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Interaction of Pu(IV, VI) Hydroxides/ Oxides with Metal Hydroxides/Oxides in Alkaline Media

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August 1998

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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the U. S. Department of Energy under
Contract DE-AC06-76RLO 1830 and a
Collaboration Agreement Made on May 20, 1997

Pacific Northwest National Laboratory
Richland, WA 99352

Summary

The interactions of Pu(IV) and Pu(VI) in alkaline media with some metal hydroxides and oxides commonly found in Hanford Site tank wastes were studied. The properties of mixed hydroxide systems of Pu(IV) with various metal ions [Ni(II), Fe(III), Co(III), Al(III), Cr(III), Zr(IV), La(III), and U(VI)] were investigated at variable component ratios using physical-chemical methods. The interactions of Pu(VI) with Al(III), Fe(III), and Cr(III) also were studied.

It was shown by infrared (IR) spectroscopy that, except for the system Pu(IV)-Ni(II), Pu(IV) interacts with all the listed metal ions and affects their interatomic bonding. The locations of IR absorption bands of the mixed hydroxides change irregularly compared with the spectra of pure components, with change in the Pu:metal mole ratio of from 1:10 to 10:1. The changes occur both for the valent and deformation vibration bands of hydroxyl ions and water at 3600 to 3100 and 1750 to 1250 cm^{-1} and for the vibrations of metal-oxygen (M-O) bridging bonds in the range of 1050 to 850 cm^{-1} . In the Pu(IV)/Ni(II) system, the IR spectra are equivalent to the sum of the individual components precipitated separately from alkaline solution.

The separate precipitation of Pu(IV) hydrous oxide and Ni(OH)_2 upon adding NaOH solution to acidic solution containing both Pu(IV) and Ni(II) nitrate was confirmed by studying the dissolution rate of the resulting precipitate in 3 M HCl at 60°C. No difference in plutonium dissolution behavior was found for pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and the products obtained by alkaline precipitation of 1:1 mole ratio Pu(IV):Ni(II) mixtures, aged for 1 hour at 70°C, over a wide range of NaOH concentrations. Similar results were obtained for the Pu(IV)-Al(III) system. Only trace amounts of aluminum were detected in $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ precipitates formed even in relatively dilute NaOH solutions.

Results in the Pu(IV)-Fe(III), Pu(IV)-Co(III), Pu(IV)-Cr(III), Pu(IV)-La(III), and Pu(IV)-U(VI) systems differed from those observed for the Pu(IV)-Ni(II) system. The dissolution rates of the precipitates obtained by NaOH addition to separate equimolar mixtures of Pu(IV) with Fe(III), Co(III), Cr(III), La(III), and U(VI) were considerably higher than those observed for pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ treated under the same conditions. Based on these results, coprecipitation of Pu(IV) with the various metal ions apparently produces the corresponding mixed hydroxides in which plutonium is distributed uniformly (on a molecular level) within the solid phases.

These conclusions are confirmed by x-ray diffraction data. The x-ray diffraction patterns for products prepared by mutual precipitation of Pu(IV) and Ni(II) consist of reflections typical for PuO_2 and Ni(OH)_2 crystalline. In all the other systems, the x-ray powder patterns of mixed hydroxides were considerably altered compared with those found for the pure components.

The formation of mixed hydroxides in the mutual alkaline precipitation of Pu(IV) and Fe(III) also was confirmed by a Mössbauer effect method using the 14.4 keV transition of ^{57}Fe . The Mössbauer spectra of mixed Pu(IV)-Fe(III) hydroxide samples, freshly precipitated from 1 to 8 M NaOH at 20 to 50°C, differ from those of pure $\alpha\text{-FeO(OH)}$ by having greater quadruple splitting. This difference can be explained by the lower symmetry of the oxygen environment of Fe^{3+} in the mixed hydroxides compared with that of pure $\alpha\text{-FeO(OH)}$. The decreased symmetry apparently is caused by the presence of plutonium in the compound structure.

As expected, plutonium distribution in the freshly prepared mixed Pu(IV)-Fe(III) hydroxide precipitate is uniform. However, in the heterogeneous mixing of the individual hydroxides, plutonium is initially concentrated in the bottom layer. During storage of a homogeneous mixed Pu(IV)-Fe(III) hydroxide sample for 90 days at room temperature, some plutonium segregation is observed. The segregation was confirmed by the fact that the bottom layer of the solid phase becomes enriched in iron. Some plutonium segregation also was noted upon thermal treatment of homogeneous mixed Pu(IV)-Fe(III) hydroxide. In this case, however, plutonium initially concentrates in the bottom layer of sediment.

The ability of Pu(VI) to form mixed compounds with Fe(III) and Cr(III) hydroxides apparently is lower than that of Pu(IV), as confirmed by measurements of Pu(VI) concentration over the precipitates. Change in Pu(VI) concentration was found only in tests with Cr(III) hydroxide. The decrease in Pu(VI) concentration likely arose by its slow reduction by oxidizing Cr(III) to chromate. It was also shown that Pu(VI) does not interact with solid phase Fe₂O₃ and Al(III) hydroxide.

Acknowledgements

This work was performed at the Laboratory of Transuranium Element Chemistry of the Institute of Physical Chemistry, Russian Academy of Sciences (IPC RAS), under an agreement between the U.S. Department of Energy and the IPC RAS. The work was supported by the U.S. Department of Energy, Office of Science and Technology, under the Office of Environmental Management.

We thank in particular Dr. Kurt Gerdes and Dr. Jerry Harness, Program Managers, Efficient Separation and Processing Crosscutting Program, for their continuing interest in our research. We also thank Dr. Jack Watson, Deputy Coordinator, for his useful advice and support. We are especially indebted to Mr. Calvin Delegard for his attention to our work and his encouraging and useful discussions of the experimental results. We also thank him for his editorial help. We acknowledge, with thanks, organizational efforts of Dr. Thomas Albert in contract implementation.

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1.0 Introduction

Though many studies have been devoted to determining plutonium behavior in different oxidation states in alkaline media, some aspects of this field are yet not clear. Thus, it is well known that many metals present in Hanford Site radioactive alkaline wastes [for example, Fe(III) and Al(III)] easily form mixed hydroxides and, in some cases, even form stoichiometric compounds (Chalyi 1972). However, there are no data concerning Pu(IV) participation in such reactions. On the other hand, many data exist on coprecipitation of plutonium with various hydroxides. In this case, however, the Pu:metal mole ratio is usually very low, so that the bulk properties of the solid phases are determined completely by the macrocomponents and the coprecipitation mechanism remains unknown. In some Hanford Site waste tanks, the NaOH concentration is high. Under these conditions, Fe(III) and Cr(III) are slightly amphoteric and can react with different metal hydroxides. Therefore, by this mechanism, Pu(IV) hydrous oxide may interact with Fe(III) or Cr(III) hydroxides despite their low solubility and the relative stability of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. In contrast, both Pu(V) and Pu(VI) form relatively soluble anionic hydroxo-complexes in alkaline solution. Therefore, the probability of their interaction with metal hydroxides or oxides is rather low.

It is important to determine the behavior of plutonium during aging in tank wastes. In particular, its formation of a distinct solid Pu(IV) hydrous oxide in the presence of different metal hydroxides and oxides must be understood. Knowledge of the rheological properties of Pu(IV) and metal hydroxide solids, though not a topic of the present research, also could help in such estimations.

It is pertinent to note that the composition and behavior of Pu(IV) hydrous oxide in pure NaOH solutions and in the presence of various additional anions were recently investigated (Krot et al. 1998). The conditions of formation and properties of many d-element hydroxides also have been investigated. Brief reviews of relevant literature are given in some reports (for example, Whyatt et al. 1996; Krot et al. 1996). Binary and multicomponent hydroxide systems also have been studied because of their possible use as starting materials to prepare oxides or in theoretical research of coprecipitation mechanisms.

The available literature data show that the formation mechanism of insoluble hydroxides is not described, even approximately, by any of the known classical precipitation theories. Two alternative mechanisms have been proposed to explain the formation and nature of insoluble hydroxides. According to the first mechanism, in the initial stages of hydrolysis, monomer "molecules" of metal hydroxide form in solutions by step hydrolysis of metal aquo ions (Baes and Mesmer 1976; Levina and Ermolenko 1955). The high formation rates of such molecules results in amorphous hydroxide precipitates. In the second mechanism, the amorphous insoluble hydroxides form inorganic polymers. The process of polymer formation proceeds through three stages: hydrolysis, formation of bridging O^- -bonds (that is, the OH^- group acts as a bridging ligand) between hydroxo complexes, and subsequent slower dehydration to form M-O-M bonds with aging (Rollinson 1956; Scott and Andrieth 1954; Sillen and Martell 1971). By this mechanism, at any given time, a wide range of polymeric compounds exists in solution. Though growth of the polymeric chains occurs, the character of bonds between the neighboring atoms

does not change. The presence of a solid phase in solution must initiate the polymerization by decreasing the charge density on polymeric forms of hydroxo complexes (Hayden and Rubin 1986). Because such polynuclear hydroxo complexes form, it has been established that the hydrolysis of most metals does not occur in a stepwise fashion (Burkov and Lilich 1968).

Some common features, determined by the chemical nature of components, were established by studying hydroxide systems containing two or more components. For example, it is known that divalent metal hydroxides crystallize easily upon precipitation. If the hydroxides are precipitated with Fe(III) hydroxide, however, crystallization is impeded. Such inhibition of crystallization is found for various systems: Co(II)-Fe(III), Ni(II)-Fe(III), Mg(II)-Fe(III), and others (Krause and Rychlewska 1953; Morrow and Levy 1968; Milligan 1951). Inhibition of crystallization also has been observed with other systems: M(III,IV)-Cr(III) (Livage and Montel 1962), Ni(II)-Al(III) (Milligan and Merton 1946), and Cr(III)-Zr(IV) (Milligan and Merten-Watt 1948). It was also noted that, as a rule, amorphous mixed hydroxides require higher temperatures to form crystalline products than do the separate individual hydroxides (Bhattacharya and Kameswari 1959; Lefevre et al. 1961).

