TREATING RADIOACTIVE CONTAMINATED SOIL BY THE PROCESS OF EXTRACTION

W. Alam, E. C. Donaldson, N. Begum, R. Hossain, R. Bouwkamp
Tetrahedron, Inc.

N. Fatherly, R. Livermore
U.S. Army Corps of Engineers, Baltimore District

ABSTRACT

A bench scale study was conducted to develop a cost effective method for treating low-level radioactive contaminated soil from a Formerly Utilized Sites Remedial Action Program (FUSRAP) site located in Maryland. Acid leaching tests for extraction were conducted on soils to evaluate the effectiveness of treatment under various conditions including: strength of the acid, addition of heat, addition of common ion salt, contact time and multi-stage extraction. It was observed that higher concentrations of acid improved extraction but the rate of increased efficiency diminished with concentration of the acid. Also, heat had a more significant effect on extraction at lower concentrations of acid. The treatment efficiency was only slightly improved by adding Common ion salt. It was further observed that a multi-stage extraction system significantly increased the treatment efficiency that would allow use of lower concentration acid in the field.

INTRODUCTION

Low-level radioactive contaminated sites have often been remediated using the "dig and haul method". Though the process works in cleaning a contaminated site, it does have certain disadvantages such as: (i) accumulating contamination at the disposal location, (ii) high exposure risk from high volume and long haul transportation, (iii) reluctance from public to allow high volume shipment through their communities, and (iv) high cost of transportation and disposal. For most sites, however, "dig and haul" remains the only choice for remediation as other alternatives are not feasible due to waste and site characteristics.

A FUSRAP site in Maryland has a disposal area containing Low Level Radioactive Waste (LLRW) generated from the process of extracting Thorium from Monazite sand. A Remedial Investigation (RI) and Feasibility Study (FS) were conducted by the US Army Corps of Engineers, Baltimore District (USACE) for the site. The Contaminants of Concern (CoC) identified during the RI were Thorium-232, Radium-226, Radium-228, Uranium-233/234, and Uranium-238 for which Primary Remediation Goals (PRGs) were established in the Baseline Risk Assessment (BLRA). During the selection of remedial alternatives for the FS, it was observed that RWDA soil characteristics, identified during the RI, indicated that "Soil Washing" was a viable alternative. A bench scale treatability study was designed and conducted by Tetrahedron to provide site-specific information needed to complete the alternative analysis for the FS. The method of treatment consisted of acid leaching of radionuclides from the contaminated soil. The results indicate that treating the soil with a multi-stage extraction system would lower the concentration of the CoC to below PRGs in most cases. As a result, a large volume of soil would not require off-site disposal. The remainder of the soil still above PRGs can be reprocessed through the system or disposed off-site at a lower concentration. The treatment system should result in substantially lowering the waste disposal cost for the site.

STUDY DESIGN

The study was conducted using soils collected from eight locations at the disposal area that indicated significantly elevated concentrations of CoC during the RI. The soil was then characterized in terms of: concentrations of CoCs by grain size, grain size distribution, Cation Exchange Capacity (CEC), pH, Total Organic Carbon (TOC), and moisture content. The samples were sieved into four fractions based on the size of the grains (< 0.075, 0.075 - 0.25, 0.25 – 2.00, and > 2.0) in millimeter. Each fraction was analyzed to see if radioactivity was concentrated in one or more of a particular sieve size that would allow treatment of only those fractions instead of the total soil volume. The initial concentration of radioactive constituent was determined from each of the four fractions from the eight samples to establish a baseline. Parameters analyzed included gross alpha, beta & gamma spectroscopy and isotopic U & Th.

Soil samples were treated with nitric acid under variable conditions to determine the most efficient method for extracting LLRW contaminants from the soil matrix. Variables studied for the acid treatment system included: (i) Concentrations of nitric acid ranging from 5% to 25% acid strength. (ii) Contact time varying between 2 minutes to 10 minutes. (iii) Effect of heat, and (iv) Effect of common ion (sodium nitrate). Results were measured in terms of Total Activity for screening purposes. A flow diagram of the study design is shown in Fig. 1.

