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Reactions of Plutonium and Uranium with Water: Kinetics and Potential Hazards

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by

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ABSTRACT

The chemistry and kinetics of reactions between water and the metals and hydrides of plutonium and uranium are described in an effort to consolidate information for assessing potential hazards associated with handling and storage. New experimental results and data from literature sources are presented. Kinetic dependencies on pH, salt concentration, temperature and other parameters are reviewed. Corrosion reactions of the metals in near-neutral solutions produce a fine hydridic powder plus hydrogen. The corrosion rate for plutonium in sea water is a thousand-fold faster than for the metal in distilled water and more than a thousand-fold faster than for uranium in sea water. Reaction rates for immersed hydrides of plutonium and uranium are comparable and slower than the corrosion rates for the respective metals. However, uranium trihydride is reported to react violently if a quantity greater than twenty-five grams is rapidly immersed in water. The possibility of a similar autothermic reaction for large quantities of plutonium hydride cannot be excluded. In addition to producing hydrogen, corrosion reactions convert the massive metals into material forms that are readily suspended in water and that are aerosolizable and potentially pyrophoric when dry. Potential hazards associated with criticality, environmental dispersal, spontaneous ignition and explosive gas mixtures are outlined.

INTRODUCTION

An awareness of the hazards associated with handling, transportation and storage of plutonium is prompted by a recent assessment of safety issues[1] and by publication of standards for storage of surplus metal and oxide.[2] Possible endangerment of workers, the public and the environment arises because of the potential for dispersing plutonium-containing particles and for redistributing nuclear material into critically unsafe configurations. Although such concerns are of reduced importance when plutonium exists as non-dispersible and critically-safe pieces of massive metal, chemical processes may cause important changes in the physical state of the material.

The chemistry and kinetics of the reaction between metallic plutonium and water are described in several reports.[3-7] In high-salt-content media such as sea water, the metal is rapidly converted to a fine black solid by a complex corrosion process. Consequences of that reaction are important for assessing potential hazards associated with situations in which plutonium metal remains in contact with water for an extended period.

The primary objective of this report is to provide essential information required to conduct hazard assessments for both normal operations and abnormal incidents involving plutonium. An effort has been made to extract relevant kinetic information from the literature, describe important unpublished experimental results, and identify potential hazards that might be enhanced by corrosion. For completeness, available information on aqueous corrosion of uranium[8-10] is also reviewed and included along with data for the reactions of plutonium hydride (PuH_x, $2 \leq x \leq 3$)[11] and uranium hydride (UH_3).[8,9] The hydrides are not considered to be suitable storage forms for nuclear material;[1] however, PuH_x and UH_3 are readily formed by reaction of the metals with hydrogen. Since hydrogen is produced by radiolytic decomposition of plastics and other organic materials,[2] significant amounts of hydride may coexist with the metals in storage and consideration of possible consequences of their presence is prudent.

EXPERIMENTAL METHODS

The experimental procedures used for characterizing the corrosion reactions of metals and hydrides are described in the original publications and will not be detailed in this report. Gravimetric and PVT (pressure-volume-temperature) techniques have normally been used to determine the rates of corrosion reactions. In a gravimetric experiment, the metal specimen is periodically removed from the test solution and weighed. In PVT tests, the build-up of hydrogen in a volume-calibrated reactor is measured as a function of time.

New experimental results were obtained using both gravimetric and PVT methods. Gravimetric tests were conducted to further investigate the effects of salt concentration, pH and temperature on the aqueous corrosion rate of plutonium. In tests at 22 °C specimens of δ-phase gallium alloy were exposed to distilled and deionized water with measured pH values near 7, a phosphate buffer solution with pH = 7.0, a borate buffer solution with pH = 10.0, a carbonate buffer solution with pH = 10.2 and a saturated LiOH solution with pH = 13.7. Tests with buffered solutions were repeated at 49 °C. Corrosion rates were determined from mass-loss data obtained after exposure periods of

7-20 days. A PVT measurement was also made with α-phase metal in 0.005 M NaCl solution at 25 °C.

In PVT tests with plutonium hydride, samples of cubic PuH_2 and hexagonal PuH_3 were prepared in situ by stoichiometric reaction of the elements in glass-lined stainless steel reactors at defined temperature and pressure conditions.[12] Whereas the cubic product was obtained by slow reaction of metal and hydrogen at temperatures less than 100 °C, the hexagonal phase was obtained by rapid reaction at temperatures above 400 °C and hydrogen pressures greater than 3.4 atm (50 psia). The hydrides were subsequently immersed in 1.0 M $CaCl_2$ solution at 25 °C without exposure to air or glovebox atmosphere. Temperature and pressure were monitored for up to a hundred days.

The behavior of unsubmerged δ-phase plutonium in the presence of submerged alloy was investigated in a PVT test with two metal specimens. One sample was immersed in 0.01 M NaCl solution and the other was suspended from the reactor lid on a stainless steel wire. Air was removed from the reactor by repeated cycles during which the solution was frozen and thawed. The hydrogen pressure was monitored for more than a year and was maintained at 150-200 psi for most of that time by periodic venting of hydrogen from the vessel.

RESULTS AND DISCUSSION

Plutonium Corrosion by Water

Chemistry of the $Pu+H_2O$ Reaction. The corrosion of plutonium metal by near-neutral liquid water at room temperature is described by Equation (1).[6,7]

$$\text{Pu (s)} + \text{H}_2\text{O (l)} \;\text{-->}\; \text{PuOH (s)} + 1/2\ \text{H}_2\ \text{(g)}. \qquad (1)$$

The solid product of the reaction is a fine black material.[6,11] X-Ray diffraction measurements give a median value of about 7 nm (70 Å) for the particles and show that the product has a face-centered-cubic structure ($a_o = 5.400 \pm 0.003$ Å) and lattice parameters similar to those of PuO_2 ($a_o = 5.397$ Å) and PuH_2 ($a_o = 5.359$ Å) . Results of characterization studies indicate that the product is an oxide hydride formed by Pu(III) cations and O^{2-} and H^- ions in a CaF_2-type lattice. When heated above 120 °C, dry PuOH decomposes with formation of gaseous hydrogen in a process similar to that observed for PuH_2. These observations show that the product is not an hydroxide or hydrated oxide, which should not exist in a fluorite-type structure and would form water during thermal decomposition.

