Conf-821107--32

TECHNETIUM BEHAVIOR IN SULFIDE AND FERROUS IRON SOLUTIONS

SUK Y. LEE AND ERNEST A. BONDIETTI
Environmental Sciences Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee, USA

CONF-821107--32

DE83 003418

ABSTRACT

Pertechnetate oxyanion ($^{99}TcO_4^-$), a potentially mobile species in leachate from a breached radioactive waste repository, was removed from a brine solution by precipitation with sulfide, iron, and ferrous sulfide at environmental pH's. Maghemite (γ-Fe_2O_3) and goethite (α-FeOOH) were the dominant minerals in the precipitate obtained from the TcO_4^--ferrous iron reaction. The observation of small particle size and poor crystallinity of the minerals formed in the presence of Tc suggested that the Tc was incorporated into the mineral structure after reduction to a lower valence state. Amorphous ferrous sulfide, an initial phase precipitating in the TcO_4^--ferrous iron-sulfide reaction, was transformed to goethite and hematite (α-Fe_2O_3) on aging. The black precipitate obtained from the TcO_4^--sulfide reaction was poorly crystallized technetium sulfide (Tc_2S_7) which was insoluble in both acid and alkaline solution in the absence of strong oxidents. The results suggested that ferrous- and/or sulfide-bearing groundwaters and minerals in host rocks or backfill barriers could reduce the mobility of Tc through the formation of less-soluble Tc-bearing iron and/or sulfide minerals.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

INTRODUCTION

The leachability of stored high-level radioactive waste from a repository will largely depend on the inherent stability of the waste forms and the reactivity of intruding groundwater. Once radionuclides are leached from the wastes, transport of the dissolved nuclides will be controlled by chemical and hydrogeological retardation factors. Long-lived ^{99}Tc (2.12×10^5 y half life) could occur in many chemical forms in high-level radioactive waste depending on pretreatment prior to disposal. The negatively charged TcO_4^- ion is, however, expected to be a predominant chemical form in aqueous leachate solutions. Since anionic species tend to be poorly retained on silicate minerals, Tc has been identified as a radionuclide that may be difficult to contain in geologic media [1]. But, recent studies [2,3] suggest that TcO_4^- could be chemically reduced to less-soluble oxidation states such as TcO_2 or $Tc(OH)_4$ in the presence of igneous rocks under anoxic conditions. Other experiments indicate that

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TcO_4^- is reduced by ferrous iron in the absence of an adequate supply of oxygen [4]. Technetium also forms sulfide compounds such as Tc_2S_7 with or without metal sulfide carriers in strong acid solutions [5,6]. Because iron and sulfur are predominant participants in natural redox processes, studies of TcO_4^--ferrous iron-sulfide interaction were initiated to provide models for *in situ* immobilization of leached TcO_4^-.

METHODS

A synthetic brine solution (5 M NaCl) containing NH_4TcO_4 (10^{-5} M) and varying concentrations of Na_2S ($n \cdot 10^{-4}$ M) was prepared. Varying amounts of $FeSO_4$ ($n \cdot 10^{-4}$ M) were added to 40-ml batches of brine solution and then the pH was adjusted to either 8.5 or 6.3 with HCl or NaOH. After 3 and again after 5 d of equilibration, 2 ml of the solutions was filtered through 0.22-μm membranes and the amounts of ^{99}Tc remaining in solution determined by beta liquid scintillation counting [4].

For the physicochemical characterizations of the Tc-bearing iron, sulfide, and ferrous sulfide precipitates, larger quantities of precipitates were prepared from 200-ml solutions having solute concentrations as follows: (A) 5×10^{-3} M $FeSO_4$ and 5×10^{-5} M NH_4TcO_4; (B) 5×10^{-3} M $FeSO_4$ and 2.5×10^{-5} M NH_4TcO_4; (C) 5×10^{-3} M $FeSO_4$ only; (D) 5×10^{-3} M $FeSO_4$, 5×10^{-5} M NH_4TcO_4, and 5×10^{-3} M Na_2S; and (E) 3×10^{-4} M NH_4TcO_4 and 6×10^{-2} M Na_2S. The pH of these solutions was adjusted to 8.5 and the resulting precipitates aged for a month at 70°C and then for 7 months at 25°C. A small portion of each precipitate was taken after both 1 week and 8 months of aging for characterization. The precipitates were washed with demineralized water and 100% ethyl alcohol for x-ray diffraction (XRD) and neutron activation analysis (NAA). The salt-free precipitates were resuspended in water and mounted on grids for transmission electron microscopy (TEM).