As shown by previous studies, an increase in the polymeric structure of Fe(III) hydroxide with time makes the stability of its amorphous state transitional. Initially, Fe(III) hydroxide consists of polymeric molecules of various lengths. Bridging bonds form between the polymers during aging and dehydration. A final crystalline product [for example, Fe(III) oxide] forms only at the latest stage. Before this time, the compound is amorphous.

Dimers with *ol* (hydroxo) bonds were found to form as intermediate products in the polycondensation of hydrolyzed Fe(III) aquo ions (Sillen and Martell 1971; Sylva 1972). Three stages were identified in the formation of Fe(III) polymeric particles (Fedotov et al. 1975). At molar ratios of $\text{OH}:\text{Fe}^{3+}$ less than 0.65, the predominant species is a dimer. By increasing this ratio, linear polymeric molecules arise from the dimers. Finally, double polymeric molecules form that can contain the anions of the initial iron salts as impurities. Polyhydroxo complexes of this sort represent double chains of $[\text{FeO}_6]$ octahedra in which the neighboring octahedra share edges. These double chains exist in the primary amorphous phase particles without substantial change in structure, composition, and size (Schneider 1984).

According to other work, a main structural element of freshly precipitated Fe(III) hydroxide is the $(\text{FeOOH})_4$ tetramer (Melikhov et al. 1976). The tetramer was confirmed by x-ray diffraction data (Feitknecht et al. 1973). Such tetramers are rather stable, as shown from the very low isotopic exchange rate of the compound with water (Misawa 1973). The orientation of the tetramers in the precipitate aggregates is completely disordered, as confirmed by the absence, in x-ray diffraction patterns, of lines other than the two arising from the ordering within the tetramer itself.

During aging of compounds, deprotonation of *ol*-bonds occurs (Misawa et al. 1974). The deprotonation accelerates Fe(III) hydroxide crystal modification. With increasing temperature, solid phase transformation to gothite ($\alpha\text{-FeOOH}$) accelerates sharply. Above 100°C , hematite ($\alpha\text{-Fe}_2\text{O}_3$) also can be formed.

Mössbauer spectroscopy studies of Fe(III) hydroxide aging has shown the compound's crystallization rate is highest at pH 13 and at 70°C. With further increase in pH, the process is interrupted (Lewis and Schwertmann 1980). At pH 14 or above, goëthite has lower solubility than amorphous Fe(III) hydroxide (Kamnev 1992). In room temperature 15 M NaOH, the alkali metal hydroxo ferrates become the stable solid phases. With increasing temperature, the threshold alkali concentration required to form hydroxo ferrate salts decreases. For example, at 90°C, the compound $K_2O \cdot Fe_2O_3 \cdot H_2O$ forms in 8.5 M KOH (Ni et al. 1976). Formation of even trace amounts of goëthite in weakly alkaline solution is prevented in the presence of Al(III) (Wolska 1981).

Study of the formation of polymeric Cr(III) ions showed that hydroxo complexes with three or more chromium atoms (for example, tetramers of the type $[Cr_4(OH)_6]^{6+}$) have a linear structure with two ol-bonds between the adjacent chromium atoms (Thompson and Connick 1981; Stuenzi and Marty 1983).

The behavior of Al(III) in alkaline media is the subject of many investigations. Under different precipitation conditions, the interaction of Al(III) with alkali proceeds through a number of states characterized by various $OH:Al^{3+}$ ratios. By increasing this ratio, the fraction of precipitated polyhydroxo complexes increases without change of structure while the monomer and dimer fraction decreases (Hayden and Rubin 1986; Fedotov et al. 1978). In dilute Al(III) solutions, condensation occurs:

The polyhydroxo complexes formed include one with a central Al^{3+} in a tetrahedral oxygen environment surrounded by four octahedral configurations each with three Al-OH bonds. The four octahedral units connect at the apexes of the central tetrahedron (Denney and Hsu 1987). Sulfate strongly interferes with formation of such hydroxo complexes and can, in general, suppress this process. Other anions are less disruptive: $SO_4^{2-} \gg Cl^- \sim NO_3^- > ClO_4^-$.

It was established that crystalline products of M(II)-Fe(III) hydroxides have composition 4M(II):Fe(III) and 2M(II):Fe(III), form layered structures, and are molecular inclusion compounds (Feitknecht 1942; Denney and Hsu 1987). Amorphous hydroxides likely have similar structure but differ by their low degree of ordering. The same researchers assert that in coprecipitated hydroxides, mixed metal ol-bonding of the type M(II)-OH-Fe(III) exists together with ol-bonding between the same metal. However, it was shown that in the structure of double M(II)-Al(III) hydroxides, the mixed M(II)-Al(III)-hydroxyl layers alternate with layers of individual hydroxides and that the arrangement of the respective metal hydroxides in the layers of the other hydroxide occurs in an ordered manner (Dzis'ko et al. 1978; Ketchik et al. 1980).

It has been postulated that the cation ratio [for example, Ni(II):Al(III)] in double hydroxides is independent of the degree of crystallinity. Despite the absence of direct structural data, the presence of an initiating metal-hydroxyl layer also has been postulated (Tomilov and Berger 1984). The initiating layer is produced from that metal which, at given pH, is first capable of forming a hydroxide phase. Preliminary precipitation of the metal hydroxide, however, is not required. It is enough that a short-lived association forms with the appropriate structural

ordering. An elementary electroneutral layer of either of the two hydroxides can act as the initiating layer, depending on the acid-base properties of individual metal hydroxides.

Numerous investigations of M(II)-M(III) hydroxide systems confirm the ability of trivalent metals to establish hydroxide layer packing in the mixed hydroxides. It is useful to test whether this property of M(III) is retained in mixed hydroxide systems with Pu(IV).

The primary goal of our investigation was to obtain data on the possibility, extent, and characteristics of interaction of Pu(IV) and (VI) with hydroxides and oxides of d-elements and other metals [Al(III), La(III), and U(VI)] in alkaline media. Such information is important in fundamental understanding of plutonium disposition and behavior in Hanford Site radioactive tank waste sludge. These results supply essential data for determining criticality safety and in understanding transuranic waste behavior in storage, retrieval, and treatment of Hanford Site tank waste.

2.0 Experimental Materials and Methods

2.1 Reagents and Equipment

Most experiments were performed using Pu(IV) nitrate solutions with known concentrations of HNO_3 . Preparation of Pu(IV) nitrate was performed by the following method. First, to ~ 0.05 M plutonium nitrate in ~ 3 M HNO_3 (purified by the common anion exchange method), hydrogen peroxide was added to 0.05 M concentration and the mixture heated in a boiling water bath. The sharp change of color from blue to brown indicated complete H_2O_2 decomposition and conversion of Pu(III) to Pu(IV). From this solution, $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ was precipitated by the slow addition, with slight heating, of ~ 1 M oxalic acid to ~ 0.1 M excess. After two hours of coagulation, the compound was separated from the mother solution by centrifugation and washed with 1 M HNO_3 containing 0.01 M $\text{H}_2\text{C}_2\text{O}_4$. The $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in boiling concentrated HNO_3 and the product solution evaporated to a small volume. After cooling, the solution was diluted four-fold with 2 M HNO_3 and treated by H_2O_2 to stabilize Pu(IV) as previously described.

Plutonium concentrations were determined gravimetrically. For this purpose, 0.1 mL aliquots of Pu(IV) stock solution were carefully (without boiling) evaporated to dryness in small Pt crucibles and the residues calcined at 800°C for about two hours to produce PuO_2 . The free HNO_3 concentrations in the Pu(IV) solutions were determined by direct titration with 0.1 M NaOH using phenolphthalein as an indicator. In determining the HNO_3 concentration, it was assumed that four moles of sodium hydroxide were consumed in the course of the titration to precipitate one mole of Pu(IV).

By this method, two Pu(IV) stock solutions were prepared with metal concentrations of 0.233 and 0.206 M, respectively. The free acid concentrations were 3.10 and 4.35 M. The tetravalent state of plutonium in the test solutions was verified by absorption spectrophotometry using a Shimadzu model UV-3100 PC UV-Vis-NIR spectrophotometer (Japan).

Working sodium hydroxide solutions were obtained by diluting 16.7 M chemical purity grade NaOH solution. The NaOH solutions were stored in plastic bottles. Standard solutions of other reagents (NaNO_2 , NaNO_3 , nitrates of Al, Fe, Ni, and other metals) were prepared by dissolving the corresponding reagent-grade salts in distilled water.

Powder x-ray diffraction patterns of solid samples were measured by a 100-mm Guinier camera, model XDC-700, using $\text{CuK}\alpha_1$ radiation (Philips PW 1140/90/96 generator, Holland); Si was used as an internal standard. Infrared spectra were recorded at room temperature with a Specord-M80 instrument (Germany).

Thermal analyses of the various compounds were obtained using a Q-1500 D derivatograph (Hungary). Thermostats of U-2 model (Germany) were used to maintain constant solution temperatures ($\pm 0.2^\circ\text{C}$) in the 20 to 80°C range.

Precipitates were separated from supernatant liquids using medical centrifuges (model CLK-1, Russia) providing a separation factor of 1,750g. Plutonium(IV) compound samples were

weighed with a microbalance having a sensitivity of 1 μg (Sartorius, Germany). The α -activities of plutonium solutions were measured by a LS-6500 scintillation counter (Beckman, USA).

