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Electrokinetic Decontamination of Concrete

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ELECTROKINETIC DECONTAMINATION OF CONCRETE

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INTRODUCTION

As a consequence of weapons production activities that occurred over the past 50 years, the U.S. Department of Energy (DOE) has accumulated more than 600 million square feet of contaminated concrete. The DOE has identified the decontamination of concrete as one of its primary problem areas that must be addressed in its Decontamination and Decommissioning Program. The problem of waste disposal of concrete rubble and debris is yet another high priority item in the same program. The cost of decontamination of concrete varies considerably with the site specific considerations. Nevertheless, the “average estimates” point to figures in range of tens of dollars per square foot. All of the above compels the development of an efficient technology for concrete decontamination.

In response to this need, ISOTRON® Corporation proposed the application of an electrokinetic transport-based mechanism to extract contaminants from concrete. The corporation has been working with the DOE Morgantown Energy Center to develop this electrokinetic technology that can provide a novel approach to the problem.

OBJECTIVES

This project is to design, develop, scale-up, and field-test a technology for the decontamination of concrete. In its fully-developed form, the process should provide benefits as follows:

- The process provides favorable economics (generally in the range of 50% of the cost of the presently used techniques).

- The process is “user friendly”, (minimal airborne releases and minimal exposure of workers to radiation).
- A semiautomatic process in the sense that the worker is not required to attend the process (minimizing worker exposure time within a rad zone).
- Minimal damage to the concrete surface, thus facilitating reuse of the surface.
- The process minimizes the volume of secondary waste generated during decontamination.
- The process achieves a solid waste form.

APPROACH

The work that started in 1993 included a comprehensive study of the mechanisms that would control this electrokinetic decontamination process. It was concluded that the process must address not only electrokinetic transport of the contaminants through the concrete, but also the solubilization of the contaminants which had been sorbed on the internals of the concrete matrix or which had precipitated in the matrix due to its high pH. It became obvious that the solubilization aspect would be the controlling issue and that the success of the electrokinetic extraction process would be determined by the ability to find a highly effective solubilization mechanism which could be delivered to the concrete in the presence of its high pH.

TECHNOLOGY DESCRIPTION

ELECTROSORB[®] Electrokinetic Extraction Technology, developed by ISOTRON[®] Corporation offers a cost-effective approach to treating contaminated concrete. The process is designed to mobilize contaminants that are deep in the concrete. Most heavy metals/radionuclides are fixed in the concrete matrix either as sorbed species or in precipitated forms. Such fixed contaminants can be extracted using this process if they are chemically solubilized. This technology utilizes metal solubilizing reagents to solubilize contaminants. (Herein these are referred to as solubilizers). A DC electric field is applied across the contaminated concrete to electrokinetically transport the solubilized contaminants from the concrete-pores to a collector placed on the concrete-surface. The process takes place inside a pad-like enclosure (SEEC pad).

The collector is an extraction pad laid on the surface of contaminated concrete. The pad provides confinement for a planar electrode and the solubilizer solution. A DC voltage is applied between this planar electrode and the concrete rebar or a metallic ground-rod. The solubilizer solution wets the planar electrode and the concrete surface, and provides electrical continuity between the two. The extraction pad is operated under a vacuum which assists in holding the pad firmly against the concrete surface while preventing leakage of the solubilizer solution out of the pad-area. The vacuum under the pad is also instrumental in providing return-flow of the circulating solubilizer solution from the concrete surface to a solution-circulation tank. The process is designed such that

it can be operated with little attendance. This reduces the workers' health hazards that are associated with more labor intensive processes.

Other features of the process include a modest rate of chemical consumption and a reduced volume of secondary waste. This is possible because the process incorporates a mechanism for recycling the solubilizer solution. The contaminant-laden solubilizer solution is pumped through a solution cleanup module comprised of ion exchange bead columns. The contaminants are stripped out of the solubilizer solution in the resin bead columns, and the processed solution is recycled back to service. When the extraction cycle is completed, the loaded bead columns can be dewatered and sent for burial.

ISOTRON[®] is working on an advancement of secondary waste treatment process, which is applicable under certain extraction scenarios. This will significantly minimize the volume of waste sent for disposal. In this case, the spent solubilizer solution will be fed to a vacuum-evaporation unit. The evaporator sludge will be solidified into a low-volume solid waste-form for disposal that complies with 10CFR PART 61 burial criteria. The distillate collected in the evaporator will be reused in solubilizer solution.

RESULTS OF THE FIELD EXPERIMENTS

A field demonstration of the concrete decontamination technology took place in the Building 21 site of the DOE's Mound facility in Miamisburg, Ohio, in June 1996. This demonstration was conducted over a period of 12 days. A prototype of the full-scale (6' x 4') extraction pad was used. The technical accomplishments from this field demonstration are summarized in this Section.

The process demonstration was organized to permit six different extraction tests. The operation parameters such as solubilizer chemistry, electrical current, and treatment time were varied through these test scenarios. The parameters which were held constant are extraction pad geometry, electrode spacing, circulation rate of solubilizer solution and its temperature. The ESM parameters including amount of cation and anion exchange beads were identical for all tests.

The thorium species present in concrete floors of Building 21 include thorium dioxide (commonly known as thoria) and thorium oxalate. These species are insoluble in water. Extraction of these species requires the use of thorium solubilizing reagents. Thoria is known as a stable, refractory material whose rapid dissolution calls for the use of mineral acid solubilizers [1,2].

In this process demonstration, two solubilizer systems were evaluated, citric acid alone, and a mixture of citric and nitric acids. The first four tests were planned to evaluate the effects of solubilizer concentration and electrical current on thorium extraction rate and efficiency. Upon arrival at the site, ISOTRON[®] staff found that the contaminated concrete floor in Building 21 was "capped" with a concrete topping material. The thorium contamination was underneath this coating. Removal of the topping material exposed the contaminated surface. The area of topping material removed from the test area was not the same for each of the first four tests. Due to this reason, an additional parameter, the ratio of electrolyte volume to treated concrete area, was reported for these tests. Two

additional tests were planned to provide a parallel comparison of cleanup level in scenarios where the effect of electrical power could be clearly shown. One of these tests would use electricity, while the other would use **no** electricity.

