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REPORT

**VOLATILIZATION OF FISSION PRODUCTS
FROM HIGH LEVEL CERAMIC WASTES**

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FEBRUARY, 1967

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VOLATILIZATION OF FISSION PRODUCTS
FROM HIGH LEVEL CERAMIC WASTES

By

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ABSTRACT

Volatilization has been established as the predominant mechanism of fission product release from simulated high level ceramic wastes when exposed to high temperatures. The volatility of cesium appears consistent and independent of ceramic composition when the ceramic is molten. The rate -- about 1%/hr from a sample 1 cm thick -- indicates the probability of diffusion control. Volatility of ruthenium is erratic and probably due to incomplete deoxidation of the ceramic. The releases of ^{90}Sr and ^{144}Ce were one thousandth or less than the rate of cesium release.

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VOLATILIZATION OF FISSION PRODUCTS FROM HIGH LEVEL CERAMIC WASTES

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INTRODUCTION

This study is directed to the determination of fission product release coefficients to aid in making realistic predictions of the possible airborne release from high level ceramic waste when exposed to high temperature.

With the increased development of power reactors and subsequent processing of spent fuel, the handling and shipping of highly radioactive waste material is assuming an ever increasing importance. With high level waste solidification processes being developed to the point of full scale demonstration, it is appropriate to examine in some detail the consequences of incidents in which these waste products may be released to the atmosphere. Although shipping casks are designed to survive the "maximum credible accident", there is nevertheless, some apprehension that an unforeseen event might allow a release of the radioactive material.

One of the release possibilities in which adequate hazards assessment data are lacking is an atmospheric release. A rather remote possibility is a situation in which a shipment of radioactive waste is

involved in a high temperature fire and the container integrity is lost. The quantity of radioactive material which would become airborne and the nature of the airborne materials, in such an unlikely event, are important considerations.

Because of difficulties in predicting the exact details of a given incident and as slight changes in the details may affect the release considerably, it is desirable to determine the release under conditions at least as favorable or somewhat more favorable for release than the conditions postulated for the maximum credible accident. In such an accident, it is assumed that the container fails prior to, or during a hydrocarbon fire. Since temperatures of about 1050 °C can be expected during such a fire⁽¹⁾, releases during exposure to somewhat higher temperatures should be measured. Experimental studies directed to the evaluation of releases of the principal radioactive constituents of the waste material were undertaken.

In order that the material used in the experimental studies be representative of actual waste material, attention has been given to the anticipated

waste composition. A promising technique for preparing the high level waste material for transportation and storage is the incorporation of the waste into a phosphate ceramic. Because of the importance of the phosphate ceramic end product, this type of waste has been emphasized in the study. Other ceramics, silicate and borosilicate glasses, are also possible end products. Two Purex-type liquid waste solutions are under consideration. A description of these solutions--PW-1 and PW-2--and the composition of the nonvolatile constituents are given in the Appendix.

SUMMARY

Simulated ceramic high level wastes were studied; and releases were evaluated for variable compositions. Volatilization is indicated to be the predominant mechanism of fission product release. Cesium-137 is indicated to be the isotope of greatest concern, although ^{106}Ru can also be important in some instances. The release of cesium appears to be independent of ceramic composition--phosphate, silicate, and borosilicate based ceramics were studied. Fractional release rates of about 1%/hr were observed when the ceramic was molten. The rate appears to be controlled by diffusion in the ceramics.

The releases of ^{106}Ru were erratic but were no greater than the cesium releases. Incomplete removal of oxidants during ceramic preparation was considered to be the cause of the ^{106}Ru releases. The releases of ^{144}Ce and ^{90}Sr , in most cases, were

less than one-thousandth the cesium releases. In the presence of the cesium, the release of these non-volatiles will be relatively insignificant.

There appears to be practically no airborne releases by means of particle entrainment. Due to the high volatility of cesium, the release of the nonvolatiles such as strontium and cerium will be relatively unimportant from a hazards standpoint. From the standpoint of airborne release from a molten ceramic waste the composition of the ceramic does not appear to have much influence on the release.

THEORETICAL ASPECTS

MECHANISMS OF ATMOSPHERIC RELEASE

Two mechanisms of airstream contamination are possible--mechanical entrainment of particles and volatilization of constituents. With the subsequent condensation of volatiles, particulate material suspended in the airstream can result from both mechanisms. Entrainment will yield released particles of essentially the same composition as the source while volatilization will be quite selective for certain constituents because the volatilities of the various constituents are not the same.

The factors giving rise to the initial release can be quite different. With entrainment, the physical properties of the source materials are important along with the airstream velocity, mechanical agitation from gas bubbles, etc. With volatilization, the physical-chemical properties of

the source and environment are important. The airstream velocity is not too significant as long as there is adequate circulation to remove vapors.

If one of these mechanisms can be shown to be relatively insignificant when compared to the other, then attention can be directed to experiments to determine the factors involved with the predominant mode. Because of the high surface tension of the ceramic and the buffering effect of the surface layer of air, loss by entrainment might be expected to be quite low. Conceivably, a crushed material or a calcine would have a much higher entrainment potential; however, one of the purposes of fusion and solidification of the waste is to reduce this possibility for release. At the temperatures of a hydrocarbon fire, around 1050 °C, the rate limiting step for volatilization of a minor constituent is most likely to be diffusion of the constituent to the ceramic surface. Since diffusion could be the controlling step, a treatment of the application of diffusion equations to this problem is given later.

CHARACTER OF THE CERAMIC

The physical and chemical properties of the solidified waste matrix and the contained fission products will govern the rate of release as the material is heated to high temperatures. The properties of melting point, viscosity, and chemical reactivity, in turn, are controlled by the complex combination of elements

in the solidified waste. Detailed theoretical prediction of release rates is difficult and inaccurate at the best because of the limited knowledge of how such complex mixtures behave at high temperatures. Some generalizations may be made, however, about some of the important constituents and their effect on properties of the solidified waste which account for some of the experimental observations.

