DOE/EW00001 - F

DOE/EW/00001--T2-Pl.1

RECEIVED

DEC 03 1998

OSTI

**Treatment Methods and Comparative Risks of Thorium Removal from
Waste Residues**

R.D. Porter, D.M. Hamby, and J.E. Martin

**Department of Environmental and Industrial Health
School of Public Health
University of Michigan
Ann Arbor, MI 48109-2029**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

**Prepared for the Department of Energy, Office of Environmental Management
Grant Number DE-FG05-96EW00001**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**Treatment Methods and Comparative Risks
of Thorium Removal from Waste Residues**

**R.D. Porter, D.M. Hamby, and J.E. Martin
University of Michigan**

July 1997

**U.S. Department of Energy
Grant Number DE-FG05-96EW00001**

TABLE OF CONTENTS

Overview	1
Introduction	2
Physical Properties of Thorium	
Radiological Decay	3
Geology and Mineralogy	3
Chemistry	5
Soil Properties	
General Soil Characteristics	5
Properties of Thorium in Soil	6
Properties of Thorium in Site-Specific Soils	7
Soil Washing	
General Description	9
Bechtel National's Soil Washing Machine	11
Other Soil Washing Machines	13
Chemical Extraction Techniques	
General Descriptions and Definitions	14
Classical Thorium Extraction Methods - Monazite Sand	17
Waste Site Thorium Extraction Methods - Process Product	21
Chemical Extraction Variations	25
Physical Removal Techniques	
The Segmented Gate System (SGS)	27
Magnetic and Electrical Properties	29
Phytoremediation	29
Summary and Applications of Treatment Methods	30
Risk Estimation Methods	
Heavy Equipment Operations	33
Local Transportation	34
Highway Transportation	34
Rail Transportation	35
Radiation Exposure	35
Risks to the General Public	38
Risk Comparison Summary	38
References	41
Appendix A	49
Appendix B	51

Table 2 lists the mineral composition and structure of some important minerals associated with thorium. Many of these structures contain the same nucleophilic elements and many of these minerals are diadochic - that is, many cationic type elements can substitute for one another in a given mineral. Rankhama and Sahama (1950) specifically note the diadochic nature of Zr-Th and U-Th and explain how this characterizes the geochemistry of thorium. Heinrich (1958) also points out the isomorphic nature of cerium with thorite, thorianite, and in a special structure with monazite. Consequently, thorium seems to share some important properties with other elements.

Table 2. Common minerals in Th geology.	
*Monazite	(La, Ce, Th, Nd)PO ₄
Ilmenite	FeTiO ₃
Rutile	TiO ₂
Quartz	SiO ₂
Zircon	ZrSiO ₄
*Thorianite	ThO ₂
*Thorite	ThSiO ₄
Uraninite	UO ₂
*Uranothorite	(U, Th)SiO ₄
*Uranothorianite	(U, Th)O ₂
*Thorogummite	ThO ₂ ·UO ₃
*Allanite	(Ca, Ce, Th) ₂ (Al, Fe, Mn, Mg) ₃ (SiO ₄) ₃ OH
*Represents principal Th containing minerals.	
Taken from Benedict et al. 1981 and Adams et al. 1954	

Chemical extraction of thorium from monazite is difficult, however, the oxides of thorium are more receptive to treatment (Bellamy and Hill 1963). Lumpkin and Chakoumakos (1988) found monazite to retain good crystallization despite its inherent alpha particle self-dosage which can alter the physical structure of the mineral. ThO₂ is a primary thorium structure and exists in monazite at about 10% with concentrations reported as high as 30%. The inherent self-irradiation of thorianite, however, results in a metamict structure that is not as stable (Fronzel 1956). This is consistent with the fact that the oxides are easier to extract than the monazite component of thorium. These types of structures may be seen in FUSRAP soils that were produced from the processing of thorium ores such as monazite, and thus an understanding of their bonding strengths is important in considering available volume reduction methods.

Thorium demonstrates properties similar to other elements, particularly Zr and Hf, Ce, and Pb. Its occurrence in nature resembles hafnium and zirconium which suggests similar natural binding properties (Rankama and Sahama 1950). This is consistent with zirconium's diadochic nature with regards to thorium. Also, minerals rich in cerium and related elements commonly contain thorium (Adams et al. 1954). This is important in thorium detection and is consistent with the cerium-thorium diadochy described above. Lead also accumulates in thorium bearing materials (Table 1) because it is the stable end product of the thorium decay series (Rankama and

Sahama 1950). Processes to remove thorium, therefore, will also remove a potential future lead contamination problem.

Chemistry

The chemical properties of thorium are very important toward understanding thorium soil extraction. The element has a relatively high melting point of 1450-1842 °C, making metallurgical processes somewhat difficult. It has multiple oxidation states, preferring the +4 valence. Thorium does not undergo chemical reactions involving oxidation state changes in solution, because it exists exclusively in the +4 valence state while in solution (Ryabchikov and Gol'braikh 1963). Based on its binding characteristics it is considered an oxyphile, binding in many types of oxide structures. Because of its chemical properties, thorium is sometimes included in the rare-earth element grouping along with yttrium and the lanthanides, and in many respects its chemistry resembles scandium (Rankama and Sahama 1950). Thorium is included with the actinides along with uranium and other transuranics, but behaves differently than them once in the environment (Whicker and Schultz 1982).

Finally, it is important to note that extrapolations between elements must be made with extreme caution. Although thorium shows similar properties with some elements, Drew and Willey (1984) found different binding characteristics between it and uranium, zirconium, and hafnium when reacted with trimethylamine. Therefore, studies involving other elements similar in chemistry may be useful, but thorium is also expected to have its own unique chemical properties.

SOIL PROPERTIES

General Soil Characteristics

Soil properties and soil types are known to vary with depth. A depth profile of soil shows that the first three divisions of earth are the soil, regolith, and bedrock. For purposes of this report, we shall focus on the soil layer. The soil layer can be divided into surface soil, subsoil, and substratum. The surface soil contains the maximum of organic accumulation and in most soils ranges from 1-6%. Soils with this type of organic content are referred to as inorganic or mineral soils. In swamps, bogs, and marshes the organic content can reach up to 95% organic material, being referred to as organic or muck soils. The organic content is important because the organic constituency can be a major phosphorous source thereby affecting ion mobilization.

The subsoil is more compact than the surface soil and contains a higher percentage of the soil minerals. Together the surface soil and subsoil are referred to as the solum which usually runs 3 to 4 feet deep in temperate regions (Buckman and Brady 1964). This region is most relevant to thorium removal processes.

Names of soils are often related to soil particle size. Stones and gravel are very coarse fractions which can be seen with the naked eye. Sands are the next smallest coarse fraction which also can be seen with the naked eye and consist of primary minerals (minerals that remain unchanged in composition). Silts are finer fractions which contain the primary minerals and secondary minerals (silicate clays and iron oxides from weathering of minerals), and which only can be seen microscopically. The final general fraction is the very fine fraction consisting of minute clays containing mainly secondary minerals. An electron microscope is required to viewing soil fines. Table 3 provides a more specific picture of soil nomenclature as a function of soil size (Buckman and Brady 1964).

Table 3. General soil names and associated sizes.	
Soil Separate	Diameter Limit (micrometers)
Very coarse sand	2000-1000
Coarse sand	1000-500
Medium sand	500-250
Fine sand	250-100
Very fine sand	100-50
Silt	50-2
Clay	<2
Taken originally from U. S. Dept. of Agriculture data in 1904. Buckman and Brady 1964.	

Other generalized size definitions are also important. A loam, for example, is a soil between sand and clay, and an ideal loam is a mixture of sand, silt, and clay. Humus is a ubiquitous ligand formed through the microbial degradation of biomass (Perdue and Lytle 1983). Humus is very fine clay that holds more water and minerals. Clay and humus are considered the finer portions of the soil matrix. Both exist in a colloidal state and contain large surface areas with charge to which water and ions are attracted. Soil contaminants preferentially adhere to the finer particles (Griffiths 1995).

Clay particles generally possess a large negative charge. The negative silicate-clay colloid particle is sometimes referred to as a micelle and the cations are usually held in a loose swarm (Buckman and Brady 1964). The preferential binding of soil contaminants for the fines is partially due to the larger surface area of the finer particles. It is believed (Eagle et al. 1993) that thorium, as well uranium and radium, adsorb to this negative charge.

Properties of Thorium in Soil

At times, and especially in the case of thorium, contaminants exhibit unique characteristics that create the need for a more specific approach to volume reduction. Although thorium generally binds to fines, like many other contaminants, it does so with a much stronger attraction. Thorium tends to bind very well with clay particles or forms insoluble oxides and hydroxides, similar to zirconium (Schulz 1965). It also lends to the theory of thorium adsorption

to negatively-charged clay or to being bound within as an insoluble oxide or hydroxide in the silicate-clay particle. In either case, the thorium is very tightly bound in the soil matrix.

The soils at many FUSRAP sites, in addition to thorium, contain uranium and radium. Whicker and Schultz (1982) classify thorium as behaving like an actinide in soil, specifically uranium and plutonium. All three form comparable insoluble compounds in the environment and are not considered biologically mobile. Furthermore, they all tend towards accumulation in the soils and sediments which ultimately serve as storage reservoirs. Subsequent movement is largely associated with geological processes. Thorium's uptake in plants is considered negligible and much less than that of uranium. Radium, however, is very mobile in the environment and has a larger plant uptake as evidenced by its accumulation in Brazil nuts.

Organic materials increase the solubility of certain heavy metals. Specifically, organic acids, exuded by plant roots and microbes in the rhizospheres, increase the solubility of zinc in mine tailings (Burckhard et al. 1995). It has also been shown that humic and fulvic acids can increase solubility of the strongly bound thorium (Tipping et al. 1995). Consequently, it is important to take into consideration the soil matrix when postulating the contaminant structure within. This may ultimately aid in determining the volume-reduction procedure of choice.

Properties of Thorium in Site-Specific Soils

Concentrations and structures of thorium contaminants differ by site. A few site analyses follow to demonstrate the need for possible site-specific alternatives and to illustrate the differences revealed thus far.

The Tonawanda, New York Site. Soils at this site have a distribution of thorium, radium, and uranium with size fractions beginning at 6,400 microns and descending to a category of less than 75 microns (Rule et al. 1995) with much of the soil consisting of finer particles (Browning 1995). It has been estimated that 48.6% of the particles were <38 microns (RUST, February 1995). All contaminants were well above acceptable limits for clean soils in all size categories. A high percentage of the weight and radioactive contaminants exist in the finest fractions (<75 microns), but there is a distribution throughout all size categories. Therefore, because the contaminants are not necessarily attached to the fines, this site cannot be classified as a predominantly fines-contamination site (Rule et al. 1995). However, Browning (1995) showed that the thorium activity per soil mass was sometimes higher in the coarser fractions.

The Tonawanda soils contain rocks, mineral grains, organic material (grasses, wood), and human-made materials (glassy and crystalline slags, concrete, and plastics). Uranium was found in both human-made and natural ore fragments, and generally was locked in a slag, gangue, or other matrix. Anderson (1996) believes that the thorium is at least partially locked in a porous matrix as well. Caution should be exercised with this data from Tonawanda, however, since most of the sample fractions contained fewer than 100 particles; these descriptions may not statistically represent the soil.

The St. Louis, Missouri Site. This soil was also contaminated with uranium, thorium, and radium, but the size fractions were divided into >150 microns, 38-150 microns, and <38 microns. Contamination was found existing in materials such as ores, slags, residues, filter cakes, and precipitates (Mardock and Dahlin 1995). However, the majority of soil particles found was in the finer fractions (Browning 1995), with about 66% of the particles in the <38 micron fraction (RUST, January 1995). Additionally, the thorium activity concentration was high in the larger fractions (30-50 pCi/g), but much higher in the finer fractions (30-240 pCi/g) (Browning 1995). Much of the contamination was rarely bound in or on the natural soil constituents. Thorium was found primarily in discrete particles of monazite with concentrations of 1-12%. This is consistent with Browning's (1996) hypothesis that some of the thorium contamination was left over monzite and zircon structures that survived industrial processing. Much of the thorium was in unidentifiable fines, but some was found locked up in matrices. On rare occasions, thorium was found involved in a siliceous, glass, iron-manganese heavy slag.

