# REMOVAL OF URANIUM AND PRIORITY POLLUTANT METALS FROM FERNALD ENVIRONMENTAL MANAGEMENT PROJECT WASTEWATER UTILIZING POTASSIUM FERRATE

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## ABSTRACT

A side-by-side treatment comparison between calcium hydroxide and TRU/Clear® "4", a potassium ferrate based wastewater treatment chemical, was performed in a process wastewater and stormwater treatment facility. Results from the full-scale plant testing demonstrated that potassium ferrate could achieve the same treatment levels as calcium hydroxide while generating 55% less sludge than the calcium hydroxide treatment. The testing also showed that utilization of potassium ferrate would minimize the volume of sludge generated and assist in the reduction of total waste management costs associated with storage, monitoring, transportation, and final disposition of generated sludge.

## INTRODUCTION

To minimize the amount of uranium and other priority pollutant metals discharged to the environment, an advanced wastewater treatment facility is being designed to treat all waters that will eventually be discharged to the environment off the Fernald Environmental Management Project(FEMP)(1). The advanced wastewater treatment facility will utilize a chemical pretreatment step to remove the majority of dissolved and suspended solids, radionuclides, and priority pollutant metals. Ion exchange will be utilized to polish the water to ensure that the concentration of uranium being discharged to the environment is less than 1.0 $\mu$g/L.

Currently, hydrated calcium hydroxide (lime, $Ca(OH)_2$) is the chemical of choice for the removal of uranium from wastewaters(2). However, the use of lime to treat wastewaters that contain radionuclides and heavy metals results in the generation of a radioactive sludge that must eventually be placed in drums and stored at secured disposal sites. The eventual goal of any treatment process is removal of contaminants from the wastewater that is discharged to the environment and minimization of the amount of waste generated during the treatment process. Minimization of generated waste assists in the reduction of total waste management costs associated with storage, monitoring, transportation and final disposition of generated sludge.

Recent work at other Department of Energy facilities has demonstrated that utilization of potassium ferrate(VI) to treat wastewaters contaminated with americium and plutonium lowered the activity of these elements from 37,000 pCi/L to less than 40 pCi/L or below present and impending future government regulations(3). This work has also demonstrated that the use of potassium ferrate would reduce the volume of radioactive sludge as much as 10 times when compared to each facility's present treatment procedure. Currently, potassium ferrate is being used at West Valley Nuclear Services as a pretreatment step to an ion exchange treatment system. The use of potassium ferrate has resulted in 85% less radioactive sludge generated than the previous ferrous sulfate treatment procedure.

A series of jar tests were performed to demonstrate the applicability of potassium ferrate to treat various waste streams at the FEMP. The jar tests simulate the types of mixing and settling conditions found in a clarifier. Based on the information obtained from the jar tests, recommendations on the implementation of potassium ferrate for full plant use were determined.

### Potassium Ferrate(VI) Chemistry

Potassium ferrate(VI) differs from other metal coagulants such as ferric (iron(III)) and ferrous (iron(II)) salts. Unlike other metal coagulants, which almost instantly form large flocs indicating the rapid precipitation of the metal hydroxide, the ferrate ion is highly soluble (~25 g/L) in solutions with a pH greater than 8. For the ferric ion to be an effective coagulant, it must collide with the negatively charged colloids in order to destabilize the colloidal particles and start the floc formation process. It is often necessary to add large quantities of the ferric salts to form a sweeping floc and ensure that flocculation is effective in removing small quantities of contaminants. Ferrate(VI), however, destabilizes colloidal particles by the formation of multicharged cation iron species when iron(VI) is reduced to iron(III). When iron(VI) is reduced in an aqueous system, it polymerizes to iron(III) by the step-by-step formation of multicharged iron species [Fe(V), Fe(VI), Fe(III)] which absorb onto the surface of the negatively-charged colloids. The absorption of the iron species eventually destabilizes the colloids through charge neutralization(4). The eventual reduction of ferrate(VI) to ferric(III) results in the formation of ferric hydroxide precipitates, which agglomerates the colloid particles into larger, settleable particles. Due to the solubility and the efficiency of the floc formation of ferrate(VI), 5 mg/L of iron as ferrate(VI) can improve or accomplish the same treatment goals as 30 mg/L or higher iron as a ferric(III) or ferrous(II) salt.