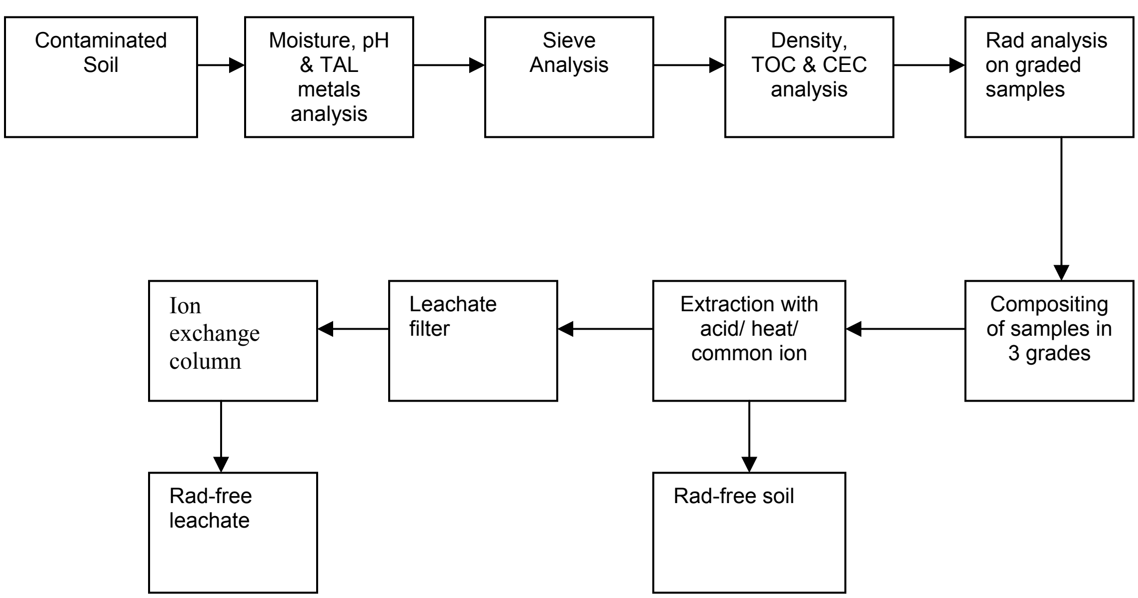

Fig. 1 Flow diagram showing the bench scale treatability system

RESULTS

The results of the soil characterization study indicated that the contaminant was randomly distributed throughout the soil matrix. Please refer to Table I. There was no significant correlation between concentration of CoC and grain size. The CEC was moderately low (~25 Meq/100gm) indicating that the contamination was not too strongly bound to the soil matrix. Also, Total Organic Carbon (TOC) was low (~1%) thereby allowing for easy separation of the extraction fluid from soil. The pH was marginally acidic. Please refer to Table II. The soil characteristics indicated that an acid extraction treatment system could be effective but the CoCs were randomly distributed throughout the soil matrix and would, therefore, require treatment of the total soil volume.

Table I Concentrations (average) of radionuclides by grain sizes

Grain Size (mm)	Th-232 (alpha)	U-238 (alpha)	U-238 gamma)	U-234 (alpha)	Ra-228
<0.075	17.28	2.69	1.96	2.91	10.09
0.075 – 0.25	5.38	1.13	2.14	1.13	9.89
0.25 – 2.0	4.08	0.86	1.25	0.95	6.34
>2.0	24.68	2.46	4.25	2.51	14.63

Table II Physical Properties (average) of contaminated soil

<table>
<tr><th colspan="2">Grain Size Distribution</th><th rowspan="2">Cation Exchange Capacity
mEv/100g</th><th rowspan="2">TOC
%</th><th rowspan="2">pH</th><th rowspan="2">Moisture
%</th></tr>
<tr><th>Grain Size (mm)</th><th>Volume %</th></tr>
<tr><td><0.075</td><td>12</td><td>55</td><td rowspan="4">1.0</td><td rowspan="4">5.9</td><td rowspan="4">37.7</td></tr>
<tr><td>0.75 - 0.25</td><td>17</td><td>29</td></tr>
<tr><td>0.25 – 2.0</td><td>45</td><td>19</td></tr>
<tr><td>>2.0</td><td>25</td><td>12</td></tr>
</table>

