

CHEMICAL EXTRACTION OF MIXED WASTE

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ABSTRACT

IT Corporation was contracted to conduct treatability studies on low level radioactive and mixed waste. A remedial investigation was initiated to develop remedial actions to control the impacts on human health and the environment. Several alternative technologies were investigated for the remediation of waste stored on site. The treatment technologies investigated by IT consisted of chemical extraction, cement based stabilization, vitrification, and soil washing.

This paper focuses on the chemical extraction study. The major constituents of concern were radium, lead, and uranium. A tiered experimental approach was used that emulates the EPA's remedy screening and remedy selection phases. Hydrochloric acid, nitric acid, acetic acid, EDTA, and KCl solutions were used to extract the radioactive components. EDTA was the most effective reagent to decrease the total activity of the waste. Acetic acid was about 80 percent as effective as hydrochloric and nitric acids. The largest radioactivity decrease was realized from sequential extractions using combinations of acids with EDTA or KCl with EDTA. The TCLP of the chemically extracted material met the TC regulatory requirements. The radium concentration in the extracted material was decreased by greater than 95 percent.

INTRODUCTION

IT Corporation was contracted to evaluate remedial technologies at a client's site. The site's material contains Resource Conservation Recovery Act (RCRA) metals, anions and radionuclides. The materials investigated were from two separate areas on the client's site. The remedial technologies to be considered were to lower the leaching of contaminants of concern (COC) from the material by reducing the COC concentration in the original matrix (chemical extraction) or by chemically fixing the COC in an altered matrix (cement-based stabilization or vitrification). This paper focuses on the chemical extraction studies.

The physical consistency of the material varied from rocks to soil-like material. The particle size was normally less than 3/8 inch. The radionuclides of interest included uranium, thorium, polonium, protactinium, actinium, and radium. The RCRA metal in the largest concentration was lead (Pb). The anions in the material included fluoride, sulfate, carbonate, phosphate, and nitrate.

OBJECTIVES

The objectives of the chemical extraction treatability study were to:

- Determine the effectiveness of various extraction solutions in removing RCRA metals and radionuclides,
- Determination of the effectiveness of various reagents to decontaminate the used extraction solutions, and
- Determine the effectiveness of various reagents to cement stabilize or vitrify the precipitate from the decontamination of the used extraction solutions.

PROGRAM DESIGN

Figure 1 shows the overall flow diagram of the program. The extracted solids, i.e., the raffinate, were analyzed for leachable RCRA metals and radionuclides using the Toxicity Characteristic Leaching Procedure (TCLP); the total radionuclide COC concentrations were also analyzed. The spent extract was decontaminated of RCRA metals and radionuclide COC's by precipitation methodology. The COC's in the precipitate were chemically fixed by cement stabilization and vitrification technologies. The leachable constituents in the

stabilized and vitrified materials were analyzed by the modified TCLP (MTCLP) and modified Product Consistency Test (MPCT). This paper will discuss the findings of the chemical extraction portion of the study. The details of the extractant decontamination (by precipitation) and chemical fixation studies of this precipitate will not be discussed in this paper.

The wastes were chemically extracted with four different acid/chelant solutions. Hydrochloric (HCl) and nitric acids (HNO₃) were selected because of their use in the uranium (U) mining industry and since most metal chloride and nitrate salts are soluble. Nitric acid has the additional benefit of being able to oxidize uranium dioxide (UO₂) to a more soluble hexavalent uranium complex. Acetic acid (HOAc) was chosen because of its mild complexing ability that might enhance the metal solubilities. Ethylenediaminetetraacetic acid (EDTA) was selected because it is widely used for decontamination in the nuclear industry and because of the strong metal-chelate complex it forms with Ra²⁺ and Th⁴⁺.

The program was conducted in two phases. An initial screening phase to determine which extractants and extraction conditions were promising and a second phase to collect more detailed data on the promising extractants and conditions. The two phases were designed to emulate the U.S. Environmental Protection Agency (USEPA) guidance for Remedy Screening and Remedy Selection studies, respectively. The USEPA's guidance is described in detail in "Guide for Conducting Treatability Studies Under CERCLA" (1).

