

INCORPORATION OF RADIOACTIVE CONTAMINANTS INTO PYROAURITE-LIKE PHASES BY ELECTROCHEMICAL SYNTHESIS

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Abstract—During electrochemical remediation of radionuclide, ²³⁵U, ²³⁸U, and ⁹⁹Tc-contaminated aqueous solutions, pyroaurite-like phases, ideally [M(II)M(III)(OH)₆CO₃·4H₂O] where M = Fe, were synthesized following coprecipitation with iron from metal iron electrodes. The effect of radionuclides on the transformation of amorphous precipitates to crystalline pyroaurite-like phases was investigated using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray analysis, Fourier-transform infrared (FTIR) spectroscopy, and fluorescence spectroscopy. The synthetic iron carbonate hydroxide phases showed primary XRD peaks at 0.7 and 0.35 nm and FTIR spectra that indicated the presence of a brucite-like sheet structure with carbonate anions occupying the interlayer. Divalent and trivalent iron, eroded from the electrode, occupies the octahedral sites of the brucite-like sheets. The carbonate anions in the interlayer balance the excess positive charge from isomorphous substitution of the Fe²⁺ or Fe³⁺ by reduced uranium (U⁴⁺) and technetium (Tc⁴⁺). Because of the lower solubility associated with crystalline phases than amorphous phases, incorporation of radioactive contaminants into pyroaurite-like phases by electrochemical syntheses represents a more effective approach for removing U and Tc from contaminated aqueous solutions than traditional technologies.

Key Words—Coprecipitation, Groundwater Remediation, Pyroaurite, Technetium, Uranium, Zero-Valent Iron.

INTRODUCTION

A variety of remedial technologies are known to remove heavy metals and radionuclides from contaminated waters (Sorg, 1990; Smith, 1996), including coprecipitation of radionuclides in water with Fe²⁺ through addition of Fe(II) salts (Lee and Bondietti, 1983). An electrochemical process has been applied recently to force coprecipitation of metals and radionuclides from contaminated waters without the addition of inorganic salts (Brewster and Passmore, 1994; Roh *et al.*, 1996). These studies showed that the electrochemical process has several advantages: (1) no chemical addition is required, (2) no secondary waste treatment is required, and (3) reaction rates may be controlled by applied current. In addition, the precipitates can be converted from an amorphous phase to crystalline pyroaurite-type phases. These phases may be synthesized through chemical mixing of Al-, Mg-, and Fe-rich compounds, although an appropriate water chemistry is vital to the formation of the pyroaurite-type compounds. To date, the influence of temperature, pH, various organic acids, silicate, and common anions (CO₃²⁻, Cl⁻, NO₃⁻, and SO₄²⁻), and the presence of Al³⁺, Mn²⁺, Mn³⁺, Cu²⁺, Zn²⁺, Ni²⁺, Co²⁺, and Ti⁴⁺ were investigated (Bish, 1977). Pyroaurite-type phases form when metal iron corrodes in the presence of O₂

and when Fe(III)-rich oxide-hydroxides, such as ferrihydrite or lepidocrocite (γ -FeOOH), are reductively dissolved through reaction with Fe²⁺ or FeOH⁺ at pH values above 6.5 (Taylor, 1980; Hansen, 1989). Pyroaurite-type phases transform to goethite (α -FeOOH), lepidocrocite (γ -FeOOH), maghemite (Fe₂O₃), or magnetite (Fe₃O₄) depending on the rate of oxidation and dehydration (Hansen *et al.*, 1994).

Pyroaurite-group minerals are composed of positively charged principal sheets interleaved with sheets of anions and H₂O molecules. The principal sheet in pyroaurite-group minerals has a brucite-like trioctahedral arrangement. Isomorphous substitution of divalent cations in the brucite-like sheet by trivalent cations creates a positive charge that is counterbalanced by an interlayer sheet of anions (mostly carbonate in natural materials), which lies parallel to the brucite-like sheet (Brown, 1980).