The Maywood Chemical Company, New Jersey Site. The major radioactive element found in these soils was thorium, but uranium and its decay products were also identified. Sand and silt appeared to have most of their radioactivity emanating from monazite and a small amount of zircon, while the smaller clay particles seems to have most of its radioactivity in the form of surface adsorbed particles. Some of these particles take the form of thorium precipitates left over from industrial extraction processing (Hay and Richardson 1993). Rule et al. (1994) found that most of the radioactivity is in the finer fraction, i.e., not distributed throughout the fractions as much as in the above mentioned sites. In fact, Browning (1995) showed that the larger fractions contained almost no thorium radioactivity while the finer fractions contained as much as 40-50 pCi/g. Also, this particular site does not consist of a higher percentage of fines as in the above two examples. The size fractions ranged from 6,300 microns to <45 microns. The activity in the fines appeared to be from uranium, thorium, and radium (Hay and Richardson 1993).

The Wayne Plant, New Jersey Site. The W. R. Grace and Company (Wayne Plant) Site in New Jersey contains particles ranging in size from 6,300 microns to <37 microns, with most of the radioactivity found in the finer fractions. The concentration of each radionuclide in the size fractions generally increased as the size decreased. The predominant contaminants were ^{232}Th in secular equilibrium with its decay products, most of which was found to be in monazite and zircon. These fell into a fine-sand-to-upper-silt size range of slightly larger than 37 microns (Cohen 1994).

Other Sites. Studies at the Monticello Mill site in Utah found differing thorium species in contaminated soils with 70-80% of ^{230}Th chemisorbed on particle surfaces. The second most prevalent state of this nuclide was in a hydrous ferric oxide, which would eventually crystallize into a goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) thus binding the thorium very tightly. A small fraction of thorium contaminants was found to be in minute particles of the original ore. This pattern is consistent with the behavior of thorium during the uranium acid leach process (to be described later) where ~90% of thorium remained in solution. It was thought that much of this thorium adsorbed onto

surfaces of minerals such as quartz and on aggregates of fine-grained materials that could have been mixtures of clays and iron hydroxides (Uranium Mill Tailings Study Panel 1986). This is consistent with Bellamy and Hill's (1963) statement that soluble thorium salts readily hydrolyze to insoluble hydrous oxides.

The above examples so that the type and distribution of thorium is certainly site-specific. In the Tonawanda and St. Louis samples the soil is mostly fines with the thorium distributed throughout many of the size fractions. At Maywood, the thorium is primarily in the fines which is a small fraction of the soil content. Chemical states of thorium vary by site, however, thorium seems to exist in its natural monazite and zircon structures along with some slag-type structures at each site. It is clear from these preliminary studies that the chosen volume-reduction procedure will be dependent on a site-specific soil characterization and possibly on a site-specific thorium matrix characterization.

SOIL WASHING

General Description

Soil washing is a recent technology developed for the purpose of physically reducing the disposal volume of contaminated soils. It has been successfully practiced in Europe for over a decade and has recent recognition in the U.S. (Fristad 1995). The recognition of its success is demonstrated by specific statutory justification for soil washing included in the Superfund Amendment and Reauthorization Act (SARA) (Griffiths 1995). Soil washing has been considered successful because, if contaminants are preferentially found in the finer soil fractions, it can significantly reduce the volume of contaminated soil which needs disposal and thus reduce the overall cost of disposal.

In an ideal scenario, all of the elevated contaminant levels would be in the finer soil fraction which could be physically separated from the larger soil fractions. The fines are defined by the particular features of a soil washing system, but generally are clays, silts, and very fine sands in the range of 40-250 microns. Soils with large concentrations of coarse material (>2000 microns) respond better to soil washing than soils with large percentages of silts and clays. It is the opinion of the EPA (1991), that soil washing is best done in soils with at least 50% coarse materials (sands and gravels). Also, it is reported that soil washing can be most cost-effective for soils with up to 40% fines, but the technique is usually applicable to soils with <20% fines (HWC 1993). This latter claim is also consistent with the EPA's (1991) report that more than 30-50% silts and clays in a soil make it unfavorable for soil washing. Soils with a high humic content are also adverse to soil washing. The two physical processes (which can be varied and combined in any particular application) for this volume reduction are particle separation and liberation.

Physical particle separations divide the soil into by particle size using screening and classification techniques. Rough screening (dry screening) uses a "grizzly" or similar device

which separates much of the rough material by literal screening techniques. Wet screening uses water to force the separation process (Eagle et al. 1993). Hydroclassification, as seen in Figure 1, applies Stoke's law of the settling velocity of a particle in a fluid, which is directly related to radius, density, and shape of the particle (Allen 1989). In this process, the finer particles do not settle as quickly and are collected and thus separated from the coarse particles.

Figure 1. Hydroclassifier using Stoke's law for particle size separation.

Hydrocyclones, as seen in Figure 2, spin the soil solution which causes the finer particles with lower specific gravity to remain in the center of the solution and be removed as the overflow; the heavier coarse particles are drained in the under-flow (Scholz and Milanowski 1983).

Froth flotation is a very sensitive metallurgical technique that uses air agitation of the soil solution to collect the fines on bubbles produced in the agitated solution. Chemicals known as "frothers" are sometimes used to stabilize the bubbles produced in the agitation. "Collectors" are chemicals used to provide separation and "modifying agents" are chemicals used to intensify the collectors and to control pH (Moore 1981).

Each of these separation techniques are commonly used in soil washing machines and some are often used more than once in a process. They are typically able to separate particles down to about 20 microns; however, smaller sizes require techniques such as separation by dielectric, electrostatic, and immiscible liquid processes.

Figure 2. Hydrocyclone schematic for particle size separation due to specific gravity.

Liberation techniques, as described by Eagle et al. (1993), literally liberate contaminated soil particles from clean particles. Washing is the most common method using mild water force to detach particles from each other. This technique is used in washers, trommels, and screw classifiers. Scrubbing is similar to washing except that other particles or a machine is used for an abrasive interface with the incoming soil. Attrition is similar to scrubbing except that a stronger force is employed on the incoming soil, as in the form of opposite-pitched turning blades. Care must be taken not to produce "extra" fines in this strong process since the added fines will reduce the volume reduction by adding clean fines to contaminated ones. Comminution (crushing and grinding) is even a stronger force and is generally used for particle size reduction. Even more so than attrition, however, it will produce extra fines.

Bechtel National's Soil Washing Machine

Bechtel National, Inc. has developed a soil washing technique for thorium contaminated soils which also works on radium and other radioactive elements. They are one of the few who have carried-out extensive testing and pilot-plant studies on thorium contaminated soils with a Volume Reduction Chemical Extraction (VORCE) device. However, it has yet to be used with chemical extraction, so that in its current state, VORCE is simply a soil washing machine that has potential for chemical extraction adaptation (Anderson 1996). Bechtel's VORCE machine for thorium contaminated soils generally follows the flow diagram shown in Figure 3.

Figure 3. Bechtel's VORCE soil washing machine schematic. (Adapted from Ryan 1995).

The soil is loaded with a front-end loader into a feed hopper. A grizzly screen separates the very large oversized clean cobble from the rest of the soil which is transported via a conveyor belt into the scrubber and trommel. Here, high pressure water is used in a liberation technique to separate the fines from the larger coarse fractions. The clean, oversized gravel is collected while the finer portions proceed on to a 250 micron separation in the primary screw classifier. Any coarse particles at the primary screw classifier are sent to an attrition mill to liberate any fine contaminants. The attrition mill products then enter the secondary screw classifier for an additional 250 micron sizing. The fine particles from the secondary screw classifier enter the flow stream with the finer particles from the primary screw classifier, and oversized particles from the secondary screw classifier are taken off as clean coarse sand.

The fine stream from both the primary and secondary screw classifiers flows into the cyclone feed sump for further size separation. The fines are routed to the final fines stream while the coarse material is transported to the hydrocyclone for more size separation. The hydrocyclone recycles its fines back to the cyclone feed sump unit for better separation efficiency while the coarser particles move onwards towards the very efficient size-separating hydrosizer where 63 micrometer separation occurs. The overflow of fines from the hydrosizer unit joins the last fines stream with fines from the cyclone feed sump while the coarse material is sized again as a polishing separation in the 74 micron vibrating screen. Fines passing through this screen move into the final fines stream along with fines from the hydrosizer and cyclone feed sump. The oversized particles from the vibrating screen are removed as clean fine sand. All of the fines from the cyclone feed sump, hydrosizer, and vibrating screen pass in the final fines stream towards the clarifier which flocculates and thickens the fine particles with the aid of an added polymer. The thickened fines then pass into a filter press for de-watering. The water is recycled while the de-watered thickened fines end up as the final product for disposal.

At the Maywood site, Bechtel has conducted a pilot-scale soil washing which is in agreement with the U.S. Bureau of Mines recommendation for treatment at this particular site (Rule et al. 1994). Significant volume reduction was obtained and the clean soil fractions contained less than 5 pCi/g of thorium radioactivity (Hay and Richardson 1993). At least part of the success of the Maywood test is due to low thorium concentrations in the coarse fractions. The pilot-plant ran at about 1000 pounds per hour and achieved a 64% volume reduction (Anderson 1996); the full scale machine would process between 5 and 40 tons per hour (Williams 1995).

Other Soil Washing Machines

Many companies have already performed soil washing processes on U.S. heavy metal contaminated soils. For example, Alternative Remedial Technologies, Inc. (ART) has used the first full-scale soil washer in the United States on the King of Prussia Superfund site in New Jersey. The EPA also has a soil washing machine for cleaning heavy metal contaminated soils,

and companies such as Bescorp, have integrated their soil washing methods with chemical extraction techniques in order to clean heavy-metal-contaminated soils.

ART's soil washers are similar in concept to the general discussion above and similar in concept to Bechtel's design. They have used mechanical and wet screening, hydrocyclones, and froth flotation units at the King of Prussia site, and in some of their systems ART has used chemical treatments to solubilize the contaminants. ART has recently conducted testing on soils containing thorium with promising results (Mann 1996). ART has also performed a pilot-plant operation at the Hanford site in Washington State targeting copper, cobalt, cesium, and uranium. Their process flow for this site was very similar to Bechtel's. The study achieved greater than 90% reduction by weight for these contaminants and was also successful in meeting the specified test performance standards. This particular device demonstrated a throughput of 10-15 tons per hour (ART 1996). It is noted that the soils and contaminants at the King of Prussia site are different than the ones Bechtel is targeting at Maywood. These differences have resulting in process design differences between the two washing techniques.

A mobile volume-reduction unit for soil washing was designed and fabricated by Foster Wheeler Enviresponse, Inc. for the EPA to clean heavy-metal and organic contaminants from soils. The volume reduction unit (VRU), as it is called, contains many similar processes described in the Bechtel and ART designs such as screening techniques, gravitational separations, and flocculations. In the field, this unit would be supported by a decontamination trailer, a mobile treatability laboratory, and a storage trailer for spare parts. It is designed to process 100 pounds of soil (dry) per hour with removal efficiencies dependent partially on soil characteristics (geology and particle size). The VRU can add an acid leaching procedure for soils not amenable to physical size separation. The unit performed "good-to-excellent" with organic and inorganic contaminants, but only "moderate-to-marginal" with various radioactive materials (Masters et al. 1991).

Finally, Brice Environmental Services Corporation (Bescorp) was the first in the United States to successfully integrate their soil washing procedure with a specific chemical extraction technique. COGNIS, Inc. provided these chemical extraction techniques used to remove lead and copper at the Twin Cities Army Ammunition Plant (TCAAP) in Minnesota. By combining the two processes, they were able to effectively treat all the soil fractions and recycle the recovered contaminants (Fristad 1995).

CHEMICAL EXTRACTION TECHNIQUES

General Descriptions and Definitions

Chemical extraction of thorium from soil can begin with a simple acidic or basic leaching procedure to bring the contaminant into solution. Soluble fractions in the soil particles are easily removed; however, often portions are bound to clay, silt, and iron oxides and are, therefore, more difficult to extract (Fahad et al. 1989). Usually, acids and bases can mobilize thorium from soils,

but it is sometimes necessary to use chelating agents. Although most information available on leaching is from laboratory or processing plant tests, it is certainly possible to perform heap leaching on a soil mound in the field.

