

DEVELOPMENTS IN TRANSURANIC ELEMENT POLISHING FROM RADIOACTIVE WASTEWATERS USING FERRATE (FeO_4^{2-}) CHEMICAL TECHNOLOGY

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ABSTRACT

Analytical Development Corporation (ADC) under exclusive license from the Los Alamos National Laboratory has continued development of a novel chemical treatment technology based on ferrate (FeO_4^{2-}) ion chemistry for the removal of trace levels of transuranic (TRU) elements from radioactive wastewater. Following development work from bench through pilot-scale, the technology has been demonstrated at the plant-scale in final polishing to consistently remove alpha-emitting TRU's to a time-weighted average of 17 pCi/l, well below Draft DOE 5400.XY discharge standards and below EPA Drinking Water Standards. Additionally, this has been achieved using small amounts of chemical by comparison to existing ferric technology. The results also indicate that based on chemical dosages, radioactive sludge generation should be reduced by factors of 3 to 20 depending on suspended solids content in the wastewater feed. The technology makes it possible to consider Zero-Discharge of transuranics as a practical engineering concept, perhaps for the first time.

SCOPE AND CHEMICAL TECHNOLOGY.

Nuclear waste management experience has shown that total containment of radionuclides in treatment of high-level waste (HLW), transuranic waste (TRU) and low-level waste (LLW) in processing facilities is extremely difficult due to the inevitable production and handling requirements of contaminated wastewaters, including by-product aqueous waste, rinse and wash waters, condensates and mop waters in large volumes. When dealing with contaminated solids or organic liquids and the like, these materials become classified as "mixed-wastes". Developed processes and equipment to treat and separate mixed wastes are available today, but they become economically and technically feasible only if the large volumes of low-level contaminated wastewater generated can be discharged or recycled. This is often not the case, and thus the separative cleanup of mixed wastes is today hampered and slowed by this problem. A typical example is shown in Fig. 1. This contaminated-soil washing process only becomes practical if a way to handle the low-level contaminated wastewater bleed that most processes of this type produce can be handled, and in a regulatory-permitted fashion. Analytical Development Corporation (ADC) has completed the development of a novel chemical treatment technology for removal of trace levels of alpha-emitting transuranic (TRU) elements from these wastewaters. The technology was originally conceived and researched by two of the authors, J. Paul Deininger and Linda K. Chatfield, at the Los Alamos National Laboratory and is being transferred to ADC for commercialization. ADC is the exclusive licensee of the Los Alamos technology. The developed technology addresses TRU wastewater problems in Department of Energy and other nuclear facilities and is intended for use in existing wastewater treatment

processes at the facilities or to be incorporated into mixed-waste treatment and remediation processes.

The technology is based on ferrate ion (FeO_4^{2-}) chemistry with TRU-removal enhancements accomplished by proprietary chemical additives into specific formulations for specific wastewaters. Ferrate chemistry has been studied for many years (1-4), but its commercial application has not occurred due to the inability to manufacture significant quantities of the material for large-scale use. The new ferrate-based chemical technology improves on existing products in three significant ways:

- (1) The new chemical is an alkaline coagulant and therefore is usable in strongly basic solutions, unlike other coagulant chemicals which are acid coagulants and are limited to more acidic wastewaters. Thus, the new technology allows exploitation of the properties of transuranic metal ions in solution to be much more insoluble in alkaline solution, enhancing the co-precipitative removal by the ferrate coagulant.
- (2) The new chemical has significant solubility in alkaline solution and degrades from the Fe^{+6} valence state (FeO_4^{2-}) to the insoluble Fe^{+3} hydrous ferric oxide at a controlled rate, thus allowing the ferrate ion to diffuse and to sweep over every portion of the wastewater at the molecular level. This is unlike the conventional ferric or alum coagulants which react to the insoluble ferric or aluminum hydroxides instantaneously, thus missing large portions of the wastewater and leaving dead spaces in the treatment process. This property contributes to the greatly improved removal of trace amounts of TRU elements from wastewater. In addition, one would expect on the basis of these comparative properties that full-plant performance of ferrate-based technology would improve upon or equal bench-scale performance, while ferric-based

