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TRENCH-WATER CHEMISTRY AT COMMERCIALLY OPERATED LOW-LEVEL RADIOACTIVE-WASTE-DISPOSAL SITES

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ABSTRACT

Water samples from the disposal trenches of two low-level radioactive waste disposal sites were analyzed for their inorganic, organic, and radionuclide contents. Since oxidation of the trench waters can occur during their movement along the groundwater flow path, experiments were performed to measure the chemical and physical changes that occur in these waters upon oxidation. Low concentrations of chelating agents, shown to exist in trench waters, may be responsible for keeping radionuclides, particularly ^{60}Co, in solution.

INTRODUCTION

Appreciable concentrations of radionuclides are reported to exist in the trench waters of shallow land burial sites. Biodegradation of organic waste results in the generation of carbon dioxide and methane. In addition, sulfate ions are reduced anaerobically into hydrogen sulfide. Subsequent formation of insoluble metal carbonates and sulfides can act to coprecipitate some radionuclides.

As reducing trench waters come in contact with more oxidized groundwaters, iron hydroxide forms. Further removal of radionuclides from solution by coprecipitation might be expected.

The effect of these precipitation reactions on the solubility of radionuclides were studied using trench waters from the disposal sites at Maxey Flats, Kentucky and West Valley, New York. These waters are of particular interest since they are strongly anoxic and contain aminocarboxylic acid chelating agents (EDTA, NTA, DTPA). Cleveland and Rees [1] have shown that the presence of these chelating agents may prevent the coprecipitation of plutonium by ferric hydroxide in the trench waters at Maxey Flats. Means et al. [2] reported that ^{60}Co may have migrated from the low-level disposal sites trenches at Oak Ridge as a chelate of EDTA.

MATERIALS AND METHODS

Trench water sampling and analyses

Collection procedures and analytical results for waste burial site trench waters have been described in a series of reports [3-9]. Briefly, water samples have been obtained from trenches and wells at commercial waste burial sites located in Maxey Flats, Kentucky, and West Valley, New York, since September of 1976. Collection procedures were developed to maintain the anoxic conditions of the groundwaters while measuring the in situ pH, Eh, conductance, dissolved oxygen and temperature. Analyses of dissolved constituents in the trench waters included radionuclides and major inorganic constituents.

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Analyses for organic chelating agents and carrier cations were performed on selected trench waters. In this particular study, water samples from Maxey Flats Trench 27 (MF 27) and West Valley Trench 8 (WV 8) were used in the oxidation experiments.

Trench water oxidation experiment

Experiments were conducted in a controlled environment chamber, which consisted of a polystyrene cylinder (~4.5 inches in diameter by 6 inches in height) equipped with ports to accommodate up to 5 electrodes. Septum ports were available to add dilute acid or base for pH adjustment, and removal of samples from the liquid phase by inserting a hypodermic needle with syringe.

Trench water (about 650 mL) was anaerobically transferred from a collection bottle into a nitrogen-flushed, controlled-environment chamber containing a combination pH and two platinum-combination electrodes. The water was stirred continuously. An initial sample was removed through the septum, filtered through a 0.45 μm membrane (Gelman Acrodisc), and analyzed for alkalinity, ferrous iron, total iron, and background radionuclide activities.

A known aliquot of the mixed spike solution, containing μCi amounts of each radionuclide (^{241}Am, ^{134}Cs, ^{137}Cs, ^{85}Sr, and ^{60}Co) was added, and the purge gas was stopped. The contents of the chamber slowly oxidized as air leaked into the chamber, resulting in a reddish-brown precipitate. Samples were removed periodically, filtered through 0.45 μm membranes, and analyzed for radionuclides and ferrous and total iron. Total iron was determined in the filtrates from a carrier-free WV 8 water experiment using atomic absorption spectroscopy. The pH and Eh were monitored throughout the experiment. Yields for ferrous and total iron were calculated from comparisons with the initial (pre-spiked) sample. Yields for Am, Co, Cs, and Sr were calculated from comparison with the reference aliquots of a mixed spike after correcting for any background radionuclides detected in the initial sample.

The experiment was terminated when the total iron, radionuclide activities, Eh, and pH reached steady-state conditions. The contents of the chamber were filtered through a 0.45 μm membrane filter and air dried. The precipitate was dissolved, analyzed for total iron by atomic absorption, and counted for specific gamma emitters.

