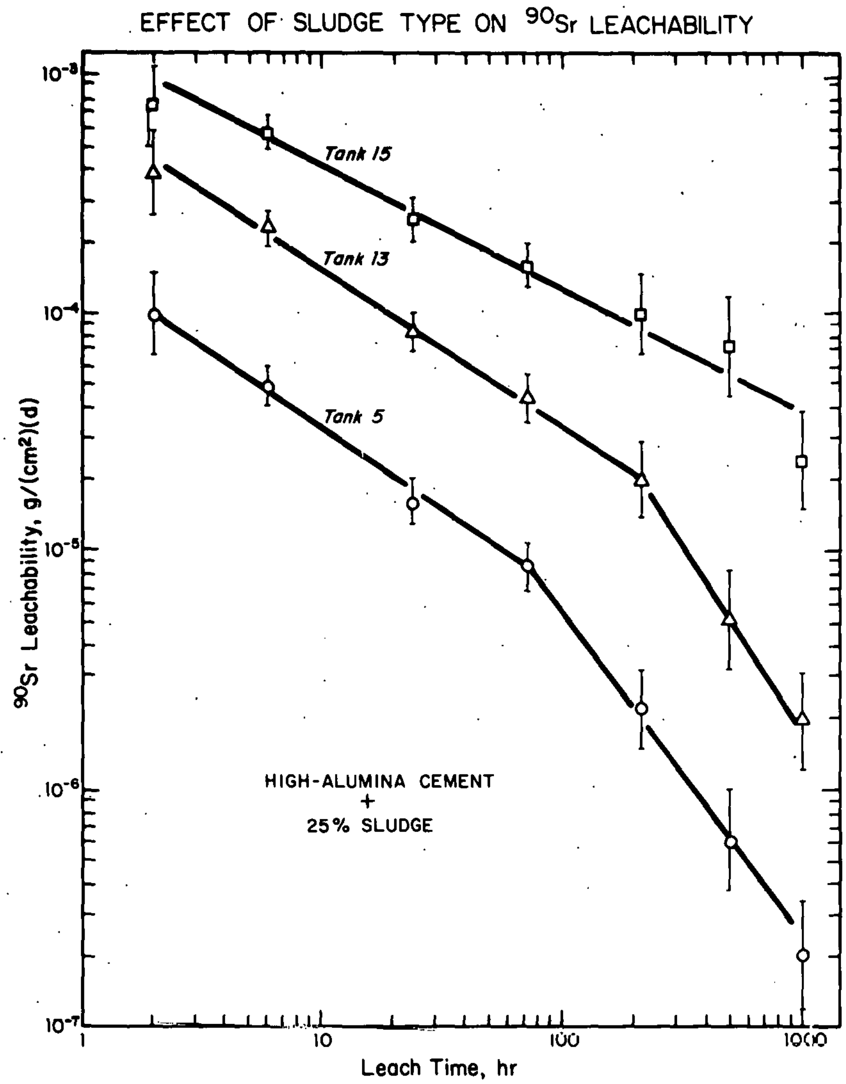


Slide 6



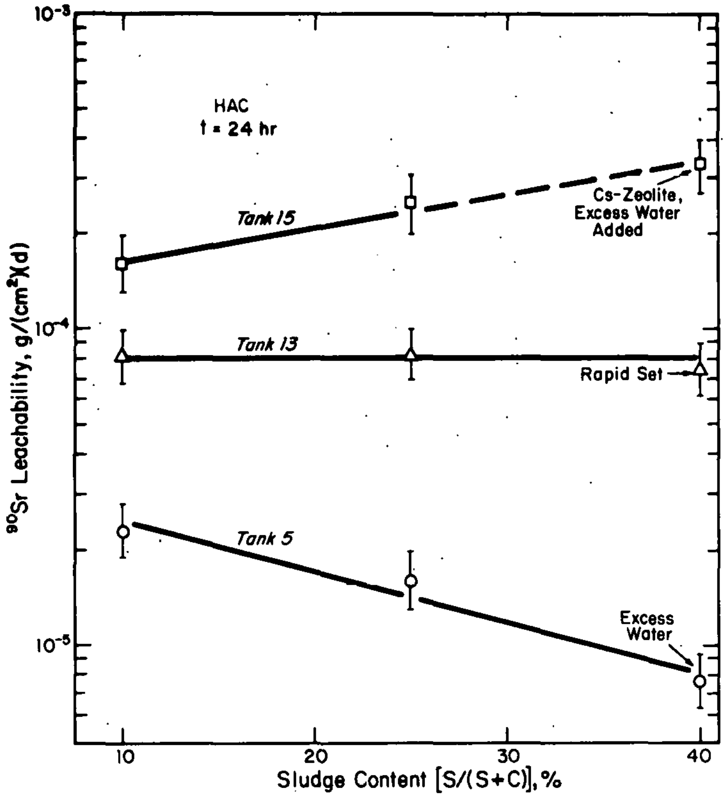
EFFECT OF CEMENT TYPE ON 90Sr LEACHABILITY
90Sr Leachability, g/(cm2)(d)
10-2
10-3
10-4
10-5
1
10
100
1000
Leach Time, hr
I-P
HAC
TANK 15 SLUDGE
(40%)

Slide 7


EFFECT OF SLUDGE TYPE ON ^{90}Sr LEACHABILITY
Tank 15
Tank 13
Tank 5
HIGH-ALUMINA CEMENT
+
25% SLUDGE
^{90}Sr Leachability, g/(cm^2)(d)
Leach Time, hr
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