Mössbauer spectra of the transition of 14.4 keV ^{57}Fe were taken with a spectrometer of constant acceleration (Mössbauer Laboratory produced by KFKI, Hungary) with a 3 mCi $^{57}\text{Co(Rh)}$ source. The detector was a NaI(Tl) crystal of 0.05 mm thickness. Certified Fe_2O_3 and sodium nitroprusside materials were used for spectrometer calibration. Isomeric shifts (δ) were determined toward sodium nitroprusside at room temperature. The data presented in this report have a spectral zero in the rate scale corresponding to the center of the sodium nitroprusside doublet (that is, the beginning of counting out of isomeric shifts). The spectra were fit (using an IBM PC AT) by a least square method assuming Lorentzian line shape. Iron enriched to 90% in ^{57}Fe content was used for sample preparation. Thus, samples containing about 0.4 mg/cm² of this isotopic enrichment have sufficient Mössbauer thickness that even in solids with high plutonium content, the spectra do not exhibit non-resonance absorption.

2.2 Experimental Methods

2.2.1 Precipitation, Coagulation, and Isolation of Pu(IV) and Metal Compounds

Pu(IV) and metal hydroxide samples were prepared by direct or reverse precipitation in plastic test tubes with an amount of NaOH calculated to obtain the chosen excess of precipitant. With direct precipitation, measured volumes of titrated sodium hydroxide were quickly added with stirring to known amounts (usually 0.3 to 0.4 mL) of the Pu(IV) and metal element stock solution diluted 3- to 5-fold by water. With reverse precipitation, Pu(IV) and metal stock solution aliquots were poured into plastic test tubes containing a solution of known NaOH concentration. In both cases, the product suspensions were stirred thoroughly and kept for a controlled period of time at a chosen temperature in a thermostat or on a boiling water bath. The solid phases then were separated by centrifugation and washed four or five times with 5 mL of water. The pH value of the final wash water was not higher than 8. Washed precipitates were collected in small glass crucibles and dried in a desiccator filled with KOH pellets when sample preparation temperatures were ambient. In the case of precipitations at elevated temperature, the samples were dried by oven heating at the temperature of formation. The dry samples thus transformed into powders and were used for subsequent experiments.

To prepare hydroxide samples under hydrothermal conditions, NaOH in a ~0.2 M excess was added to 0.3 to 0.4 mL of mixed Pu(IV) and metal stock solution. The resulting mixtures were diluted to 5 to 7 mL with water. After stirring and coagulation at room temperature, the precipitate was separated from the mother solution by centrifugation and washed once with 5 mL of water. The solids then were suspended in 1 mL of standardized sodium hydroxide solution and transferred into a Teflon test tube with 6-mm outer diameter. The test tube was sealed in a glass ampoule and heated for several hours at a controlled temperature ranging from 100 to 220°C. After cooling, the ampoule was opened, and the aged suspension was washed and dried as described previously for the solids produced by heating under atmospheric pressures.

2.2.2 Measurements of the IR Spectra of Pu(IV) and Metal Hydroxide Compounds

Precipitates of the various mixed hydroxides were dried 1 to 3 days in a desiccator over KOH pellets if the temperature of sample preparation was ambient. The samples prepared at 100°C or higher were dried in plastic test tubes in a boiling water bath. From 1.5 to 2.8 mg of dried compound was mixed with 200 mg of special purity-grade NaCl or KBr and ground into powder for 2 to 5 minutes in an agate mortar. The product mixture was pressed into a 2-cm-diameter transparent disk about 1 minute at 190 kP/cm². The IR spectra were recorded in the range of 4000–400 cm⁻¹ (NaCl matrix) or 4000–300 cm⁻¹ (KBr matrix) and compared with spectra from blank disks prepared from pure NaCl or KBr of the same weight as the samples' disks.

2.2.3 Determining the Sedimentation Rate of Pu(IV) and Metal Hydroxide Samples

Sedimentation rates of hydroxides obtained by the described methods were determined in glass test tubes after washing in distilled water and mixing. After sedimentation was complete, the samples were centrifuged to increase the precipitates' compaction. Measured volumes of precipitate were dissolved in heated 3 M HCl and the dissolved Pu(IV) and Fe(III) determined by spectrophotometry.

2.2.4 Study of the Dissolution Rate of Pu(IV) and Metal Hydroxide Precipitates

Measured volumes of standard Pu(IV) and metal element solution, usually containing 0.06 mmole of each component, were mixed with known amounts of NaOH by direct or reverse precipitation to obtain hydroxide under the controlled conditions described previously. Preliminary tests showed that optimum coagulation occurred in one hour at 70°C. The product precipitates were dissolved in 3 M HCl at 60°C to prevent disproportionation and oxidation of Pu(IV). Dissolutions required no more than two hours under these conditions. The kinetic measurements were performed by visible spectrophotometric monitoring of colloidal Pu(IV) transformation into true solution.

3.0 Results and Discussion

Experimental results for various Pu-metal systems are presented separately for experimental methods based on IR spectrometry, dissolution rate, sedimentation rate, Mössbauer spectrometry, and thermal and x-ray analyses.

3.1 IR Spectra of the Mixed Hydroxides

In general, freshly precipitated hydroxide compounds, excluding Mg, Cd, and In hydroxides (Chalyi 1972), have no crystal structure immediately after precipitation. This is also true for freshly precipitated Pu(IV) hydroxide (Ockenden and Welch 1956). Therefore, infrared spectroscopy, which, unlike x-ray diffractometry, does not require crystalline compounds, often is used to determine important structural properties of amorphous compounds.

The following data give evidence that mixed hydroxide compounds with Pu(IV) are formed in alkaline media in all studied systems except with Ni(II). However, this conclusion must be confirmed by other methods.

3.1.1 The Fe(III)-Ni(II) System

The IR spectrum of Fe(III) hydroxide precipitated from 1 M NaOH has an intense band with a maximum at 3452 cm^{-1} and half-width of $\sim 280\text{ cm}^{-1}$. The maximum is at higher energy than the $\nu(\text{HOH})$ maxima of 3049 or 3095 cm^{-1} found for $\alpha\text{-FeOOH}$, gothite (Glemser 1959; Schwarzmann 1962), and for $\gamma\text{-FeOOH}$, lepidocrocite, 3125 to 3120 cm^{-1} (Russell 1979). This shows that Fe(III) hydroxide is more disordered than the oxyhydroxides, and that the hydroxide contains bridge and ending OH groups. A band at 1642 cm^{-1} , attributed to $\delta(\text{HOH})$, confirms the presence of molecular water in the Fe(III) hydroxide.

A weak band at 1350 cm^{-1} has been attributed to out-of-plane distortion (bending) vibrations of hydroxyl ions (Yukhnovich 1973). This band also may be caused by carbonate (formed by sorption of CO_2) in the precipitate. In such a case, however, the spectra of other metal hydroxides obtained under similar conditions should have greater uniformity than shown in this frequency region.

Two distinct bands at 890 and $805\text{-}790\text{ cm}^{-1}$ can be attributed to in-plane deformation (bending) vibrations of hydroxyl ions. The absorptions at 890 and 797 cm^{-1} have been found for gothite (Cabannes-Ott 1957). Absorption bands at $625\text{-}615\text{ cm}^{-1}$ correspond to libration vibrations of water. Deformation vibrations of the Fe-O bond are not evident above the large background absorption found below 600 cm^{-1} .

The spectrum of freshly precipitated Ni(II) hydroxide contains many bands considering that the crystal $\text{Ni}(\text{OH})_2$ has a hexagonal lattice (Cabannes-Ott 1960). Bands with maxima at 3410 and $1638\text{-}1600\text{ cm}^{-1}$ can be assigned to valent and deformation vibrations of water occluded in the amorphous hydroxide. The very narrow intense band at 3600 cm^{-1} corresponds to the

unperturbed valent vibrations of the OH group. For crystalline $\text{Ni}(\text{OH})_2$, the brucite-type layered structure (Kober 1965) and the absence of hydrogen bonding between hydroxyl ions are typical. It is likely that the principal features of $\text{Ni}(\text{OH})_2$ already are displayed in amorphous $\text{Ni}(\text{II})$ hydroxide. The band at 525 cm^{-1} represents libration vibrations of OH groups. The IR spectrum of coprecipitated $\text{Fe}(\text{III})$ - $\text{Ni}(\text{II})$ hydroxide evidently undergoes some changes caused by the mutual influence of the two components (Figure 3.1.1).

Figure 3.1.1. The Infrared Spectra of Hydroxide Compounds in the $\text{Ni}(\text{II})$ - $\text{Fe}(\text{III})$ System at Different $\text{Ni}(\text{II})$: $\text{Fe}(\text{III})$ Ratios (NaCl matrix - approx. 210 mg)

- 1 - 1:4 (2.12 mg)
- 2 - 2:3 (2.29 mg)
- 3 - 4:1 (2.19 mg)
- 4 - $\text{Ni}(\text{OH})_2$ (2.41 mg)

Ni:Fe = 1:4

The high frequency band with maximum at 3420 cm^{-1} and with fine structure elements has the same width as in the case of pure $\text{Fe}(\text{III})$ hydroxide. The intensity of the water deformation vibration band remains practically unchanged, though long wavelength components occur at 1640 and 1625 cm^{-1} . In the 1160 to 900 cm^{-1} range, a series of weak bands is displayed that is not present in the spectra of the individual hydroxides. These bands can be attributed to in-plane deformation vibrations of hydroxyl ions, assuming the existence, in the hydroxide ensemble, of OH groups in various environments. The shift of the water libration vibration band to 615 - 550 cm^{-1} correlates with splitting of the $\delta(\text{HOH})$ band.

Ni:Fe = 2:3

The intensity, shape, and location of the main absorption bands change slightly with increase in the fraction of nickel in the mixed hydroxide. The only essential spectral change is the further complication of the $\delta(\text{HOH})$ band, caused, most likely, by the mutual perturbation of hydroxyl ions and water molecules.