In all six tests, the electrolyte was replaced periodically. ISOTRON[®] scientists adopted this process control measure to ensure that the electrolyte could be maintained within a specified pH range (as per the process protocol). Replacement of contaminant-laden electrolyte with clean electrolyte would shift the chemical equilibrium to favor dissolution of the contaminant. It should be noted that a spent batch of electrolyte was processed in the solution recycle module comprising of ion exchange columns. After the electrolyte was processed it was reused.

Results from Tests 1 through 4

The relationship between thorium extraction and treatment time for Tests 1 through 4 is depicted in **Figures 1 through 4**. The slope of the curve at any point in time provides the corresponding extraction rate. **Table 2** shows the time-averaged thorium and calcium extraction rates normalized by the area of exposed concrete surface in the four tests. A comparison of the normalized thorium and calcium extraction rates in the four tests is presented in **Figure 5**. The quantity of calcium extracted is significant in that it strongly influences the amount of secondary waste generated. One can conclude that the ratio of thorium to calcium extraction is an indicator of extraction efficiency. A higher value of this ratio represents the preferred operational regime.

These test results reveal the effects of the process variables on thorium extraction rate and efficiency, and thus point toward those parameters that will improve the process. The notable features are as follows:

- A reduction in thorium extraction rate is observed as the electrolyte becomes exhausted. Periodic replacement of exhausted electrolyte ensures continued extraction of thorium at an efficient rate. (See Figures 2 through 4 which correspond to Tests 2 through 4.)
- Solubilizer concentrate addition extends the active-life of the electrolyte. This provides continuity in contaminant extraction (as evident from Figures 3 and 4, see concentrate addition regime).
- An increase in solubilizer concentration results in an increased thorium extraction rate (as evident from Figures 3 and 4, see concentrate addition regime).
- The ratio of electrolyte volume to treated surface area has an effect on thorium extraction and secondary waste generation (as can be seen from the data presented in Table 2 for Tests 1 through 3 carried out under the same electrical current). The extraction of thorium is enhanced. Unfortunately, the volume of secondary waste is also increased.

- The use of a higher electrical current improves the contaminant extraction efficiency. The ratio of thorium to calcium extraction increases as the electrical current is raised (as indicated by the data presented in Table 2). The solubilizer concentration was lower in Test 4 as compared to Test 3. In spite of a lower solubilizer concentration, the thorium extraction rate was greater in Test 4 than in Test 3. The ratio of electrolyte volume to concrete area was higher in Test 4 which would tend to explain part of the trend. However, this alone does not account for the magnitude of the increased thorium extraction rate. One cannot ignore the possibility that the enhanced thorium extraction rate might be a result of the presence of any "hot spots" (thorium-enriched spots) in the Test 4 area. If this possibility is ignored, one can conclude that the use of a higher electrical current caused the higher thorium extraction rate.
- The use of nitric acid in the electrolyte facilitates thorium extraction (as can be seen from Figure 3).

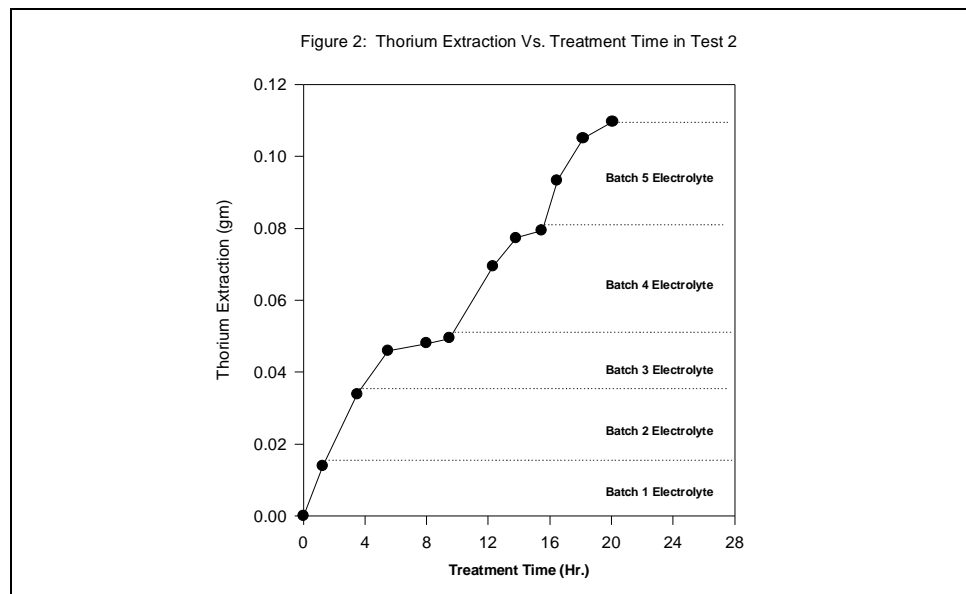
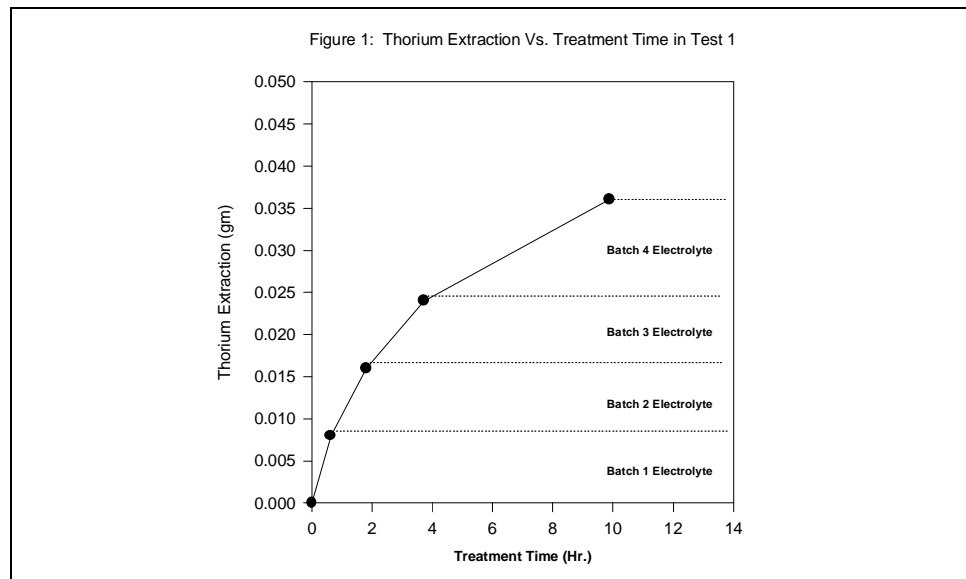