Since contamination was randomly distributed, soils from the eight locations were composited into three samples based on their similar characteristics for conducting the extraction study. Composite #1 consisted of soils with grain size less than 2 mm from the eight locations, Composite #2 consisted of soils of grain size greater than 2 mm from the eight locations, and Composite #3 consisted of soils of grain size greater than 2 mm from locations 1 through 4. Locations 1 through 4 had the highest levels of radionuclides and this composite represented the worst-case scenario. The purpose of separating composites 1 and 2 based on grain size was to find out if extraction efficiency could be affected by the extraction fluid not being able to reach the core of the grain in larger particle contamination. Total Activities of the three composite samples before treatment and the results of the extraction study using the process of acid leaching are given in Table III and Table IV respectively.

Table III Total activities of the composite samples prior to treatment

Sample ID	**Total Activity (pCi/g)**
Composite #1	185 ± 17.3
Composite # 2	238 ± 24.0
Composite #3	1200 ± 37.3

Table IV Results of total activity from treated soils

Sample ID	Treatment	Leach Time	RL pCi/g	Total Activity pCi/g
Composite #1	15% HNO3 treated	2 minute leach	5	159 ± 6.11
Composite #1	15% HNO3 treated	5 minute leach	5	84.3 ± 4.97
Composite #1	15% HNO3 treated	10 minute leach	5	73.2 ± 4.50
Composite #3	15% HNO3 treated	2 minute leach	5	700 ± 16.5
Composite #3	15% HNO3 treated	5 minute leach	5	899 ± 20.6
Composite #3	15% HNO3 treated	10 minute leach	5	685 ± 16.1
Composite #3	15% HNO3 treated	20 minute leach	5	693 ± 16.3
Composite #3	5% HNO3 treated	5 minute leach	5	962 ± 21.6
Composite #3	5% HNO3 treated	10 minute leach	5	937 ± 20.9
Composite #3	5% HNO3 treated	20 minute leach	5	1100 ± 24.2
Composite #3	15% HNO3/NaNO3 w/heat	20 minute leach	5	306 ± 36.7
Composite #3	15%HNO3/NaNO3 w/o heat	20 minute leach	5	758 ± 33.6
Composite #3	20%HNO3/NaNO3 w/heat	20 minute leach	5	231 ± 20.7
Composite #3	20%HNO3/NaNO3 w/o heat	20 minute leach	5	404 ± 24.9
Composite #3	20% HNO3 w/heat	20 minute leach	5	297 ± 24.1
Composite #3	20% HNO3 w/o heat	20 minute leach	5	396 ± 24.6
Composite #3	25% HNO3 w/heat	20 minute leach	5	186 ± 19.9
Composite #3	25% HNO3 w/o heat	20 minute leach	5	227 ± 21.6
Composite #2	20% HNO3/NaNO3	20 minute leach	5	56.2 ± 6.26

DISCUSSIONS OF THE RESULTS

The total activity was found to be lowest in Composite #1 and highest in Composite #3 of the untreated soil samples. Effect of increasing the acid concentration on extraction efficiency can be seen from the above data. The study also evaluated the effects of heat and common ions on extraction efficiency. Following observations were made from the results of this study:

Effect of Contact Time on Leaching Efficiency

Results show that the length of acid contact time of over five minutes minimally affects the extraction efficiency. Please refer to Table IV. It should be noted that the soil was sieved making it easy for the acid to reach all the grains instantaneously.

Effect of Adding Heat to and Increasing the Concentration of Nitric Acid on Extraction Efficiency

It can be seen that at lower concentrations of nitric acid, heat (resulting in temperature of 70 C) seems to enhance the extraction process. At higher concentrations of nitric acid, this effect seems minimal. Please refer to Fig. 2. It is estimated that at about 25% nitric acid concentration, heat has minimal effect, if any, on the extraction efficiency.

Effect of the Adding the Common Ion (NaNO3 to the HNO3) and Increasing the Concentration of Nitric Acid (with and without heat) on Extraction Efficiency

Affect of common ion (adding $NaNO_3$ to HNO_3) was evaluated to see if lower concentration acid, in conjunctions with, common ions could be used in the field to get high extraction efficiency. It was observed that common ions enhance the extraction efficiency at lower acid concentration. However, the efficiencies are not high (<50%) enough at these concentrations for making the process viable. At higher acid concentrations (greater than 15%), common ions have minimal effect on the extraction efficiency. At 25% nitric acid concentration, incremental efficiency obtained from common ions is only about 2% and, therefore, the advantage of the use of common ion is marginalized. Please refer to Figure 3.