Ni:Fe = 4:1

The IR spectrum of the 4:1 mixed hydroxide was expected to closely resemble the spectrum of pure $\text{Ni}(\text{OH})_2$. However, the characteristic narrow hydroxyl ion valent vibration band above 3600 cm^{-1} is not observed while the position and shape of the 3450 cm^{-1} band confirm the absence of appreciable amounts of free hydroxyl groups (i.e., hydroxyl groups lacking hydrogen bonds). There is a further narrowing of the $\delta(\text{HOH})$ band, and the weighted center of the band is shifted towards shorter wavelengths. Because $\text{Ni}(\text{II})$ hydroxide has only one type of OH group, whereas the number of OH group types is great in polymeric $\text{Fe}(\text{III})$ hydroxide, it is assumed that including $\text{Ni}(\text{OH})_2$ in the $\text{Fe}(\text{III})$ hydroxide creates new hydroxyl groups with intermediate OH-O distances and bond energies.

As shown in Figure 3.1.1, a very strong IR band of unknown nature appears at 1375 cm^{-1} in the 80% $\text{Ni}(\text{II})$ mixed hydroxide. The band could be attributed to valent vibrations of carbonate. In such a case, the change of the $\delta(\text{HOH})$ band could be caused by the presence of additional $\text{HOH-O}_3\text{C}$ bonds. However, it is not clear why, of the various mixed $\text{Fe}(\text{III})$ - $\text{Ni}(\text{II})$ hydroxides prepared under similar conditions, only hydroxides of this Ni:Fe ratio absorb such a high amount of carbonate. Absorption bands at 1500 to 1000 cm^{-1} in the IR spectra of böhmite-type hydroxides (including $\gamma\text{-FeOOH}$, lepidocrocite) have been attributed to in-plane deformation vibrations of hydroxyl (Hund 1959; Chalyi 1959). In this case it is assumed that even in $\text{Fe}(\text{III})$ - $\text{Ni}(\text{II})$ mixed hydroxides having a large fraction of nickel, the $\text{Ni}(\text{OH})_2$ brucite layer structure is not a major component. More likely, $\text{Fe}(\text{III})$ hydroxide determines the structural features of the mixed hydroxide. Based on the available data, it is impossible to choose between these two explanations. However, it is obvious that even small fractions of $\text{Fe}(\text{III})$ inhibit the brucite layer formation of $\text{Ni}(\text{OH})_2$ and decrease the overall structure of the system.

3.1.2 The Pu(IV)-Fe(III) System

The $\text{Pu}(\text{IV})$ - $\text{Fe}(\text{III})$ hydroxide system was studied with initial component Pu:Fe ratios of 1:10, 1:2, 1:1, 2:1, and 10:1 (Figure 3.1.2). As shown in the following discussion of the individual systems, the $\text{Pu}(\text{IV})$ - $\text{Fe}(\text{III})$ mixed hydroxides undergo a number of changes depending on the metal ratio. However, the $\text{Pu}(\text{IV})$ - $\text{Fe}(\text{III})$ mixed hydroxides behave as a rather homogeneous system with properties differing from those of the individual hydroxides. In this connection the question arises whether only $\text{Fe}(\text{III})$ hydroxide provides a strongly protective action or whether $\text{Fe}(\text{III})$ and $\text{Pu}(\text{IV})$ each provide a mutually protective action that inhibits the precipitation of the individual hydroxides.

Figure 3.1.2. The Infrared Spectra of Hydroxide Compounds in Pu(IV)-Fe(III) System at Different Pu(IV):Fe(III) Ratios (NaCl matrix - approx. 210 mg)

- 1 - 10:1 (2.98 mg)
- 2 - 2:1 (2.18 mg)
- 3 - Fe(OH)₃ (2.32 mg)
- 4 - 1:2 (2.44 mg)
- 5 - 1:10 (2.01 mg)

Pu:Fe = 1:10

Comparing the IR spectrum of this mixed hydroxide (Figure 3.1.2, scan 5) with the spectra of the individual Pu(IV) and Fe(III) hydroxides (Figures 3.1.5, scan 1, and 3.1.2, scan 3, respectively) shows that the Pu(IV) and Fe(III) mutually influence each other. The $\nu(\text{HOH})$ band for the mixed hydroxide is split into at least three components at 3450, 3410 and 3380 cm^{-1} . Overall, the band is wider and has lower intensity than was found for the individual materials. Other low-intensity absorption bands are observed at 1500 to 1200 cm^{-1} ; some of these are found in the spectrum of pure Fe(III) hydroxide. The two rather intense bands at 870 and 780 cm^{-1} in the mixed hydroxide's spectrum can be attributed to M-OH bond vibrations. Strong absorptions are observed in the low-frequency region, including hydroxyl ion libration vibration bands at 610 to 500 cm^{-1} and M-O valent vibration bands at 448 to 430 cm^{-1} .

Pu:Fe = 1:2

This mixed Pu(IV)-Fe(III) hydroxide has a spinel-like component ratio. Bands typical for valent and deformation vibrations of water are practically absent (Figure 3.1.2, scan 4). Deformation bands caused by the vibrations of various hydroxyl groups have shapes similar to the corresponding bands in the spectrum of pure Pu(IV) hydrous oxide. However, their maxima are shifted to longer wavelengths.

Pu:Fe = 1:1

The IR spectrum of this mixed hydroxide (not depicted) has the same water valent and deformation vibration bands and bands at 880 and 780 cm^{-1} as found in the 1:10 Pu:Fe system.

Pu:Fe = 2:1

Changes in the spectrum (Figure 3.1.2, scan 2) are displayed by splitting two components of hydroxyl ion deformation vibration bands at 1100 to 1000 cm^{-1} . This splitting indicates non-equivalence in the OH groups. In addition, only one band of M-OH vibrations (maximum at 840 cm^{-1}) is observed.

Pu:Fe = 10:1

The spectrum of the 9% Fe(III) mixed hydroxide (Figure 3.1.2, scan 1) is still not identical to the spectrum of Pu(IV) hydroxide by itself. In the range of 1250 to 1100 cm^{-1} , two new bands are displayed. The whole series of OH group deformation vibrations shifts toward the shorter wavelength area and correlates with the Pu(IV)-O distance (Neu 1997). It is assumed that several non-equivalent M-OH bonds exist in this compound. The well-resolved band at 1720 cm^{-1} is difficult to explain.

3.1.3 The Pu(IV)-Ni(II) System

The intense narrow hydroxyl ion vibration bands in the IR spectrum of pure $\text{Ni}(\text{OH})_2$ at about 3600 cm^{-1} can serve as a convenient benchmark to indicate the formation of $\text{Ni}(\text{OH})_2$ layers in coprecipitation with another metal. At a Pu:Ni ratio of 2:1 (Figure 3.1.3), a perturbed $\nu(\text{HOH})$ band with maxima at 3640, 3560, 3430, 3360, and 3190 cm^{-1} appears in the spectrum of the mixed hydroxide. The intensity of the component at 3640 cm^{-1} , typical for vibrations of the "free" hydroxyl group, is lower than that of the main band.

Figure 3.1.3. The Infrared Spectra of Hydroxide Compounds in the Pu(IV)-Ni(II) System at Different Pu(IV):Ni(II) Ratios (NaCl matrix - approx. 210 mg)

1 - 1:2 (2.34 mg)

2 - 1:1 (2.46 mg)

3 - 2:1 (2.17 mg)

Upon decreasing the Pu:Ni ratio to 1:1, the intensity of the $\nu(\text{OH})$ band grows and the main $\nu(\text{HOH})$ band becomes less perturbed. Further increase of Ni(II) content leads to the expected growth in the intensity of the free hydroxyl ion absorption band. Interesting changes occur in the frequency region of 1150 to 950 cm^{-1} . These bands, attributed to in-plane deformation vibrations of the OH group, are distinctly displayed in the IR spectrum of pure Pu(IV) hydroxide but are absent in the $\text{Ni}(\text{OH})_2$ spectrum. In spectra of mixed Pu(IV)-Ni(II) hydroxides, these bands have low intensity and are shifted somewhat toward shorter wavelengths with increasing Ni(II) fraction. An intense band in the range of 600–500 cm^{-1} is rather sensitive to the composition of the mixed hydroxide. For pure $\text{Ni}(\text{OH})_2$, this band has a maximum at 525 cm^{-1} and can be assigned to libration vibrations of hydroxyl groups (Kober 1965). In Pu-Ni hydroxides with 1:2 and 2:1 ratios, the position of the band is unchanged, but its intensity decreases. Without additional investigations, it is not known why, in the IR spectra of 1:1 Pu:Ni mixed hydroxides, this band's shape is close to that found in the spectrum of pure $\text{Ni}(\text{OH})_2$ but is shifted by 50 cm^{-1} toward shorter wavelengths.

The experimental results indicate that a hydroxide phase of uniform structure does not form in the coprecipitation of Ni(II) and Pu(IV). However, some slight component interaction occurs.

3.1.4 The Pu(IV)-Ni(II)-Fe(III) System

The Pu(III)-Ni(II)-Fe(III) three-component system was investigated with component ratios of 1:1:1 and 2:1:1. In both cases, no "free" hydroxyl ion vibration bands were found in the IR spectra (Figure 3.1.4). Libration vibration bands for $\gamma(\text{OH})$ in the $560\text{--}525\text{ cm}^{-1}$ region also do not appear in a background of strong absorption below 600 cm^{-1} . Intense deformation vibration bands of various hydroxyl groups are found at 1520 , 1350 , 1150 , and 1050 cm^{-1} in the spectrum of the 1:1:1 system. With increasing Pu(IV) content to the 2:1:1 ratio, the intensities of the 1520 and 1350 cm^{-1} bands observed for pure Pu(IV) hydroxide grow appreciably. Slight but distinct bands at 1050 , 845 and 720 cm^{-1} can be assigned to vibrations of bridge hydroxo groups with varying M-O bond lengths.