In the second of two experiments performed using trench water WV 8, sufficient $CoCl_2 \cdot 6H_2O$ and CsCl carriers were added, prior to adding the mixed radionuclides, to obtain a concentration of 10^{-5} M for each metal in the trench water. Previous analyses [3] indicated concentrations of $<10^{-6}$ M Cs and 2×10^{-5} M Sr in this trench water. The concentration of cobalt was not determined.

RESULTS AND DISCUSSION

Due to the bacterial degradation of organic material in the waste, the trench waters sampled at Maxey Flats and West Valley disposal sites exhibit strongly reducing conditions. The anoxic water condition is characterized by the absence of oxygen, low redox potential (Eh), low nitrate and sulfate concentrations, increased ammonia and alkalinity, and the presence of sulfide. Appreciable ferrous iron concentration can result when the corrosion of buried steel drums is significant. Low concentrations of some organic chelating agents are also present due to the widespread use of these substances for decontamination purposes. The chemical characteristics of Maxey Flats and West Valley trench waters are presented in Table I.

TABLE I
Chemical characteristics of Maxey Flats and West Valley trench waters

	Trench Water	
	WV 8	MF 27
pH	6.9	5.1
Eh (mV)	−6.3	140
Dissolved oxygen (ppm)	0.05	0.15
Fe (ppm)	130	1400
NH_3 (ppm)	290	60
Alkalinity (ppm as $CaCO_3$)	2000	300
NO_3 (ppm as N)	<0.02	0.75
SO_4 (ppm as N)	<5	2.2
Sr (ppm)	1.6	6.7
Cs (ppm)	<0.1	<0.5
NTA[a] (μg/g)	0.06	<0.01
DTPA[b] (μg/g)	0.40	0.20
EDTA[c] (μg/g)	0.10	<0.01

[a] NTA - nitrilotriacetic acid as free chelating agent.
[b] DTPA - diethylenetriaminepentaacetic acid as free chelating agent.
[c] EDTA - ethylenediaminetetraacetic acid as free chelating agent.

Burial site trench waters, upon migration, may encounter a relatively more oxidizing environment, thus resulting in the oxidation of ferrous iron to ferric iron to form ferric hydroxide. The pH of the solution may decrease due to the release of hydrogen ions following the reaction:

$$Fe^{+2} + 1/4\ O_2 + 2\ 1/2\ H_2O \rightleftharpoons Fe(OH)_3 + 2H^+ \qquad (1)$$

However, the H^+ concentration must exceed the buffering capacity of the pore water alkalinity for the pH to drop significantly. This effect is illustrated in Table II.

The changes in Eh, pH, alkalinity, and metal concentrations before and after the oxidation of the WV 8 and MF 27 trench waters are reported in Table II. The important differences in these trench waters are high alkalinity and relatively low iron concentration for WV 8 and high iron concentration and low alkalinity for MF 27. Also, MF 27 has a lower initial redox potential than WV 8. The observed changes, upon oxidation, as a function of time are shown in Figure 1 for the MF 27 experiment and in Figures 2 and 3 for the WV 8 experiments.

During oxidation of MF 27 trench water (Figure 1), the most pronounced changes are observed in dissolved iron concentration, pH, and Eh during the first 25 hours, followed by a gradual change approaching equilibrium conditions. The ferrous iron concentrations range from 98.0 to 103% (mean 99.5%; 1 standard deviation = 1.2 for 14 samples) of the total dissolved iron concentrations indicating that all iron is present in the ferrous state. The yields for ferrous and total iron are 79 ± 3% for the last seven samples shown in Figure 1. Co, Cs, and Sr do not exhibit removal from solution.

Table II
Changes in alkalinity, metal concentrations, and redox potential measured before and after oxidation of WV 8 and MF 27 trench waters

Component	Concentrations (moles/L)[a]					
			West Valley Trench 8			
	Maxey Flats Trench 27		Carrier-Free Exp.		Carrier Exp.[b]	
	Before	After	Before	After	Before	After
Total Iron	2.7×10^{-2}	2.2×10^{-2}	2.0×10^{-3}	$<6\times10^{-5}$	2.1×10^{-3}	4×10^{-6}
Ferrous Iron	2.7×10^{-2}	2.2×10^{-2}	c	c	2.1×10^{-3}	4×10^{-6}
Am[d]	7×10^{-9}	4×10^{-9}	6×10^{-9}	e	---	---
Cs[f]	$<1\times10^{-6}$	$<1\times10^{-6}$	1×10^{-6}	1×10^{-6}	1×10^{-5}	1×10^{-5}
Co[e]	c	c	c	c	1×10^{-5}	1×10^{-5}
Sr[f]	8×10^{-5}	8×10^{-5}	2×10^{-5}	2×10^{-5}	2×10^{-5}	2×10^{-5}
pH (unitless)	8.0	3.7	7.8	6.5	7.9	7.0
Eh (mV, NHE)	-400	+400	-100	+275	-150	+360
Alkalinity (meq/L)	3	0	c	c	44	c

