

ACTINIDE REMOVAL FROM WASTE SOLUTIONS BY FERRITE TREATMENT

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ABSTRACT

The ferrite waste treatment process was investigated in the laboratory in a continuous mode to evaluate the effectiveness of this method for removing plutonium and americium from aqueous waste. Experiments using actual process waste samples indicated that plutonium concentrations could be lowered consistently from around 10^{-4} g/l to the 10^{-7} - 10^{-8} g/l range. Three to four grams of solids were produced per liter of solution treated as compared to 15.7 g/l observed for the flocculant precipitation technique now in use at Rocky Flats. Less cement was required for the immobilization of ferrite solids resulting in further reductions in waste generation.

INTRODUCTION

The term "ferrite" refers to a class of mixed valence iron oxide compounds of which iron ferrite, $\text{FeO-Fe}_2\text{O}_3$, is an example. One or more of the iron atoms can be replaced by most other metals without drastically affecting the general chemical and structural characteristics. Ferrites are very insoluble crystalline materials having a cubic crystal structure like that of the mineral spinel, $\text{MgO-Al}_2\text{O}_3$.¹⁻³ The one feature which distinguishes ferrites from most other types of compounds is the fact that they are strongly magnetic.

The use of ferrites for waste treatment is a relatively new development which has been investigated extensively for a variety of applications.³ The ferrite treatment technique has been used for the removal of metal ions, organic compounds, biological materials, and particulate matter from aqueous media. In addition, ferrites can be used as catalysts for the decomposition of noxious gases in waste gas streams. With aqueous media ferrites remove contaminating species from solution either by adsorption onto the ferrite surface or by chemical incorporation into ferrite compounds. Because ferrites can be made within the waste medium itself or be prepared separately and added in slurry form, it is possible to use ferrite in a wide variety of chemical environments. In addition, ferrites are not as susceptible to leaching as are the sludges obtained from other waste treatment processes.

Among the various applications of ferrites for waste treatment, metal removal has received the greatest attention.^{3,8} For example, cadmium, lead, and mercury were removed from fly leach solution and effluent from flue gas scrubbers at electrical generating plants.^{4,5} The success realized in metal removal prompted the investigation of ferrite treatment for actinide removal from waste solutions at Rocky Flats.

At present, a flocculant precipitation technique is used to treat actinide containing process waste at Rocky Flats. This waste is primarily composed of an acidic waste stream, a basic waste stream, and steam condensate along with waste streams from the various buildings on plantsite. Although this technique is effective, at least two treatments are required to

achieve the desired level of actinide removal. The solid by-product from this treatment process is a hygroscopic sludge which is difficult to filter and dry. Even with the addition of filter-aid and flocculating agents, the filtration is slow, and the resulting sludge contains around 60 percent water. Recent operating history has shown that an average of 15.7 g/l (dry weight) of solids is produced.

EXPERIMENTAL

In order to minimize chemical interference from other dissolved species, the preformed ferrite addition technique was used in experiments with actual plant waste solutions. In this technique, iron ferrite is prepared separately and added to the waste solution. Ferrite solids were prepared by quickly adding 50% NaOH solution to a solution containing ferric and ferrous ions in a 2:1 molar ratio until the pH was between 9 and 13. After standing for 10 minutes, 2.0 g ferrite solids were added per liter of actinide containing waste which had been made alkaline. Removal of solids after an additional 10 minutes under gentle agitation yielded a solution with a substantially lower actinide concentration.

Laboratory studies on process waste were performed in a continuous mode. Waste solution and preformed ferrite slurry were pumped into an agitated reaction vessel. Simultaneously, the reaction mixture was removed at a rate equal to the addition rate and transferred to a separator. After a settling time of approximately 30 minutes, the slurry of solids was transferred to second separator. Supernatant liquid from both separators was transferred to a receiver and fed at 10 ml/min through a glass column packed with 431 stainless steel wool. The column was placed between the poles of an electromagnet, and a field strength of 2000 Gauss was applied.

Two sets of experiments were carried out with the preformed ferrite addition technique. Waste stream components were obtained from the plant and mixed according to design data for the new processing facility at Rocky Flats. A second set of waste mixtures was prepared, based on plant operation over a recent 16 month period. The relative amounts of each component in the design and actual waste mixtures are given in Table I.

Table I

Relative Amounts of Components in Waste Stream Mixture

Waste Component	Design Mixture	Actual Mixture
Acid	0.061	0.302
Base	0.319	0.091
Laundry	1.0	---
Condensate	---	1.0

RESULTS AND DISCUSSION

Using the preformed ferrite method or the *in situ* ferrite technique, ferrite treatment can be applied to a wide variety of waste media. While the *in situ* method does not require a separate slurry handling procedure as does the preformed ferrite technique, it is more sensitive to the chemistry of the waste solution. For example, complexing, oxidizing, or reducing agents can react with the cationic iron species and prevent or impair ferrite formation. Metal ions which form insoluble hydroxides can coprecipitate with ferrous and ferric ions during the initial step of ferrite formation. While most of these metal ions do form ferrites, they do not form as readily as iron ferrite. As a result, these metal ions can impair ferrite formation by the *in situ* method. The threshold levels of some metal ions which allow for good ferrite formation and reduction in plutonium concentrations from 1.0×10^{-4} g/l to the 10^{-8} g/l range are given in Table II.

