# Solidification of Radioactive Waste by Inorganic Binders (Literature Survey)

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by

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# Verfestigung radioaktiver Abfälle mit anorganischen Bindern

## (Literaturübersicht)

## Zusammenfassung

Es wird eine Übersicht gegeben über die Verfestigung von radio-
aktiven Abfallösungen, Schlämmen und Tritiumwässern mittels
Zement und anderen anorganischen Bindemitteln.

Einem allgemeinen Überblick über die in der Literatur beschrie-
benen Möglichkeiten folgt eine etwas ausführlichere, durch
persönliche Informationen ergänzte Beschreibung der Arbeiten
an vier Forschungsstätten in den Vereinigten Staaten, nämlich
Oak Ridge National Laboratory, Savannah River Laboratory,
Brookhaven National Laboratory und Atlantic Richfield Hanford
Company.

Weitere Abschnitte beschreiben die Erfahrungen mit den verschie-
denen Zementsorten und die Möglichkeiten zur Verbesserung der
Verfestigungsprodukte durch Vorfixierung der toxischen Nuklide
(Umwandlung in unlösliche Produkte oder Absorption);ferner
gibt es die Möglichkeit einer Nachbehandlung durch Polymer-
Imprägnation.

Schließlich werden Definition und Bestimmung der Auslaugbarkeit
angegeben und einige Ergebnisse zusammengestellt.

# Solidification of Radioactive Waste by Inorganic Binders
## (Literature Survey)

## Abstract

A survey is presented of the solidification of radioactive
waste solutions, sludges and tritiated liquid effluents by
means of cement and other inorganic binders.

A general survey of the possibilities outlined in the litera-
ture is followed by a more detailed description with addi-
tional personal information of the work carried out at four
research centers in the United States, i.e., Oak Ridge National
Laboratory, Savannah River Laboratory, Brookhaven National
Laboratory, and Atlantic Richfield Hanford Company.

Other chapters describe the experience accumulated in the
use of various types of cement and the possibilities available
to improve the solidification products by prefixing toxic
nuclides (conversion into insoluble products or adsorption);
moreover, there is a possibility of subsequent treatment by
polymer impregnation.

Finally, definitions of and techniques for assaying the
leachability are given and some results are compiled.

# Contents

## 1. Introduction

The use of cement and similar inorganic binders for the so-
lidification of radioactive waste has been known since the
early days of nuclear technology. Surveys of the techniques
then known were written in 1968 (1), 1971 (2) and 1976 (3).

The present literature survey was compiled within the frame-
work of development activities on a technique of solidifying
intermediate level waste by means of inorganic binders, which
would also include tritiated waste. The survey is a general
description of the possibilities existing around the middle
of 1977. More specific information is presented mainly in
Chapter 4, which lists the experience accumulated in the
United States.

## 2. Solidification of Radioactive Waste by Inorganic Binders

### 2.1. Fixing Waste Solutions

In one of the earliest studies of the use of cement as a
solidifying agent also the technique of fixing alkaline
waste solutions is covered. Approximately 95 l of waste
solution plus some 172 kg of Portland cement is filled into
a drum of approximately 210 l capacity. After closing the
drum is rotated for 15 minutes at 3 revolutions per minute
(4).

Another older technique solidifies acidified waste (acid
concentration $\leq$ 2 N) without any stirring.

A drum with a volume of approximately 114 l is filled with
some 57-64 l of waste solution. Next, a mixture of Portland
cement and vermiculite (weight ratio 10:1) is added. This
must be done very slowly in the beginning, because there is
considerable heat generation (5).

Also, in Chalk River, Canada, large amounts of acidified
waste solutions were solidified in cement, some of them
with high contents of ammonium nitrate (up to 4 moles/l)
(6). In this case, a mixing ratio of 3.8 l of waste solution,
6.8 kg of Portland cement and 0.136 kg of bentonite turned
out to be advantageous. Mixing is done by means of a pro-
peller mixer. Again, a marked increase in temperature is
found. Since there is relatively strong leaching, a water-
tight enclosure must be provided. In a large scale process
the filled drums were cemented into large monolithic blocks.

At Los Alamos a technique has been developed and implemen-
ted to solidify a concentrated solution with a high percen-
tage of nitric acid and containing plutonium and americium.
The solution was neutralized by 50% caustic soda solution
prior to solidification. A drum of 208 l volume was filled
with 130 kg of Portland cement, 4.1 kg of vermiculite and
two half bricks as stirring aids; subsequently 75 l of
waste solution was added, and the drum was shaken for 15
minutes after closing (7). At a later date a continuous
technique was developed in which the cement and the waste
solution are mixed in a pug mill and pumped into holes in
the ground over a distance of 50 m (8).

The Moscow storage facility for radioactive waste reports
about the combined solidification of low level waste solutions
(salinity 45 g/l, pH 7 to 10) and solid waste. The solution:
cement ratio is 0.75. The solid waste is filled into a steel
reinforced concrete vessel submerged in the ground and filled
up with a cement mix (9).

Experiments have been described in Japan which are aimed at cementing waste solutions from reprocessing plants for subsequent ocean dumping (10). Simulated waste solutions acidified with nitric acid were neutralized and solidified with cement while various parameters were varied. When neutralizing with $Ca(OH)_2$, which also accelerates curing, the stability of the final product is increased most by high salinity and a low ratio of waste relative to cement. When neutralizing the waste with NaOH, the most important parameters to be observed are a low waste/cement ratio and a relatively long curing time.

Other techniques for the solidification of waste solutions, which differ from those described above only in some specific details, are reported by France (11), Norway (12), and Germany (13). In the early years of nuclear technology radioactive waste solutions were frequently cemented in drums later dumped into the ocean (14).

At the Brookhaven National Laboratory (15) evaporator concentrate containing 30% of solids is solidified in rectangular concrete vessels with a wall thickness of 15 cm and a volume of 2.27 $m^3$. For this purpose, Portland cement and vermiculite are mixed in the dry state in a ratio by volume of 1:3 and filled into the vessel; the liquid is filled from the bottom through a tube extending almost down to the bottom. The vessel completely filled up is closed with a layer of concrete of the same composition as that of the walls of the vessel. A typical charge consists of 0.91 $m^3$ of Portland cement, 2.7 $m^3$ of vermiculite and 1250 l of concentrated waste.

Besides cement also plaster is sometimes suggested as an agent for the solidification of radioactive waste solutions. The drawback that, according to the equation

$$CaSO_4 \cdot 1/2 \ H_2O + 1.5 \ H_2O \longrightarrow CaSO_4 \cdot 2 \ H_2O,$$
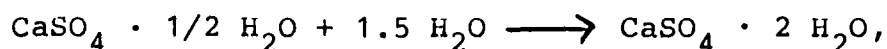
a maximum of approximately 15% of water can be bound chemically is avoided by adding adsorptive agents.

The solidification of acid and alkaline aqueous solutions
and organic compounds soluble in water with a minimum water
content of 50% is said to be possible in a mixture of plaster
and pumice or plaster and water glass, especially in small
quantities (16). 1 kg of a mixture of plaster and pumice in
a 1:1 ratio will solidify 500 ml of radioactive waste solution.
When applying a plaster-water glass mixture, 200 to 300 ml of
soda water glass are stirred batchwise into 1 kg of plaster;
and to the partly granular, partly pulverulent mixture can
then be added up to 500 ml of a radioactive aqueous solution.

In Japan, plutonium bearing waste solutions are solidified
by means of gypsum and vermiculite (17). For this application,
a 20 l steel tank lined with asphalt is used to prepare a mix-
ture of calcined dental gypsum and burnt vermiculite (1:1 vo-
lume ratio) with 10 l of waste solution (neutralized with
caustic soda solution). The solidification time is one hour.
By 1970, 1000 tons of plutonium waste had been solidifed in
this way.

For the solidification of a waste solution containing mainly
sodium nitrate and sodium hydroxide, the Hydraulic Fracturing
process was developed at the Oak Ridge National Laboratory
(18), about which more will be said below (page 11).

## 2.2 Fixing Sludges

The solidification of sludges arising from chemical preci-
pitation by cement has been implemented on an industrial
scale in various places and offers relatively few problems
(1). Frequently a mix of cement and vermiculite is used as
a solidifying agent. Difficulties mainly arise from mixing
the sludge with cement.