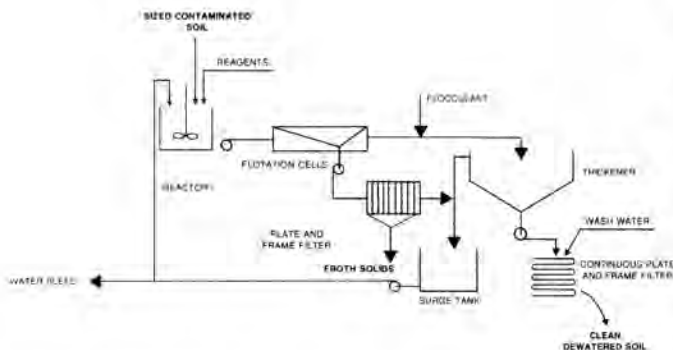


Fig. 1. Typical Soil Washing Process: Examples of Mixed-Waste Treatment Technology.

technology, needing well-designed flash mixing, would decline in performance upon full-plant scale-up.

- (3) The dosage amounts needed to achieve this performance are greatly reduced by comparison to existing usages of coagulant chemicals, largely because of the properties just discussed. For instance, only 5 to 10 parts per million (ppm) as iron of ferrate is needed in most projected applications as compared with conventional 20 to 40 ppm as iron of ferric sulfate used routinely in most mainline treatment processes. This significantly reduces the production of radioactive (LLW or TRU) or mixed-waste sludge contributed by the coagulant chemical itself. Estimates based on plant mass balances range from 3:1 to 20:1 reduction in sludge depending directly on the suspended solids content of the incoming wastewater feed, its particular chemical content and the coagulants chemicals used. In yearly costs associated with accrued drums of radioactive sludge, this could contribute to an enormous savings in waste management costs.

The novel ferrate chemistry which is exploited in this technology operates via a degradation chemical reaction in which the strongly oxidizing ferrate ion reacts with water to an insoluble hydrated ferric oxide, hydroxide ions and oxygen gas:



The rate of this reaction is directly catalyzed by trace metal ions which may be present in solution. In the presence of organic or inorganic reducing agents, the rate of degradation and its stoichiometry can be influenced radically as well. The reaction mechanisms discovered to date during

investigation of ferrate chemistry and application indicate a possible violation of equilibrium solubility behavior as it is understood today. The experimental results indicated that transuranic metal elements can be removed using this chemistry to lower concentrations in solution than can be predicted by equilibrium solubility constants which are empirically measured. It is believed that several mechanisms are operating simultaneously in the system which contribute to the overall removal characteristics of the technology, including localized kinetically controlled reactions. These mechanisms are being investigated presently in conjunction with the engineering development of the technology. The total engineering effect of these mechanisms and properties is precipitative removal of transuranic elements from wastewater to unprecedented low concentrations, not predictable by standard analysis.

The technology defines a new chemistry and chemical technology as applied to water treatment which allow new kinds of engineering thinking along the lines of Zero-Discharge of transuranics, while also possibly allowing reductions in overall waste management costs in many cases. It is thus possible to consider in a practical way an overall concept of closed-loop waste management of transuranics, as schematically shown in Fig. 2. Waste treatment and management is handled using standard technologies available for the most part today, and process streams and remedia-

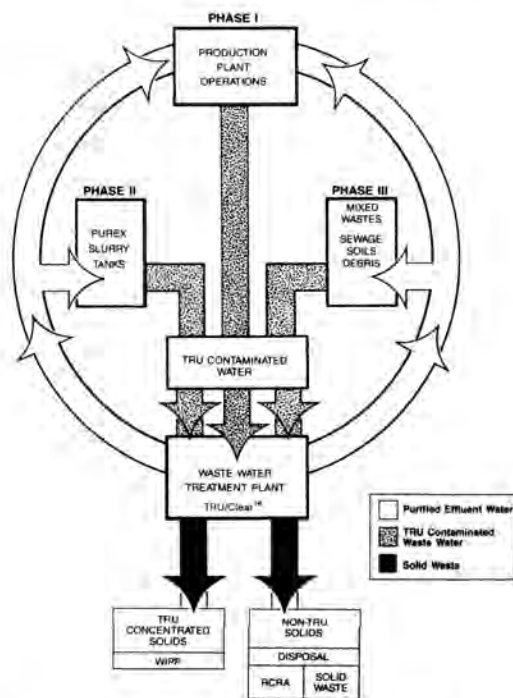


Fig. 2. Conceptual Closed-Loop TRU Waste Management and Process System Using FeO_4^{2-} Technology.