Figure 3.1.4. Infrared Spectra of Hydroxide Compounds in the Pu(IV)-Ni(II)-Fe(III) System at Different Pu(IV):Ni(II):Fe(III) Ratios (NaCl matrix - approx. 210 mg)

1 - 1:1:1 (2.93 mg)

2 - 2:1:1 (2.79 mg)

In the case of pure Pu(IV) hydrous oxide, such a band is observed at 970 cm^{-1} . In the spectrum of crystalline PuO_2 obtained by calcination of Pu(IV) hydrous oxide at 700°C , a similar absorption band occurs at ~ 1100 to 1020 cm^{-1} and corresponds to a decrease in the Pu-O interatomic distance (Figure 3.1.5). Based on these observations of IR spectra, we concluded that the mutual influence of all three components is observed in the Pu(IV)-Ni(II)-Fe(III) system. Thus, despite the high mutual affinity of Fe(III) and Ni(II), Pu(IV) hydrous oxide does not form in the three component Pu(IV)-Fe(III)-Ni(II) system.

Figure 3.1.5. Infrared Spectra of Plutonium(IV) Compounds (NaCl matrix - approx. 210 mg)

1 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ (2.478 mg)

2 - PuO_2 obtained by calcination of the $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ at 700°C (1.507 mg)

3 - PuO_2 obtained by calcination of the Pu(IV) oxalate at 700°C (1.581 mg)

3.1.5 The Pu(IV)-Co(III) System

This system is similar to the Pu(IV)-Ni(II) system in many respects. A narrow absorption band at 3620 cm^{-1} , which can be attributed to valent vibration of "free" hydroxyl, $\nu(\text{OH})$, is observed in the IR spectrum of the Pu:Co mixed hydroxide at the 1:10 ratio (Figure 3.1.6). This band's intensity decreases with increasing Pu(IV) fraction. As a result, only a shoulder on the high-frequency side of the water valent vibration band is observed in the spectrum of the 2:1 Pu:Co mixed hydroxide; the $\nu(\text{OH})$ band is not observed at all for the 10:1 Pu:Co mixed hydroxide. The character of the water valent vibration band alters as well. The band's intensity increases somewhat and the maximum is shifted to longer wavelengths. Such effects are usually explained by the formation of additional hydrogen bonds (Yukhnovich 1973).

3.1.6 The Pu(IV)-La(III) System

The Pu(IV)-La(III) system was investigated at Pu(IV):La(III) ratios of 1:10, 1:2, 2:1, and 10:1. The IR spectra of the coprecipitated hydroxides are presented in Figure 3.1.7. According to the literature, the crystal structures of both $\text{La}(\text{OH})_3$ and LaOOH are simple, and their IR spectra contain few absorption bands. The hydroxide bands are usually observed at about 3600 cm^{-1} for the valent vibrations of hydroxyl ions, in the region of $745\text{--}615\text{ cm}^{-1}$ for the

Figure 3.1.6. Infrared Spectra of Hydroxide Compounds in the Pu(IV)-Co(III) System at Different Pu(IV):Co(III) Ratios (NaCl matrix - approx. 210 mg)

- 1 - 1:10 (2.98 mg)
- 2 - 1:2 (2.83 mg)
- 3 - 1:1 (4.94 mg)
- 4 - 2:1 (2.04 mg)
- 5 - 10:1 (2.08 mg)

deformation vibration $\delta(\text{OH})$, and near 400 cm^{-1} where complex structure bands for valent M-O bond vibrations are observed (Nakamoto 1986). The hydroxyl groups in $\text{La}(\text{OH})_3$ do not form hydrogen bonds. The absence of hydrogen bonds in $\text{La}(\text{OH})_3$ was shown by a neutron diffraction technique (Atoji and Williams 1959). Two absorption bands would be expected in the region of the M-O deformation vibrations because of the two different M-OH distances in the hydroxide's structure. However, only one band is found. The reason for this discrepancy is not satisfactory explained (Klevtsov et al. 1967).

Figure 3.1.7. Infrared Spectra of Hydroxide Compounds in the Pu(IV)-La(III) System at Different Pu(IV):La(III) Ratios (NaCl matrix - approx. 210 mg)

- 1 - $\text{La}(\text{OH})_3$ (2.96 mg)
- 2 - 1:10 (2.31 mg)
- 3 - 1:2 (2.42 mg)
- 4 - 2:1 (1.87 mg)
- 5 - 10:1 (2.07 mg)

The spectrum of pure La(III) hydroxide, precipitated under the same conditions as the mixed Pu(IV)-La(III) hydroxides, also is presented in Figure 3.1.7. However, the spectrum in the figure differs from that given in the literature (Klevtsova et al. 1967). Besides the narrow intense absorption band of "free" hydroxyl at 3600 cm^{-1} , a band of similar intensity is observed in the region of 3480 to 3400 cm^{-1} . An additional band, typical for deformation vibrations of water, is found at 1650 - 1625 cm^{-1} . It is likely that the La(III) hydroxide precipitated by the present technique is a nonstoichiometric compound of form $\text{La}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ and that its dehydration occurs at temperatures higher than the 70°C specified in the technical literature (Chalyi 1972).

Two bands occur in the spectrum in the 1530 to 1460 and 1400 to 1355 cm^{-1} regions. These bands likely are caused by carbonate arising from CO_2 sorption by the hydroxide. The complex structure of these bands indicates the formation of hydrogen bonds between carbonate and the water present in the structure of $\text{La}(\text{OH})_3 \cdot x\text{H}_2\text{O}$. A very strong and split band in the region of 670 to 605 cm^{-1} likely can be ascribed to deformation vibrations of the nine hydroxyl ions forming the coordination polyhedron around La^{3+} . Another, more intense absorption band is found at about

400 cm^{-1} . A similar band is found in the LaOOH spectrum (Klevtsova and Klevtsov 1964). Thus, the structure of La(III) hydroxide produced for the present tests differs from those of both La(OH)_3 and LaOOH .

The valent vibration band intensities of "free" hydroxyl ions decrease sharply even with 9% Pu(IV) content. Simultaneously, the $\nu(\text{HOH})$ band widens and splits into four components. The shape of the water deformation vibration band, $\delta(\text{HOH})$, also is altered. Presumably, carbonate formation on the La(III) hydroxide displaces this band to a lower frequency region, decreases its intensity, and eliminates its fine structure. These changes manifest the effects of carbonate ion coordination.

When the Pu(IV) content in mixed hydroxide reaches about 30%, the $\nu(\text{OH})$ band practically disappears and the M-O vibration band shifts towards higher frequencies. The shift can be explained by the decrease in the interatomic metal-oxygen distance upon formation of the double hydroxide.

The most appreciable change in the mixed hydroxide IR spectra is observed at the 2:1 Pu:La ratio. As in the Pu(IV)-Fe(III) system, a very slight and wide absorption band is observed in the region of 3500 to 3200 cm^{-1} . Absorption bands for both water and hydroxyl ion deformation vibrations practically disappear. With further increase of plutonium fraction up to 10:1 Pu:La , water valent and deformation vibration bands, perturbed by hydrogen bonds, reappear in the mixed hydroxide spectra. In the region of 500 to 400 cm^{-1} , the M-O vibration band character becomes complicated and slightly more intense. Even so, the spectrum of the 10:1 Pu:La mixed hydroxide still differs from the spectrum of pure Pu(IV) hydroxide.

The IR spectra results indicate that mixed hydroxides form in the Pu(IV)-La(III) system at various component ratios. It is noted that, in contrast to the literature, absorption bands in the region of 1550 to 1350 cm^{-1} likely do not arise from carbonate formation in the precipitate but indicate OH deformation vibrations. In any case, changes in the intensity and form of these bands, as well as in the valent and deformation vibration bands of water, with changing Pu:La ratio indicate component interactions in the mixed hydroxides. As will be shown, these observations and explanations also apply to the Pu(IV)-Cr(III) and Pu(IV)-Zr(IV) systems.

3.1.7 The Pu(IV)-Cr(III) System

In Figure 3.1.8, the IR spectra of mixed Pu(IV)-Cr(III) hydroxides are presented for component ratios 10:1, 2:1, 1:1, 1:2, and 1:10. Values of $\nu(\text{HOH})$, $\delta(\text{HOH})$, $\delta(\text{OH})$, and $\nu(\text{Cr-O})$ for pure Cr(III) hydroxide were reported to be 3350, 1620, 1400, and 520 cm^{-1} , respectively. The deformation vibrations of the OH ion are observed at 2100 to 1600 cm^{-1} for the rhombohedral $\alpha\text{-CrOOH}$ and at ~ 1000 cm^{-1} for rhombic $\gamma\text{-CrOOH}$ (Cabannes-Ott 1960). Thus the IR spectra should be sensitive to reorganization of the Cr(III) hydroxide structures.

Figure 3.1.8. Infrared Spectra of Hydroxide Compounds in the Pu(IV)-Cr(III) System at Different Pu(IV):Cr(III) Ratios (NaCl matrix - approx. 210 mg)

- 1 - 10:1 (2.12 mg)
- 2 - 2:1 (2.58 mg)
- 3 - 1:1 (2.91 mg)
- 4 - 1:2 (2.34 mg)
- 5 - 1:10 (2.08 mg)

As shown in Figure 3.1.8, the form and position of the $\nu(\text{HOH})$ vibration bands remain practically unchanged with changing Pu(IV):Cr(III) ratio. The maxima also appear in a narrow interval of $3450 \pm 10 \text{ cm}^{-1}$, which indicates that the water molecules in all cases likely are associated with each other in similar manner. A wide complex band with maxima at 1148, 1075, 1060, and 980 cm^{-1} appears in the IR spectra of mixed hydroxides with small chromium content. Such splittings are typical of vibrations of different M-O bonds. Increasing the hydroxide's chromium content leads to a non-monotonous change in the spectra. Based on published findings (Milligan and Merten-Watt 1948), the changes observed in the spectrum of the mixed hydroxides at about 10% Cr are characteristic of multiphase systems. The existence of multiple phases can explain the finding of only one case (at 1:1 Pu:Cr) of M-O bond deformation vibration at 520 to 490 cm^{-1} .

The intense absorption band at about 1400 cm^{-1} may result from valent vibrations of carbonate (if CO_2 absorption occurs only at 2:1 Pu:Cr) or from deformation vibrations of the OH

group. As discussed for the analogous Pu(IV)-La(III) results, the presence of this band in only some spectra indicates that specific interactions occur between Pu(IV) and Cr(III).