EPA Guidance - Remedy Screening and Remedy Selection

Remedy Screening is the first step in the tiered approach to treatability studies. Its purpose is to determine the feasibility of the treatment alternative. These small-scale studies are designed to provide a qualitative evaluation of the technology and are conducted with minimal levels of Quality Assurance/Quality Control (QA/QC). Tests conducted under this tier are generic in nature (not vendor specific). If the feasibility of the treatment cannot be demonstrated, the alternative generally will be eliminated.

The Remedy Selection tier is designed to determine whether a treatment alternative can meet the cleanup goals and at what cost. The purpose of this tier is to generate the performance data and data for the estimation of the cost at a

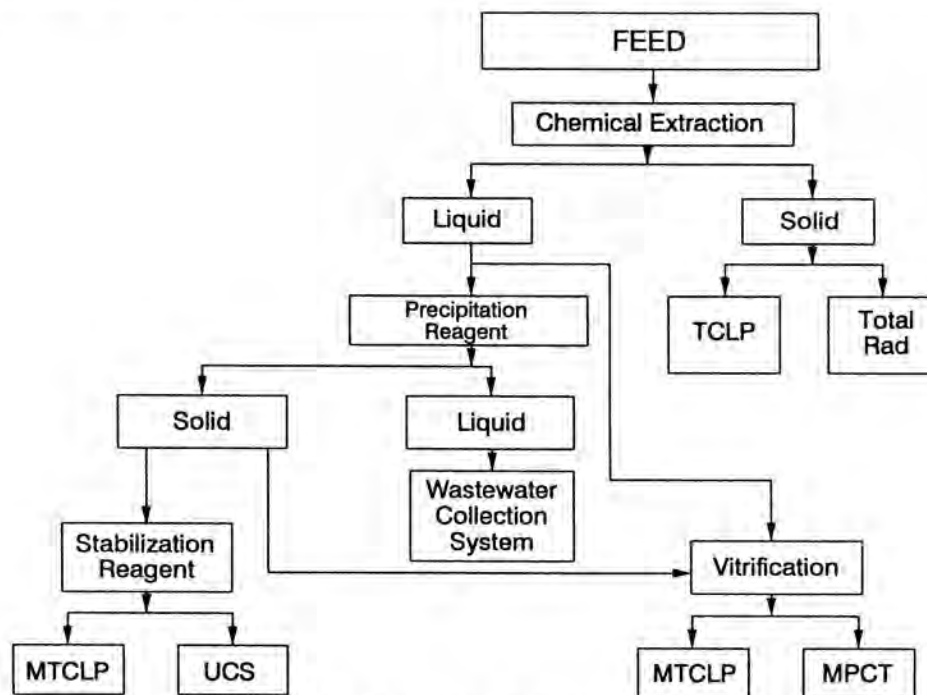


Fig. 1. Treatability flowsheet.

+ 50/-30 percent accuracy. The levels of QA/QC are moderate to high.

Remedy Screening Analyses

Only target analytes were used in this phase. The target analytes were U, Pb, gross alpha and gross beta. The spent extractants were analyzed for all four target analytes; the raffinates were analyzed for gross alpha and beta. Uranium and Pb were selected as the target analytes because they were present in greater concentrations than the other COC's.

Remedy Selection Analyses

The raffinate was analyzed for Th-total, U-total, Pb-210, Po-210, Pa-231, Ac-227, Ra-226 and Ra-228, and gross alpha and beta. Selected spent extractant solutions were analyzed for U and Pb as in the Remedy Screening phase.

EXPERIMENTAL DESIGN

Remedy Screening - Stage I

In Stage I, HCl, HNO₃, and HOAc were investigated. EDTA was not investigated in Stage I. The acid leaching experiments were conducted to determine which acids had promise and the effects of temperature and acid concentration on the metal solubilities. In the initial tests with the concentrated acids, the effect of temperature was measured by testing at room temperature and 80°C. The effect of acid concentration was measured by testing each acid at three concentrations. The three acid concentrations were concentrated, and concentrated acid diluted with 1 part and with 3 parts water. The experiments were conducted at 2:1 and 4:1 (w/w) extractant to waste ratio (dose rate).

