# DEMONSTRATION OF CHEMICAL TREATMENT PROCESS DEVELOPMENT DESIGNED TO GENERATE A BELOW REGULATORY CONCERN (BRC) WASTE FROM RADIOLOGICAL AND MIXED WASTES

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## ABSTRACT

EcoTek, Inc., has performed numerous process development treatability studies for private and government clients designed to develop chemical treatment processes to extract radionuclides from both radiological and mixed waste sediments, sludges and soils. The primary purpose of process development studies for radiological and mixed wastes is to cost effectively produce a leached residue activity which is consistently BRC. An optimum treatment process which generates a BRC residue allows alternate disposal options for both waste types as either a non-radiological, or hazardous waste. Secondary process development objectives are to identify resource recovery potential from residue and aqueous waste streams, minimize waste stream volumes and avoid generating waste streams which are characteristic hazardous wastes.

The treatment process identified for each waste type has been successfully demonstrated at bench and pilot scale levels. Results of two process development treatability studies for a radiological and a mixed waste are outlined below. The radiological waste was a uranium bearing fuel fabrication waste in a calcium fluoride matrix. A sulfuric acid leaching process was developed for this waste which produced a residue activity allowing disposal in a chemical landfill. In addition to producing a BRC waste, this process selectively recovers uranium from the leachate for recycle back to the fuel fabrication cycle. A pilot plant is under construction to demonstrate scaleup operations. A sulfuric acid leaching process was developed for a mixed waste soil contaminated with uranium, thorium, PCB, heavy metals, and other listed hazardous organics. The process was optimized on a laboratory scale basis and demonstrated via laboratory and large scale batch tests. The optimum treatment process produced a residue total activity upper limit (95% UL) below 34 $\mu Ci/m^3$ (36 pCi/g). Total activity was defined as the sum of gross alpha + gross beta + gross gamma activities.

## BACKGROUND

Extensive development work has been performed on various radiological and mixed waste soils, sediments and sludges to identify, optimize and demonstrate specific chemical treatment processes to remove the radioactive contaminants. The primary objective is to define a cost effective process for each waste which will allow disposal of the residue as a BRC waste in either a municipal or chemical landfill. A secondary objective for many radiological wastes is to selectively recover uranium for recycle back to the fuel cycle. Resource recovery of uranium or other species from treatment process aqueous waste streams is not always possible due to technical and economic issues. However, achieving the primary objective 1) can result in significant cost savings compared to low-level waste burial in the case of a radiological waste and 2) provides a disposal option for mixed wastes which otherwise have no current means of disposal.

Results, observations and conclusions resulting from process development treatability studies performed on a mixed waste soil and a radiological sediment typical of those generated by fuel fabrication activities are presented in this paper.

## MIXED WASTE SOILS

### Introduction

The mixed waste soil was predominantly contaminated with depleted uranium (60 ppm) and organics (i.e., PCB, phenol, phthalates, fluoranthene) and classified as an EPA F001 hazardous waste. The purpose of the process development tests were to identify, optimize and demonstrate a chemical treatment process capable of generating a leached residue total activity below regulatory concern. Total activity was defined by the client to be gross alpha + gross beta + gross gamma activities. Process development goals were 1) identify an optimum treatment process via a statistically valid experimental design, 2) demonstrate a large scale ambient temperature leach process and 3) characterize the residue and aqueous wastes.

Roasting and leaching processes were investigated using sulfuric and nitric acids and sodium carbonate/bicarbonate. These treatment processes are common to the uranium mining industry; however, additives and reaction

conditions were modified to enhance the overall effectiveness.

## Test Plan

Mixed waste soil samples were obtained and initially analyzed for chemical and radiological characterization to confirm soil contaminant concentrations and determine soil homogeneity. Extensive screening, grinding and blending was required to achieve a homogeneous feed material for process development testing. A minimum of five samples were analyzed for gross alpha, beta and gamma activity and the results statistically compared to verify soil homogeneity. This soil was used in subsequent scoping and optimization test phases.

The process development test plan was divided into three phases; scoping, optimization and large batch tests. Scoping tests were performed on 200g samples of homogeneous soil to investigate numerous combinations of reaction conditions (i.e., acid type, acid concentration, contact time, temperature, oxidant, etc.) and define ranges for these variables to be used during the optimization tests. Optimization tests were defined by a factorial experimental design and conducted with three factors (i.e., acid concentration, contact time, and temperature) and two levels (i.e., high and low conditions). The high-low values for each factor were combined to establish eight reaction conditions for the optimization test phase. Optimization tests were conducted on 200g samples of homogeneous soil with high-low reaction conditions listed in Table I. Two large batch tests were performed on approximately 23 kg of soil per batch. The leach temperature for all batch tests was limited to ambient temperature due to health and safety and environmental concerns associated with the levels of mercury, PCBs and other listed wastes. The purpose of the large batch tests was to investigate and quantify leach process variability associated with scale up.

