Title

THERMODYNAMIC PROPERTIES OF CHEMICAL SPECIES IN NUCLEAR WASTE. TOPICAL REPORT. THE SOLUBILITIES OF CRYSTALLINE NEODYMIUM AND AMERICIUM TRIHYDROXIDES

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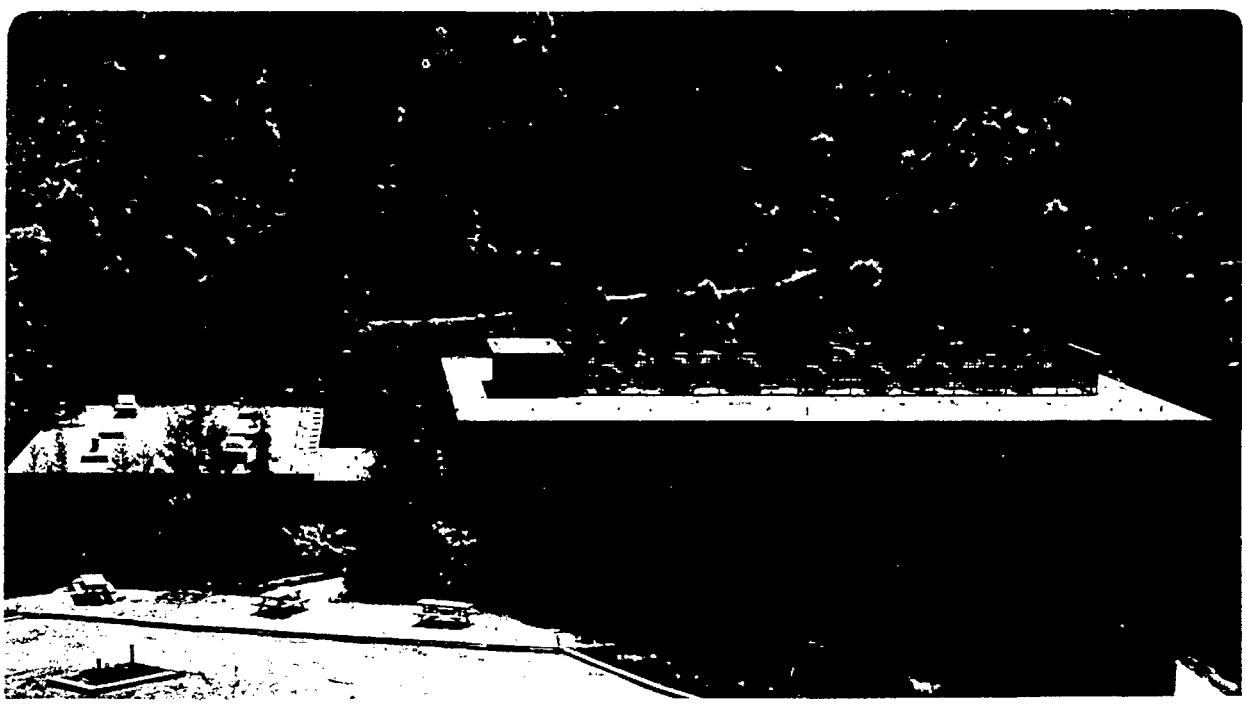

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THERMODYNAMIC PROPERTIES OF CHEMICAL SPECIES IN NUCLEAR WASTE

TOPICAL REPORT

THE SOLUBILITIES OF CRYSTALLINE NEODYMIUM AND AMERICIUM TRIHYDROXIDES

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ABSTRACT

The solubilities of crystalline $Nd(OH)_3$ and $Am(OH)_3$ were measured at 25 ± 1° C in aqueous solutions of 0.1 M $NaClO_4$ under argon as a function of pH by determination of the solution concentrations of Nd and Am. Prior to use in the solubility measurements, the solid materials were characterized through their x-ray powder patterns. Analyses of the solubility data with the computer code MINEQL allowed estimates of the solubility product constants, K_{s10}, and the second and third hydrolysis constants, K_{12} and K_{13}, for Nd^{3+} and Am^{3+}. Upper limits for the fourth hydrolysis constants were also estimated. For Nd, they are: log K_{s10} = 16.0 ± .2, log K_{12} = -15.8 ± .5, log K_{13} = -23.9 ± .2 and log K_{14} < -34. For Am, they are: log K_{s10} = 15.9 ± .4, log K_{12} = -16.0 ± .7, log K_{13} = -24.3 ± .3 and log K_{14} < -34.5.

The crystalline $Nd(OH)_3$ was found to be a factor of 100 to 300 less soluble than predicted from previously reported thermodynamic data over much of the pH range of environmental interest. The measured solubility of crystalline $Am(OH)_3$ was also considerably less than predicted from the previously estimated solubility product constant, i.e., a factor of ~ 600. For Am, the solubility of the crystalline material was a factor of ~ 30 less than the amorphous material.

The solubilities of crystalline $Nd(OH)_3$ and $Am(OH)_3$ as a function of pH were found to be very similar and $Nd(OH)_3$ should be a good analog compound for $Am(OH)_3$.

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1.0 INTRODUCTION

1.1 BACKGROUND

The disposal of high-level radioactive waste in a waste package emplaced in a deep geologic formation appears to be a technically feasible method for the long-term isolation of the waste from the biosphere[1]. In the event that the canister and waste form fail to contain the radioactive waste materials, radionuclides will enter the local groundwater system and, if moving, the groundwater is expected to provide the mechanism by which the nuclear waste could be transported from the underground storage facility to the accessible environment[1]. The radionuclides can react with various components of the groundwater, and possibly host rock, to form insoluble compounds and solution species, which will provide major controls on the solution concentrations and migration rates of the radionuclides. The identities and solubilities of compounds and the solution species will depend on the oxidation states of the radionuclides, the redox properties of the groundwater and surrounding geomedia, and the nature and concentrations of precipitating ions and complexing ligands in the groundwater system, i.e., the groundwater composition. Precipitation of stable solid phases will retard the migration of radionuclides relative to the average velocity of groundwater movement; on the other hand, formation of aqueous complexes will tend to reduce this retardation effect. In addition, the nature of the solution species will determine to a large extent the degree of sorption of the radionuclides

by the host rock and engineered barrier.

The formation of insoluble phases and their equilibria with solution species are much more complicated processes in groundwaters than in the solutions normally encountered in laboratory measurements. It would be misleading to suggest that thermodynamic data obtained in static laboratory measurements can alone accurately predict behavior in dynamic field situations. However, thermodynamic data obtained in the laboratory form the building blocks for delineating the important interactions and parameters of the systems, for interpreting the results of field measurements and sorption data, and for modelling calculations. Therefore, thermodynamic data on the solubilities of compounds and solution complexes of the waste radionuclides likely to form in the groundwaters are needed to adequately assess and predict the ability of the storage site to meet established site characteristics and standards for rates of release of radioactive materials as required for licensing by the U. S. Nuclear Regulatory Commission in 10 CFR 60[2] and the U.S. Environmental Protection Agency in 40 CFR 191[3].

Studies of natural analog elements can potentially provide useful information for the prediction of the migration behavior of waste radionuclides over extremely long time periods, information not accessible through short-term laboratory measurements[4]. However, laboratory-generated thermodynamic information on the nature, solubilities, and solution complexes of the waste radionuclides likely to form under repository conditions, compared with those of naturally

occurring elements, can be used to select possible natural analogs.

A number of long-lived actinides, actinide decay products, and fission products are present in spent reactor fuels and high-level reprocessed wastes in sufficient quantities to remain a radiological hazard, even after 1,000 years, if placed in an underground repository. Several attempts have been made to rank the waste radionuclides as to overall hazard on the basis of the amount of the radionuclide in the waste, the half-life, the biological toxicity, and the potential mobility. They are summarized in reference 5. Taken as a group, the actinides U, Np, Pu, Am, and Cm represent the largest potential long-term hazard.

A number of inorganic components will be present in groundwaters that can form insoluble compounds and solution complexes with the waste radionuclides. Hydroxide, carbonate, phosphate, fluoride, sulfate,[6] and possibly silicate would be the important groundwater anions for the actinides. Since hydroxide is common to all groundwaters, this anion is expected to play a dominant role in determining the speciation and solubilities of the important actinides[6]. The information on hydroxides is needed before one can proceed to the other anion systems.

One of the important actinides in nuclear waste from a long-term hazards point of view is americium. If trivalent Am behaves like the trivalent lanthanides, and there is good reason to expect that it will[7], Am would be expected to form an insoluble hydroxide under environmental conditions. Unfortunately, there has been no systematic

investigation of the solubility of well-characterized $Am(OH)_3$ reported in the literature. The objective of this work was (1) to measure the solubility of well-characterized, crystalline $Am(OH)_3$ as a function of pH and obtain a value for the solubility product constant and (2) to measure the solubility of well-characterized crystalline $Nd(OH)_3$ as a function of pH and, by comparing the results with (1) above, determine if it is a good analog compound for $Am(OH)_3$.

1.2 PRIOR WORK

1.2.1 Background

A knowledge of the solubility product constant, K_{s10}, for the reaction

$$Am(OH)_3(s) + 3H^+ = Am^{3+} + 3H_2O$$

is not sufficient by itself to calculate the solubility of $Am(OH)_3$ in aqueous, noncomplexing solution over a wide pH range. Hydrolysis of Am^{3+} occurs in neutral and basic solution and, in addition to the Am^{3+} ion, the hydrolysis products contribute to the total solution concentration of americium. Therefore, values for the formation constants of the hydrolyzed species are needed, e.g., the possible reactions,

$$Am^{3+} + H_2O = Am(OH)^{2+} + H^+;\ K_{11}$$

$$Am^{3+} + 2H_2O = Am(OH)_2^+ + 2H^+;\ K_{12}$$

$$Am^{3+} + 3H_2O = Am(OH)_3^0 + 3H^+;\ K_{13}$$

$$Am^{3+} + 4H_2O = Am(OH)_4^- + 4H^+;\ K_{14}$$

$$2Am^{3+} + 2H_2O = Am_2(OH)_2^{4+} + 2H^+;\ K_{22}$$

$$3Am^{3+} + 5H_2O = Am_3(OH)_5^{4+} + 5H^+;\ K_{35}$$

All of these equations must be solved simultaneously for a given temperature, pressure and pH in order to calculate the concentration of the individual species since they can occur together in solution. The total solution concentration of americium, i.e., the solubility, is the sum of the concentration of all the species.

1.2.2 Measured Solubility of Am(III) in Near Neutral and Basic Solutions

In FY 80, the solution concentration of Am was measured as a function of pH at 25° C in aqueous solution using 0.1 M $NaClO_4$ as supporting electrolyte. Two solutions of purified Am(III) were prepared with initial concentrations of $1.023 \pm 0.031 \times 10^{-5}$ M. The pH of these solutions was adjusted to cover the range 5 to 10 in steps of 1 pH unit starting with a pH of 5. After each pH change, the solutions were allowed to equilibrate for a time and the concentration of Am in solution was determined. Precipitation of Am occurred for pH values greater than 7. The details of this work and results have been reported previously[8,9].

The results of these measurements are displayed as the points in Figure 1. These data were assumed to represent the solubility of amorphous $Am(OH)_3$, however, chemical analysis of the solid phase was not feasible due to the very small amount of amorphous precipitate available.

In 1978, Allard reported estimates for the hydrolysis constants for Am^{3+} in aqueous solution, as well as for the solubility product

of $Am(OH)_3$[10]. His estimates are given in Table 1. Using the computer program MINEQL[11], a computer program for the calculation of chemical equilibrium compositions of aqueous systems, the solubility limit for Am in an aqueous 0.1 M $NaClO_4$ solution was calculated as a function of pH from Allard's estimates. The results of the calculation are shown in Figure 1 as the curve marked A.

Baes and Mesmer[12] have also estimated the solubility product for $Am(OH)_3$ from a comparison with a lanthanide ion of nearly the same ionic radius, i.e., Nd^{3+}, and their estimate is given in Table 1. Unfortunately, the lanthanide data used for the estimates were for "aged" precipitates and not characterized, crystalline material. It seemed reasonable to go a step further and to use the measured or estimated values for the hydrolysis constants for Nd as estimates for Am. This approach has also recently been taken by Allard[6]. These values, taken from Baes and Mesmer[12], are also shown in Table 1. The solubility limits for $Am(OH)_3$ in 0.1 N $NaClO_4$ were calculated as a function of pH using these estimates and are shown in Figure 1 as the curve labelled B. Clearly, our experimental data favored the solubility limit line calculated from the Baes and Mesmer estimates (curve B) over the line calculated using Allard's estimates (curve A). If the solubility product constant of $Am(OH)_3$ estimated by Baes and Mesmer was decreased about a factor of 10, i.e., log K_{s10} decreased from 18.7 to 17.5, the calculated curve labelled C resulted. This curve was a better fit to the data. Therefore, our best estimate for the solubility product constant of amorphous $Am(OH)_3$ for 25° C and zero ionic strength from this work was log $K_{s10} = 17.5 \pm 0.3$.