The experiments were conducted using Hach[®] chemical oxygen demand test vials with a magnetic stir bar in each vial. A waste sample of 1.5 or 3 grams (g) was placed in each vial, and 6 g of acid were added. The samples were agitated and heated for two hours. After two hours of agitation the samples were removed and centrifuged for 10 to 25 minutes as needed. An aliquot of each sample was filtered through a 0.45 micron

syringe filter and analyzed for Pb and U. Ion chromatography (IC) was used to obtain U values and Pb was analyzed by inductively coupled plasma (ICP).

If it was apparent from the analytical results that a particular acid was not successfully leaching the metals, the acid was eliminated from further testing. If the analytical results indicated that a particular extract contained more U and Pb than another extract at similar conditions, then that extract and condition were considered promising. Those promising extracts and conditions were investigated further during Stage II testing.

Remedy Screening - Stage II

Stage II testing began with duplication of promising tests from Stage I using different waste samples. Stage II testing was performed using the same equipment and same basic methodologies described under Stage I testing. All experiments were conducted at a 4:1 dose rate, 80°C, and extracted for 4 hours unless otherwise noted. The 4:1 dose rate and 80°C conditions were used because the extraction efficiencies at these conditions were better than at the 2:1 dose rate and ambient temperature conditions.

The gross alpha and beta values of the raffinate were not sufficiently decreased by any of the three acids investigated. Therefore, EDTA (0.2 and 0.8 M at pH 8.5 to 9) which forms strong complexes with Ra²⁺ and Th⁺⁴ was investigated in Stage II to improve the total radiological removal from the raffinate.

In addition, analysis of the data indicated that to achieve substantial reductions in the total radiological activity of the extracted waste, sequential extraction steps were required. The extractants investigated were 27 percent HCl, 30 percent HNO₃ and 0.8 M EDTA. The eight sequential extraction treatment schemes investigated are as follows:

- Six HCl extractions (6-HCl)
- Six HNO₃ extractions (6-HNO₃)
- Six 0.8 M EDTA extractions (6-EDTA)

- Potassium chloride (KCl in a 15 percent solution) pretreatment followed by six EDTA extractions (KCl/EDTA)
- Six HCl extractions followed by one EDTA extraction (HCl/EDTA)
- Six HNO₃ extractions followed by one EDTA extraction (HNO₃/EDTA)
- Six EDTA extractions followed by HNO₃ extractions (EDTA/HNO₃)
- HNO₃ extraction followed by two water rinses then by six EDTA extractions (HNO₃/RINSE/EDTA)

Potassium chloride pretreatment followed by EDTA was investigated because this treatment has previously been used to extract RaSO₄ from soils (2). These experiments were conducted at 80°C, a 4:1 dose rate and 4 hours extraction time. The HNO₃/RINSE/EDTA experiment was conducted after the selection of experiments for the Remedy Selection phase study.

Further experiments were conducted to determine if the effectiveness of the sequential extraction process was being limited by the saturation of the extractant. Two sets of multiple extraction tests at 80°C were conducted where the dose rate was increased from 4:1 to 10:1 and the time of extraction was increased from 4 to 24 hours. These additional tests were investigated using two different extraction sequences, six sequential EDTA extractions and KCl/EDTA. The EDTA was at 0.8 M at pH 8.5 - 9. The KCl was a 15 percent solution.

Remedy Selection

The goal of the Remedy Selection testing was to demonstrate on larger samples (400 g) that the extracted solids were nonhazardous materials as defined by RCRA and that uranium, lead, thorium, polonium, protactinium, actinium, and radium were successfully extracted from the solids. The two treatments from the Remedy Screening Stage II tests that yielded extraction solutions with the highest concentrations of Pb and U and raffinate with the lowest gross alpha and beta were repeated on a larger scale. All experiments were conducted at a 4:1 dose rate, 80°C, and extracted for 4 hours. The KCl/EDTA and EDTA/HNO₃ extraction processes were carried forward into the Remedy Selection phase.