A very important chemical additive to solidified waste formulations is phosphorus as phosphoric acid. The addition of phosphoric acid to the waste during the solidification process materially affects the ceramic properties of the waste over a wide-spread concentration range. Melting point may be reduced, viscosity controlled, and a true glass may be formed through phosphoric acid addition. When the waste solution containing phosphoric acid is calcined to remove the more volatile constituents of water, nitric acid, and sulfuric acid and then is fused, an ionized melt results. The cations are the metal ions and the anions are primarily oxygen ions (some molybdate ions may also be present). With P_2O_5 the oxygen ions react to form $PO_4^{=}$

Each phosphorus atom is surrounded by four oxygen atoms. When all of the oxygen ions have been consumed and additional P_2O_5 is added, a cross linking of the phosphate occurs because each phosphorus is still coordinated to four oxygens. A glass is formed when this cross linking

hinders the orderly arrangement necessary for crystal formation upon cooling.

Because of the importance of P_2O_5 on the characteristics of the final product, waste compositions have come to be characterized by expressing the ratio of metal oxide to phosphate ratio, M_xO/P_2O_5 (sometimes abbreviated to M^+/P). Meta-phosphate is represented by a ratio of 1.0, pyrophosphate by a ratio of 2.0, and orthophosphate by a ratio of 3. In the orthophosphate all free oxygen ions have been consumed and all phosphate is present as PO_4^{3-} ; therefore, no cross linking will be expected.

The property of the fission product elements of greatest significance in determining rate of release at high temperature is probably the equilibrium vapor pressure of the oxides. Although vapor pressure data for the constituents of interest in these complex ceramics are unavailable, the relative volatilities are indicated by the vapor pressures of the pure oxides. The vapor pressure of fission products can be expected to be less from the ceramic waste than from the oxide; otherwise, the oxide would appear as a stable phase.

Equilibrium vapor pressure data⁽²⁾ indicate that, of the principal isotopic constituents being considered for release-- ^{137}Cs , ^{106}Ru , ^{90}Sr , ^{144}Ce --, only cesium is capable of any significant volatility at the temperature of concern. Cs_2O , the stable oxidized form, is in equilibrium with two gaseous species-- Cs and CsO --, whose combined partial pressures are about 1.5 atm at 1500 °K

(1227 °C). This equilibrium is represented by

The relative abundance of the two gases is dependent upon the oxidizing conditions of the environment.

Even though their relative abundance can be varied, their total pressures remain about 1.5 atm; and, thus, the volatility of cesium may be independent of the oxidizing conditions.

The indicated stable form of ruthenium oxide is RuO_2 which does not have an appreciable vapor pressure. The higher oxides-- RuO_3 and RuO_4 --are volatile; however, since they are metastable except under high oxygen pressures, no predictions can be made as to their vapor pressures. If present in a ceramic, they could volatilize before they were reduced to a stable state. The incorporation of the fission products into the ceramic is expected to reduce their capability of volatilization by lowering the vapor pressure of the constituent by dilution in the solution and by hindering the diffusion of the volatiles to the surface.

DIFFUSION IN CERAMICS

As soon as the minor constituents of a ceramic begin to vaporize, the surface can become deficient in the species of the constituent. With constituents of very low vapor pressures, equilibrium with the gas phase is probably approached with very little

mass transfer and no appreciable concentration changes will take place. On the other hand, a constituent with an appreciable vapor pressure, such as an alkali metal, can volatilize at a higher rate; and mass transfer in the liquid or solid state can quickly become the rate limiting step. With sufficient sweep gas to remove vaporized material, the assumption of zero concentration at the interface can be made. Thus, application of diffusion theory may predict limiting mass transfer rates. Should a surface reaction rather than diffusion be a rate limiting step, then the rate would be lower than predicted by diffusion. Certain other qualifying assumptions regarding the heat and mass transfer analogy used in the derivations must be ~~measured~~ ^{recognized}.

Diffusivity coefficients have been measured for various constituents in solid and liquid ceramics. The values vary with temperature and composition. Monovalent ions tend to have the highest diffusivity rates. Diffusivity rates for the species of concern in the glasses and ceramics under consideration for waste fixation are not readily available. It seems reasonable to assume, that cesium diffusivity would be approximately that of sodium.

Sodium diffusivity in silicate glasses was determined to be about $3 \times 10^{-6} \text{ cm}^2/\text{sec}$ at 1100°C .⁽³⁾ Extrapolated values indicated that $10^{-5} \text{ cm}^2/\text{sec}$ could be expected at 1200°C . Other ceramics will probably have somewhat different values of the diffusivity coefficient. It is believed that the value for cesium will be between 10^{-7} and $10^{-5} \text{ cm}^2/\text{sec}$. The diffusivity of calcium, which is

likely analogous to strontium, was found to be about $3.5 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 1350°C in a molten silicate.⁽⁴⁾

The diffusivity of aluminum was found to be about $10^{-6} \text{ cm}^2/\text{sec}$ at 1480°C .⁽⁵⁾ Since the diffusivity of the polyvalent ions would be lower at lower temperatures and as cesium is the constituent with the highest expected volatility, attention to the theoretical diffusivity will be especially directed to estimation of the anticipated rates for cesium.

Diffusion from molten ceramics suddenly exposed to the atmosphere can be predicted from unsteady-state mass-transfer theory. Two solutions of Fick's second law are applicable: (1) diffusion from a slab of infinite thickness covers conditions where depletion of the source is not a problem. (2) diffusion from a slab of finite thickness with mass transfer in one direction only is applicable where the diffusion rate is sufficiently high that the depth of the material can affect the rate. These solutions are analogous to comparable heat transfer problems to which appropriate solutions have been made.⁽⁶⁾ The concentration profile for the case of infinite depth is given by:

$$\frac{C}{C_0} = \text{erf} \frac{x}{2\sqrt{Dt}} \quad (4)$$

where

x = distance from surface, cm

D = diffusivity coefficient, cm^2/sec

t = time, sec

C = concentration, $f(x,t)$

C_0 = initial concentration.