1
10
100
1000

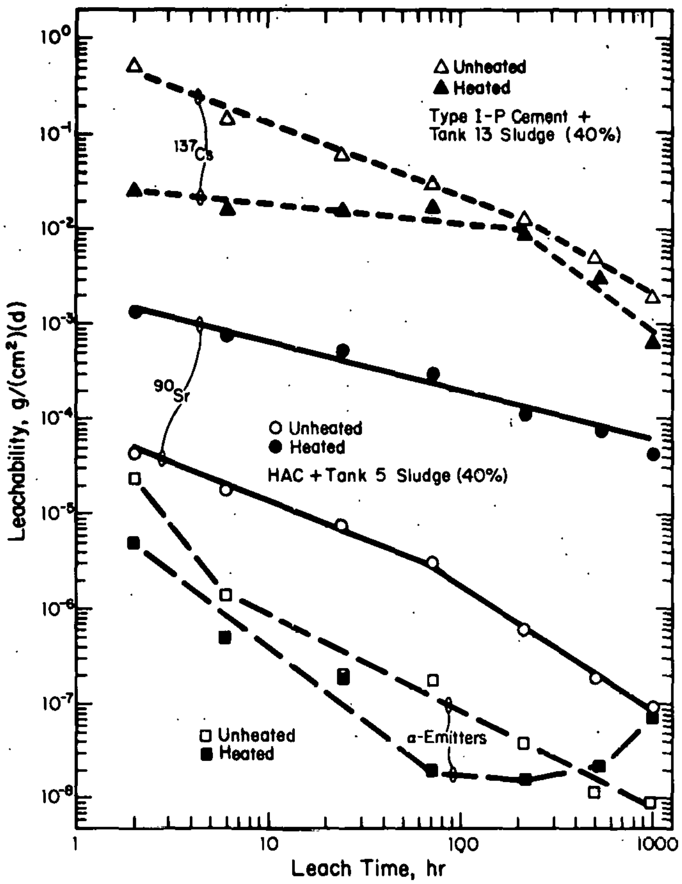
Slide 8

EFFECT OF SLUDGE CONTENT ON ^{90}Sr LEACHABILITY



Slide 9

EFFECT OF PROLONGED HEATING AT 400°C ON LEACHABILITY



Slide 10

CONCRETE FOR SRP WASTE

Favorable Characteristics

- Compressive Strength
- ^{90}Sr Leachability
- α-Emitter Leachability
- Thermal Stability
- Radiation Stability

Unfavorable Characteristics

- ^{137}Cs Leachability
- Gas Generation
- Set Times