Like plutonium dioxide, the oxide hydride is apparently insoluble in near-neutral water. The plutonium concentration measured in synthetic sea water solution after 140 hours in contact with the solid product is 1.4 $\times 10^{-5}$ mol/ liter (3.3 mg Pu/liter).[5] This concentration is attributed to the presence of fine particles of suspended product or to traces of plutonium hydroxide polymer,[13] not to plutonium in solution.

PuOH is the first in a sequence of oxide hydride and oxide products formed by hydrolysis.[6,7] Each successive reaction increases the oxygen to plutonium ratio in the solid and generates additional hydrogen at a slower rate than the preceding process. For example, the reaction PuOH to form $Pu_7O_9H_3$ and H_2 begins only after Equation (1) is complete and proceeds at a rate that is thirteen times slower than the rate of Pu corrosion. The reactions apparently proceed in sequence by progressive insertion of oxygen into the lattice until CaF_2-type PuO_2 is reached. Since the lattice dimensions of the terminal phases (PuOH and PuO_2) are similar, all intermediate reactions probably occur without spallation or significant change in particle dimensions.

The behavior of oxide hydride upon exposure to air is somewhat uncertain. Wet PuOH does not react with air, and the dry product can be handled in an air atmosphere if appropriate care is exercised.[6] However, observations suggest that PuOH may be pyrophoric when rapidly exposed to air.[14]

Dependence of the Pu+H_2O Rate on pH. Results of gravimetric corrosion tests show that aqueous corrosion of plutonium in buffered solutions (pH 7, 10 and 10.2) is strongly pH dependent. In these media, freshly burnished plutonium surfaces remain untarnished for periods of several hours at 22 °C. Thereafter, a light golden discoloration becomes evident and the surface hue progresses slowly through a sequence of colors that change from shades of gold to brown as the product layer increases in thickness. These color changes occur more rapidly in neutral buffers than in basic media and are accelerated by increasing the temperature. At pH 7, the product layer appears dark golden after two weeks at room temperature and dark brown after one week at 49 °C. Since the products are not black, the reactions occurring in neutral to basic buffered solutions may not be accurately described by Equation (1).

Certain features of the corrosion process in buffered media are defined by gravimetric results. The observation of constant specimen masses (± 0.01 mg/g Pu) implies that the golden to brown product layers did not spall during the experiments. Mass measurements made after careful burnishing of samples tested at 49 °C imply that the brown to dark brown adherent layers are 0.2 to 0.5 µm thick. These observations are generally consistent with the correlation of oxide thickness with color with product thickness described by Larson and Cash for plutonium oxidation.[15] For buffered solutions at pH 7 and 10, the average corrosion rates during a one-week period at 49 °C are 2×10^{-3} and 7×10^{-7} mg Pu/cm^2 h, respectively.

A strong pH dependence of plutonium corrosion is evident across the pH range. Whereas massive metal dissolves within minutes in strong acids such as HCl, dissolution in intermediate-strength systems such as trifluroacetic and sulfamic acids is moderately rapid and usually leaves an insoluble residue or sludge that may be pyrophoric.[13] Attack is slow in weakly acidic solutions such as acetic acid. In unbuffered near-neutral water, the metal corrodes with formation of insoluble oxide hydride. At pH 10, corrosion occurs very slowly with formation of an adherent product layer on the metal surface. The behavior in high pH solutions is demonstrated by experimental results for freshly burnished metal in saturated LiOH solution. Detectable quantities of hydrogen were not generated and the clean surface appeared untarnished after a three-week test at pH 13.7.

Dependence of the Pu+H_2O Rate on Salt Concentration. Prior studies show that the corrosion rate in near-neutral aqueous systems is an exponential function of the molar salt concentration, [salt]. Results of gravimetric and PVT measurements are consistent with this dependence. However, redetermination of the corrosion rate, R, for distilled and deionized water ([salt] = 10^{-7}) shows that the value at 25 °C ($7.2 \pm 0.8 \times 10^{-3}$ mg Pu/cm^2 h) is a hundred fold greater than reported previously.[6] The rate measured for α-phase metal in 0.005 M NaCl solution is 0.85 mg Pu/cm^2 h. These values and previously reported results for salt solutions[6] are presented as $\log_{10}$R-$\log_{10}$[salt] data in Figure 1. The dependence of R on salt concentration is described by Equation (2):

$$R = 7.25[\text{salt}]^{0.43}. \qquad (2)$$

Although data are limited, the corrosion rates shown for α-phase plutonium in Figure 1 are consistently higher than those for δ-phase alloy and suggest that R may have a slight dependence on the metallurgical form of plutonium.

Dependence of the Pu+H_2O Reaction on Temperature. The temperature dependence of Equation (1) is defined in earlier reports and by results of this study. Rate data obtained by Barlow and Sackman[3] using ocean water are presented in Figure 2. Arrhenius analysis of the results yields an activation energy, E_a, of 6.9 kcal/mol . Corrosion data reported by Haschke et al.[6] for 1.0 M $NiCl_2$ solution give an E_a of 5.3 kcal/mol. A value of 5.7 kcal/mol is derived from mass-loss rates measured with distilled and deionized water at 22 °C (7.2 × 10–7 mg Pu/cm^2 h) and at 49 °C (0.05 mg/cm^2 h) in this study. The combined results give an average E_a of 6.0 ± 0.9 kcal/mol for Equation (1).

The observation of similar E_a values with substantially dissimilar aqueous systems suggests that the same corrosion process occurs in all cases. Whereas the corrosion reaction of plutonium changes dramatically with pH, the fundamental process is not altered by changing the salt concentration. As suggested previously,[6] Equation (1) is apparently catalyzed by dissolved salts and the rate is further increased by the presence of cations such as Fe(III) and Ni(II). The fifty-fold rate enhancement observed for 1.0 M $NiCl_2$ solution compared to 1.0 M $CaCl_2$ solution is attributed a slight pH decrease induced by an hydrolysis reaction that forms $Ni(OH)_x^{(x-2)-}$ ions and H^+.

Prediction of Corrosion Rates for the $Pu+H_2O$ Reaction. Evaluation of potential hazards associated with plutonium corrosion is assisted by rate data appearing in Table I. Rates for several near-neutral aqueous solutions of interest are presented in three units: μm H_2/cm^2 h, mg Pu/cm^2 h and mm Pu /h. The first value facilitates calculation of the amount of hydrogen formed over time and the second provides similar capability for plutonium. The third rate permits rapid calculation of the time required for corrosion to penetrate a given thickness of plutonium. The corrosion rate for synthetic sea water exceeds that for actual sea water by a factor of five. The source of more aggressive behavior for the synthetic solution is unknown.