Solid/liquid separation after each extraction step was accomplished using vacuum filtration. The raffinate were rinsed three times (4:1 dose rate) at the end of the extraction process. During successive rinses, filtration became increasingly difficult. Therefore, the liquid separations during rinsing operations were continued using centrifugation. Filter aids and polymers were not tested at this time because of possible interferences with analysis of the residue. The extracted solids were subjected to TCLP, with the extract being analyzed for metals and radionuclides. The solids were also analyzed for total radionuclide concentrations.

RESULTS AND DISCUSSION

Remedy Screening

Results from range finding tests in the Remedy Screening Stage I indicated the HCl and HNO₃ were more effective extracting U and Pb than HOAc. Acetic acid, which is a weak acid used in the TCLP procedure, was about 80 percent as effective as the two strong acids, HCl and HNO₃. Acetic acid was dropped from the program, since it was less efficient at U and Pb removal.

Of the three acid concentrations investigated, the target metals were most effectively extracted with 27 percent (concentrated) HCl and 30 percent (1 part acid to 1 part water) HNO₃. Approximately 80 percent of the U and Pb were extracted in a single 27 percent HCl or 30 percent HNO₃ extraction. The efficiencies for extractions of Pb were similar for HCl, HNO₃, and EDTA. However, the strong mineral acids, HCl and HNO₃, were substantially more effective at extracting U than EDTA. The 4:1 dose rate was more effective at extracting U and Pb in a single extraction step. It is postulated that at the 2:1 dose rate, the liquid is becoming saturated with metal ions and is therefore limiting the solubility of the U and Pb.

In the single acid extraction step experiments, the conditions and acid type for the maximum decrease in the measured gross alpha and gross beta of the raffinate were not the same as for maximum Pb and U removal. The best extractant for reduction in gross alpha and beta in a single extraction step was 2 M HOAc at 80°C. The best performing acids based on the amount of Pb and U in the extract were HNO₃ and HCl at 80°C. At closer inspection of the gross alpha and beta data for the raffinate, it was observed that approximately half of the values after one extraction step were higher than the untreated waste. A possible explanation for this phenomenon is the extraction of shielding elements, such as natural lead, which are more soluble than the radionuclides, thus increasing the concentration and effective availability of the radionuclides for the analysis. The extractant also may have caused the waste to break up into smaller particles, exposing more surface area.

The reduction in the raffinate gross alpha and beta by the three acids tested was not satisfactory. EDTA solutions (0.2 and 0.8 M at pH 8.5 - 9) were significantly more efficient at lowering the raffinate gross alpha and beta activity than the acids investigated. The 0.8 M solution was generally better than the 0.2 M solution.

Analysis of the data indicated that a single extraction by any of the three acids or by EDTA would not be successful. In order to achieve substantial reductions in the total radiological activity of the waste, multiple extraction steps using EDTA by itself or EDTA combined acid extraction steps would be required.

The eight sequential extraction treatment schemes were as follows: 6-HCl, 6-HNO₃, 6-EDTA, KCl/EDTA, HCl/EDTA, HNO₃/EDTA, EDTA/HNO₃, and HNO₃/RINSE/EDTA. (See Remedy Screening - Stage II). The least reduction in gross alpha and gross beta of the raffinate were measured for six sequential extractions with the acids, HCl/EDTA, and HNO₃/EDTA. The acid extractions were not efficiently extracting the radium from the waste; therefore, the activity of the waste was not sufficiently decreased. Also the EDTA was not effective because in the HCl/EDTA and HNO₃/EDTA experiments the pH of the raffinate was not adjusted to near neutral conditions before addition of EDTA. Therefore, it is highly likely that most of the EDTA precipitated on the solid residue instead of effectively penetrating the particle to extract the metals. The maximum reductions in total gross alpha and beta activity in the raffinate after six or seven extractions at 4:1 dose rate and four hour extraction time were from the KCl/EDTA, EDTA/HNO₃, and HNO₃/RINSE/EDTA. The latter extraction sequence was more effective than HNO₃/EDTA since the two water rinses raised the pH of the solid above the precipitation pH for EDTA.

