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ELECTRICAL-CONDUCTIVITY MEASUREMENTS OF LEACHATES FOR THE RAPID ASSESSMENT OF WASTEFORM CORROSION RESISTANCE*

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ABSTRACT

Measurements of the electrical conductivity of leachate solutions as a function of time can be used as an efficient, informative means of evaluation and comparison in the development of nuclear waste forms and in the preliminary analysis of their corrosion resistance in distilled water. Three separate applications of this technique are described in this work. These are: (1) its use in the optimization of the corrosion resistance of a crystalline wasteform (monazite); (2) a study of the protective ability of the surface layer ("gel layer") which forms on the nuclear waste glass Frit 21 + 20 wt. % SRW in distilled water, and (3) making comparisons of the overall corrosion resistance of three different nuclear wasteforms (i.e., monazite, SYNROC, and borosilicate glass). A complete solution analysis of the borosilicate glass leachate and a straightforward analysis of the conductivity results agree to within $\pm 20\%$. In the absence of a complete, time consuming solution analysis, conductivity measurements can be used to estimate reliably the total ionic concentration in the leachate to within a factor of 2.

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INTRODUCTION

One of the major criteria that determines the suitability of any candidate nuclear waste form is its ability to retain hazardous radioactive nuclei during prolonged periods of exposure to aqueous conditions. The rate of wasteform corrosion in an aqueous environment is usually measured by analytical determinations of the concentration of each element present in solution after leaching the material for a given time period. While this method provides detailed quantitative information about the effects of the corrosion process, it is time consuming, generally very expensive, and often provides more information than is required. For example, in order to determine how a change in the preparation procedure alters the relative corrosion resistance of a wasteform, a full scale quantitative analysis of the leaching solution can be avoided. Solution conductivity measurements can provide the required comparative information quickly and simply. Although the individual leach rates of specific ions cannot be obtained using solution conductivity measurements, the overall dissolution rate of the wasteform matrix can be reliably determined to within a factor of 2. Measurements of the leachate conductivity as a

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function of time are closely related to measurements of the total mass loss of the wasteform due to corrosion (i.e., to the "bulk leach rate"). Leachate conductivity measurements, however, have two important advantages over mass loss measurements: These are, first, the ability to continuously monitor the dissolution rate of the wasteform matrix in situ and, second, a detection limit that is several orders of magnitude lower than that for mass loss measurements. One limitation of the conductivity technique is that it is only useful when distilled water is the leachant. Nevertheless, solution conductivity measurements can be a powerful tool in general studies of the problem of wasteform corrosion in an aqueous environment.

EXPERIMENTAL

General. As a nuclear wasteform (or other material) corrodes in distilled water, mobile ions are released into solution resulting in an increase in the solution conductivity. For total ionic concentrations lower than 10^{-3} moles/liter the effects of ion-ion interactions on the solution conductivity can be neglected and the activity coefficients of all ions taken to be unity. In this dilute limit, the solution conductivity, σ , is then:

$$\sigma = \sum_i |q_i| \sigma_i N_i \quad (1)$$

where q_i is the charge of the anion or cation in solution, N_i is the concentration in moles/cm³ of the i 'th type of ion in solution, and σ_i is the ionic conductance per charge of the i 'th ion in the dilute limit. With the exception of the H^+ and OH^- ions, the values for σ_i at 25°C of almost all cations and anions in solution are between 40 and 80 cm²-mho/mole [1]. The concentration of the H^+ and OH^- ions, however, can be determined directly by measuring the solution pH. When the total ionic concentration in solution is greater than about 10^{-2} moles/liter, the effects of ion-ion interactions in solution must be considered as is done, for example, in the Debye-Hückel theory [2,3].

If the average charge of the ions in solution is known, then Eq. (1) can be used to estimate the total ionic concentration. For example, if a monazite wasteform is leached, a reasonable charge to assume for the ions in solution would be 3. Thus, if the solution conductivity rises by 100 μ mho/cm at room temperature, an average value for σ_i of 60 cm²-mho/mole can be assumed which implies a total concentration of ions in solution of 0.5×10^{-6} moles/cm³ (i.e., 0.5×10^{-3} moles/liter). Because of the weak variation of σ_i from ion to ion, this estimate should be accurate to within a factor of 2.

The conductivity measurements were made using a standard MCC-1 type Teflon corrosion container that was modified slightly to allow two 0.5 mm diameter Pt wires to be inserted in the solution. The conductance was measured with a YSI Model 32 conductance meter, and the cell constant for each Teflon container was determined using a solution of known conductivity (10^{-2} N, KCl at 25°C). A change in the solution conductivity of 0.1 μ mho/cm could be measured easily. This corresponds roughly to a 50 ppb change in the total ionic concentration.