Pyroaurite-type mineral precipitation under reducing conditions may act as a sink for certain heavy metals and phosphate by their incorporation into the hydroxide layers and interlayers, respectively (Myneni *et al.*, 1997). In anoxic soils and sediments, pyroaurite-type minerals may also reduce nitrite or nitrate to ammonium and dechlorinate chlorinated organic compounds, at rates similar to or exceeding microbial reduction rates (Hansen *et al.*, 1994, 1996; Erbs *et al.*, 1999). Thus, pyroaurite-type phases are considered a possible important reductant for nitrate and heavy metals in subsoils, sediments, or aquifers where microbiologically mediated reduction rates are slow.

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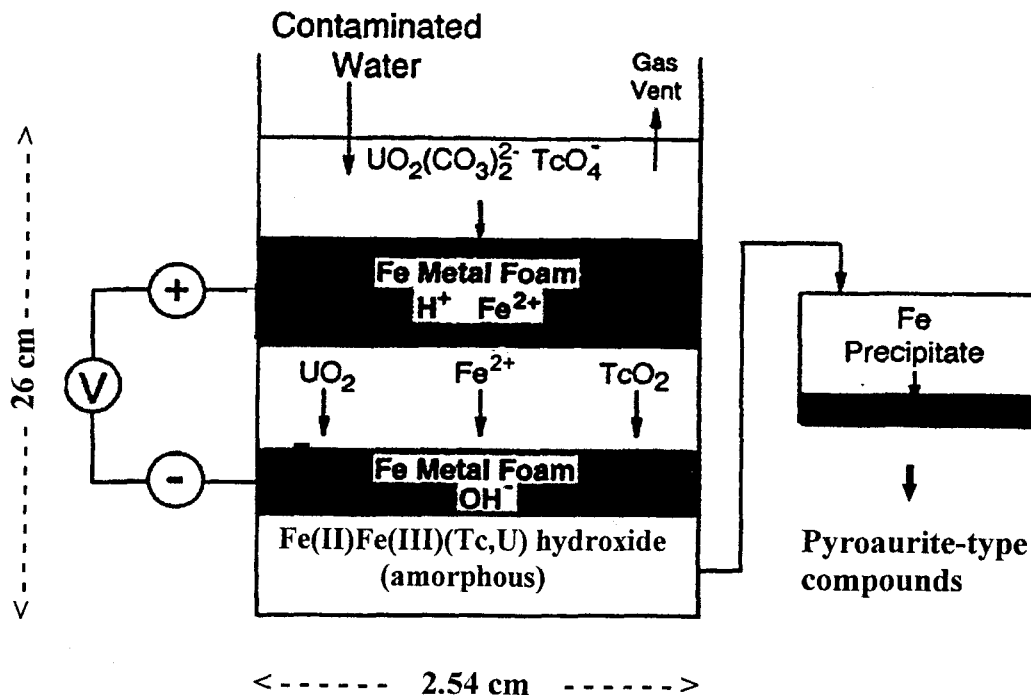


Figure 1. Schematic diagram showing the electrochemical system.

The objectives of this study were to characterize the products of an electrochemical process to synthesize pyroaurite-like phases and to understand the effect of water chemistry on the initial precipitation and subsequent phase transformation.

MATERIALS AND METHODS

The following four solutions were prepared to precipitate iron-bearing phases by an electrochemical process: (1) uranyl carbonate [$\text{UO}_2(\text{CO}_3)_2^{2-}$]: 5 mL of uranyl-nitrate [$\text{UO}_2(\text{NO}_3)_2^{2-}$] solution were added to 9 mL of 0.5 M sodium carbonate and pertechnetate (TcO_4^-) solution diluted with tap water (200 mL) to produce a final ^{235}U concentration equal to 2300 mg L^{-1} and a Tc concentration of $7 \times 10^{-6} \text{ mg L}^{-1}$; (2) cobaltic carbonate: oxidation of a cobaltous salt (2 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was placed in sodium bicarbonate (2 mM NaHCO_3) (Young, 1961); (3) 2 mM $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ solution; and (4) 2 mM Na_2CO_3 . In addition, uranyl-nitrate [$\text{UO}_2(\text{NO}_3)_2^{2-}$] solution (^{235}U concentration equal to 2300 mg L^{-1}) was used to determine anion effects on precipitation of iron-bearing phases by the electrochemical process. Solution samples and precipitates containing ^{235}U and ^{99m}Tc were analyzed using a high-purity intrinsic germanium gamma-ray detector equipped with a Nuclear Data Model 6700 microprocessor programmed in 4096 channels (Cutshall and Larsen, 1980). The counting error (2σ) was maintained of $<2\%$ for the analysis of each solution. For the pertechnetate anion, sodium pertechnetate