A number of laboratory studies were conducted on the solidi-
fication of precipitation sludges, most of which were con-
cerned with the choice of a suitable grade of cement or with
assessing the leachability of the products generated. It was
often found that product properties could be improved by ad-
ditives; limestone has been recommended (19) as well as ab-
sorbent materials such as sawdust in the case of phosphate
sludges (20)

The vacuum suction technique can be applied for direct ce-
mentation of sludges from suspensions (21). In this tech-
nique, for instance, a suspension with a water content bet-
ween 95 and 98% is mixed with 1.5 kg of Portland cement per
liter of suspension, agitated with a propeller mixer, and
the mix is sucked off under a vacuum. This produces 0.5 l
of filtrate. The volume of the residual cement mix is 1 l.
After 12 hours the solidified blocks can be taken from the
mold, after 48 hours they can be transported. The mechanical
properties and the leaching resistance are improved by this
treatment.

At the Savannah River Laboratory large amounts of waste
are stored in tanks which have separated into sludge and super-
natant liquid. These two phases are to be solidified separate-
ly; cf. p. 18.

## 2.3 Fixing_Other_Wastes

The fixation of spent ion exchangers as a preparation for
ocean dumping was investigated on a laboratory scale (22). One
volume fraction of mixed bed exchanger can be solidified into
a hard block with good leaching properties by two volume frac-
tions of Portland cement and one volume fraction of water.

For the solidification of fission product solutions resul-
ting from flushing a reactor core a method was proposed
in which a highly radioactive cement block is surrounded
by a shell of non-radioactive concrete and stainless steel.
A pozzolanic cement is used to which barite is added to in-
crease self-shielding (23).

Cementation is being discussed also as a possible alter-
native for the solidification of highly radioactive waste
solutions from reprocessing plants (24). Cement has also
been proposed as a substance to be used in solidifying highly
radioactive calcinates (25).

## 3. Fixing Tritiated Liquid Effluents

Tritium, the superheavy hydrogen isotope, is produced in
reactor operation as a fission product as well as from lithium,
boron or other substances as a consequence of neutron cap-
ture reactions and occurs as a highly diluted solution in
reprocessing. In principle, isotopic enrichment is possible
and is said to be quite attractive also costwise (26,27).

A discussion of the different fixing agents eligible for the
solidification of tritiated water is found in a report pub-
lished in 1973 (28):

- Generation of carbon-hydrogen bonds.
- Mechanical adsorption (e.g. on sawdust, silica gel or
  alumina).
- Hydrate formation (calcium sulfate), especially of hydro-
  genated silicates (Portland cement, zeolites, clays).
- Formation of metal hydrides (e.g. zirconium hydride).
- There is also the possibility of preventing the exchange
  between fixed tritium and the environment by adopting
  suitable measures.

Most studies of the practical possibilities at hand in
tritium fixation were only compiled in the past few years.
A survey of the methods applied in practice in tritium
treatment up until 1973 is available (29).

## 3.1 Fixing_in_Organic_Materials

Fixing tritium by generating C-H bonds was studied in great
detail at the Battelle Institute of Richland, Washington
(27, 30). Because of the easy execution, first of all tech-
niques were studied in which acetylene generated from cal-
cium carbide and tritiated water represented the first stage.
In one process this is converted into acetaldehyde by cata-
lytic addition of water, from which a reaction with resor-
cinol and formaldehyde produces a bakelite-type plastic. As
an alternative, polyacrylonitrile can be produced by the ad-
dition of hydrocyanic acid to acetylene and subsequent poly-
merization. From the outset, all these techniques are en-
cumbered with the drawback that, in the reaction of calcium
carbide with HTO, only half of the hydrogen goes to acetylene,
the other half going to calcium hydroxide which, for this
reason, has to be recycled. In addition, there were diffi-
culties (incomplete reaction) in the addition reactions of
water and hydrocyanic acid, respectively, with acetylene.

Another method of generating C-T bonds is the catalytic
hydrogenation of polystyrene, which is based on the electro-
lytic production of elemental hydrogen.
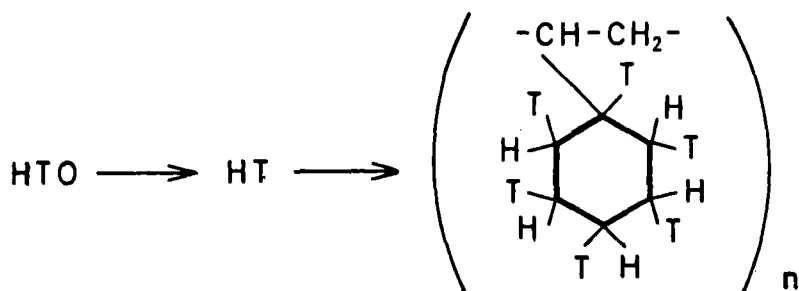
A catalyst (Rh on $Al_2O_3$) was found which allows the reaction
to proceed at atmospheric pressure and room temperature,
albeit at a lower rate.

The most positive of the techniques studied by Battelle is
based on the addition of water to isocyanates. Thus from
phenyl isocyanate and tritiated water through the intermediate
stage of an amine, finally diphenyl urea is generated. A polymer
type of polyureylene is generated from substituted phenyl
diisocyanates, in both cases tritium being bonded to nitrogen:

$$2 \ RNCO \ + \ HTO \longrightarrow RNHCONTR + CO_2$$
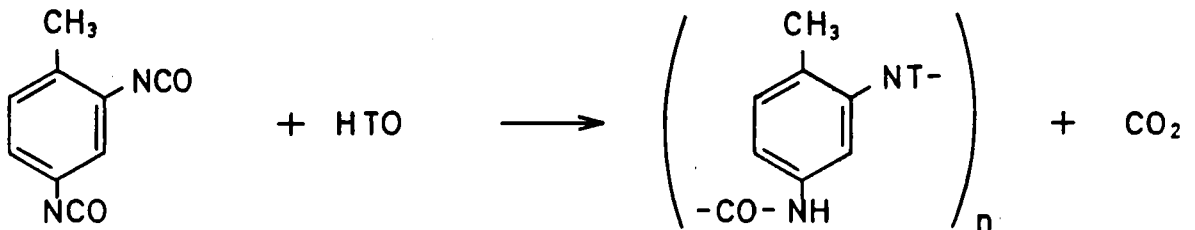


These products are powders with high exchange rates for tritium.
Products which can be fused to compact blocks are produced if
some of the water in the reaction of tolylene-2,4-diisocyanate
is substituted by ethylene glycol:
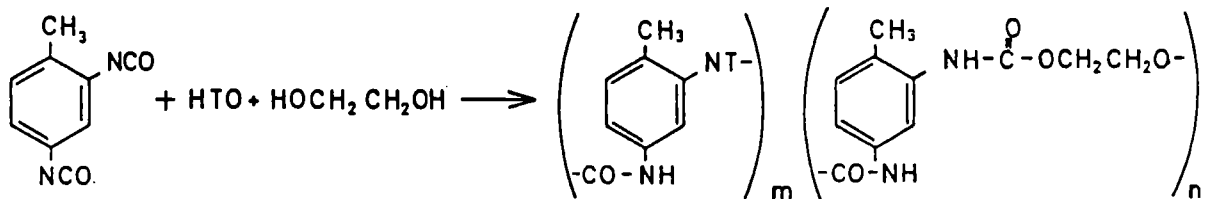
The components are made to react in acetone, the ratio between water and ethylene glycol being a maximum of 4:1. The powder produced is compacted in a cylindrical mold into a block of the density 1.15 at $220^{\circ}C$ and 1500 atm within 15 or 20 minutes. Compared with cement, such polymer offers the advantage of being impervious to water. Moreover, the reaction is very quick. The main drawback are the high costs which limit the application to small amounts of highly concentrated tritium solutions.

Studies of direct polymerization of tritiated acetylene were carried out at the Brookhaven National Laboratory (31). The acetylene made from calcium carbide and water can be polymerized by irradiation with $^{60}Co$ or catalytically by means of cupric oxide at about 240 to $280^{\circ}C$. The product, whose molecular weight is unknown and certainly has a broad distribution, is inert and non-volatile. It decomposes at approx. $325^{\circ}C$ and is flammable. The tritium cannot be exchanged. For further protection the substance can be embedded in cement or a polymer. Drawbacks of the technique are not listed explicitly, but there is mention of a number of gaseous secondary products generated in polymerization.

## 3.2 Fixing_in_Cement

The use of tritiated water in producing a cement block results in a product which still contains free water and easily exchangeable hydrogen atoms and, for this reason, is hardly useful in fixing tritium in an unmodified form. To reduce the exchange of tritium and its environment, it has been attempted to design a suitable coating for the cement blocks. Asphalt turned out to be most useful among a number of materials studied; also wax and paraffin can be used. (32)

As far as the product is concerned, a better method of re-
ducing the leachability of tritium is the generation of a
polymer-impregnated tritium cement (PITC) (31). For its
production a cement block with a relatively low ratio of
0.18 of water (with HTO) to cement after curing is soaked
with styrene containing 0.5% benzoyl peroxide as a starter.
In a cement block of approx. 45 cm diameter this soaking
takes about 3 to 4 hours; styrene amounts to some 15% of
the total weight. This step is followed by polymerization
which takes 24 hours at 50°C.