Solutions of this equation for three assumed diffusivities-- 10^{-7} , 10^{-6} , and 10^{-5} cm^2/sec --are given in Figures 1, 2, and 3.

Since the experimental depth of the ceramics in this study was about one centimeter and as the depletion extends to a greater depth with a diffusivity as great as 10^{-5} cm^2/sec , the solution involving finite depth is appropriate. A solution of the concentration profile for a slab of thickness $\underline{l}$ and diffusion in one

direction only is the same as a solution for a slab of thickness $\underline{2l}$ with no net mass transfer across the central plane since this latter solution yields a profile symmetrical about the central plane. This solution is:

$$\frac{C}{C_0} = 1 - \sum_{n=0}^{n=\infty} (-1)^n \left\{ \text{erfc} \frac{(2n+1)\underline{l} - x}{2(Dt)^{1/2}} + \text{erfc} \frac{(2n+1)\underline{l} + x}{2(Dt)^{1/2}} \right\} \quad (5)$$

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FIGURE 1. Concentration Profile for Diffusion from a Slab of "Infinite Thickness" ($D = 10^{-7}$ cm^2/sec)

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FIGURE 2. Concentration Profile for Diffusion from a Slab of "Infinite Thickness" ($D = 10^{-6} \text{ cm}^2/\text{sec}$)

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FIGURE 3. Concentration Profile for Diffusion from a Slab of "Infinite Thickness" ($D = 10^{-5} \text{ cm}^2/\text{sec}$)

where

l = 1/2 thickness

x = distance from central plane
(distance from bottom of
crucible), cm

D = diffusivity coefficient,
 cm^2/sec

t = time, sec

c = concentration, $f(x,t)$

C_0 = initial concentration.

Concentration profiles for this
solution are given in Figure 4.

From these concentration profiles
the fraction of release and, also, the
total quantity of released material
can be calculated. The area above a
concentration profile for a desired

time can be graphically integrated.

The resultant area has the units of
length. When this area is multiplied
by C_0 , the total amount of released
material is determined; and, when this
area is divided by the depth of
ceramic, the fraction of release is
found. The integrated areas above the
profile curves for all of the solu-
tions are given in Figure 5. For
convenience and also to avoid con-
fusion with other terms used in this
report, this integrated area is
designated as the "loss factor."

These theoretical solutions required
several simplifying assumptions. A
zero concentration at the surface was

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FIGURE 4. Concentration Profile for
Diffusion from a Slab 1 cm Thick
($D=10^{-5}$) cm^2/sec)

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FIGURE 5. Loss Factor as a Function of Time and Diffusivity for a 1 cm Thick Slab

assumed. If the concentration is not zero at the surface, the diffusion of the more volatile constituents from the body of the melt would be lowered. Although the concentration gradient is thus lowered, there may be greater availability of the volatile constituents for release. The assumption of a stagnant, nonstirred melt was made which is doubtless an over-simplification in view of the bubbles formed in several cases. Stirring would tend to make the concentration uniform; and, if the transfer in the liquid phase is controlling, an increase in release rate would occur. The increased stirring could assist in depleting the constituent in the

ceramic if this action reduces the surface mass transfer resistance. Comparison with experimental results may show the importance of diffusion within the ceramics as a rate controlling phenomenon. (See Appendix B for further comment on possible deficiencies in release estimates based on the analogy with heat transfer.)

EXPERIMENTAL

Laboratory scale experiments were conducted which involved the exposure of simulated waste material to high temperatures and the measurement of the released fission product isotopes. The experimental studies were carried

out in three stages: First, cursory studies involving ceramic-metal crucible compatibility were made, and furnace operation and sampling techniques were refined. Second, release studies were carried out in which individual fission product isotopes were incorporated into the ceramic and the fractional release was measured. Third, release studies were performed in which portions of actual high level solidified waste were incorporated into the ceramic and the fractional releases of all of the principal isotopes were measured.

A controlled atmosphere induction powered furnace was used to heat samples of simulated ceramic waste in these fission product release studies. Figure 6 is a sectional drawing of the furnace assembly. After a metal crucible containing a previously prepared ceramic waste sample was inserted in the furnace, the assembly was sealed by replacing the cover which includes the airstream-release sampling apparatus. With argon flowing through the furnace the sample was heated to, and, and held at, the release temperature for the desired release period--one or two hours. When air was desired for the environmental atmosphere, the argon was switched off when the sample reached temperature. After the heat, the airstream-sampling apparatus was disassembled and the glass fiber filter and washings from the quartz chimney were analyzed for the particular isotope under study. (Repeated analyses of backup condenser washings and a backup filter indicated that the released material was trapped on

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FIGURE 6. Furnace for Fission Product Release Studies

the first filter and chimney). Figure 7 is a photograph of the furnace assembly, and Figure 8 shows furnace covers with the airstream-sampling apparatus.

To maintain a similarity between the experiments and an actual situation, metal crucibles were used in the release tests. One of the potential container materials, 304-L stainless steel, was used in some of the studies; and nickel was used in

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FIGURE 7. Furnace Assembly for Fission Product Release Studies

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FIGURE 8. Airstream Sampling Assemblies

the others. As the release rates are expected to be geometry dependent, the same cross-sectional area, 5 cm^2 , and same quantity of ceramic was used. Since the specific gravity of the solidified material is about 3, the 15-g samples have a volume of 5 cm^3 and a depth of 1 cm.