Chelating agents are chemical compounds which bind metal cations. They can be simple compounds forming single bonds or ligands to centralized metal ions. Other chelators are often larger organic structures which bind a metal ion multiple times forming a chelating complex. They can be negative, neutral, or positive depending on their functional groups; those which are neutral combine easier with organic solvents (De 1961). Chelating agents frequently bind metals tightly and thus make efficient leaching agents; however, they must be removed to <0.1% by weight from thorium wastes before disposal (Bechtel 1996).

The desired metal in a leach solution may require separation from the unwanted dissolved particles, especially if a pure metal is to be recovered. This process is common in the area of hydrometallurgy, which involves purifying the desired metal from its ore while leaving the unwanted gangue material behind (Moore et al. 1981). Solvent extraction, ion exchange, and various electrometallurgical techniques are commonly used procedures for this type of separation.

Solvent extraction involves the use of a chelating agent to *pull* the desired metal or metals from one solution to another. The chelator is usually mixed with an organic solvent and combined with the metal-bearing aqueous solution. Upon mixing, the chelating agent bonds with the metal, but has a preference for staying in the organic solvent. The distribution of the metal between the two solvents (aqueous and organic) is described by its distribution or partitioning coefficient, K_D (Mayo et al. 1989):

$$K_D = [\text{Concentration of metal in organic phase}] / [\text{Concentration of metal in aqueous phase}]$$

The concentration of the metal in the organic phase usually involves the metal/chelant complex, but technically can involve any metal which dissolves in this layer (usually low amounts). Likewise, the aqueous concentration of metal usually involves its aqueous species, but it also can include any chelating complex which remains in the aqueous phase (De 1961). Chelating agents are usually organic solvents and thus have low dielectric constants, i.e., a weak ability to disperse the force of attraction between oppositely charged particles. Aqueous solutions generally have high dielectric constants while organic solutions generally have low dielectric constants (Carey 1992).

Solvent extraction can be carried-out in either a batch or continuous process. The batch extraction is simply a mixing of the two liquids to obtain the phase separation of the metal, and then the subsequent separation of the two liquid phases. This method works well in situations with large distribution coefficients. The continuous method involves the continuous flow of the two immiscible liquids against one another; this method works well for low K_D situations.

After extraction, the metal is removed from the chelating complex usually by "stripping" or destroying the complex. The organic solvent is then evaporated away or, if non-volatile, is mixed with an acidic solution to bring the metals back into an aqueous solution (De 1961). As mentioned earlier, the primary goal of solvent extraction is purification, but a well performed extraction can also lead to a volume reduction. Peppard et al. (1953) obtained an 800-fold volume reduction for removal of ^{230}Th from pitchblende residue using tributyl phosphate and hydrofluoric acid.

Ion exchange can be described as an exchange of ions between a solid (resin or ion exchange material) and a solution, but with no physical change occurring in the solid (De 1961). In effect, soil and clay behave as exchange resins, exchanging metal cations with the solutions they absorb - perhaps this ion exchange process is the way thorium became structured in the soils at the various sites. Use of ion exchange for volume reduction would involve an exchange between a metal contaminant and an ion exchange resin. The ion exchange resin is generally a high molecular weight tightly cross-linked polymer with an appropriate exchange capacity for the desired ions. Cation exchangers are thought of as polyvalent anions with adhering positively charged hydrogen ions (counter ions). Negative exchangers can be considered polyvalent cations with negative counter ions or high molecular weight polymers containing amine groups and anions (De 1961).

The exchange procedure, like solvent extraction, can be performed by batch or continuous processes. The continuous process is most extensively used in metal refining by flowing the metal-bearing solution through a resin column. The pH of the solution must be compatible with the chelant and resin in order to get a good ion exchange, as noted with an ethylenediaminetetraacetic acid (EDTA) and thorium complex (Gordon et al. 1956). The feed solution should have a low solid content for radioactive waste sites (Rodger 1954). After the metal ions are adsorbed onto the column, the column is washed with distilled water to displace any remaining solution and irreversibly adsorbed particles. The resin is then washed with an electrolyte solution in order to regain the desired metal ion into the more pure solution. This step may not be necessary, however, unless recovery of the metal or resin is desired, or further significant volume reduction is gained. The washing solutions are usually acids, salts, or complexing agents. De (1961) reports the strong adsorption of thorium on a Dowex-50 (Dow Chemical Company) styrene based column and on a Amberlite IR-100 (Rohm & Haas Company) sulphonated phenolic column. Although exchange resins are a powerful tool, it has been found in one study that solvent extraction reached equilibrium more rapidly than ion exchange with regard to thorium and uranium extractions (Peppard et al. 1957). This result does not necessarily indicate, however, that this would be the case for every solvent extraction and ion exchange method compared.

Finally, the desired metal can be precipitated from a purified solution or the precipitation can be performed as part of a purification process. Complex purification steps may not be necessary for thorium waste products and thus a simple precipitation from a leach solution may be all that is necessary for significant volume reduction. The process is dependent on the

precipitate formed and on the pH of the solution resulting in the ability to manipulate the reaction such that certain products can be precipitated while leaving others behind in solution, thus purifying and volume reducing.

Several compounds exist which precipitate thorium out of solution. Burger (1973) mentions some of the more exotic organic compounds, for example, arsonic acids or arsenazo which changes color upon precipitation for photometric determination. In both of these cases, the pH can be adjusted to separate out the rare earths. Sebacic acid ($\text{COOH}(\text{CH}_2)_8\text{COOH}$) was a very early discovery as an excellent compound for thorium precipitation (Smith and James 1912). Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is another early thorium precipitation discovery which has become a favorite for thorium precipitations. Simple precipitates such as hydroxides and phosphates are historically found in many thorium precipitation processes (Gordon 1947).

Classical Thorium Extraction Methods - Monazite Sands

Thorium has been refined from monazite sand by chemical extraction since the early 1900's. Much experimentation was performed yielding some very good extraction methods. Some of the FUSRAP sites contain monazite and other pristine thorium materials which may allow thorium removal by these original extraction processes. Even so, the more modern methods for extraction do not deviate much from the original techniques. Originally, methods involved the cracking of the monazite structure with a strong acid or base to put the thorium in solution. Miller (1986) emphasizes that although some of the metal may be easily dissolved, heavy metals must be put as completely as possible into solution for good extraction. Since these early methods were concerned with obtaining a pure thorium metal product, many purification steps were included after the acid or base treatment.

The caustic soda process, was used on a large scale in Brazil and India, and has also been investigated extensively at the Battelle Memorial Institute on a pilot-plant scale (Benedict et al. 1981). The Battelle procedure has been modified throughout the years, but the original process is described in Figure 4.

Grinding of the sand is the first step in the process. Water is then added at a weight ratio of water-to-sand of 1.7, and the slurry charged to a reaction vessel where 73% NaOH is added at a ratio of 1.5, NaOH-to-sand by weight. The mixture is heated to a temperature of about 280 °F (~140 °C) and agitated for a time that is sufficient for the sand to react completely with the caustic soda. Battelle (Calkins et al., Volume I, 1950) described the reaction as listed below in which R represents the thorium as well as rare earths and other elements which may be present in the monazite sand reactants:

with the reaction being described specifically for thorium by Bellamy and Hill (1963) as:

The Battelle reaction may be more functional in showing the product as a hydrous oxide. Thorium hydrous oxides are generally very bulky and dense, and hence easily filterable (Gordon 1947). The slurry then is diluted and digested at 220 °F (~ 105 °C) for one hour to facilitate filtration. The filtration is carried out under pressure at a temperature of 180 °F (~ 80 °C) to keep the caustic soda and trisodium phosphate in solution for NaOH recycling. The filtrate is then washed with water until all solubles are removed from the filter cake, and then blown dry. Recovery percentages from the monazite sand are given in Table 4.

Figure 4. Battelle's caustic soda process for Th extraction from monazite sand.

If thorium purification is of interest, the filter cake is then placed in a Pfaudler kettle and dissolved with 37% hydrochloric acid (ratio of acid-to-sand is 1.5 by weight). This mixture is heated at 175 °F (~ 80 °C) for one hour facilitating complete dissolution. The mixture is then diluted with water and the pH adjusted with NaOH to afford selective precipitation and to remove the rare earths (Calkins et al., Volume I, 1950). At a pH of 5.8 all the thorium and uranium, and only 3% of the rare-earths, are precipitated. This pH is consistent with the subsequent ranges listed by Ryan and Rai (1987) for the hydrous oxide solubility of thorium and is well above the pH of 3.5 listed by Britton (Part I, 1925) as the precipitation pH for thorium hydrous oxides. The Battelle thorium and uranium precipitation pH is also below the precipitation pH's for many rare earths (> pH 6.8) which allows this purification step (Britton, Part II, 1925). The uranium and thorium cake was filtered and washed multiple times, and upon drying, the cake consisted of 36.4% thorium by weight while other constituents occurred in smaller amounts.

Table 4. Percent recovery in filter cake from NaOH treatment of monazite sand (Calkins et al., Volume I, 1950).

Constituent	% Recovered in Hydrous Oxide Cake
Thorium	100%
Uranium	96.90%
Rare earths	100%
Phosphorus	0.30%

With a goal of thorium purification, this filter cake must undergo additional purification steps. It is now dissolved in 9.0 molar HNO₃, heated to 175 °F (~ 79 °C) for one hour, cooled, and filtered. The filter cake now consists of unwanted gangue material and the nitric-acid solution is carried over for uranium solvent extraction techniques. This solution carries about 90% of the thorium and 75% of the uranium from the original sand charge.

The next procedure consists of three steps of countercurrent liquid-liquid solvent extraction. The organic solvent is a mixture of 50% by volume tributyl phosphate (TBP) (the chelating agent) and 50% by volume Gulf Spray naphtha (GSN), 50-50 TBP-GSN (Calkins et al., Volume I, 1950). This technique is similar to the "Thorex" process developed at Oak Ridge National Laboratory (ORNL) where TBP is diluted in a solvent of the paraffin series resulting in a more than 99% extraction of uranium and thorium (Ryabchikov and Gol'braikh 1963). The extraction into the organic phase of uranium and thorium occurs because of their larger distribution coefficients than those of the surrounding impurities.

The organic phase of the mixture is then washed in dilute HNO₃, allowing the thorium to be displaced from the organic phase into an aqueous phase, while the uranium remains in the organic phase. The uranium is later stripped with deionized water for its recovery. The aqueous thorium solution is then mixed with a 5% excess of 10% oxalic acid solution for direct

precipitation of thorium oxalate. Oxalic acid is used because the oxalate form of thorium is the most desirable when considering subsequent thorium metal production. The resultant thorium oxalate precipitate is filtered, washed, and recovered.

Battelle has also made modifications to their technique by using ion exchange resins for the metal separations process. As in the original method, the sand is dissolved preferentially in NaOH and the subsequent cake dissolved in HCl, however, the solution is then precipitated with ammonium hydroxide (NH₄OH) instead of NaOH (Calkins et al., Volume II, 1950). The resulting precipitate contains primarily thorium and uranium with the rare earths left behind. This solution is then dissolved in a sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) solution, as described by:

The same reaction occurs for uranium. This reaction solubilized about 80% of the uranium hydrous oxide and 70% of the thorium hydrous oxide. The solution is then poured over an Amberlite IRA-400 resin column resulting in >99.93% of the uranium binding to the resin while leaving essentially all of the thorium in solution for subsequent precipitation.

Battelle also experimented with an alternative resin method described by Poirier and Bearse (1950) in which thorium is selectively adsorbed by an Ionac A-300 anion exchange resin. The experiment resulted, however, in only 65% recovery of thorium and did not show desired purification levels. This result would be expected when one considers De's (1961) statement that thorium prefers cation exchange type resins, showing a tenacious binding tendency.