3.1.8 The Pu(IV)- Zr(IV) System

Because plutonium and zirconium ions form both polymeric structures during hydrolysis and hydroxides with similar properties, formation of their mixed hydroxides was expected. The IR spectra of coprecipitated Pu(IV) and Zr(IV) hydroxides at various Pu:Zr ratios (1:10, 1:2, 2:1, and 10:1) are shown in Figure 3.1.9.

Figure 3.1.9. Infrared Spectra of Hydroxide Compounds in the Pu(IV)-Zr(IV) System at Different Pu(IV):Zr(IV) Ratios (NaCl matrix - approx. 210 mg)

- 1 - 1:10 (2.26 mg)
- 2 - 1:2 (2.18 mg)
- 3 - 2:1 (2.04 mg)
- 4 - 10:1 (1.97 mg)

The composition of zirconium hydroxide is known to be $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$. The compound consists of ZrO_2 crystallites that retain a nonstoichiometric amount of water (Blumenthal 1958). The water valent vibration band intensity decreases and shifts to shorter wavelengths with increasing plutonium content. This change indicates a change in the number of nonstoichiometric water molecules and their bonding in the mixed hydroxides. In mixed hydroxides with up to 30% plutonium content, appreciably split bands are observed at 1050 to 950 cm^{-1} in the IR spectra. These bands can be attributed to $\text{M}=\text{O}$ bond vibrations (Kondo et al. 1990). With further

increase of plutonium content, these bands practically disappear, indicating that a fundamental change in the coordination of functional groups occurs in the mixed hydroxide. Another indication of component interaction in the investigated system is given by the appearance, only for 1:2 Pu(IV):Zr(IV), of a strong absorption band in the region 1400 to 1350 cm^{-1} .

3.2 Dissolution Rates of Pu(IV) and Metal Hydroxide Precipitates

One technique for understanding the possible interaction between Pu(IV) hydroxide and other metal hydroxides is comparing the dissolution rates of the mixed hydroxides and the respective pure hydroxides. A significant difference in the rates suggests that an interaction exists between the Pu(IV) and metal hydroxides. Initial experiments have shown that the NaOH concentration used to age the precipitates has only slight influence on the rate of dissolution of pure Pu(IV) hydroxide (Figure 3.2.1).

Figure 3.2.1. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$

- 1 - Prepared in 1 M NaOH
- 2 - Prepared in 10 M NaOH

The first studied system was Pu(IV)-Ni(II) hydroxide. No differences were observed in the behaviors of pure Pu(IV) hydroxide and 1:1 molar mixture of Pu(IV) and Ni(II) hydroxides prepared in either 1 M NaOH (Figure 3.2.2) or 10 M NaOH (Figure 3.2.3). All Ni(II) reported completely to the solid phase.

Figure 3.2.2. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Ni(II) Hydroxide Prepared in 1 M NaOH [1 - pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$; 2 - 1:1 mixed Pu(IV)-Ni(II) hydroxides]

Figure 3.2.3. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Ni(II) Hydroxide Prepared in 10 M NaOH
 1 - Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$
 2 - 1:1 mixed Pu(IV)-Ni(II) hydroxide

Similar results were obtained for the Pu(IV)-Al(III) system. However, only trace amounts of aluminum were detected in the precipitate, even in those precipitates prepared in relatively dilute NaOH. Because of the virtual absence of an Al(III) solid phase, no difference was revealed in the kinetics of dissolution between pure Pu(IV) hydroxide and the precipitate obtained in the Pu(IV)-Al(III) system.

The Pu(IV)-Fe(III) hydroxide system also was studied. The dissolution rates of equimolar Pu(IV) and Fe(III) hydroxide mixtures treated in 1 and 10 M NaOH were found to be considerably greater than those of similarly prepared pure Pu(IV) hydrous oxide (Figure 3.2.4). Comparable results were obtained for the Pu(IV)-Cr(III) hydroxide system. The dissolution rate of pure treated Pu(IV) hydrous oxide is markedly lower than the dissolution rate of the mixed compositions (Figure 3.2.5). Additional tests showed that the dissolution rates of the mixed Pu(IV)-Fe(III) and Pu(IV)-Cr(III) hydroxide compositions treated in different concentration alkalis are similar. Thus, it can be supposed that Fe(III) and Cr(III) inhibit Pu(IV) hydroxide phase formation, at least in cases of molar ratio Pu(IV):M(III) less than 1.

Figure 3.2.4. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Fe(III) Hydroxides Prepared in 1 and 10 M NaOH
 1 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from 1 M NaOH
 2 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from 10 M NaOH
 3 - Pu(IV)-Fe(III) hydroxides from 1 M NaOH
 4 - Pu(IV)-Fe(III) hydroxides from 10 M NaOH

Figure 3.2.5. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Cr(III) Hydroxides Prepared in 1 and 10 M NaOH
 1 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from 1 M NaOH
 2 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from 10 M NaOH
 3 - Pu(IV)-Cr(III) hydroxides from 1 M NaOH
 4 - Pu(IV)-Cr(III) hydroxides from 10 M NaOH

It is known that Co(II) hydroxide can be oxidized by atmospheric oxygen to Co(III) . Therefore, the precipitate formed by alkali treatment of acidic Pu(IV) and Co(II) mixtures quickly acquires the brown color typical of Co(III) hydroxide. It is also reasonable to suppose that plutonium, a multivalent element, might catalyze the oxidation of Co(II) to Co(III) . Like the Fe(III) and Cr(III) mixed hydroxide systems, acceleration of plutonium dissolution in the Pu(IV)-Co(III) mixed hydroxide systems again was observed (Figure 3.2.6).

The dissolution rates of equimolar Pu(IV)-Zr(IV) mixed hydroxide and of pure Pu(IV) hydrous oxide are not significantly different after treatment in 1 M NaOH; however, a slight effect was observed for the systems treated in 4 M and 10 M NaOH (Figure 3.2.7). It is possible that the low rate of Pu(IV)-Zr(IV) mixed hydroxide dissolution is caused by rapid aging of the solid phase with the concurrent formation of the mixed plutonium and zirconium hydrous dioxide.

Figure 3.2.6. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Co(III) Hydroxide Prepared in 1 M NaOH
 1 - Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$
 2 - 1:1 mixed Pu(IV)-Co(III) hydroxide

Figure 3.2.7. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-Zr(IV) Hydroxide Prepared in 4 M NaOH
 1 - Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$
 2 - 1:1 mixed Pu(IV)-Zr(IV) hydrous oxide

The dissolution kinetics in hydrochloric acid also were tested of mixed Pu(IV)-U(VI) and Pu(IV)-La(III) compositions prepared in alkaline media. The experiments again showed the lower dissolution rate of pure Pu(IV) hydrous oxide compared with the respective mixed products (Figures 3.2.8 and 3.2.9, respectively).

In summary, the dissolution kinetics in hydrochloric acid show that, in all cases in which a kinetic effect was observed [i.e., for Fe(III), Cr(III), Co(III), La(III), Zr(IV), and U(VI)], plutonium dissolution from the mixed compositions proceeded faster than the analogous dissolutions of pure Pu(IV) hydrous oxide. This means that the PuO₂ structure was not preserved in the coprecipitation with the various metal ions or that the respective metal ions inhibited the formation of the PuO₂ structure during the homogeneous precipitation of the compound. For mixed systems with Ni(II) and Al(III), however, Pu(IV) apparently precipitated as the pure hydrous oxide.

Seemingly, there is little similarity between the alkaline chemistry of Fe(III), Cr(III), and Co(III), on one hand, and the diverse alkaline chemistries of La(III), Zr(IV), and U(VI). Only the low solubilities of their respective hydroxide compounds and their abilities to form inorganic polymers are in common for all the mentioned elements. These qualities seemingly control the formation of mixed hydroxides with Pu(IV).

Subsequent experiments were conducted to study the leaching, by carbonate solutions, of Pu(IV) from homogeneously precipitated solids containing U(VI), Fe(III), or Al(III). The precipitates were obtained from 1 M HNO₃ solutions by treatment with excess NaOH and subsequent water washing. The compositions of the test samples are given in Table 3.2.1.

Figure 3.2.8. Kinetic Dissolution Curves of Pure PuO₂·xH₂O and Pu(IV)-U(VI) Coprecipitate Prepared in 1 M NaOH
 1 - Pure PuO₂·xH₂O
 2 - 1:1 mixed Pu(IV)-U(VI)

Figure 3.2.9. Kinetic Dissolution Curves of Pure $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and Pu(IV)-La(III) Hydroxide Prepared in 1 and 10 M NaOH

- 1 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in 1 M NaOH
- 2 - $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ from 10 M NaOH
- 3 - Pu(IV)-La(III) hydroxides in 1 M NaOH
- 4 - Pu(IV)-La(III) hydroxides in 10 M NaOH

Table 3.2.1. Composition of Samples Prepared for Carbonate Dissolution

Sample Number	Solids Content, mg			
	Pu(IV)	U(VI)	Fe(III)	Al(III)
1	0.020	20	0	0
2	0.020	20	0	0.9
3	0.020	20	1.8	0
4	0.020	20	1.8	0.9

The samples were placed in test tubes and aliquots of 0.5 or 0.25 M NaHCO_3 added. After 20 minutes of intense agitation, the mixtures were centrifuged and supernates analyzed by radiometry. In preliminary experiments without plutonium, U(VI) dissolved very quickly and completely from precipitates of the same composition in similar bicarbonate solutions.

The precipitates in samples 1 and 2 dissolved completely in bicarbonate solution, and about 95% of the plutonium reported to the solution phase. A portion of the solid phase in samples 3 and 4 remained undissolved, and only about 5 to 8% of the plutonium dissolved. Similar results were obtained for both 0.25 and 0.5 M NaHCO_3 . Heating samples 3 and 4 in the bicarbonate solution did not increase plutonium dissolution. These results point to the formation of strong Pu-O-Fe bonds in the mixed Pu(IV) and Fe(III) hydroxide that are stable to carbonate leaching.

