

SUCCESSFUL REMEDIATION OF A THORIUM
CONTAMINATED 40 ACRE SITE

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ABSTRACT

A 40 acre storage site located in Madison, Illinois was successfully remediated by removing the contaminated material and shipping it to an approved landfill in Utah. Initial estimates indicated that there were approximately 150,000 cubic yards of magnesium slag and soil contaminated with thorium-230 and thorium-232. The slag was the by-product of a thorium-magnesium alloying process. Concentrations of thorium (Th) on-site varied from less than background to several thousand pCi/g. Because barium (Ba) was used as a fluxing agent, there was a concern for leachable Ba. This paper will describe the project management process and tools used to accomplish the remediation. Radiological analysis of the slag was performed using alpha spectroscopy for isotopic thorium and gamma spectroscopy using a germanium (Ge) detector to determine the concentration of daughters. In addition, 3 inch sodium iodide (NaI) detectors coupled to multichannel analyzers were used for on-site analysis. By setting a window on the 2.61 MeV gamma photon of the thallium-208 daughter, the concentration of Th-232 could be estimated using one minute counts. This method was used for site characterization and for the remediation work. Although not used in the remediation of the site, a chemical volume reduction method was developed. This involved selectively extracting magnesium (Mg) as the bicarbonate after exposing the aqueous slag slurry to CO₂. The process has the advantage of inexpensive and innocuous reagents (H₂O and CO₂) which can be recycled. Volume reductions of 80% were achieved in the laboratory and >99.9% MgCO₃·3H₂O was recovered free of radioactivity. A patent has been allowed for the process and although it was never used on this site, it may prove valuable in the remediation of other similar sites. Characterization of the site was accomplished by sampling at 20 foot intervals and analyzing the samples using the on-site NaI method and the Ge detector. This work identified large areas of the site where the slag was free of radioactivity. Non radioactive slag was placed in a vault on-site. Remediation of the site was accomplished by selective excavation of contaminated material. The on-site NaI method was used to guide the excavation ensuring that the contaminated material was removed and over-excavation minimized. Material was analyzed on-site then sent by rail to Envirocare of Utah for disposal. Verification

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that a section of the site was remediated was accomplished by sampling and analyzing for isotopic Th. The Illinois Department of Nuclear Safety (IDNS) released the site for unrestricted use based on IDNS personnel sampling and analyzing approximately 10% of the site.

INTRODUCTION

A contaminated magnesium slag storage site, owned by Consolidated Aluminum Corporation, (CAC) has been remediated and released for unrestricted use. The Dow Chemical Company (Dow), a previous owner, shared in the management and cost of the remediation.

The 40-acre site consisted of approximately 150,000 cubic yards of magnesium slag. A portion of the slag was contaminated with thorium residues from a magnesium-thorium alloying process. In addition, PCB contaminated soil was discovered on-site.

Considerable efforts were expended over a 6-year period in site characterization, remedial alternative assessments and remedial technology development. While alternative technologies were being developed which would have resulted in significant waste volume reduction, all materials above the site cleanup criteria were eventually excavated and transported to licensed disposal sites.

The storage site, located in Madison, Illinois was managed under a source materials license issued by the Illinois Department of Nuclear Safety. Upon discovery of the PCB contamination, the remediation of the PCB contaminated soil was done under the guidance of the Illinois Environmental Protection Agency (IEPA) under an IEPA-USEPA agreement.

The cleanup criteria in the radioactive materials license called for removal of all material with a total thorium (Th-230 plus Th-232) concentration greater than 10 pCi/g above background with an administrative limit of 5 pCi/g above background. The cleanup criterion for the PCB contaminated soil was 10 ppm.

PROJECT MANAGEMENT

The 40 acre site contained slag from the production of a magnesium/thorium alloy used for special applications. The Dow Chemical Company (Dow) owned and operated the site from 1952-1969, storing material under an NRC license. Consolidated Aluminum (CAC) purchased the site and continued production and storage until 1979 when newly generated slag began to be shipped off site for disposal. In 1986 CAC sold the facility but maintained ownership of the 40 acre storage site. In 1987 Dow and CAC signed an agreement to jointly remediate the site, with Dow responsible for project management.

A project management team (PMT) was formed including CAC management, Dow research and development (R&D), Dow environmental engineering, Dow regulatory affairs, Dow communications and legal council. Consultants were used to provide expertise where appropriate. Regular PMT meetings were conducted and new challenges required flexibility.