tive cleanups are accomplished via aqueous washing processes. The TRU-contaminated wastewater is shunted to a wastewater treatment process employing ferrate technology. Purified wastewater is recycled or discharged to the environment. The final low volume waste solids contain the suspended solids and inorganic metals, which upon further separation, radionuclides and priority pollutant metals should be able to be recycled for reuse. While the concept is probably not purely achievable in practice, ferrate technology may allow movement of TRU waste management toward this ideal, which has never been possible before. The development program and results described in this paper include bench jar-test screening and pilot 50-gallon test results and culminate with results of full plant testing of ferrate technology in the Los Alamos TA-50 Low-Level Waste Treatment Plant.

EXPERIMENTAL PROCEDURES.

Experimentation began with early screening experiments on TA-50 wastewaters to compare ferric sulfate and lime treatment with ferrate treatment on incoming raw feed samples and on polishing of clarifier weir overflows. Figure 3 shows a schematic diagram of the Los Alamos TA-50 wastewater plant, possessing two clarifiers which can be run with wastewater flows either in parallel or in series. In normal operations, the plant runs these clarifiers in parallel with ferric sulfate and lime coagulant additions by rapid mixing in the flash mixers, then about 3-6 hours of coagulation, flocculation and settling of the formed sludge. The sludge consists of ferric hydroxide gel from the reaction of ferric sulfate and lime, suspended solids which enter with the raw wastewater feed, and some salts and reaction products which precipitate during the treatment process. The decantant wastewater is then passed through a sand-particle filter to remove any particulates which may have carried over from the clarifier. The final effluent is then analyzed such that it meets the current radioactivity regulations before discharge to the environment. A full description of this plant may be found in Ref. 5. The most important of these regulations governing this operation is DOE Order 5480.1 which allows discharge of treated wastewater at no more than about 300 pCi/liter of alpha-emitting radionuclides to an uncontrolled area. In Los Alamos wastewater, these nuclides are primarily Pu^{239} , Pu^{238} and Am^{241} . A revisionary Draft DOE Order 5400.XY is imminent which lowers the discharge limit to about 100 pCi/l. EPA Drinking Water Standards (40 CFR 141) on alpha-emitters specifies about 45 pCi/l on alpha-emitters, which could be the federal limit imposed in the near future. These early screening experiments showed that ferrate dosages in the range of 5 to 40 ppm Fe as ferrate gave good TRU removal results with no apparent incremental benefits at higher treatment levels. Thus, standardized jar-tests were begun using a standard 1.0 liter, 6-vessel jar-test apparatus with stainless-steel flat

-blade 3-inch width impellers with adjustable speed of 0 to 400 RPM. 1.0 liter Pyrex or polyethylene beakers were used in all experiments. To simulate actual TA-50 plant operations as much as possible, the jar tests were performed throughout using an approximately 5 minute flash mixing time (about 250-300 RPM), then about 1 hour coagulation and flocculation time (about 25 RPM mixing), and 2-4 hours of quiescent settling time. The dry chemicals were added in weighed appropriate amounts. The settled slurries were decanted by pouring or pipetting the clarified liquid into sample bottles. The 800 to 1000 ml sample liquids were stabilized using about one half ml of concentrated nitric acid in all cases. The ferrate used was synthesized using a literature method (1) and assayed according to a standard method (3). The ferric sulfate and lime were standard commodity materials obtained in large quantities from a manufacturer for TA-50 plant operations.