The other major process for monazite dissolution leading to thorium extraction is the acid digestion process developed largely at Iowa State in Ames, Iowa. Scientists at Iowa State were largely responsible for developing industrial methods of uranium purification as well as thorium purification during the Manhattan project (Impé 1954). The Iowa State process involves, first, grinding of the sand to affect dissolution for the extraction process. It is then transferred to a stirred reaction vessel for digestion with 93% H₂SO₄ for 4 hours at 210 °C where the following reaction occurs (Bellamy and Hill 1963):

A similar reaction occurs for the lanthanides and other minerals. Although many types of acids have been investigated for liberating thorium from monazite sand, sulfuric acid (H₂SO₄), which has been used industrially in Europe, Australia, and the United States, was the acid of preference in the Iowa State process (Benedict et al. 1981).

The product is then cooled to 70 °C and diluted with 10 kg of cold water per 1 kg of monazite. Nearly all of the thorium, uranium, and rare earths are dissolved into the water solution leaving the unwanted gangue behind (silica, rutile, zircon, and some unreacted monazite). The resulting

solution is decanted for further purification (Benedict et al. 1981). The phosphoric acid (H_3PO_4) produced in the reaction makes subsequent separation procedures difficult; however, some good separation efficiencies have been achieved. It is estimated that up to 15% of the monazite can go unreacted in this procedure (Bellamy and Hill 1963).

A very reliable separation method involves precipitation using oxalic acid that was first bench tested by Gordon (1947) and then developed industrially at the U.S. AEC's Ames, Iowa, Laboratory. The Ames process begins with diluting the acidic solution (generally containing about 50 to 60 g of thorium and rare earths per liter) with about 4.5 volumes of water, and then adding NH_4OH until a pH of 1.5 is reached. Sodium oxalate and oxalic acid in a 10% aqueous solution is then added to obtain precipitation of thorium and the rare earths while leaving uranium behind in solution. The precipitate is washed in a solution of 1% oxalic acid and 0.3 N nitric acid and treated with a stoichiometric equivalent of NaOH. This precipitate, too, contains both thorium and the rare earths and, therefore, must undergo further dissolution and solvent extraction steps in order to separate the two (Benedict et al. 1981).

Another popular purification method involves a solvent extraction using alkyl amines. In this "AMEX" process, scientists at ORNL experimented with many amine chains but found that primary amines, in particular Primene JM, worked best for thorium extraction. Di(tridecyl)amine demonstrated a lower extraction coefficient for thorium, but was more selective toward the rare earths (Crouse and Brown 1959). In this procedure, the monazite acid solution generally consists of 5.9 g per liter of thorium, 0.2 g per liter of uranium, and about 34-45 g per liter of rare earth oxides. The organic solvent used for the amine extractant is 97% kerosene and 3% tridecanol, and the Primene JM is generally at a concentration of about 0.1 M. The organic phase is made to flow through the aqueous phase to produce a saturated thorium concentration (~ 3 g per liter) in the organic phase. An organic-to-aqueous flow ratio of 80:59 is established to achieve this goal. The organic solvent is subsequently washed with 0.2 M H_2SO_4 to remove any adhering uranium or rare-earth elements, and the thorium is finally stripped out with 0.75 M Na_2CO_3 back into an aqueous phase (Benedict et al. 1981).

As an example of the compounds and processes involved, Wylie (1959) presents an equation for the stripping of the thorium complex out of a di(tridecyl)amine organic extractant:

Crouse and Brown (1959) report >99.8% thorium recovery from this process and describe subsequent thorium precipitation with an ammonia solution followed by a reslurrying in 0.5 M NaOH. The precipitate was found to be 91.4% thorium oxide.

Waste Site Thorium Extraction Methods - Process Product

The methods of extracting thorium from monazite sand cannot necessarily be applied to thorium extraction from the waste residues at process sites. Unreacted monazite is one form of

thorium in the residues; however, the wastes may contain other species of thorium as well as various slags, soils, and other compounds which tightly bind the element. Therefore, a different chemical process may be required to bring thorium into a process solution.

Battelle has used HNO_3 for the dissolution of Brazilian monazite sludge from rare-earth processing facilities rather than NaOH , because caustic soda did not remove significant levels of thorium from the sludge product (Meeley et al. 1954). However, even though HNO_3 was a poor reagent for dissolving monazite sand (Calkins et al., Volume II, 1950), Battelle found this acid worked well on the process-product sludge (Meeley et al. 1954). The sludge Battelle was using contained about 20% unreacted monazite and, since about 12% of this monazite contained thorium, only about 2-3% of the thorium resisted reaction with HNO_3 . Also, the nitrate solution generated by the nitric acid reaction was the solution of choice for subsequent purification steps.

Before the nitric acid reaction could be performed, Battelle found it beneficial to pre-treat the sludge with NaOH in order to remove significant chloride and phosphate contaminants. The chloride, if left in the sludge, reacted with the HNO_3 to yield even more corrosive reaction conditions. Phosphate, however, could seriously reduce the distribution coefficient of thorium in the subsequent extraction procedures. The addition of NaOH performed the function of solubilizing the chloride and phosphate while leaving the desired products as solids, and thus a filtering was all that was necessary for removing the unwanted ions. Battelle found that chloride removal did not appear to be dependent on the amount and concentration of NaOH , however a NaOH -to-solid ratio of 0.5 was optimum for removing the phosphate ion.

The procedure was done with 5-25% NaOH in 2 hour digestions. The solid product was washed 5 times with 100 mL of water per 70 g of dry solids for each wash. It was also found that sodium chlorate pre-treatment in lieu of NaOH pre-treatment showed promise for chloride removal (Meeley et al. 1954) and that the pre-treatment allowed for subsequent nitric acid digestion. Many of the subsequent HNO_3 treatment parameters were then investigated and an optimum digestion method prescribed. The optimal HNO_3 amount and concentration was determined to be 0.7 g of anhydrous nitric acid per gram of dry solids and 0.25 g of anhydrous nitric acid per gram of water. The following slurry was digested for 30 minutes with no heat applied. This procedure was found to solubilize up to 97% of the thorium, which then could be removed by one of many procedures described in the preceding section (Meeley et al. 1954).

While the Battelle treatment was being devised, the French Atomic Energy Commission was using nitric acid to dissolve thorium from oxide and silicate minerals (not monazite). The minerals were finely ground and digested with 60% HNO_3 at 115 °C for 8 hours (Wylie 1959). Thorium was almost completely dissolved by this process. Although these oxide and silicate minerals were not process products, the FUSRAP mill tailing sites may contain thorium in these or similar states. Although HNO_3 did not seem to perform well with monazite, it did work well with process products and thorium in oxide and silicate forms.

The HNO_3 technique has been tested on the Tonawanda site, but has not met cleanup criteria at the bench level. The process also created problems by dissolving much of the soil matrix itself (Browning 1995). Currently, the EPA has performed successful experimentation with the nitric acid digestion process on certain heavy metal contaminated soils. However, the method is not favorable due to the corrosive nature of HNO_3 and other associated problems (Browning 1996). This is a similar situation with that of the U.S. Bureau of Mines nitric acid system which requires the use of 15-30% HNO_3 (COGNIS 1996). Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) has also been tested at the Tonawanda site at the bench scale. The test results were similar to the HNO_3 test results - cleanup criteria were not achieved and significant dissolution of the soil matrix was encountered (Browning 1995). The actual processes used in these trial runs were not obtainable.

Many types of subsequent recovery steps have been outlined in the previous section, but a particular solvent extraction method involving HNO_3 solutions has been developed using tri-n-octyl amine (TOA) that warrants consideration. The TOA is actually a nitrate complex often existing as $(\text{TOAH})\text{NO}_3$, with "TOAH" representing $\text{NH}(\text{C}_8\text{H}_{17})_3$ (Verstegen 1964a). Chloroform makes a poor organic-phase solvent for this particular extractant, but benzene derivatives (nitrobenzene, o-dichlorobenzene, etc.) are often found useful for metal extractions. Thorium in the nitric acid solution will form a complex with the TOAH resulting in the structure $(\text{TOAH})_2\text{Th}(\text{NO}_3)_6$ (Verstegen 1964b). Although TOA has been used to selectively remove uranium from thorium in certain solutions (Crouse and Brown 1959), Verstegen (1964c) reports thorium having higher distribution coefficients than uranium for benzene-derivative organic solvents.

Aside from the general acidic extraction processes, chelating agents have also been employed recently in the investigation of thorium removal from process product. Three different chelators were combined with tailing site soils: EDTA, TIRON (4,5-Dihydroxy-1,3-benzenedisulfonic acid), and HEDPA (1-Hydroxyethane-1,1-diphosphonic acid). These investigations were performed at the Tonawanda and St. Louis sites. Chen and Hong (1995) found that extraction of lead and copper from soils was more dependent on chelator concentration than pH and solid concentration. Chelator was used at a concentration of 0.1 M and 0.5 M CO_3^{2-} was added as NaHCO_3 (sodium bicarbonate) in order to aid complexing and to selectively enhance the dissolution of the radioactive elements. Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was also added in 0.1 M quantities to aid dissolution.

It is hypothesized that sodium dithionite helps to release contaminants from iron, manganese, and aluminum oxide matrices which may be present in the soils (RUST January 1995). Tessier et al. (1979) make a consistent claim that these types of oxides are excellent scavengers for trace metals, thus "cementing" the compounds. They have used $\text{Na}_2\text{S}_2\text{O}_4$ to aid the extraction of heavy metals from similar slag matrices. The $\text{Na}_2\text{S}_2\text{O}_4$ was found to be beneficial at the Tonawanda site, but not at the St. Louis site, where it actually depressed the overall thorium removal. This may be due to the soil differences at the two sites - Tonawanda conceivably possessing more of the oxide-type matrices described above.

Soils at both the Tonoawanda and St. Louis sites were most responsive to the EDTA/ CO_3^{2-} solution versus the HEDPA/ CO_3^{2-} and TIRON/ CO_3^{2-} solutions. St. Louis demonstrated an 88-98.4% ^{230}Th removal, however residual thorium concentrations were 81-2,686 pCi/g, and therefore still well above cleanup criteria (RUST January 1995). Multi-stage extractions, however, were able to achieve cleanup goals in some instances (Browning 1995). The EDTA demonstrated up to 49% ^{230}Th removal in some of the Tonawanda tests, leaving final thorium soil values of 255-700 pCi/g (RUST February 1995). Although EDTA was the preferred chelator at both sites, HEDPA was shown to remove up to 68% of the thorium in some Tonawanda samples. The generalized process flow diagram (Figure 5) shows how the procedure could be performed on a larger scale (RUST February 1995). Wet screening would remove about 2% of the soil as oversize, and the de-watering step would employ a polymeric flocculent as a filter aid. Chelant recycling would occur via acidification or precipitation of EDTA from the retentate using a specified reagent. Recovery of 95% of the EDTA is predicted with a proposed operating capacity of about 5-10 tons per hour.

Figure 5. Proposed process flow diagram for chelant treatment of site soils (Adapted from RUST, February 1995).

Chemical Extraction Variations

Procedure, extractant choice, and system combination are all relevant issues for thorium removal from monazite and waste residues regardless of which chemical extraction process is employed. The procedures reviewed herein involve primarily batch style applications. For example, nitric acid treatment of process product was performed in a stirred reaction vessel. However, this may not be the most efficient method for chemical extraction, as shown by Tuin and Tels (1991). They use solutions of 0.1-0.3 N HCl to treat clay contaminated with heavy metals for three scenarios: 1) two continuous stirred-tank reactors in series; 2) a countercurrent column for the acid/soil slurry exchange; and 3) a combination of a continuous stirred-tank reactor followed by a countercurrent exchange. Countercurrent alone worked slightly better than stirred-tank reactor alone, but the combination of the two provided the best result. Tuin and Tels (1991) state that metal fractions difficult to treat could possibly be treated more effectively with a countercurrent system.

Another interesting alternative is that of system combination, particularly that of physical separation and chemical extraction. Bescorp and COGNIS were the first to successfully integrate the two systems in the cleanup of the Twin Cities Army Ammunition Plant (see Figure 6). The soil is fed into the trommel where attrition breaks the fragments down into their constituent particles. The clean oversized particles are removed and the finer fractions are moved to a vertical separation chamber which separates the finer particles from the sands by physical hydraulic settling forces.