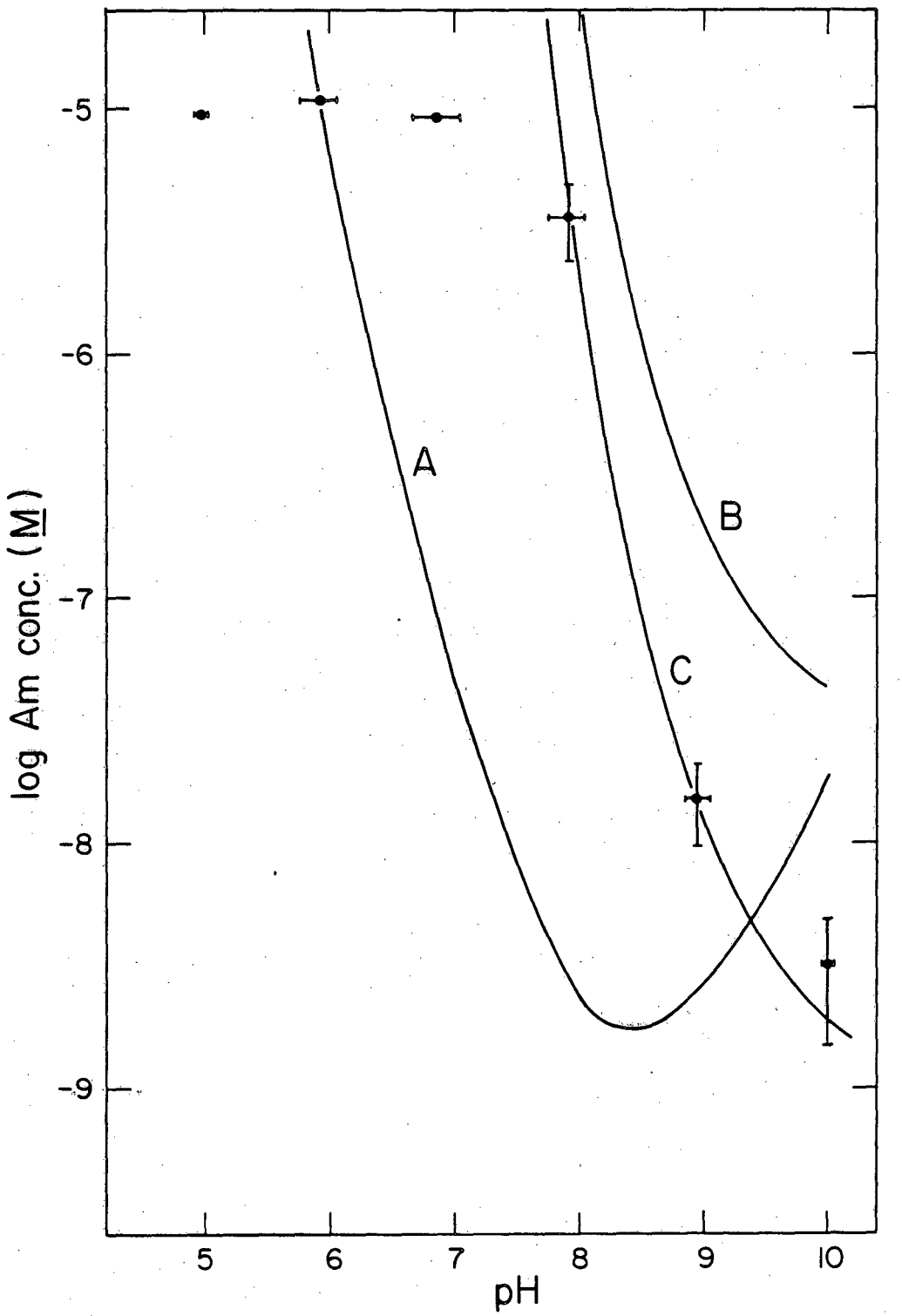

Figure 1. Plot of the Logarithm of the Solution Concentration of Am in Aqueous 0.1 M $NaClO_4$ Solutions as a Function of pH at 25°C.

Table 1. Estimates of Hydrolysis and Solubility Constants of Am^{3+} for 25° C and Zero Ionic Strength.

Reaction	log $k^{(10)}$	log $k^{(12,13)}$
Hydrolysis		
$Am^{3+} + H_2O = Am(OH)^{2+} + H^+$	-5.80	-8.0
$Am^{3+} + 2\ H_2O = Am(OH)_2^+ + 2\ H^+$	-13.0	-16.9
$Am^{3+} + 3\ H_2O = Am(OH)_3^o + 3\ H^+$	-21.0	-26.5
$Am^{3+} + 4\ H_2O = Am(OH)_4^- + 4\ H^+$	-30.0	-37.1
$2\ Am^{3+} + 2\ H_2O = Am_2(OH)_2^{4+} + 2\ H^+$	-11.0	-13.8
$3\ Am^{3+} + 5\ H_2O = Am_3(OH)_5^{4+} + 5H^+$		<-28.5
Precipitation		
$Am(OH)_3(s) + 3H^+ = Am^{3+} + 3\ H_2O$	+12.0	+18.7

2.0 EXPERIMENTAL SECTION

2.1 BACKGROUND

Measurement of the solubility of a compound in aqueous solution involves basically the following steps: formation or preparation of the solid phase, characterization of the solid phase, equilibration of the solid phase with an aqueous phase, separation of the solid and aqueous phases, and analyses of the aqueous phase for the concentrations of dissolved species. The most commonly used method for determining solubility is to first prepare the compound by some standard method using purified components. The material is characterized, e.g., by measurement of its x-ray diffraction pattern, and then an excess of the solid is placed in contact with an aqueous solution of the appropriate composition. The aqueous phase should be free of complexing ligands, because the formation of solution complexes can increase the solubility. Since thermodynamic constants are a function of solution ionic strength, a noncomplexing supporting electrolyte is normally used as the aqueous phase in order to maintain a constant ionic strength. Some of the solid phase dissolves, and the system is allowed to come to steady state before the aqueous phase is analyzed for the concentration of the element of interest and the precipitating counter-ion. From the concentrations, a solubility product can be calculated if the species are known.

For reliable results, it should be demonstrated that (1) the separation of solid and aqueous phases is adequately effective and (2) that equilibrium has been achieved. If the measured solution

concentration of a component remains constant for two or more different separation techniques, e.g., centrifugation and filtration, or for variation of a technique, e.g., filtration using several decreasing pore sizes, it is usually taken as verification of effective separation. When the solution concentration of components are measured as a function of time and remain constant for several weeks or months, i.e., a steady state achieved, it is assumed that equilibrium has been established.

2.2 MATERIALS AND REAGENTS

The neodymium used in these experiments was obtained from United Mineral and Chemical Company of New York City, New York as the oxide and was stated to be > 99 percent pure. After dissolution in HCl, a 50 µg sample was submitted for spectrochemical analysis. The results of the analysis are given in Table 2.

Approximately 20 mgs of americium, primarily ^{243}Am, was obtained through the Department of Energy's National Heavy Element Production Program at Oak Ridge. Prior to receipt, elemental purification had been made via cation-exchange chromatography using ammonium alpha-hydroxyisobutyrate as eluant[14]. Before use, a final purification was made to remove remaining contaminants, e.g. silica, salts, etc. The americium was first precipitated as the hydroxide. The hydroxide was washed with CO_2-free distilled water and dissolved in 6 M HCl. Final purification was accomplished by ion-exchange chromatography. The Am was loaded on a Dowex 50 x 8

Table 2. Spectrochemical Analyses of Nd and Am Stock Solutions

Nd		Am	
Element	Wt. percent	Element	Wt. percent
Al	< 0.2	Al	< 0.1
Bi	< 0.1	Bi	< 0.2
Ca	< 0.1	Ca	0.02
Nb	< 0.1	Ce	< 0.2
Cd	< 1	Cr	< 0.02
Co	< 0.02	Dy	< 1
Cr	< 0.02	Eu	< 0.02
Dy	< 0.1	Fe	< 0.1
Fe	0.1	La	< 0.1
Mg	0.1	Mg	< 0.02
Mn	< 0.02	Mn	< 0.02
Mo	< 0.02	Na	< 2
Na	< 1	Nd	< 0.2
Ni	< 0.1	Ni	< 0.1
Ob	< 0.2	Pb	< 0.2
Si	< 0.02	Si	< 0.02
Sn	< 0.2	Sm	< 0.1
Ti	< 0.1	Sn	< 0.2
Yb	< 0.1	U	< 2
Y	< 0.02	Yb	< 0.1
Zn	< 1	Y	< 0.02
Zr	< 0.02		

cation-exchange resin column from 0.1 M HCl. The column was first washed with three column volumes of 0.1 M HCl and then three column volumes of 3 M HCl. The Am^{3+} was then eluted with 6 M HCl. The eluate was taken to near dryness, and a stock solution was prepared with 0.1 M HCl. Alpha pulse height analysis of samples taken from the stock solution showed the amount of Am to be 18.8 mgs and the isotopic composition to be 99.83 percent ^{243}Am, 0.14 percent ^{241}Am, and 0.025 percent ^{244}Cm by weight. A 50 μg sample was also submitted for spectrochemical analysis. The results are given in Table 2.

The ^{147}Pm, 10 mci, used in these experiments was obtained from New England Nuclear of Boston, Massachusetts as carrier free material in 0.1 ml of 0.1 M HCl. Radionuclidic purity was stated as 99.0000 and radiochemical as 99.000.

All solutions were prepared with deionized-distilled water from which CO_2 had been removed by boiling for approximately two hours while being purged with pure argon. The water was stirred and continued to be purged with argon for several days. It was stored in a thick walled glass bottle under argon. Before use, the water was filtered through 0.1 μm pore size Nucleopore filters under an argon atmosphere. This was done to remove particulate material, e.g. silica or dust particles, suspended in the water that could adsorb Nd or Am ions to form pseudocolloids.

Ultra pure reagents were used to prepare solutions and compounds and for pH adjustments, i.e. ultrex hydrochloric acid (J.T. Baker Chemical Company of Phillipsburg, New Jersey), ultrapure (30 percent)

sodium hydroxide in water (Alfa Products of Danvers, Massachusetts) and hydrated sodium perchlorate (G. Frederick Smith Chemical Company of Columbus, Ohio). Cation-exchange resins were obtained from Bio-Rad Laboratories of Richmond, California.

2.3 EQUIPMENT

When measurements were to be isolated from air, a model HE-43-2 inert-atmosphere box obtained from Vacuum Atmospheres Company of Hawthorne, California was used. The pH measurements were made with a Beckman model 39505 microcombination glass electrode coupled to a Beckman model 4500 pH meter. Centrifugations were made with an Eppendorf (Brinkmann) model 5412 microcentrifuge obtained from Scientific Products, Sunnyvale, California. Filters were of two types: (1) polysulfone acrodiscs from Gelman, Ann Arbor, Michigan and (2) polycarbonate films from Nuclepore Company, Pleasanton, California. Samples were shaken with a Junior Orbit Shaker obtained from Lab-line, Incorporated, Melrose Park, Illinois.

Alpha energy analysis of spectra from dried samples were obtained with Au-silicon surface barrier detectors (Oak Ridge Technical Enterprises Corporation, Oak Ridge, Tennessee) coupled to a low noise preamplifier, main amplifier and biased amplifier of LBL designs. Spectra were recorded and analyzed with a model TN-1710 multichannel analysis system from Tracor Northern Incorporated of Middleton, Wisconsin. Liquid samples were counted for alpha or beta activity

with a microprocessor-controlled liquid scintillation counter model 460 C obtained from Packard Instrument Company, Downers Grove, Illinois. The scintillating cocktail used was "betaphase" obtained from Westchem Products, a division of Interchem Enterprises Incorporated of San Diego, California.

Optical viewings of solid samples were made with a Zeiss Standard Universal M microscope obtained from Brinkmann Instruments, Westbury, New York. Scanning electron microscopy (SEM) investigations of the solid compounds were made with a Model 1000 SEM from AMR Corporation, Bedford, Massachusetts. X-ray powder patterns of the solid compounds were obtained with an 11.4 cm diameter Debye-Scherrer camera mounted on a Norelco III x-ray generator (both from Philips Electronics Incorporated, Mount Vernon, New York). Copper x-rays with a nickel filter were used.