The products generated in this way have tritium leaching
rates as measured by the IAEA standard of approximately
$2 \times 10^{-4}$ (g $\cdot$ cm$^{-2}$ $\cdot$ d$^{-1}$). Thermogravimetric and differen-
tial thermal analyses indicate that water will become vo-
latile only above 120°C; there is complete decomposition
above 538°C. The compressive strength is increased by poly-
mer impregnation from a few hundred psi to 16,000 or 20,000
psi (1125 to 1400 kp/cm$^2$). When prepared with a common
water/cement ratio of 0.5 the types of cement used exhibited
after solidification compressive strengths of about 8000 to
12,000 psi (560 to 850 kp/cm$^2$). The resistance of the product
to radiolysis, frost and acid attack is excellent.

## 3.3   Fixing_by_Production_of_Metal_Hydrides

Fixing tritiated hydrogen as zirconium hydride is an obvious
choice, because it would allow the removal of spent zircaloy
fuel element claddings at the same time (33). The Zr/H phase
diagram indicates that two ZrH$_2$ phases have a stability range
extending between room temperature and approximately 900°C,
which makes them eligible for fixing hydrogen (34). However,
the practical implementation of hydride formation is not al-
together simple; the process is particularly sensitive to im-
purities (35).

The conditions under which zirconium hydride of the composition $ZrH_{1,5}$ to $ZrH_{1,9}$ will form quickly, i.e., within 20 minutes, have been determined (33, 36). Products with sufficient strength arise from the isothermal absorption of hydrogen at 760 torr and 600°C or in the addition of hydrogen at 760 torr by raising the temperature starting from 600°C until absorption is complete. In this case, the hydride is essentially free from cracks.

The stability of tritiated zirconium hydride to distilled water, saturated salt solutions and dilute acids and alkaline solutions turned out to be excellent (37).

Work on fixing tritium by means of zirconium was also carried out at Brookhaven (p.29 )

4.   **Present Status in the United States of America of**
      **Radioactive Waste Solidification by Inorganic Binders**

Because of the special significance of the development work carried out in the United States of America this will be described in a separate chapter based both on information from the literature and on personal information (38).

4.1  **Oak Ridge National Laboratory**
      **Hydraulic Fracturing Process**

Detailed descriptions of the technique can be found in (18) and (39).

Only waste generated in the plant is processed at Oak Ridge. It is collected in central tanks into NaOH solution. Concentration by a factor of 20 to 25 is achieved by evaporation. The distillates with approximately $2.5 \times 10^{-7}$ Ci/l are discharged into the main canal by way of ion exchangers. The concentrates have specific activities of 0.25 to 0.75 Ci/l; the $\beta/\gamma$-activity is mainly due to cesium-137.

The Hydraulic Fracturing process is carried out batchwise. Approximately 400 $m^3$ are injected within 8 hours; the injection rate is around 700 l/min. The binder/MAW mix is injected into shale formations about 250 m deep.

Four injections are made into one layer. The next injection is made about three meters higher. So far, a total of approximately 4000 $m^3$ of MAW have been processed by this technique. The injections are made through a coaxial tube. This allows the solidification of the binder-waste mix to be monitored; if necessary, the water released in the curing process may be returned through the second pipe. It is known from experience that this is generally less than 5% of the total volume injected. The layer spreading in the shale is traced through an observation borehole (approx. 30 m from the injection point) by means of a γ-probe. There has only been one case of plugging of the injection pipe in the shale layer in the course of plant operation because of too rapid curing of the mix.

The compositions of wastes and the cement-clay mixes used are shown in Tables 1 and 2. TBP serves as a curing retarder in order to ensure sufficiently long pumping capability. The compressive strengths of the products generated are relatively bad, being around 20 $kp/cm^2$. This is due to the high water/cement ratio (W/C ∿ 3) .

Table 1: Composition of Liquid MAW Concentrate at the Oak Ridge National Laboratory

Salinity:

∿ 125 g of salt/l, of which

∿ 70 g/l  $NaNO_3$

∿ 30 g/l  $Na_2CO_3$

∿ 13 g/l  $Na_2SO_4$

Distribution of Major Nuclides:

| Solution | | Sludge | |
|----------|---|--------|---|
| $^{137}Cs$ | 1 Ci/gal | $^{137}Cs$ | 0.1 Ci/g |
| $^{90}Sr$ | 0.1 Ci/gal | $^{90}Sr$ | 1 Ci/g |
| $^{244}Cm$ | 1 mCi/gal | $^{244}Cm$ | 0.1 Ci/g |

Table 2: Composition of the Binder Mix for Hydraulic Fracturing

| | |
|---|---|
| Portland cement | 38.5 wt.% |
| fly ash | 38.5 wt.% |
| attapulgite | 15.4 wt.% |
| pottery clay | 7.7 wt.% |
| retarder (TBP) | 0.05 wt.% |

## Laboratory Studies

Extensive laboratory studies were conducted at Oak Ridge in
connection with the Hydraulic Fracturing technique which re-
lated mainly to the leaching behavior of simulated products
of Hydraulic Fracturing.

Theoretical studies furnished a number of models for the
leaching process which were based on the assumption of pure
diffusion, diffusion with a concentration-dependent disso-
lution rate, and a number of other parameters (40,41).

The leaching experiments (42, 43) were carried out on a
simulated waste solution whose composition is indicated
in Table 3. The composition of the binder resembled that
indicated in Table 2; the retarder was a sugar; besides
pottery clay also other clay materials were investigated.
Binder and waste solution were mixed in a ratio of 6 lb/gal
(720 g/l), which is a very high water/cement ratio. The
leaching technique used was similar to the IAEA method (44).
To accelerate the method, smaller samples with a higher sur-
face-to volume ratio were used and the entire surface was ex-
posed to leaching.

Table 3: Composition of the Simulated Waste Solution Used
at Oak Ridge

| | | |
|---|---|---|
| 68.85 | g/l | $NaNO_3$ |
| 27.0 | " | $Na_2CO_3$ |
| 13.25 | " | $Na_2SO_4$ |
| 7.2 | " | NaOH |
| 5.44 | " | NaCl |
| 2.78 | " | $Al(NO_3)_3 \cdot 9H_2O$ |
| 0.24 | " | $NH_4NO_3$ |

pH 11.52                    density 1.085 g/ml

From the test results obtained by varying a number of para-
meters the following conclusions can be drawn:

- The cementitious grouts prepared from simulated interme-
  diate level waste, cement, fly ash and suitable clay mi-
  nerals led to leaching rates comparable with those of
  wastes incorporated in borosilicate glass.

- The addition of suitable clay minerals can greatly re-
  duce the leaching rate for cesium. There were major dif-
  ferences among the substances examined, namely grundite
  (an illitic type of clay), pottery clay and Conasauga
  shale (Fig. 1)

- The leaching rates of the radionuclides studied decrease
  in the order Cs, Sr, Cm, Pu

- An aging period of up to 28 days in a moist atmosphere
  before the onset of leaching will reduce the leached
  fractions.

- The IAEA standard leaching method may result in leaching
  rates which are too low, probably because of the low
  ratio of leaching liquid to surface of the specimen and
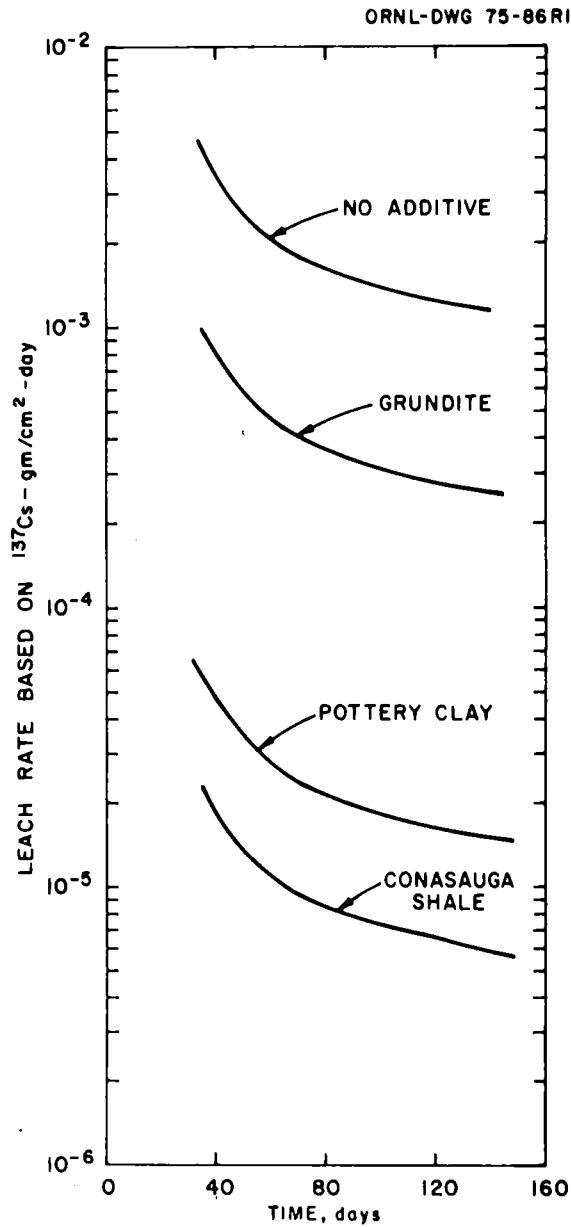  the insufficient frequency of water changes.