RESULTS

By varying both the pH and the amounts of sulfide and/or ferrous iron added to the brine solution containing TcO_4^-, differing amounts of TcO_4^- were removed from the solutions as a result of precipitation with iron, sulfide, and ferrous sulfide (Table I). Although the initial black color of the iron and iron sulfide precipitates changed to brown within 4 d of equilibration, the amounts of TcO_4^- remaining in the solution were not noticeably affected by the color change. The black precipitates in the solutions containing only Na_2S and NH_4TcO_4 did not change color during equilibration. The loss of TcO_4^- from solutions increased with increasing initial sulfide and ferrous iron concentrations, and the loss was larger when the solution contained both sulfide and ferrous iron. Ferrous iron removed TcO_4^- more effectively than sulfide at pH 8.5, but at pH 6.3, significant amounts of TcO_4^- were lost only when the ferrous iron solution contained a considerable amount of sulfide (Table I).

TABLE I
Percent TcO_4^- removed from brine solutions by precipitates after 5 d equilibration

Initial Na_2S concentration ($n \times 10^{-4}$ M)	Initial $FeSO_4$ concentration ($n \times 10^{-4}$ M)				
	pH = 8.5				pH = 6.3
	0	1	3	6	3
0	1	1	52	90	0
1.9	3	14	95	78	2
7.5	23	57	95	97	81
15.0	31	66	82	98	95

All five of the precipitates prepared for the characterization studies initially had a black color and removed more than 90% of Tc from the solutions. Precipitates A, B, and C (from the ferrous iron solutions with 5×10^{-5} M Tc, 2.5×10^{-5} M Tc, and without Tc, respectively) gradually changed to a brown color. These precipitates were ferromagnetic both before and after color changes. The black ferrous sulfide precipitate (D) turned bright red, while the technetium sulfide precipitate (E) remained black. After 7 d aging, the black precipitates were examined by XRD and TEM. The XRD indicated the presence of poorly crystalline maghemite (γ-Fe_2O_3) in precipitates A, B, and C, but no x-ray crystalline minerals in precipitate D and E (although precipitate D had a very weak electron diffraction pattern).

The TEM showed that precipitate A (containing Tc) was a mixture of very fine (0.01-0.1 μm) distorted cubic maghemite and lath-like goethite crystals (Fig. 1a). The crystals precipitated without Tc had similar morphology, but their size, particularly goethite crystals, was much larger (0.05-1.0 μm) and their structure appeared to be well ordered (Fig. 1c). Precipitate D, obtained from the TcO_4^--ferrous iron-sulfide batch, was composed of a mixture of irregular platy ferrous sulfide and acicular iron hydroxide crystals (Fig. 1b).

During 8 months of aging, the initial solution pH of 8.5 decreased gradually to near 2.2 as a result of hydrolysis and sulfate formation; about 40 and 70% of the Tc that had been removed by the iron precipitates (A and B) and ferrous sulfide precipitate (D), respectively, returned to the aqueous phase. The Tc initially removed by sulfide alone, however, remained with the precipitate (E). The XRD, after eight months aging, showed significant improvements in the crystallinity of the minerals in the precipitates (Fig. 2), except precipitate E which remained x-ray amorphous (not shown). Goethite (α-FeOOH) and maghemite (γ-Fe_2O_3) were major components in precipitates A, B, and C, while goethite and hematite (α-Fe_2O_3) predominated in precipitate D. The goethite and maghemite lines became weaker and broader (width at half height) as the initial concentration increased, indicating that the added Tc had substituted for Fe in the structure, resulting in a decreased crystallinity. Similar