The initial plan (1987) was to construct an on-site storage facility, but significant regulatory concern over the long term acceptability of on-site storage due to proximity of neighbors and the flood plain required a change in direction. Dow R&D outlined a plan to evaluate management options. Initially, off-site disposal was not an option due to constraints of the Low Level Rad Waste Policy Act. R&D identified a process for volume reduction. A pilot plant and preliminary engineering were initiated.

In 1991 an off-site disposal option became available. Engineering and R&D developed a plan for off-site disposal which occurred from April until December 1992. Approximately 100,000 cubic yards of low level slag were shipped by rail to Utah without incident.

ANALYTICAL METHODS

Alpha spectroscopy was performed in The Dow Chemical Company, Freeport, Texas facility using a passively implanted planar silicon (PIPS) detector coupled to a multichannel analyzer. The method for sample preparation was developed by doing a comprehensive literature search and customizing the procedures to fit our matrix. A significant portion of the procedure came from journal articles by Claude W. Sills of the Radiological and Environmental Sciences Laboratory, Department of Energy, Idaho Falls, Idaho. The 23 step sample preparation procedure followed by counting on the PIPS detector allowed baseline resolution of the alpha emissions from Th-232, Th-230 and Th-228. Th-234 was used as a tracer to determine the chemical efficiency of the separation. The efficiency calibration for the detectors was accomplished using a purchased pre-calibrated Th-232 standard (Isotope Products, Burbank, CA) which was traceable to the National Institute of Standards and Technology. Samples analyzed by IDNS and Oak Ridge National Laboratories gave isotopic Th results that were within experimental error of the results obtained by this method. The method was used to guide research and for final verification of site clean up. In addition, the method was used to determine the average ratio of Th-230 to Th-232 on site samples. The average ratio was about 2.2 for samples with higher radioactivity and about 1.4 for the verification samples.

Gamma spectroscopy was also conducted in Freeport, Texas using a 51.5 mm diameter by 54.5 mm deep germanium (Ge) detector coupled to a multichannel analyzer. The samples were counted for 1000 seconds in 2-liter Marinelli beakers. The detector was calibrated using 2-liter Marinelli beakers filled with multinuclide standards (Isotope Products Laboratories, Burbank, CA) in epoxy resin. The concentration of five Th-232 daughters and two Th-230 daughters could be determined by this method. These included actinium-228, bismuth-212, lead-212, thallium-208 and radium-224 for the Th-232 series. Lead-214 and bismuth-214 were detectable from the Th-230 series. Since the Th-232 series was determined to be in secular equilibrium, the average concentration of Th-232 in the samples was estimated by averaging the five daughters after correcting for the branching ratio of thallium-208. Total Th was estimated by assuming a conservative ratio of Th-230:Th-232 of 3:1, based on site characterization work. This method was used early on for site characterization, then for preliminary screening of verification samples and for calibrating the NaI detectors on site.

Due to the cost, fragile nature, and necessity for cooling, a Ge crystal was not practical for site use. Because it was critical to have an on-site radiological analysis, a method for estimating Th-232 was developed using NaI detectors. To overcome the intrinsic poor resolution of NaI detectors, a technique was developed using the 2.6145 MeV gamma photon emitted by thallium-208. This is the highest energy photon of the two series and can be resolved from the other emissions with a NaI crystal. Thus a 3-inch NaI crystal coupled to a multichannel analyzer was used. A window was selected for this high energy peak and the samples were weighed into 2-liter Marinelli beakers and counted for 1-5 minutes. Reference standards for calibrating the systems were prepared by obtaining samples from the site of varying Th concentrations and determining the Th-232 concentration using the Ge detector in Freeport, TX. A linear relationship was observed between the counts from the Tl-208 peak and the Th-232 concentration. This method was found useful in determining Th-232 concentrations down to 0.25 pCi/g. Using a 3:1 Th-230:Th-232 ratio, this method was utilized for site characterization and for remediation.

SITE CHARACTERIZATION

The radiological characterization of the site was done using a phased approach over several years. Figures 1 and 2 show the decay schemes for Th-230 and Th-232. The decay of these radionuclides eventually results in the entire series of radionuclides with a multitude of alpha, beta, and gamma emissions. The freshly separated thorium material was placed on the site from the 1950's to the 1970's, allowing essentially 100 percent ingrowth of all Th-232 daughters. This allowed the use of gamma-ray spectrometers for analyzing the Th-232 concentrations in the materials rather than performing alpha spectroscopy which requires difficult radiochemical separations of the sample. However, due to the long half life of Ra-226 in the Th-230 decay chain, the concentration of Ra-226 and the other Th-230 daughters were less than 1 percent of the Th-230 concentrations. Therefore the Th-230 concentrations were determined by alpha spectroscopy. After an adequate data base existed, the Th-230 concentrations could be estimated using the measured Th-232 concentrations and a conservative value for the Th-230 to Th-232 ratio of 3:1.