Soil, leached residue and leachate were analyzed on site for gross alpha, gross beta and gross gamma activity. Residue total activity for this project was defined as the sum of gross alpha + gross beta + gross gamma activities. The residue total activity upper limit (UL 95%) was defined as 34 $\mu Ci/m^3$ which for this particular soil density (1.05 g/cc) is equal to 36 pCi/g. On site gross radiological analyses were performed with a Tennelec LB 5100 Series III Alpha/Beta Counting System and a Canberra Hyper-Pure Germanium (HPGe) System. Planchettes were prepared using 100mg of soil/residue and 2ml of leachate per a modified procedure detailed in Ref. 1. For each gross alpha/beta analysis, a minimum of five planchettes were prepared and counted for 1 hour each. The results for the five planchettes were combined statistically to establish the sample alpha and beta activity 95% upper limit. Gamma activity was determined by counting samples in either 250 or 500ml containers depending upon the amount of material available. Off site gross radiological analyses were performed to independently confirm results performed on site. All chemical analyses of soil, residue and leachate were performed off site by a contract laboratory in accordance with SW-846 analytical methods and quality assurance requirements. Blank, spike and duplicate samples were included with each batch of samples sent for off site analysis.

## Discussion of Results

Initial soil gross radiological analyses indicated that the material was not homogeneous. Extensive screening, grinding, and blending was required to produce a homogeneous material for subsequent scoping and optimization testing. A statistical evaluation was performed on gross radiological results of multiple samples to verify homogeneity. The mixed waste soil mean total activity was 215 pCi/g (95% UL). Beta activity comprised over half of the total activity with alpha and gamma activities accounting for approximately 40% and less than 10% of the total activity, respectively. The majority of gamma activity was due to naturally occurring K-40.

Scoping tests were performed to establish high-low conditions for acid concentration, contact time and temperature to be used during the optimization test phase. No ambient temperature leach, regardless of acid concentration, oxidant or contact time, produced a residue which approached the 36 pCi/g activity limit. Therefore, all optimization tests were conducted at elevated temperature. Oxidant addition to elevated temperature leaches did not produce a statistically significant effect on total activity reduction. However, the addition of oxidant to ambient temperature leaches did improve the reduction in total activity. Based on these findings, oxidant was added to the large batch ambient temperature leach tests but not added to the optimization leach tests. High and low contact times were chosen based on scoping test results. Scoping tests indicated that multiple stage treatments were required to achieve the residue activity limit. Each treatment stage included either a nitric or sulfuric acid roast plus a sulfuric acid leach. Nitric and sulfuric acid roasts were performed at elevated temperature.

The limits defined by scoping test results were implemented through a factorial experimental design shown in Table I. Experimental conditions for acid concentration, contact time and temperature were investigated based on eight combinations of high-low factors. Residue total activity for each optimization test defined by Table I is shown graphically in Fig. 1. Two optimization tests produced a residue total activity upper limit (95% confidence limit) which were less than 36 pCi/g. Test condition "abc" generated a residue activity of 36 pCi/g. This test was repeated with an oxidant added and designated as HNO3 in Fig. 1

with a residue activity of 35 pCi/g. The least aggressive reaction conditions which met activity limit was a double sulfate roast/sulfuric acid leach process. The double roast/leach conditions were defined as the optimum treatment process for this mixed waste soil and activity limit.