Fig. 1:  $^{137}$Cs leaching rates from cement specimens with
various additions of clay (from (39)).

- The ORNL leaching technique has proved to work satis-
  factorily for fast and for systematic studies alike,
  furnishing reproducible values in a short period of
  time.

- The total amounts leached of cesium and strontium will
  decrease with increasing curing time and will increase
  if the specimen was kept dry during curing.

- In specimens aged 28 days a theoretical relationship
  is followed, if two daily water changes are made, which
  is based on the assumption of a diffusion mechanism.

- The amounts leached of cesium and strontium depend on
  the leachant in this sequence: distilled water > tap
  water > grout water (obtained by mixing freshly prepared
  cement grout with distilled water).

- Short time experiments indicated that an increase in
  the bulk waste concentration hardly affects the leacha-
  bility of strontium and cesium. However, the addition of
  stable strontium reduces strontium leaching, whilst the
  addition of stable cesium increases cesium leaching.

- A short time experiment conducted on a fraction of real
  "Hydraulic Fracturing" product confirmed the laboratory
  experiments which had been carried out on simulated waste.

- Long time leaching experiments (550 days) performed by
  the IAEA test method confirmed the reliability of extra-
  polations of data obtained over shorter experimental
  periods (140 days ).

## 4.2. Savannah_River_Laboratory

The Savannah River Laboratory has 30 large tanks for storing
HLLW (high level liquid waste). In these tanks a layer of
sludge and a supernate have formed. The Savannah River La-
boratory considers three basic options for the treatment
of HLLW:

(1)  continued tank storage

(2)  bedrock storage

(3)  solidification

Among the potential alternatives for fixation borosilicate
glass and cement have been determined as favorites.

The treatment concept is based on separate treatment of the
supernate and the sludge. For this reason, studies were con-
ducted of methods of sludge separation. A suitable technique
turned out to be the use of centrifuges fed from the bottom
and discharged through the bottom. So far, hot tests have been
conducted with throughputs between 2 and 6 liters per minute.
A total volume of approximately 700 l has been processed; this
resulted in 8 kg of sludge. It was possible to separate more
than 99% of the solids in the centrifuges. The filtrate is
largely cleaned by a downstream sand bed filter. A non-radio-
active centrifuge with a 25 times higher capacity is due to
be started up in 1977. In summary, the centrifuge experiments
produced the following results:

With respect to separation capability, real sludge behaves
very much like simulated sludge; the separation effect is
limited by mechanical effects (vibrations of the centrifuge).
Different types of sludge show a very similar behavior with
respect to centrifuging capability. The addition of floccu-
lating agents hardly affected the centrifuge action.

## Experiments on Simulated Sludges

A comprehensive review of the cementing experiments conducted at Savannah River was published recently (45).

Table 4 shows the simulated types of sludge studied in the dried form. The types of cement studied are listed in Table 5.

To prepare the test specimens, cement and dry sludge were mixed (sludge content 10, 25 or 40 wt.%), water was added until the desired consistency had been achieved, and the mixture was left to cure in a moist atmosphere for 28 days.

Experiments made to determine the compressive strength indicated a marked drop with increasing sludge content. Also the type of cement used has a tremendous influence, high alumina cement resulting in the highest strength values. Other parameters, such as the type of sludge and the water content, only have minor influences.

Strontium leaching was determined in an accelerated test using specimens 2.52 cm long and 2.38 cm in diameter, the entire surface of which was exposed to leaching by distilled water. Spectral analytical measurements were made to determine the leached fraction of the natural strontium content in the cement.

Table 4: Composition of the simulated sludges studied at Savannah River.

Type I    50 mole-% $Fe(OH)_3$,  50 mole-% $Al(OH)_3$

Type II   40 mole-% $Fe(OH)_3$,  40 mole-% $Al(OH)_3$,  20 mole-% $HgO$

Type III  50 mole-% $Fe(OH)_3$,  50 mole-% $MnO_2$

Table 5: Types of cement used in Savannah River.

Type I   Portland cement        : standard Portland cement
Type II  Portland cement        : low heat generation
Type III Portland cement        : curing fast
Type V   Portland cement        : resistant to sulfate
Type I-P pozzolanic cement      : 80% type I, 20% fly ash
"Lumnite" high alumina cement   : mainly $CaO \cdot Al_2O_3$

The leaching rates were around $10^{-5}$ to $10^{-2}$ $g \cdot cm^{-2} \cdot d^{-1}$.
The dependence on the sludge content in cement of the Sr
leaching rate is shown in Fig. 2. It is remarkable to see
that type III sludge containing $MnO_2$ has the lowest leaching
rates and that in this case the leaching capability decreases
with increasing sludge content. Again, high alumina cement
offers the most advantageous properties among the different
types of cement; the water/cement ratio has only a minor in-
fluence in this respect.

Specimens which had been kept at $100^{\circ}C$ for several months in
a forced-draft laboratory oven suffered a weight loss on the
order of 6 to 16% and a reduction in compressive strength by
about 25%. After irradiation with $10^{10}$ rads of $^{60}Co$ radiation
no change in compressive strength was to be found; the leacha-
bility of strontium decreased by a factor of 2 to 20.

In all these experiments high alumina cement was superior to
the Portland cement varieties. I-P pozzolanic cement showed
some slight advantages over the other types of Portland cement.
For this reason, further studies were limited to these two
types of cement.

Under the solidification concept the cesium present in the
supernate waste solution is to be absorbed on zeolites which
should be fixed in cement together with the sludge. No major
difficulties were encountered in the experiments conducted
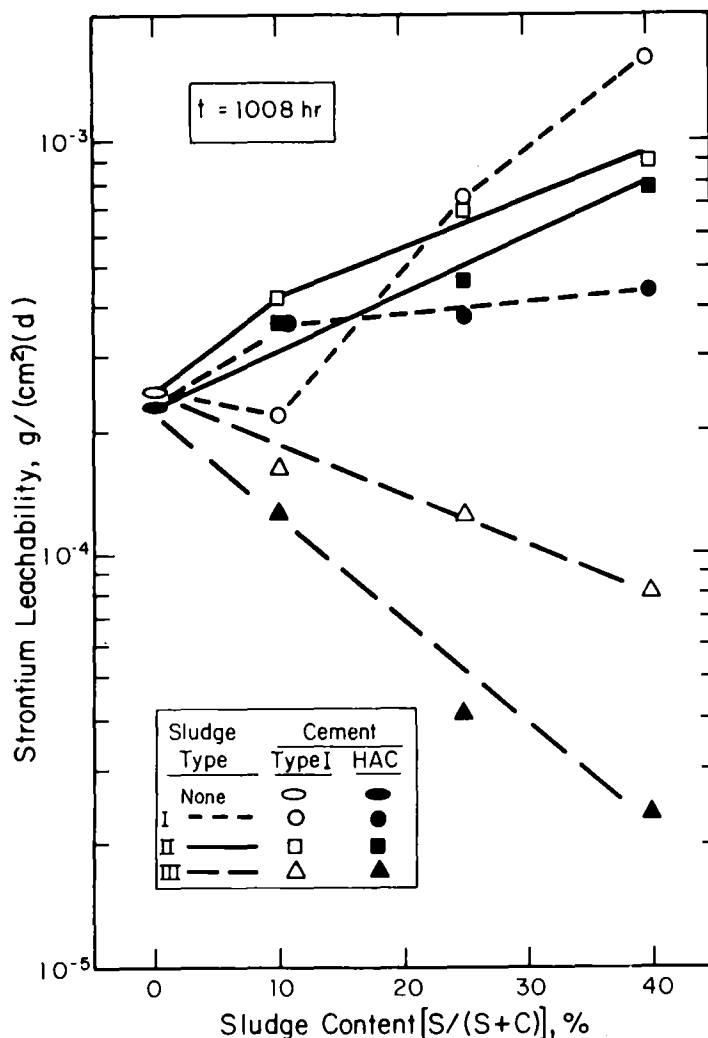for this purpose.