Figure 3: Thorium Extraction Vs. Treatment Time in Test 3

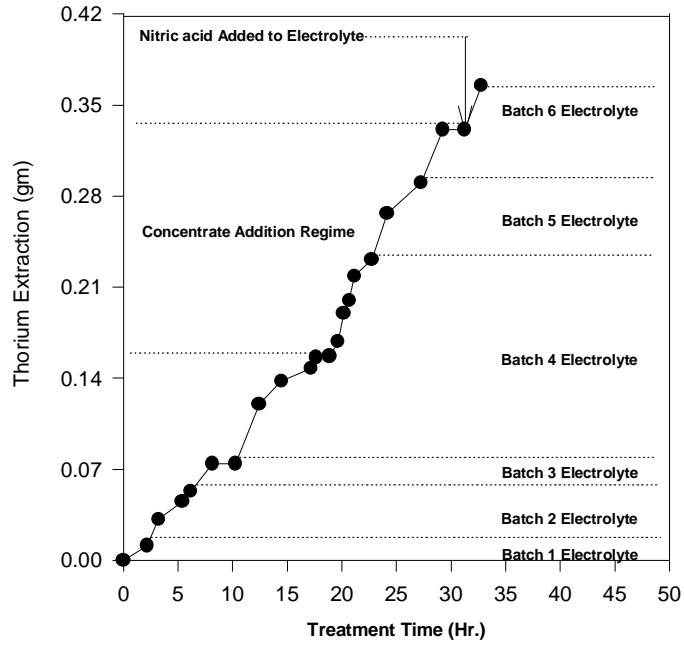
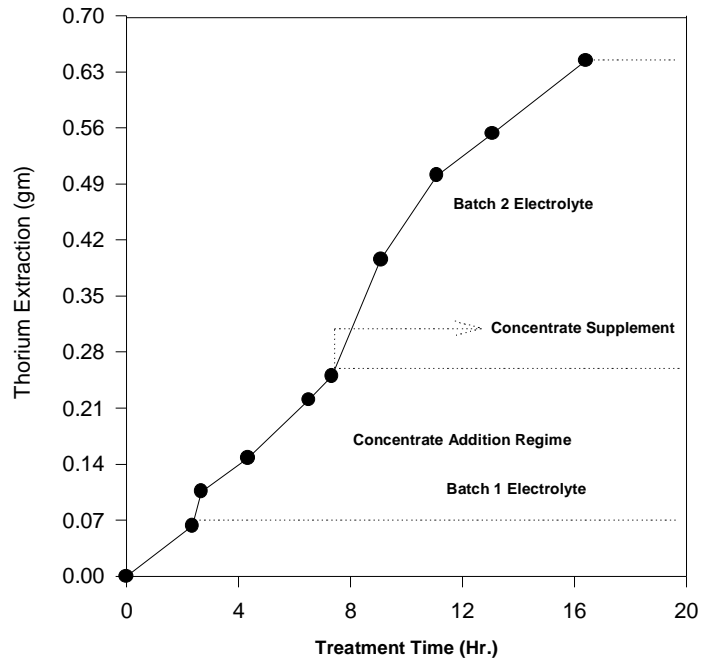


Figure 4: Thorium Extraction Vs. Treatment Time in Test 4



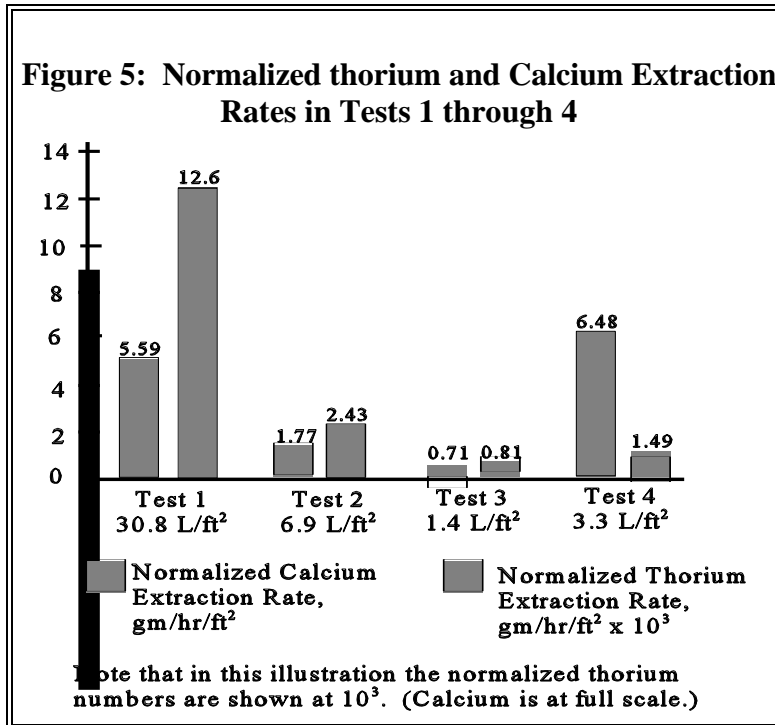


Table 2: Thorium and Calcium Extraction in Tests 1 through 4

Test No.	Exposed Concrete Area, ft ²	Time-Averaged Citric Acid Concn., M	Electrolyte Volume : Concrete Area, L/ft ²	Current, A	Normalized Th & Ca Extraction Rates, gm/hr/ft ²	Th : Ca Extraction Ratio
1	0.65	0.05	30.8	5.5	559 x 10 ⁻⁵ (Th) 12.6 (Ca)	45 x 10 ⁻⁵
2	2.89	0.08	6.9	5.5	177 x 10 ⁻⁵ (Th) 2.43 (Ca)	73 x 10 ⁻⁵
3	15	0.42	1.4	5.5	74 x 10 ⁻⁵ (Th) 71 x 10 ⁻⁵ (Th)* 1.02 (Ca) 0.81 (Ca)*	73 x 10 ⁻⁵ 88 x 10 ⁻⁵ *
4	6.07	0.19	3.3	8.5	648 x 10 ⁻⁵ (Th) 1.49 (Ca)	435 x 10 ⁻⁵

*The nitric acid regime is eliminated.