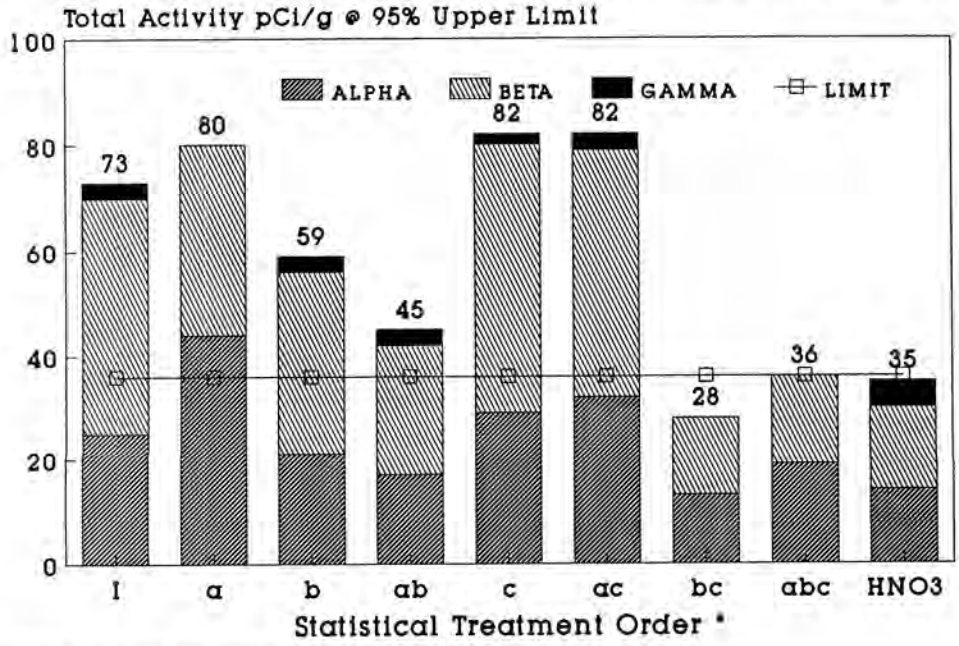
**TABLE I**
Optimization Test Factorial Experimental Design

| Symbol For Test Combinations | High/Low Levels For Factors | | |
|---|---|---|---|
| | Hours | Temp | Acid Conc. |
| I = Low Initials | Low | Low | Low |
| a = High Hours | High | Low | Low |
| b = High Temp | Low | High | Low |
| ab = High Hrs&Temp | High | High | Low |
| c = High Acid | Low | Low | High |
| ac = High Hrs&Acid | High | Low | High |
| bc = High Temp&Acid | Low | High | High |
| abc = High Initials | High | High | High |

Several general statements can be made based upon the residue activity data presented in Fig. 1. Alpha activity was more easily removed than beta activity. Low temperature leach combinations (i.e., I, a, c, and ac) were ineffective in removing beta activity. Beta activity represents the largest component of residue total activity. Because this soil was predominately contaminated with depleted uranium (i.e., U-238), a substantial portion of the beta activity is due to its short-lived daughters Th-234 and Pa-234. This is significant in that most test conditions generated residue total activities which were less than the activity goal if the beta activity is not included. Given the short half lives for these two beta emitters, the residue beta activity after six months of decay will be essentially equal to the alpha activity assuming a 50% split in alpha activity between U-234 and U-238. No statistically significant difference in overall activity removal was found between the most aggressive and the intermediate conditions.

Two large scale batch tests were performed at ambient temperature using a one stage leach with sulfuric acid, oxidant and 24 hour contact time. The leach temperature reached a mean temperature of 75°C due to the heat of reaction of the acid, soil and water. No external heat was applied. Based on the large scale batch test mass balance, one $m^3$ of dry leached residue and 13,240 liters of aqueous waste are generated per unit volume ($m^3$) of untreated soil processed. Waste water treatment required to meet NPDES discharge requirements was not investigated in this project. It is important to note that soil treatment did not result in an increased residue volume compared to the original feed volume.

Three grab samples of leached residue and one composite leachate sample from each large scale batch test were




* Order Symbols are defined in TABLE I

Fig. 1. Soil Optimization Test Results.

analyzed in house and by a contract laboratory for gross alpha, gross beta and gross gamma activity. The contract laboratory also performed isotopic thorium and uranium, total mercury, phenol, PCB, and TCLP analysis for metals. In house and contract laboratory gross radiological analyses correlated which validated the accuracy of the in house analyses. Residue total activity was reduced by 80%; however the mean residue total activity of 66 pCi/g (95% UL) was not less than the activity goal of 36 pCi/g. Leached residues and composite leachate from both large batch tests had TCLP results below the regulatory thresholds for all metals. Residue and leachate analyses for PCB and total mercury reported mean concentrations of 0.50 ppm and 0.30 ppm, respectively.

**Observations and Conclusions**

The residue total activity goal 34 $\mu Ci/m^3$ (36 pCi/g) is too restrictive. Background total activity was determined to be 74 pCi/g (95% LL) which is greater than twice the activity goal. The intent of any soil remediation project should be to remove activity attributable to manmade operations. Therefore, a practical activity goal equal to background is reasonable and justifiable. Reviewing the optimization test results summarized in Fig. 1, reveals that all eight treatment processes produced residue total activity below 74 pCi/g. A single 10 wt. % sulfuric acid leach at 65°C would meet the new activity goal. Much less aggressive and more cost effective treatment processes are able to meet the new activity goal.