[a] Except where units are specified.
[b] Sufficient $CoCl_2\cdot6H_2O$ and CsCl salts were added to make the trench waters 10^{-5} M in cobalt and cesium.
[c] Analysis not performed.
[d] Calculated from ^{241}Am activity.
[e] Below detection.
[f] Based on earlier work [Czyscinski et al., (1981); Weiss and Colombo (1980)].

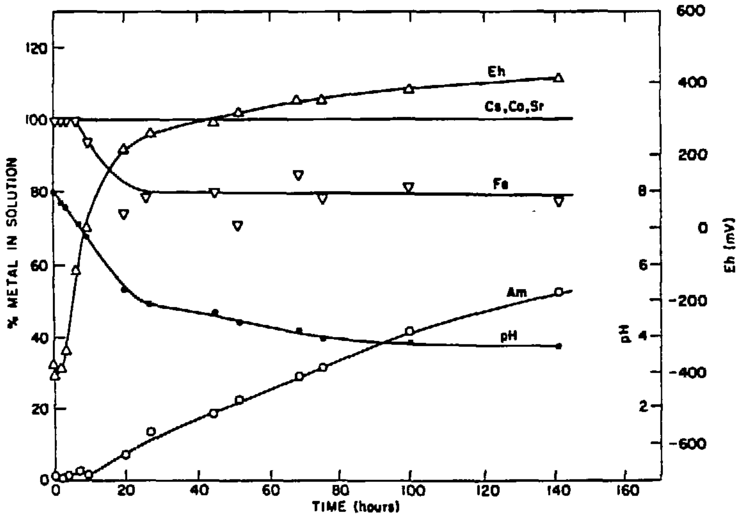

Figure 1. Changes in the pH, Eh and metal concentrations as a function of time during the oxidation of trench 27 water (MF 27) from the Maxey Flats disposal site.

The Am concentration drops off sharply and remains low during the first 10 hours followed by a gradual increase. The Am behavior is believed to be pH dependent, since the observations are in agreement with relative solubilities of americium oxides and hydroxides as a function of pH as reported by Ames and Rai [10]. The relative solubilities are based on thermodynamic data and decrease rapidly with increasing pH. The yields for metals in the trench water and in the precipitate, after steady-state conditions are reached, are reported in Table III. Small amounts of iron are lost on the 0.45 μm membranes during the filtration of the aliquots removed from the chamber. No attempt was made to recover the iron from the membranes or the Am that is adsorbed on these iron precipitates or on the chamber walls.

Table III
Yield for various metals in the filtrate and precipitate from oxidized Maxey Flats Trench 27 water (MF 27)

Metal	Yield (%) Precipitate	Yield (%) Filtrate	Yield (%) Total
Fe_{Total}	14	79 ± 3[a]	93
Am	29	62 ± 2[b]	91
Co	0.3	99 ± 2[c]	100
Cs	0.1	100 ± 3[c]	100
Sr	<0.08	110 ± 14[c]	110

[a] Mean and standard deviation for the last eight filtrates.
[b] See Table 5.
[c] Mean and standard deviation for 13 filtrates.

As shown in Table IV, oxidation of the MF 27 trench water beyond 140 hours shows no further change in the dissolved metal concentrations. In addition, all the iron remained in the ferrous state even after prolonged bubbling of air through the filtrate.

The results in Figures 2 and 3 for the carrier-free and carrier experiments using WV 8 trench water indicate similar trends with time, but the rate of oxidation was faster in the carrier experiment, probably due to greater diffusion of oxygen into the chamber. Cs and Sr remained in solution while all the dissolved iron precipitated. The ratio of ferrous to total iron is 1.00 ± 0.02 for the first seven samples removed from the carrier-experiment chamber. The pH values stabilized between 6.5 and 7.0 and the Co concentrations stabilized at 83% and 88% for the carrier-free and carrier experiments, respectively. About 80% of the Am was removed from the solution during the first hour, followed by a gradual decrease in Am concentration until about 1% remained after 10 hours. The concentration of metals in the ferric oxyhydroxide precipitates and in the oxidized trench waters are listed in Table V. Small amounts of ferric oxyhydroxide precipitates were lost on the membrane filters during the filtration of each aliqout removed from the chambers.