The fines are routed to a series of leaching clarifiers, and the sand is fed to a mineral jig for further separation. The coarse sand passes through the jig, but the finer sand is moved down a spiral to remove metallic particles. The overflow from the jig goes into the metal collection while the finer sand is leached (as the fines were above). Both the fines and the finer sand are de-watered and neutralized before returned to the environment as clean product. The leachant from the two streams is sent to an electrochemical reduction unit for metal separation and recycling. Although this particular system was developed for heavy metal recovery, it is an example of what a soil washing and chemical extraction process may involve for thorium removal. The EPA has designed a prototype machine with similar treatment combinations for arsenic and phenol, but without a metal recycling system (Scholz and Milankowski 1983). A chemical treatment system can be added to Bechtel's soil washing machine (Anderson 1996), and many of ART's designs also have this capability.

Figure 6. COGNIS/Bescorp process flow diagram for the soil washing and chemical extraction methods used at TCAAP (Adapted from Fristad 1995).

Finally, choosing an extracting mechanism may be more complicated than selecting a procedure that works best for the element in question. In particular, COGNIS believes that since every site is different, a two phase treatability study is required for each site. Phase I characterizes the soil and contamination for determining an optimum leaching procedure, while Phase II scales up the proposed procedure, incorporates a metal recovery system, proves the recyclability of all operational streams, and determines a cost estimate (COGNIS 1996). This philosophy emphasizes that a certain procedure may not work at every site. In studies performed at the sites mentioned above, soil washing worked best at some sites and leaching worked best at others, but both did not work everywhere.

One possible problem relating to chemical extraction is that of low thorium soil concentrations. The activity may be relatively high, but the thorium concentration in the particular soil sample may be quite small - perhaps in the parts per billion (ppb) range. This small amount could make a simple extraction procedure not possible by significantly increasing the free energy (Anderson 1996), which is given by

$$Q = \frac{C^c D^d}{A^a B^b}$$

$$\Delta G = RT \ln\left(\frac{Q}{K}\right)$$

where ΔG is the Gibbs free energy of the reaction, R is the gas constant, T is the absolute temperature in Kelvin, K is the thermodynamic equilibrium constant for the particular reaction and temperature, and Q is the reaction quotient as described in the first two equations (Kotz and Purcell 1987). Therefore, if reactant A is thorium and its concentration approaches zero (extremely small values), Q gets large and ΔG becomes positive. When this is the case, the reaction spontaneity does not allow the reaction to proceed. Similarly, Tuin and Tels (1991) show an extraction efficiency E for a counter-current acid extraction column in their heavy metal soil extraction studies:

$$E = x(C_{ki})^p (C_{H+})^q$$

where x is a proportionality constant, C_{ki} is the initial metal concentration in the clay soil, C_{H+} is the H^+ concentration in the column, and p and q are constants. When the initial metal concentration in the clay soil decreases substantially, so does the counter-current extraction efficiency. These examples may demonstrate, at least partially, why the nitric acid and EDTA bench scale results were not always favorable.

PHYSICAL REMOVAL TECHNIQUES

The Segmented Gate System (SGS)

This final section will describe the segmented gate system (SGS), a physical separation process which is already in place at a few radioactively contaminated sites. The segmented gate system does not rely on particle size differences, but rather on the heterogeneity of the soil. Such a machine has been tested very successfully on Johnston Atoll (JA), an unincorporated territory of the United States about 825 nautical miles from Honolulu, contaminated with weapons grade plutonium from an aborted Thor rocket launch in 1962 (Moroney et al. 1993).

The contaminated soil is dispersed on a conveyer belt in a thin layer which passes by 15 sodium iodide detectors. The units are overlapped in two rows, providing a complete survey of the passing soil. Any soils which contain radiation levels above the detector set point, as determined by the cleanup criteria, would be detected and rerouted by a segmented gate towards a disposal drum. The clean soil continues on its normal path towards a soil recycling area, where it is monitored again before being returned to the environment (Thermo Analytical). The original unit processed about 800 metric tons per week with a day-to-day volume reduction of 93-99%

(Moroney et al. 1993). Technical developments allow one main computer to control four SGS conveyor belts and increase the throughput to about 2000 tons per week (Moroney et al. 1994).

According to Moroney et al. (1994) the system can be applied effectively to any soil or dried sludge matrix, coarse or fine, as long as the radiation can be detected; however, site treatment is heavily dependent on the lack of uniformity in radioactivity concentration. The SGS would simply not be effective on homogeneous soils. Soils at Los Alamos have been treated successfully in a pilot study with regard to uranium removal, and the SGS system is currently being tested on thorium soils at the New Brunswick, New Jersey FUSRAP site (Rogers 1996). Some of the piles in those tests, however, are believed to be blended into a homogenous mixture which may likely result in failure of the SGS functionality.

The application at JA was to remove ^{239}Pu and ^{241}Am particulates and their decay products, but the general approach may be useful at thorium sites. The SGS is designed to detect gamma radiation which is associated only with the decay products of the alpha-emitting americium and plutonium isotopes. But, since the decay products are intermingled with the parent radionuclides, they too are removed. Thorium is an alpha emitter, but its immediate daughters include gamma emitters which could be detected by the SGS. Daughters of thorium were used to detect it in monazite in the early days of thorium mining (U.S. AEC 1955). Calkins et al. (1954) found that the thorium daughters build rapidly enough to be detected by scintillation counters from pure thorium solutions. And, it was found at the Wayne Plant site, that ^{232}Th was in secular equilibrium with its daughters (Cohen 1994). Therefore, the site soils in question could very well have enough daughter activity to make the SGS a plausible alternative.

Similar to the thorium cleanup criteria, the cleanup criteria on JA was near 14 pCi/g for alpha activity from plutonium and americium (Moroney et al. 1994). Therefore, with similar cleanup standards, the SGS may be adaptable to thorium soils. However, Kohli (1996) notes that the soils on JA were relatively pure with regard to the targeted contamination while that of the thorium sites may contain other radionuclides which might cause problems in removing only thorium by these methods. Finally, the SGS can be coupled with a soil washing or chemical extraction mechanism in order to further volume reduce the soil.

Soil homogeneity could be a serious problem for the Segmented Gate System. Soils at Los Alamos have been successfully treated in a pilot study with regard to uranium removal. More importantly, thorium soils are currently being tested at a New Brunswick, New Jersey FUSRAP site (Rogers 1996). Some of the piles being tested, however, are believed to be blended into a homogeneous mixture and this could cause a problem with attaining cleanup criteria. Nonetheless, the pilot study has recently begun (June 1996) and, therefore, the results are inconclusive. Even if this were a problem, treatment of an untouched site - that is, a site without a blended pile already formed for the incoming crew - may yield very different results (Dillon 1996).

Magnetic and Electrical Properties

Soil washing and chemical extraction techniques are used to handle the problem of thorium removal from soils; however, they do not guarantee decontamination consistent with current cleanup criteria. Therefore, other possible methods need to be considered that could replace or augment existing proposals for thorium remediation.

Magnetic techniques have been explored for thorium separation in monazite sands. These methods rely on utilizing the strong paramagnetic properties of magnetite and ilmenite in monazite ores to separate them from the less paramagnetic monazite. The residual then contains diamagnetic zircon, rutile, sillimanite, and garnet (Bellamy and Hill 1963). It is also possible to separate out the finer monazite, which was less magnetic, from the larger monazite by using magnetic fields of varying strengths (Benedict et al. 1981). This process works well for such complex ores as the monazite beach sands (Ryabchikov and Gol'braikh 1963). This technique has been considered for removal of monazite remnants at the Wayne Plant site (Cohen 1994) described earlier, and may also one day prove valuable in separating thorium locked in slag matrices.

Because of the expense involved, electrometallurgical techniques of thorium removal have not gained much attention. The standard technique generally yields a very pure product by employing electrolysis to extract the metal from an electrolyte. Once the thorium is put into solution, a good electrolytic technique may heighten extraction efficiencies over that of chemical methods. More research is needed before this process can be applied to thorium extraction, however.

Electro-Pure Systems, Inc. has studied, for the EPA's Superfund Innovative Technology Evaluation (SITE) Program, an alternating current electrocoagulation (ACE) technology for agglomerating and removing colloidal solids, metals, and certain organics. An alternating current is applied to a soil slurry resulting in a coagulation of metals and clay particles, which then fall out of solution as a large conglomerate. This technology has been developed to recover primarily heavy metals (lead, chromium, copper, and cadmium) from the environment (Farrell 1991). This technology might find application following soil washing. The current soil washing schemes involve a last step of flocculating the final slurry with a polymer to create a filter cake. The ACE technology yields a more compact filter cake that is easier to de-water than that from polymer treatment. The filter cake volume, expressed as a percentage of the pre-filtered sludge volume, was 7-9% less for heavy metal treated slurries (Farrell 1991), which could mean further volume reduction of the waste product.

Phytoremediation

A possible biological alternative for extraction of certain heavy metals is the utilization of vegetation for soil remediation. Several authors have proposed this alternative in one form or

another (Dudka et al. 1996; Coghlan 1996; Raskin 1996; Boyd 1996; Carey 1996; Rouhi 1997). Under this approach, plants could be grown in contaminated sites, harvested mechanically like hay, and dried. The biomass, then, could be burned to produce ash with a high content of recoverable metal. The economic value of the metal and of the heat produced during ashing may be sufficient to pay for the cleanup expense (Rouhi 1997).

The U.S. Department of Agriculture is experimenting with plants that naturally scavenge heavy metals like cadmium and zinc from the soil. Called hyperaccumulators, the plants can store as much as 2.5 percent of their dry weight in leaves without yield diminutions. It is the plants' metal-storage ability that could provide a financial return to help counteract cleanup costs. Researchers are concentrating on pennycress, a short-stature weed typically found growing in such alpine areas as the Rocky Mountains and central Europe (Boyd 1996).

Plants may be the key to a better, cheaper approach to cleaning up contaminated soil. Phytoremediation, the process of enlisting nature's flora to cleanse polluted soil, is becoming increasingly widespread. This method is extremely efficient: Even if the polluting metals absorbed by the plants are not recovered, there is a 98 percent reduction in the amount of waste, as it is contained in the form of contaminated plants rather than dirt (Carey 1996). The effectiveness of phytoremediation on thorium removal, however, may be questionable.

SUMMARY AND APPLICATIONS OF TREATMENT METHODS

Various methods have been investigated for thorium removal or volume reduction from contaminated site soils, but none of these methods is universally applicable. Nitric acid and EDTA have promise, but have not always achieved cleanup criteria. Bechtel's soil washing machine has demonstrated good volume reduction at the Maywood site, but, because of variations in soil type and soil chemistry, probably will not perform as well at all sites; recommendations have been made at other sites not to soil wash based on bench scale tests. All of the potential problems need to be considered for specific sites, and the final remediation technique may involve a combination of methods reviewed herein or may involve other processes still under study.

The EDTA bench scale results presented by Browning (1995), could possibly be modified to obtain better yields. For instance, the soil samples were treated without an initial grinding step (Browning 1996). This, as has been noted by Wylie (1959), is a principal factor in metal extraction from soils. Grinding the fractions into smaller particles may increase the surface area for chemical reaction. It is interesting to note that EDTA did perform up to the cleanup criteria at the St. Louis site but not at the Tonawanda site. St. Louis had a higher percentage of fine particles than Tonawanda; the St. Louis soil had about 66% of its particles less than 38 microns, while the Tonawanda soil had only about 48%. The higher amount of fine particles may be the reason for better EDTA performance at the St. Louis site. Grinding, prior to treatment, therefore, may demonstrate better results. However, grinding also could require additional

product handling and may cause severe clogging in the process mechanism requiring frequent cleaning (Browning 1996).

Other modifications may also increase yield. For example, the use of countercurrent techniques in the EDTA application procedure resulted in different extraction yields. Chemical application methods may also affect yield and grinding followed by countercurrent application may increase yield and applicability. Cost and practicality may preclude some approaches from full scale operations. There are simply not enough plants to treat spent acid and adding additional chemical procedures to separate the thorium may generate too much secondary waste to justify the process (Kohli 1996).