Further experiments were conducted to determine if the multiple extraction process was being limited by the saturation of the extractant. Two sets of multiple extraction tests at 80°C

were conducted where the dose rate was increased from 4:1 to 10:1 and the time of extraction was increased from 4 to 24 hours. The Pb and U concentrations in the first extraction step for the 10:1 dose rate experiments were only slightly improved over the 4:1 experiments. It can be concluded that solubilities of Pb and U in the EDTA extractants at 80°C were limited due to saturation of the solutions. The 10:1 dose rate experiments were not studied further since this high dose rate was believed to be impractical in the field operations.

The raffinate from the first 24 hour extraction had higher gross alpha and gross beta values than for the first 4 hour extraction. By the third extraction step, the gross alpha and beta of the raffinate was substantially lower for the 24 hour than the 4 hour extraction steps. A possible explanation of these observations is that several materials dissolved relatively quickly. When these dissolved materials were allowed to stand for longer periods of time (24 hours), some of the dissolved material reprecipitated. By the third extraction step, the concentrations of cations and anions in the extraction solution were low enough that the rate of reprecipitation was diminished or effectively terminated thereby allowing a permanent removal of the COC from the waste. Further experiments using 24 hour extraction times were not conducted because it was believed that long extraction times were impractical for large field operations.

Based on the reduction in the raffinates' gross alpha and beta, KCl/EDTA and EDTA/HNO₃ were carried forward into the Remedy Selection extractions. Further small-scale investigations, conducted after the selection of the Remedy Selection experiments, indicated that the HNO₃/RINSE/EDTA may be the most effective process to remove U from the waste and the most cost-effective process of the processes investigated.

Remedy Selection

With the 400 gram samples used in the Remedy Selection phase, the KCl/EDTA was more effective at removing the radionuclide than EDTA/HNO₃. Both extraction processes, KCl/EDTA and EDTA/HNO₃, were successful at meeting the goal of yielding a raffinate that had TCLP leachate concentrations less than the toxicity characteristic (TC) regulatory limit. The TCLP leachate concentrations were less than 5 percent of the TC regulatory limit.

The measured concentrations of most of the radionuclides in the total constituent analyses were reduced by the chemical extraction process. The average percent reductions are listed in Table I. In particular, note that Ra-226 was reduced by greater than 96 percent. The table shows measured concentration increases for two of the radioisotopes: specifically, total thorium and total uranium. It is postulated that radionuclides which are not extracted are concentrated in the solids fraction by the removal of the more chelatable and more acid soluble substances. Also, elements that are detected by measurements that are influenced by self-absorption or self-attenuation can exhibit increased measured activity when the absorbent or attenuating materials are removed from the surface of the particle being measured, as for example, Pb by EDTA extraction.

PROPOSED PROCESS

The current extraction processes, KCl/EDTA or EDTA/HNO₃, are limited due to inefficient extraction of U. An improved process would extract the majority of all the radionuclides COCs. A slight modification of the HNO₃/RINSE/EDTA process should achieve this goal. The

TABLE I
Radionuclide Percent Reduction

Radionuclide	KCl/EDTA (%)	EDTA/HNO ₃ (%)
Ac-227	42.10	50.73
Pb-210	82.42	78.90
Po-210	96.22	95.78
Ra-226	97.63	96.63
Th-total	-922.61	-3.73
U-total	-100.09	3.20

process would include a 30 percent HNO₃ extraction (4:1 dose rate), followed by two water rinses (2:1 dose rate), followed by KCl pretreatment, and three KCl and EDTA extractions.

From previous work, approximately 80 percent of the U and Pb can be extracted in a single step with 30 percent HNO₃ at 80°C, 4 hour extraction time, and 4:1 dose rate. This initial acid extraction would extract most of the U and Pb from the feed. The remaining Pb and U would be extracted in the subsequent EDTA extractions. The HNO₃ spent extract will be decontaminated with standard hydroxide precipitation techniques. The majority of the Pb and U would be isolated in these hydroxide precipitates. The addition of an initial acid extraction step would satisfy the goal of improving the U extraction efficiency over that of the KCl/EDTA or EDTA/HNO₃ processes.