($^{99m}\text{TcO}_4^-$, half life = 61 d) purchased from Du Pont NEN Products (Boston, Massachusetts) was used in these experiments because the fission product ^{99}Tc constitutes a potential long-term environmental hazard owing to its long half-life ($2.13 \times 10^5 \text{ y}$).

Each of the four solutions was added sequentially to the electrochemical column to coprecipitate radionuclides and heavy metals. The electrochemical column (2.54-cm diameter and 26-cm long) had two iridium-coated titanium-oxide electrodes (anode and cathode), and both electrodes were in direct contact with 9 g "Fe⁰ foam" (Cercona of America, Inc., Dayton, Ohio). The "Fe⁰ foam" has the following characteristics: (1) 92% Fe⁰ and 8% aluminosilicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); (2) 0.9-g cm^{-3} bulk density; and (3) $0.5\text{-}1 \text{ m}^2 \text{ g}^{-1}$ estimated specific-surface area. The Fe⁰ is composed of mainly metal iron (Fe⁰) with Fe_2SiO_4 (fayalite) and FeAl_2O_4 (hercynite). Both electrodes were connected to an external power supply (Figure 1). Solutions were pumped from the container open to the atmosphere to the column using a MasterFlex Digi-Staltic pump (Cole-Parmer, Vernon Hills, Illinois) at a flow rate of 3.24 mL min^{-1} as determined by measuring the discharge rate. A direct current (DC) power supply (30 V/11 mA) was used to accelerate the dissolution of the "Fe⁰ foam". Oxidation of the Fe⁰ (*i.e.*, corrosion) at the electrodes causes the reduction of the target contaminants, thereby converting these contaminants to less soluble forms. The contaminants are then coprecipitated from solution with dissolved Fe. The precipitate was left to age in the treated

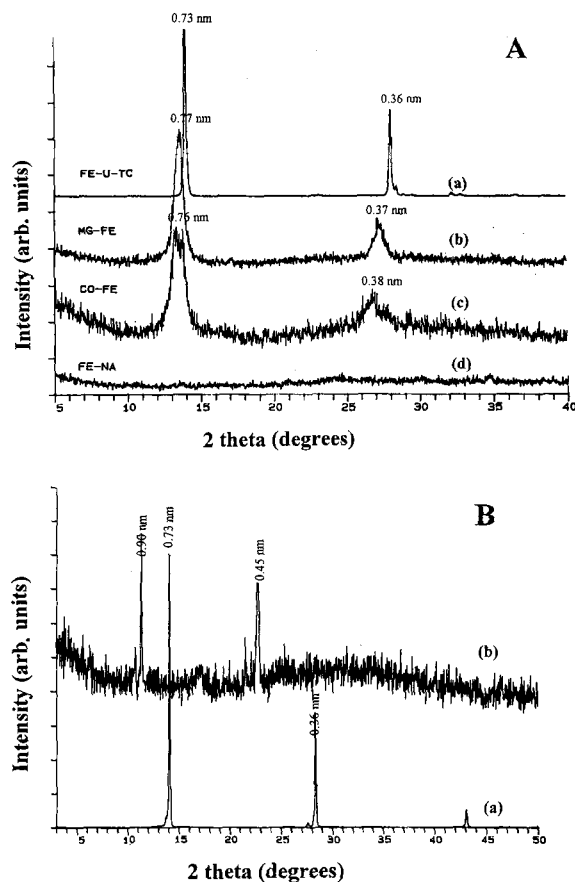


Figure 2. (A) X-ray diffraction patterns of the crystalline precipitates: (a) U, Tc, Fe-rich carbonates, (b) Mg, Fe-rich carbonates, (c) Co, Fe-rich carbonates, and (d) Na, Fe-rich carbonates; (B) XRD patterns of U, Tc, Fe-rich carbonates: (a) before glycerol treatment and (b) after glycerol treatment.