Experimental Conditions for Tests 5 and 6

These two tests were carried out under identical conditions except that an electric field was not applied during Test 6. The operating conditions for these tests are presented in **Table 3**.

Table 3: Operating Conditions for Tests 5 and 6

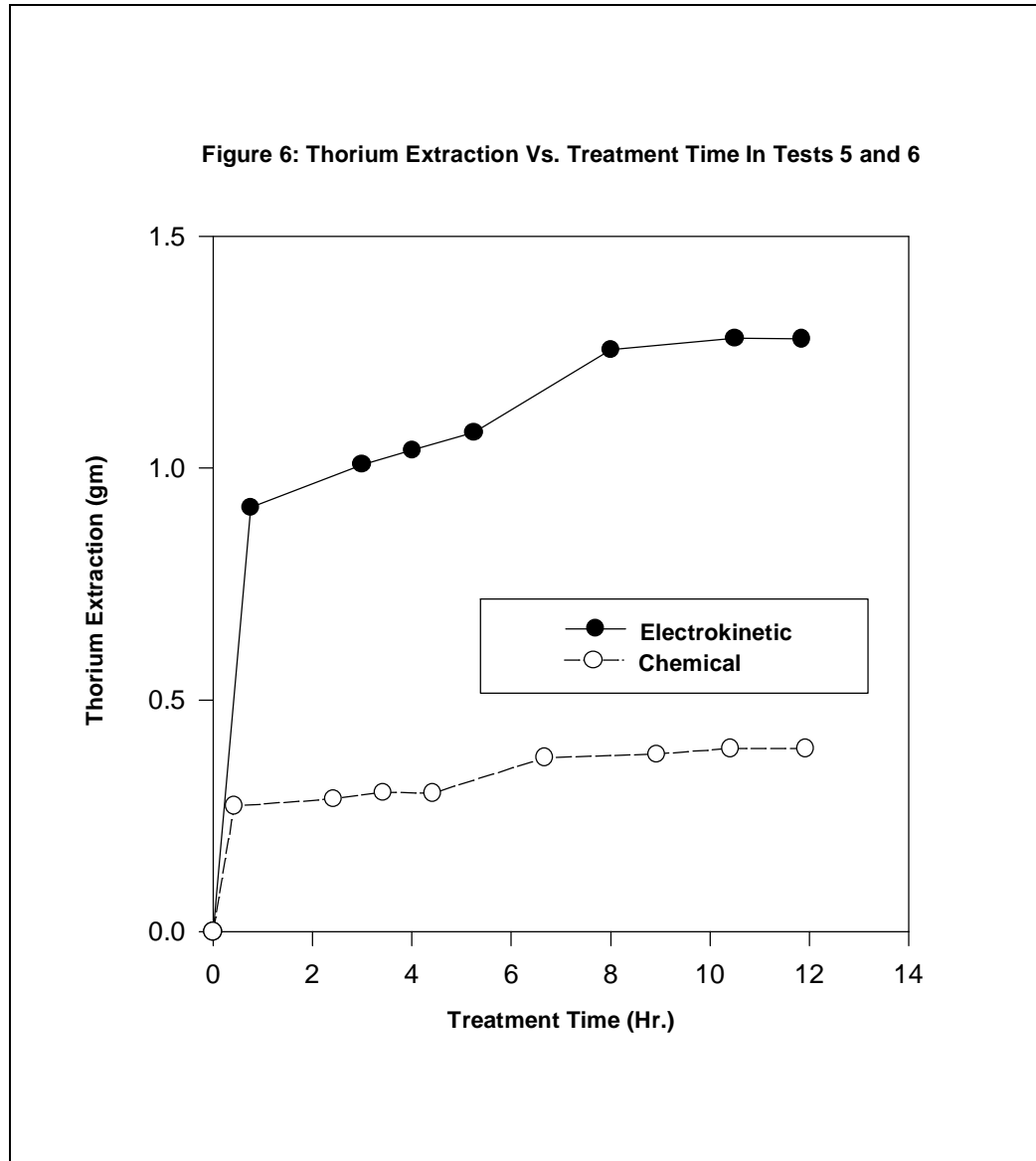
Test No.	Electrolyte, Concentration, Duration of Use	Current, Time-Averaged Voltage	Duration, hr.	Electrical Energy, kW-hr
5	5% Nitric Acid + 0.2 M Citric Acid 1st Batch: 5.3 hr. 2nd Batch: 6.6 hr.	7.5 A 96 V	11.9	8.57
6	5% Nitric Acid + 0.2 M Citric Acid 1st Batch: 4.4 hr. 2nd Batch: 7.5 hr.	0 A 0 V	11.9	0

Results from Tests 5 and 6

Figure 6 shows a comparison of the extent of thorium extraction in the two tests. **Table 4** shows the time-averaged thorium and calcium extraction rates normalized by the area of an exposed concrete surface in the two tests. The thorium to calcium extraction ratio is also presented.

Table 4: Thorium and Calcium Extraction in Tests 5 and 6

Test No.	Exposed Concrete Area, ft ²	Solubilizer Conc., M	Electrolyte Volume : Concrete Area, L/ft ²	Current, A	Normalized Th & Ca Extraction Rates, gm/hr/ft ²	Th : Ca Extraction Ratio
5	15	5 % Nitric Acid + 0.2 M Citric Acid	1.4	7.5	720 x 10 ⁻⁵ (Th) 4.44 (Ca)	162 x 10 ⁻⁵
6	15	5 % Nitric Acid + 0.2 M Citric Acid	1.4	7.5	220 x 10 ⁻⁵ (Th) 3.69 (Ca)	60 x 10 ⁻⁵



A significant amount of thorium was extracted in a relatively short time during Test 5. As expected, the amount of thorium extracted in Test 6 fell short of the same in Test 5. These two tests were carried out under identical process conditions except that an electric field was not applied during Test 6. The thorium to calcium extraction ratio was much higher in Test 5 than in Test 6 (see Table 4). The above findings are in agreement with the key inference drawn from the Test 4 results. These results showed that the use of a higher electrical current augments the contaminant extraction rate and efficiency.

