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LEACH RATE CHARACTERIZATION OF SOLID RADIOACTIVE WASTE FORMS[†]

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INTRODUCTION

Leaching of radioactive material from solidified waste represents the most probable mechanism for transport of hazardous radionuclides from waste to the biosphere. While it is not clear that acceptable waste management techniques will require a waste form with an extremely low leach rate, the assessment processes for the waste handling system will certainly require a sound knowledge of what the actual leach rate is. Therefore the determination of the leach rates of proposed waste forms is of importance to the security of these waste forms. The elements of major concern in high level waste are strontium (^{90}Sr), cesium (^{137}Cs), the rare earths (Sm, Eu), uranium, plutonium (^{239}Pu) and the transplutonium actinides (Am, Cm). Other elements, having radioactive isotopes, [e.g. technetium (^{99}Tc) iodine (^{129}I), selenium (^{79}Se) etc.] have significantly lower relative toxicities and hence are of lesser interest (1). Since the leach rates can vary greatly among the elements in the same waste form, it is necessary that the rate be determined for each element of concern. It is also desirable to measure the leach rates for the waste form in its original (fabricated) state. Pulverizing or other destructive measures often employed to increase the rate of reaction may significantly alter the physical characteristics, and hence the leach rate of the waste form. This is especially true for inhomogeneous waste forms.

A neutron activation analysis (NAA) technique has been employed in order to measure the leach rates for specific elements in proposed waste forms without physically altering the waste matrix prior to leaching. The details of the NAA technique together with a critique of its advantages and disadvantages have been reported previously (1). This technique involves five basic steps.

- (1) Neutron irradiation of unaltered solid waste forms of simulated waste to produce activation of the elements present in the sample matrix.
- (2) Quantitative determination of the activation products in the solid waste form using instrumental [i.e. lithium drifted germanium (GeLi) gamma counting] techniques.

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- (3) Leaching of the solid matrix for a suitable time interval using the appropriate leaching conditions.
- (4) The leaching medium is then analyzed instrumentally (GeLi) and/or radiochemically for the specific activation products leached from the matrix.
- (5) Leach Rates (L) are then calculated from the ratio of the activated species found in the leachant (A_t) to the species in the solid matrix (A_0), the time interval of leaching (t), the surface area of the solid matrix (S), and weight of the solid matrix (W) according to the equation:

$$L = A_t W_0 / A_0 S t = (fr/t) \div (S/W_0) \quad (1)$$

The term (fr/t) identifies the fraction leached per unit time (i.e. incremental leach rate) and (S/W_0) represents the specific surface area (i.e. cm^2/g) of the solid matrix. The ratio (fr/t) is not independent of time or surface area and hence is not an adequate comparison of different waste forms. The ratio may, however, provide indications of the importance of physical changes in the waste form. For example similar values of (fr/t) for pellets and powdered forms of the same waste indicates very rapid reaction of the particular element under study. Further, the magnitude of (fr/t) gives an indication of the extent of leaching more easily pictured than the conventional leach rate, L. It is often convenient, for comparison purposes, to report the incremental leach rate (fr/t) since meaningful surface areas are difficult to determine. These units (fr/t) will be designated as L.R. and are readily converted to the commonly accepted units of L (i.e. g/cm^2d) by dividing L.R. by the specific surface area (S/W_0) . In order to make comparisons with (or extrapolations to) waste forms of significantly different specific surface area it is, of course, necessary to use the conventional units of L (g/cm^2d).

EXPERIMENTAL RESULTS and CONCLUSIONS

Several waste forms using a variety of leaching media have been studied employing this NAA technique. The data reported here will be restricted to results obtained from distilled water as the leaching medium and instrumental techniques (GeLi counting) for determination of the radioactive species. Initial studies were made using experimental waste forms provided by Battelle Pacific Northwest Laboratories (PNL).

These waste forms were of three types. The first consisted of 80%PW-4b spray calcined simulated waste (2) mixed with 10% silica and 10% borosilicate glass frit and sintered at $1100^\circ C$. The results of the leach studies on this material have been reported in reference 1.