A combination of surface sampling analyses and bore-hole gamma logging and core sampling were used to determine the vertical and aerial extent of contamination. Large regions of the slag were found to be free of radioactive contamination using surface samples taken at 20-ft intervals and gamma-logging techniques. Two on-site gamma-ray spectrometers were used for the analysis of many of these site characterization samples. Analysis of samples on-site was found to be very cost effective, resulting in data at a small fraction of the cost compared to off-site analysis. An example of site characterization and the utility of the on-site analytical is given below.

A fraction of the site (about 10% of the area) in the northwest portion was characterized as follows. The area was surveyed and wooden identification stakes were placed at 20 foot intervals. Two-liter samples (from 0-6 inches in depth) were collected at each stake and the samples were sent to Freeport, Texas for gamma analysis using the germanium method described above. The area was divided into 60 foot X 60 foot grids and the average of 16 evenly spaced samples was used to estimate the Th concentration of each grid. The results from 405 samples were used to predict that a large portion of this part of the site was free from contamination. It was also predicted that an additional 4 grids required only selective excavation. These grids had localized "hot spots" that could be easily removed. For this work, sampling took about one week and counting using one Ge detector required about 5 months.

A second small area (again about 10%) in the southwest portion of the site was also characterized. By this time, the on-site NaI method had been developed and was used for the analysis. The area was surveyed and stakes were placed at 20 foot intervals and two-liter samples were taken. This time the samples were analyzed using 5 minute counts on two NaI detectors that were set up on-site. Even though the number of samples were about the same, the sampling and analysis was accomplished in 5 days compared to 5 months for the northwest part of the site. Thus the on-site NaI analysis was found to be a useful tool and it was decided that it would be used in the remediation efforts for selective excavation.

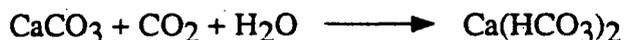
In addition to the sampling strategy and analysis described above, borehole sampling and analysis were also performed to estimate the contamination below grade. With the aide of topographical maps, the amount of material in these two sections of the site was estimated to be about 74,500 cubic yards (cy). Combining all the data, it was estimated that 38,000 cy were free of contamination, 4,500 cy was slightly contaminated and 32,000 cy were heavily contaminated.

Because a large portion of this area was not contaminated, careful selective excavation was recommended. Similar characterization was done on the rest of the site.

REMEDIAL ALTERNATIVES

CO₂ Process

Although not used on this site, it is worthwhile to describe the process since it may have applications for other sites. Classical chemical separations for this material would involve dissolving the slag with aqueous acids prior to accomplishing the separation. The amount of acid required plus the necessity for an extremely selective separation method make this not only impractical but impossible. Thus a separation method that uses inexpensive and safe reagents that can be recycled was envisioned. The idea evolved from examining the chemistry involved in stalagmite and stalactite formation in caves. Thus, in nature calcium carbonate is dissolved in water that has absorbed carbon dioxide from the atmosphere by forming soluble calcium bicarbonate.



Release of carbon dioxide, or the reverse reaction, yields the insoluble carbonate. (i.e. stalagmites and stalactites).



The major component of the Mg slag on site was found to be hydromagnesite. Similar reactions could be envisioned for this material.



Since Th and its daughters were not expected to undergo this reaction, a separation was envisioned based on this chemistry. Recovery of the Mg as a solid could be accomplished by removing carbon dioxide.



The reaction product is written as the trihydrate based on analytical data.

Runs were made in a 300 ml Parr bomb. The slag was slurried in water and placed in the bomb then pressured with CO₂ and stirred for a predetermined amount of time. After this, the pressure was released, the vessel was opened and the solids were separated from the aqueous layer by filtration. The formation of a white solid in the filtrate (MgCO₃·3H₂O) was aided by purging the solution with air. Materials were weighed and analyzed for metals and for radiation. Figure 3 shows the weight reduction of the slag after each run using 240 g of slag, 1194g of water, 145 psig of CO₂, and stirring for 2 hours. After 10 extractions, enough Mg was removed such that the radioactivity was contained in only 22.5% of the original weight.