Table IV
Composition of the filtrate after removal of the ferric oxyhydroxide precipitate from Maxey Flats Trench 27 water (MF 27)

Component	Hours After Start of Experiment					X^a	$\pm S^b$
	914	1078	1249	1251	1509		
Am (%)	c	64	61	60	63	62	2
Cs (%)	c	100	100	105	100	100	3
Co (%)	c	105	104	104	105	104	1
Sr (%)	c	103	106	109	113	108	4
Fe^{2+} (%)	d	79	81	81	80	80	1
Fe_{Total} (%)	c	80	82	81	80	80	1
Eh (mV)	+540	+540	+542	+546	a		
pH	3.1	3.0	2.8	2.9	a		

^{a}X = Mean.
^{b}S = Standard deviation.
^{c}Analysis not performed.
^{d}Pipette malfuntioned.

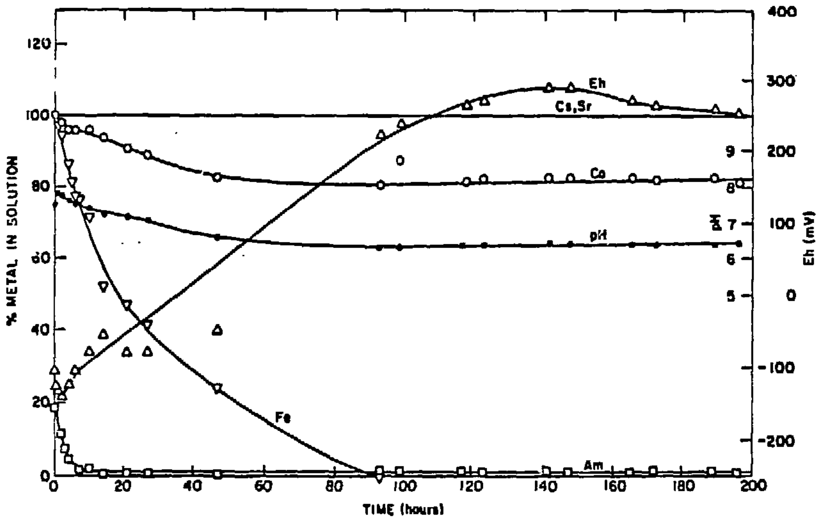

Figure 2. Changes in the pH, Eh and metal concentrations as a function of time during the oxidation of trench 8 water (WV 8) from the West Valley disposal site.

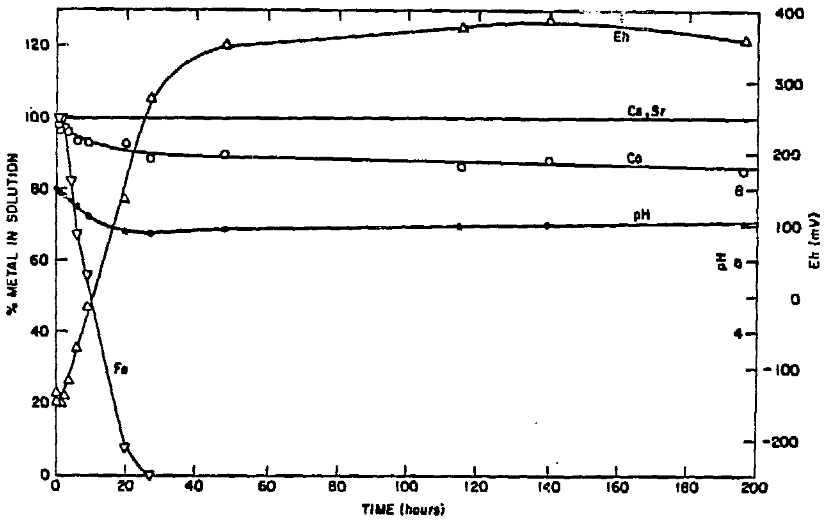

Figure 3. Changes in the pH, Eh, and metal concentrations as a function of time during the oxidation of trench 8 water (WV 8) from the West Valley disposal site with added 1 x 10^{-5} M Cs^+ and Co^{+2}.