**Fig. 2:** Effects on strontium leachability of the type of sludge (from (45)).

It is remarkable to find that the leachability of cesium decreases with increasing zeolite content in fixing Cs-loaded zeolite in cement (see Fig. 3). A possible explanation offered is this: as the cement/zeolite ratio decreases, less exchange capacity of the zeolite is claimed by calcium ions.

The zeolite used was 20-50 mesh Linde AW-500, a synthetic chabasite. It turned out to be the most suitable type with respect to sorption rate, leachability and influence upon the compressive strength of cement, along with Zeolon 900, a synthetic mordenite, among several Zeolites that have been studied (46).

Studies of the behavior of cement specimens at elevated temperatures also indicated that the specimens remain mechanically stable at 200°C and 400°C for several months (more than 150 days). At 600°C, the specimen will fail after a few weeks,, at 800°C after a few hours, and at 1000°C after some minutes. Also the pressure build-up during the heating phase in a closed vessel was measured. It was between 30 and 35 atm at 240°C, which roughly corresponds to the water vapor pressure. Heating to 150°C before closing allows so much water to be removed that the pressure at 240°C is now only 3.5 atm.

## Experiments on Real Sludges

A number of experiments were also conducted on real dried sludge from the storage tanks. No major new findings were made over the non-radioactive experiments.

Fig. 4 shows the leaching rates for cesium, strontium and α-emitters from high alumina cement specimens containing real sludge.

The curing times of the specimens containing high alumina cement were around 30 minutes and could be extended to more than 4 hours by the addition of 1.5 wt.% (relative to the solids) of a commerical organic retarder.

## Other Studies

The dependence of the curing times of various cement mixes on a number of parameters was studied, in this case two types of cement, two types of simulated waste sludges, the presence of a set retarder, the water content and the mixing technique used (mixing the cement with wet or dry sludge) (47). It was found that high alumina cement set much more rapidly than pozzolanic cement and that mortars with an insufficient amount of water set much more rapidly than those whose water content was sufficient to form a cement grout easy to process. The
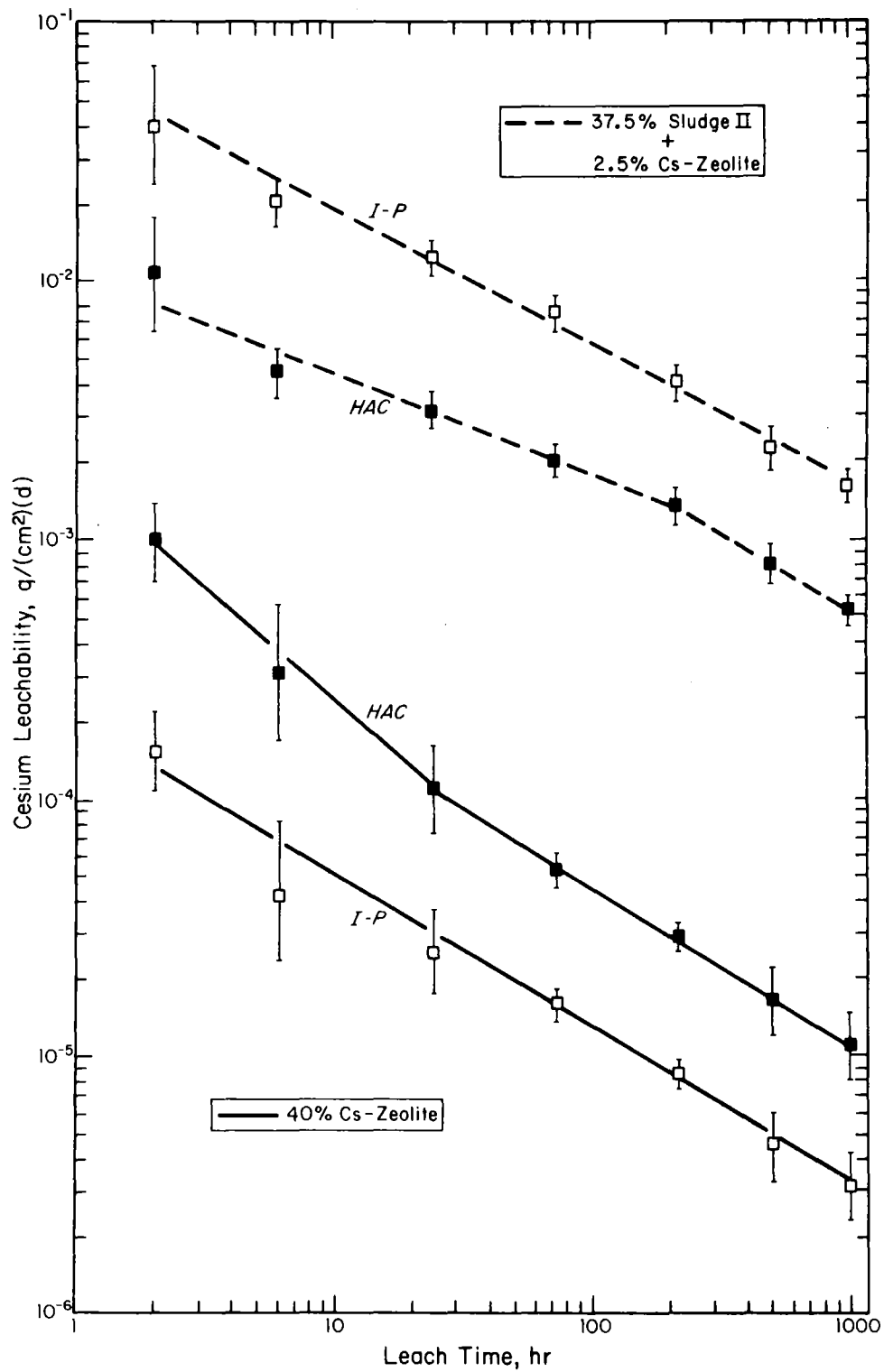
Fig. 3: Cesium leaching from cement specimens
containing Cs-loaded zeolite.

impacts of the other factors remain below the limit of statistical significance. This applies in particular to the set retarder, which was ineffective at the concentration recommended by the manufacturer; a retarding action could only be achieved by adding 5 to 10 times the recommended dose.

A study of the impact strength of various glass and cement specimens (48) indicated that the newly formed surface A was largely proportional to the energy E spent, so that the A/E ratio may be important in safety assessments. Both in glass and in pure cement specimens it was an average of 9.6 $cm^2$/Joule in cement specimens containing 40 wt.% of waste sludge it was an average of 25.7 $cm^2$/Joule.

Radiolysis of Cement Sludge Products

Experiments were conducted with external $\gamma$-radiation from a cobalt-60 source and with curium-244, real sludges and cement. The experiments were performed in such a way that the cement sludge mixtures were sealed in steel tanks and the pressure build-up as a result of radiolysis was measured. In external $\gamma$-radiation the only radiolysis product discovered was hydrogen. An equilibrium hydrogen pressure was established after irradiation with integral doses of up to 2 x $10^{10}$ rads. The equilibrium hydrogen pressure was dependent on the dose rate; it is dependent of the gas volume (see Fig. 5). Extrapolation of the data for dose rates of real sludge (Fig. 6) indicates that equilibrium pressures between 0.5 and 2 atm will occur for the first 100 years, due primarily to the decay of $^{90}$Sr and $^{137}$Cs. Experiments conducted on real radioactive sludge resulted in radiolysis data consistentwith those found with external $\gamma$-radiation. The equilibrium pressure observed, which is approximately 0.5 atm, is in the range extrapolated from the external $\gamma$-radiation experiment. The effect of $\alpha$-radiolysis due to curium-244 on cement-waste products is seen from Fig. 7. In the case of $\alpha$-irradiation also oxygen occurs as a radiolysis gas, but there