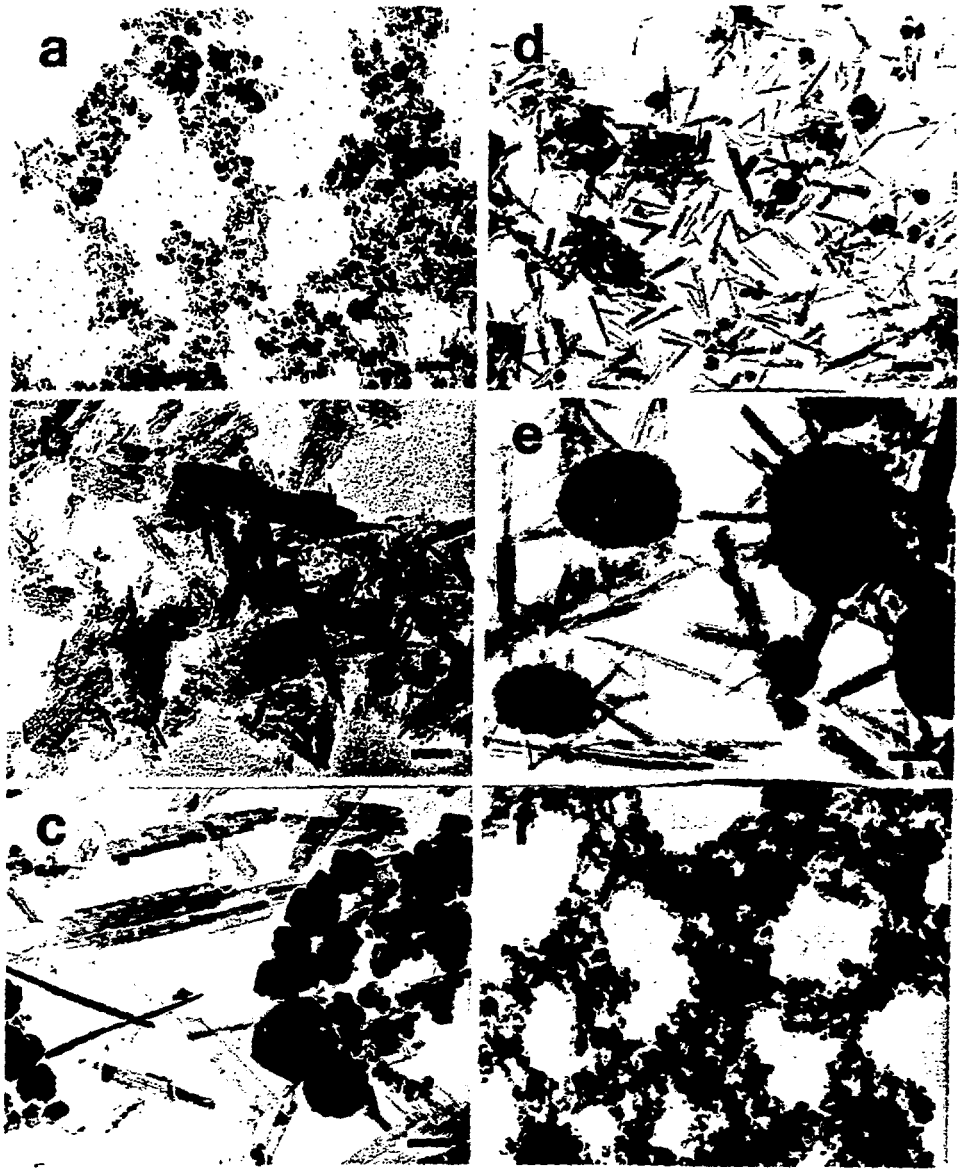

Fig. 1

Fig. 1. Transmission electron micrograph of (a) precipitate A, (b) precipitate D, (c) precipitate C after aging 7 d, and (d) precipitate A, (e) precipitate D, (f) precipitate E after aging 8 months (bar unit = 0.1 μm).

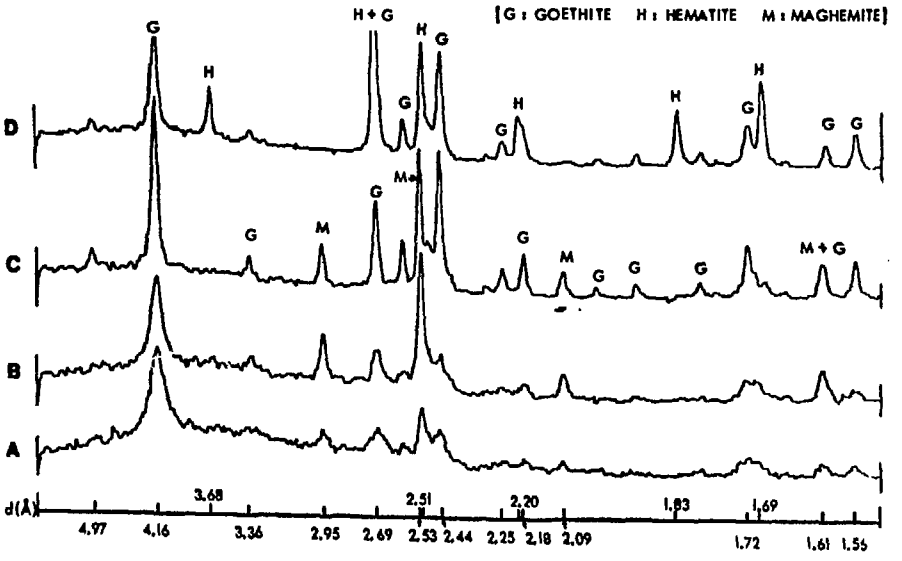
[G : GOETHITE H : HEMATITE M : MAGHEMITE]
D
C
B
A
d(Å)
4.97
4.16
3.68
3.36
2.95
2.69
2.53
2.51
2.44
2.25
2.20
2.18
2.09
1.83
1.72
1.69
1.61
1.56