Table V
Yield for various metals in the filtrate and precipitate from oxidized West Valley Trench 8 water (WV 8)

	Yield (%)					
	Carrier-Free Experiment			Carrier Experiment		
Metal	Fe ppt	Filtrate	Total	Fe ppt	Filtrate	Total
Fe_{Total}	>97	<3	>97	96	0.2	96
Am	96	1.2±0.2[a]	97	0	0	0
Cs	0.6	100.6±0.7[b]	101	0.2	100.0±0.6[c]	100
Co	18.0	83 ±2[a]	101	12	88 ±1[c]	100
Sr	1.8	99 ±3[b]	101	2	98 ±1[c]	100

[a] Mean and standard deviation for last 10 filtrates.
[b] Mean and standard deviation for 35 filtrates.
[c] Mean and standard deviation for 10 filtrates.

The iron concentrations as a function of Eh for the MF 27 and WV 8 experiments are shown in Figure 4. Slight decreases in the dissolved iron concentrations occur between -100 and +200 mV in the MF 27 experiment. In the WV 8 experiments, sharp decreases in dissolved iron concentrations were observed between approximately -140 and +135 mV for both the carrier-free and carrier systems.

This observed decrease in the dissolved iron concentration of WV 8 trench water, upon oxidation, can be attributed to the initially high buffering capacity of these waters. Upon oxidation, the resultant pH drop is not significant to the extent that it affects the precipitation of ferric hydroxide. In contrast, the MF 27 trench water has an initially low buffering capacity. As a result, upon oxidation of MF 27 trench water, a sharp drop in pH is observed, thus inhibiting the formation of ferric hydroxide.

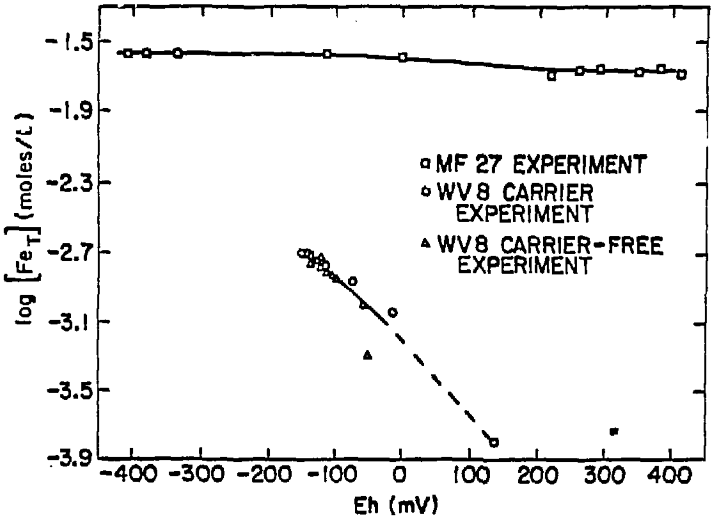

Figure 4. Dissolved iron concentrations as a function of Eh during the oxidation of trench waters from the Maxey Flats and the West Valley disposal sites. Dashed line represents extrapolation to the last data point.

The lack of removal of dissolved radionuclides even in the presence of ferric hydroxide precipitate resulting from the oxidation of WV 8 trench water implies that complexation of radionuclides with chelating agents can prevent their coprecipitation. Similar observations were reported by Cleveland and Rees [1] for dissolved plutonium at Maxey Flats.

CONCLUSIONS

- The Maxey Flats and West Valley trench waters (MF 27 and WV 8) exhibit strongly reducing conditions and share many characteristics in common with naturally occurring anoxic waters such as low redox potential (Eh) and high titration alkalinity. These waters also contain aminocarboxylic acid chelating agents (NTA, EDTA, DTPA).

- Upon oxidation of MF 27 trench water, significant changes in pH and Eh were observed with time. However, no significant removal of radioactive Cs, Co, and Sr and dissolved iron solution was observed. The lack of removal of radionuclides and iron from solution can be attributed to the initially low buffering capacity of MF 27 trench water. Because of this, a sharp drop in pH is observed upon oxidation which, in turn, inhibits precipitation of iron hydroxide and coprecipitation of radionuclides.

- Significant removal of dissolved iron was observed upon oxidation of WV 8 trench waters. This can be explained by the high buffering capacity of WV 8 trench waters, which neutralizes the released H^+ resulting from the iron oxidation reaction. As a result, iron hydroxide is formed.

- The lack of removal of radionuclides from solution upon oxidation of both WV 8 and MF trench waters indicates that highly acidic conditons in MF 27 inhibits radionuclide coprecipitation and that complexation of radionuclides with chelating agents may prevent their removal from solution in WV 8 trench water.

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