solution in a sealed glass bottle without headspace at room temperature ($\sim 25^{\circ}\text{C}$). A small portion of each precipitate was sampled periodically for chemical analysis in the first month of aging. The pH measurements used a combination of pH electrode and an ORION EA 920 expandable ion analyzer (Orion Research, Beverly, Massachusetts), standardized with pH buffer 7 and the appropriate buffer of either pH 4 or pH 10. Eh values were measured using platinum micro-electrodes (Microelectrodes, Inc., Londonerry, New Hampshire). Precipitates in each sample were collected on a 0.45- μm Millipore filter and washed three times with deionized water prior to characterization.

Coprecipitated phases were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, Fourier-transform infrared (FTIR) spectroscopy, and fluorescence spectroscopy to identify phases and to determine the chemical composition and morphology of the precipitates. Well-crystallized phases were solvated with glycerol at room temperature for 12 h and 180°C for

2 h for XRD examination (Koch and Hansen, 1996). X-ray diffraction analyses were performed using a Scintag XDS2000 diffractometer (Scintag Corporation, Sunnyvale, California) equipped with $\text{CoK}\alpha$ radiation (45 kV, 40 mA) at scan rate at $2^{\circ}2\theta/\text{min}$. A JEOL JSM-35CF (Tokyo, Japan) SEM (20 kV) was used to determine morphology of the coprecipitated forms. EDX analysis determined the elemental composition of each precipitate.

Infrared spectra of synthesized phases were obtained with a FTIR (Nicolet Magna-IR 760 spectrometer, Madison, Wisconsin) with a spectral range from 4000 to 400 cm^{-1} . The pressed-pellet technique was used to prepare samples for infrared examination by mixing 2 mg of the synthetic with 200 mg of KBr in an agate mortar prior to forming a 12-mm diameter KBr disk by pressing. In addition, a fluorescence spectrometer was used to probe the oxidation state of U in the precipitates. A pulsed nitrogen laser (Model 165, Spectra Physics, Mountain View, California) was used as the excitation source. This laser operated at a wavelength of 337 nm with a pulse duration of 5 ns. Pyroaurite-like phases were air-dried for 2 d and their steady-state luminescence spectra were measured by a fiber-optic probe (Dai *et al.*, 1996; Gu *et al.*, 1998). Steady-state luminescence spectra of uranyl-carbonate and uranyl-nitrate solutions were also measured.

RESULTS

Fe-(U,Tc)-CO₃ system

The solution containing U-rich carbonate and pertechnetate as contaminants generated coprecipitates containing U and Tc with Fe^{2+} and Fe^{3+} from the oxidized Fe^0 . Gamma activity of the ^{235}U and $^{95\text{m}}\text{Tc}$ isotopes in the solutions before and after treatment showed that $\sim 99\%$ ($C_0 = 2300\text{ mg L}^{-1}$ and $C = 25\text{ mg L}^{-1}$ where C_0 = influent contaminant concentration and C = effluent contaminant concentration) of ^{235}U and 87% ($C_0 = 7 \times 10^{-6}\text{ mg L}^{-1}$ and $C = 9 \times 10^{-7}\text{ mg L}^{-1}$) of $^{95\text{m}}\text{Tc}$ was removed during electrochemical treatment. Gamma activity of the aged precipitates showed that 1470 mg kg^{-1} of ^{235}U and $3.6 \times 10^{-7}\text{ mg kg}^{-1}$ of $^{95\text{m}}\text{Tc}$ were incorporated in the iron precipitates. The precipitates were initially X-ray amorphous, but these precipitates transformed into a phase with an XRD peak at 0.7 nm within an aging period of 2 wk when left in the treated water (Figure 2). Analyses by SEM and EDX showed that this crystalline phase contains U and Tc with a keg-shape or barrel-shape morphology and a pronounced platy habit (Figure 3a). These particles contain significant quantities of uranium and iron, as determined by EDX (Figure 3b). Technetium is probably incorporated in this phase but was below the detection limit. X-ray diffraction analysis of an oriented particle-aggregate sample shows sharp and intense reflections, attesting to the highly crystalline