Fig. 4: Typical leaching rates of cement products containing radioactive waste (from (45)).
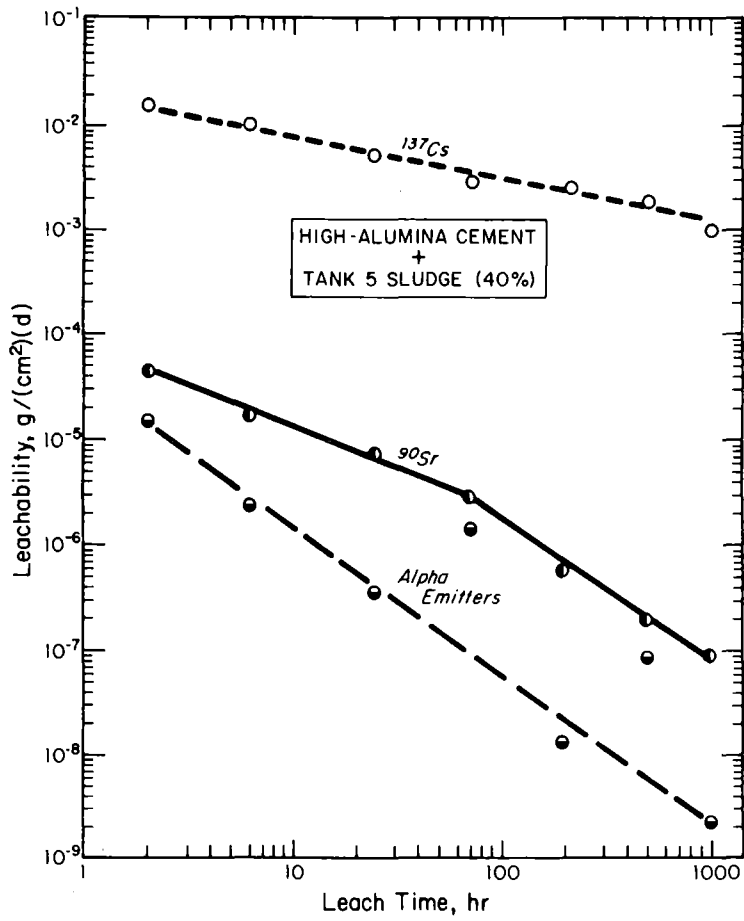
Fig. 4: Typical leaching rates of cement products containing radioactive waste (from (45)).

is no equilibrium pressure as in the case of $\gamma$-irradiation;
the pressure rises linearly with the dose. The final partial
hydrogen pressure resulting from $\alpha$-irradiation ($^{239}$Pu) may
be around 110 atm after $10^5$ years, the oxygen partial pressure
around 30 atm. The rise in the integral $\alpha$-dose is shown in
Fig. 6.
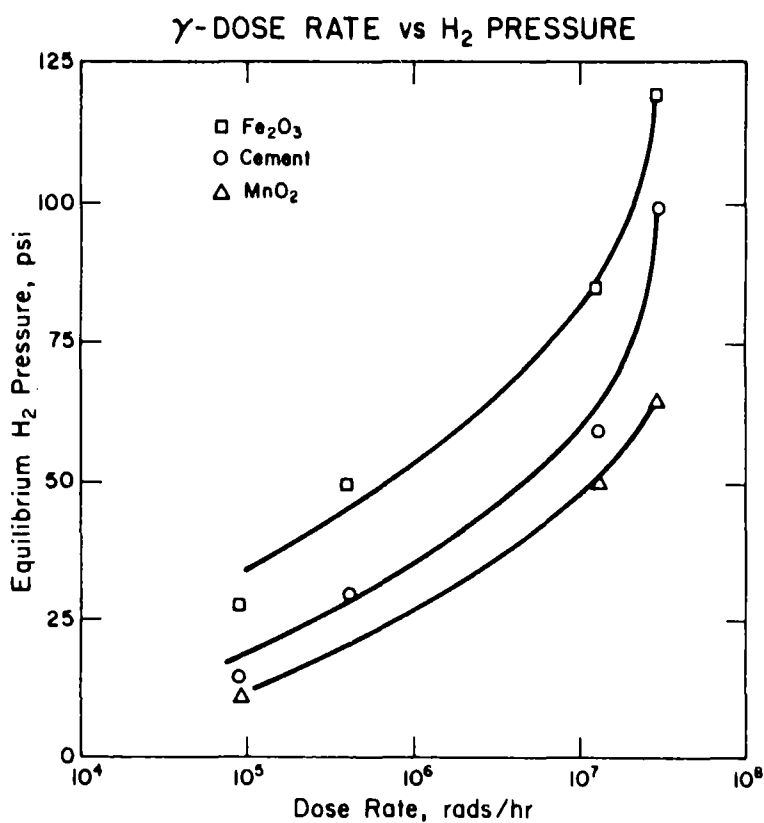


Fig. 5: Influence of the dose rate on the hydrogen
equilibrium pressure.

**ACCUMULATED DOSES TO CONCRETE WASTE FORMS**



Fig. 6: Accumulated radiation dose in cement
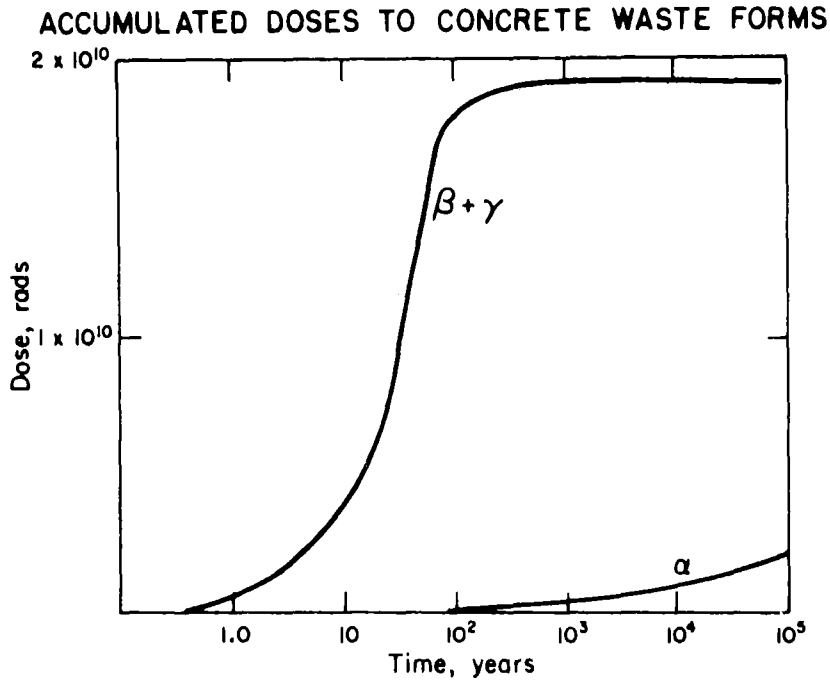blocks containing Savannah River waste.

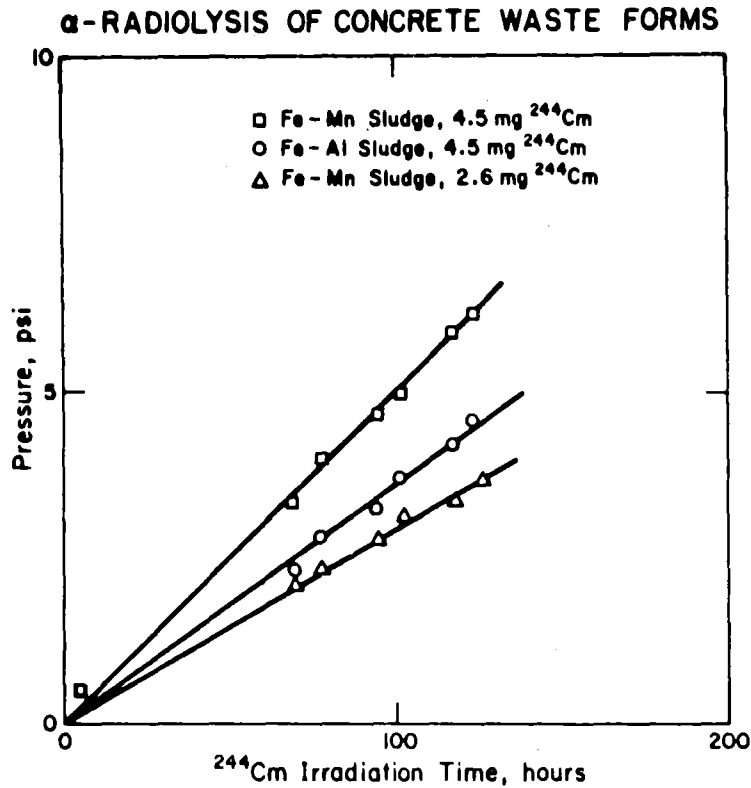**α-RADIOLYSIS OF CONCRETE WASTE FORMS**



Fig. 7: α-radiolysis of cement specimens containing
simulated Savannah River waste.

## 4.3. Brookhaven National Laboratory

In 1976 BNL started a program to determine the properties of radioactive waste products and of containers. Most of the initial studies were concerned with waste products generated in the solidification of liquid effluents from nuclear power plants. Various materials were studied for fixing purposes: type II Portland cement, urea-formaldehyde, bitumen, Tiger Lock, and polyester.