Wasteform Optimization. In order to prepare an optimized crystalline wasteform such as monazite a determination of the effective average valence for the various cations present in the waste must be made. This information is very important since it determines the correct amount of phosphate that must be added to form the waste-loaded synthetic monazite. The effect on the total ionic release due to varying the cation valence was investigated using three different types of simulated nuclear waste in a LaPO₄ host matrix. These wastes and concentrations were: 20 wt. % composite SRW with Al removed, 20 wt. % composite SRW without Al removed, and 10 wt. % PW-4b. The compositions of

Fig. 1. Leachate conductivity vs time for synthetic monazite ceramics loaded with three types of simulated nuclear wastes with different assumed values for the average waste valence. These results show how the solution conductivity technique can be used to quickly determine the optimum composition for a given wasteform type.

these simulated nuclear wastes have been reported previously [4,5]. Several samples of synthetic monazite were prepared for each waste composition using assumed values for the average cation valence that lay in the range between 1.5 and 3.5. Ceramic monazite pellets were made by cold pressing powders prepared by the urea precipitation procedure [6]. Sintering for 60 h at 900°C for pellets containing SRW and at 1100°C for pellets loaded with PW-4b waste was sufficient to produce high-density ceramic materials.

The variation of the solution conductivity with time at 90°C for the ceramic pellets is shown in Fig. 1. An assumed valence of between 2.0 and 2.5 for the Savannah River waste cations appears to produce the most corrosion resistant form of synthetic monazite. For the PW-4b waste there is very little variation in the corrosion behavior as the assumed cation valence is changed between 1.5 and 3.5. With these wasteforms no conductivity measurements were attempted for times longer than about 100 h since, after this time period the background corrosion rate of the Teflon container was larger than the synthetic monazite corrosion rate.

Protective Ability of the "gel layer" on Borosilicate Glass. When borosilicate glasses corrode in distilled water, a layer of metal complexes has been observed to form on the glass surface. The question of how important or effective this layer (sometimes called the "gel layer") is in protecting the remainder of the glass network from continuing dissolution is crucial in assessing the long-term performance of borosilicate glass wasteforms. The role of this layer cannot be properly evaluated by simply monitoring the decrease in the leach rate with time in a static MCC-1 type leach test since approaching the solution solubility limit for Si also slows the effective rate of corrosion. In order to determine how effective this surface layer is in "protecting" a prototype nuclear waste glass, several samples were precorroded in distilled water at 90°C for various lengths of time. During this precorrosion process a gel layer formed on the glass surface. The precorroded glass with its altered surface layer intact was then re-exposed in fresh distilled water, and the total release of ions into solution was monitored using the solution conductance technique. The solution conductivity vs time curves for the precorroded glasses were then compared to the conductivity curve of an uncorroded piece of the same glass.

The glass specimens (Frit 21 + 20 wt. % simulated composite SRW with Al removed) were prepared by melting the appropriate amounts of oxides or carbonates in a Pt crucible at 1160°C and then pouring the material into a preheated carbon mold. After an anneal at 550°C for 2 h, four samples measuring 0.5x1.0x0.2 cm³ were cut from the resulting glass billet and ultrasonically cleaned in acetone and ethanol. Three of the samples were precorroded in distilled water at 90°C for 8 h, 2 days and 42 days. Rutherford backscattering measurements on this same glass have shown that the surface layer formed under these conditions is about 0.4 µm thick after 8 h, 1.6 µm thick after 2 days, and extends several microns below the outer surface after 42 days of corrosion. This surface layer is highly enriched in Fe, Ni, Mn, Ti, and U but is strongly depleted of Si, Na, and probably B.

The variation of the solution conductivity with time is shown in Fig. 2 for the uncorroded and precorroded glass samples. It is evident from these results that the 0.4 and 1.6 µm thick surface layers afford little or no protection for the underlying glass matrix. The thick surface layer present on the glass precorroded for 42 days does appear to reduce the glass matrix dissolution rate by about a factor of 2. Since in a static MCC-1 leach test, the 28-day leach rate for Si is about 4 or 5 times less than the 1-day value, about half of this decrease is due to the gel layer information and about half to the approach of

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Fig. 2. Leachate conductivity vs time for borosilicate glass with and without precorroded surfaces. After a 42-day formation period for the altered surface layer the "protective" ability provided by this layer only produces a drop in the leach rate of about a factor of 2.

the solubility limit for Si. If the leach rate for Si from PNL 76-68 glass is compared in a static MCC-1 vs a flowing MCC-4 corrosion test, a similar conclusion is reached concerning the relative importance of the surface layer [7].