In the earlier studies, the simulated phosphate waste samples were prepared in the same metal crucibles that were used in the subsequent tests. The makeup materials including a spike of the isotope being studied were slurried and thoroughly mixed; then the samples were dried and baked on a hot plate to remove volatiles and, finally, were fused and held at a molten temperature for one hour in the induction furnace. The fraction of tracer isotope released during this initial fusion was measured and found in every case to be so low as to immaterially reduce the tracer content remaining in the ceramic for the subsequent fusions. The samples were then considered representative of a phosphate ceramic waste material and were ready for the release studies.

In these earlier studies two simulated solidified waste materials--a phosphate and a calcined oxide--were used in the sample makeup where convenient. The use of these materials, both PW-1 type, facilitated sample preparation in that only small additions were required to obtain the desired composition. Where necessary, the samples were prepared by adding the metal oxide constituents either as oxide, nitrate, or phosphate to the required amount of phosphoric acid.

In the later studies where actual solidified waste was used to trace the releases, a different technique was used in the sample preparation. Simulated waste materials representing eight different compositions were prepared. Five phosphate formulations were prepared along with one silicate and two borosilicates. The silicate, PW-2 type, was formulated in the following molar ratio: 3 moles SiO_2 to 1 mole Na_2O . The borosilicate formulations, both PW-2 type, were made up as follows: in B-Si-1, 1 mole Na_2O to 1 mole SiO_2 to one mole B_2O_3 ; and in Bi-Si-2, 1 mole metal oxide (M_2O) to 1 mole SiO_2 to 1 mole B_2O_3 . These were mixed with a previously weighed sample of actual waste calcine which had been carefully diluted with inert ceramic waste material. After the mixed samples were counted to determine the relative radioactivity, they were placed in the metal crucibles for the release studies.

The preparation of these later samples involved fusion and heating to 1200°C with subsequent cooling and grinding to -100 mesh. Porcelain crucibles were found to be satisfactory for the preparation step as there was no adverse corrosion of the crucibles by the ceramic. For the fusion an induction powered pot furnace was constructed by using a nickel crucible for a susceptor and a clay crucible for a heat insulator.

The preparation of the actual radioactive waste material which was obtained from waste fixation experiments⁽⁷⁾ involved grinding to -100 mesh and the diluting with ground inert waste material. Two successive 10 to 1

dilutions were made so that 10:1 material and 100:1 material were available for tracing the samples.

The analyses of the radioactive constituents in the release samples were determined by a combination of gamma and beta counting techniques*. All of the release samples were gamma counted prior to the release tests. The activities of the samples were compared to the known weights of actual material used to trace the sample and agreement within satisfactory limits were found--4% maximum deviation from the average.

The activities of ^{137}Cs were used in the intersample comparisons. The spectra of six of these samples were further examined and quantitative values were assigned for the ^{137}Cs , ^{144}Ce , and ^{106}Ru . These values were averaged and ratios between the isotopes were calculated. Four samples of the actual waste were dissolved and after chemical separation had been made, the ^{90}Sr and ^{137}Cs content was determined.

Because of counting geometry considerations and interference from other isotopes, the latter analysis for ^{137}Cs was considered to be better than the one obtained by counting the experimental samples. On the basis of the known weight of actual waste, the ratios between the isotopic contents and the latter analysis, the isotopic content of the experimental samples was calculated. These values

will be given subsequently in Table IV.

The quantities of radioactive constituents released during the experiments were also determined by gamma and beta counting procedures. The ^{137}Cs and ^{106}Ru release were found by gamma analyses. Chemical separations with subsequent beta counting were required to determine the ^{90}Sr and ^{144}Ce releases.

RESULTS AND DISCUSSION

After a series of preliminary release tests which involved samples traced with individual isotopes-- ^{137}Cs , ^{144}Ce , ^{106}Ru , and ^{85}Sr --, fourteen release samples of simulated waste which were traced with actual high level radioactive waste were studied. The results of these studies indicated that an average release rate of about 1%/hr for cesium could be expected while the ceramic was molten--1050 to 1200 °C.

The release of ^{144}Ce and ^{90}Sr were found to be much lower than those of the ^{137}Cs . The highest releases of these two constituents were about 1/1000 that of the cesium and the lower releases were barely, if at all, detectable. The releases of ^{106}Ru were erratic. Some releases of ruthenium were as high as the cesium while others were undetectable. The release rates for the principal isotopes indicate that ^{137}Cs and ^{106}Ru will be the isotopes of greatest radiological concern from the standpoint of airborne release during a fire.

The large difference in the release rates of cesium and those of cerium and strontium establishes volatilization as the predominant release

*Chemical analyses were provided by the Chemical Analysis Unit of the Chemistry Department, and by the Radiological Analysis Unit of Environmental and Radiological Sciences Department, both of Battelle-Northwest.

mechanism for cesium. Had entrainment been important, the release rates of the isotopes would have been more nearly equal, as the particles would have essentially the same composition as the source.

Measurable releases were not detected when attempts were made to measure an entrainment rate. Gas-stream flows of about $400 \text{ cm}^3/\text{min}$ were used with the apparatus arrangement indicated in Figure 1 for the preliminary studies. The apparatus was slightly modified so that a smaller quartz chimney was extended down into the crucible just above the ceramic and the argon flow was increased to $3000 \text{ cm}^3/\text{min}$. Even under these conditions no release was detected with a ceramic containing ^{85}Sr .

In conjunction with the preliminary release studies, the interaction between the ceramic and the metal crucible was briefly studied. To maintain similar conditions between experimental and projected accident conditions, stainless steel (304-L) was selected as one of the crucible materials. This steel is one of the possible materials for containing the ceramic waste. It was found that the molten phosphate severely attacked the stainless steel. As the reaction proceeded, the ceramic changed appearance greatly. The melt fluid at first thickened and appeared to solidify with time. A clinker-like mass resulted which contained inclusions of iron and iron-nickel phosphide. Nickel was found to be more durable and was used whenever repeated or

prolonged heating was planned. Some of these test crucibles are shown in Figure 9 which includes some different compositions of ceramic. The size and position of air bubbles give an indication of the fluidity of the ceramic.