Table I. Corrosion Rates of Plutonium and Uranium in Near-Neutral Aqueous Media at 25 ± 3 °C

		Corrosion Rate			
Metal	Medium	μmol H_2/cm^2 h	mg metal/cm^2 h	mm metal/h[a]	Reference
Pu	distilled water	0.015	$7.2 \pm 0.8 \times 10^{-3}$	4.5×10^{-6}	this study
Pu	tap water[b]	1.1	0.52	3.3×10^{-4}	4
Pu	lake water[c]	1.5	0.70	4.4×10^{-4}	--[c]
Pu	sea water[d]	2.5	1.2	7.6×10^{-4}	3
Pu	syn. sea water[b]	13	6.3 ± 1.3	4.0×10^{-3}	5
Pu	$CaCl_2$ solution[b]	65	31 ± 5	0.019	6
Pu	$NiCl_2$ solution[b]	390	186 ± 33	0.12	6
U	distilled water[d]	0.3	0.03 ± 0.02	2×10^{-5}	8,9
U	syn. sea water[b]	0.011	$1.3 \pm 0.5 \times 10^{-3}$	6.8×10^{-7}	10

a. Linear corrosion rates are calculated using values of 15.80 and 19.05 g/cm^3 for the densities of δ-phase Pu and α-phase U, respectively. The linear rate for α-phase Pu should be approximately 80% of that for the δ-phase alloy, but this density difference is probably offset by a slightly faster corrosion rate for unalloyed Pu.

b. The molar concentrations of tap water, synthetic sea water, calcium chloride and nickel chloride solutions are 0.0013 (23 ppm), 0.6, 1.0 and 1.0 M, respectively.

c. Rates for lake or river water are estimated and assumed to be slightly greater than those for tap water because the pH may be reduced by acids from decaying organic matter.

d. The rate at 25 °C is calculated using an Arrhenius relationship based on the rate at 100 °C and on an activation energy of 14.5 ± 2.5 kcal/mol.

A relationship describing the temperature dependence of plutonium corrosion in synthetic sea water is derived from the average E_a for Equation (1) and the rate for 25 °C in Table I. The result is defined by the dashed line in Figure 2 and by Equation (3):

$$\ln R \text{ (R in mg Pu/cm}^2\text{ h)} = 11.98 + [(3020 \pm 350/T]. \qquad (3)$$

For the temperature range near 25 °C, a two-fold change in the corrosion rate is expected for each change of ten degrees Celsius in water temperature. Since E_a is apparently not altered by the salt concentration of a near-neutral aqueous system, this general rule is applicable to all plutonium corrosion rates listed in Table I.

Plutonium Corrosion by Product Hydrogen

The possibility of a secondary reaction between corrosion-produced hydrogen and unsubmerged plutonium metal is of concern in certain situations. In one potentially hazardous scenario, rapid hydriding initiates after a substantial quantity of H_2 has been formed. A hydride-catalyzed reaction of plutonium with water ensues as the reactive hydride product falls into water, forms plutonium oxide hydride or oxide and regenerates hydrogen that propagates continued reaction. Although evaluation of system chemistry suggests that the likelihood of such an event is remote, experimental investigation is prudent.

Results of the laboratory-scale test designed to examine the corrosion of plutonium by product hydrogen suggest that hydriding does not occur in the presence of water, even at H_2 pressures up to 13.6 atm (200 psi). Hydrogen was produced steadily during the year-long test and the absence of a pressure decrease suggested that a reaction had not occurred. This conclusion is verified by the unaltered mass and geometry of the suspended plutonium specimen after the test. The sample was covered with a green product layer characteristic of corrosion products formed under humid conditions.

The experimental results are consistent with the chemical behavior of plutonium and other actinide elements.[12] From a thermodynamic perspective, the hydrides should not exist in the presence of excess oxygen or oxygen-containing species. The most stable chemical configuration is established by forming plutonium oxide. A non-equilibrium state involving hydride might exist if the rate of hydriding is more rapid than that for oxidation of hydride by water. However, this possibility is doubtful because induction periods for hydriding of the actinides are extended by oxide layers on the metal and by oxygen-containing impurities in the hydrogen.

Plutonium Hydride Corrosion by Water

Chemistry of the PuH_x+H_2O Reaction. Products of the reaction between plutonium hydride and liquid water are not well defined. The formation of oxide hydride instead of oxide is anticipated, but has not been confirmed experimentally. The behavior is further complicated by the possibility of partial hydrogen retention in the cubic PuH_x phase. Two possible reactions are described by Equations (4) and (5):

$$PuH_x\ (s) + H_2O\ (l) \dashrightarrow PuOH\ (s) + (1+x)/2\ H_2\ (g). \qquad (4)$$

$$PuH_x\ (s) + y\ H_2O\ (l) \dashrightarrow y\ PuOH\ (s) + (1-y)\ PuH_{x+\delta} + y/2\ H_2\ (g). \qquad (5)$$

Equation (4) is expected if hydrogen from both the hydride and water is released as gaseous product. However, when hydride reacts with oxygen and other gases that do not contain hydrogen, H_2 is not formed, even at elevated temperatures.[16] As oxide or other solid plutonium-containing product forms at the gas-solid interface, the hydrogen produced from water is released as H_2. Hydrogen formed at the product-hydride interface moves inward and increases the stoichiometry of unreacted hydride remaining in the hydride particle. At any point in time, the change in hydride stoichiometry, δ, depends on the fraction of the hydride particle reacted and increases until $x+\delta$ approaches three.

For cubic hydride, preference is given to Equation (5). X-Ray diffraction results for the product obtained after extended reaction of $PuH_{2.0}$ ($a_o = 5.359$ Å) with 1.0 M $CaCl_2$ solution at 25 °C shows a cubic product with $a_o = 5.345 \pm 0.003$ Å corresponding to the $PuH_{2.5\pm0.1}$ composition.[17] The behavior of the system is uncertain as the limiting hydride composition is approached; however, based on observations for the reaction of oxygen,[16] reaction of each particle is expected to stop when its internal stoichiometry approaches PuH_3. Therefore, each mole of observed H_2 is assumed to correspond to formation of two moles of PuOH. The formation of PuOH could not be verified because the diffraction pattern of the surface product was not resolved.

The uncertainty in behavior at high stoichiometry exists for the reaction of hexagonal trihydride. Since additional hydrogen cannot be accommodated by the solid phase, the process must be described by Equation (4) with each mole of H_2 corresponding to the formation of a half mole of PuOH.

