LBL--16690

CONF-831174--51

DE84 004882

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Presented at the Materials Research Society Annual
Meeting, Symposium D, Scientific Basis for
Nuclear Waste Management, Boston, MA,
November 14-17, 1983; and to be published in
the Proceedings

THE BEHAVIOR OF AMERICIUM IN AQUEOUS CARBONATE SYSTEMS

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November 1983

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ABSTRACT

The solubilities of crystalline $Am(OH)_3$ and $AmOHCO_3$ were measured at 25° C in aqueous solutions of 0.1 M $NaClO_4$ by determination of the solution concentrations of Am. Prior to use in the measurements, the solid materials were characterized by their x-ray powder diffraction patterns. The solubility product quotients were calculated from the experimental data. The hydrolysis quotients of Am^{3+} were also estimated from the hydroxide solubility data. Using the thermodynamic data derived from these experiments and the recently reported formation constants for the Am^{3+} carbonate complexes, the solid phases and concentrations of solution species of americium in several aqueous carbonate systems were calculated using the computer code MINEQL.

INTRODUCTION

In the event that the canister and waste form fail to contain radioactive waste materials, radionuclides will enter the local groundwater system. The radionuclides will react with various components of the groundwater, dissolved waste form materials, and the host rock to form insoluble compounds and solution complexes that can control concentrations and migration rates of the waste radionuclides. Since the time scale being considered is a 1000 years or longer, predictions based on realistic modelling studies provide the main avenue of assessment. Thus, reliable data on the nature and solubilities of compounds as well as the nature and formation constants of complexes of the waste radionuclides that form in natural systems are needed as a first step in the prediction of the amounts and rates of release of radionuclides from a proposed underground repository.

Computer calculations show that the actinides, U-Cm, are major contributors to the radioactivity of the waste for storage times of 10^3 years or greater [1,2]. Although a number of inorganic components will be present in groundwaters which can form insoluble compounds and solution complexes with the actinides, hydroxide and carbonate are common to all groundwaters and are expected to play a dominant role in determining the speciation and solubilities of the important actinides [3,4]. However, reliable thermodynamic data on the solubilities of trivalent actinide hydroxide and carbonate compounds have not been available.

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The purpose of this paper is to present the results of recent investigations of the solubilities of crystalline americium(III) hydroxide and hydroxycarbonate compounds. Using thermodynamic data derived from these investigations and other reported data, predictions of the solid phases and solution species formed by Am^{3+} in several different aqueous carbonate systems were made using the computer code MINEQL[5]. These results are also presented here.

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SOLUBILITY STUDIES

$Am(OH)_3$

The solubility of crystalline $Am(OH)_3$ was measured at 25 ± 1°C and 1 atmos. pressure in aqueous solutions of 0.1M $NaClO_4$ under argon. The solution concentrations of americium were followed to steady state over a 48 day period and over the pH range 7 to 9.5 in batch type experiments. The x-ray powder diffraction pattern obtained from the solid, prior to the solubility measurements, was nearly identical to that reported for $Am(OH)_3$ [6] and $Nd(OH)_3$ [7].

An analysis of the solubility data was made in terms of the solubility product and first four hydrolysis reactions of Am^{3+} using the speciation computer code called MINEQL [5]. The first hydrolysis constant for Am^{3+} has not been measured, however, this quotient has been reported for Cm^{3+} at an ionic strength of 0.1 M [8]. Since Am and Cm are adjacent actinides of nearly the same ionic radius, the value for Cm^{3+} should be a good approximation for Am^{3+} and was used in the analysis. From the results of the analysis, values for the solubility product quotient, Q_{s10}, and the second and third hydrolysis quotients, Q_{12} and Q_{13}, were estimated. An upper limit for the fourth hydrolysis quotient was also obtained. The reactions used in the analysis and the resulting estimates of the quotients are given in Table I. The quotients were calculated from the molar concentrations of the constituents. A more detailed description of these studies are given in reference 9. The work of Rai et al. indicate that the solubility product quotient for amorphous $Am(OH)_3$ is about a factor of 10 larger than reported here for the crystalline material [10].

$AmOHCO_3$

The solubility of crystalline $AmOHCO_3$ was measured at 25 ± 1°C and 1 atmos. pressure in aqueous solutions of 0.1 M $NaClO_4$ and $2.08 \pm .09 \times 10^{-4}$ M HCO_3^-. Initial experiments indicated that this compound, rather than $Am_2(CO_3)_3$, was the stable solid phase in dilute aqueous solutions of bicarbonate. The measurements were conducted at a fixed pH, 6.12 ± .03. The pH and HCO_3^- concentration were sufficiently low to avoid significant hydrolysis and carbonate complexation of the Am^{3+}. The pH was controlled with a potentiostat and the bicarbonate fixed by contacting the solution with an atmosphere of 0.792 percent CO_2 and 99.2 percent Ar.