The releases of the four principal isotopes from the individually traced samples are given in Table I, the releases of cesium from the samples with variable phosphate contents are given in Table II, and the cesium releases from the samples having variable simulated irradiation levels are given in Table III. The apparent change in the release level of the cesium between the earlier and later tests was probably at least partially due to a slight change in sample preparation technique. At the onset of the studies it was assumed that complete mixing would take place during the fusion step and that an ideal dispersion of the tracer would result. Because a crust of salt appeared at the top of the samples after the drying and baking steps, the possibility of concentration of cesium--a soluble phosphate--in the boundary layer became apparent. To minimize this concentration possibility, the salt crust was rinsed down during the drying step in the preparation of the samples shown in Table II and III. The possibility of the lack of mixing or internal stirring of the molten ceramic became apparent because of the spread of the results--from 0.05%/hr to 2.2%/hr.

Neg 0660055-3

- A. One Hour in Air at 1200 °C,
SS-304-L Crucible $M^+/P = 2.7$
PW-1 Ceramic

Neg 0660055-2

- B. One Hour in Argon at 975 °C,
SS-304-L Crucible, $M^+/P = 2.7$
PW-1 Ceramic

Neg 0660055-1

- C. One Hour in Argon at 950 °C,
Nickel Crucible, $M^+/P = 2.4$
PW-1 Ceramic

Neg 0660055-5

- D. One Hour in Argon at 925 °C,
Nickel Crucible, $M^+/P = 2.0$
PW-1 Ceramic

FIGURE 9. Examples of Ceramic-Crucible Interaction and Typical Solidified Ceramic Material

TABLE I. Release of Radioisotopes from Simulated Waste Samples^(a)

Run	Crucible	Temperature, °C	Time, min	Atmosphere	Release Rate, fraction/hr
Cs-1	SS 304-L	1075	60	argon	6×10^{-3}
Cs-2	SS 304-L	1200	60	argon	4×10^{-3}
Cs-3	SS 304-L	1075	60	air	6×10^{-3}
Cs-4	SS 304-L	1200	60	air	1×10^{-2}
Cs-5	SS 304-L	1150	60	air	1×10^{-2}
Cs-6a	Nickel	990	60	argon	4.7×10^{-3}
Cs-6b	Nickel	1000	120	argon	4.8×10^{-3}
Cs-6c	Nickel	1050	60	argon	1.1×10^{-2}
Cs-6d	Nickel	1050	120	argon	1.1×10^{-2}
Cs-6e	Nickel	1100	120	air	1.7×10^{-2}
Cs-7a	Nickel	900	60	argon	2.4×10^{-3}
Cs-7b	Nickel	900	120	argon	1.9×10^{-3}
Cs-8	SS 304-L	1200	60	argon	2.6×10^{-2}
Sr-1a	SS 304-L	1050	120	argon	6×10^{-6}
Sr-1b	SS 304-L	1050	60	air	9×10^{-6}
Sr-2a	Nickel	1100	120	argon	5×10^{-6}
Sr-2b	Nickel	900	120	argon	not detected
Ru-1	SS 304-L	1100	60	air	1.6×10^{-5}
Ce-1	SS 304-L	1100	60	air	not detected

(a) 15 g samples of PW-1 type having a phosphate content represented by M⁺/P of about 2.7. Fission product content was equivalent to 20,000 MWd/tonne irradiation.

TABLE II. Release of Cs¹³⁷ from Simulated Waste Samples with Varying Phosphate Contents^(a)

Phosphate Content, M ⁺ /P	Run	Crucible	Temperature, °C	Release Rate, fraction/hr
1.0	Cs-24	Nickel	1200	2.2×10^{-2}
1.48	Cs-12a	Nickel	1100	2.9×10^{-3}
	Cs-12b	Nickel	1100	3.1×10^{-3}
1.96	Cs-10a	Nickel	1100	1.8×10^{-3}
	Cs-10b	Nickel	1100	2.1×10^{-3}
	Cs-10c	Nickel	1150	2.5×10^{-3}
2.50	Cs-9	Nickel	1100	3.4×10^{-3}
2.50	Cs-14 ^(b)	SS 304-L	1100	2.6×10^{-3}
2.50	Cs-15 ^(b)	Nickel	1100	2.2×10^{-3}
2.53	Cs-13	Nickel	1100	2.2×10^{-3}
2.74	Cs-20a	Nickel	1100	3.8×10^{-3}
	Cs-20b	Nickel	1200	2.5×10^{-3}
2.74	Cs-21	SS 304-L	1100	0.7×10^{-3}
2.80	Cs-22	SS 304-L	1100	0.5×10^{-3}
3.00	Cs-19	Nickel	1100	4.5×10^{-3}
3.40	Cs-11a	Nickel	1100	1.0×10^{-2}
	Cs-11b	Nickel	1100	8.6×10^{-3}
	Cs-11c	Nickel	1150	8.1×10^{-3}

(a) Fission product content equivalent to 20,000 MWd/tonne irradiation.

(b) PW-2 type ceramic waste, all others PW-1 type.

TABLE III. Release of Cs¹³⁷ from Simulated Phosphate Ceramic Wastes with Varying Fission Product Contents^(a)

Run	Simulated Irradiation Level, MWd/tonne	Temperature, °C	Release Rate, fraction/hr
Cs-13	20,000	1100	2.2×10^{-3}
Cs-14 ^(b)	20,000	1100	2.6×10^{-3}
Cs-15 ^(b)	20,000	1100	2.2×10^{-3}
Cs-16	50,000	1100	2.0×10^{-3}
Cs-17	75,000	1100	4.1×10^{-3}
Cs-18	100,000	1100	5.0×10^{-3}

(a) Phosphate content corresponds to M⁺/P of 2.5.