The acid extracted material would be rinsed twice with water at a 2:1 dose rate. Two rinses would be used to more effectively remove the soluble Pb and U and to lower the concentration of acid on the raffinate. Prior to KCl and EDTA treatment, the pH of the raffinate would be raised to 8.5-9 by sodium hydroxide and ammonia additions.

Pretreatment with KCl followed by EDTA would be used to extract the Ra and Th from the acid extracted material. Instead of KCl being added only as a pretreatment step, KCl would be added each step of the EDTA extraction sequence. The number of EDTA extractions would be reduced from six to three since previous data indicates most of the metals are extracted in the first three EDTA extractions. In addition, many of the soluble metals would have been extracted in the initial acid extraction. The addition of KCl with each EDTA extraction step was not investigated in this study.

It has been demonstrated from small scale tests that the extraction of U and Pb were improved by using increasing contact times for subsequent extractions. Therefore, in the proposed process, the KCl and EDTA extraction times would be double for each of the KCl and EDTA extraction steps to minimize potential reprecipitation problems and to increase the extraction of kinetically limited species. The liquids from the pH adjustment and first KCl addition would not be filtered from the raffinate prior to KCl and EDTA addition. This would be done to increase the dose rate of the first EDTA extraction and to minimize the solubility limitation of Pb and U in the extraction fluid. The subsequent EDTA extraction would use a 4:1 dose rate as before.

SUMMARY AND CONCLUSIONS

The objectives of the chemical extraction treatability study were to:

- Determine the effectiveness of various extraction solutions in removing RCRA metals and radionuclides,

- Determination of the effectiveness of various reagents to decontaminate the used extraction solutions, and
- Determine the effectiveness of various reagents to cement stabilize or vitrify the precipitate from the decontamination of the used extraction solutions.

The treatability study was successful. The efficiencies of various extractants and extraction conditions were determined. The goal of determining an extraction process to yield a raffinate that had TCLP leachate concentrations below the TC regulatory limit was met. The effectiveness of reagents to decontaminate the extractants and to stabilize/vitrify the precipitate were determined. The decontamination data were not discussed in this paper. The decontamination and the vitrification processes did meet the project goals.

Three acids, HCl, HNO₃, HOAc, a chelant, EDTA, and combinations of acids or KCl with EDTA were investigated. Acetic acid proved to be ineffective at Pb and U removal. The extraction efficiencies of Pb were similar for HCl, HNO₃, and EDTA. The strong acids were significantly more effective than EDTA at U extraction. The acids were not effective at removing Ra from the waste.

Under the conditions of the tests investigated, sequential extraction steps were necessary to remove the majority of radionuclides. The largest decrease in the gross alpha and beta values

for the extracted solid materials were derived from extractions with six sequential EDTA extractions followed by one HNO₃ extraction (EDTA/HNO₃), KCl pretreatment followed by six sequential EDTA extractions (KCl/EDTA), and a HNO₃ extraction, followed by a rinse and six EDTA extractions (HNO₃/RINSE/EDTA).

The KCl/EDTA and EDTA/HNO₃ experiments were scaled-up for TCLP and total radionuclide determinations. The extracted insoluble residues passed the TC regulatory limits and most of the radionuclide concentrations were significantly reduced in the raffinate.

The use of a single extractant, i.e., the use of only an acid or EDTA, limits the extraction of the constituents of concern. It is proposed that a modification of the HNO₃/RINSE/EDTA process will improve the extraction efficiencies and will be the most efficient and cost effective process investigated in this study.

REFERENCES

1. U.S. ENVIRONMENTAL PROTECTION AGENCY, "Guide for Conducting Treatability Studies under CERCLA," EPA/540/R-92/071a, EPA (1992).
2. K.E. HAQUE, "Radium(226) Removal from a Contaminated Soil," EPA (1988).