3.3 Sedimentation Rate of Pu(IV) and Fe(III) Hydroxide Precipitates

Table 3.3.1 contains information on the sedimentation of 1:1 mixed Pu(IV)-Fe(III) hydroxide in water and various alkaline solutions simulating Hanford Site tank waste. The mixed hydroxide precipitates were aged 1 hour in 70°C 0.2 M NaOH.

Data on the sedimentation kinetics of 1:1 mixed Pu(IV)-Fe(III) hydroxide precipitate aged 1 hour in 70°C 1 M NaOH are presented in Table 3.3.2. The sedimentation process was performed in the same media as in the previous experiments.

Data for 1:1 mixed Pu(IV)-Fe(III) aged at 70°C for one hour in 3M NaOH are given in Table 3.3.3. The sedimentation data show that increasing the alkali concentration used for thermal treatment (aging) of the precipitates decreases their sedimentation rates and decreases their densities. These phenomena indicate that additional hydration of the solid phase occurs in the more concentrated alkalis.

Table 3.3.1. Sedimentation of Mixed Pu(IV)-Fe(III) Hydroxide Aged in 0.2 M NaOH

In H ₂ O		In 1 M NaOH	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.75	0	1.75
1	0.50	1	0.83
2	0.45	2	0.60
3	0.40	3	0.54
5	0.38	5	0.45
10	0.36	10	0.43
30	0.35	30	0.40
60	0.35	60	0.35
after centrifugation	0.18	after centrifugation	0.18
In 3 M NaOH		In 3 M NaOH + 3 M NaNO ₃	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.75	0	1.75
2	0.60	3	0.60
3	0.50	5	0.50
4	0.45	10	0.43
5	0.42	30	0.35
10	0.40	60	0.35
30	0.35		
after centrifugation	0.19	after centrifugation	0.19

Table 3.3.2. Sedimentation of Mixed Pu(IV)-Fe(III) Hydroxide Aged in 1 M NaOH

In H ₂ O		In 1 M NaOH	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.80	0	1.80
1	1.52	1	1.45
2	1.35	2	1.10
3	1.20	3	0.92
4	1.11	4	0.82
5	1.05	5	0.76
10	0.89	10	0.63
30	0.81	30	0.60
60	0.81	60	0.60
after centrifugation	0.25	after centrifugation	0.25
3 M NaOH		In 3 M NaOH + 3 M NaNO ₃	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.80	0	1.80
4	0.70	5	0.58
5	0.58	10	0.50
10	0.50	20	0.45
20	0.44	30	0.44
30	0.44	40	0.42
after centrifugation	0.25	after centrifugation	0.25

Sedimentation rates for 1:1 mixed Pu(IV)-Fe(III) solids obtained by homogeneous precipitation of both components and of the individual components, precipitated separately and then mixed, are presented in Figure 3.3.1. Because the precipitates' sedimentation rates and final centrifuged volumes (0.19 mL for the homogeneous coprecipitate and 0.33 mL for the mixed solids) differ considerably, an interaction apparently takes place between the components in homogeneous solution at the stage of hydroxide formation. For separately precipitated and then mixed hydroxides, the rate of the precipitate front movement is similar to that of pure Fe(III) hydroxide.

A marked layering also occurs upon settling for Pu(IV) and Fe(III) hydroxides that were separately precipitated and then mixed (Figure 3.3.2, curve 1). The heavier Pu(IV) hydrous oxide particles settle more rapidly than the Fe(III) hydroxide particles with the plutonium concentrating on the bottom. In contrast, hydroxides freshly prepared from homogeneous solution settle quickly without separation as shown by the fairly uniform volumetric distribution of the Fe and Pu components (Figure 3.3.2, curve 2). Increase in iron concentration near the bottom after 100 days of aging of coprecipitated Pu(IV) and Fe(III) mixtures at room temperature obviously is connected with a segregation process and the formation of a dense crystalline iron

Table 3.3.3. Sedimentation of Mixed Pu(IV)-Fe(III) Hydroxide Aged in 3 M NaOH

In H ₂ O		In 1 M NaOH	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.75	0	1.75
10	1.70	10	1.67
30	1.53	30	1.56
60	1.34	60	1.33
90	1.22	120	1.09
150	1.15		
24 hours	1.10	24 hours	1.10
after centrifugation	0.35	after centrifugation	0.30
3 M NaOH		In 3 M NaOH + 3 M NaNO ₃	
Time, min	Volume, mL	Time, min	Volume, mL
0	1.80	0	1.80
10	1.75	30	1.54
30	1.58	60	1.15
60	1.37	120	0.92
90	1.29	150	0.89
120	1.15		
150	1.10		
24 hours	1.00	24 hours	0.85
after centrifugation	0.30	after centrifugation	0.30

Figure 3.3.1. Sedimentation Curves for Solids Aged 1 Hour in 70°C 0.2 M NaOH
 1 - Pure Fe(III) hydroxide
 2 - 1:1 Pu(IV)-Fe(III) hydroxide, homogeneously precipitated from solution
 3 - 1:1 Pu(IV)-Fe(III) hydroxide, obtained from separately precipitated and then mixed hydroxides

Figure 3.3.2. Fe and Pu Vertical Distribution in Sedimented Layers

- 1 - 1:1 Pu(IV)-Fe(III) hydroxide obtained from separately precipitated and then mixed hydroxides
- 2 - 1:1 Pu(IV)-Fe(III) hydroxide homogeneously precipitated from solution, no aging
- 3 - 1:1 Pu(IV)-Fe(III) hydroxide homogeneously precipitated from solution, aged 100 days
- 4 - 1:1 Pu(IV)-Fe(III) hydroxide homogeneously precipitated from solution, 1 hr thermal treatment

oxide (Figure 3.3.2, curve 3). It was also found that the homogeneously precipitated mixed Pu(IV)-Fe(III) hydroxide will segregate after one hour's thermal treatment. In this case the lower layer becomes enriched in plutonium (Figure 3.3.2, curve 4).

3.4 Mössbauer Spectroscopy Study of the Interaction of Pu(IV) and Iron Hydroxides

Many papers describe Mössbauer spectroscopy studies of pure and mixed iron hydroxides but the results are somewhat contradictory. For example, it was indicated that α -FeO(OH) at 300°C gives a spectrum with magnetic hyperfine splitting corresponding to an inner magnetic field of 360 ± 15 kOersted (Nakamura and Shimizu 1964). According to another source, the spectrum of α -FeO(OH) at room and liquid nitrogen temperature exhibits a doublet caused by quadrupole splitting in the absence of magnetic splitting (Taraban 1995). Therefore, we attempted to verify these results by first preparing pure α - and γ -FeO(OH) and α - and γ -Fe₂O₃ according to published methods. We succeeded only for the more stable α -forms of these compounds.

The α -FeO(OH) was identified by x-ray diffraction. Its Mössbauer spectrum (Figure 3.4.1) had the parameters (in mm/sec): isomeric shift (δ) 0.62, quadrupole splitting (Δ) 0.62, line width (Γ) 0.53 mm/sec. Some ambiguity exists in the literature regarding the thermal stability, method

of preparation, and identity of Fe(III) hydroxide compounds. Our results show that both α -FeO(OH) and α -Fe₂O₃ give Mössbauer spectra. In fact, α -FeO(OH) exhibits at least two forms, one of which is active only at low temperatures. This difference can be attributed to the extent of crystallinity of this oxyhydroxide. In agreement with previous studies for the pure Fe(III) system (Ujihira and Ohyabu 1978), we observed the transformation of amorphous primary hydroxide products of Fe(III) into α -FeO(OH) and α -Fe₂O₃ during the storage of pure and mixed Fe(III)-Pu(IV) samples. Pure or mixed Fe(III)-Pu(IV) hydroxides precipitated at different molar ratios in 1 to 8 M NaOH at 20 to 50°C in each case formed amorphous materials that do not have a room temperature Mössbauer spectrum. However, at liquid nitrogen temperature, spectra with broad doublets are observed (Figure 3.4.2). In the absence of Pu(IV) quadrupole splitting, the spectra are similar to those exhibited by crystalline α -FeO(OH) at room temperature. Splitting in spectra of the mixed Fe(III)-Pu(IV) hydroxides is larger and does not change by varying the Pu(IV):Fe(III) molar ratio from 4:1 to 1:8 (Table 3.4.1). It is postulated that, in mixed hydroxides, the oxygen environment surrounding Fe³⁺ is less symmetric than in pure Fe(III) hydroxide. At the same time, the isomeric shifts of pure α -FeO(OH) and the mixed oxides are similar, confirming the constancy of effective charge on the Fe(III) ions. The change of isomeric shifts with decreasing temperature is attributed to the so-called temperature shift.

Figure 3.4.1. Mössbauer Spectra at 300K of α -FeO(OH)

1 - Pure α -FeO(OH)

2 - A mixture of α -FeO(OH) with α -Fe₂O₃

Figure 3.4.2. Mössbauer Spectra at 80K of Amorphous Pu/Fe Hydroxides Prepared at 20°C in 1 M NaOH (Pu:Fe mole ratio shown on the right)

Table 3.4.1. Mössbauer Parameters at 80K of Freshly Prepared of Mixed Hydroxides of Fe(III) and Pu(IV) at Various Mole Ratios

Pu(IV):Fe(III) Mole Ratio	Mössbauer Parameters, mm/s		
	Isomeric Shift, δ	Quadrupole Splitting, Δ	Experimental Line Width, Γ
0:1	0.71	0.66	0.56
1:1	0.71	0.74	0.49
1:2	0.72	0.75	0.51
1:4	0.71	0.76	0.54
1:8	0.71	0.75	0.56
4:1	0.71	0.75	0.52

It was found that initially amorphous samples that are not Mössbauer active or which exhibit only the $\alpha\text{-Fe}_2\text{O}_3$ line at room temperature will exhibit the $\alpha\text{-FeO(OH)}$ doublet (in pure samples) or a doublet with larger quadrupole splitting (in mixed hydroxides) after several days of storage at room temperature. Such observations may be explained by an increase in $\alpha\text{-FeO(OH)}$ crystallite size during storage. For samples prepared under conditions in which only $\alpha\text{-Fe}_2\text{O}_3$ is stable (for example, those undergoing several hours of hydrothermal treatment at 200°C in 1 M NaOH), some fraction of the Fe(III) still is present as the amorphous hydroxide. With time, the amorphous material crystallizes and will then produce the Mössbauer spectrum.