(b) PW-2 type, all others PW-1 type.

Insufficient mixing to establish and maintain ideal dispersion of the tracer isotope and also the nonactive constituents were verified by adding 2 mm of inactive ceramic to the top of a sample after a release run and then repeating the procedure. The release rate from a 2 hr exposure at 1200 °C which was made after 3 hr high temperature exposure with the inactive material covering the traced ceramic was ten-fold lower than the previous releases. The possibility of the cesium release being associated with a ceramic-metal crucible interaction was greatly minimized by the test since the ceramic surface to metal crucible surface was not appreciably changed.

With the establishment of insufficient stirring or mixing to assure dispersion of constituents, the sample preparation techniques were changed to produce samples which would not have to depend on this mixing to produce ideally dispersed

samples. The simulated waste samples were fused and then ground to -100 mesh. The actual high level waste was ground to -100 mesh and diluted with ground ceramic material. By mixing the diluted active waste with the sample the tracer was dispersed throughout the sample. All of the sample material had been subjected to the temperatures that would be expected in a waste solidification process; and all of the constituents were in the same form--either a glass or a microcrystalline solid--as expected from the solidification.

The analyses of the principal radioactive constituents are given in Table IV. The results of the release runs on the 14 samples are given in Table V.

The release rate of cesium appears to be fairly consistent at about 1%/hr for all of the compositions. The samples in the stainless steel crucibles appeared to have lower release

rates. This is quite possibly associated with a composition change because of the ceramic reaction with the crucible which in turn causes the ceramic to solidify. In most cases the rates decrease with increased exposure at the same temperature and also the rates generally increase with an increase in temperature. This would be expected with diffusion as the rate limiting step. The highest observation for cesium was 3.5%/hr with the borosilicate (B-Si-1) and the lowest rate was 0.17%/hr with the silicate. These extremes are attributed to the ceramic compositions. The borosilicate (B-Si-1) constantly fumed during all three runs, and the fume (probably B_2O_3) could have carried the cesium with it. With the silicate, a small quantity of a second phase--a molten salt--floated on top of the molten glass. This floating second phase could have acted as a diffusion barrier to the cesium escaping from the glass.

Volatility appears to be the mechanism of cesium release with diffusion in the ceramic; likely the rate limiting step. Because of convection in the ceramic and, also, because the generation of bubbles from within the ceramic provides mixing mechanisms, the assumption of an unstirred melt is not quite valid; however, this assumption with an assumed diffusivity value of about $10^{-7} \text{ cm}^2/\text{sec}$ for cesium will result in a close prediction of the actual release rates. The total quantity releasable with diffusion control would be directly related to the

TABLE IV. Analyses of Ceramic Samples Used for Release Tests

Sample	Weight of High Level Waste For Tracing, mg	Activity Disintegrations/min			
		^{137}Cs $\times 10^{-8}$	^{106}Ru $\times 10^{-8}$	^{90}Sr $\times 10^{-8}$	^{144}Ce $\times 10^{-8}$
10 mg of High Level Waste	10.000	3.65	1.79	2.84	5.62
H-1	9.404	3.43	1.68	2.67	5.29
H-2	9.765	3.56	1.75	2.77	5.49
H-3	10.956	4.00	1.96	3.11	6.16
H-4	10.895	3.98	1.95	3.09	6.13
H-5	6.927	2.53	1.24	1.97	3.89
H-6	11.616	4.24	2.07	3.30	6.53
H-7	10.906	3.98	1.95	3.10	6.13
H-8	11.336	4.14	2.03	3.22	6.37
H-9	11.336	4.14	2.03	3.22	6.37
H-10	8.087	2.95	1.45	2.30	4.54
H-11	9.646	3.52	1.73	2.74	5.42
H-12	10.646	3.89	1.91	3.02	5.98
H-13	9.386	3.42	1.68	2.67	5.27
H-14	9.766	3.56	1.75	2.77	5.49

TABLE V. Fractional Release Rates Observed from Various Samples of Simulated Waste Traced with Actual High-Level Waste