Effect of the a Two Stage Process on Extraction Efficiency

A two-stage process using nitric acid at concentrations between 20% to 25% brings extraction efficiency up to 95%. Please refer to Fig. 4. Extrapolation of the data shows that approximately 98% extraction efficiency can be obtained using a three-stage process.

Effect of Contaminate Distribution on the Process

The CoCs were randomly distributed throughout the soil matrix. Therefore, all contaminated soil at the site must be treated to reduce COCs. Segregation of "clean soils" from treatment will not be cost effective volume reduction strategy.

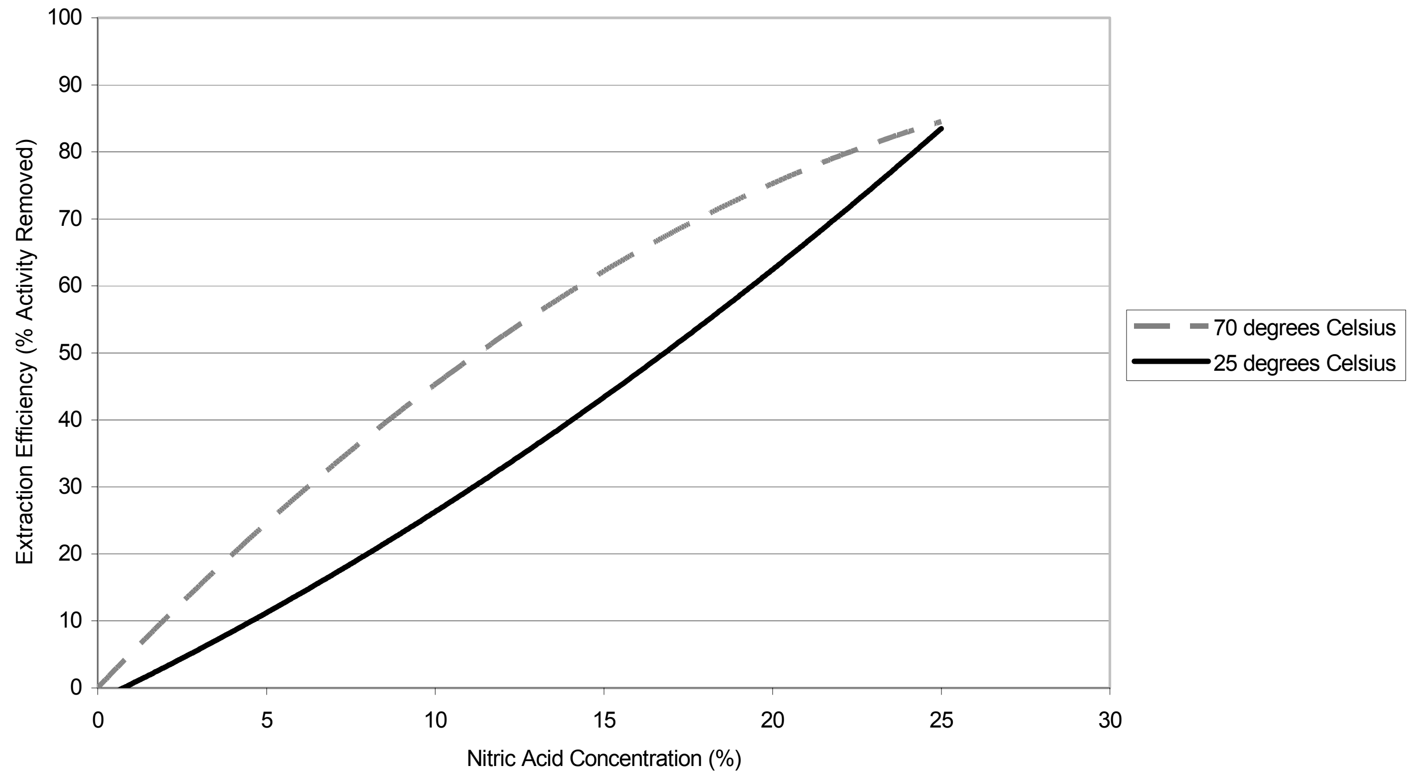

Fig. 2 Effect of heat and nitric acid concentration on extraction efficiency

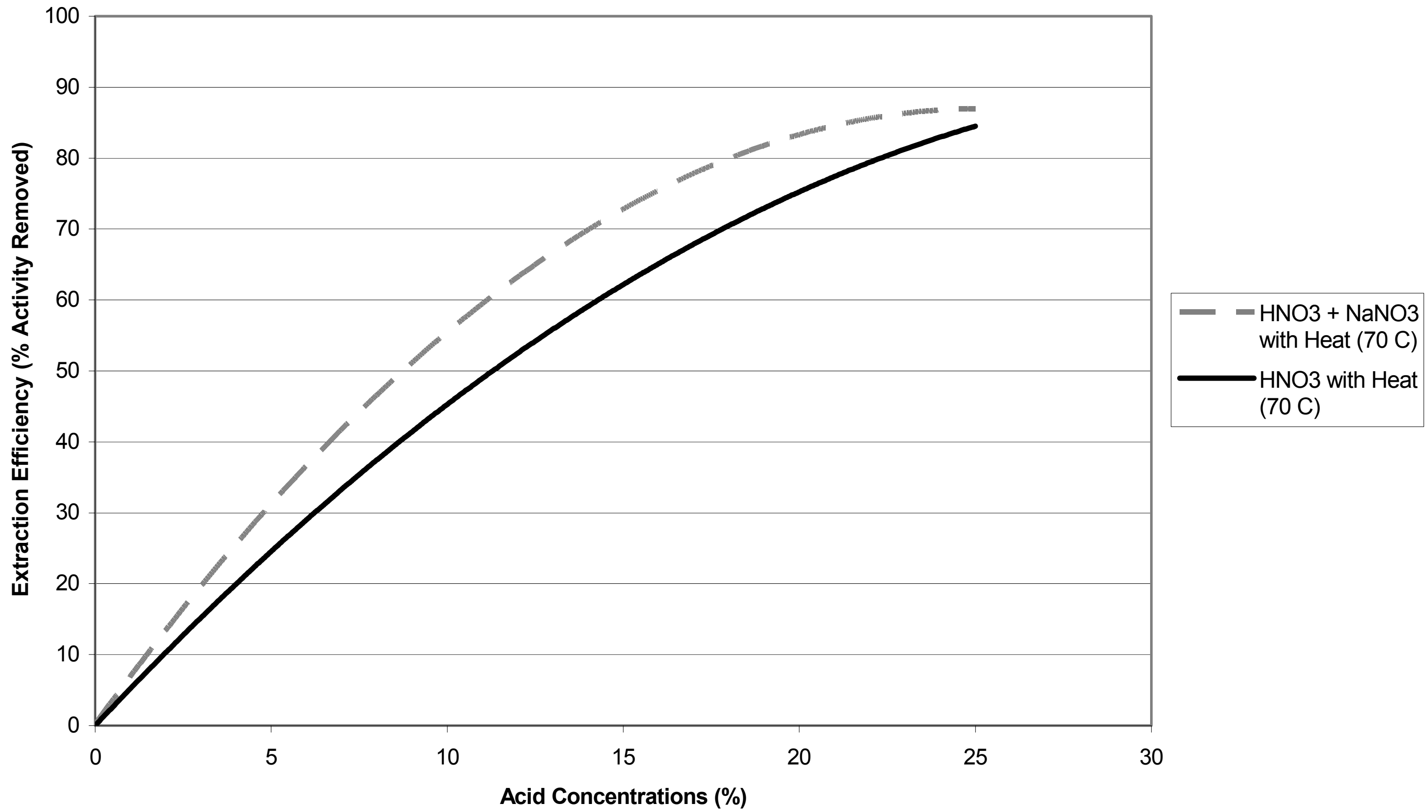

Fig. 3 Effect of common ion and nitric acid concentration on extraction efficiency