A number of possible causes can be speculated for the observed enhancement in contaminant extraction in the case of electrokinetic extraction over chemical extraction. These are narrated under the following heading.

Contributory Features of Electrokinetics

- In an electrokinetic extraction process, protons are generated at the anode due to the electrolysis of water. The anode therefore serves as a proton source. Due to this continuous supply of protons by the anode, their facilitating effect on contaminant dissolution would be greater in the case of electrokinetic extraction.
- Solubilization of contaminants from concrete matrix by a solubilizer solution represents a two-phase chemical reaction. The concentration gradient of species between the two phases often governs the rates of these chemical reactions. The higher the concentration gradient, the greater is the dissolution rate. Electrokinetics is instrumental in maintaining an elevated concentration gradient of dissolving species between the concrete-solid phase and the solution phase. Electrokinetic transport of dissolved species results in their removal from the vicinity of a dissolution site. This in turn creates a local concentration gradient of these species (near a dissolution site), which is greater than that achieved in the absence of such transport. The result is an enhancement in contaminant dissolution.
- It is also expected that electrokinetics provides for treatment of concrete strata deep within the matrix. The contaminants dissolved in concrete pore solution deep in the matrix can be electrokinetically driven up to the concrete surface and recovered. This may not be achievable in non-electrical extraction processes. Application of an electric field facilitates material transport which is otherwise limited to diffusion and convection.

Further observations from Test 5 are as follows: The thorium extraction rate was greater in Test 5 than in Test 3. The ratio of electrolyte volume to concrete area was the same for the two tests, although the electrical current was 7.5 A in Test 5 as compared to 5.5 A in Test 3. Enhancement of thorium extraction is seen in Test 5 as compared to Test 4. The electrical current, as well as the electrolyte volume to concrete area ratio, was higher in Test 4 than in Test 5, yet the thorium extraction rate was greater in the latter test. The increased thorium extraction rate in Test 5 is therefore attributed to the solubilizer chemistry used in this test, namely to the incorporation of nitric acid as a solubilizer component.

Decontamination Effectiveness

The concrete surface treated in Test 5 was reported clean. This conclusion is based on the following.

- The mean radiation count from the Test 5 area was reduced to "near-background" level. Figure 7.2 shows the results of radiation count measurements made by ISOTRON® (these were later verified by an independent contractor hired by the DOE).
- Mass balance of thorium. The amount of thorium extracted during Test 5 is nearly 83% of the entire inventory of thorium that is expected to be present in the treated area (based on site survey results [3]).

- The thorium extraction vs. treatment time curve was seen to level off in spite of the fact that the process conditions were maintained highly conducive to thorium extraction. The conclusion is that the thorium "source" has been depleted.

Details on the observations on reduction in radiation level are presented below.

Radiation Level

The concrete surface affected by Tests 5 and 6 was grid-marked. The radiation count from each of the grid units was recorded (using BICRON Surveyor 50 radiation counter) before and after treatment. These radiation counts are presented in **Figures 7 and 8**. The data indicate that the radiation count was reduced to the background level (200-250 cpm) at a majority of the sampled locations in the Test 5 area. This corresponds to approximately 84% reduction in radiation count.

A survey of the Building 21 floor for radiation level was also carried out by third party contractor-personnel, both before and after treatment. The results are provided in the survey report [3]. The concentration data for locations in the Test 5 area showed nearly 82% reduction (from 14.98 pCi/g to 2.77 pCi/g) in radiation level. This is in good agreement with the results presented in Figure 7.