Although nitric acid dissolves thorium very well, the high concentrations required to put thorium in solution also tend to dissolve the soil matrix itself. Dissolving the whole soil matrix is a severe problem because it precipitates with the thorium when attempting precipitation and no volume reduction is gained (Browning 1996). Another precipitation method needs to be found or thorium separation attempted before precipitation.

The high concentrations of HNO_3 necessary to put thorium into solution is also very corrosive, thus requiring use of costly stainless steel reaction vessels and careful attention to worker safety. Special clothing and respirators would be necessary as well as time for dressing and undressing which would effectively shorten the work day (Browning 1996).

Soil washing has seen its share of problems as well, especially with regards to Tonawanda and St. Louis sites. The U.S. Bureau of Mines has recommended no soil washing at either site and, in fact, has recommended no treatment at all for the Tonawanda site (Rule et al. 1995) and chemical treatment alone for the St. Louis site (Mardock and Dahlin 1995; Browning 1995). Bench-scale physical size separation techniques like those used in a full scale soil washer were performed at both sites. These involved physical size separation, attrition scrubbing, and density separations. All of these treatments were ineffective at the St. Louis sites, while limited effectiveness was found for density separation and attrition scrubbing at the Tonawanda sites. This may be due to the high percentage of fine material found at these sites.

Soil washing at full scale is most effective when 50% or more of the material is coarse material. Tonawanda showed limited effectiveness, but also had only about 48% of fine particles; St. Louis soils had a much higher percentage of fines. Finally, Anderson (1996) believes the soil washing problem to be in part due to a porous slag matrix binding the thorium. This porous matrix, when moist, can change its density and cause an inefficient volume reduction.

Bechtel was able to achieve good results with the soil washing technology at the Maywood site, probably due, at least in part, to that of the soil properties. They reported a 64% volume reduction while successfully meeting cleanup criteria. This site differed significantly from the above two sites in that Maywood did not have a high percentage of fines and that there was not a large amount of radioactivity, if any, in the larger fractions. These two properties

make this an ideal soil for the washing techniques, however, blending of the soil as it moves through the soil washing machine dispersed the radioactivity in the coarse fractions (Browning 1996); that is, dilution may have brought the coarse fraction to cleanup criteria. Therefore, soil washing may not have been solely responsible for meeting the standard.

No one process can be used to remediate all of the FUSRAP sites. Chemical extraction (EDTA) appears to work on soils with larger percentages of fines, and may be used at such sites or in concert with preliminary soil grinding. Sites that fit the Maywood characteristics could use soil washing which may be more economical than chemical extraction. These variations require a treatability study for each site before treatment and different processes used depending on the circumstances. However, chemical extraction with EDTA requires further study to determine its feasibility for full scale applications.

Combined procedures, like the COGNIS/Bescorp process, are likely to be the best approach. At the Maywood site, soil washing followed by chemical extraction could possibly further reduce the volume of waste needing permanent disposal. However, this would be useful only if the fine soils met the treatment criteria after processing. The extraction process, therefore, would have to be complex to reduce these concentrated fines to cleanup standards. Other combinations of various remediation methods may also prove beneficial.

Treatment may be more problematic at sites similar to Tonawanda. Again, soil grinding followed by EDTA extraction may be promising, but more investigation is required. These investigations may find techniques for all sites and better efficiency for the ones now deemed treatable. For instance, soil washing and proper management of the remaining hot coarse particles may reduce future radiation exposures. A simple dilution of the remaining hot particles could be achieved by mixing fresh soil with the remaining coarse particles, or by dispersing the hot particles in large river. Perhaps proper land management of the remaining coarse particles would be better than dilution in some areas, and maybe a combination of dilution and land management in others. Instead of these last two methods occurring after soil washing, dilution and land management may be used after EDTA extraction which did show reduction in thorium levels. These techniques could achieve a residual concentration that may offer significant exposure benefits, rather than arguing that the technique failed because residuals were still above what may be an arbitrary concentration criteria which were set based on a past and different scenario. Nitric acid and the Segmented Gate System (SGS) may play a role at these tougher sites, but both require further study.

Based on the above information, the recommendation for site remediation begins with treatability studies at each site. Treatment decisions then would be dependent on soil and contaminant types. Sites which have properties similar to the Maywood site may be considered for soil washing, but sites which seem undesirable for this process may be treatable with EDTA (although more work needs to be done for a full scale process including the consideration of secondary waste generation), the SGS process, or combinations of any of these. It may be necessary to treat certain soils with a process not perfectly suited for that site, but with

subsequent dilution and management allowing it to meet more realistic goals. Judging by the difficulties at some sites, this may occasionally be the only option. However, it is much better by future waste and cost considerations than transporting all of the soil to a waste facility. And, if the current treatment criteria are altered based on upcoming risk reports, treatment options may be changed or not necessary at certain sites.

RISK ESTIMATION METHODS

The risk estimates provided in this section are order-of-magnitude approximations. Given the large uncertainties involved in any risk assessment and the variability of exposure situations at various FUSRAP sites, the methods below are used to illustrate the relative risks to remediation workers and, if the no-action alternative were chosen, risks to the potential site visitor. The risk comparison shows that transportation risks clearly outweigh the cancer risks to remediation workers.

The typical environmental remediation worker at FUSRAP sites likely will be involved in the broad work categories of either operating heavy earth-moving equipment, operating soil treatment devices, or transporting large volumes of contaminated soil to disposal sites. Accident statistics, therefore, have been compiled for these types of occupations throughout the United States. In order to compare with risk estimates for radiation exposure, statistics have been gathered to relate probabilities of fatal injuries occurring on-the-job or in highway-traffic accidents of professional truck drivers. Except for transportation risks, workers at FUSRAP sites are assumed to be exposed to occupational and radiological risks 8 hours per day for 250 days of the year.

Statistics from the National Safety Council (NSC), the Bureau of Labor Statistics (BLS), and the Occupational Safety and Health Administration (OSHA) have been obtained from their respective computer systems via the Internet. The most current data for death rate as a function of hours worked is from 1993. The databases contain statistics back to 1980, however, because of various safety programs, death rates have declined over the years. As we have done in this report, it is, therefore, more appropriate to use data from the most recent year available rather than an average over many years.

Heavy Equipment Operations

In 1993, the death rate for on-the-job injuries was 0.04 per million hours exposed (NSC). This death rate includes all occupations and all injury types. In 1992, injuries classified as "struck by object", "caught in or compressed by equipment or objects", or "non-highway transportation accidents" made up 22% of the total fatal occupational injuries. Additionally, 39% of these fatal injuries were for the occupation classifications of "forestry & logging", "machine operators and tenders", "truck drivers", "material moving equipment operators", or "laborers" (BLS).

With a death rate of 0.04 per million exposure hours for on-the-job occupational injuries and about 39% of fatal occupational injuries being for those classified in occupations similar to those for environmental remediation, with 22% of those being fatalities by "contact with objects", "crushings", or "non-highway transportation", a worker at a site where heavy equipment is being utilized would have a risk of fatal injury of approximately $3.5\text{E-}9$ per exposure hour. If it is assumed that a worker is exposed 2000 hours per year, the worker's risk of on-the-job fatality from heavy equipment operations is $7\text{E-}6/\text{yr}$.

Local Transportation

Risks from the transport of FUSRAP waste material are determined per 100,000 cubic yards of waste transported. Estimates indicate that 100,000 cubic yards of material can be moved in 186 days, assuming work continues for 8 hours per day with a productivity adjustment factor (PAF) of 50% (Wright 1997). The PAF takes into account delays due to weather, unsafe conditions, job sequencing, and utility interruptions. Risks calculated per 100,000 cubic yards are, therefore, multiplied by the factor 1.34 to convert to annual risk estimates.

It is assumed that smaller trucks would be used to transport waste material to a local disposal site. Estimates of fatality rates for smaller trucks (10-20 cubic yards capacity) are taken from the correspondence of Science Applications International Corporation (SAIC; Wright 1997). This document quotes a risk of $1.09\text{E-}7$ fatalities per mile for local transportation. This work also indicates that more than 5,500 trips would be required to transport 100,000 cubic yards of material in a 20 yd³ dump truck, and requiring about 1,500 hours (Wright 1997) to load the material.

If it is assumed that the local disposal site is between 1 to 100 miles from the originating FUSRAP site, total miles traveled to dispose of 100,000 cubic yards of material would be in the range of 11,000 to 1.1 million miles. Using the fatality rate quoted above, this mileage results in a fatality risk ranging between 0.0012 and 0.12 per 100,000 cubic yards of waste material transported. If 100,000 cubic yards can be transported in 186 days, the annual risk is between $2\text{E-}3/\text{yr}$ and $2\text{E-}1/\text{yr}$. When loading hours are included, using a death rate of $3.5\text{E-}9/\text{hr}$ obtained in the previous section, the fatality risk is not significant relative to the driving risks.

Highway Transportation

In 1992, about 18% of fatal occupational injuries were from highway accidents. Data from the National Highway Traffic Safety Administration (NHTSA) from 1975 to 1993 show that for large trucks involving fatal crashes, the average involvement rate is 4.2 fatal crashes per 100 million vehicle miles traveled. This involvement rate over the 20 years of study, however, is continually declining, thus, making an average from the past 5 years more indicative of current risks. Therefore, the most recent 5-year average fatal-crash involvement rate is 3.0 fatal crashes per 100 million miles traveled. The NHTSA data also indicate that the average fatality rate from

1975 to 1993 was 0.86 fatalities per 100 million vehicle miles traveled (decreasing each year since 1975) and that the recent 5-year average was 0.46 fatalities per 100 million miles.

If it is assumed that a professional truck driver transports radioactive waste to a burial site that results in 1,000 to 5,000 miles round-trip and a single truck is capable of transporting no more than 100 cubic yards of waste material, then a total of 1 to 5 million miles per 100,000 cubic yards will have been driven in performing the task of transporting FUSRAP waste to its permanent burial site. The risk to the drivers of large trucks of being involved in a fatal crash, therefore, is between approximately 0.042 and 0.21, and their risk of dying in a traffic accident is from about 0.0046 to 0.023 per 100,000 cubic yards of waste material transported. If 100,000 cubic yards can be transported in 186 days, the annual fatality risk is between $6\text{E-}3/\text{yr}$ and $3\text{E-}2/\text{yr}$.

Rail Transportation

Transportation of waste material by train requires that materials be removed from the site with a front-end loader, put into dump trucks and taken to a staging area where it is again moved by front-end loader into rail-car gondolas. The process of moving 100,000 cubic yards of material in this manner requires a total of approximately 16,400 loading hours and about 1,700 rail-car gondolas, each with a capacity of 60 cubic yards (Wright 1997). One train typically includes six gondolas for a total of about 280 train trips with an associated fatal train crash risk of $4.52\text{E-}8/\text{mile}$ (Wright 1997).

Assuming that the train staging area is between 1 and 50 miles from the originating FUSRAP site, the risk of fatality during transportation by dump truck ranges from 0.0012 to 0.06 per 100,000 cubic yards. The incremental risk for the 16,400 loading hours is an insignificant 0.00006. Assuming that the trains travel round-trip distances between 1,000 and 5,000 miles, the fatality risk for train travel is 0.012 to 0.06. Therefore, the total risk for transporting FUSRAP wastes by rail is estimated to be between 0.013 and 0.12 per 100,000 cubic yards. If 100,000 cubic yards can be transported in 186 days, the annual fatality risk is between $2\text{E-}2/\text{yr}$ and $2\text{E-}1/\text{yr}$.

Radiation Exposure

Fatal cancer risk factors for workers exposed to Thorium-230/232 and their decay products have been estimated for individuals involved in the remediation of contaminated soils. Estimates are based on multiplicative models similar to those used for CERCLA human health risk assessments. We have chosen to calculate risk factors in units of fatal cancer risk/yr per unit concentration in soil. Risk factors are calculated in this manner so that relative contributions to radiation risk can be estimated since soil concentrations will vary from site to site. The source is assumed to contain both ^{230}Th and ^{232}Th along with all daughter products at secular equilibrium. The major contributor to external radiation exposure from the ^{230}Th chain is bismuth-214, while the major contributors from the ^{232}Th chain are actinium-228 and thallium-208.