2.4 PREPARATION AND CHARACTERIZATION OF SOLID COMPOUNDS

2.4.1 $Nd(OH)_3$

Several schemes were tested for the preparation of stable, crystalline hydroxides using natural Nd, and a suitable procedure was worked out. Approximately 20 mg of $Nd(OH)_3$ were prepared by precipitation from 3 mls of 0.05 M HCl containing dissolved $NdCl_3$ by the addition of 0.5 mls of 1 M NaOH. The resulting precipitate was stable and did not peptize after three washings with CO_2-free distilled water. Examination of small samples of the gelatinous precipitate with an optical microscope showed the material to have no apparent crystal structure. The precipitate was slurried in 5 ml of 5 M NaOH and

transferred to a Teflon bottle that was fitted with a reflux condenser. The slurry was boiled (~ 100°C) for 19 days. The resulting material was washed twice with CO_2-free water. Examination by an optical microscope showed the precipitate had converted to a microcrystalline structure. It was composed of rod-like particles of approximately 0.01 mm length and 0.001 mm diameter. A few micrograms of the material were placed in a 0.3 mm diameter quartz capillary tube and the tube sealed by heating with an oxy-butane microtorch. An x-ray powder pattern of the dried material was obtained. A comparison of the measured d-spacings and relative intensities calculated from the powder pattern with literature values for $Nd(OH)_3$[15] is made in Table 3. There was no evidence in our powder pattern for the presence of $Nd(OH)CO_3$. The sample appeared to be pure, microcrystalline $Nd(OH)_3$.

A more detailed study of the rate of conversion of freshly prepared $Nd(OH)_3$ precipitates to microcrystalline forms using the method described above was made. Samples of the precipitates were examined daily with an optical microscope for 4 weeks. Using this method of preparation, it required about 3 weeks to complete the conversion. Since this conversion process requires high temperatures of concentrated alkaline solutions in plastic containers in the presence of Am radiations, some degradation of the container surfaces could occur. We tried changes in the process in an attempt to substantially reduce the conversion time and, thus, to minimize deterioration of the plastic containers and possible contamination

Table 3. Comparison of X-ray Powder Patterns of Nd and Nd*(^{147}Pm) Precipitates With Reported Pattern for $Nd(OH)_3$.

Nd Precipitate		Nd* Precipitate		Reported for $Nd(OH)_3$[15]	
d(Å)	Intensity[a]	d(Å)	Intensity[a]	d(Å)	Intensity[b]
5.55	s	5.57	s	5.57	80
3.20	s	3.21	s	3.20	65
3.09	s	3.10	s	3.08	85
2.78	m	2.78	m	2.76	10
2.44	w	2.43	w	2.45	5
2.23	s	2.23	s	2.22	100
2.10	m	2.10	w	2.09	10
1.87	w				
1.85	m	1.85	m	1.85	50
1.83	s	1.83	s	1.84	100
1.77[c]	w	1.77	w		
1.62	m	1.61	m	1.61	30
1.61	w				
1.55	w	1.55	w	1.54	10
1.43	m	1.43	m	1.42	20
1.40	w	1.40	w	1.39	10
1.32	m	1.32	m	1.31	15
1.30	w	1.30	w	1.29	10
1.28[c]	w				
1.22[c]	m	1.22	m		
1.21[c]	m	1.21	m		

(a.) Visually estimated. s = strong; m = medium; w = weak.

(b.) Relative intensities determined by diffractometer.

(c.). Not previously reported but calculated to be present from lattice parameters.

of the solutions. It was found that microcrystalline $Nd(OH)_3$ could be prepared in 3 to 4 days if the freshly precipitated material was slurried in 2 mls of 5 M NaOH, transferred to a Teflon bottle fitted with a cap containing a 0.1 mm hole to reduce the flow of exit vapor, and the slurry evaporated to near dryness (~ 0.5 ml final volume) over a period of 3 to 4 days. Crystalline $Nd(OH)_3$ was prepared for the solubility measurements by this method. After washing, samples of the material were examined with an optical microscope and an SEM at various magnifications. Figure 2 was made from a polaroid picture of a sample taken at a magnification of 500 through the optical microscope. A number of scans of the samples were taken with the SEM at magnifications of 2000, 6500 and 10,800. Figure 3 was made from a polaroid picture of a scan of one portion of a sample taken at a magnification of 6500. An x-ray powder pattern of this material was identical in every respect to the $Nd(OH)_3$ formed by the slower process.

Measurements of the solubility of this non-radioactive $Nd(OH)_3$ were carried out over the pH range 6 to 9.5 in steps of 0.5 pH units. This sample served two functions in the solubility measurements. Firstly, the samples at pH values of 6 and 6.5 were used to determine the Nd solution concentrations by colorimetric titration. However, this method, nor any other readily available analytical methods, gave the sensitivity needed for determining the low Nd concentrations expected for pH values of 7 and higher, i.e. $< 10^{-5}$ M. Samples of $Nd(OH)_3$ "spiked" with ^{147}Pm were used for these measurements. Secondly, we wished to know if changes in the Am or Nd crystals occurred during the solubility measurements, e.g., changes that might suggest the formation of secondary solid phases. It

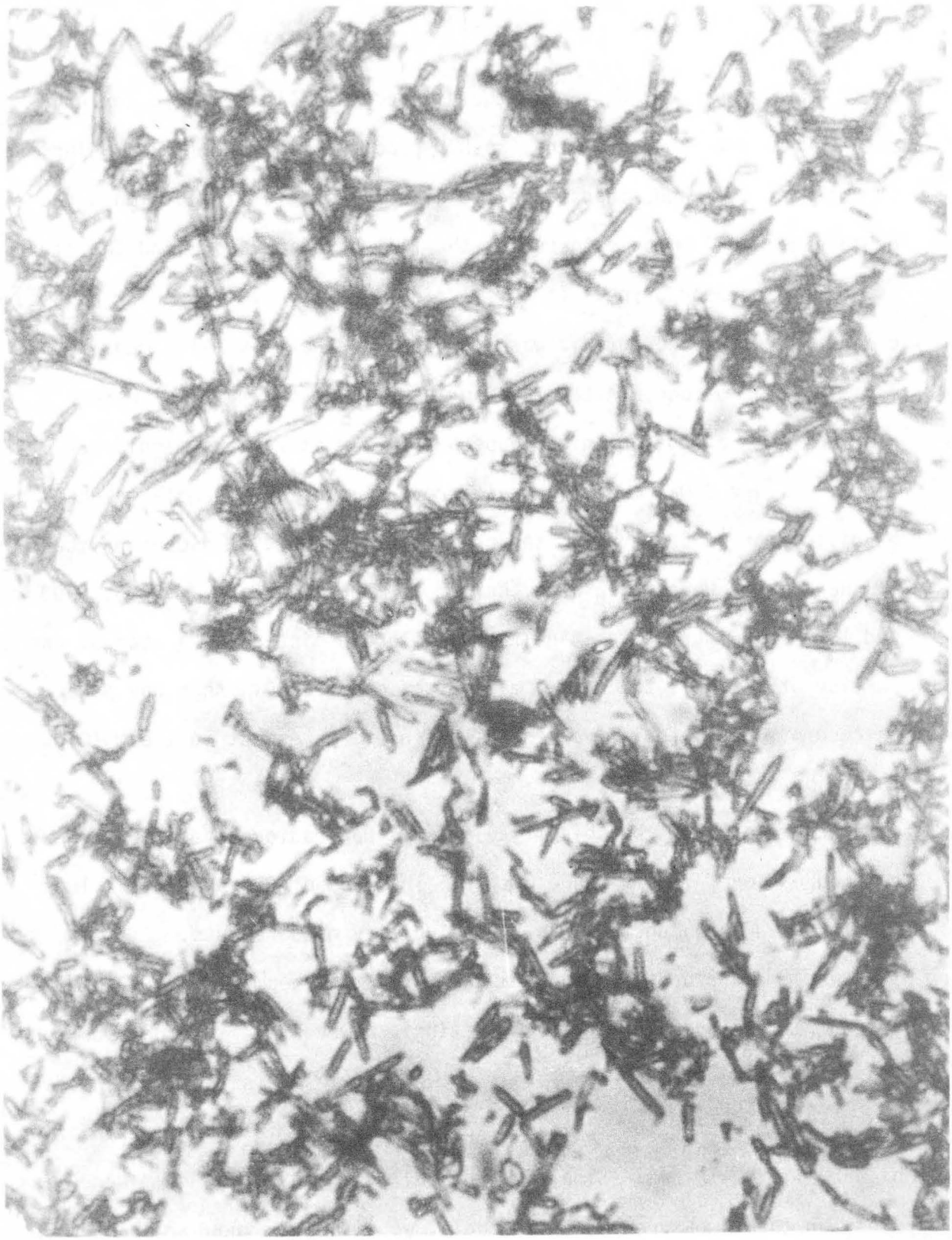

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Figure 2. $Nd(OH)_3$ Crystals as Viewed with an Optical Microscope at a Magnification of 500.

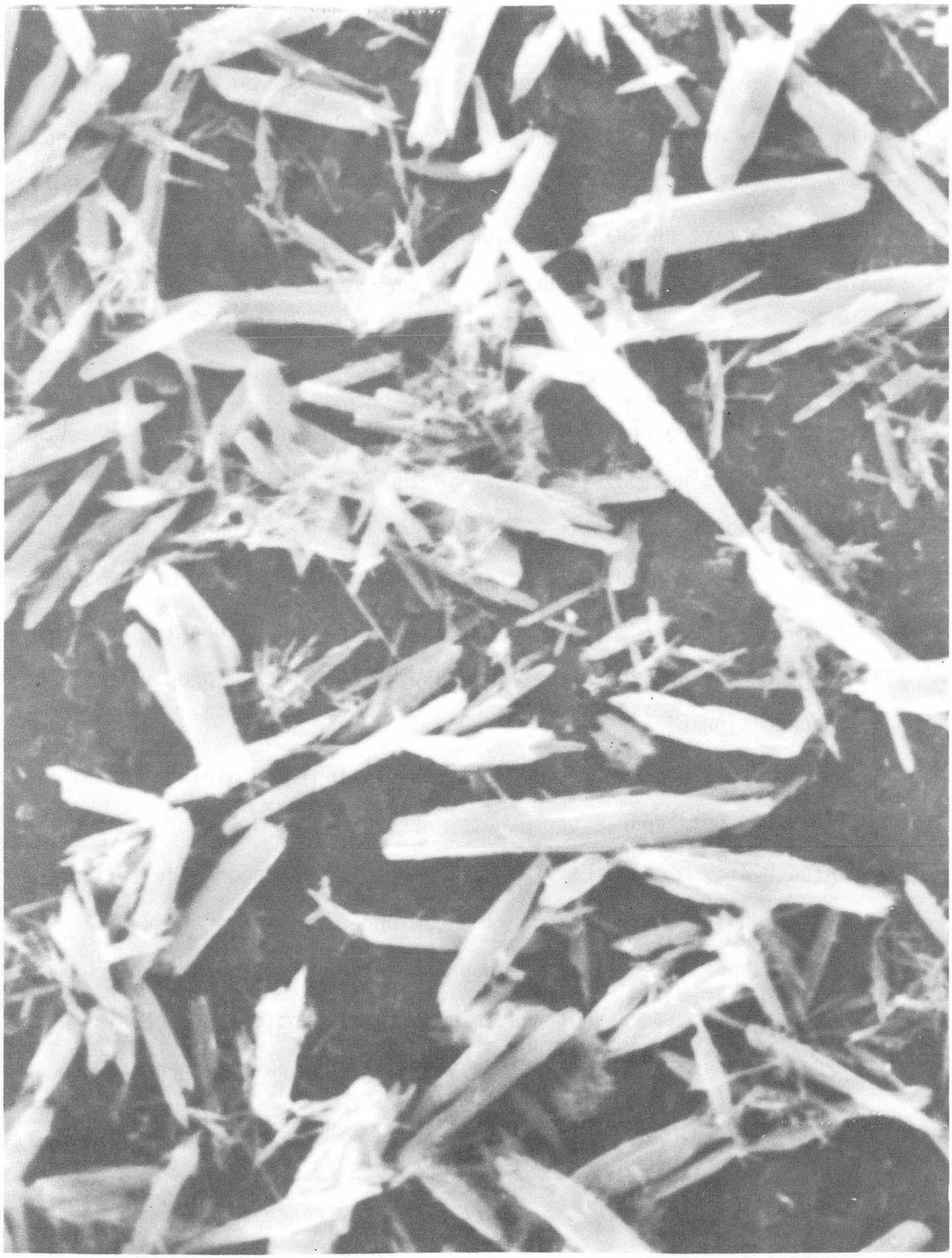

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Figure 3. $Nd(OH)_3$ Crystals as Viewed with an SEM at a Magnification of 6,500.

was planned to achieve this by SEM studies. However, the SEM is not available for the investigation of radioactive samples. Therefore, the nonradioactive $Nd(OH)_3$ samples, treated as nearly as possible the same as the radioactive $Nd(OH)_3$ and $Am(OH)_3$ samples, were used for the SEM studies at the end of the solubility measurements.