In the pilot tests, two 55-gallon drums equipped with polypropylene liners and overhead agitators with stainless steel 2.5 inch diameter propeller mixers were used. Exactly 50 gallons of TA-50 clarifier weir overflow fluid was used in the vessels. Flash mixing was carried out for about 5 minutes, slow coagulative mixing for about 20 minutes, then settling for about 2 hours was allowed. Decantant samples were pulled from the top of the drum fluid for analysis after a minimum of two hours of settling, which was hopefully representative of a ferrate-treated clarifier weir overflow. These samples were preserved with nitric acid in similar manner as given above.

In the scaled-up full plant test, a 55-gallon drum was used to make up a dissolved aqueous feed which contained about 22 grams per liter of potassium ferrate in solution. A small peristaltic metering pump was used to accurately administer the liquid ferrate solution into the plant flash mixer No. 2, adjusting for plant flow rate to maintain a target dose of 5 ppm Fe as ferrate ion. As shown in Fig. 3, the plant was run in series at about 80 GPM wastewater flow, and ferrate was used only in the second clarifier to polish out the last traces of TRU elements. A major experimental problem had to be faced which has to do with historical effects on the ferrate plant test by previous operations in the plant equipment. In previous small-scale work, it had been shown that ferric/lime treatment left radionuclides in the final effluent wastewater in the neighborhood of 200 to 600 pCi/l, and raw feeds had been used for years on both clarifiers running in parallel. At the levels of removal expected with ferrate from small-scale work of considerably less than 100 pCi/l, it was thought that the ferrate treated overflows could be recontaminated by passing through the sand filter, both by mixing with "hotter" solution from the filter and by contact with contaminated solids in and on the filter itself. In order to avoid recontamination of the ferrate-treated clarifier weir overflow No. 2 by the sand filter, the plant test samples of the overflow were drawn and filtered on standard medium-

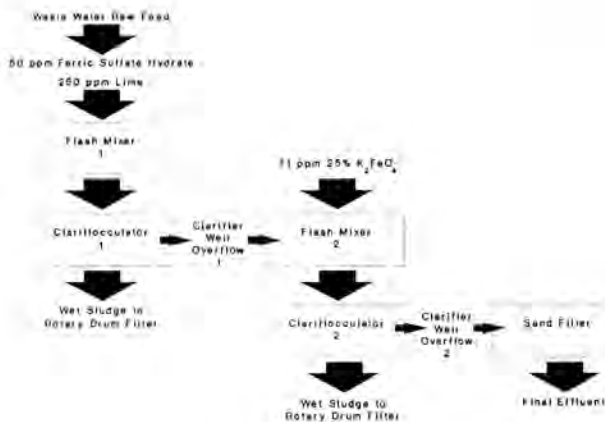


Fig. 3. Schematic of Los Alamos TA-50 Low-Level Waste Water Plant Operations with Ferrate Polishing Option.

density filter paper before stabilization with nitric acid and radiochemical analysis, thus simulating the use of a very clean plant filter. In this way, recontamination of the samples is avoided. Alpha-emitters analysis of the samples was completed on the samples by standard gross-alpha plating counting. In earlier work, a technique for direct analysis of Pu^{239} , Pu^{238} , and Am^{241} involving concentration of the sample followed by ion-exchange, elution and counting was run on a large number of samples which had also been analyzed by gross-alpha counting. This allowed a correlation between gross alpha and concentrative methods to be constructed such that a better approximation of actual total nuclide activity at low levels could be made when values from gross alpha analyses were obtained.

RESULTS AND DISCUSSION

Early screening tests indicated that the ferrate technology could not easily treat a high suspended-solids wastewater to extremely low effluent TRU concentrations in a single treatment step. Development work reported here was focused on the first step, toward working out the optimum operating parameters for a 2-stage process using ferrate as a polishing treatment in the second clarifier in series, following ferric/lime treatment in the first clarifier in series. The second development task remaining after this is a 2-stage process using ferrate in both clarifier stage. A summary of the optimum results of these tests with various options and scales is given in Table I. The first set of 1-liter jar-test results are single-stage treatment of TA-50 raw feed with ferrate and ferric/lime. It is evident that ferrate can be as effective as ferric/lime at lower iron dosage levels, but as yet no outstanding advantage in single-stage treatment to

very low effluent levels could be realized. This can be understood by recognizing that good removal of heavy suspended solids is mechanical and required high bulk material to enhance co-precipitation. Recent work, however, indicates that single-step treatment is feasible and the development work is continuing.