Figure 7-1: Radiation Count in the Test 5 Area before Treatment

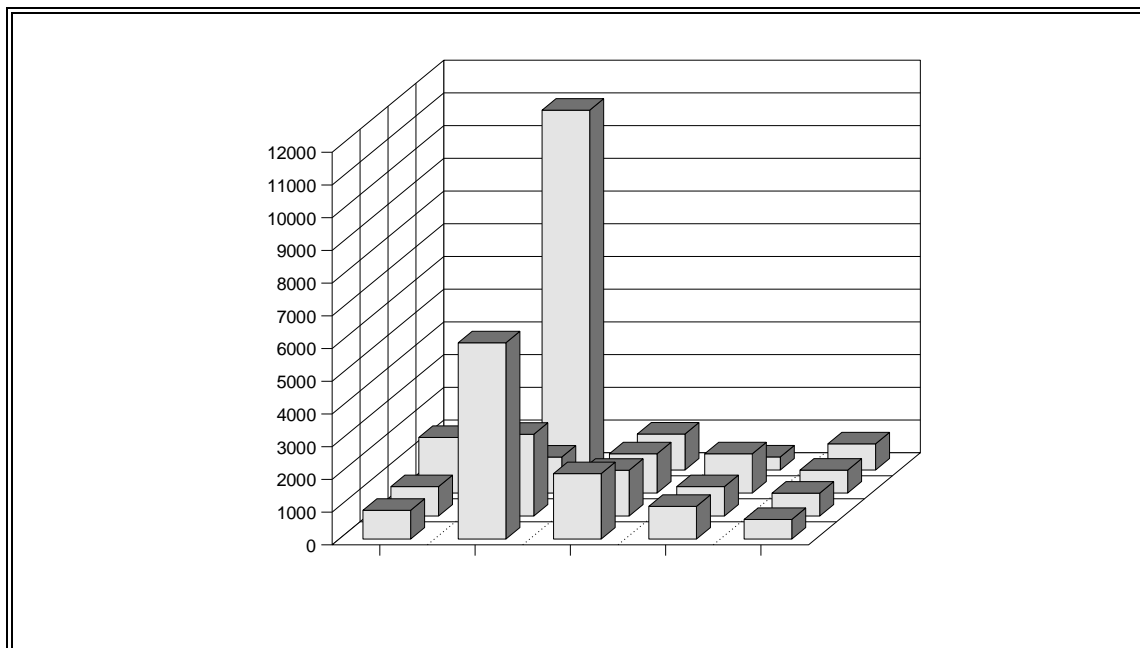


Figure 7-2: Radiation Count in the Test 5 Area after Treatment

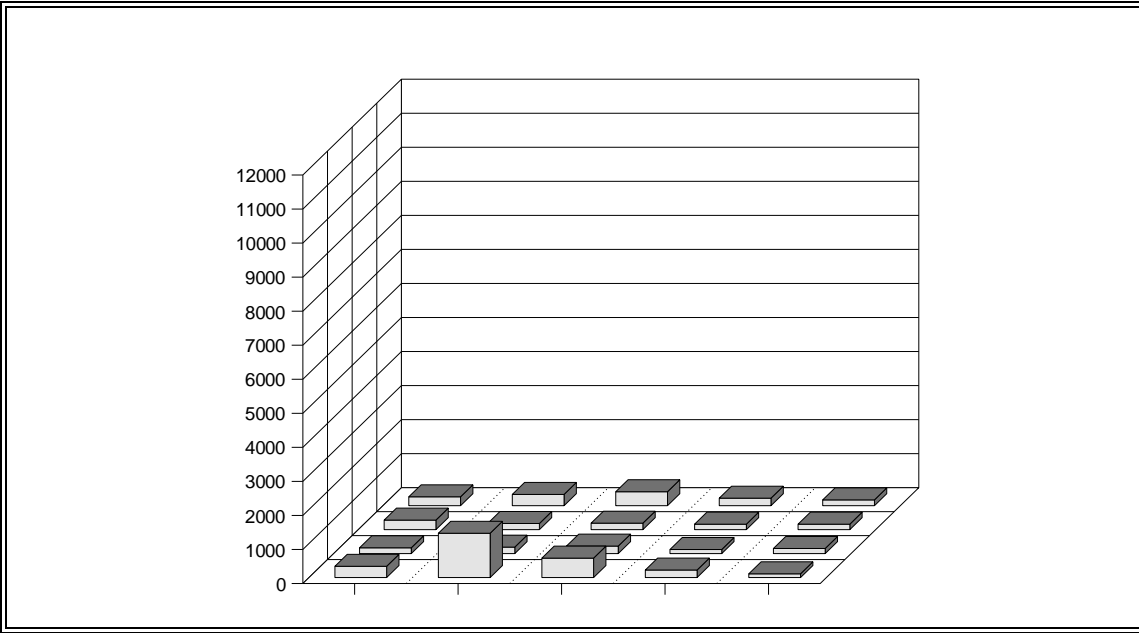


Figure 8-1: Radiation Count in the Test 6 Area before Treatment

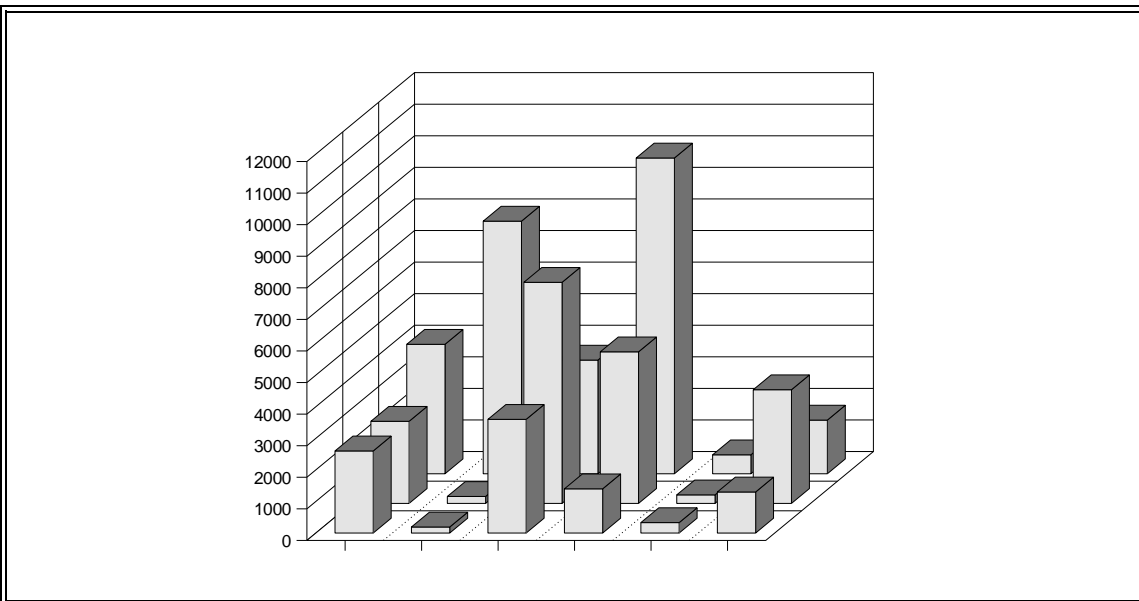
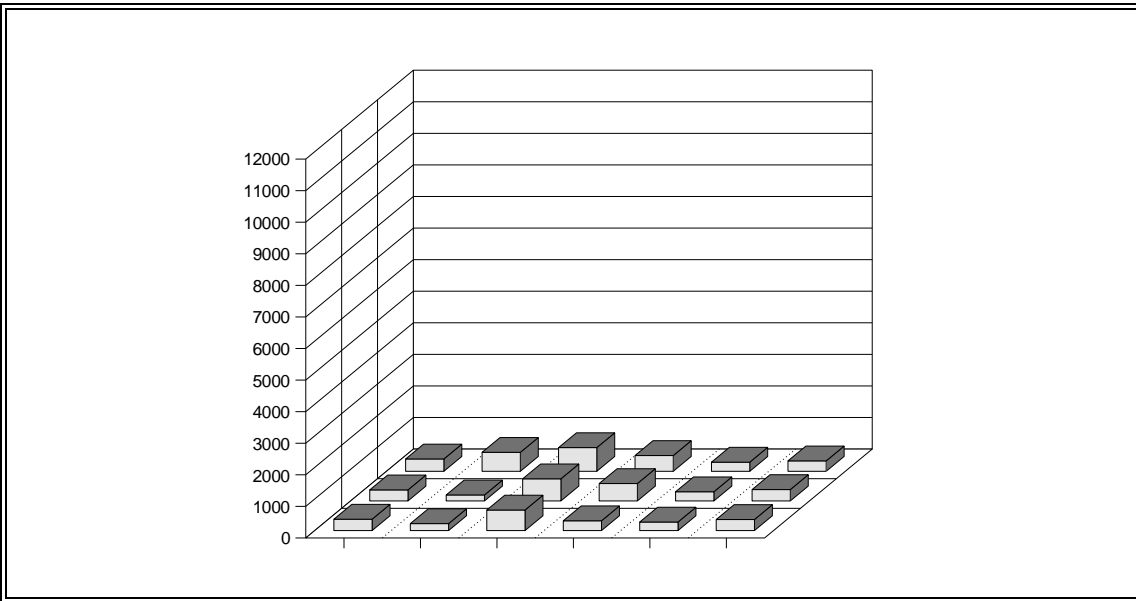