2.4.2. $Nd^*((OH)_3$

As stated in the previous section, neodymium hydroxide "spiked" with ^{147}Pm, denoted as $Nd^*(OH)_3$, was used in the solubility measurements for pH values of 7 and greater. The $^{147}Pm(OH)_3$ should be isostructural with the $Nd(OH)_3$ and should be distributed uniformly in the $Nd(OH)_3$, since they are adjacent lanthanide elements of nearly the same ionic radii. The concentration of Nd should be directly proportional to the concentration of ^{147}Pm.

Fifty microliters of the ^{147}Pm stock solution, containing a total of 9.368×10^9 beta counts per minute, were added to 3 mls of .05 M HCl containing 0.2185 millimoles of Nd. The precipitation and crystallization of the $Nd^*(OH)_3$ was then carried out under as nearly the same conditions as possible as for the nonradioactive $Nd(OH)_3$. Because of the radioactivity, it was not possible to obtain optical or scanning electron microscope pictures of this material. A few micrograms were dried and an x-ray powder pattern measured. The results of an analysis of the pattern are given in Table 3. The pattern agreed very well with published data for $Nd(OH)_3$[15]. There was no evidence in the pattern for the presence of the hydroxycarbonate. The sample appeared to be pure, microcrystalline $Nd(OH)_3$. This material was used in the

solubility measurements of $Nd(OH)_3$ for pH values between 7 and 9.5.

2.4.3. $Am(OH)_3$

Purified Am was used to prepare approximately 22 mg of $Am(OH)_3$ following the procedures as nearly as possible as developed with $Nd(OH)_3$. The resultant amorphous precipitate was converted to a microcrystalline form in 4 days again using the short procedure developed with $Nd(OH)_3$. Because of the radioactive nature of the sample, it was not possible to obtain optical and scanning electron microscope pictures. A few micrograms of the material were dried and an x-ray powder pattern was obtained. The powder pattern was not as clear with the Am sample as with the $Nd(OH)_3$ samples due to fogging of the film by the 75-KeV gamma rays emitted in the decay of ^{243}Am; however, 16 lines were visible in the pattern. A comparison of the measured d-spacings and relative intensities obtained from the powder pattern with values obtained by Milligan[16] from electron diffraction patterns of $Am(OH)_3$ is made in Table 4. The pattern was similar to that of the $Nd(OH)_3$. The sample appeared to be pure, microcrystalline $Am(OH)_3$. This material was used in the solubility measurements of $Am(OH)_3$ for pH values between 7 and 9.5.

2.5 SOLUBILITY MEASUREMENTS

2.5.1. Preparation and Treatment of Solutions

The preparation of all solutions and the solubility measurements were conducted in an inert atmosphere box under Ar in order to exclude

Table 4. Comparison of X-Ray Powder Pattern of the Am Precipitate With Reported Electron Diffraction Pattern of $Am(OH)_3$.

Am Precipitate		Reported for Am(OH) [16]	
d(Å)	Intensity[a]	d(Å)	Intensity[b]
5.55	m	5.57	4
3.21	m	3.21	10
3.10	s	3.11	10
2.77	w	2.78	1
2.69	m		
		2.44	1
2.23	m	2.24	7
2.10	w	2.10	3
1.90	m		
1.85	w	1.86	8
1.83	m	1.83	7
		1.77	1
1.62	m	1.62	1
		1.61	2
1.55	w	1.55	1
1.42	w	1.43	1
		1.40	5
1.34	w	1.32	2
1.23	w	1.28	2
1.20	w	1.21	1

(a.) Visually estimated. s = strong; m = medium, w = weak.

(b.) Relative intensities determined by microphotometer.

CO_2 and minimize the carbonate complexation of Am.

Before beginning the experiments, the inert box was flushed with several hundred cubic feet of pure Ar until the O_2 content of the box atmosphere was about 4 ppm. The O_2 concentration was measured with a trace oxygen analyzer from Teledyne Analytical Instruments. Since we have no method for determining the exact concentration of CO_2 at very low levels in the box atmosphere, it was assumed that the CO_2 to O_2 ratio in the box was the same as the original room air, i.e. 1.69×10^{-3}, since nothing was intentionally done to change this ratio. Therefore, we estimated the CO_2 partial pressure in the box after flushing was about 7×10^{-9} atmosphere. The box was maintained at a slight positive pressure so as to avoid leakage of room air into the box. Even so, under operating conditions, the O_2 content rose to a more or less steady value of 50-60 ppm or about 1×10^{-7} atmos. of CO_2. At equilibrium, this partial pressure would result in CO_3^{2-} solution concentrations of about 10^{-13} M at a pH of 6 and about 10^{-7} M at a pH of 9.

Samples of the three materials, i.e., $Nd(OH)_3$, $Nd^*(OH)_3$ and $Am(OH)_3$, were separately placed in contact with 15 mls of 0.1 M $NaClO_4$ solutions (pH=10) as a noncomplexing, supporting electrolyte in teflon bottles. The pH of the solutions in contact with the $Nd(OH)_3$ were adjusted to values from 6 to 9.5 in 0.5 pH unit steps by addition of HCl, i.e., one bottle for each pH step, eight bottles total. The pH of the solutions in contact with the $Nd^*(OH)_3$ and the $Am(OH)_3$ were adjusted from 7 to 9.5 in 0.5 pH unit steps with HCl.

The amount of salts formed by the addition of HCl did not significantly change the ionic strength. It was not possible to go to lower pH values for the Am, since, because of its high solubility, the large amounts of Am required could not be safely handled in our present setup due to the 75-KeV gamma radiation associated with the decay of ^{243}Am. The amounts of solid and the initial pH values for the three materials are given in Table 5.

After the initial pH adjustments, the samples were rotated continuously at 150 RPM with a Junior Orbit Shaker. The pH values of the samples were subsequently checked nearly daily and readjusted to near the original values when necessary by the addition of microliter amounts of 0.05 M NaOH or 0.05 M HCl.

2.5.2. Sampling of Solutions

After equilibration times of roughly 2 weeks, 4 weeks and 6 weeks, aliquots of the solution phases were taken and analyzed for Nd or Am concentrations. This was done to follow the reactions to steady state. The aliquots taken at the 2 and 4 week periods were from the $Nd^*(OH)_3$ and $Am(OH)_3$ samples. About 1.25 mls of the solutions of the various pH values between 7 and 9.5 were centrifuged at 15,000 RPM for 15 minutes. For our centrifuge system, it was estimated that particles of about 0.1 μm diameter and larger should be precipitated[17]. Portions of the centrifuged solutions were taken and acidified in counting bottles. The exact volume analyzed depended on the nuclear count rate since the resolving time of the counting instrument placed

Table 5. Quantities of $Nd(OH)_3$, and $Nd^*(OH)_3$ and $^{243}Am(OH)_3$ and Initial pH Values Used in the Solubility Measurements

	Quantity of Solid (mgs)							
pH	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
Solid								
$Nd(OH)_3$	500	50	8	4	2	2	2	2
$Nd^*(OH)_3$	-	-	8	4	2	2	2	2
$Am(OH)_3$	-	-	4	2	2	2	2	2

an upper limit on the acceptable total count rate. It ranged from 20 microliters for the lowest pH values to 1 ml for the higher pH values. Then, 10 mls of scintillation cocktail were added to the counting bottles and the nuclear count rate determined with the Packard 460 liquid scintillation counter. Since nuclear disintegration rates are directly related to half-lives and the number of atoms, the solution concentrations of ^{243}Am and ^{147}Pm could be calculated from the measured count rates per volume. Knowing the ratio of Pm to Nd atoms in the initial solution, the Nd concentration could be calculated from the Pm concentration.

Since the beta emitting ^{239}Np daughter of ^{243}Am could contribute to the counting rate and was not necessarily in equilibrium with the Am, the ^{243}Am was purified by cation-exchange chromatography before counting. One ml of the aliquots (0.1 M in HCl) were passed through 3 mm diameter by 5 cm long Dowex 50 x 8 cation-exchange resin columns and the Am adsorbed onto the top of the resin beds. The columns were then washed with 2 ml of 1 M HCl to elute the Np, and the Am eluted with 1 ml of 6 M HCl. This procedure was found to consistently give greater than 95 percent recovery of the ^{243}Am.

At the end of the 6 weeks equilibration period, 5 ml samples were taken of the solutions in contact with the $Nd^*(OH)_3$ and $Am(OH)_3$ and centrifuged as before. A portion of the centrifuged supernatant solutions were also counted as before. The remaining portions were split into two fractions. One fraction was passed through a 0.2 μm acrodisc filter while the other fraction was passed through a 0.015 μm

Nuclepore filter. The first 0.5 mls through the filters were discarded and a portion of the remaining filtrate analyzed by liquid scintillation counting. This procedure was follows to test the effectiveness of the separation of solid and aqueous phases.

Also at the end of the 6 weeks period, 5 ml aliquots of the solutions in contact with the $Nd(OH)_3$ samples initially at pH values of 6 and 6.5 were taken. These aliquots were centrifuged as before and passed through 0.2 μ acrodisc filters. The Nd concentrations in the aliquots were determined by making complexometric titrations of each sample.

2.5.3. Determination of Solution Concentrations

The concentration of Nd in the solutions in contact with $Nd(OH)_3$ at initial pH values of 6.0 and 6.5 were determined from the results of three complexometric titrations of one ml volumes of each solution using 0.00999 M DTPA (diethylenetriaminepentaacetic acid) as tritrant and erichrome black T as endpoint indicator. Knowing the exact concentration of the DTPA and the volume of DTPA solution needed to reach the endpoint, the number of equivalents of Nd in the solutions were calculated. The concentrations and standard deviations were determined from the averages of the three titrations and the root mean square deviations from the averages.

The Nd concentrations in the solutions in contact with $Nd^*(OH)_3$ at initial pH values of 7.0, 7.5, 8.0, 8.5, 9.0 and 9.5 were calculated from the results of the ^{147}Pm count rate determinations.

Since both the number of millimoles of Nd and the disintegration rate of ^{147}Pm are directly related to the number of atoms present and these values were accurately known for the initial stock solution, the concentration of Nd could be calculated from the solution disintegration rates, i.e.

$$\underline{M}(Nd) = \frac{A(Pm)}{V} \times \frac{Nd_o}{Pm_o}$$

where

$\underline{M}(Nd)$ = concentration of Nd (mmoles/ml = moles/liter)

$A(Pm)$ = Pm solution count rate (counts/minute)

Nd_o = total mmoles of Nd in initial stock solution
= 0.2185 mmoles

Pm_o = total Pm count rate in initial stock solution
= 9.368×10^9 c/m

V = solution volume analyzed (mls)

The ^{147}Pm decays with a half-life of 2.62 years[19]. Therefore, corrections were made for the loss of Pm atoms in the samples due to decay during the various equilibration times.

The concentrations of Am in the solutions in contact with $Am(OH)_3$ at initial pH values of 7.0, 7.5, 8.0, 8.5, 9.0 and 9.5 were calculated from the measured alpha particle disingration rates of the solutions, i.e.,

$$\underline{M}\ (Am) = \frac{A(Am)}{V \times C}$$

where

$\underline{M}(Am)$ = concentration of Am(mmoles/ml = moles/liter)

$A(Am)$ = ^{243}Am solution count rate (disintegrations/minute)

C = disintegration rate of ^{243}Am per mmole (disintegrations/minute/mmole) = 1.077×10^{11} d/m/mmole

V = solution volume analyzed (mls)

The counting efficiency of the LSC was experimentally determined to be 100 percent to an accuracy of 3.7 percent. Since energy analysis of the alpha particle spectrum of the initial Am stock solution showed that 86.3 ± 0.3 percent of the total alpha count rate was due to ^{243}Am, a correction to the measured solution count rates was made to obtain the ^{243}Am count rates.

2.5.4. Testing of Solution Sample Purity

Portions of the aliquots of the solutions in contact with the $Nd^*(OH)_3$ samples initially at pH values of 9 and 9.5, that had been centrifuged and passed through the 0.2 μm acrodisc filters, were tested for radioactive purity. These samples were selected as being the most sensitive to impurities since they exhibited the lowest count rates, i.e. 200-300 counts per minute. This was accomplished by a cation-exchange column separation using NH_4-alphahydroxyisobutyrate as the eluting agent. This technique is routinely used to separate individual lanthanide elements and is highly selective[18]. From a knowledge of column dimensions and the concentration and pH of the eluting solution, the elution position of a given lanthanide element

can be accurately predicted. Separations were carried out on 0.25 ml volumes of the two samples. The separations were made on a 3 mm diameter by 6 cm long Dowex 50 x 12 cation exchange resin column using 0.436 $\underline{M}$ NH_4-alphahydroxyisobutyrate at a pH of 4.11 as the eluting solution. The column eluate was collected in fractions and the fractions counted in the liquid scintillation counter. The fractions predicted to contain the ^{147}Pm did indeed show substantial increases in count rates over the fractions that eluted both before and after. In fact, the count rates of these latter fractions were essentially the background count rate of the Packard 460, i.e., ~ 30 counts per minute. The count rates of the fractions containing the ^{147}Pm were summed and compared with the count rates of the corresponding unseparated samples of equal volumes. It was found that 76.3 ± 3.9 percent and 77.0 ± 3.9 percent of the radioactivity of the unseparated samples initially at pH values of 9.0 and 9.5, respectively, appeared in the separated Pm fractions. The nature of this column separation is such that some loss of sample usually occurs, normally of the order of 10 percent. Therefore, a large percentage, ~ 90 percent, of the radioactivity of these two samples could be directly attributed to the ^{147}Pm.