The second set of 1-liter jar-test experiments in Table I performed on ferric/lime treated clarifier weir overflows shows clearly that small concentrations of ferrate from 2 to 10 ppm Fe as FeO_4^{2-} will remove the final traces of alpha-emitting elements to the detection limit of the Pu and Am concentrative analytical methods of 5 pCi/liter. In comparison, properly administered ferric sulfate/lime will also do this job at the 1.0 liter scale, using 20 ppm Fe as ferric with 300 ppm of lime addition. Thus, it appears that ferrate can accomplish the job of removing the TRU's well below DOE 5400.XY and EPA Drinking Water Standards at lower dose levels than required by standard ferric technology. These experiments became the basis of a Los Alamos patent application (6).

The third set of experiments accomplished the ferrate polishing treatment scaled up to 190 liters or 50 gallons. This scale-up was successful and shows equal performance compared to the 1.0 liter experiments at both the 5 and 25 ppm Fe as ferrate dosage levels. Regrettably, 50 gallon scale-up data was not obtained using standard ferric/lime treatment. It should be noted, however, that the degradation time of the soluble ferrate ion in these experiments are all in the range of around 10 to 100 minutes, which is much longer than the reaction time to ferric hydroxide for a ferric salt (almost instantaneous). Thus it can be expected that the ferric technology will decrease in performance on trace level removals as it is scaled up, due to dead spaces and fluid bypassing. This expectation is born out in the TRU-polishing plant test data.

The successful 50 gallon scale-up data on clarifier weir effluent led directly to the decision to proceed with full-scale plant testing of the 2-stage option using ferric/lime in the first clarifier stage and ferrate at 5 ppm Fe in the second clarifier stage. Data from the plant test underway is given in Table II. On the days of operation, four samples are collected for analysis: the influent Raw Feed, the decantant overflow from Clarifier No. 1, the decantant overflow from Clarifier No. 2 which is filtered on paper before analysis, and the collected Final Effluent which has been sand-filtered before discharge to the environment. The simulated Final Effluent data from Clarifier No. 2 clearly are extremely low in concentration. Using the correlation of gross alpha values with TRU species concentrative analysis, averaged values of about 17 pCi/l in this effluent are obtained. This value is well below 5400.XY and Drinking Water standards, and thus the ferrate technology is successfully polishing the final TRU's out of the wastewater. The sand-filtered

TABLE I
Summary of Optimum Bench and Pilot Results of Ferrate Treatment of
Los Alamos Low-Level Radioactive Wastewater.

1.0 Liter Wastewater Feed Tests	Product Trt.	pH	Gross α (pCi/l)	Pu 239	Pu 238	Am 241	FeO ₄ ⁻² Degradation Time (mins.)
1-Raw Feed to Clarifier No.1	--	9.3	212,000	67,000	16,000	100,000	--
A. Treatment.	15ppm Fe as FeO ₄ ⁻²	12.0	340±92	--	--	--	90
B. Treatment.	20ppm Fe as Ferric, 300ppm Lime	11.7	680±290	150±20	36±9	220±30	--
C. Treatment.	15ppm Fe as FeO ₄ ⁻²	10.2	860±300	--	--	--	8
2-Clarifier No. 1 Weir Overflow Feed to No. 2.	--	11.5	340±220	170±20	120±15	75±10	--
A. Treatment.	2ppm Fe as FeO ₄ ⁻²	11.7	14±61	2±5	3±5	8±4	20
B. Treatment.	5ppm Fe as FeO ₄ ⁻²	11.7	4±80	16±4	8±3	9±3	47
C. Treatment.	10ppm Fe as FeO ₄ ⁻²	11.7	0±80	12±9	0±9	12±3	51
D. Treatment.	20ppm Fe as Ferric, 300ppm Lime	11.7	0±60	4±2	2±2	2±2	--
50 Gallon Wastewater Feed Tests							
3-Clarifier No. 1 Weir Overflow Feed to No. 2	--	12.0	160±87	78±54	62±49	--	--
A. Treatment.	5ppm Fe as FeO ₄ ⁻²	12.0	47±58	3±7	0±6	--	60
B. Treatment.	25ppm Fe as FeO ₄ ⁻²	12.0	0±41	8±5	3±4	--	108