Relative Corrosion Rates of Different Wasteform Matrices. Solution conductivity measurements can also provide information regarding the relative corrosion resistance of different types of wasteforms. Borosilicate glass (Frit 21 + 20 wt. % composite SRW with Al removed), synthetic monazite (LaPO_4 + 20 wt. % composite SRW with Al removed), and SYNROC B were corroded in distilled water at 90°C. The SYNROC B sample did not contain simulated waste and was prepared and provided by the Lawrence Livermore Laboratory. Solution conductivity vs time plots at 90°C are shown in Fig. 3 for all three materials. Due to the significant differences in the chemistry of the three wasteforms, relating changes in the solution conductivity to the leach rate of a particular element is not feasible. The overall bulk corrosion rate of both synthetic monazite and SYNROC B is, however, clearly less than that of borosilicate glass by a significant amount. A rough estimate of the total concentration of ions in solution after 100 h of corrosion in distilled H_2O is: borosilicate glass - 2×10^{-3} moles/liter, synthetic monazite - 2×10^{-6} moles/liter, SYNROC B - 6×10^{-6} moles/liter.

SOLUTION CONDUCTIVITY AND SOLUTION ANALYSIS

In order to test the validity of solution conductivity measurements as a comparative technique, the leachate solutions for both the monazite and glass wasteforms were analyzed. The solution analysis was performed using an inductively coupled plasma (ICP) technique. After 100 h of corrosion the concentration in $\mu\text{g/ml}$ of each element in solution was: for glass: (Si-18, B-3.4, Na-19, Al-1.5, Li < 4.0, Ca-0.6, Ti-0.03, Fe-0.07, Sr-0.1, Cs-0.2, Mn < 0.002, U < 0.2); and for monazite (La < 0.1, P < 0.4, Fe-0.06, Al < 0.061, Mn < 0.002, Ni < 0.04, Na < 4, Sr < 0.001, Cs < 0.1, U < 0.2, Ca < 0.07.) In the case of the monazite leachate the concentrations of most of the elements in solution were below the detectability limit of the ICP technique and hence a meaningful comparison between the solution analysis and solution conductivity results was not possible. For the glass leachate, however, the concentration of elements in the leachate was sufficiently high that a comparison was possible. At room temperature the conductivity and pH of the glass leachate were $152 \pm 5 \mu\text{mho/cm}$ and 9.85, respectively. A breakdown of the conductivity calculated using the solution analysis and the measured pH is shown in Table I.

TABLE I

Element	Moles/cm ³	Ion	Conductivity ($\mu\text{mho/cm}$)
Si	0.64×10^{-6}	H_3SiO_4^-	40
Na	0.8×10^{-6}	Na^+	40
-	0.07×10^{-6}	OH^-	13.8
B	0.31×10^{-6}	H_2BO_3^-	19.5
Li	0.32×10^{-6}	Li^+	12.5
Al	0.06×10^{-6}	Al^{+3}	12
Ca	0.015×10^{-6}	Ca^{+2}	1.8
All others			$\leq 1 \mu\text{mho/cm}$
Total	$2.2 \times 10^{-6} \text{ mole/cm}^3$		$140 \mu\text{mho/cm}$

Fig. 3. Leachate conductivity vs time for a borosilicate glass, SYNROC B, and synthetic monazite. Both the glass and monazite samples contain simulated waste while the SYNROC B specimen does not. The total ionic release into distilled water is clearly much greater for the borosilicate glass.

In preparing Table I a value of $63 \text{ cm}^2\text{-mho/mole}$ has been assumed for the conductance of the H_3SiO_4^- and H_2BO_3^- ions, and the leach rate for Li was taken to be the same as the leach rate for Na. The calculated conductivity of $140 \text{ }\mu\text{mho/cm}$ compares quite favorably with the measured value of $152 \text{ }\mu\text{mho/cm}$. In general, however, this type of comparative analysis should only be accurate to about $\pm 20\%$.

From the data shown in Table I it is evident that conductivity measurements only determine the overall release rate of wasteform matrix. To obtain information concerning the leach rate of specific elements of interest that are present in small amounts in the wasteform (i.g., Cs, Sr, U, etc.), a solution analysis is required.

Leachate conductivity measurements obviously do not replace solution analyses in the development of nuclear wasteforms and a complete leachate analysis is often essential. In some situations such as those described in the present work, however, solution conductivity measurements can be a valuable, time saving method for comparing the general leaching characteristics of nuclear wasteforms.

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