Figure 8-2: Radiation Count in the Test 6 Area after Treatment



BENEFITS

The ELECTROSORB[®] Electrokinetic Extraction Technology offers distinct advantages over the baseline and/or other innovative technologies. Alternative technologies can be classified under three broad categories: 1) chemical, 2) mechanical, and 3) heating. The limitations and/or drawbacks of these alternatives are some combinations of the following:

- limited to surface or shallow contamination;
- not effective for removing sorbed contaminants;
- result in airborne debris and dust problems;
- energy and/or labor intensive, especially when applied to large contaminated areas;
- high risk of personnel-exposure hazards;
- generate large volume of secondary waste (including dust, rubble, and wastewater).

The ELECTROSORB[®] process provides a solution to these problems.

Figure 9 depicts the total cost of the ELECTROSORB[®] process against a backdrop of the baseline and emerging technologies. Figure 10 shows the breakdown of the total cost. The cost estimates presented in Figure 10 are based on the cleanup of 600 sq. ft. of concrete per day. The additional elements of total process cost are as follows: Thirty extraction pads, each having a footprint of 20 sq.ft. are operated. Three solution circulation and processing modules (i.e., ten pads per module) are used. The capital cost is based on 3 years life-span for process equipment and taking 100 working days per year. Labor is based on a 2-person team at \$43.75/hour (8 hours per day). The disposal cost of the solid waste is based on the rate of \$ 300.0/ft³. The electricity cost is based on the rate of \$0.08/kw-hr. The disposal cost is applicable to the process features which incorporate

a vacuum-evaporator unit and waste solidification in a proprietary cement material. The evaporator unit has a processing capacity of 300 gallons/24 hours. The waste loading capacity of the cement matrix is 50% by weight. (See Table 5 for a projected secondary waste volume.) The chemical cost includes the costs of solubilizer and solid waste-form making chemicals. The vaporization energy is based on manufacturer's energy demand rating of 0.85kw-hr/gallon.

The cost figures (shown in Figure 9) for CO₂ blasting and Microwave Scabbling methods are based on data presented in [4]. However, it appears that these costs do not include the cost of radioactive secondary waste disposal. Considering that these methods involve physical removal of concrete matrix, the secondary waste volume and its disposal cost will be significant. The baseline used here, Mechanical Scabbling, is a widely used technology for concrete cleanup. It is reported in [5] that this method results in removal of approximately 0.5 cm of concrete, and the cleanup rate is approximately 30 sq. ft. per hour. The cost of this technology as presented in Figure 9 has been estimated based on the above data on concrete mass removed and productivity, and for the cleanup of 600 sq. ft. of concrete. (It is assumed that the bulk density of the removed concrete material is 1.4 gm/cc. Also, 200 sq. ft. of concrete is cleaned per day with a 2-person team. This considers that there will be non-working time in a 8-hour period due to rad-zone operation. The cost of chemical extraction process is also based on data presented in [4].