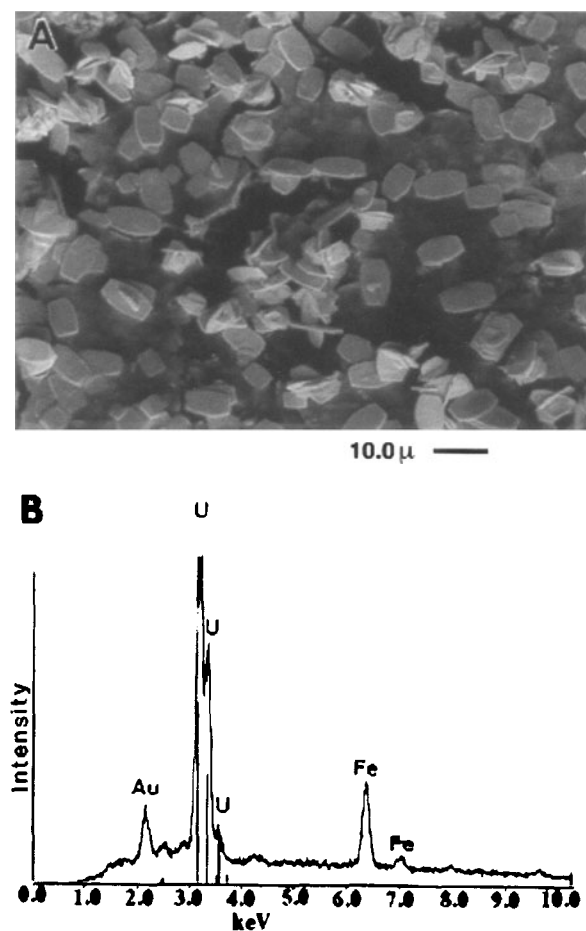


Figure 3. (A) Scanning electron micrograph of the coprecipitates displaying barrel-shape or keg-shape morphology and (B) EDX spectra showing the chemical composition of the precipitate is primarily iron- and uranium-rich.

nature of the precipitate (Figure 2). During the electrochemical process, the influent solution of pH 5.8 increased to 8.5–9.8 in the effluent. The redox potential decreased from +400 mV in the influent to between –200 and –400 mV in the effluent.

Fe-Mg-CO₃ system

When the solution containing dissolved Mg-rich carbonate passed through the electrochemical column, the dissolved Mg coprecipitated with the Fe from the “Fe⁰ foam” as amorphous precipitates. These precipitates transformed into a crystalline phase with an XRD peak of 0.7 nm within a 1-wk aging period (Figure 2A). The crystalline phase contains Mg and Fe and has a pseudo-hexagonal morphology and platy habit. SEM revealed that these phases are <1 μm in diameter (data not shown).

Fe-Co-CO₃ system

Dissolved Co also coprecipitated with the Fe from the “Fe⁰ foam” and crystallized from an amorphous

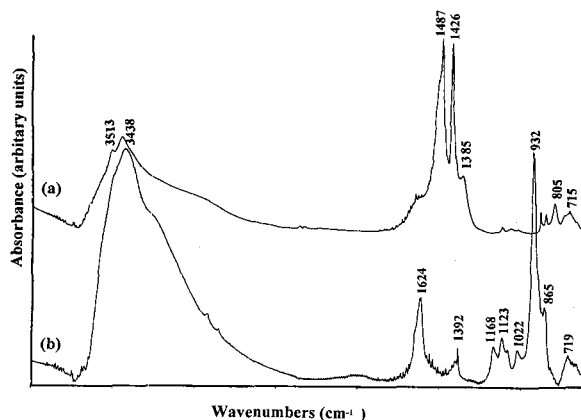


Figure 4. FTIR spectra of pyroaurite-like phases: (a) Co, Fe-rich carbonates and (b) U, Tc, Fe-rich carbonates.