Dependence of the PuH_x+H_2O Reaction on the Hydride Phase. As suggested by the preceding discussion of properties, reaction kinetics of the cubic and hexagonal hydrides are distinctly different. Since the two hydride forms are obtained at different experimental conditions, the preparative history of a hydride sample is an important determinant of the chemical behavior following immersion in water.

The reaction of cubic plutonium dihydride, $PuH_{2.0}$, with aqueous media at 25 °C is defined by the results of PVT tests with $CaCl_2$ solution. Although a very rapid reaction might be anticipated, hydrogen evolution occurs more slowly than with metal at identical conditions. Pressure-time data show two kinetic regimes. For about 0.5 hour, P increases with t at a constant rate of 70 μmol H_2/g PuH_2 h. A quantitative comparison of this result with the corrosion rate of metal is possible because PuH_x samples obtained at the conditions used for hydride preparation consistently have specific surface areas in the range 0.2 ± 0.1 m^2/g.[18] Normalization for surface area and use of the stoichiometric ratios defined in Equation (5) give a reaction rate of 0.017 mg Pu/cm^2 h, a value that is more than a thousand times slower than for plutonium metal in 1.0 M $CaCl_2$ solution at 25 °C.

After a transition period of a few hours, the reaction enters a parabolic kinetic regime. A parabolic time dependence is indicated by the linear relationship between extent of reaction and square root of time in Figure 3. This dependence is characteristic of a process in which the reaction rate is controlled by diffusion of reactive species through a layer of solid product that progressively increases in thickness with time. These data indicate that the product layer grows on the cubic hydride without spallation, an observation consistent with structural properties of PuH_2, PuOH and PuO_2. Whereas formation of the oxide hydride or oxide on unalloyed metal is accompanied by a volume increase of about 40% and spallation of the low-density solid product, formation of these phases on the dihydride occurs with a volume change of less than 3% and formation of an adherent product layer.

PVT data for reaction of hexagonal PuH_3 with aqueous 1.0 M $CaCl_2$ solution at 25 °C indicate that the rate is also diffusion controlled. However, three distinct linear regions are observed in the extent of reaction-$t^{1/2}$ results. The slopes for the initial thirty minutes, for 0.5 -24 hours and for 1-15 days are 9.2, 0.40 and 0.11 mol H_2/mol Pu $d^{1/2}$, respectively. The appearance of three linear regions is attributed to a trimodal distribution of particles in the trihydride. After reaction of extremely fine particles is complete, the active surface area of the sample is reduced and a region of lower slope is entered. In a similar way, the change occurring after one day is attributed to complete reaction of particles with an intermediate distribution of sizes.

Prediction of Rates for the PuH_x+H_2O Reaction. Prediction of rates for the reaction between plutonium hydride and water is limited by a lack of knowledge about the kinetic dependence on pH , temperature and other parameters. The task is made more difficult by the need for information on preparative history of the hydride.

Available information for evaluating potential hazards associated with reaction of plutonium hydride and water at 25 °C is presented in Table II. The total quantities of hydrogen generated and the estimated percentages of hydride consumed are listed for the cubic and hexagonal hydrides at selected points in time following immersion in water. Although the kinetic dependence on salt concentration is unknown, the results for 1.0 M $CaCl_2$ solution approximate those for sea water. Extrapolation of the data for the cubic phase suggests that the reaction will be complete in approximately 575 days, but behavior of the $PuH_{x+\delta}$ product at times greater than the hundred-day experimental period is uncertain.

Table II. Hydrogen Quantities and Extents of Reaction Measured for the Cubic and Hexagonal Hydrides of Plutonium Immersed in Water for Different Periods of Time at 25 °C

	Total Hydrogen Generated ($mmol\ H_2/g\ PuH_x$)		Hydride Reacted[a] (%)	
Elapsed Time	Cubic PuH_2	Hexagonal PuH_3	Cubic PuH_2	Hexagonal PuH_3
1 h	0.04	0.6	2	7
1 d	0.1	2	5	24
10 d	0.3	3	14	36
50 d[b]	0.6	5	29	60

a. Percentages of reaction for the cubic and hexagonal hydrides are based on Equations (5) and (4), respectively.
b. Values for PuH_3 are based on extrapolation of data beyond the experimental range of 15 days.

Uranium Corrosion by Water

Chemistry of the $U+H_2O$ Reaction. The corrosion of uranium by liquid and gaseous water at temperatures up to 240 °C is described by Equation (6).[8,9]

$$U\ (s) + 2\ H_2O\ (l) \dashrightarrow UO_2\ (s) + 2\ H_2\ (g). \qquad (6)$$

This is an idealized description of the reaction because the experimental data are consistent with formation of a black solid product containing $UO_{2.06\pm0.02}$ and 2 to 9% UH_3. The oxide composition is apparently based on X-ray diffraction data showing a CaF_2-type product with a cubic lattice parameter corresponding to that for the slightly superstoichiometric oxide. The solid product is finely divided, as indicated by line broadening of X-ray reflections and a specific surface area of 30 m^2/g.

However, several observations closely parallel those for the plutonium system[6,7] and suggest that the solid product may be an oxide hydride, not a mixture of UO_2 and UH_3. Solids formed at low temperatures (110-150 °C) contained the highest amounts of hydrogen and "considerable amounts" of H_2 were released when products were heated at temperatures as low as 120 °C in static vacuum.[8] Hydrogen pressures in excess of 10 torr were generated. These observations are inconsistent with thermodynamic properties of UH_3, which has an equilibrium hydrogen pressure of 1.0×10^{-5} atm (7.6×10^{-3} torr) at 120 °C.[19] In addition, the rate of hydrogen formation by UH_3 is extremely slow at this temperature (2×10^{-8} mol H_2/g UH_3 sec).[20] The estimated time to reach the equilibrium pressure with a 5-g sample containing 10% UH_3 is on the order of 10 to 100 h for a 100 cm^3 vessel at 120 °C.

Although the authors attribute the formation of large amounts of H_2 during heating of the material in vacuum at 120 °C to reaction of residual UH_3 with water adsorbed on the product surface,[8] that explanation must be questioned. The UH_3+H_2O reaction should have occurred while the material was being prepared at 110-150 °C in the presence of excess water. If the product of Equation (6) is an oxide hydride instead of a 91% UO_2-9% UH_3 mixture, its composition ($UO_{1.80}H_{0.30}$) is reasonable and similar to that of the plutonium product ($PuO_{1.39}H_{0.43}$) formed by reaction of PuOH with water.