The second waste form consisted of 85% PW-7a spray calcined waste (2) and 15% glass frit, pelletized and sintered for one hour at 1000°C. These granules which were about 4mm in diameter and about 80 mg (average weight) have been identified as SWF (PW-7a). The specific surface area based on the assumption of a solid impervious spherical shape was calculated to be about 6 cm²/g. (The BET measured surface area for these granules using krypton as the sorbent was 0.9 x 10⁴ cm²/g). Some of these SWF (PW-7a) granules were pulverized and leached using a commercial Soxhlet extractor. The surface area of the pulverized material was calculated from the measured particle size distribution assuming spherical particles (4). This calculated specific surface area was 150 cm²/g. (The BET measured surface area for this pulverized material using krypton as the sorbent was 2 x 10⁴ cm²/g). The calculated surface area for this waste form increased a factor of twenty five by pulverizing, however the BET measured surface area only increased a factor of two. The BET measured surface area for both materials was significantly greater than the calculated surface area. While calculated surface areas are probably low because of uncertainties associated with porosity, nevertheless surface areas determined by assuming solid geometric shapes result in conservative estimates of leach rates (i.e. the calculated leach rate is an upper limit for the true leach rate). Conversely reported leach rates based on BET surface area measurements are likely to be unrealistically low.

Some of the SWF(PW-7a) granules (54g) were incorporated into a metal matrix by casting about 300 beads (close packed) in molten lead. The beads were left exposed at the outer radius of the ingot for these studies. No attempt was made to leave an outer envelope of lead around the ingot as has been suggested for metal matrix encapsulation (5). The resulting cylindrical ingot measured 3 cm diameter by 5cm, weighed 284g and is identified as a "composite". The specific surface area for this ingot was calculated (geometrically) to be 0.23 cm²/g. However the geometric surface areas of composite ingots do not represent areas in which solution and waste are in contact. The resulting calculated leach rate is not comparable to leach rates obtained by direct reaction with the waste form. The specific surface areas of ingots could be useful in comparisons of leach rates under varying leaching conditions for identical waste forms.

The third waste form consisted of a PNL waste glass (composed of PW-8a-3 calcine and 76-68 glass) containing uranium. The composition of this material is defined by PNL (3) and is identified in this report as PNL-Glass. Samples of this material used in the leach studies were 1.2 cm diameter discs and weighed about 0.5 g (specific surface area 5 cm²/g).

These waste forms were all subjected to sequential leach tests generally using 25°C quiescent distilled water (the soxhlet tests, of course, were done at the temperature of the condensing water in the soxhlet extractor). The results of the initial (about 1 week) leach test for each waste form are given in Table 1. The results are reported both as incremental leach rates (fr/d) and mass leach rates (g/cm²d). Radioisotopes of twenty different elements were determined during the course of these measurements. Among these elements, those of most significance for nuclear waste management studies are strontium (⁸⁵Sr), Cesium (¹³⁴Cs), Cerium (¹⁴¹Ce), Europium (¹⁵²Eu) and Uranium (²³⁷U). The other elements

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Table 1. Leach Rates For Various Waste Forms Using
Quiescent Distilled Water As Leachant