TABLE II
Results from Los Alamos TA50 Low-Level Wastewater Plant
Operations with Ferrate TRU-Polishing Option

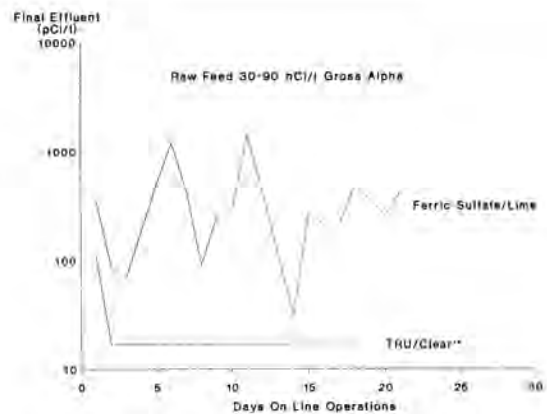
Total Alpha Activity in pCi/l:

Day On-Line	Raw Feed	Ferric/Lime (300ppm Total) Clarifier No. 1 Weir Overflow	Ferrate (5ppm Fe) Paper-Filtered Clarifier No. 2 Weir Overflow	Sand-Filtered Final Effluent
1	77,000	2,800	90±70 (110)	100±99
2	71,000	1,600	20±50 (17)	100±99
3	185,000	2,400	20±50 (17)	--
4	2,850,000	650	77±76 (25)	680±170
5	--	--	--	--
6	330,000	150	20±60 (17)	100±90
7	900	30±70 (17)	0±60 (17)	1200
8	--	520	30±50 (17)	480±150
9	--	--	--	--
10	36,000	70±70 (120)	0±40 (17)	420±150
11	142,000	260±110	260±110 Sludge Reduction	500±150
12	103,000	0±70 (17)	0±70 (17)	240±110
13	55,000	40±60 (17)	0±40 (17)	260±170
14	93,000	150±90	0±50 (17)	--

final effluent is analyzing considerably higher than the simulated final effluent, and thus it may be suspected that sand filter-laden residual activity is being picked up by the clarified wastewater as it passes through the sand filter. Similar final effluent data was observed in a previous plant test using ferric/lime in both clarifiers in series.

To test the validity of direct comparison of the filter-paper filtered Clarifier No. 2 simulated effluents from ferrate with the sand-filtered effluents from ferric/lime operations, composited final effluents from the ferric/ferric in series operation and from the ferric/ferrate in series plant operations were both filtered on standard filter paper, and gross-alpha activity was measured on the samples before and after this process. No change in gross alpha count was observed on the ferric/ferric sample, while significant decrease in gross alpha count was observed on the ferric/ferrate sample. Thus, while the ferric/ferric process is successfully producing large particulated solids which are easily filtered on the large void-volume sand filter, the data indicate that finer filtration does not additionally remove and polish the final traces of TRU's from the effluent. It is not known whether this is due to the TRU carry-over as extremely fine particles which pass through paper filters, or whether the TRU is remaining soluble in the effluent wastewater. By contrast, with ferric/ferrate treatment, the paper filtration process is successfully removing the remaining TRU's to very low concentrations and these are associated directly with the suspended colloidal particles in the wastewater. Therefore, it appears that the ferric/ferric technology is removing TRU's only to the hundreds of pCi/l range in plant performance and use of a finer filtration system would be ineffective in achieving better performance. The ferric/ferrate technology, however, is removing TRU down to the tens of pCi/l range and use of a finer filtration system, or improvement in flocculation and coagulation to larger particles in the clarifier, would be successful in achieving this excellent performance consistently at the plant scale. In any case, however, it appears that the TRU elements in the ferrate-treated operation are all associated with removable solids in the effluent, while much of the TRU content in the ferric-treated operation are not removable even by fine filtration. Hence, direct comparison of paper-filtered ferrate clarifier overflow with sand-filtered ferric overflow is valid.