Portions of the aliquots of the solutions in contact with the $Am(OH)_3$ samples initially at pH values of 9 and 9.5, that had been centrifuged and passed through the 0.2 μm acrodisc filters, were also tested for radioactive purity. As with the $Nd^*(OH)_3$, these samples would be the most sensitive to impurities since they exhibited the

lowest count rates, i.e., 100-300 counts per minute. This was accomplished by measurement of the alpha particle energy spectra of dried aliquots of the two samples. The energy spectra of both samples were essentially identical to the energy spectrum of the initial Am stock solution.

2.5.4. Data Analysis Methods

The equilibrium between the solid Nd or Am hydroxides and the species in solution, i.e. the uncomplexed cation and the hydroxide complexes, can be represented by the general reaction

$$xM(OH)_3(s) + (3x-y)H^+ = M_x(OH)y^{(3x-y)+} + (3x-y)H_2O$$

The constant that governs the concentration of each solution species in equilibrium with the solid is

$$K_{sxy} = \frac{[M_x(OH)_y^{(3x-y)+}]}{[H+]^{(3x-y)}}$$

These equilibrium constants are related to the solubility product constant, K_{s10}, and the hydrolysis constants, K_{xy}, by the equation

$$K_{sxy} = {}^xK_{s10}K_{xy}$$

The total metal concentration in a saturated solution is

$$\underline{M}(satd) = \sum x\ K_{sxy}[H^+]^{3x-y}$$

Thus the total Nd or Am concentration at any pH is the sum of terms, one for each species, including the unhydrolyzed cation, and each with a power dependence on [H+] equal to 3x-y. As a result, the curve representing the variation of the logarithm of $\underline{M}$ (sat'd) with pH is a composition of a series of straight lines beginning with a slope of 3 for the uncomplexed cation and decreasing in slope with increasing pH, one for each species. The following features are observed: (1) At the low pH values, the predominant species is the unhydrolyzed cation (often polynuclear species are important for high metal ion concentrations) and $\underline{M}$ (sat'd) is controlled primarily by the solubility product reaction, i.e. $M(OH)_3(s) + 3H^+ = M^{3+} + 3H_2O$; (2) As the pH is increased and $\underline{M}$ (sat'd) decreases, the predominant species are ordered according to decreasing 3x-y values, i.e. first $M(OH)^{2+}$, followed by $M(OH)_2^+$, etc.; (3) The slope, d log $\underline{M}$ (sat'd)/dpH, becomes less negative, with a value equal to the average -(3x-y) for the species present; (4) there is a minimum in the curve determined by the neutral mononuclear hydrolysis product, $M(OH)_3^o$, the concentration of which is independent of pH; (5) if anionic complexes are formed, the curve will rise with a further increase in pH. In general, several species can coexist in solution and must be considered together in any analysis.

The results of the measurements of the solubilities of $Nd(OH)_3$ and $Am(OH)_3$ were analyzed in terms of solubility product and

proposed hydrolysis reactions. Since this involves the solution of a number of coupled equations simultaneously, the calculation of the concentrations of solution species and solubilities from the thermodynamic data were made using a computer program called MINEQL[11]. MINEQL is a computer code designed to accept a list of components of a solution and their total analytical concentrations, solve the appropriate set of mass balance and equilibrium constant expressions, and produce a list of the identities and concentrations of all species formed by interactions among the components and between them and/or water. Data processing involves reading the input solution composition, identifying the complexes expected, fetching the required stability constants, connecting the stability constants to the ionic strength imposed, and deriving the appropriate mass balance expressions. The resulting set of stability and mass balance expressions is solved by the Newton Raphson method, using the correctness of the mass balances as the criterion of successful solution. Ionic strength corrections are made by the Davies equation[20].

3.0 RESULTS

3.1 SOLUBILITY MEASUREMENTS

3.1.1 $Nd(OH)_3$

The results of the measurements of the solubility of crystalline $Nd(OH)_3$ at 25 ± 1°C as a function of pH and for equilibration times of 16, 24 and 35 days are given in Table 6. Because the solutions were unbuffered, there was a certain amount of drift in the pH values between readjustment periods. The pH values given in Table 6 are the average values observed during the equilibration periods. The errors in the pH values were estimated from the inherent reproducibility of measurements with the pH meter and probe (0.04 pH units) and the root mean square deviations of the daily measurements from the averages.

The Nd concentrations for the pH values of 5.67 and 6.42, measured at the 35 day equilibration period, were determined on solutions in contact with the pure $Nd(OH)_3$. The values are averages of three titrations of each sample and the errors are the root mean square deviations from the averages. The remaining Nd concentrations were determined for solutions in contact with $Nd^*(OH)_3$, i.e., "spiked" with ^{147}Pm, and the values were calculated from the ^{147}Pm concentrations measured by nuclear counting methods. The errors result from assignment of standard deviations to (1) errors associated with counting statistics, (2) uncertainty in counting efficiency, (3) reproducibility of sampling volumes and (4) uncertainties in the measured values of the Nd and Pm concentrations in the inital stock solutions.

Table 6. Solution Concentration (Moles/Liter) of Nd(III) in Contact with Crystalline $Nd(OH)_3$ as a Function of pH and Equilibration Time Measured at 25 ± 1° C and 0.1 M Ionic Strength

Equilibration Time							
16 days		24 days		35 days			
pH	M[a]	pH	M[a]	pH	M[a]	M[b]	M[c]
				5.67 ± .15		$3.90 \pm .08 \times 10^{-2}$	
				6.42 ± .14		$4.88 \pm .75 \times 10^{-3}$	
7.38 ± .10	$3.32 \pm .25 \times 10^{-6}$	7.22 ± .08	$1.86 \pm .14 \times 10^{-5}$	7.11 ± .10	$2.02 \pm .15 \times 10^{-5}$	$1.86 \pm .14 \times 10^{-5}$	$1.93 \pm .15 \times 10^{-5}$
7.52 ± .09	$1.49 \pm .11 \times 10^{-6}$	7.46 ± .08	$2.19 \pm .17 \times 10^{-6}$	7.44 ± .07	$2.69 \pm .20 \times 10^{-6}$	$2.42 \pm .18 \times 10^{-6}$	$1.49 \pm .11 \times 10^{-6}$
7.93 ± .13	$2.20 \pm .17 \times 10^{-7}$	7.89 ± .13	$2.11 \pm .16 \times 10^{-7}$	7.85 ± .13	$1.78 \pm .13 \times 10^{-7}$	$1.47 \pm .12 \times 10^{-7}$	$1.24 \pm .10 \times 10^{-7}$
8.41 ± .13	$3.03 \pm .23 \times 10^{-8}$	8.38 ± .12	$2.18 \pm .17 \times 10^{-8}$	8.36 ± .12	$3.68 \pm .29 \times 10^{-8}$	$1.68 \pm .14 \times 10^{-8}$	$2.45 \pm .19 \times 10^{-8}$
8.99 ± .10	$2.40 \pm .19 \times 10^{-8}$	8.94 ± .06	$1.34 \pm .11 \times 10^{-8}$	8.96 ± .06	$2.21 \pm .18 \times 10^{-8}$	$1.14 \pm .10 \times 10^{-8}$	$1.04 \pm .09 \times 10^{-8}$
9.52 ± .06	$2.18 \pm .17 \times 10^{-8}$	9.50 ± .04	$1.03 \pm .08 \times 10^{-8}$	9.48 ± .04	$1.60 \pm .13 \times 10^{-8}$	$1.00 \pm .09 \times 10^{-8}$	$1.29 \pm .10 \times 10^{-8}$

[a]Centrifugation; [b]Centrifugation plus 0.2 μm filtration; [c]Centrifugation plus 0.015 μm filtration.

Standard methods for the assignment of standard deviations and for propagation of errors were used to obtain the reported errors[21]. From the results given in Table 6, it is clear that much larger errors of unknown origin were involved in the measurements. For samples of nearly the same final pH values, the measured Nd concentrations for the different equilibration times and the different separation techniques agreed to no better than about a factor of two.

For samples of very nearly the same final pH values and separated by centrifugation, the variations between the measured Nd solution concentrations for the three different equilibration times did not show any apparent trends toward an increase or decrease with time and the values generally agreed to within better than a factor of two. Apparently, steady state was achieved within the first 16 days of equilibration.

At the end of the 35 day equilibration period, aliquots of the samples at the various final pH values were subjected to separations by three techniques, i.e., centrifugation at 15,000 RPM for 15 minutes, centrifugation plus filtration through 0.2 μm pore size filters, and centrifugation plus filtration through 0.015 μm pore size filters. In general, the centrifuged samples tended to yield slightly larger Nd concentrations than the filtered samples, particularly at the higher pH values. However, the three techniques gave results that agreed to better than a factor of two in general. This result was taken as a demonstration that the solid and aqueous phases had been effectively separated.

3.1.2 $\underline{Am(OH)_3}$

The results of the measurements of the solubility of crystalline $Am(OH)_3$ at 25 ± 1°C as a function of pH and for equilibration times of 17, 28 and 48 days are given in Table 7. As with the $Nd(OH)_3$ samples, drifts in the pH values occurred between readjustment periods. However, with the $Am(OH)_3$ samples, the drift was much larger, was nearly always toward lower pH values, and was quite regular with time. In the near neutral pH region, where the solutions were least buffered, the drifts were as much as a half to three quarters of a pH unit per day. This behavior has been reported previously[22] and was said to be due to alpha particle radiolysis in air-equilibrated aqueous solutions which produced nitric acid from N_2. Since our solutions had been purged with argon and had been isolated from air in the inert atmosphere box, this mechanism seems unlikely in our case. It may have to do with the radiolysis of the water itself since it is known that densely ionizating radiation, such as alpha particles, causes the decomposition of H_2O with the formation of peroxide[23].

The pH values given in Table 7 are the average values observed during the equilibration periods. The errors in the pH values were estimated from the inherent reproducibility of measurements with the pH meter and probe (0.04 pH units) and the root mean square deviations of the daily measurements from the averages.

The errors assigned to the Am solution concentrations are standard deviations resulting from a compounding of errors due to

Table 7. Solution Concentration (Moles/Liter) of Am(III) in Contact with Crystalline $Am(OH)_3$ as a Function of pH and Equilibration Time Measured at 25 ± 1° C and 0.1 M Ionic Strength

Equilibration Time							
17 days		28 days		48 days			
pH	M[a]	pH	M[a]	pH	M[a]	M[b]	M[c]
7.25 ± .10	7.17 ± .47 x 10^{-6}	7.09 ± .12	1.22 ± .08 x 10^{-5}	7.05 ± .11	1.50 ± .10 x 10^{-5}	1.60 ± .10 x 10^{-5}	1.46 ± .10 x 10^{-5}
7.44 ± .15	1.87 ± .12 x 10^{-6}	7.33 ± .16	3.34 ± .22 x 10^{-6}	7.19 ± .18	3.73 ± .24 x 10^{-6}	3.46 ± .23 x 10^{-6}	2.25 ± .15 x 10^{-6}
7.68 ± .30	6.13 ± .40 x 10^{-7}	7.60 ± .32	1.55 ± .10 x 10^{-6}	7.49 ± .33	1.45 ± .10 x 10^{-6}	1.29 ± .08 x 10^{-6}	8.73 ± .57 x 10^{-7}
8.09 ± .32	1.14 ± .07 x 10^{-7}	8.03 ± .35	2.26 ± .15 x 10^{-7}	7.91 ± .36	3.26 ± .21 x 10^{-7}	2.55 ± .17 x 10^{-7}	1.12 ± .07 x 10^{-7}
8.85 ± .15	3.79 ± .25 x 10^{-9}	8.88 ± .16	8.65 ± .57 x 10^{-9}	8.82 ± .16	8.34 ± .55 x 10^{-9}	3.76 ± .25 x 10^{-9}	4.13 ± .27 x 10^{-9}
9.43 ± .06	3.07 ± .21 x 10^{-9}	9.42 ± .07	6.73 ± .44 x 10^{-9}	9.43 ± .06	8.77 ± .58 x 10^{-9}	3.02 ± .20 x 10^{-9}	2.76 ± .19 x 10^{-9}

[a]Centrifugation; [b]Centrifugation plus 0.2 μm filtration; [c]Centrifugation plus 0.015 μm filtration.