Table II

Threshold Interference Levels for Various Metal Ions in g/l

Metal Ion	In situ	Preformed
Na ⁺	>50	>50
K ⁺	>50	>50
Be ⁺²	0.004	5.0
Ca ⁺²	1.0	1.0
Mg ⁺²	1.0	5.0
Cr ⁺³	1.0	5.0
Zn ⁺²	1.0	5.0
Al ⁺³	1.0	5.0
Cd ⁺²	1.0	5.0
La ⁺³	5.0	5.0
UO ₂ ⁺²	5.0	5.0

These data indicate that preformed ferrite, whose formation occurs outside the waste medium, is not affected as greatly by the presence of other metal ions.

Most common anions do not interfere with ferrite formation. However, anions such as phosphate, fluoride, and silicate, which form sparingly soluble compounds with ferrous and/or ferric ions, immobilize the iron in a less soluble form which is not totally free to undergo *in situ* ferrite formation. Because of the chemical sensitivity of the *in situ* ferrite method, the preformed ferrite addition technique was employed in the experiments with plant waste solutions.

In laboratory scale experiments, ferrite treatment was superior to flocculant precipitation, as indicated by the data in Table III.

Table III

Comparison of Waste Treatment Processes

Process	Treatment Steps, No.	Pu Conc., g/l		Solids g/l
		Initial	Final	
Floc.Pptn ^a	2 ^b	1.0×10^{-3c}	2.2×10^{-7c}	15.7
Ferrite ^d	1	1.0×10^{-4}	3.4×10^{-9}	3.2
Ferrite ^e	1	4.9×10^{-4}	7.0×10^{-8}	3.6
Ferrite ^f	1	5.5×10^{-4}	1.7×10^{-7}	3.2

^a Plant operation

^b Minimum

^c Maximum

^d *In situ* ferrite with simulated waste (Ref.1)

^e Preformed ferrite with "design" waste

^f Preformed ferrite with "actual" waste

The same degree of plutonium removal achieved in one step of ferrite treatment required at least two flocculant precipitations as observed in plant operation. Americium levels were similarly reduced by three to four orders of magnitude. At the same time, significantly lower amounts of solids were generated.

The solids produced by flocculant precipitation as well as ferrite treatment are transuranic or "TRU" waste and require immobilization prior to their removal from plantsite. Preliminary studies using cementation and the inert carrier process⁹⁻¹⁰ have shown that cement matrices containing up to 60 percent ferrite can be obtained. On the other hand, maximum loadings of only 40 percent are possible with the sludge from flocculant precipitation. These data are summarized in Table IV.

Table IV

Amounts of Solids Generated by Waste Treatment Processes

Process	Solids, g/l	Loading in Cement, %	Immobilized Solids, g/l
Floc.Pptn ^a	15.7	40	39.3
Ferrite ^b	3.2	60	5.3
Ferrite ^c	3.6	60	6.0

^a Plant operation

^b "Actual" waste

^c "Design" waste

This combination of reduced solids generation and greater loading possible during immobilization amounts to a very significant reduction in the weight of solids produced. Since the densities of both forms of solid waste are approximately the same, significant volume reductions can also be realized.

Compared with flocculant precipitation, ferrite treatment can be performed with the addition of less reagents. In plant operation over a recent 16 month period, an average of about 11.5 grams of reagents were added per liter of solution treated. On the other hand, ferrite treatment requires the admixture of only 10.0 g/l. This includes 2.0 g ferrite along with 4.9 g by-product Na₂SO₄, which is very soluble, and 3.1 g water arising either from ferrite formation or as water of hydration.

SUMMARY

In laboratory tests, ferrite treatment was effective in removing actinides from Rocky Flats process waste. Plutonium concentrations were consistently lowered from over 10^{-4} g/l to the 10^{-7} to 10^{-8} g/l range. At the same time, 3.2 to 3.6 g/l solids were produced as compared to 15.7 g/l observed over a recent 16-month period for waste treatment by flocculant precipitation. Whereas ferrite treatment required only one treatment step, at least two treatment steps are needed for flocculant precipitation to achieve the same results. Greater loadings of ferrite in a cement matrix were obtained so that very significant weight and volume reductions in immobilized solid TRU waste were observed.

In addition to its effectiveness in actinide removal, ferrite waste treatment has shown considerable versatility, which would facilitate its application to a variety of waste media. There are two methods of introduction which enable ferrite waste treatment to be used in different chemical environments. Whereas the *in situ* method is affected by the presence of other metal ions, the preformed ferrite addition technique is much less sensitive to the chemistry of the waste medium. Because of their strongly magnetic nature, ferrite solids can be separated magnetically in addition to techniques such as filtration and centrifugation.

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