For aqueous waste streams containing low concentrations of suspended and dissolved solids, a formulation of potassium ferrate and magnesium salts (TRU/Clear® "4", Analytical Development Corporation, Colorado Springs, Colorado) is used. In order for the coagulation and flocculation process to be efficient in these waste streams, the size of the colloidal particles must increase in size to encourage the growth of settleable agglomerates. Magnesium acts as a seed crystal to ensure the formation of colloidal particles and eventual floc formation.

## LABORATORY TESTS

To demonstrate the applicability of potassium ferrate (TRU/Clear® "4") to treat FEMP waste streams, a series of jar tests were performed to evaluate the effectiveness of TRU/Clear® "4" in the removal of uranium and priority pollutant metals from several waste streams at the FEMP. These waters originated from three sources: Storm Water Retention Basin(SWRB), Biodenitrification Plant effluent(BDN), and Manhole-175. Manhole-175 is a point on the site where wastewater throughout the site is combined and mixed to form a single liquid stream that is discharged to the Great Miami River.

Jar tests were performed to simulate actual operating conditions of a one or two-stage clarification treatment process with each treatment step utilizing one-half hour of flocculation and one hour of settling of the resulting floc. Prior to the addition of TRU/Clear® "4", the pH of the waste stream was adjusted to the range of 10.6 to 11.2 with sodium hydroxide. At this pH, the water becomes depleted of carbonate and the chemical state of the uranium species in water is converted to uranyl hydroxide $(UO_2)_3(OH)_5^+$ which is more easily removed from water using coagulation than the soluble uranium carbonate complexes(2). In the first treatment step, TRU/Clear® "4" was added at a concentration of 120 mg/L (17.7 mg/L $K_2FeO_4$, 5 mg/L of $Fe^{6+}$). The treated sample was decanted after the resulting floc had settled to be either analyzed for uranium or treated a second time with 120 mg/L TRU/Clear® "4" (5 mg/L $Fe^{6+}$). The results obtained from these jar tests are listed in Table I.

### TABLE I

Jar Tests Treatment Results Using TRU/Clear® "4" To Treat Fernald Environmental Management Project Wastewaters

| Waste Stream | Initial U Concentration (µg/L) | U Concentration 1-stage treatment (µg/L) | U Concentration 2-stage treatment (µg/L) |
|---|---|---|---|
| SWRB | 490 | 71 | 11 |
| BDN | 160 | 45 | 4 |
| Manhole-175 | 62 | 14 | <1 |

The jar tests performed demonstrated that TRU/Clear® "4" was able to remove 72 to 86 percent of the uranium in the wastewater using a single-step treatment. Treating these waste streams a second time with TRU/Clear® "4" resulted in greater than 98% of the uranium being removed from these wastewaters.

## FULL SCALE DEMONSTRATION

The results from the jar tests demonstrated the applicability of using TRU/Clear® "4" to treat FEMP wastewaters. To demonstrate the applicability of this technology as a possible pretreatment stage in the advanced wastewater treatment facility, Plant 8 wastewater was treated with TRU/Clear® "4". Plant 8 currently treats process wastewaters and storm water with lime addition to remove uranium, heavy metals and suspended solids.

Initially, a side-by-side comparison of TRU/Clear® "4" and lime treatments was performed. Twelve thousand gallons of wastewater were transferred from the General Sump to two treatment tanks. The pH of 6,000 gallons of wastewater was adjusted to a pH of 10.8 to 11.2 on the average with 23 pounds of sodium hydroxide (NaOH) in one treatment tank. In another treatment tank, 6,000 gallons of similar wastewater was adjusted to the same pH range on the average with 26 pounds of lime ($Ca(OH)_2$). Six pounds of TRU/Clear® "4" were added to the sodium hydroxide, pH-adjusted wastewater at a concentration of 5 mg/L $Fe^{6+}$. The wastewater in both treatment tanks was agitated for one to two hours. Once the potassium ferrate had degraded from $Fe^{6+}$ to $Fe^{3+}$, the potassium ferrate treated wastewater and the resulting floc were processed through a rotary drum vacuum filter that had been precoated with diatomaceous earth. The lime treated wastewater and the resulting floc were processed through a similar filter. Effluent waters from both treatment processes were collected in separate holding tanks for analytical testing to ensure that the wastewater met discharge specifications. The generated sludge was removed from the rotary drum filters and the volume of sludge from each treatment process was measured and processed according to standard operating procedures at FEMP.

Initial results from the first 12 runs of the full scale plant test are summarized in Table II. These results show that potassium ferrate treatment is able to replace the current lime treatment procedures with no modifications to plant operations. Both treatment processes removed greater than 98% of the uranium in the wastewater. However, no reduction in the volume of sludge was seen using TRU/Clear® "4" versus lime treatment. Both treatment procedures generated approximately 80 pounds of sludge per 1000 gallons of wastewater treated (36 kg/3785 liters).