The exposure scenario for a remediation worker assumes an exposure time, ET, of 8 hours per work day and an exposure frequency, EF, of 250 work-days per year. The worker is assumed to be exposed externally while standing on contaminated soil and while working in the vicinity of burial drums, earth-moving equipment, and soil-remediation process streams. Internal exposures are assumed to occur as a result of the incidental ingestion of contaminated soil and the inhalation of dust/dirt that becomes airborne due to heavy equipment traveling over dry soil.

Radiation risk factors for external exposure are estimated by,

$$\text{Risk [risk-g/yr-pCi]} = \text{SF [risk-g/hr-pCi]} * \text{ET [hr/d]} * \text{EF [d/yr]}$$

for ground-shine exposures and for exposures from other sources such as burial drums, process lines, or earth-moving equipment. Slope factors, SF, for ground-shine exposures come from EPA's HEAST tabulations, while SFs for other sources are calculated by estimating photon flux at a specific distance from burial drums, process lines, etc. Estimation of photon flux is carried out in accordance with the methods of Kase and Nelson (1978). Calculational details can be found in Appendix B.

The risk factor for incidental ingestion of soil is calculated using,

$$\text{Risk [risk-g/yr-pCi]} = \text{SF [risk/pCi]} * \text{Soil Ing. Rate [g/d]} * \text{EF [d/yr]}$$

assuming the EPA standard soil-ingestion rate of 50 mg/day for workers.

A mass-loading model is used to estimate the risk factor for inhalation,

$$\text{Risk [risk-g/yr-pCi]} = \text{SF [risk/pCi]} * \text{L [g/m}^3\text{]} * \text{IR [m}^3\text{/hr]} * \text{RF} * \text{ET [hr/d]} * \text{EF [d/yr]}$$

where it is assumed that the dust loading in air, L, is 100 times higher when heavy vehicle traffic is present than the ambient level of approximately 2E-4 g/m^3 . An inhalation rate, IR, of 10,000 $\text{m}^3\text{/yr}$ is used to approximate the annual average breathing rate of a remediation worker while on the job. A reduction factor, RF, of 0.01 has been included to account for the removal of 99% of particulates by having workers wear cloth respirators.

Slope factors from EPA's HEAST tables (see Table 5) for inhalation, ingestion and external ground-shine pathways are utilized to convert activity intake to fatal cancer risk. Risks from other external exposures are estimated from photon flux and dose calculations converted to annual risk. The dose/risk conversion is accomplished using the risk factor from ICRP (1991) of 5%/Sv. All slope factors and calculated risk factors include contributions from daughter products except those from external ground shine. Internal slope factors include contributions from daughters once the parent is assimilated.

Table 5. HEAST Slope Factors and Calculated Risk Factors for ^{230}Th and ^{232}Th .

Pathway	^{230}Th	^{232}Th	Units
Inhalation	1.72E-8	1.93E-8	risk/pCi
Ingestion	3.75E-11	3.28E-11	risk/pCi
External*	5.02E-15	2.25E-15	risk-g/hr-pCi
Calculated risk factors			
External-drum†	4.2E-15	9.5E-15	risk-g/hr-pCi
External-pipe††	2.1E-14	3.7E-14	risk-g/hr-pCi

* does not include contributions from daughter products

† calculated for exposures at 3 meters from a standard rad. waste drum

†† calculated for a line source at 1 meter, with no attenuation

Calculated, pathway-specific radiation risks per pCi/gram of ^{230}Th and ^{232}Th , at secular equilibrium with their respective daughter products, are given in Table 6. The dominating pathway is shown to be the inhalation of airborne contamination. The risk values for ingestion and inhalation also include the contributions from internally deposited alpha and beta emitters following assimilation of ^{230}Th or ^{232}Th .

An estimate of the minimum risk to workers from radiation exposure can be obtained by assuming that soil concentrations are no less than 5 pCi/g (or else remediation would not be taking place). Given this assumption, risk to remediation workers from radiation exposures would be no less than about 4E-8/yr from gamma emitters.

To estimate a maximum radiation risk to remediation workers, an assumed maximum concentration must be determined. Contaminated FUSRAP sites have ^{230}Th or ^{232}Th soil concentrations of up to a few hundred picocuries per gram. We will arbitrarily assume, therefore, that the maximum thorium concentration is 500 pCi/g and that no respiratory protection is used, resulting in an estimate of the maximum risk of approximately 5E-4/yr.

Table 6. Summary of Relative Radiation Risks to Workers
(per pCi/g of ^{230}Th and ^{232}Th in soil)

Radiation Risk Summary (^{230}Th):		
<u>Pathway</u>	<u>Fatal Cancer Risk</u> (^{230}Th)	<u>Fatal Cancer Risk</u> (^{232}Th)
External (ground shine)	1.0E-11/yr	4.5E-12/yr
External (drum)	1.1E-12/yr	2.4E-12/yr
External (process)	5.3E-12/yr	9.3E-12/yr
Dust Inhalation	7.8E-9/yr	8.8E-9/yr
Dust Ingestion	4.7E-10/yr	4.1E-10/yr
TOTAL	8.3E-9/yr	9.2E-9/yr

Risks to the General Public (no-action alternative)

The radiation risk to a site intruder would be approximately equal to the risk calculated for remediation workers for the exposure pathways of external ground-shine, inhalation (without respiratory protection), and incidental ingestion, but for exposure times much less than those for workers. Therefore, utilizing Table 2 and assuming a maximum concentration of 5 pCi/g, the radiation risk to a site intruder, assuming no remediation takes place, will be no greater than 4E-6/yr.

The risk from airborne material transported downwind is also worthy of consideration. Typical dilution factors for atmospheric dispersion are on the order of $1\text{E}6$, therefore, the risk to individuals living downwind would be orders of magnitude lower than the risk to workers from inhalation. The estimated risk to a worker via the inhalation pathway is about 9E-9/yr at 1 pCi/g. Therefore, assuming that the exposure time is 24 hours rather than 8 hours, the soil concentration is 5 pCi/g, no respiratory equipment is worn, and the dust loading factor is $2\text{E}-4 \text{ g/m}^3$, the risk to an individual downwind would be no greater than approximately 1E-13/yr.

RISK COMPARISON SUMMARY

Estimated risks are tabulated in Table 7 and displayed graphically in Figure 7. Maximum annual risks are estimated to result from transportation of waste materials, which are more than two orders of magnitude greater than risks to the general public with the no-action alternative.

Table 7. Risk estimate summary.

Source	Annual Risk
Heavy Equipment	7×10^{-6}
Local Trans.	$2 \times 10^{-3} - 2 \times 10^{-1}$
Highway Trans.	$6 \times 10^{-3} - 3 \times 10^{-2}$
Rail Trans.	$2 \times 10^{-2} - 2 \times 10^{-1}$
Rad Exposure (worker)	$4 \times 10^{-8} - 5 \times 10^{-4}$
Rad Exposure (public)	$< 4 \times 10^{-6}$

Figure 7. Comparison of remediation risk to workers and members of the general public from remediation and no-action alternatives.

REFERENCES

- Adams, J.; Ahrens, L.H.; Arnold, J.R.; Bell, K.G.; Birch, F.; Bowie, S.H.U.; Daniels, F.; Davis, F.J.; Faul, H.; Flint, R.F.; Friedman, I.; Holland, H.D.; Hurley, P.M.; Johnson, D.H.; Koczy, F.F.; Larsen, E.S.; Marble, J.P.; Pettersson, H.; Phair, G.; Tilton, G.R.; Tittle, C.W.; Thode, H.G.; Urey, H.C.; Wasserburg, G.J.; Whitehead, W.L.; and Zeller, E.J. Nuclear Geology. John Wiley & Sons, Inc.; 1954.
- Allen, S.E. Chemical Analysis of Ecological Materials. 2nd Edition. Blackwell Scientific Publications, Oxford, England; 1989.
- Anderson, R. Personal communication. Waste Treatment Specialist. Bechtel Environmental, Inc. Oak Ridge, TN; April 1996.
- ART (Alternative Remedial Technologies, Inc.). Statement of Qualifications and Experience: Soil Washing. Tampa, FL; 1996.
- Bearse, A. E.; Calkins, G.D.; Clegg, J.W.; Filbert, R.B. Thorium and rare earths from monazite. Chemical Engineering Progress 50(5):235-239; 1954.
- Bechtel National, Inc. Basic Ordering Agreement for Estimate Development and Field Demonstrations FUSRAP Wide. Report No. 14501-191-SC-560. Oak Ridge, TN; May 1996.
- Bellamy, R. G.; Hill, N.A. Extraction and Metallurgy of Uranium, Thorium, and Beryllium. International Series of Monographs on Nuclear Energy. Pergamon Press, Oxford; 1963.
- Benedict, M.; Pigford, T.H.; Levi, H.W. Nuclear Chemical Engineering. 2nd Edition. McGraw-Hill Book Company; 1981.
- Boyd, V. Pint-sized plants pack a punch in fight against heavy metals: USDA research with metal-scavanging weeds. Environmental Protection 7:38-39; 1996.
- Britton, H.T.S. Electrometric studies of the precipitation of hydroxides. Part I. Precipitation of magnesium, manganous, ferrous, cobalt, nickel, and thorium hydroxides by use of the hydrogen electrode. J. Chem. Soc. 127:2110-2120; 1925.
- Britton, H.T.S. Electrometric studies of the precipitation of hydroxides. Part II. The precipitation of the hydroxides of zinc, chromium, beryllium, aluminum, bivalent tin, and zirconium by use of the hydrogen electrode, and their alleged amphoteric nature. J. Chem. Soc. 127:2120-2147; 1925.

- Browning, D. FUSRAP Soil Characterization Summary. A presentation to the DOE at Oak Ridge National Laboratories. Scientific Applications International Corporation (SAIC), Oak Ridge, TN; November 1995.
- Browning, D. Personal communication. Science Applications International Corporation (SAIC), Oak Ridge, TN; 1996.
- Bruyn, K. Uranium Country. University of Colorado Press, Boulder Colorado; 1955.
- Buckman, H.O.; Brady, N.C. The Nature and Properties of Soils. 6th Edition. The MacMillan Company, New York, NY; 1964.
- Burckhard, S. R.; Schwab, A.P.; Banks, M.K. The effects of organic acids on leaching of heavy metals from mine tailings. Journal of Hazardous Materials. 41:135-145; 1995.
- Burger, K. Organic Reagents in Metal Analysis. Pergamon Press, Ltd.; 1973.
- Calkins, G. D.; Filbert, R.B.; Bearse, A.E.; Clegg, J.W. Final Report on Recovery of Thorium and Uranium from Monazite Sand. Volume I. BMI-243. Battelle Memorial Institute, Columbus, OH; 1950.
- Calkins, G. D., Filbert, R.B.; Bearse, A.E.; Clegg, J.W. Final Report on Recovery of Thorium and Uranium from Monazite Sand. Volume II. BMI-243A. Battelle Memorial Institute, Columbus, OH; 1950.
- Calkins, G. D., Poberskin, M.; Gates, J.E.; Blackmore, R.H.; Duffee, J.H. The Distribution of Thorium-Decay Products in the Thorium-Purification Process. BMI-967. Battelle Memorial Institute, Columbus, OH; 1954.
- Carey, F.A. Organic Chemistry. 2nd Edition. McGraw-Hill, Inc.; 1992.
- Carey, J. Can flowers cleanse the earth? Business Week. 54; Feb. 19, 1996.
- Chen, T-C; Hong, A. Chelating extraction of lead and copper from an authentic contaminated soil using N-(2-acetamido)iminodiacetic acid and S-carboxymethyl-L-cysteine. Journal of Hazardous Materials. 41:147-160; 1995.
- Coghlan, Andy. How plants guzzle heavy metals. New Scientist 149:17; Feb 17, 1996.
- COGNIS. Terramet Remediation Systems. Sales Pamphlet. COGNIS, Inc., 2331 Circadian Way, Santa Rosa, CA, 95407; 1996.