phase to a phase with an XRD peak of 0.7 nm within a 7-d aging period (Figure 2A). The chemical composition of this phase is mainly Fe and Co. It has a pseudo-hexagonal morphology and a pronounced platy crystal habit. Scanning electron microscopy showed a crystallite size of <1 μm (data not shown).

Fe-Na-CO₃ system

In contrast, the solution containing Na-rich carbonate generated only Fe-hydroxide precipitate which remained X-ray amorphous after 2 wk aging (Figure 2A).

Analysis by XRD of the three crystalline precipitates revealed that each phase is similar to a pyroaurite-type mineral or green rust I (Figure 2). The two main XRD peaks for green rust I, Fe(II)Fe(III) hydroxy carbonate, are 0.750 and 0.376 nm (Schwertmann and Cornell, 1991). For the U- and Tc-bearing phases, glycerol treatment at 180°C (Koch and Hansen, 1996) replaced the interlayer anions and H₂O molecules and produced expansion to 0.9 nm (Figure 2B). The crystalline precipitate containing Mg and Co produces the same pattern of expansion after hot glycerol treatment (data not shown). The FTIR spectra showed that the crystalline phase with U, Tc, Co, and Mg also contains carbonate ions. The carbonate anion showed an absorption at 1640, 1392, and 719 cm⁻¹ for the U- and Tc-bearing phase and 1487, 1426, 1385, and 715 cm⁻¹ for the Co-bearing phase (Figure 4), corresponding to carbonate-stretching and carbonate-bending vibrations similar to carbonate phases (Huang and Kerr, 1960; Farmer, 1974; Nakamoto, 1997). The U- and Tc-bearing phase has a large absorption band at 1624 cm⁻¹ owing to molecular H₂O (Bish, 1977), absorption bands at 1168, 1123, and 1022 cm⁻¹ owing to structural OH (Farmer, 1974), and absorption bands at 932 and 865 cm⁻¹ owing to uranyl cations (Farmer, 1974).

Fluorescence spectroscopy identified the oxidation state of U in the crystalline precipitate and in the con-

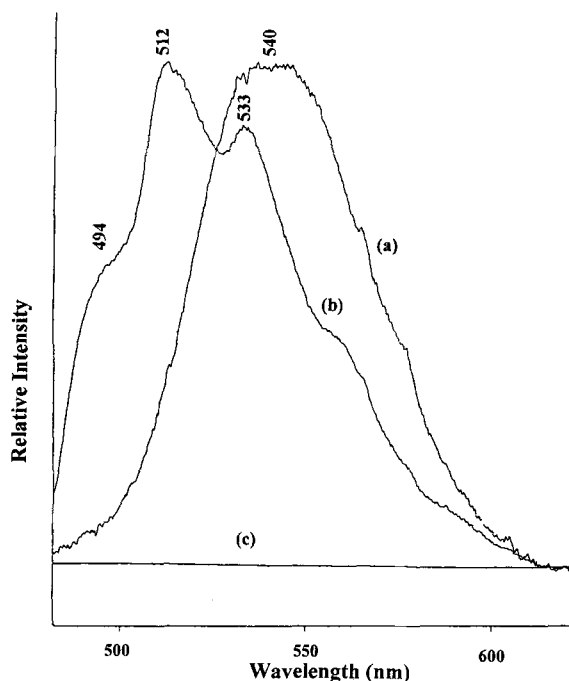


Figure 5. Comparison of fluorescence spectra of (a) uranyl nitrate, (b) uranyl carbonate, and (c) crystalline phase.

taminated solutions, particularly the uranyl-carbonate and uranyl-nitrate solutions. As expected, uranyl nitrate and uranyl carbonate showed strong fluorescence because the U is in an oxidized state (Figure 5), but no fluorescence was observed for U in the crystalline phase. Thus, the U in the crystalline precipitate is in a reduced state, U(IV), as predicted from the electrochemical reaction. Fluorescence spectra showed that soluble uranyl nitrate was reduced and coprecipitated with the iron. The precipitates, however, remained amorphous after aging for 2 wk.