No lines were observed in a Mössbauer spectrum obtained at room temperature for a Pu-Fe hydroxide precipitate of mole ratio 1:2.5 prepared in 1 M NaOH at 100°C . After nine days of storage at room temperature, however, the Mössbauer spectrum consisted of a doublet with large quadrupole splitting and a sextet caused by hyperfine magnetic splitting (Figure 3.4.3). The inner magnetic field strength was 357 kOersted, correlating well with values observed for $\alpha\text{-FeO(OH)}$ (Danon 1968). The Mössbauer spectra and associated parameters for $\alpha\text{-FeO(OH)}$ and mixed Fe(III)/Pu(IV) hydroxides aged at room temperature are shown, respectively, in Figure 3.4.4 and Table 3.4.2.

Figure 3.4.3. Mössbauer Spectrum at 300K of 1:2.5 Pu:Fe Mixed Hydroxide after Nine Days of Aging in Air at Room Temperature (no Mössbauer spectrum found immediately after preparation)

Figure 3.4.4. Mössbauer Spectra at 300K of Metal Hydroxides before and after Room Temperature Aging in Air

- 1 - Pu:Fe = 2:1, 1 M NaOH, 100°C, 9 days; freshly prepared sample gave no spectrum
- 2 - Fe(III) without Pu, 4 M NaOH, 140°, freshly prepared; lines correspond to α -Fe₂O₃
- 3 - Same as 2 but after 4 days; central doublet parameters correspond to those of α -FeO(OH)
- 4 - Pu:Fe = 1:1, 4 M NaOH, 180°C, 10 days; freshly prepared sample gave spectrum similar to (2)

Table 3.4.2. Mössbauer Spectra Parameters at 300K of α -FeO(OH) and Mixed Fe(III)/Pu(IV) Hydroxides Aged at Room Temperature

Composition and Preparation Conditions	Aging Time, days	Other Phases	Mössbauer Parameters, mm/s		
			δ	Δ	Γ
α -FeO(OH)	--	None	0.62	0.62	0.53
Pu:Fe = 0:1, 1 M NaOH, 100°C	9	α -Fe ₂ O ₃	0.59	0.62	0.53
Pu:Fe = 1:1, 4 M NaOH, 180°C	11	α -Fe ₂ O ₃	0.62	0.85	0.51
Pu:Fe = 1:2.5, 1 M NaOH, 100°C	9	None	0.63	0.89	0.61
Pu:Fe = 2:1, 1 M NaOH, 100°C	9	None	0.63	0.88	0.60
Pu:Fe = 1:1, 1 M NaOH, 200°C	6	α -Fe ₂ O ₃	0.62	0.84	0.52

From these data, it is evident that in the course of hydrolytic formation of mixed Fe(III)-Pu(IV) hydroxides, homogeneous component distribution occurs on a molecular level, at least in the case of FeO(OH). Interaction of Pu(IV) hydrous oxide with Fe₂O₃ phases was not observed.

In further tests, pure Fe(III) and Pu(IV) hydroxides were prepared separately in 1 M NaOH and then mixed at a 1:1 Pu:Fe mole ratio. This mixture was periodically agitated for five hours at room temperature. The mixture's Mössbauer spectrum showed only the doublet of pure α -FeO(OH). Interaction of the components evidently did not occur in this short time scale. However, after four days in storage, the mixture exhibited a Mössbauer spectrum doublet with large quadrupole splitting. This confirms that separate solid phase precipitates of Fe(III) and Pu(IV) interact in the blended solid phase system to slowly form a mixed hydroxide.

In additional tests, pure Fe(III) hydroxide and a mixed Pu(IV)/Fe(III) compound (Pu:Fe mole ratio of 1:1) were separately aged five hours in 1 M NaOH at 220°C to reach dehydration. The samples' Mössbauer spectra are presented in Figure 3.4.5. Based on these spectra, the mole ratio α -FeO(OH): α -Fe₂O₃ was estimated to be 1:9 for the pure Fe(III) hydroxide and 1:3 for the Pu(IV)/Fe(III) mixed hydroxide. It is evident that interaction between Fe(III) and Pu(IV) hydroxides inhibits the dehydration process.

Figure 3.4.5. Mössbauer Spectra at 80K of Metal Hydroxides after Five Hours of Aging in 1 M NaOH at 220°C
1 - Fe(III) without Pu
2 - Pu(IV):Fe(III) = 1:1

3.5. Thermal and X-Ray Diffraction Studies of Mixed Systems Containing Pu(IV) Hydrous Oxide

The thermal behavior of homogeneously precipitated hydroxides from mixed acid solutions of Pu(IV) with Ni(II), Fe(III), Al(III), or U(VI) at a 1:1 Pu(IV):metal mole ratio was studied by differential thermal analysis. In all cases, the thermal analysis scans were superpositions of the scans of the respective individual hydroxides [Figure 3.5.1 illustrates these observations with data from Pu(IV)-Fe(III)]. For this reason, the thermal properties of the mixed systems were not studied further.

Figure 3.5.1. Thermal Analysis Scans of Hydroxide Compounds Precipitated in 1 M NaOH and Aged 1 Hour at 100°C

1 - Pure Fe(OH)₃ · xH₂O

Initial weight 49.481 mg

Final weight 34.686 mg

Rate of heating 2.5°C/min

2 - Homogeneously precipitated 1:1 Pu:Fe

Initial weight 47.354 mg

Final weight 39.967 mg

Rate of heating 2.5°C/min

The x-ray diffraction patterns of the mixed hydroxides are fixed in many cases by the nature of the Pu(IV) hydrous oxide. After some aging, this product consists of small PuO_2 crystallites. The mass percentage of the metal hydroxide coprecipitated with the Pu(IV) hydrous oxide in mixed samples is low at Pu:metal molar ratios of 1:1 (especially for low atomic weight aluminum). Furthermore, plutonium has a high atomic number and thus is an effective x-ray absorber. Therefore, even in mechanical mixtures of Pu(IV) with other metal hydroxides, the lighter metal's x-ray diffraction pattern may be masked. The mixed systems of Pu(IV) with Al(III), Fe(III), and Ni(II) were studied by x-ray diffraction techniques. In mixed hydroxides freshly precipitated at room temperature, no definite x-ray diffraction lines were observed. The x-ray diffraction patterns of materials formed by heating these samples above 100°C in air or alkaline solution showed lines of oxyhydroxides or oxides like $\text{AlO}(\text{OH})$, $\text{FeO}(\text{OH})$, and Fe_2O_3 . Only one system, Pu(IV)-Ni(II), exhibited the diffraction pattern of the metal hydroxide together with that of PuO_2 . This was observed by aging the sample in 1 M NaOH at 155°C for one hour (Figure 3.5.2). The high crystallinity of $\text{Ni}(\text{OH})_2$ and its relatively high thermal stability (Chalyi 1972) allowed this hydroxide to be observed.

The crystallographic results confirm the formation of mixed hydroxides in alkaline precipitation of Pu(IV) with the studied metals. In these limited tests, the mixed hydroxides apparently decompose into their respective components by hydrothermal aging at elevated temperatures. However, further investigations are required to enhance understanding of this process.

3.6 Interaction of Pu(VI) with Hydroxides and Oxides

No interaction of Pu(IV) or Pu(VI) with Fe_2O_3 was observed in alkaline hydrothermal treatment. As noted in Section 3.4, the Mössbauer spectra of Fe_2O_3 remained unchanged in samples prepared under various conditions in the presence of Pu(IV). Because Mössbauer spectroscopy is very sensitive to change in the coordination sphere of iron, the interaction of Pu(IV) with Fe_2O_3 must be negligible. The interaction of Pu(VI) with Fe_2O_3 also was found to be negligible.

Figure 3.5.2. Powder X-Ray Diffraction Pattern of the Mixed Pu(IV)-Ni(II) Hydroxide (top) and $\text{Ni}(\text{OH})_2$ (bottom)

The interactions of Pu(VI) with hydroxides of Al(III), Fe(III), and Cr(III) also were insignificant. The hydroxides of Fe(III) and Cr(III) were precipitated and washed by 1 M NaOH at room temperature; Fe₂O₃ was prepared by heating of Fe(III) hydroxide at 220°C for about five hours in 1 M NaOH; and Al(III) hydroxide was precipitated and washed by dilute alkali at room temperature. To each precipitate, 5x10⁻³ M Pu(VI) in 1 M NaOH was added and the mixtures were stirred periodically at room temperature. The change of Pu(VI) concentration in the centrifuged supernatant was determined by spectrophotometry. Only in the case of Cr(III) hydroxide was a change in Pu(VI) concentration observed. This change, a decrease, was attributed to a relatively slow oxidation of Cr(III) to CrO₄²⁻. A slow dissolution of precipitate was observed for Al(III) hydroxide, as expected by its amphoterism, to form the aluminate anion.

The lack of interaction of Pu(VI) with the metal hydroxides and oxides would be expected because the ionic form of Pu(VI) in alkaline solutions, PuO₂(OH)₄²⁻, does not change in the range of 0.5 to 15 M NaOH (Budantseva et al. 1997). The hydroxide-coordinated Pu(VI) solution species should not interact with hydrolyzable cations in the presence of high OH⁻ concentrations.

4.0 References

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