Composition	Run	Crucible	Exposure		Release Rates, Fraction/hr			
			Temp., °C	Time, hr	¹³⁷ Cs	¹⁰⁶ Ru	⁹⁰ Sr	¹⁴⁴ Ce
PW-1 Phosphates								
M*/P								
1.0	H-8a	Nickel	1100	1	8.1 x 10 ⁻³	ND	3.1 x 10 ⁻⁷	1.2 x 10 ⁻⁶
	H-8b		1100	1	7.7 x 10 ⁻³	ND		
	H-8c		1200	1	1.3 x 10 ⁻²	ND		
2.5	H-1a	Nickel	1100	1/2	2.4 x 10 ⁻³	1.6 x 10 ⁻²	2.0 x 10 ⁻⁵	1.1 x 10 ⁻⁵
	H-1b		1100	2	6.0 x 10 ⁻³	3.4 x 10 ⁻⁴	4.7 x 10 ⁻⁶	2.5 x 10 ⁻⁶
	H-1c		1100	2	1.5 x 10 ⁻²	2.8 x 10 ⁻⁴	3 x 10 ⁻⁶	
	H-1d		1200	2	1.2 x 10 ⁻²	ND	5 x 10 ⁻⁶	1.6 x 10 ⁻⁶
2.5	H-14a	Nickel	1100	1	3.1 x 10 ⁻³	ND		
	H-14b		1150	1	4.8 x 10 ⁻³	ND		
	H-14c		1200	1	5.6 x 10 ⁻³	ND		
2.5	H-2a	SS-304L	1100	1	1.5 x 10 ⁻³	2.4 x 10 ⁻²	2 x 10 ⁻⁶	
	H-2b		1100	2	1.6 x 10 ⁻²	ND	1.8 x 10 ⁻⁷	
	H-2c		1200	2	2.1 x 10 ⁻³	ND	7 x 10 ⁻⁷	
4.0	H-9a	Nickel	1100	1	6.2 x 10 ⁻³	ND	4.0 x 10 ⁻⁷	3.8 x 10 ⁻⁷
	H-9b		1100	1	3.9 x 10 ⁻³	ND		
	H-9c		1200	1	8.2 x 10 ⁻³	ND	1.8 x 10 ⁻⁷	2.3 x 10 ⁻⁷
4.0	H-13a	SS-304L	1100	1	1.9 x 10 ⁻³	1.6 x 10 ⁻⁴		
	H-13b		1150	1	4.4 x 10 ⁻³	ND		
	H-13c		1200	1	5.8 x 10 ⁻³	ND		
PW-2 Phosphates								
M*/P								
1.0	H-10a	Nickel	1100	1	2.8 x 10 ⁻³	1.1 x 10 ⁻³	6.2 x 10 ⁻⁷	1.3 x 10 ⁻⁶
	H-10b		1100	1	4.1 x 10 ⁻³	ND	1.5 x 10 ⁻⁷	3.1 x 10 ⁻⁷
	H-10c		1150	1	1.4 x 10 ⁻²	ND		
2.5	H-3a	Nickel	1100	1	6 x 10 ⁻³	8.1 x 10 ⁻³	3.9 x 10 ⁻⁶	
	H-3b		1100	2	5 x 10 ⁻³	ND	1.1 x 10 ⁻⁶	
	H-3c		1100	2	4.1 x 10 ⁻³	ND	1.9 x 10 ⁻⁶	
	H-3d		1100	2	4.0 x 10 ⁻³	ND	1.3 x 10 ⁻⁶	
2.5	H-4a	SS-304L	1100	1	1.2 x 10 ⁻²	1.7 x 10 ⁻²	7.4 x 10 ⁻⁶	
	H-4b		1100	1	2.4 x 10 ⁻²	ND	1.6 x 10 ⁻⁶	
PW-2 Silicate								
Si-1	H-5a	Nickel	1150	1	1.1 x 10 ⁻²	6.8 x 10 ⁻⁴	7 x 10 ⁻⁵	9 x 10 ⁻⁶
	H-5b		1150	2	2.9 x 10 ⁻³	ND	1.8 x 10 ⁻⁶	5.7 x 10 ⁻⁶
	H-5c		1200	1	4.7 x 10 ⁻³	ND	2.9 x 10 ⁻⁶	3.8 x 10 ⁻⁶
Si-1	H-11a	SS-304L	1100	1	2.5 x 10 ⁻³	1.2 x 10 ⁻³	2 x 10 ⁻⁷	1.4 x 10 ⁻⁶
	H-11b		1150	1	1.7 x 10 ⁻³	3.4 x 10 ⁻⁴	5 x 10 ⁻⁶	1.1 x 10 ⁻⁶
	H-11c		1200	1	7.0 x 10 ⁻³	ND		
PW-2 Borosilicates								
B-Si-1	H-6a	Nickel	1100	1	1.0 x 10 ⁻²	ND	1.8 x 10 ⁻⁶	1.0 x 10 ⁻⁶
	H-6b		1100	1	3.5 x 10 ⁻²	1.1 x 10 ⁻²		
	H-6c		1100	1	2.6 x 10 ⁻²	1.1 x 10 ⁻²		
B-Si-2	H-7a	Nickel	1100	1	2.0 x 10 ⁻²	ND	1.9 x 10 ⁻⁶	8 x 10 ⁻⁷
	H-7b		1100	1	9.0 x 10 ⁻³	ND		
	H-7c		1150	1	1.6 x 10 ⁻²	ND		
B-Si-2	H-12a	SS-304L	1100	1	5.1 x 10 ⁻³	2.0 x 10 ⁻³		
	H-12b		1150	1	8.0 x 10 ⁻³	7.8 x 10 ⁻⁴		
	H-12c		1200	1	1.1 x 10 ⁻²	5.4 x 10 ⁻⁴		

Note 1: ND (Not Detectable) indicates that there was an insufficient amount of ^{106}Ru activity to be detected in the presence of the ^{137}Cs activity. In all cases this means that the ruthenium release was less than 5% of the cesium release and in some cases less than 2%.

Note 2: Accuracy of most strontium releases is on the order of $\pm 25\%$; however, some of the very low releases may approach $\pm 100\%$.

Note 3: Accuracy on most cerium releases is about $\pm 25\%$.

surface. At this low diffusivity rate, only a very thin layer near the surface will be depleted in the volatilizing constituent.

The releases of ruthenium were erratic. In some instances the releases were as high or slightly higher than those of the cesium while at other times a ruthenium release was not detected. In analyzing the gamma spectrum from the release samples, it was not generally possible to detect ^{106}Ru in the presence of ^{137}Cs when the ruthenium activity was less than about 5% of the cesium activity. There were a few instances, however, where ruthenium activities were detected at about 2% of the cesium.

The lower valent forms of ruthenium-- RuO_2 and Ru --are supposedly not volatile and the ruthenium releases are obviously due to volatilization since the strontium and cerium would have been released in the same magnitude by means of entrainment. It is believed that these ruthenium releases are associated with either incomplete reduction to the lower valent forms during the preparation of the ceramic or incomplete removal of oxidizing agents which were present before the ceramic preparation. In essentially all of the runs where ruthenium was released, bubbling of the ceramic was observed. This bubbling is probably associated in some manner with the release, either in contributing oxidizing agent or as a carrier gas to sparge the ceramic.

With but one exception, the release of ^{90}Sr was at least a thousand-fold less than the corresponding cesium

release. In this one exception, the silicate--a second liquid phase--was present during the run. This second phase, which floated on top of the molten glass, could have conceivably been concentrated in strontium; and, thus, the small entrained particles would also be concentrated in strontium. It appears that with most compositions the strontium release will be relatively insignificant when compared to the cesium release.