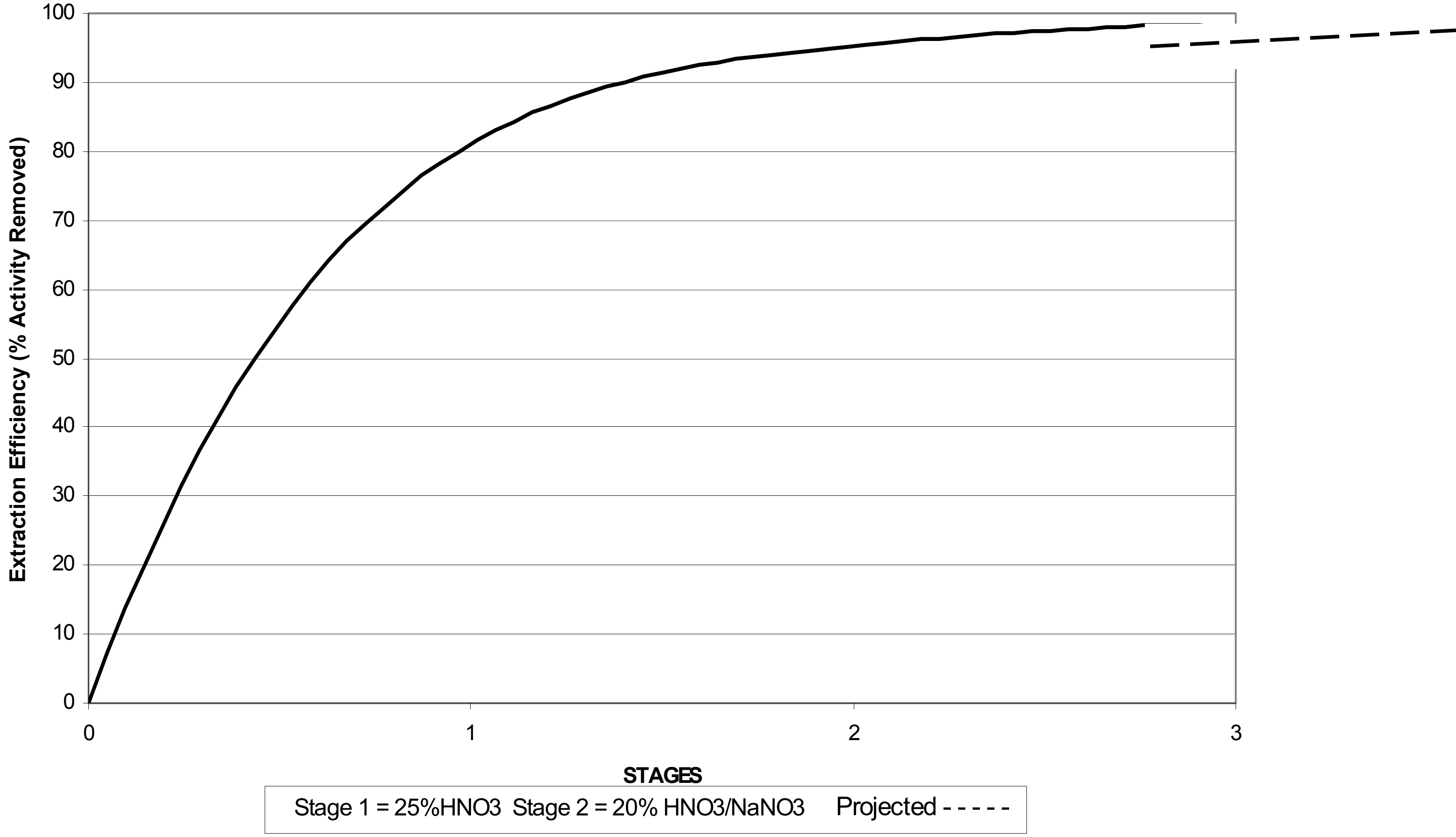

Fig. 4   Effect of multi-stage process on extraction efficiency

CONCLUSION

Acid leaching tests for extraction were conducted on soils to evaluate the effectiveness of treatment under various conditions including: strength of the acid, addition of heat, addition of common ion salt, multi-stage extraction and grain size. It was observed that:

- Nitric acid is able to effectively remove the radionuclides from the soils.
- A treatment efficiency of over 95% can be achieved in a 2-stage treatment.
- Multiple stage treatment enhances treatment efficiency.
- Treatment efficiency increases with higher concentration of acid. The rate of increase diminishes at higher concentrations of acid.
- Application of heat improves treatment efficiency.
- At higher concentrations of acid (25% and over), effect of heat on treatment efficiency is insignificant
- Contact time of 5 minutes or over is sufficient for recovery in a batch system.
- Common ions increase the treatment efficiency insignificantly at higher concentrations of acid.
- Distribution of CoC in soils is random.