Figure 4 shows the concentration of radionuclides in the slag as a function of extraction number for a similar run. This data is consistent with an increase of the radionuclide concentration in the solids as a function of extractions. The concentration of Tl-208 is lower than the other daughters due to its branching ratio. When a small amount of BaSO₄ was added to prevent any of the

radioactive daughters from dissolving in the aqueous layer, it was possible to recover 99.9% pure $MgCO_3$ as the trihydrate free of any radioactive contamination.

Preliminary experiments were performed to begin optimizing the parameters of the process. In short, CO_2 pressures of 200 psig were sufficient, extractions were complete in less than one hour, and the slag to water ratio was only limited by the ability to stir the thick slurry. The highest ratio used in these experiments was 0.8 to 1. Based on this, a miniplant was designed and built to study the possibility of a continuous process. Miniplant data has not been collected.

The process described above could be used to reduce the volume of the radioactive slag by about 80%. It has the advantages that the only reagents needed, carbon dioxide and water, are non-toxic and recyclable. Also, the process produces a high grade of magnesium carbonate which may have some commercial value. A patent (U.S. 5,223,181) has been issued covering this technology. As mentioned earlier, this technology was not used to remediate this site. Instead, the radioactive material was selectively excavated and sent to Envirocare of Utah for reasons described below. However the potential use of this technology at other sites is being explored.

Off-Site Disposal Option

Envirocare of Utah, Inc. was selected as the disposer of all radioactively contaminated material. An analysis of the regulatory situation at the time revealed that the radioactive waste "Compacts" would have the authority to assess fees for disposal after January 1, 1993. Any treatment or chemical separation would result in significant quantities of highly concentrated radioactive materials, requiring disposal after the January 1, 1993 deadline. The uncertainty in the regulatory process related to treatment, and the availability and cost for disposing of the concentrated wastes were the primary reasons for selecting the off-site disposal option.

REMEDICATION

The first remediation effort was aimed at clearing approximately 2 acres on the southwest corner of the site for the construction of a laboratory building and access road. An administrative goal of 5 pCi/g total Th above background was established. The area to be cleared was surveyed and two NaI crystals housed inside tents were used to guide the remediation. This ensured that the amount of contaminated material generated during this phase was kept to a minimum. The construction equipment consisted of one trackhoe with a 2 foot wide bucket and a 4 foot wide bucket plus a 7 yard capacity dump truck. The contaminated soil was removed and trucked to one of several waste piles on site. Geotextile fabric was placed on the ground prior to placement of the material. Verification samples of the cleaned areas were collected and sent to Freeport, TX for isotopic Th analysis using alpha spectroscopy. In addition, trenching and trench soil samples were obtained and analyzed to assure that there was no contamination below grade. After the remediation of this area was successfully completed, a laboratory building was constructed on-site. Once the laboratory building was in place, it became headquarters for operations and it was used for all on-site analytical work.

After the laboratory was in place, full scale remediation of the site began. Thin layers of contaminated soils were removed under the guidance of hand held radiation monitors. Once the area was thought to be below the administrative limit, samples were obtained and analyzed on site using NaI spectroscopy. If the results were above the clean up criteria, further excavation was done. If the results were below the clean up criteria, verification samples were taken and sent to Freeport, TX for isotopic Th analysis. After determining that an area met the clean up criteria,

the area was trenched, monitored and samples taken and analyzed to ensure that there was no buried contamination.

Contaminated soils were transferred to a part of the site designated for mixing. Here material that was contaminated above the license limit for Envirocare was mixed with contaminated material that was below the Envirocare limit using earth moving equipment. Samples were taken to ensure proper mixing and the material was transferred to the loading stock pile. In addition, leachable Ba was measured and it was determined that each rail car was below 100 ppm. Non-radioactive slag was placed in a vault on site. This material was not used for mixing.

SUMMARY

Remediation of a 40 acre site contaminated with Th was accomplished with the use of a multidisciplined project management team. The amount of radioactive material was minimized by careful characterization of the site followed by "selective excavation" which was made possible by the utilization of rapid and reliable on-site analytical methods. After doing their own sampling and verification, the Illinois Department of Nuclear Safety (IDNS) released the site for unrestricted use. This accomplishment was due to talented individuals including managers, chemists, office professionals, health physicists, lawyers and engineers that worked together as a team.