Fig. 2

Fig. 2. X-ray diffractogram of precipitates A, B, C, and D after 8 months aging (G = goethite, M = maghemite, and H = hematite).

crystallinity changes were observed when goethite was precipitated from ferrous iron-aluminum solutions [7,8,9].

After aging 8 months the morphology of precipitate A (Fig. 1d) as well as precipitate B and C (not shown) did not change although XRD showed improved crystallinity. On the other hand, drastic alterations occurred to precipitate D (Fig. 1e) where hexagonal platy hematite and lath-like goethite appeared to have replaced the irregular platy crystals (x-ray amorphous FeS) observed in the fresh precipitate (Fig. 1b). Precipitate E consisted of very fine (about 0.05 μm in diameter), defined circular platy particles (Fig. 1f) that did not produce either characteristic electron diffraction or x-ray diffraction lines. The TEM observations confirmed the XRD results in terms of mineral composition as well as crystallinity of minerals in the precipitates.

The NAA results (Table II) showed that the molar ratio (Tc/Fe) of precipitate A was not noticeably different from that of precipitate B, although the initial Tc concentration of solution A was twice that of solution B at the same initial iron concentration.

TABLE II
Neutron activation analyses results (NAA) for the precipitates after aging 8 months

Precipitate (solutes in initial solution)	Composition (mg/g)[a]			Molar ratio	
	Fe	S	Tc	Tc/Fe	Tc/S
A ($FeSO_4$, high NH_4TcO_4)	579	-[b]	5.1	4.9×10^{-3}	-
B ($FeSO_4$, low NH_4TcO_4)	528	-	3.8	4.1×10^{-3}	-
C ($FeSO_4$)	521	-	-		-
D ($FeSO_4$, NH_4TcO_4, Na_2S)	558	-	1.1	1.1×10^{-3}	-
E (Na_2S, NH_4TcO_4)	-	341	330	-	0.31

[a] Samples were dried at 70°C for 24 h.
[b] Not present or not applicable.

The Tc/Fe molar ratio of precipitate D obtained from the solution, which had the same Tc and Fe concentrations as solution A, was about one-fifth that of precipitate A. The lower molar ratio could have resulted from either lesser isomorphous substitution or dilution by a mineral that did not contain Tc. However, precipitate D started as an iron hydroxide and ferrous sulfide mixture; later the ferrous sulfide was recrystallized by dissociation and oxidation to hematite during equilibration as indicated by TEM and XRD.

In the other iron precipitates, goethite and maghemite improved their crystallinity but did not recrystallize to form new minerals. Therefore, one could speculate that the Tc associated with ferrous sulfide was released to solution during the ferrous sulfide-hematite transformation and only the Tc incorporated into the goethite phase remained with the precipitate. The

Tc/S molar ratio (0.31) of precipitate E is approximately that calculated for the Tc_2S_7 compound (0.29), suggesting that Tc(VII) in the sulfide solution was not reduced to a lower oxidation state to form a sulfide compound. A reduced form of technetium sulfide compounds would be TcS_2 where the molar ratio is 0.5.

DISCUSSION

The experimental results clearly demonstrate that the pertechnetate oxyanion can be removed from solution by both iron and ferrous sulfide. The degree of removal depended on the concentration of ferrous iron and/or sulfide at constant TcO_4^- concentrations (Table I). Equilibration pH also influenced the removal rate, but it is not clear whether the pH influence was related to redox potential of the system or to solubility of the iron precipitates as influenced by pH.