Older activities relate to polymer impregnated cement and to the fixation of tritiated water (p. 9 ). Moreover, some work was carried out at Brookhaven about the waste stored at Savannah River (15).

### Polymer Impregnated Cement

BNL has accumulated much experience in the field of polymer impregnated cement. Originally this material was developed as a construction material. Due to the large volumes of tritiated liquid effluents produced by the Mound Laboratories, the suitability of polymer impregnated cement for fixing tritiated water has recently been studied.

Three types of polymer products are distinguished (49):

- Polymer Impregnated Concrete (PIC)
  is produced by impregnating a cured block of cement with a suitable monomer which is subsequently polymerized. If the concrete block is dried and evacuated, the accomodation of monomers is about 6%. Monomers which can be used include methylmethacrylate, styrene, acrylonitrile, t-butyl styrene. Polymerization may be brought about by irradiation, heating or chemical induction. In a product made with standard concrete this treatment increases the compressive strength from 350 kg/cm$^2$ to 1400 kg/cm$^2$. Water absorption is reduced by 99%.

- Polymer Cement Concrete (PCC)
  is a term relating to products in which the monomer is
  mixed with the cement grout prior to curing. The results
  so far obtained are hardly convincing, because organic
  substances are incompatible with aqueous systems; either
  polymerization or cementation will be upset.

- Polymer Concrete (PC)
  is a term used for products regarded as concrete, in which
  a polymer has assumed the place of cement.

Fixing_Tritium_by_Zirconium

BNL has begun to study a method of fixing tritium which is
based on the electrolysis of tritiated water to HT. HT is sub-
sequently added to sintered zirconium. In some preliminary
experiments it was found that the absorption capacity is highly
dependent on the purities of zirconium and HT. Even minute
traces of oxygen block the fixing capabilities of zirconium.
The leaching properties of a zirconium-HT product, which is
a hydride compound, are excellent even in a sodium chloride
bearing solution. A laboratory scale system is presently under
construction; experiments on this system are due to be started
in late 1977. Fixing relatively pure tritium by means of zir-
conium is being investigated also in view of the fact that this
would represent a source of tritium for possible later use in
a fusion reactor, because tritium can be removed relatively
easily by heating. Work on using zircaloy fuel elements for
conditioning purposes is not carried out at BNL (see also
p. 10 ).

4.4. Atlantic_Richfield_Hanford_Company

Hanford is concerned mainly with treatment of the following
three types of waste:

(1)   salt cake (mainly sodium nitrate, approx. $190 \times 10^6$ l),

(2)   high level sludge (approx. $40 \times 10^6$ l),

(3)   soil contaminated by actinides.

One major objective of this waste treatment is the attempt
to change the waste into a retrievable form. The short term
goal is the conversion of the present types of waste into a
less mobile form. The materials that have been studied for
fixing purposes are clays combined with other binding agents
and glass.

A method of fixing salts was developed by ARHCO which uses
the inclusion of salts into the crystal lattice of certain
silicates (50). A substance particularly useful for this pur-
pose is cancrinite, which is produced in the reaction of waste
(in an aqueous solution) with such clay minerals as kaolin or
bentonite in crystals of approximately 0.5 mm size with the
approximate composition of $2 (NaAlSiO_4) \cdot 0.52 NaNO_3 \cdot 0.68 H_2O$.
Two moles of NaOH are consumed for each mole of cancrinite
generated. The leaching rates of cancrinite for sodium or
cesium are $10^{-7}$ to $10^{-9}$ $g/cm^2 \cdot d$ relative to the BET surface.

Three possibilities have been proposed for the practical imple-
mentation of the reaction with clay minerals (51):

-   The "Rich Clay Process", i.e. a reaction of the waste solu-
    tion with a stoichiometric excess of clay mineral. It has
    the advantage of being easy to perform, but the drawback
    of generating a product of moderate quality as a result of
    the excess of clay mineral.

-   "Lean Clay Process", i.e., a reaction of waste solution
    with a deficit of clay mineral. This produces relatively
    pure cancrinite in small crystals; excess salts are re-
    cycled. The product quality can be improved by binding
    the cancrinite by means of polystyrene, polymethylmetha-
    crylate, Portland cement, waterglass + zinc oxide or calcium
    oxide.

- "Clay Calcination Process", in which solid or liquid
  waste is mixed with a clay mineral and burnt to nepheline
  at 600 to 1000°C. This is a process which is relatively
  sophisticated in terms of process engineering. Calcination
  must be brought about by two burning processes which re-
  sults in dust problems. The product, however, has a number
  of advantages. Thus, there is no $NO_x$ radiolysis in this
  product; in addition, the leaching rates are better than
  those for products from low temperature processes.

The planned installation of a prototype facility for imple-
mentation of the Rich Clay Process has been completed, but
the plant has not been put in operation. For clay products
(cancrinite) leaching rates were measured over more than a year.
No destruction of the matrix was observed. However, there were
some problems with a few products of the Rich Clay Process.
Occasionally, swelling of the clay in water was observed.

## 5. Properties of Various Types of Cement

The following pages contain a summary of information found
in the literature about the properties of various types of
cement as far as they are relevant to solidification.

### Portland Cement

This most common type of cement is generally meant by loose
reference to cement.

Portland cement exhibited the highest strength among all
usual types of cement at high nitrate contents and after long
aging periods, whilst other types have better retention capa-
bilities for radionuclides (52). Leaching of strontium de-
creases markedly with increasing age of the cement block.
The presence of larger quantities of calcium nitrate impairs
the mechanical strength of the Portland cement products.

Portland cement was found to be suitable for the solidifi-
cation of precipitation sludges designed for ocean dumping
(53).

In the solidification of phosphate sludge pure Portland cement
has better values in terms of leaching capability, hardness
and volume increase than has Portland cement with sand addi-
tives. The addition of small quantities of waterglass greatly
reduces leaching losses (54).

Also in liquid effluents of various kinds solidification with
Portland cement plus waterglass offers advantages over the
use of pure Portland cement; however, few details are communi-
cated (55).

As mentioned on page 19, four varieties of Portland cement
used in the United States were investigated at Savannah River.
Compared with high alumina cement and pozzolanic cement, the
four are regarded as being less suitable (45, 56).

Eisenportland-Zement

The leaching behavior of simulated evaporator concentrates so-
lidified by means of Eisenportland-Zement (a Portland cement
containing less than 35% of blast furnace slag)      was
measured (57).

Blast Furnace Cement  is preferred to solidify evaporator con-
centrates for ocean dumping because of its chemical stability.
To prevent demixing, shale dust (probably vermiculite) is added.
However, Portland cement lends itself better to the solidifi-
cation of precipitation sludges (53).

## Pozzolanic Cement

One type of pozzolanic cement and one type of ferric pozzo-
lana cement were selected for the solidification of fission
product solutions for their resistance to aggressive waters,
which is known from conventional cement technology (23).

In the solidification of precipitation sludges, certain types
of trass (pozzolanic) cement are said to offer advantages over
Portland cement, such as higher water capacity, higher compres-
sive strength, better leaching resistance (45, 58).

## High Alumina Cement

In the United States (Savannah River) a type of cement rich
in alumina (trade name "Lumnite") is preferred for the soli-
dification of dried sludges from a reprocessing plant because
of its short curing time and its chemical resistivity (59).
The product has higher compressive strength and lower leacha-
bility for for strontium than Portland cement (45). The same
type of cement is also used to solidify concentrated sodium
nitrate solutions (60).

## Magnesia Cement

A mixture of magnesium oxide and magnesium chloride was in-
vestigated for its suitability in the solidification of phos-
phate sludges, but was found to be unsuitable: curing is
slow and irregular, the volume increase is large (54).

## 6.    Prefixing and Product Posttreatment Steps

### 6.1  Prefixing_by_Reaction_with_Clay_Minerals

There is an extensive bibliography about the transformation
of radionuclides into insoluble silicates (61). The literature
compiled in that bibliography relates to three processes which
can be applied to incorporate radionuclides, especially cesium
and strontium, into suitable synthetic minerals:

- Hydrothermal Syntheses.

    Example: CsOH, NaSiO$_3$ · 9 H$_2$O and Al(OH)$_3$ · H$_2$O in a
    molar ratio of 1:2:1 will produce pollucite with the
    cesium firmly locked in place at 90$^\circ$C and atmospheric
    pressure within two weeks.

- Gel Process.

    Aluminum hydroxide-silicic acid hydrogels can also re-
    act to crystalline substances in the presence of Cs , Sr
    and other ions, whose nature depends on the temperature
    and on the alkali concentration.