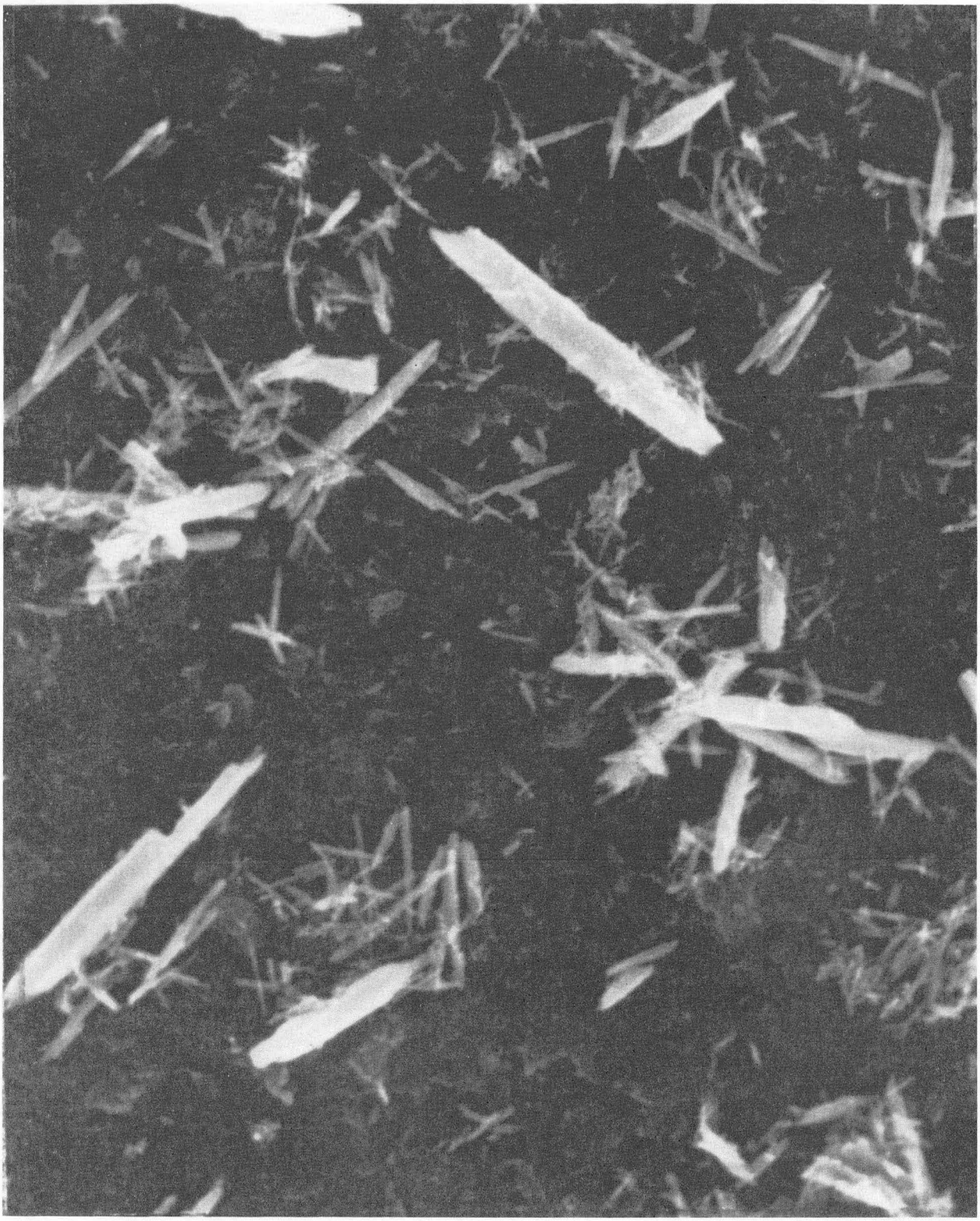
(1) counting statistics, (2) reproducibility of sampling volumes, (3) counting efficiency and (4) the measured ^{243}Am concentration in the initial stock solution. As was the case with the Nd, the results given in Table 7 indicate larger errors of unknown origin since samples of about the same pH values agreed to no better than about a factor of three. This factor is larger than for the $Nd(OH)_3$ and may be in part due to the larger uncertainties in the final pH values for the Am samples. Since the solution concentration of Am varies with pH, small differences in pH between samples can produce large differences in Am concentrations.

For samples of very nearly the same final pH values and separated by centrifugation, the variations between the measured Am solution concentrations for equilibration times of 28 and 48 days agreed to within better than a factor of 1.5; for the 17 day equilibration period, the Am concentrations tended to be about a factor of 2 less than those of the longer periods. From the results, steady state was considered to have been achieved within a month.

At the end of the 48 day equilibration period, aliquots of the solutions of the various pH values were subjected to separation by the three techniques. The results agreed reasonably well except at the two highest pH values where the centrifuged samples gave concentrations a factor of about three larger than the filtered samples. Since the nature of this variation is unknown, the results using the three techniques were given equal weight in subsequent analyses. The separations of solid and aqueous phases were considered to be adequate.

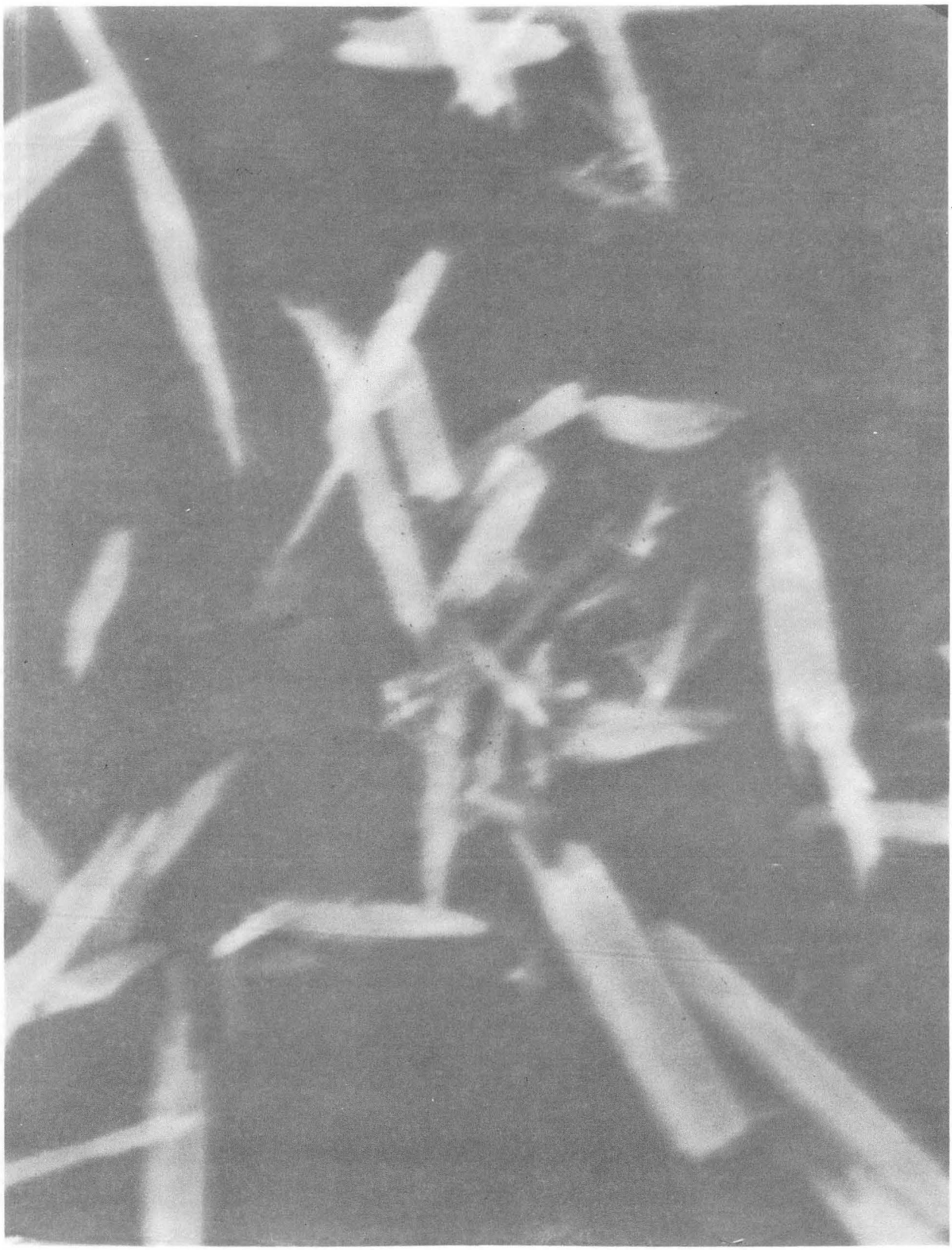
3.2 SEM STUDIES

The final pH values (and errors) of the aqueous phases in contact with the pure $Nd(OH)_3$ samples for 35 days were 5.67 ± .15, 6.42 ± .14, 7.14 ± .11, 7.40 ± .12, 7.88 ± .14, 8.38 ± .11, 8.94 ± .07 and 9.46 ± .06. A few micrograms of the solid material in the samples with the pH values of 6.42, 7.40, 8.38 and 9.46 were taken from the bottles, dried under a heat lamp and samples prepared for study with the SEM. A number of scans of the samples were taken with the SEM at magnifications of 2000, 6500 and 10,800. Examples of the scans taken at a magnification of 6500 for pH values of 6.42, 7.40, 8.38 and 9.46 are shown in Figures 4, 5, 6 and 7, respectively. A visual comparison of the scans of the crystals at these 4 pH values with scans of the original $Nd(OH)_3$ crystals used in the initial preparation of these samples did not reveal any apparent change in the shapes, sizes, or surfaces of the crystals. Assuming the formation of secondary phases would have produced an observable change in the appearance of the crystals, it was concluded that the nature of the crystals before and after the solubility measurements were the same and no further investigations of other samples were made. Since the $Nd^*(OH)_3$ and $Am(OH)_3$ samples were treated the same as the $Nd(OH)_3$ samples during the solubility measurements, it was assumed that there was no change in the nature of the crystals in these samples either.



XBB 820-9718

Figure 4. $Nd(OH)_3$ Crystals as Viewed with an SEM at a Magnification of 6,500 After Equilibration at a pH of 6.42 for 35 Days.

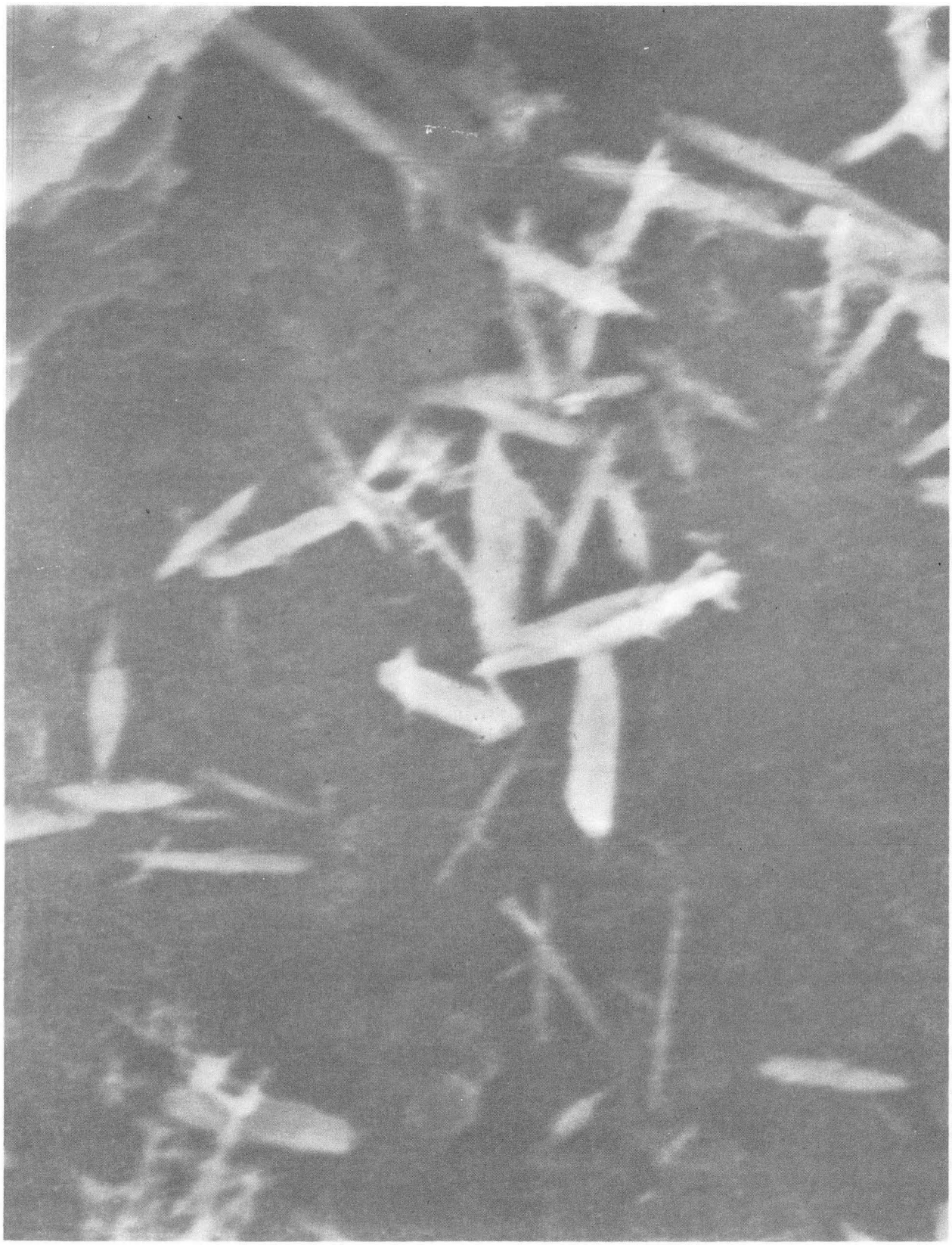


XBB 829-8048

Figure 5. $Nd(OH)_3$ Crystals as Viewed with an SEM at a Magnification of 6,500 After Equilibration at a pH of 7.40 for 35 Days.