The solubility studies were conducted in two parts. The first involved following to steady state the solution concentration of Am over a period of 30 days in a solution initially free of the element, undersaturation conditions, but which had been placed in contact with the crystalline solid. The second part involved following to steady state the solution concentration of Am over a period of 51 days in a solution initially supersaturated in Am with respect to the precipitation of a solid phase but with no solid initially present. At the beginning and end of part 1 and the end of part 2, x-ray powder diffraction patterns were obtained from the solids. The three patterns were nearly identical to each other and to that reported for $NdOHCO_3$ [11]. From the molar concentrations of Am^{3+}, HCO_3^- and H^+, a solubility product quotient was calculated. The reaction and the quotient obtained from averaging the results of part 1 and 2 are given in Table I. A more detailed description of these studies are given in reference 12.

MODELLING CALCULATIONS

In order to test the effect of the presence of carbonate on the solubility of Am^{3+}, a series of speciation calculations were performed

TABLE I. Thermodynamic data used in MINEQL calculations (25°C, 0.1 M ionic strength).

Reaction	log Q	Reference
$Am^{3+} + H_2O = AmOH^{2+} + H^+$	-7.7 ± .3	8
$Am^{3+} + 2H_2O = Am(OH)_2^+ + 2H^+$	-16.6 ± .5	9
$Am^{3+} + 3H_2O = Am(OH)_3^{\bullet} + 3H^+$	-24.8 ± .2	9
$Am^{3+} + 4H_2O = Am(OH)_4^- + 4H^+$	< -35	9
$Am^{3+} + CO_3^{2-} = AmCO_3^+$	6.1	13
$Am^{3+} + 2CO_3^{2-} = Am(CO_3)_2^-$	10.1	13
$Am(OH)_3(c) + 3H^+ = Am^{3+} + 3H_2O$	16.5 ± .2	9
$AmOHCO_3(c) + 2H^+ = Am^{3+} + HCO_3^- + H_2O$	2.74 ± .17	12
$Am^{3+} + F^- = AmF^{2+}$	3.9	19
$Am^{3+} + 2F^- = AmF_2^+$	6.4	19
$Am^{3+} + 3F^- = AmF_3^{\bullet}$	9.3	19
$Am^{3+} + SO_4^{2-} = AmSO_4^+$	2.6	19
$Am^{3+} + 2SO_4^{2-} = Am(SO_4)_2^-$	3.7	19
$Am^{3+} + Cl^- = AmCl^{2+}$	0.5	19
$Am^{3+} + 2Cl^- = AmCl_2^+$	-0.1	19

for several pH values and carbonate concentrations. Only the solid phases $Am(OH)_3$ and $AmOHCO_3$ were considered and only hydrolysis and carbonate complexing of Am^{3+} were considered. The reactions and constants used in the calculations are given in table I. Since this involves the solution of a number of coupled equations simultaneously, the calculation of the concentration of solution species and solubilities from the thermodynamic data were made using a computer code called MINEQL [5].

Data on the first and second formation constants, β_1, and β_2, for the carbonate complexes of Am^{3+} have been obtained from studies carried out in 1 M $NaClO_4$ [13]. Unfortunately there are no data on mean activity coefficients of appropriate Am salts in mixed electrolyte systems which could be used to correct the quotients obtained in 1 M $NaClO_4$ to 0.1 M $NaClO_4$. As the next best approximation, it was decided to use mean activity coefficients of $LaCl_3$-HCl mixtures that have been measured experimentally [14] for dilute solutions of $LaCl_3$ in 1 M and 0.1 M HCl. The mean activity coefficient for appropriate carbonate species in a mixed electrolyte were estimated using Pitzer's equations [15]. Ion interaction parameters used in the calculations for carbonate species [16] and $NaClO_4$ [17] are reported in the literature. The single ion activity coefficients for $AmCO_3^+$ and $Am(CO_3)_2^-$ were taken equal to that of Na^+. The values for the carbonate formation quotients given in Table I were calculated from the data in reference 13 using these activity coefficients.

Figure 1(a) shows a plot of the logarithm of the calculated concentrations of the various Am solution species (dashed curves) and the sum of the concentrations of the solution species (solid curve), i.e., the solubility line, in the absence of carbonate using the $Am(OH)_3$ solubility and hydrolysis quotients given in Table I. The solid curve is labelled with the stable solid phase. Figure 1(b) shows a plot for a fixed partial CO_2 pressure of $10^{-3.5}$ atmosphere, i.e., normal concentration in air. Figures 1(c) shows a plot for a constant total carbonate concentration of 2×10^{-3}M, or about 120 ppm.

Finally, a MINEQL calculation was made for a simulated groundwater with a composition similar to that reported for a Hanford Basalt groundwater with a pH of about 9.5 [18]. In addition to hydrolysis and carbonate complexation, fluoride, sulphate and chloride complexations were included. The reactions and quotients for 0.1 M ionic strength [19] are given in Table I. The solution composition was taken to be 42 parts per million (ppm) F^-, 199 ppm SO_4^{2-}, 297 ppm Cl^- and 157 ppm total carbonate. The results of these calculations are shown in figure 1(d).