<u>Dependence of the U+H_2O Reaction on pH.</u> Results for uranium immersed in aqueous media at 100 °C show that the corrosion rate is rather insensitive to pH.[9] Unlike plutonium, the slowest rates are for dissolution in acidic systems below pH 2. Between pH 2 and 3, the rate increases about ten fold to the maximum value (4.15 mg U/cm^2 h) associated with Equation (6). The corrosion rate remains constant in the pH 3 to 7 range and decreases gradually by 10-15% over the pH 7 to 13.5 range.

<u>Dependence of the U+H_2O Reaction on Salt Concentration.</u> Studies with uranium and with the Mulberry alloy (2.5% Zr, 7.4% Nb, 90.1% U) immersed in synthetic sea water (3% salinity) at 25 °C show that the corrosion rate for unalloyed metal is seven to eight times faster than for the alloy.[10] For uranium metal, the average corrosion rate determined from data presented in the report is $1.3 \pm 0.5 \times 10^{-3}$ mg U/cm^2 h. As shown by data in Table I, this value is thirty times slower than the rate derived for distilled water at 25 °C and suggests that corrosion of uranium is suppressed by dissolved salts. This result is supported by observation of a decreased corrosion rate in sodium carbonate solution,[9] but additional studies are needed to adequately define the dependence on salt concentration.

<u>Dependence of the U+H_2O Reaction on Temperature.</u> The temperature dependence of uranium corrosion is derived from the results of studies by Baker et al. with distilled

water.[8,9] Different batches of uranium are reported to have activation energies in the 12 to 17 kcal/mol range, but absolute reaction rates are not presented. However, the Arrhenius relationship given by Equation (7) is derived from the E_a results and a corrosion rate extracted from graphical data for the pH dependence of corrosion at 100 °C:

$$\ln R \text{ (R in mg U/cm}^2\text{ h)} = 20.99 - [(7300 \pm 1260)/T]. \qquad (7)$$

The corrosion rate presented for distilled water at 25 °C in Table I is calculated using this equation.

Prediction of Corrosion Rates for the U+H_2O Reaction. Corrosion rates for uranium immersed in distilled water and synthetic sea water in Table I provide reference points for evaluating potential hazards and for comparing the corrosion behavior of uranium and plutonium. The kinetic effect of pH is negligible and absent in mildly acidic media. The corrosion rate is apparently reduced by increasing the salt concentration. A ten-degree change in temperature is accompanied by two-fold change in rate.

The kinetic dependence on water pressure is also described by Baker et al.[9] The corrosion rate in saturated vapor (100% relative humidity) equals that observed for metal immersed in water at 100 °C. The corrosion rate remains constant as the relative humidity decreases to 70% and then drops steadily by a factor of two between 70 and 25%. Kinetic data are not reported for low water pressures.

Uranium Hydride Corrosion by Water

Chemistry of the UH_3+H_2O Reaction. The reaction of uranium hydride with water is described by Baker and coworkers[8,9] and by Newton et al.[21] These authors define the process by Equation (8):

$$UH_3\text{ (s)} + 2\ H_2O\text{ (l)} \dashrightarrow UO_2\text{ (s)} + 7/2\ H_2\text{ (g)}. \qquad (8)$$

However, this equation is not consistent with extent of reaction-time data reported for UH_3 immersed in distilled water at 100 °C. Reaction stops at 84 ±1% of the completion point for Equation (8) and approaches completion only as the humidity is decreased and the temperature is increased.[8,9]

The results suggest that the solid reaction product may be an oxide hydride of uranium. The lack of agreement between Equation (8) and the observed products is attributed to incomplete reaction of the hydride, but an explanation is not offered for why a certain fraction of the UH_3 reactant is consistently active while the remainder is stable. Furthermore, the conditions identified for complete reaction (4% relative humidity and 240 °C) cause an oxide hydride to decompose and force the reaction to comply with Equation (8). If the product obtained at 84% completion is assumed to be an oxide hydride of tetravalent uranium, its stoichiometry is $UO_{1.2}H_{0.6}$. This composition is consistently observed for products formed at 100-150 °C and 100% relative humidity and is anticipated for the product formed at 25 °C, unless a more hydrogen-rich phase is not stable.

Certain kinetic features of the reaction are deduced from reported observations.[8,9] At 25 °C, the reaction is rapid initially, but becomes slow after a few minutes, implying that the rate is controlled by diffusion through the product layer. However, kinetic data for 100 °C show that the extent or reaction is linear with time until the limiting percentage of reaction (84 ± 1%) is approached. These observations suggest that the kinetics are paralinear, a region of parabolic time dependence followed by a linear regime. A constant rate is observed in the linear region because a product layer of fixed average thickness is maintained by a balance of continuous spallation and reaction.

Dependence of the UH_3+H_2O Reaction on Temperature. The temperature dependence of the reaction between the trihydride and water is derived from extent of reaction-time data for 100 °C and from information on kinetic behavior at room temperature.[9] The calculated reaction rate at 100 °C is 40 mg U/g UH_3 h, a value equivalent to 8×10^{-3} mg U/cm^2 h for hydride with a specific area of 0.5 m^2/g. A rate at 25 °C is obtained from the statement that "after two weeks only 15-20% of the UH_3 reacted." For 17.5 ± 2.5% reaction, $R = 0.5 \pm 0.1$ mg U/g UH_3 h (1×10^{-4} mg U/cm^2 h). Arrhenius analysis of these data gives an activation energy of approximately 13 kcal/mol and yields Equation (9):

$$\ln R \text{ (R in mg U/cm}^2\text{ h)} = 12.3 - (6420/T). \qquad (9)$$

Dependence of the UH_3+H_2O Reaction on Hydride Quantity. Observations reported by Newton et al.[21] suggest that the kinetic behavior outlined in the preceding paragraphs may only apply to small amounts of uranium trihydride. These authors report that visible reaction was not observed when UH_3 samples of less than 25 g were covered with water. However, immersion of larger quantities usually resulted in "a deflagration" that produced "sudden red heat" and broke glass containers. A large sample (400 g) was successfully immersed by adding water in a drop-wise process that limited the rate at which heat was generated by the reaction.

These observations suggest that large samples of UH_3 enter an autothermic or pyrophoric regime if they are rapidly immersed in water. Heat generation is sufficiently rapid that the sample temperature exceeds the ignition point at which self-sustained reaction occurs. In addition to hydride quantity, factors that determine ignition behavior include the activation energy, specific surface area of the hydride and the rate of heat transfer from the reaction zone.