Isotope Analyzed	Incremental Leach Rate (fr/d)				Mass Leach Rate (g/cm ² d)			
	Pellet	SWF(PW-7a) Pulverized	Composite	Glass PNL	Pellet (6) ^b	SWF(PW-7a) Pulverized (150) ^b	Composite (0.23) ^{b,c}	Glass PNL (5) ^b
²² Na	d	d	d	8.9E-7 ^e	d	d	d	1.8E-7
⁵¹ Cr	8.0E-2	2.4E-1	1.5E-2	9.3E-6	1.3E-2	1.6E-3	6.5E-2	1.9E-6
⁵⁹ Fe	d	4.7E-5	d	d	d	3.1E-7	d	d
⁶⁰ Co	5.0E-5	6.1E-5	1.5E-6	2.4E-5	8.3E-6	4.1E-7	6.5E-6	4.8E-6
⁶⁵ Zn	4.0E-5	1.7E-4	5.9E-6	2.6E-5	6.7E-6	1.1E-6	2.6E-5	5.2E-6
⁷⁵ Se	d	d	2.0E-3	d	d	d	8.7E-3	d
⁸⁵ Sr	2.0E-4	2.0E-4	d	d	3.3E-5	1.3E-6	d	d
⁸⁶ Rb	d	d	d	3.0E-6	d	d	d	6.0E-7
⁹⁵ Zr	1.0E-4	1.8E-3	d	2.2E-6	1.7E-5	1.2E-5	d	4.4E-7
⁹⁹ Mo	d	d	d	1.2E-5	d	d	d	2.4E-6
¹⁰³ Ru	d	5.5E-4	d	5.8E-6	d	3.7E-6	d	1.2E-6
¹¹⁰ Ag	6.0E-5	2.7E-4	d	d	1.0E-5	1.8E-6	d	d
¹²⁴ Sb	1.7E-4	1.1E-4	1.6E-5	d	2.8E-5	7.3E-7	7.0E-5	d
¹³¹ I	2.2E-2	5.9E-2	d	7.2E-6	3.7E-3	3.9E-4	d	1.4E-6
¹³¹ Ba	2.0E-4	1.9E-4	d	d	3.3E-5	1.3E-6	d	d
¹³⁴ Cs	3.0E-2	4.2E-1	1.0E-2	3.8E-6	5.0E-3	2.8E-3	4.3E-2	7.6E-7
¹⁴¹ Ce	6.0E-5	6.1E-5	2.7E-6	2.9E-6	1.0E-5	4.1E-7	1.2E-5	5.8E-7
¹⁵² Eu	2.3E-5	4.6E-5	3.3E-7	2.5E-6	3.8E-6	3.1E-7	1.4E-6	5.9E-7
²³⁷ U	d	d	d	7.4E-7	d	d	d	1.5E-7
²³⁹ Np	d	d	d	7.4E-6	d	d	d	1.5E-6

- a. Initial leach rates based on approximately one week leaching.
b. Specific surface area (cm²/g) based on calculated surface area.
c. This specific surface area is extremely unrealistic because of uncertainties related to particle to particle contact and the resulting diffusion of the leachant through the ingot.
d. These data were not resolved from the gamma spectrum.
e. 8.9E-7 corresponds to 8.9×10^{-7} .

are of generic concern in establishing the characteristics of specific waste forms. Because of inconveniences associated with data analysis all elements were not determined for all samples.

The incremental leach rates for the SWF(PW-7a) pellets range from $3\text{E-}2$ for cesium to $2\text{E-}5$ for europium (cf. Table 1). This wide range (three orders of magnitude) indicates that either there are strong diffusion effects for certain elements (e.g. cesium) within the solid matrix or there are present multiple phases with varying solubilities. These results emphasize the variations in behavior among waste constituents in this particular waste form. If elements shown to easily mobilized from this waste form are believed to be important, the results point to the need provide a more stable environment for them.

The incremental leach rates for the pulverized form of SWF(PW-7a) are at best marginally greater than the leach rates for the pellets (cf. Table 1) in spite of a twenty five fold increase in calculated surface area. These results indicate that pulverizing this waste form might be significantly changing its leaching characteristics and conversion of leach rate data to a specific surface area basis can result in gross errors.

The incremental leach rates for the composite waste form [i.e. SWF(PW-7a) pellets in a lead matrix] can be compared with the leach rates for the unencapsulated pellets by reviewing the data in Table 1. Cesium (the most leachable element in this waste form) is leached from the composite at substantially the same rate as from the pellet whereas the leach rate for europium (the least leachable element in this waste form) is leached significantly more slowly (i.e. two orders of magnitude) from the composite. However long term sequential leach tests of the pellets and the composite (i.e. greater than 100 days) indicate that the leach rates for each of the radioisotopes studied are asymptotically approaching the same values for these two waste forms. During the course of these long term experiments it was determined that greater than 10% of some elements (e.g. cesium) leached out of the composite whereas only parts per million (PPM) of other elements (e.g. rare earths) were leached from the same composite. The results of the leach tests of this composite waste form indicate that there is no significant reduction in leaching of some elements from these pellets by casting them in a metal ingot (i.e. the leach rates from the composite are comparable to those from the dispersed waste form). Also, the leach rates for all elements of concern must be determined in order to establish the integrity of any proposed waste form. Leach rates determined from experiments carried out for at least 100 days are necessary for reliable results. Additional experiments are needed to establish the time required to reach steady state for specific waste forms.