During 8 months of aging, considerable amounts of Tc associated with the precipitates, particularly amorphous FeS, returned to the solution phase as the pH dropped from 8.5 to the 2.2 to 2.6 range, due to hydrolysis and sulfide oxidation. However, a separate experiment did show that most of the Tc remained with the solid phase after 1 month when the aqueous phase was maintained at a pH above 6.5 during sulfide dissociation from the iron phase and subsequent goethite formation (unpublished observation). The precipitation removal of Tc from solution by the addition of ferrous iron or finely ground magnetite is well known and practiced during Tc-bearing waste separation [10]. The particle size and crystallinity differences between minerals formed with and without the presence of Tc indicated that the Tc was incorporated into the goethite and maghemite structure in the sulfide-free ferrous iron system (Figs. 1 and 2) and that the pertechnetate oxyanion in solution was reduced to a lower oxidation state before this structural incorporation. Such a mechanism has been proposed on the basis of redox potential measurements involving Tc(VII)/Tc(IV) and Fe(III)/Fe(II) equilibria and similarity of ionic radii of Fe(III) and Tc(IV) [4]. The ineffectiveness of other hydroxide-forming but nonreducing transition metals including ferric iron for removing TcO_4^- (unpublished data) also indicates that the reduction of Tc(VII) to a lower oxidation state is a prerequisite for incorporation into the iron mineral structure because goethite can grow from both ferrous and ferric iron solutions [11] but Tc is precipitated only when ferrous iron is present.

The Tc-bearing ferrous sulfide, an initial precipitate in the TcO_4^--ferrous iron-sulfide batch, was unstable under ambient laboratory conditions but could be a stable phase under differing conditions in natural geologic media. Nevertheless, sulfide gradually dissociated from the precipitate leaving behind goethite and hematite (Figs. 1 and 2). The crystallinity of the hematite and the low Tc content of the precipitate after 8 months aging (Table II) suggested that Tc incorporated into ferrous sulfide was liberated to the solution during the ferrous sulfide-hematite transformation. Although determination of environmental conditions necessary for such a transformation is the subject of another investigation, formation of hematite is not expected to be favored in moderately reducing geologic environments [12].

The blackish precipitate (E) obtained from the TcO_4^--sulfide batch was a technetium sulfide compound with an apparent Tc/S molar ratio of 0.31 and was insoluble in strong acid and alkaline solutions without strong oxidants. The precipitate appeared to be amorphous Tc_2S_7, suggesting that Tc(VII) can be removed as a sulfide compound without being reduced to a lower oxidation state. The reported Tc_2S_7 compound has been synthesized in a strong acid solution [6], but formation of such a compound under environmental conditions has not yet been reported. Thermodynamic stabilities and crystal structures of technetium-substituted iron and sulfide minerals is the pertinent subject for further investigation. However, experimental evidences to date have suggested that the mobility of TcO_4^- in waste leachate could be reduced by interaction with ferrous- and/or sulfide-bearing groundwaters and minerals in host rocks or backfill barrier materials under relatively reduced repository environments.

ACKNOWLEDGEMENT

We thank D. H. Newman and B. Fellows, Chemical Technology Division, for providing TEM service and J. Switek for reading the manuscript and offering helpful suggestions. Research was supported by a subcontract with the Office of Nuclear Waste Isolation's Waste Rock Interaction Technology Program, Battelle Memorial Institute, for the U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation. Publication No. 2048, Environmental Sciences Division, Oak Ridge National Laboratory.

REFERENCES

1. Energy Research and Development Administration, Publication 76-43, vol. 4 (ERDA, Washington, D.C. 1976).

2. E. A. Bondietti and C. W. Francis, Science 203, 1337 (1979).

3. B. Allard, H. Kigatsi, and B. Torstenfelt, Radiochem. Radioanal. Lett. 37, 223 (1979).

4. C. W. Francis and E. A. Bondietti, Task 4 Third Contractor Information Meeting, vol. 2, CONF-7910160 (PNL, Richland, Washington 1979) pp. 81-132.

5. E. Jacobi, Helv. Chim. Acta 31, 2118 (1948).

6. S. Fried, J. Am. Chem. Soc. 70, 741 (1951).

7. G. W. van Oosterhout, Acta Crystallogr. 13, 932 (1960).

8. R. Thiel, Z. Anorg. Allg. Chem. 326, 70 (1963).

9. M. V. Fey and J. B. Dixon, Clays Clay Miner. 29, 91 (1981).

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a non - exclusive, royalty - free license in and to any copyright covering the article.

10. S. J. Rimshaw, U.S. Patent 3,005,683 (1961).

11. D. G. Lewis and U. Schwertmann, J. Colloid Interface Sci. 78, 543 (1980).

12. U. Schwertmann and R. M. Taylor, in: Minerals in Soil Environments, J. B. Dixon, S. B. Weed eds. (Soil Sci. Soc. Am., Madison, Wisconsin 1977) pp. 145-176.