Figure 1. Decay Scheme For Th-230

Th-230 7.52 x 10 ⁴ years				
↓ α				
Ra-226 1622 years				
↓ α				
Rn-222 3.825 days				
↓ α	At-218 1.3 seconds			
Po-218 (0.02%) 3.05 minutes	↓ α	Po-214 1.6x10 ⁻⁴ seconds		Po-210 138.4 days
↗ β ⁻				
(99.98%) ↓ α	Bi-214 (99.96%) 19.7 minutes	↓ α	Bi-210 5.01 days	↓ α
	↗ β ⁻		↗ β ⁻	
Pb-214 26.8 minutes	(0.04%) ↓ α	Pb-210 22 years	(5x10 ⁻⁵ %) ↓ α	Pb-206 Stable
		↗ β ⁻		
	Tl-210 1.32 minutes	(1.8x10 ⁻⁶ %) ↓ α	Tl-206 4.3 minutes	
		↗ β ⁻		
		Hg-206 8.5 minutes		
		↗ β ⁻		

Figure 2. Decay Scheme for Th-232

Th-232 1.4×10^{10} years		Th-228 1.90 years		
α ↓	Ac-228 6.13 hours β ⁻ ↗	α ↓		
Ra-228 6.7 years β ⁻ ↗		Ra-224 3.62 days		
		α ↓		
		Rn-220 54.5 seconds		
		α ↓		
		Po-216 0.158 second		Po-212 3.0×10^{-7} second
		α ↓	Pb-212 (66.3%) 10.6 hours β ⁻ ↗	α ↓
		Pb-212 10.6 hours β ⁻ ↗	(33.7%) α ↓	Pb-208 Stable
			Tl-208 3.1 minutes β ⁻ ↗	

Figure 3. % Weight of Slag -vs- Extraction Number

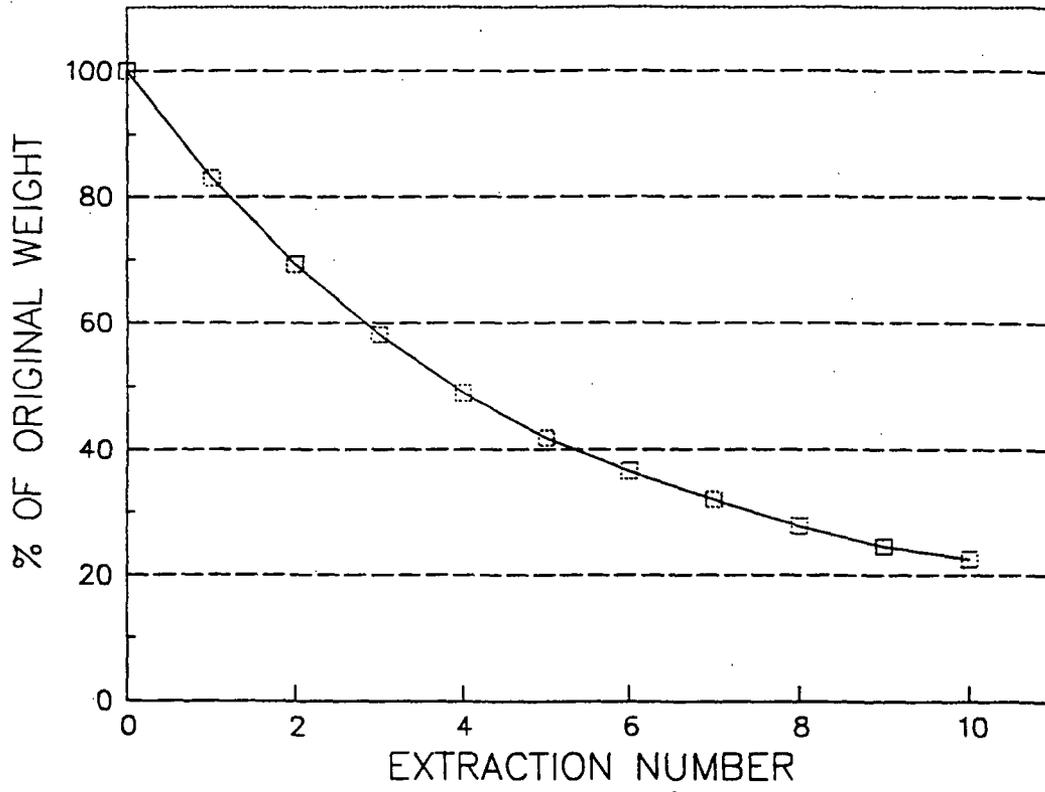


Figure 4. Concentration of Th-232 Daughters in Solids -vs- Extraction Number