The releases of cerium were in all instances less than one thousand-fold smaller than the corresponding cesium release. It is believed that cerium along with strontium will present no great airborne release problem due to the overwhelming abundance of the cesium.

CONCLUSIONS

Whenever a high level ceramic waste is exposed to the temperature attainable in a hydrocarbon fire, there will be a release of cesium. The rate of release appears to be fairly independent of ceramic composition; and, for a ceramic with a thickness of 1 cm, the rate appears to be about 1%/hr at temperatures of 1100 °C or above.

The release of ruthenium appears to be erratic. The greatest release rate is about the same as experienced by cesium and therefore the airborne release of ruthenium from the ceramic waste will present no greater problem than the release of cesium.

SUGGESTIONS FOR FUTURE STUDY

To better assess the possibilities and consequences of a release, further

study in the following areas is suggested:

1. A study related to the behavior of a loaded cask when exposed to the anticipated fire temperatures would be extremely helpful in predicting both cask failure possibilities and also the expected exposed surface of ceramic. The possibility of cask failure due to internal corrosion resulting from a high temperature exposure has been indicated in the ceramic-crucible compatibility tests.
2. The behavior of the cesium-bearing vapors after they leave the ceramic surface is another area of concern.
3. Basic studies of the physical-chemical properties of the various ceramic constituents are important. The diffusivity and vapor pressures of the constituents of concern with regards to overall ceramic composition are important properties.

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APPENDICES

APPENDIX A

HIGH LEVEL WASTE COMPOSITION

The composition of two typical high level waste solutions are given in Table A-I. These are representative of Purex waste solutions resulting from the processing of a fuel after a 20,000 MWd/tonne irradiation and after an aging of 6 yr*. The solution concentrations have been normalized to a hypothetical 100 gal/tonne fuel for the purpose of comparison. These solution compositions are used in conjunction with the waste solidification studies.

The amount of process constituents resulting from the treatment of a fixed amount of fuel is expected to be about constant. The amount of fission products can be expected to vary with the irradiation level of the fuel. The composition of the nonvolatile constituents of the principal process constituents is given in Table A-II, and the composition of the nonvolatiles from the fission products is given in Table A-III. The proportions of these constituent groups necessary for simulated waste sample preparation at different irradiation levels are given in Table A-IV.

* Private communication from C. R. Cooley, Manager, Waste Solidification Battelle-Northwest, Richland, Washington

TABLE A-I. Typical Purex Waste Solutions^(a)

Principal Process Constituents	PW-1, M	PW-2, M
H ⁺	5.00	5.00
Fe ³⁺	0.93	0.445
Cr ³⁺	0.012	0.024
Ni ²⁺	0.005	0.010
Na ⁺	0.138	0.930
NO ₃ ⁻ , NO ₂ ⁻	8.80	6.44
SO ₄ ²⁻	--	0.87
PO ₄ ³⁻	0.003	0.006
SiO ₃ ²⁻	0.010	0.010

Principal Fission Products

(Rb + Cs) ⁺	0.0416	0.0416
Sr ²⁺	0.0155	0.0155
Ba ²⁺	0.0195	0.0195
(R. E. + Y) ³⁺	0.1185	0.1185
Zr ⁴⁺	0.065	0.065
Mo ⁶⁺	0.065	0.065
Ru ⁴⁺	0.032	0.032

^(a) Normalized to 100 gal/tonne fuel and fission products from 20,000 MWd/tonne fuel irradiation with 6 yr aging.

TABLE A-II. Relative Composition of Process Oxides (weight percentages of principal constituents)

	PW-1	PW-2
	wt%	
Fe ₂ O ₃	92.28	52.62
Cr ₂ O ₃	1.13	2.69
NiO	0.47	1.11
Al ₂ O ₃	0.06	0.07
Na ₂ O	5.32	42.62
SiO ₂	0.74	0.89
	100.00%	100.00%

TABLE A-III. Relative Composition of Fission Product Oxides (weight percentages of principal constituents)

	wt%
Cs ₂ O (incl. Rb as Cs)	11.36
SrO	3.11
BaO	5.80
RuO ₂	8.25
(R.E.) ₂ O ₃	37.85
MoO ₃	18.14
ZrO ₂	15.49
	100.00%

TABLE A-IV. Weight of Fission Product Oxides Required for each 100 g of Process Oxides in Order to Achieve Desired Simulated Irradiation Level

Irradiation Level, MWd/tonne	PW-1	PW-2
20,000	64	76
50,000	160	190
75,000	192	229
100,000	320	382

APPENDIX B

COMMENTS ON HEAT-MASS TRANSFER ANALOGY

The development of a concentration gradient with depth of a relatively nonvolatile solute initially distributed uniformly in a viscous molten glass would seem to be entirely analogous to the formation of a temperature gradient in a uniformly heated slab when a heat sink is placed against one surface. The heat diffusivity model, however, requires that the loss of heat to the sink occur with virtually zero resistance to heat flow due to the junction. This situation is at best an imperfect analog of the diffusing solute situation since the solute transfer is impeded by resistance at the surface. Mass transfer of a solute into the space above a liquid surface will be influenced by the transfer rate of

the solute in the liquid and the rate of transfer across the interface. An assumption of zero resistance for transport from the liquid to the gas phase will result in a higher estimate of release rate than actually experienced. This appears to be consistent with the observations. The diffusivity of cesium in the molten ceramic can only be inferred from data for sodium, and a relatively large uncertainty is introduced from this source, too. The observed release is more consistent with a diffusivity of 10^{-7} cm²/sec if surface transfer resistance is assumed minor. This diffusivity is likely too low an estimate based on sodium data and we must conclude that the interface transfer resistance is also of importance in determining the release rate.

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