Prediction of Rates for the UH_3+H_2O Reaction. Prediction of reaction rates for the reaction of uranium trihydride with water is also limited by lack of knowledge. Estimated quantities of hydrogen generated and percentages of hydride reached at selected points in time following immersion of UH_3 in water at 25 °C are presented in Table III. The estimates, which do not include a contribution from the rapid initial rate, are based on the constant (linear) rate determined for the reaction and on the validity of Equation (8). Reaction is expected to become immeasurably slow or stop after the extent of reaction reaches 84%.

Table III. Estimated Hydrogen Quantities and Extents of Reaction for Uranium Trihydride Immersed in Water at 25 °C[a]

Elapsed Time (days)	Total Hydrogen Generated (mmol H_2/g PuH_x)	Hydride Reacted[b] (%)
1	0.2	1
10	1.7	12
50	8.4	60

a. The hydrogen generation rate is based on Equation (9).

b. The percentage of reaction is calculated by assuming that the reaction is described by Equation (8).

POTENTIAL HAZARDS

Several potential hazards related to product properties and reaction kinetics described in this report are identified. In many cases, the hazardous potential of the situation is expected to depend strongly on the specific conditions of the incident. Situations of concern are not evaluated; that task is left to experts in the appropriate fields of hazard assessment.

Criticality. The finely divided oxide hydride or oxide products of metal corrosion, as well as the powdered hydride reactants, may become dispersed in water. For example, the black product formed by corrosion of plutonium deposits as a sludge-like mass that is dispersed in water by agitation and settles very slowly. Like aqueous solutions of uranium or plutonium, such suspensions are capable of moderating and reflecting neutrons and their formation may impact criticality safety.

Dispersibility . Aqueous corrosion of uranium and plutonium transforms these non-dispersible materials into dispersible forms. The fine particles formed by reactions of the metals and hydrides with water are capable of being spread by water currents when in suspension and may be aerosolized and transported by air currents when dry. Qualitative observations suggest that large fractions of the products are potentially dispersible and respirable. Accurate assessment of the risk due to airborne material is difficult because the particles dry slowly, coalesce as a hard solid mass when dry and readily adhere to surfaces. However, the potential for exposing workers and the public to radioactive materials and for dispersing contamination into the environment is of concern.

Chemical Reactivity. Two types of chemical reactivity are recognized and each has a unique potential for creating hazardous situations. One concern is the possible occurrence of a violent reaction when a large quantity of hydride is immersed in water. The other is related to the pyrophoric tendency of the hydridic products formed by reaction of the metals and hydrides with water.

A violent exothermic reaction is reported to occur when uranium trihydride is submerged in water.[21] However, the only quantified parameter is the amount of UH_3 (approximately 25 g) required to initiate autothermic reaction. Important factors such as preparative history of the hydride, immersion rate, configuration of the hydride mass, thermal transport, etc. are not defined. Although additional understanding of the reaction and of the kinetic parameters controlling its rate is needed before a detailed safety assessment can be made, hazards associated with its occurrence merit consideration.

An important question related to the hydride-water chemistry is whether a sufficiently large quantity of plutonium hydride might also react violently when immersed in water. This question cannot be answered, but a qualitative assessment of the potential can be made by comparing certain parameters such as reaction rate, heat of reaction, activation energy and ignition temperature with those of uranium hydride. Kinetic results presented in this report show that the reaction rate of plutonium hydride (34 mg Pu/g PuH_x h) with salt water at 25 °C is about sixty times faster than that of uranium trihydride (0.5 mg U/g UH_3 h); however, the R for UH_3 is the long-term constant value, not the more rapid initial rate. The quantities of heat generated by Equation (5) for PuH_x (x = 2 and y = 1) and Equation (8) for UH_3 are comparable at -38 and -44 kcal/mol, respectively. The effect of product heat in accelerating the reaction rate cannot be compared with that of UH_3+H_2O because E_a is not known for the PuH_x+H_2O reaction.

The largest uncertainty in comparing properties of the PuH_x+H_2O and UH_3+H_2O reactions is in the ignition temperature, the point at which self-sustained reaction begins, and in the mechanism by which that temperature is reached. For the reactions of interest, heat may also be derived from the combustion of product hydrogen. If the heat of forming gaseous water is combined with the enthalpies of Equations (5) and (8), the total heats of reaction are -67 and -246 kcal/mol for PuH_x and UH_3, respectively. The difference in thermal consequences may be larger than suggested by these values because decomposition of UH_3 is relatively facile. The 30 torr equilibrium H_2 pressure required to form a flammable mixture of 4% H_2 in air is reached at 303 °C with UH_3 and at 685 °C with PuH_2.[19] If the ignition points of the hydrides are related to these temperatures, the behavior of PuH_x will differ markedly from that of UH_3.

Violent reaction is anticipated if sufficient uranium hydride is rapidly immersed in water and similar behavior may be encountered with plutonium hydride. Inclusion of these possibilities as part of hazard assessment seems prudent and should be augmented by studies that define conditions for violent reaction and investigate the potential for dispersing of nuclear materials into the environment.

Concerns also exist about potential pyrophoricity of dry hydridic products such as oxide hydrides or mixtures of oxide and hydride. The ignition of hydrogen produced by plutonium corrosion is attributed to pyrophoric nature of PuOH.[14] In addition to creating sparks and localized heating, pyrophoric materials may also act as ignition sources for autothermic reaction of metal. Oxidation reactions involving trivalent plutonium oxide (Pu_2O_3) and hydride on plutonium surfaces are identified as thermal sources that may heat the metal above its ignition point of 500 ± 25 °C.[22,23] The ensuing autothermic reaction of the metal with air causes a thermal excursion that continues until all metal is consumed.[16,24] The possibility exists for ignition of plutonium and uranium by hydridic corrosion products, their rapid conversion to dispersible forms, and subsequent dispersal of nuclear material into the environment.

Hydrogen Generation. The primary concern associated with hydrogen generation is the possibility of forming explosive mixtures with air. The potential hazard is enhanced by the presence of hydridic material that may act as an ignition source.

CONCLUSIONS

As evidenced by this report, much is known about the reactions of water with the metals and hydrides of plutonium and uranium and about relevant properties of the reactants and products. The knowledge base has been expanded by presentation of new results for Pu and PuH_x. The corrosion rate of uranium by sea water at 25 °C is approximately a thousand times slower than that of plutonium. The reaction rates of PuH_x and UH_3 with water are more comparable, but the effects of salt concentration and other parameters are unknown.