XBB 829-8046

Figure 6. $Nd(OH)_3$ Crystals as Viewed with an SEM at a Magnification of 6,500 After Equilibration at a pH of 8.38 for 35 Days.



XBB 829-8050

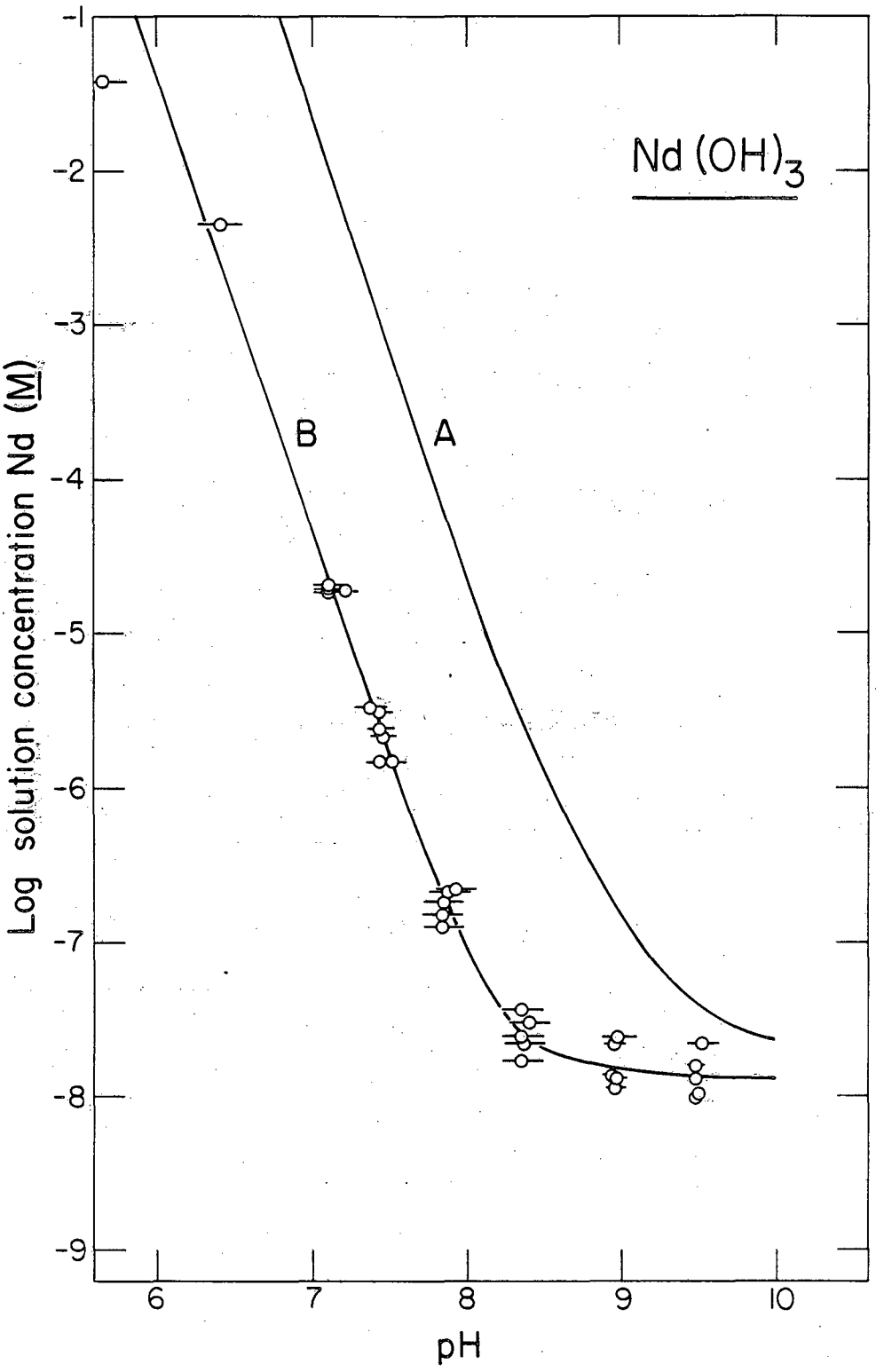
Figure 7. $Nd(OH)_3$ Crystals as Viewed with an SEM at a Magnification of 6,500 After Equilibration at a pH of 9.46 for 35 Days.

3.3 DATA ANALYSIS AND DISCUSSION

3.3.1 $Nd(OH)_3$

Figure 8 shows a plot of the logarithm of the measured solution concentrations of Nd (Table 6) as a function of the pH (open circles). These experimental data were analyzed in terms of the solubility product and hydrolysis reactions proposed by Baes and Mesmer[24] and are given in Table 8. Baes and Mesmer have reported measured or estimated constants for these reactions for 25° C and zero ionic strength[13]; they are also given in Table 8. Using these thermodynamic constants, the solution concentrations of Nd, including Nd^{3+} and hydrolysis products, were calculated for an ionic strength of 0.1 using the computer code MINEQL. The result of this calculation is represented by the solid curve labelled (A) in Figure 8. Clearly, the predicted solubility of $Nd(OH)_3$ was considerably higher than that measured in our experiments. The value for K_{s10} given by Baes and Mesmer comes from the work of Aksel'rud[25]. A potentiometric titration method was used to study the solubility of $Nd(OH)_3$ precipitates aged at room temperature for up to 120 days. These solids were not proven to be crystalline.

Further analysis of the solubility data presented here was made using MINEQL in an attempt to obtain values for the solubility product and hydrolysis constants that more closely represented our data. The recently measured value of -7.7 ± .3 for the first hydrolysis constant, K_{11}, of Nd^{3+}[9] was used in these further calculations. The values of the constants for reactions (2), (3), (4), (5), (6) and



XBL 8210-1200

Figure 8. Plot of the Logarithm of the Solution Concentration of Nd in Aqueous 0.1 M $NaClO_4$ Solutions as a Function of pH at 25°C.

Table 8. Measured and Estimated Solubility Product and Hydrolysis Constants of Nd^{3+} for 25° C and Zero Ionic Strength

Reaction	log K[13] (Baes and Mesmer)	log K (this work)
(1) $Nd^{3+} + H_2O = Nd(OH)^{2+} + H^+$; K_{11}	-8.0	-7.7±.3[9]
(2) $Nd^{3+} + 2H_2O = Nd(OH)_2^+ + 2H^+$; K_{12}	(-16.9)*	-15.8±.5
(3) $Nd^{3+} + 3H_2O = Nd(OH)_3^0 + 3H^+$; K_{13}	(-26.5)*	-23.9±.2
(4) $Nd^{3+} + 4H_2O = Nd(OH)_4^- + 4H^+$; K_{14}	-37.1	< -34
(5) $2Nd^{3+} + 2H_2O = Nd_2(OH)_2^{4+} + 2H^+$; K_{22}	-13.8	
(6) $3Nd^{3+} + 5H_2O = Nd_3(OH)_5^{4+} + 5H^+$; K_{35}	< 28.5	
(7) $Nd(OH)_3(s) + 3H^+ = Nd^{3+} + 3H_2O$; K_{s10}	18.6	16.0±.2

*Values in parentheses are estimates.

(7) were varied systematically from the Baes and Mesmer values to obtain the best fit to our experimental points. The species $Nd_2(OH)_2^{4+}$ and $Nd_3(OH)_5^{4+}$, i.e., reactions (5) and (6), were calculated to be minor components of the solution over the pH range of investigation and the calculated solution concentrations were rather insensitive to small variations in the values of their formation constants, i.e., variations of 100 or less. Therefore, no information could be obtained from the analysis concerning these constants. Thus, the experimental data were fit primarily by varying the values of K_{s10}, K_{12}, K_{13}, and K_{14}. The values for these constants that resulted in the best fit to the experimental data are given in Table 8. Probable errors were estimated by varying the values of the constants so that the calculated solution concentrations at the various pH values just remained within the extremes in the measured solution concentrations. The fitting of the calculations to the experimental data was quite sensitive to the value of K_{s10} for pH values of ~ 8 or less and to the value of K_{13} for pH values of ~ 8.5 or greater. Thus reasonably good values could be extracted for these two constants. The fitting was much less sensitive to the value of K_{12} resulting in a rather large assigned error. Contrary to the other solution species, the concentration of $Nd(OH)_4^-$ increases with increasing pH. This would cause an increase in the solubility of $Nd(OH)_3$ with increasing pH at the higher pH values. Since this did not appear to occur, only an upper limit could be assigned to the value of K_{14}. The solid curve labelled (B) in Figure 8 results from

calculations using these values. The calculated concentrations of the various solution species as a function of pH are represented by the solid lines in Figure 9. The concentrations of $Nd_2(OH)_2^{4+}$ and $Nd_3(OH)_5^{4+}$ were calculated using the values for K_{22} and K_{35} given by Baes and Mesmer (13).

3.3.2 $Am(OH)_3$

Figure 10 shows a plot of the logarithm of the measured solution concentrations of Am (Table 7) as a function of pH (open circles). Since it was expected that Nd and Am should exhibit similar behavior, these experimental data were analyzed in terms of the solubility product and hydrolysis reactions given in Table 9. Analysis of the solubility data for $Am(OH)_3$ were made using the computer code MINEQL to obtain values for the solubility product and hydrolysis constants that best represented our experimental data. The recently measured value of -7.7 ± .3 for the first hydrolysis constant, K_{11}, of Cm^{3+}(9) was used in the calculations. Curium is adjacent to Am in the periodic table and has nearly the same ionic radius. It was assumed in the calculations that the species $Am_2(OH)_2^{4+}$ and $Am_3(OH)_5^{4+}$ would be minor solution components as was the case with Nd. The values of the constants for reactions (2), (3), (4), and (7) were varied systematically as in the Nd analysis to obtain the best fit to our experimental points. The resulting values are given in Table 9. Probable errors were estimated by varying the values of the constants so that the calculated solution concentrations at the various pH