DISCUSSION

During preliminary development of this electrochemical process for groundwater treatment, a crystalline pyroaurite-like phase formed after a short aging period instead of an amorphous U- and Tc-bearing Fe-oxide or hydroxide phase. As expected, most of the U (>99%) and Tc (>87%) was removed as a coprecipitate of an Fe-oxide phase (Roh *et al.*, 1996). Other metals, including Co and Mg, also coprecipitated with iron from Fe⁰ in the electrochemical column and crystallized into a pyroaurite-like phase.

The precipitate was initially amorphous, but crystallized within a 2-wk aging period at room temperature. The crystalline precipitates have similar XRD patterns as the pyroaurite-group minerals. Corrosion of the electrode foam produced Fe²⁺ and Fe³⁺ of the brucite-like hydroxide sheet. Presumably, isomorphous substitution of the iron by U⁴⁺ and Tc⁴⁺ in the brucite-

like sheet generated excess positive charge, which is balanced by the carbonate anion in the interlayer. Magnesium and Co also coprecipitated with Fe and crystallized into a pyroaurite-like phase in a 2-wk aging period. However, soluble uranyl nitrate was reduced and coprecipitated with Fe, but these precipitates remained X-ray amorphous throughout the aging period. Therefore, carbonate anions seem essential for generating pyroaurite-like phases via electrochemistry.

Coprecipitation by reduction of uranyl carbonates with oxidized Fe is a thermodynamically favorable reaction (Langmuir, 1978; Cantrell *et al.*, 1995), particularly as U(IV) readily forms oxy-hydroxide precipitates from solution (Gu *et al.*, 1998). Because the chemical composition of the crystalline phase is primarily U⁴⁺, Co²⁺, Co³⁺, Mg²⁺, Fe²⁺, Fe³⁺, and the carbonate ion, we conclude that the removal of radionuclides occurred via coprecipitation by reduction in the presence of iron. In turn, the precipitates crystallize into a carbonate mineral.

Another pyroaurite-type mineral, green rust, often forms as an intermediate product during the hydrolytic oxidation of Fe²⁺ solutions to FeOOH (Taylor, 1980). This mineral converts to goethite (α -FeOOH), lepidocrocite (γ -FeOOH), maghemite (γ -Fe₂O₃), or magnetite (Fe₃O₄), depending on the rate of oxidation and dehydration of pyroaurite (Hansen *et al.*, 1994). Thus, pyroaurite-type compounds are a possible inorganic reductant for nitrate, chlorinated organic compounds, and heavy metals in anoxic subsoil, sediments, and aquifers where microbial reduction rates are limited by low carbon content (Hansen *et al.*, 1996). Pyroaurite has considerable potential for applications such as water-purification processes, gas adsorbents, catalysis, and designed drug and pesticide delivery systems (Koch and Hansen, 1996).

CONCLUSIONS

Synthesis of Fe-rich carbonate phases through this electrochemical process is an effective approach to remediate contaminated aqueous solutions. This process generates a waste form that may be more stable to a leaching process than conventional wastewater-precipitation processes as a result of crystallization. The formation of well-crystallized waste products is fortuitous because the solubility of crystalline products is expected to be much lower than that of an amorphous (Fe oxide) phase, thereby immobilizing the entrapped contaminants more effectively. Further research is required to assess the effect of the electric current on coprecipitation and crystallization of the heavy metals and radionuclides with iron, the solubility of the electrochemically synthesized pyroaurite-like phases as a waste form, and the determination of the Fe-oxidation state in the synthetic pyroaurite-like phases.

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