Final effluent comparisons of the ferric/ferric-in-series plant test data with the ferric/ferrate plant test data are shown in Graph 1. The results clearly show that the ferric/ferric sand-filtered final effluents during the test ran on average at about 340 pCi/l, slightly above 5400.XY. The ferric/ferrate paper-filtered final effluents during the test ran on average at about 17 pCi/l based on species correla-

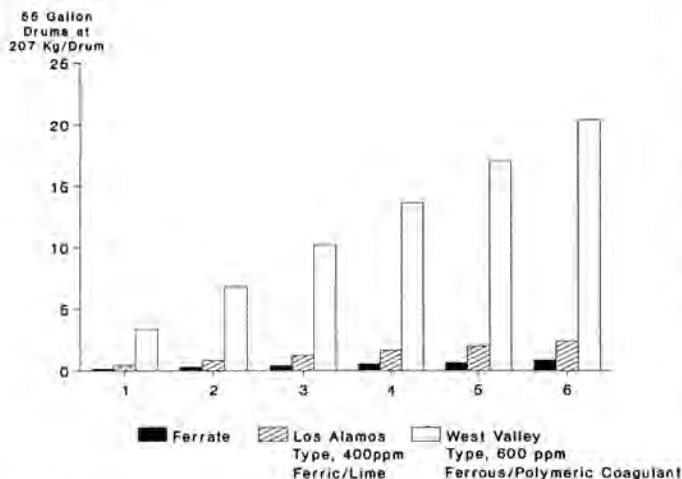


Graph 1. TA-50 Low Level Aqueous Waste Treatment Plant Results of Series Operations Tests.

tion to gross alpha measurements as described in Section III of this discussion.

CONCLUSIONS AND FUTURE WORK

The process development of ferrate chemical treatment technology for TRU wastewater removal has proceeded through screening, bench-scale, pilot-scale, and finally to the full wastewater plant scale testing. The work has climaxed in a successful plant demonstration of ultra low TRU removal from Los Alamos wastewater to below DOE 5400.XY and EPA Drinking Water effluent standards, in second-stage ferrate polishing of primary ferric/lime treated radioactive wastewater. Consistent day to day simulated final effluent concentrations at approximately the 17 pCi/l gross alpha level have been achieved using a targeted 5 ppm Fe as ferrate concentration in the wastewater. The available data to date appears to indicate that the ferrate chemical treatment technology consistently outperforms standard ferric/lime treatment both at the final polishing effluent concentration and in the minimization of radioactive/mixed-waste generation. Projected normalized comparisons of sludge generation as 207-kg drums, which accrue in volume, weight and cost as well as inflation of cost per drum are shown in Graph 2. The projections are made based on assumptions for chemical dosages inherent in ferric/lime, ferrous and ferrate (2 stages at 5 ppm Fe as ferrate each) chemical treatment technology by completing mass balances across typical radioactive wastewater treatment plants. Los Alamos represents a type whose wastewater is fairly high on average in suspended solids. West Valley represents a type whose wastewater is fairly low in suspended solids. The projections clearly show how ferrate chemical treatment technology could contribute to minimizing sludge drum generation and the astronomical and rising costs associated with sludge drum generation, disposal, storage, monitoring, and transportation. This tech-



Graph 2. Projected Normalized Sludge Comparisons for 10 ppm Fe as Total Ferrate Based on Plant Material Balances: Los Alamos-Type Waste Water and West Valley-Type Waste Water.

nology, as it stands, can greatly contribute to TRU wastewater and solid waste management today!

Significant development work in several areas can only enhance the efficiency and broaden the scope of this new technology. Development at the bench-scale of 2-stage operations with ferrate in both clarifiers in series will continue on to scale-up plant demonstration and operation with this option. Development of single-stage options will continue. Sludge reduction measurements and verification of projections; studies of sludge filtration, dewatering and leaching; development of ferrate technology for additional applications in TRU wastewater systems; development of the tech-

nology and associated equipment for mixed-waste separation treatment processes will all require intensive development work.

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