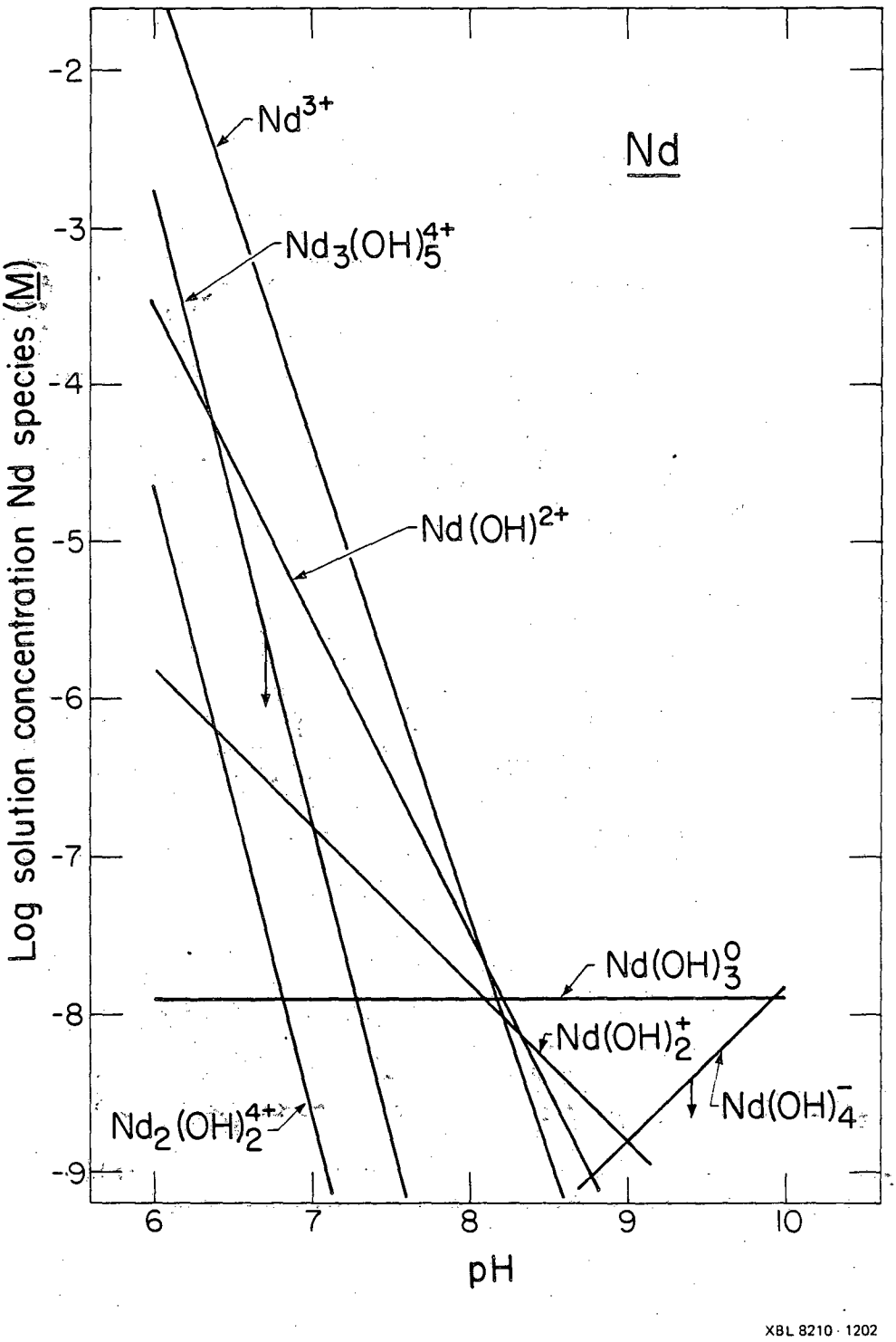


Figure 9. Plot of the Logarithm of the Calculated Concentrations of Nd Solution Species in 0.1 M $NaClO_4$ as a Function of pH at 25°C.

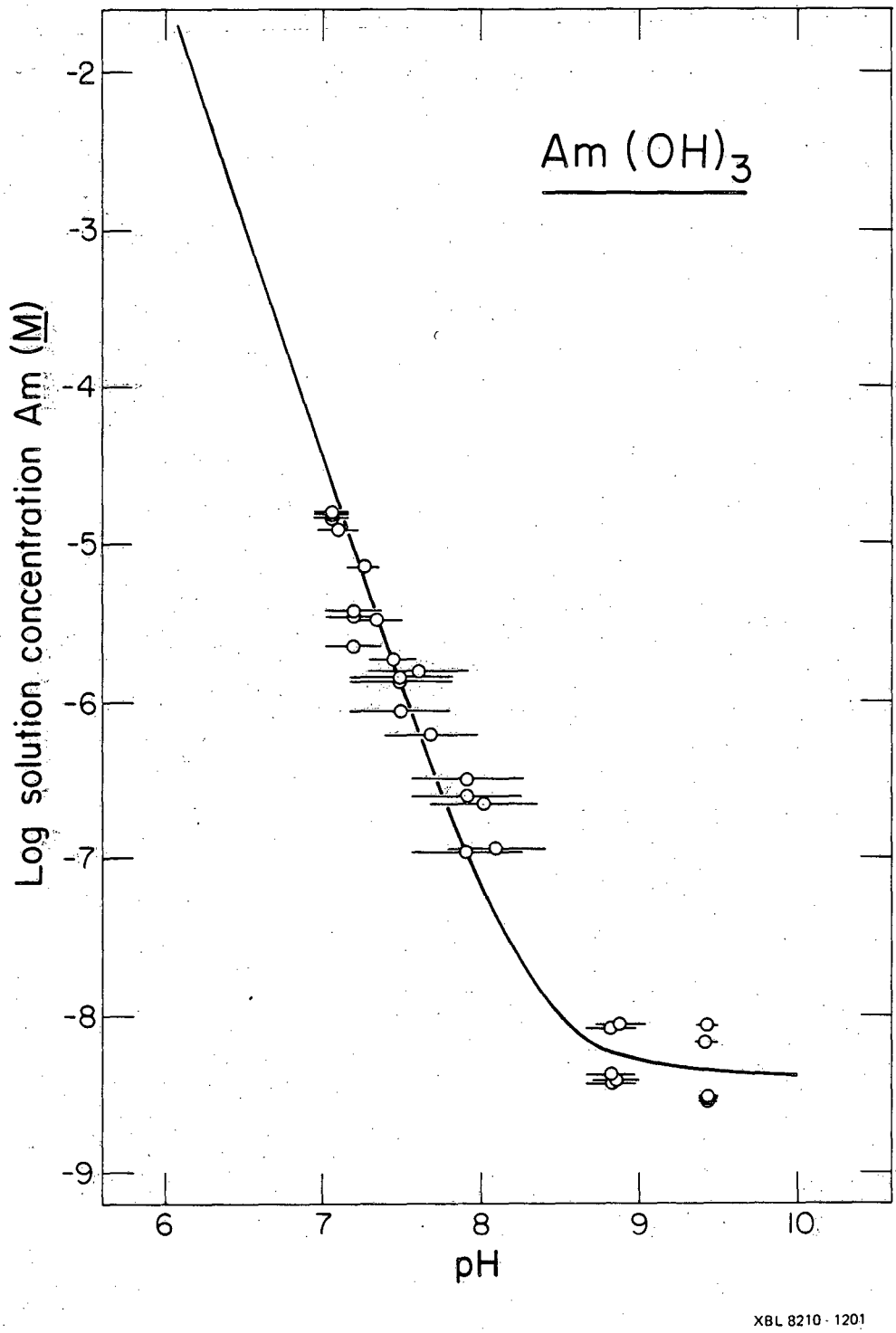


Figure 10. Plot of the Logarithm of the Solution Concentration of Am in Aqueous 0.1 M $NaClO_4$ Solutions as a Function of pH at 25°C.

Table 9. Solubility Product and Hydrolysis Constants of Am^{3+} for 25° C and Zero Ionic Strength

Reaction	log K
(1) $Am^{3+} + H_2O = Am(OH)^{2+} + H^+$; K_{11}	$-7.7 \pm .3$[9]
(2) $Am^{3+} + 2H_2O = Am(OH)_2^+ + 2H^+$; K_{12}	$-16.0 \pm .7$
(3) $Am^{3+} + 3H_2O = Am(OH)_3^o + 3H^+$; K_{13}	$-24.3 \pm .3$
(4) $Am^{3+} + 4H_2O = Am(OH)_4^- + 4H^+$; K_{14}	< -34.5
(5) $2Am^{3+} + 2H_2O = Am_2(OH)_2^{4+} + 2H^+$; K_{22}	-13.8*
(6) $3Am^{3+} + 5H_2O = Am_3(OH)_5^{4+} + 5H^+$; K_{35}	< 28.5*
(7) $Am(OH)_3(s) + 3H^+ = Am^{3+} + 3H_2O$; K_{s10}	$-15.9 \pm .4$

*Values for Nd taken from reference 13.

values just remained within the extremes in the measured solution concentrations. As with Nd, the fitting was quite sensitive to values of K_{s10} and K_{13} but not K_{12}. As was the case for Nd, an increase in the solubility of $Am(OH)_3$ at the high pH values did not appear to occur and, thus, only an upper limit could be assigned to the value of K_{14}. The solid curve in Figure 10 results from calculations using these values. The calculated concentrations of the various solution species as a function of pH are represented by the solid lines in Figure 11. The concentration of $Am_2(OH)_2^{4+}$ and $Am_3(OH_5)^{4+}$ were calculated using the values for K_{22} and K_{35} given by Baes and Mesmer for Nd(13).

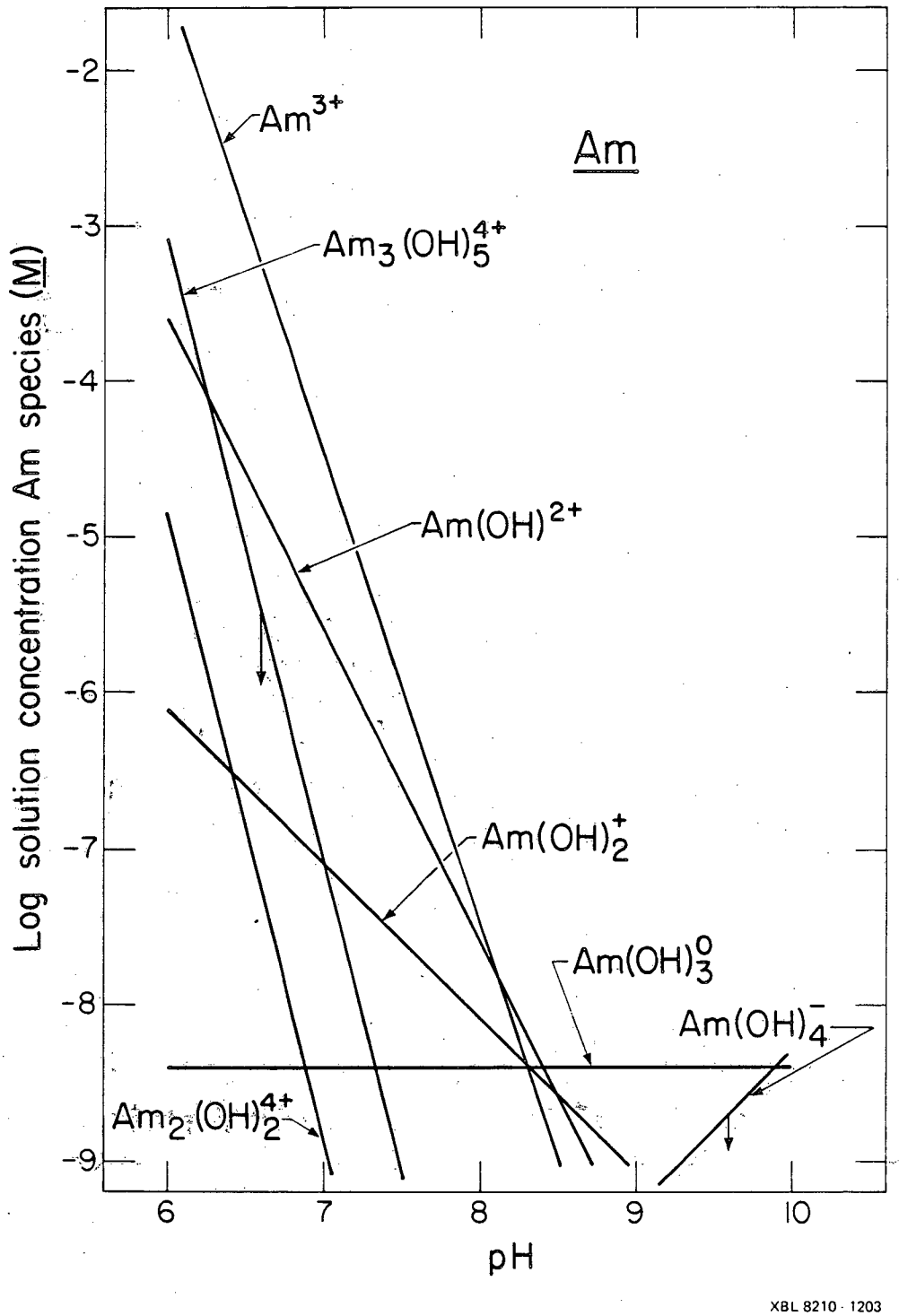


Figure 11. Plot of the Logarithm of the Calculated Concentrations of Am Solution Species in 0.1 M $NaClO_4$ as a Function of pH at 25°C.

4.0 CONCLUSIONS

(1) The measured solubility of crystalline $Nd(OH)_3$ was considerably less than that predicted from the usually accepted thermodynamic constants for the solubility product and hydrolysis constants given by Baes and Mesmer[13], i.e., a factor of 100-300 less soluble over much of the pH range of environmental interest.

(2) The measured solubility of crystalline $Am(OH)_3$ was also considerably less than that predicted from the solubility product constant, K_{s10}, estimated by Baes and Mesmer[12], i.e., a factor of ~ 600. The solubility of the crystalline material appears to be a factor of about thirty less than the amorphous material.

(3) The solubility of crystalline $Nd(OH)_3$ and $Am(OH)_3$ are quite similar and are virtually identical over much of the pH range of environmental interest. Therefore, $Nd(OH)_3$ should be a good analog compound for $Am(OH)_3$.

(4) For pH values of about 8.5 or less, positively charged ions would be expected to be the dominant solution species for Nd and Am; for pH values of about 8.5 and greater, the neutral complexes would be expected to be the dominant solution species.

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