It was decided that the sludge removal process from the rotary drum vacuum filter needed to be optimized. It was speculated that the cutting blade of the rotary drum filters was actually cutting more filter precoat off the rotary drum filters than sludge, and the sludge from the TRU/Clear® "4" treatment displayed better dewatering characteristics than the sludge from the lime treatment process. To minimize the volume of filter precoat being cut off the rotary drum filters, the operators of the facility decided when to cut sludge from the rotary drum filters rather than having the cutting blade of the filters set at a constant cut rate. The results from the next eight runs are summarized in Table III. The results demonstrate that TRU/Clear® "4" is able to treat the wastewater flowing into Plant 8 and achieve approximately the same treatment results as the lime treatment procedure. One benefit that TRU/Clear® "4" treatment has over the lime treatment is the reduction of the calcium concentration in the Plant 8 effluent, which flows to the Biodenitrification Plant. Treatment systems such as biodenitrification are sensitive to high calcium levels.

Optimization of the cutting procedure for sludge removal off of the rotary drum filters resulted in the TRU/Clear® treatment generating approximately 55% less drums of sludge than the lime treatment. The TRU/Clear® process generated 41 pounds of sludge per 1000 gallons of wastewater treated (19 kg/3785 L) whereas the lime treatment process generated 91 pounds of sludge per 1000 gallons of wastewater treated.

The sludge reduction and removal results from Runs 13 through 20 provided the data needed to operate Plant 8 utilizing only the TRU/Clear® "4" treatment procedure to treat the next 30 batches of wastewater. The results from Runs 21 through 50 are summarized in Table IV. The results from these 30 plant treatment runs demonstrate that potassium ferrate can be utilized to treat the wastewater that flows into Plant 8 on a day-to day basis removing greater than 94% of the uranium flowing into the facility. The results also show that once the operations of the rotary drum vacuum filter were optimized, Table IV states 41 pounds of sludge were generated treating 1,000 gallons of wastewater with potassium ferrate (TRU/Clear® "4").

## ANNUAL TOTAL WASTE MANAGEMENT COST COMPARISON

An economic comparison of the TRU/Clear® "4" and lime treatment procedures treating 6,200,000 gallons of wastewater per year in Plant 8 is shown in Table V. Based on chemical costs only, treating the Plant 8 wastewater with TRU/Clear® "4" would cost $0.036 per gallon versus less than $0.001 per gallon using a lime treatment procedure. Based on wastewater treatment chemical costs per gallon only, the use of potassium ferrate to treat Plant 8 wastewater would be difficult to economically justify.

However, treatment chemical costs do not take into account the cost for monitoring, analyzing, treatment and the eventual transportation and disposal of the resulting sludge from a flocculation treatment procedure. The TRU/Clear® "4" treatment procedure would generate approximately 349 drums of sludge on an annual basis treating Plant 8 wastewater. A lime treatment procedure would generate 775 drums of sludge treating the same volume of Plant 8 wastewater. At FEMP, the sludge is processed through a rotary kiln that further reduces the volume of sludge another 30%. The dry sludge is then placed into a 55 gallon drum and transported to a secure disposal site.

Current estimated costs for private industry to transport and dispose of one drum of Low Level Radioactive Waste (LLW) is approximately $1060 per drum with each drum containing 7.3 cubic feet of sludge. Currently, there is no definitive data on disposal costs of hazardous waste for Department of Energy facilities. Estimated costs for disposal of LLW from a DOE facility have ranged from $100 to $2000 per drum.

The total waste management cost of the treatment procedures based on the eventual disposal of 244 drums of dry

**TABLE II**

Plant 8 Treatment Results - Average of Runs 1-12

| | Lime Treatment | | Potassium Ferrate (VI) Treatment | |
|---|---|---|---|---|
| | Effluent (mg/L) | Effluent (mg/L) | Influent (mg/L) | Effluent (mg/L) |
| Uranium | 230 | 2 | 160 | 2 |
| Calcium | 240 | 170 | 240 | 37 |
| Copper | 6 | 0.2 | 4 | 0.1 |
| Iron | 370 | 1 | 300 | 0.5 |
| Magnesium | 540 | 43 | 450 | 24 |
| Sludge Generated - | 80 lb./1000 gal. | | 80 lb./1000 gal. | |