The leach rates for the PNL-Glass samples are reported in Table 1. Since the calculated specific surface area for these glass samples ($5\text{ cm}^2/\text{g}$) are approximately the same as for the SWF (PW-7a) pellets ($6\text{ cm}^2/\text{g}$) the mass leach rates can be compared directly with the incremental leach rates for these two waste forms. The leach rates as determined for the fourteen radioisotopes analyzed in the PNL-Glass (cf. Table 1) span only about one order of magnitude and in all cases are significantly lower than the leach

rates determined for the SWF (PW-7a) pellets. In fact the leach rate for cesium (usually the most leachable element) and europium (usually the least leachable element) are (within experimental error) the same for this waste form. These results indicate that this glass appears to be relatively homogenous and incorporates the fission product elements fairly uniformly, presumably by solution in the vitreous phase. Long term leach rate studies currently in progress using this PNL-Glass indicate little if any change in leach rate with time under these test conditions. These results confirm the leach resistance of this waste form.

Leach rates have also been determined using this (NAA) method for several other materials of interest in radioactive waste disposal. Among these are Zircaloy (^{95}Zr as radioactive tracer), aluminum - 12½% silicon alloy (^{59}Fe from trace iron in the alloy as radioactive tracer), lead (^{124}Sb from trace antimony in the lead as radioactive tracer), borosilicate glass (^{22}Na from sodium in the glass as radioactive tracer), and a lead rare earth silicate $[\text{Pb}_3\text{RE}_6(\text{Si}_4\text{O}_4)_6]$ compound formed in the reaction zone between calcine waste pellets and molten lead (4) (^{147}Nd as radioactive tracer). The mass leach rates ($\text{g}/\text{cm}^2\text{d}$) for these materials are presented in Table 2. The lead-rare-earth silicate compound formed in the reaction zone between calcine waste and molten lead (4) has a leach rate significantly lower than that of borosilicate glass. Hence this compound would not be detrimental to the overall leaching characteristics of waste encapsulated in metallic lead if it were formed in any significant concentration in the actual waste. The most leach resistant material studied thus far is Zircaloy with a leach rate two orders of magnitude below that of borosilicate glass. Among the metals studied, lead is the least leach resistant. However this leach rate of $3\text{E}-4 \text{ g}/\text{cm}^2\text{d}$ should be adequate to satisfactorily control the waste as long as the surface to volume ratio exposed to the leaching medium is reasonably small.

Sequential leach tests were performed on all the waste forms reported here. These tests generally showed a slow decrease in leach rate leveling off to a constant value after about 100 days. The PNL-Glass samples however showed little if any change in leach rate over 70 days of testing.

The leach rates reported here using instrumental techniques were obtained from relatively small samples (e.g. the PNL-Glass was 0.5 g with 2.3 cm^2 surface area). In spite of this, leach rates of $10^{-7} \text{ g}/\text{cm}^2\text{d}$ were easily determined. With minor modifications (e.g. radiochemical separations and beta counting) leach rates of less than $10^{-10} \text{ g}/\text{cm}^2\text{d}$ could be determined (1).

Accurate determination of the surface area exposed to the leaching medium remains as a major uncertainty in the conversion of experimental results to true leach rates. Until this problem is solved the use of simple geometric shapes rather than gas sorption surface areas (BET) are recommended since only the former yield conservative (i.e. upper limit) estimates for the true leach rate. In any case, optimization (i.e. minimization) of the surface to volume ratio for any final waste form is a major factor in maintaining the leaching process under control.

Table 2. Leach Rates (g/cm²d)^a For Various Matrix Materials Using
25°C Quiescent Distilled Water As Leachant

Matrix:	Zircaloy(⁹⁵ Zr) ^b	Alumimum (⁵⁹ Fe) ^c	Lead(¹²⁴ Sb)	Glass(²² Na)	Pb ₃ RE ₆ (SiO ₄) ₆ ^d (¹⁴⁷ Nd)
Leach Rate:	2E-9	2E-6	3E-4	2E-7	4E-8

- a. Initial leach rates based on approximately one week leaching.
- b. Radioisotope assayed is given in parenthesis following each matrix designation.
- c. Aluminum - 12½% silicon alloys were used in these measurements.
- d. Lead rare earth silicate (compound formed in the reaction zone between calcine waste pellets and molten lead (4).

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