Additional studies are needed to resolve uncertainties and questions in several important areas. Unlike plutonium, the corrosion rate of uranium is slower in sea water than in distilled water. This behavior should be verified and the reactions of PuH_x and UH_3 should be further investigated to establish their dependencies on temperature and salt concentration. Characterization of the violent reaction of water with large quantities of UH_3 is needed to adequately assess the potential hazard. Parallel studies with large quantities of PuH_x are essential.

Several potential hazards associated with immersion of plutonium and uranium in water are identified. Possible emergency procedures are suggested by the effects of kinetic parameters. The corrosion reaction of plutonium is relatively rapid and forms a fine hydridic solid plus hydrogen; the hydrides of uranium and plutonium may react violently with water. Suspension of solid products in water may result in a criticality or in dispersal of nuclear material in the environment. In addition to becoming aerosolized and dispersed, dried products may be pyrophoric and provide an ignition source for unreacted metal or product hydrogen. The sludge-like corrosion products dry slowly, even in dynamic vacuum. Pyrophoric ignition and aerosolization are not anticipated if products remain wet, but hydrogen continues to be formed. If plutonium must remain immersed in water or cannot be thoroughly dried, the reaction rate can be suppressed by making the aqueous phase basic. Results for uranium suggest that its corrosion rate might be reduced by adding salt to the water.

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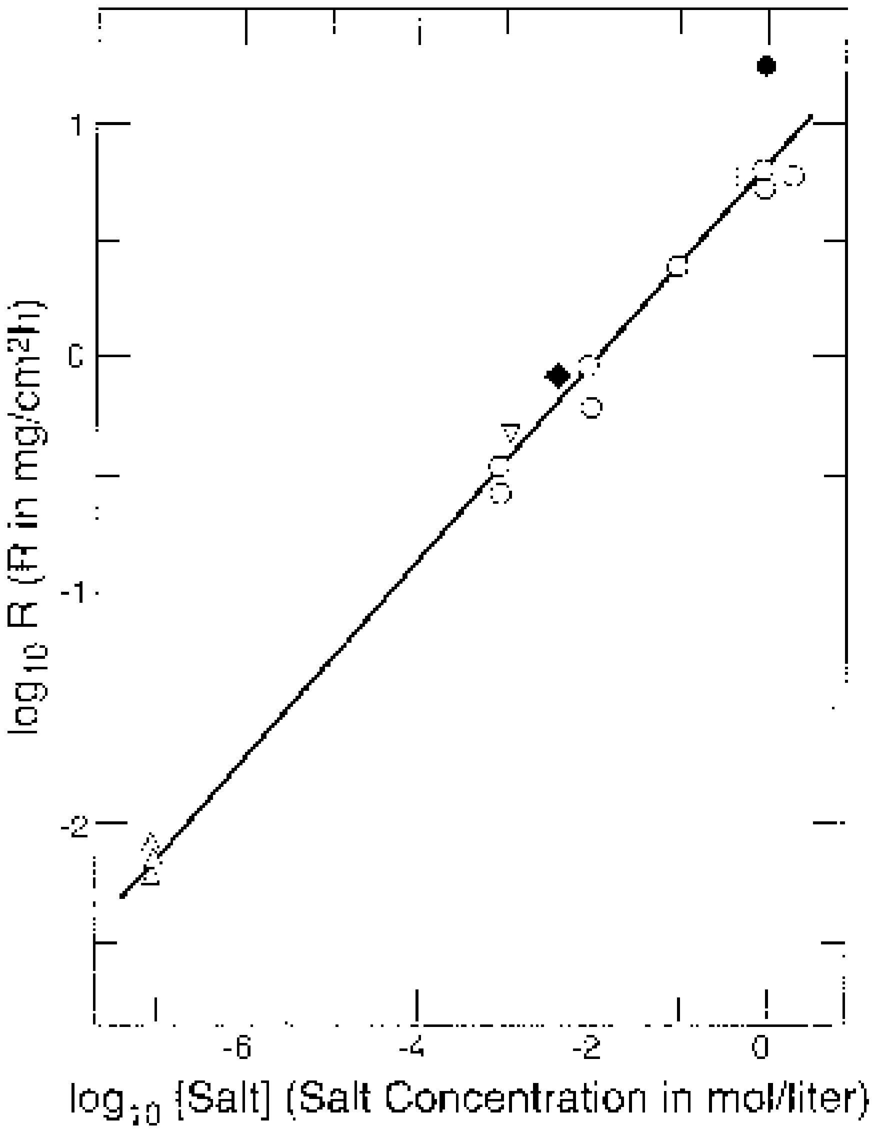

Figure 1. Dependence of the plutonium corrosion rate on molar salt concentration of the aqueous solution at 25 °C. Rates for alpha- and delta-phase metals are indicated by solid and open symbols, respectively. Upright triangles, circles, the inverted triangle, the diamond and the square are for distilled-deionized water, calcium chloride solutions, tap water, sodium chloride solution and synthetic sea water, respectively.