**TABLE III**

Plant 8 Treatment Results - Average of Runs 13-20

| | Lime Treatment | | Potassium Ferrate (VI) Treatment | |
|---|---|---|---|---|
| | Effluent (mg/L) | Effluent (mg/L) | Influent (mg/L) | Effluent (mg/L) |
| Uranium | 100 | 2 | 59 | 4 |
| Calcium | 130 | 110 | 160 | 10 |
| Copper | 8 | 0.1 | 5 | 0.1 |
| Iron | 40 | 0.5 | 39 | 0.8 |
| Magnesium | 91 | 32 | 170 | 30 |
| Sludge Generated - | 91 lb./1000 gal. | | 41 lb./1000 gal. | |

**TABLE IV**

Plant 8 Treatment Results - Average of Runs 21-50

| | Potassium Ferrate (VI) Treatment | |
|---|---|---|
| | Influent | Effluent |
| Uranium | 26 | 1 |
| Calcium | 44 | 27 |
| Copper | 3 | 0.04 |
| Iron | 11 | 0.1 |
| Magnesium | 38 | 17 |
| Sludge Generated - | 41 lb./1000 gal. | |

**TABLE V**

Annual Total Waste Management Cost Comparison

| | TRU/Clear® @ $35/lb. | Lime @ $0.05/lb. |
|---|---|---|
| CHEMICAL COSTS: | | |
| TRU/Clear® | $217,000 | $0 |
| Sodium Hydroxide | $8,010 | $0 |
| Lime | $0 | $5,170 |
| Drums of Sludge Produced | 349 | 775 |
| Monitoring Costs ($5/drum) | $1,745 | $3,880 |
| Rotary Kiln Operating Costs ($50/drum) | $17,450 | $38,750 |
| Drums of Dry Sludge | 244 | 543 |
| Disposal Costs ($145/cu.ft.) | $258,270 | $574,770 |
| Total Waste Mgmt. Costs* | $502,475 | $622,570 |
| Treatment Cost | $0.08/gal | $0.10/gal |
| *6.2 million gallons of wastewater treated per year | | |

sludge per year using the TRU/Clear® "4" treatment is $0.08 per gallon versus $0.10 per gallon using a lime treatment procedure that generates 543 drums of dry sludge. This would result in an annual savings of $120,095 in total waste management costs for the FEMP site.

## SUMMARY

TRU/Clear® "4", a potassium ferrate based wastewater treatment chemical, was utilized in day-to-day operations in Plant 8 to treat process wastewater and stormwater. When compared to lime treatment, TRU/Clear® "4" obtained the same removal results for uranium, copper, and iron while generating 55% less contaminated sludge. TRU/Clear® "4", unlike the lime treatment, did lower the concentration of calcium in the Plant 8 effluent. High calcium concentrations in the Plant 8 effluent, which is eventually treated using biodenitrification can negatively effect the efficiency of this process.

Implementation of TRU/Clear® "4" could eventually result in utilizing equipment that does not require a filter precoat which would further reduce the volume of sludge generated in Plant 8. Even though the operations of the rotary drum filters were optimized, it is highly probable that a significant amount of the filter cake was due to the filter precoat being cut off the rotary drum filter.

Treating 6.2 million gallons of wastewater, the potassium ferrate based treatment procedure would generate 244 drums of dry sludge whereas a lime treatment procedure would generate 543 drums of dry sludge. The total waste management cost, based not only on the treatment chemical costs, but also on the cost to monitor, treat, and dispose of the resulting sludge, was calculated at $0.08 per gallon using the TRU/Clear® "4" treatment and $0.10 for the lime treatment procedure.

## REFERENCES

1. T. A. DUGAN, G. L. GELS, J. S. OBERJOHN, and L. K. ROGERS, "Feed Materials Production Center Annual Environmental Report for Calendar Year 1989," FMPC-2200/Special UC-707, NTIS: Springfield, VA (October 1990).
2. T. J. SORG in *Radon, Radium and Uranium in Drinking Water;* C. R. Cothern and P. A. Rebers, Ed.; Removal of Uranium from Drinking Water by Conventional Treatment Methods; Lewis Publishers: Chelsea, MI, 1990; pp. 173-191.
3. M. E. POTTS and J. P. DEININGER. "Removal of Radionuclides in Wastewater Utilizing the TRU/Clear® Chemical Process," Air & Waste Management Association, Vancouver, B.C. June 16-21, 1991.
4. T. D. WAITE in *Chemistry in Water Reuse*; W. Cooper, Ed.; Treatment of Domestic Wastewater for Reuse with Iron(VI) Ferrate; Butterworth: London; Chapter 25.