Establishing an unrealistic activity goal which is below natural background results in greater analytical uncertainties as the method detection limit (MDL) is approached. Reporting analytical data and associated uncertainties at these low levels results in a large confidence interval when a high confidence level is required. Gross alpha and beta analytical methods required to support field activities can be associated with poor sensitivity and high variability. An activity goal should be selected and reevaluated to account for the uncertainties inherent in gross alpha and beta analytical methods at levels approaching MDLs.

Defining residue total activity equal to the sum of gross alpha + gross beta + gross gamma activities is unclear and results in over estimating the total activity actually present. This definition is unnecessarily conservative. Activity units of $\mu Ci$ refers to the number od atoms of a radioisotope disintegrating per unit time. Alpha and beta activities are equal to the number of atoms disintegrating by those decay modes. Gamma activities do not have this direct relationship. The gamma emitting radionuclides are also detected by either their alpha or beta emissions. Summing the radionuclide activities determined by gamma spectroscopy to gross alpha and gross beta measurements has the effect of doubling the true activity of those isotopes. Therefore, "gross gamma" activities should not be summed to the gross alpha and gross beta activities to evaluate a limit expressed in units of $\mu Ci$.

The 34 $\mu Ci/m^3$ activity limit does not address the issue of radionuclide daughters. The potential to upset the parent (U-238) - daughter (Th-234, Pa-234) equilibrium activities by of the leaching process can have a significant impact on residue total activity. If the U-238 parent is preferentially leached, which is likely the case for this soil, the remaining beta activity due to Th-234 and Pa-234 will decay in approximately six months. The net effect of this relationship is that residue total activity is lower after six months than immediately after treatment. Therefore, credit should be taken for this decay in residue total activity by expressing the activity based upon the leached residue ppm uranium.

## RADIOLOGICAL WASTE

**Introduction**

The fuel fabrication waste sediments were primarily composed of uranium isotopes and associated daughters in a calcium fluoride matrix. A process has been successfully adopted for removing uranium from calcium fluoride sediment typically generated in the nuclear fuel manufacturing industry. The three process development goals were 1) decrease uranium levels in the sediment residue to permit its disposal as a chemical waste, 2) process aqueous and solid wastes must pass EP Toxicity tests for heavy metals and 3) offset processing costs by recovering uranium from leach solutions for recycle.

Two basic chemical treatment processes, sulfuric acid and carbonate leaching common to the uranium mining industry, were investigated for applicability to fuel fabrication waste sludges. Carbonate leaching methods proved to be unsatisfactory for this application due to high residual radioactivity levels. A treatment process derived from basic sulfuric acid leaching methods yielded results which met the first two process development goals. A counter-current solvent extraction process has proved viable in recovering uranium in a form amenable to recycle. EcoTek is currently

in the final stages of constructing a pilot plant to process sediment for scale-up demonstration and evaluation.

**Discussion of Results**

The sulfuric acid leaching process developed for the fuel fabrication waste consists of four basic steps:

- Leaching of the uranium bearing solids with sulfuric acid.
- Selective extraction of the uranium from the leachate via a solvent extraction system.
- Recovery of the uranium by precipitation as the diuranate.
- Treatment of all process liquid effluent streams with lime.

As with many process development studies, several factors unique to this waste type had to be overcome before a suitable process could be developed.

Examples of these were:

- High levels of fluorides resulting in extremely corrosive leaching conditions.
- High levels of zirconium which interfered with the solvent extraction process.
- Other miscellaneous materials that caused emulsion problems during the solvent extraction process.

These problems were overcome by the addition of a variety of proprietary reagents to the basic sulfuric acid leaching process and by employing various solvent scrubbing techniques.

The resulting process consistently produced residues containing activity levels suitable for burial at a non-radiological waste disposal site from feed material containing uranium levels as high as three percent. The process waste streams were non-hazardous as defined by EPA criteria in Ref. 2. A high quality uranium product was produced which was suitable for reuse by the fuel manufacturing industry. These results satisfied the process goals of creating a residue waste suitable for burial at a non-radiological disposal site, generating a non-hazardous waste and recovering uranium for recycle to offset treatment costs. A resource recycle scenario for the leached residue is being investigated.

## SUMMARY

Chemical treatment processes to remove radioactivity from mixed and radiological waste sediments, soils and sludges have been developed, optimized and demonstrated. Alternate waste disposal options and resource recovery/recycle are possible for mixed and radiological wastes. The optimum process requirements for each waste type must be investigated via laboratory scale tests to determine initial feasibility. Resource recovery potential, waste water treatment requirements and aqueous/solid waste stream hazardous waste evaluation should be determined during the laboratory scale tests.

## REFERENCES

1. Standard Methods For the Examination of Water and Wastewater, 16th Edition, American Public Health Association, Washington, DC, 1985.
2. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods SW-846, 3rd Edition, November 1986, USEPA.