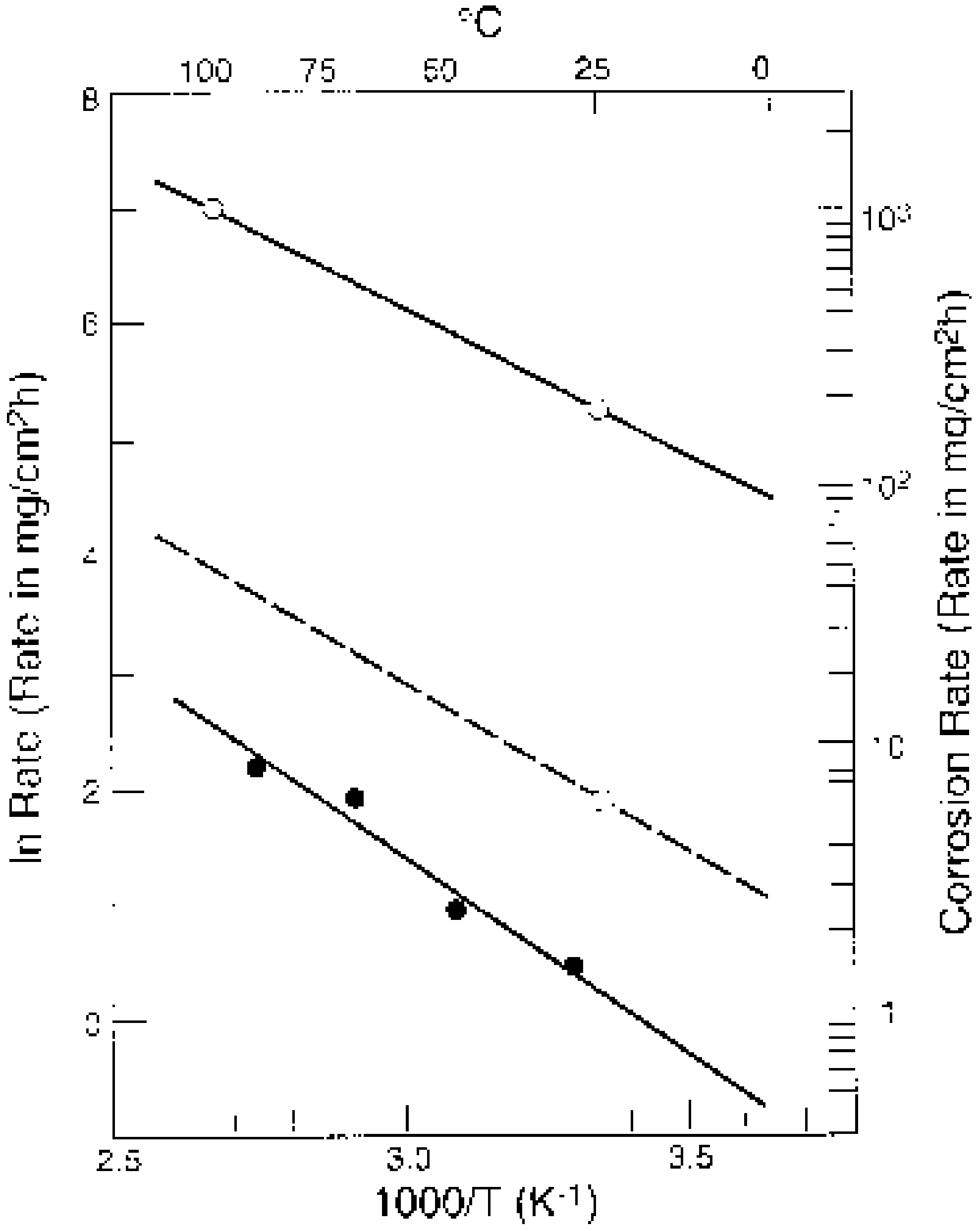

Figure 2. Arrhenius dependence of plutonium corrosion in selected salt solutions. Data for ocean water (Reference 3) and 1.0 M nickel chloride solution (Reference 6) are indicated by solid and open circles, respectively. The temperature dependence for synthetic sea water is derived from the rate (Reference 5) shown by the square symbol and the dashed line based on the average activation energy of 6.0 kcal/mol for near-neutral solutions.

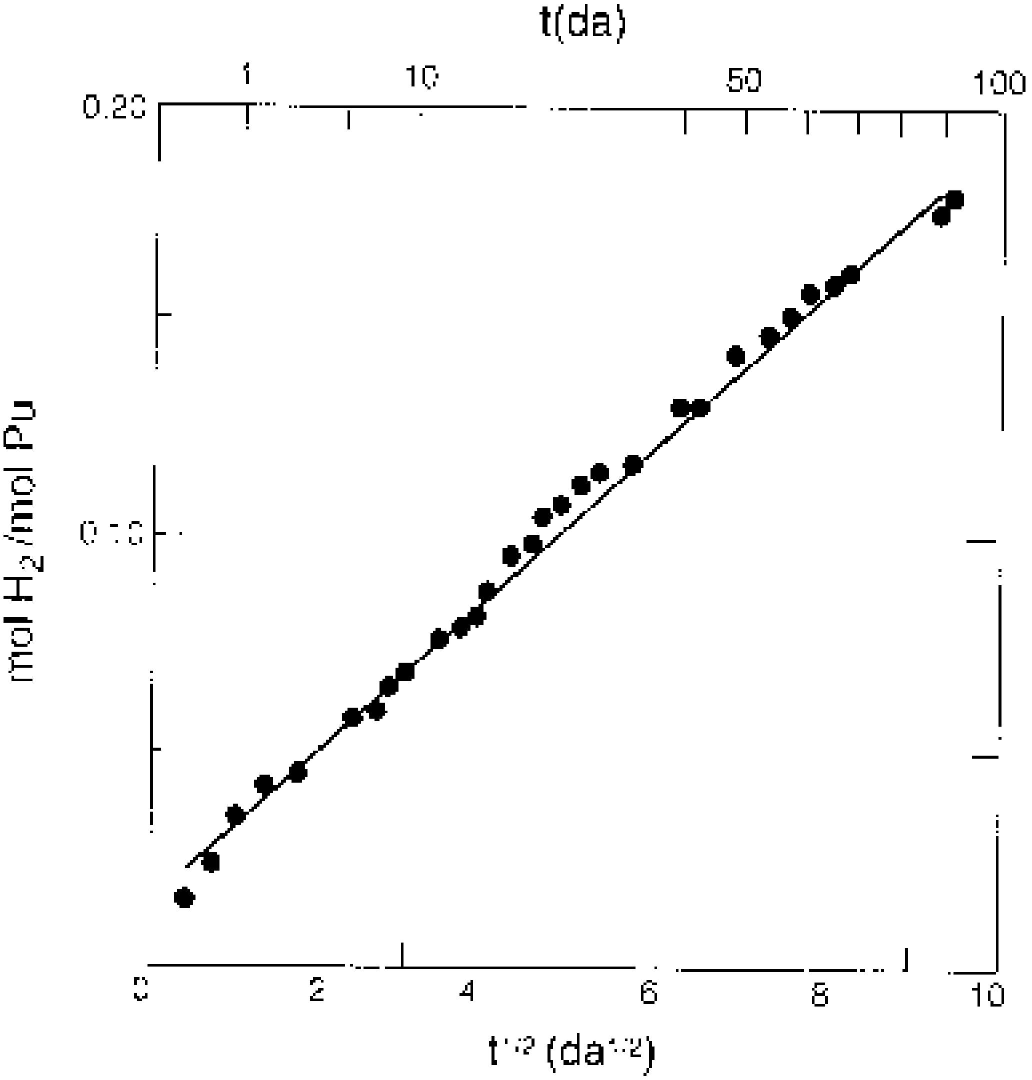

Figure 3. Dependence of the reaction extent for PuH_x+H_2O on the square root of time in days. The data are for $PuH_{2.0}$ immersed in 1.0 M calcium chloride solution at 25 °C.

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