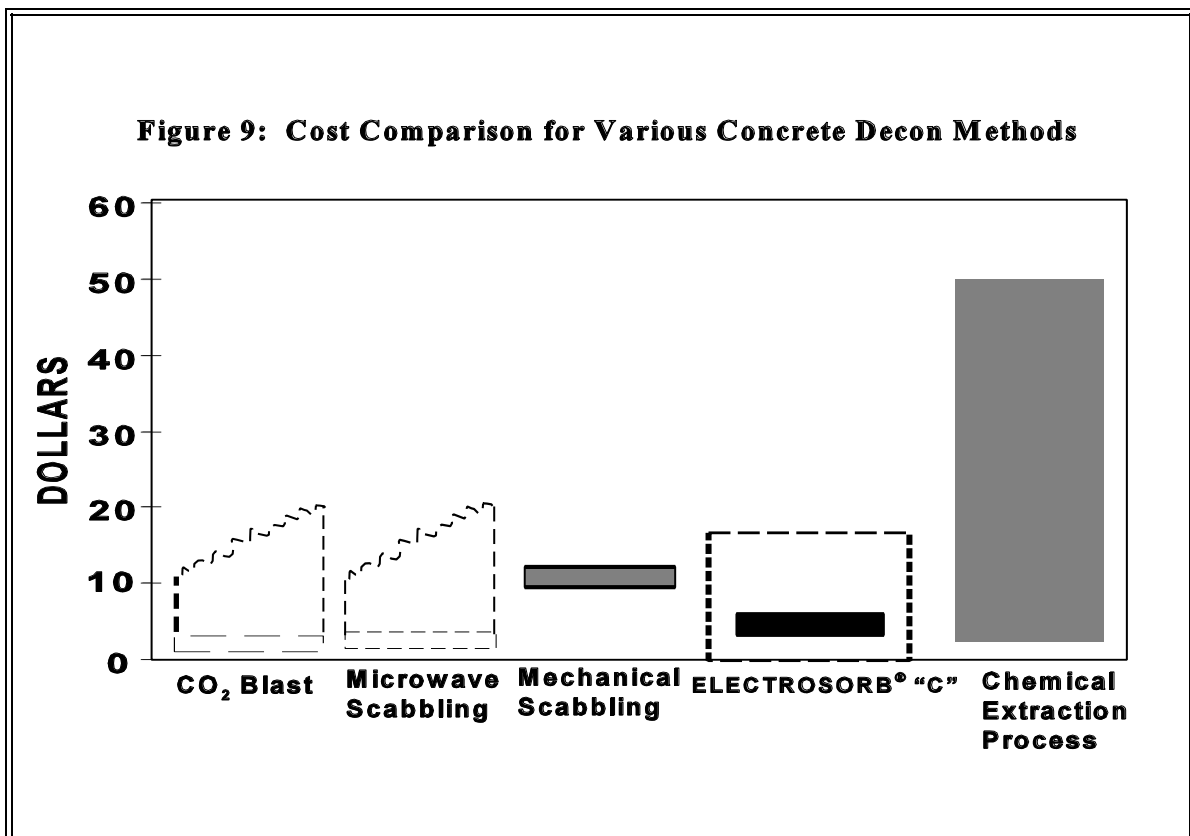


Figure 10: Cost Breakdown for the ELECTROSORB® Process

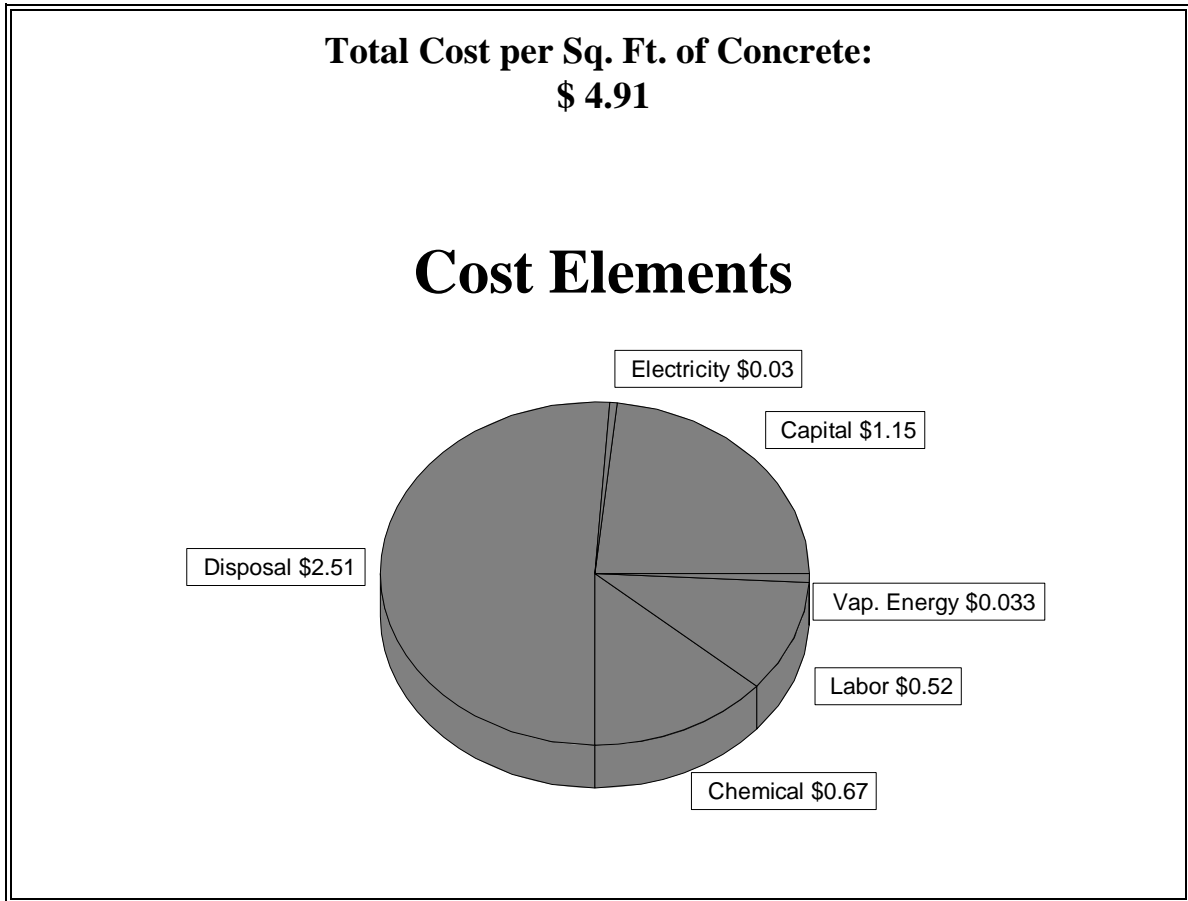


Table 5: Comparison of Projected Secondary Waste Volume for ELECTROSORB® Process versus Baseline Technologies

Technology	Volume of Secondary Waste Generated, ft ³ /ft ²
Scarifying ^a	0.081
Grit Blasting ^a	0.03
ELECTROSORB® (for thorium extraction)	0.04 ^b - (0.01) ^c

a: Source:[4]

b: This figure is based on a waste-form comprising of loaded ion-exchange beads.

c: This figure is appropriate when waste-form is a cement-based solid.

It should be noted that the ELECTROSORB® Process is applicable to the extraction of most radioisotopes typically found in concrete contamination scenarios, such as uranium, technetium, cesium, cobalt etc. The process has been demonstrated for uranium and technetium extraction [6].

FUTURE ACTIVITIES

ISOTRON[®] is presently working on an advanced extraction pad and electrolyte recycling system (ESM). This will be coupled to an advanced secondary waste processing technique. In this approach, a closed-loop cold vaporization unit is used for separating the dissolved solids (including the contaminants) from the spent electrolyte. The distillate is recycled for making solubilizer solution. The evaporator sludge is solidified either in a ceramic or in a cement matrix. The matrix offers a relatively high waste loading capacity. The final waste-form is a low-volume solid whose disposal complies with 10CFR PART 61 burial criteria.

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