CONCLUSIONS

The results of the measurements and the MINEQL calculations lead to the following conclusions:

(1) The presence of carbonate, at normal groundwater concentrations, can have a substantial effect on the nature and solubility of Am^{3+} compounds as well as solution species. Since actinides in the same valence state tend to exhibit similar chemical properties [20], this result should be true for other actinides in the trivalent state as well.

(2) The solid phase $AmOHCO_3$ is predicted to be more stable than $Am(OH)_3$ over the pH range 6 to 9.5. Factors of 10 to 10^4 lower solubilities (depending on the pH and carbonate concentration) compared to $Am(OH)_3$ could be expected.

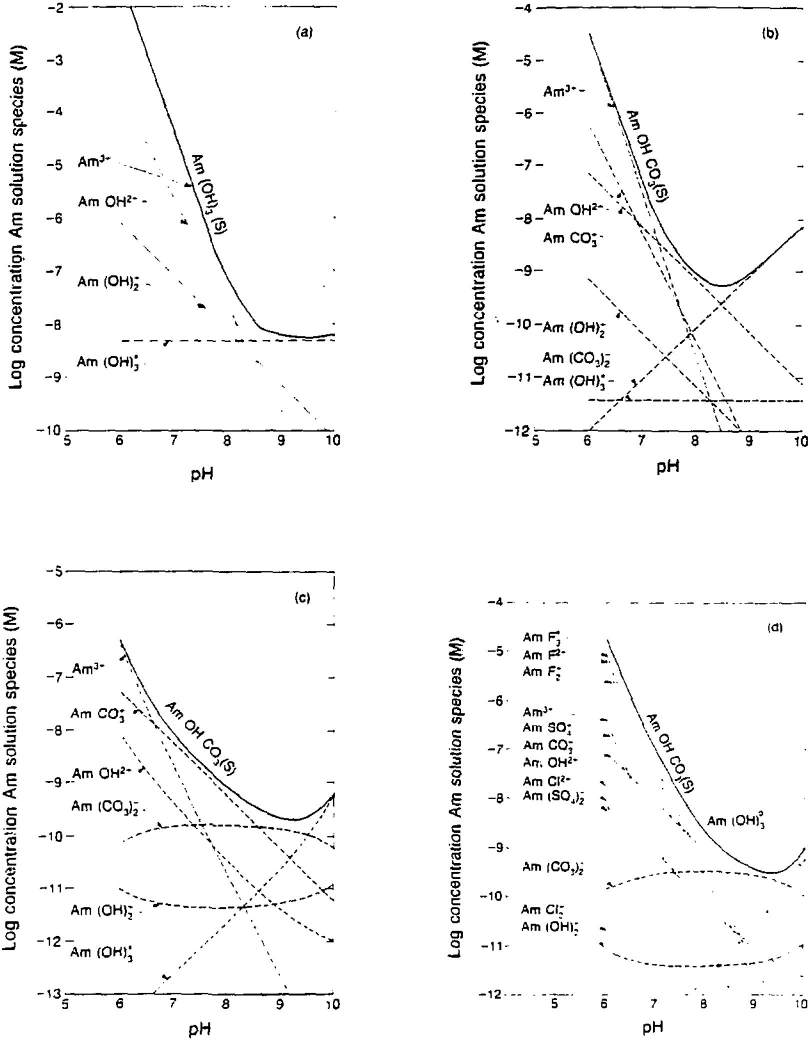

Fig. 1. Calculated concentrations of Am solution species (dashed curves-labelled with species) and their sums (solid curves-labelled with the controlling solid phase) for 0.1 M ionic strength as a function of pH. (a) P(CO_2) = 0 atmos.; (b) P(CO_2) = $10^{-3.5}$ atmos.; (c) $\Sigma CO_3 = 2 \times 10^{-3}$ M; (d) simulated ground water of low dissolved solids: $Cl^- = 8.4 \times 10^{-3}$ M, $SO_4^{2-} = 2.1 \times 10^{-3}$ M, $F^- = 2.2 \times 10^{-3}$ M, $\Sigma CO_3 = 2.6 \times 10^{-3}$ M.

(3) The carbonate complexes of Am, $AmCO_3^+$ and $Am(CO_3)_2^-$, are predicted to be major solution species for pH values of about 7 and higher for low dissolved solid groundwaters.

ACKNOWLEDGMENTS

The author wishes to thank J.J. Bucher for helpful advise on estimating activity coefficients and H. Nitsche for calculation of the activity coefficients of the carbonate species. The investigations of the solubility of $Am(OH)_3$ were supported by the U.S. Department of Energy, under contract No. DE-AC03-76SF00098, and administered by the Office of Nuclear Waste Isolation, Battelle Memorial Institute. The remainder of the work was supported by the Division of Health, Siting and Waste Management, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, under Contract FIN No. B 3040-0.

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