- Cohen and Associates, Inc. Preliminary Characterization of Soil Samples Within and Under the Storage Piles at the W. R. Grace and Company (Wayne Plant) Site. Prepared for the U.S. EPA National Air and Radiation Environmental Laboratory (NAREL). Sanford Cohen and Associates, McLean, VA; 1994.
- Crouse, D.J.; Brown, K.B. The amex process for extracting thorium ores with alkyl amines. *Industrial and Engineering Chemistry*. 51(12):1461-1464; 1959.
- De, A.K. Separation of Heavy Metals. Pergamon Press. New York; 1961.
- Dillon, M. Personal communication. Segmented Gate System pilot study. New Brunswick, New Jersey FUSRAP site manager; 1996.
- Donivan, S.; Hollenbach, M.; Costello, M. Rapid determination of thorium-230 in mill tailings by α spectrometry. *Anal. Chem.* 59:2556-2558; 1987.
- Drew, M.B.; Willey, G.R.. A seven-co-ordinate actinoid complex: crystal and molecular structure of tetrachlorotris (trimethylamine) thorium (IV). *J. Chem. Soc. Dalton Trans.* 727-729; 1984.
- Dudka, S.; Piotrowska, M.; Terelak, H. Transfer of cadmium, lead, and zinc from industrially contaminated soil to crop plants: a field study. *Environmental Pollution*. 94(2):181-188; 1996.
- Eagle, M.C.; Richardson, W.S.; Hay, S.S.; Cox, C. Soil washing for volume reduction of radioactively contaminated soils. *Remediation*. 3(3):327-344; 1993.
- Fahad, A. A.; Ali, A.W.; Shihab, R.M. Mobilization and fractionation of ^{137}Cs in calcareous soils. *Journal of Radioanalytical and Nuclear Chemistry*. 130(1):195-201; 1989.
- Farrell, C.W. Alternating current electrocoagulation for Superfund site remediation. EPA/600/9-91/002. Electro-Pure Systems, Inc.; 1991.
- Fristad, W.E. Case Study: using soil washing/leaching for the removal of heavy metal at the twin cities army ammunition plant. *Remediation*. Autumn:61-72; 1995.
- Frondel, C. The mineralogy of thorium. *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy. Geology of Uranium and Thorium*. Volume 6:568-577; 1956.
- Gordon, L. The Precipitation of Hydrous Oxides of Tin and Thorium from Homogenous Solution by the Hydrolysis of Non-ionizable Compounds. Doctoral Dissertation. The University of Michigan, Ann Arbor, MI; 1947.

- Gordon, L.; Firsching, F.H.; Shaver, K.J. Concentration of microgram amounts of rare earths in thorium: precipitation and ion exchange procedures. *Analytical Chemistry*. 28(9):1476-1479; 1956.
- Griffiths, R.A. Soil washing technology and practice. *Journal of Hazardous Materials*. 40:175-189; 1955.
- Hay, S.; Richardson, W. Characterization of Soil Samples from the Maywood Chemical Company Site. Prepared for the U.S. EPA National Air and Radiation Environmental Laboratory (NAREL). Steven Cohen and Associates, McLean, VA; 1993.
- Heinrich, E.W. *Mineralogy and Geology of Radioactive Raw Materials*. McGraw-Hill Book Company, Inc.; 1958.
- HWC. Full Scale Soil Washing System Remediates Superfund Site. *The Hazardous Waste Consultant*, November/December: 1.1-1.3; 1993.
- Impe, J.V. Uranium and fabrication. *Chemical Engineering Progress*. 50(5):230-240; 1954.
- International Commission on Radiation Protection. 1990 Recommendations of the International Commission on Radiation Protection. ICRP Report No. 60; 1991.
- Kase K.R.; Nelson, W.R. *Concepts of Radiation Dosimetry*. Pergamon Press. New York. 1978.
- Kohli, R. Personal communication. Battelle Memorial Institute. Columbus, OH; 1996.
- Kotz, J.C.; Purcell, K.F. *Chemistry and Chemical Reactivity*. Saunders College Publishing; 1987.
- Lumpkin, G.R.; Chakoumakos, B.C. Chemistry and radiation effects of the thorite-group minerals from the Harding pegmatite, Taos country, New Mexico. *American Mineralogist* 73:1405-1419; 1988.
- Mann, M.J. Personal communication. Alternative Remedial Technologies (ART), Inc., Tampa, FL; 1996.
- Mardock, C.L.; Dahlin, D.C. Characterization of Soil Samples from the St. Louis, Missouri, FUSRAP Site. DOE IA No: DE-A105-930R22161. U. S. Bureau of Mines, Albany Research Center; 1995.
- Masters, H.; Rubin, B.; Gaire, R.; Cardenas, P. EPA's Mobile Volume Reduction Unit for Soil Washing. EPA/600/9-91/002; 1991.

- Mayo, D.W.; Pike, R.M.; Butcher, S.S. *Microscale Organic Laboratory*. 2nd Edition. John Wiley & Sons, Inc.; 1989.
- Meeley, W. A.; Snyder, M.J.; Filbert, R.B. Recovery of Thorium from Brazilian Monazite Sludge by Nitric Acid Digestion. BMI-946. Battelle Memorial Institute, Columbus, OH; 1954.
- Melillo, J.T. The Environmental Legacy of the Nuclear Weapons Complex. A presentation to the University of Michigan School of Public Health. Executive Secretary, U.S. Department of Energy; 1995.
- Miller, W. P.; Martens, D.C.; Zelazny, L.W. Effect of sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am. J.* 50:598-601; 1986.
- Moore, J. J.; Boyce, E.A.; Brooks, M.J.; Perry, B.; Sheridan, P.J. *Chemical Metallurgy*. Butterworth and Co., Ltd.; 1981.
- Moroney, K.S.; Moroney, J.D.; Johnson, N.R. Remediation of transuranic-contaminated coral soil at Johnston Atoll using the segmented gate system. Johnston Atoll Plutonium Soil Cleanup Project - Reprinted from WM'93 Conference Proceedings. February/March. Tucson, AZ; 1993.
- Moroney, K.S.; Moroney, J.D.; Turney, J.; Johnson, N.R. Processing plutonium-contaminated soil on Johnston Atoll. *Radwaste Magazine*. July:69-92; 1994.
- Peppard, D. F.; Asanovich, G.; Atteberry, R.W.; Dutemple, O.; Gergel, M.V.; Gnaedinger, A.W.; Mason, G.W.; Meschke, V.H.; Nachtman, E.S.; Winsch, I.O. Studies of the solvent extraction behavior of the transition elements. II. Isolation of gram quantities of ²³⁰Th (ionium) from a pitchblende residue. *J. Amer. Chem. Soc.* 75:4576-4578; 1953.
- Perdue, E.M.; Lytle, C.R. Distribution of binding protons and metal ions by humic substances. *Environ. Sci. Technol.* 17:654-660; 1983.
- Poirier, R. H.; Bearse, A.E. Topical Report on Anion-Exchange Studies on the Separation and Purification of Uranium and Thorium. BMI-242. Battelle Memorial Institute. Columbus, OH; 1950.
- Rankama, K.; Sahama, T.G. *Geochemistry*. University of Chicago Press; 1950.
- Raskin, Ilya. Plant genetic engineering may help with environmental cleanup. *Proceedings of the National Academy of Sciences of the United States of America*. 93:3164-3166; April 16, 1996.

- Rodger, W. A. Radioactive wastes: treatment, use, disposal. *Chemical Engineering Progress*. 50(5):263-266; 1954.
- Rogers, S. Personal communication. Segmented Gate System Engineer. TMA. Albuquerque, NM; 1996.
- Rouhi, A. M. Plants to the rescue: Crops in soil cleanup. *Chemical and Engineering News*. 75:21-23. Jan. 13 1997.
- Rule, A. R.; Dahlin, D.C.; Henn, J.J. Conceptual Design and Economic Analysis of a Process to Treat Radiation-Contaminated Soils at Maywood, New Jersey. DOE IA No.: DE-AI05-930R22161. U.S. Bureau of Mines, Albany Research Center; 1994.
- Rule, A. R.; Dahlin, D.C.; Summers, C.A. Characterization of Soil Samples from the Tonawanda, New York Site. DOE IA No.: DE-AI05-930R22161. U.S. Bureau of Mines, Albany Research Center; 1995.
- RUST Clemson Tech. Center. DOE FUSRAP - St. Louis Site Treatability Study. Interim Characterization Report. RUST-CTC 851150. RUST Clemson Tech. Center. Anderson, SC; 1995a.
- RUST Clemson Tech. Center. DOE FUSRAP - Tonwanda Site Treatability Study. Interim Characterization Report. RUST-CTC 851608. RUST Clemson Tech. Center. Anderson, SC; 1995b.
- Ryabchikov, D. I.; Gol'braikh, E.K. The Analytical Chemistry of Thorium. International Series of Monographs on Analytical Chemistry. The MacMillan Company, New York; 1963.
- Ryan, J.L.; Rai, D. Thorium (IV) hydrous oxide solubility. *Inorg. Chem.* 26:4140-4142; 1987.
- Scholz, R.; Milanowski, J. Mobile System for Extracting Spilled Hazardous Materials from Excavated Soils. Environmental Protection Agency. Report No. EPA-600/2-83-100. Washington, DC; 1983.
- Schulz, R.K. Soil chemistry of radionuclides. *Health Physics*. 11:1317-1324; 1965.
- Sky and Telescope. News and Notes Section. *Sky and Telescope*. 78:349-350; 1989.
- Smith, T.O.; James, C. A new method for the separation of thorium. *J. Am. Chem. Soc.* 34:281-286; 1912.
- Tessier, A.; Campbell, G.C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. 51(7):844-851; 1979.

- Thermo Analytical, Inc. A Cost Effective Approach to Remediation of Radiologically Contaminated Soil. Video. Thermo Analytical, Inc. Ann Arbor, MI.
- Tipping, E.; Woof, C.; Kelly, M.; Bradshaw, K.; Rowe, J.E. Solid-solution distributions of radionuclides in acid soils: application of the WHAM chemical speciation model. *Environ. Sci. Technol.* 29:1365-1372; 1995.
- Tuin, B.J.W.; Tels, M. Continuous treatment of heavy metal contaminated clay soils by extraction in stirred tanks and in a countercurrent column. *Environmental Technology*. 12:178-190; 1991.
- Uranium Mill Study Panel. Board on Radioactive Waste Management. National Research Council. Scientific Basis for Risk Assessment and Management of Uranium Mill Tailings. National Academy Press. Washington, DC; 1986.
- U.S. Atomic Energy Commission. Manual of Analytical Methods for the Determination of Uranium and Thorium in their Ores. New Brunswick Laboratory; 1955.
- U.S. Department of Energy. Closing the Circle on the Splitting of the Atom. Office of Environmental Management. Washington, DC; 1995.
- U.S. Department of Energy. FUSRAP Fact Sheet. Office of Environmental Management. Washington, DC; 1995.
- U.S. Environmental Protection Agency. Guide for Conducting Treatability Studies Under CERCLA: Soil Washing. Prepared by Science Applications International Corporation for the Environmental Protection Agency. Report No. EPA/540/2-91/020A. Washington, DC; 1991.
- U.S. Government. Code of Federal Regulations 40, Parts 190-259. Office of the Federal Register National Archives and Record Administration. Washington, DC; 1994.
- Verstegen, J.M.P.J. Distribution of nitric acid between water and organic solvents containing tri-n-octyl amine - II. *J. Inorg. Nucl. Chem.* 26:1085-1102; 1964a.
- Verstegen, J. M. P. J. 1964. Metal nitrates in tri-n-octyl amine nitrate solution. *J. Inorg. Nucl. Chem.* 26:1589-1599; 1964b.
- Verstegen, J. M. P. J. Extraction of Thorium and Uranium by Means of Tri-n-Octyl Amine. Institute for Atomenergi. Kjeller Research Establishment, Kjeller Norway; 1964c.

Whicker, F.W.; Schultz, V. Radioecology: Nuclear Energy and the Environment. Volume I. CRC Press, Inc., Boca Raton, FL; 1982.

Williams, L. Soil Wash Test at K-25. The Oakridger. Oak Ridge National Laboratories. Oak Ridge, TN; 1995.

Wright, R.D. FUSRAP-Risk Analysis Data. Science Applications International Corporation. Letter to James Martin. Number 1044.970408.001. April 8, 1997.

Wylie, A.W. Extraction and purification of thorium. Reviews of Pure and Applied Chemistry 9(3):169-212; 1959.