REFERENCES

1 EPA. 1989. Innovative Technologies: Soil Washing, OSWER Directive 9200.5-250FS.

2 EPA. 1989. Soils Washing Technologies for: Comprehensive Environmental Response, Compensation, and Liability Act, Resource Conservation and Recovery Act, Leaking Underground Storage Tanks, Site Remediation.

3 EPA, 1990. Soil Washing Treatment. Engineering Bulletin, EPA, OERR, Washington, D.C. EPA/540/2-90/017. Available from NTIS, Springfield, VA. Order No. PB91-228056.

4 EPA, 1991. Biotrol Soil Washing System. EPA RREL, series includes Technology Evaluation Vol. I, EPA/540/5-91/003a, PB92-115310: Technology Evaluation Vol. II, Part A, EPA/540/5-91/003b, PB92-115328: Technology Evaluation Vol. II, Part B, EPA/540/5-91/003c, PB92-115336: Applications Analysis, EPA/540/A5-91/003; Technology Demonstration Summary, EPA/540/A5-91/003; and Demonstration Bulletin, EPA/540M5-91/003.

5 EPA, 1992. Bergmann USA Soil/Sediment Washing System, EPA RREL, Demonstration Bulletin, EPA/540/MR-92/075.

6 EPA, 1997. Best Management Practices (BMPs) for Soil Treatment Technologies: Suggested Operational Guidelines to Prevent Cross-media Transfer of Contaminants during Clean-up Activities, EPA OSWER, EPA/530/R-97/007.

7 Raghavan, R., D.H. Diez, and E. Coles.1988. Cleaning Excavated Soil Using Extraction Agents: A State of the–Art Review, EPA Report, EPA 600/2-89/034.

8 INEL-96/0273. 1997. Biagi, C. Integrated Non-thermal Treatment System Study.

9 Krstich, M.A. 1995. The Integration of Innovative Technologies into a Physical-Separation-Based Soil Washing System. Fernald Environmental Restoration Management Corporation Report No. FEMP-2410, U.S. DOE.

10 Musich, M.A. 1997. Systems Analysis of Environmental Management Technologies. DOE/MC/31388-5766.

11 Baylock, B. P. 1995. U. S. Department of Energy Worker Health Risk Evaluation Methodologies for Assessing Risks Associated with Environmental Restoration and Waste Management. ORNL 6833.

12 DOE/EM-0282. 1995. Description of recommended non-thermal mixed waste treatment technologies: Version 1.0.

13 ORNL/TEM –13201. Evaluation of the Act-De-Con^R Process for Treating tank Sludge, NTIS, Springfield, VA.

14 DOE/MC/30097. 1997. W.E. Schwinkendorf . Comparison of Alternative Treatment System for DOE Mixed Low-Level Waste. Idaho National Engineering Laboratory. Lockheed Martin Idaho Technology Company. Idaho.

15 DOE/MC/30097-5162. 1996. Rindt, J. R. Mixed Waste: Topical Report : April 1994-Sept.1995.

16 *Technical Reports from Argonne National Laboratory, Environmental Assessment Division, Chicago.

17 *Technical Reports from National Council on Radiation Protection and Measurement.

18 *Technical Reports from Nuclear Regulatory Commission.*Directives and Orders form U.S. Department of Energy.

19 *FUSRAP Soil Washing Database.

20 Perry, R.H., and C. H. Chilton (Eds). Chemical Engineers' Handbook, Fifth Ed. McGraw-Hill Book Company, New York.

21 Corbitt, R. A.(Ed.). Standard Handbook of Environmental Engineering. McGraw-Hill Book Company, New York.

22 Rossiter, A.P. (Ed.). Waste Minimization through Process Design. McGraw-Hill Book Company, New York.