- Clay Reaction Process

    The term is used to describe the formation of new products
    by reaction of the ions to be fixed with suitable clay
    minerals, such as the formation of pollucite from bentonite
    and cesium hydroxide.

The bibliography also includes literature about fixation by
heating and about the cation exchange properties of clay
minerals.

Conversion with clay minerals is a particularly suitable pro-
cess for rendering insoluble the toxic components of radio-
active waste solutions (50). As mentioned above, the reaction
between bentonite and cesium hydroxide will produce pollucite,
a cesium mineral in which the cesium ions are chemically firmly
bound (62). From other starting materials and waste composi-
tions other ultimate products will be generated, such as zeo-
lite, sodalite, cancrinite. Thus, waste solutions containing
NaOH, NaNO$_3$, NaNO$_2$ and NaAlO$_2$ can be converted into cancrinite
within a few hours at 30 to 100$^\circ$C by means of clay minerals
(preferably kaoliniteor bentonite dehydrated for 48 hours at
600$^\circ$C), which cancrinite traps in its cyrstal lattice the ions

of the saline solution and, accordingly, shows a very low leaching capability (63, 64) (see also page 30 ).

## 6.2 Prefixing_by_Absorption

A large number of products occurring in nature have ion exchange properties enabling them to directly accept and retain radioactive ions in solution (65). Especially the selectivity of many clay minerals and zeolites for cesium should be stressed; on the other hand, pyrolusite (natural $MnO_2$) is said to be an effective adsorption agent for strontium.

In Hydraulic Fracturing the cement grout contains illite, a clay mineral, to retain cesium, and fly ash to improve the retention of strontium (18, 42) (see page 11 ).

The addition of mordenite, a natural zeolite, to cement grout will reduce to approximately one fiftieth the leaching rate for cesium (66).

## 6.3 Polymer_Cement

A major improvement in cement properties can also be achieved by polymer impregnation (see also page 28 ).

To prepare a polymer impregnated type of concrete (67), which contains sludges to be fixed, the ratios of sand: crushed rock = 1, (sand + crushed rock): cement = 3 and sludges: cement = 0.8 are observed. After curing the cement block is dehydrated at 30 torr and at least $150^{\circ}C$. Impregnation with styrene or methylmethacrylate can be carried out in a vacuum and will have reached a level of 90% after 15 minutes and will be completed after 2 1/2 hours. Even without venting the degree of impregnation is 80% after 15 minutes. Polymerization is achieved by $\gamma$-radiation or induced chemically. The product exhibits an increase in compressive strength by up to 174%.

Irradiation to $2.6 \cdot 10^8$ rads does not give rise to any changes. Leaching of cesium (at 85°C in 24 hours) is reduced to one tenth compared with untreated concrete.


## 7. Leaching Behavior of LAW, MAW Fixation Products

For leaching tests carried out on products generated in the solidification of radioactive waste IAEA has proposed a standard method (44). It provides the following procedure for cement specimens: the specimen is placed in a cylindrical container with a diameter of 5 cm and a height of 5 cm; the open side faces upward and is covered by at least 5 cm of the leachant. The ratio of (volume of leachant): (exposed surface area of specimen) should not exceed 10 cm. The cement specimen should fill the specimen container completely. The exposed surface shall be smoothed with a spatula, and subsequently the specimen must cure for 28 days in a water-vapor saturated atmosphere. If a gap has formed between the specimen and the container as a result of shrinkage, it should either be filled with a waterproof, firmly adhering substance, or the specimen should be removed and coated with a waterproof substance on all surfaces but the one designed for leaching. The leachant shall be demineralized water at ambient temperature; it is not stirred. The leaching solution is changed daily during the first week, once per week in the following eight weeks, and then once per month during the following six months and then, twice per year, as long as is considered necessary.

The criticism voiced against this technique alleges that it furnished values which are too low because the ratio of leaching agent volume to surface of the specimen was too low and the specimens were not exchanged frequently enough (42).

The results of leaching can be represented in accordance with the IAEA standard by plotting the differential leaching rate $R_n$ versus the time t:

$$R_n = \frac{a_n/A_o}{(F/V) \cdot t_n} \quad (cm \cdot d^{-1})$$

$a_n$ : radioactivity leached during the $n^{th}$ period

$A_o$ : radioactivity originally found in the specimen

F : surface of the specimen exposed to leaching $(cm^2)$

V : volume of specimen $(cm^3)$

$t_n$ : leaching period in days.

If $\frac{a_n}{A_o}$ is plotted versus $\sqrt{t}$, this sometimes results in a straight line. In that case, leaching follows the diffusion laws, and a leaching factor L can be calculated from the slope m of this straight line:

$$L = \frac{\pi \cdot m^2 \cdot V^2}{4 \, F^2} \quad (cm^2 \cdot d^{-1})$$

This diffusion equation can be extended to cases with a concentration dependent dissolution rate and with a rate of transfer across the surface directly proportional to the difference in concentration between the surface and the surrounding medium. Moreover, it may be necessary to account for radioactive decay (40,41).

Other methods of testing the leaching capability for various solidification agents and for representation of the results can be found in a survey article (68).

Another unit frequently used to denote leaching capability is the leaching rate expressed in $(g \cdot cm^{-2} \cdot d^{-1})$. However, this indication is not unequivocal; the following definitions are possible, of which the last one is the most common one:

$$\frac{\text{grams of substance leached}}{\text{area} \quad x \quad \text{time}}$$

$$\frac{\text{activity leached}}{\dfrac{\text{total activity}}{\text{grams of waste}} \quad x \quad \text{area} \quad x \quad \text{time}}$$

$$\frac{\text{activity leached}}{\dfrac{\text{total activity}}{\text{grams of solids}} \quad x \quad \text{area} \quad x \quad \text{time}}$$

The resulting figures would be different in each case. For this reason, the leaching rate as proposed in the standard IAEA procedure should be preferred, which can also be written down as follows:

$$\frac{\text{activity leached}}{\dfrac{\text{total activity}}{\text{volume of solid}} \quad x \quad \text{area} \quad x \quad \text{time}}$$

In many studies quoted above the results of leaching tests are simply indicated as the fraction leached of the bulk activity under the respective experimental conditions. Under these conditions it is practically impossible to compare the leaching results obtained by various authors.

In leaching experiments under static and dynamic conditions it was found that trass (pozzolanic) cement has a lower leaching rate than Portland cement. The leaching rate for Cs is relatively high, those for Sr and Nb are intermediate, whereas it is very low for Ru (58).

In a different study, trass cement had the lowest leaching rate for Cs among various types of cement, whereas Portland cement had the lowest leaching rate for Sr. Leaching of strontium from specimens of Portland cement decreased very strongly with aging time and was no longer measurable after one year (52).

The leaching rate of products obtained by solidification of ferric hydroxide and phosphate sludges with cement in various ratios , sometimes with the addition of sawdust, was measured and, after 91 days,was on the order of $10^{-5}$ $(g \cdot cm^{-2} \cdot d^{-1})$ (20). Model solutions containing $NaNO_3$ or NaCl were solidified in "Eisenportland-Zement". In leaching experiments it turned out that Co and Sr with diffusion coefficients on the order of $10^{-8}$ $(cm^2 \cdot d^{-1})$ are bound very firmly, whereas the diffusion coefficients of Cs, NaCl and $NaNO_3$ are on the same order of magnitude as in an aqueous solution (57).

In the solidification of waste solutions containing boric acid curing is greatly impaired; however, the leachability is deteriorated only for Cs, but hardly so for Co and Sr (69).

In Japan a number of leaching experiments were conducted on cement specimens with a view to the planned ocean dumping program. It was found that the leachability of cesium can be reduced by selecting a proper type of cement (Portland cement or blast furnace cement), by reducing the water/cement ratio and the salt concentration as well as by adding zeolite. Moreover, the curing time plays a role (70,71). However, the leachability of cobalt is hardly dependent on the composition of the cement specimen (72). In both nuclides the leachability is directly proportional to the surface/volume ratio (73).

Diffusion coefficients for Cs were found to be between 2.7 x $10^{-8}$ and 8.3 x $10^{-7}$ $(cm^2 \cdot s^{-1})$, depending on the type of saline solution solidified. Vermiculite and glauconite have high selective exchange capabilities for Cs (74).

High alumina cement, in which 29.8 wt.% of $NaNO_3$ had been solidified, was measured to have a leaching rate for sodium nitrate of 0.08 $(g \cdot cm^{-2} \cdot d^{-1})$ after 7 days. Irradiation to $10^9$ rads did not change the leaching behavior and the compressive strength(60), but see also p. 20.

Reference is again made to the extensive leaching experiments carried out at Oak Ridge (p. 14) and Savannah River (p.[19] ).

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