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HAZARDOUS WASTE SITE
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THE APPLICATION OF X-RAY FLUORESCENCE TECHNOLOGY IN THE CREATION
OF SITE COMPARISON SAMPLES AND IN THE DESIGN OF
HAZARDOUS WASTE TREATABILITY STUDIES

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ABSTRACT

Site Comparison Samples (SCS) and treatability studies are contemporary tools used in the investigation and remediation of hazardous waste sites. Each depends on the development of large volume samples which are characteristic of the most difficult conditions at a site to treat. The use of X-ray fluorescence spectrometers (XRF) to identify sample locations at a major Superfund site is described. The subsequent processing of samples into SCS materials and treatment samples is presented.

INTRODUCTION

As byproducts of a growing technological society continue to find their way into the environment, the Environmental Protection Agency (EPA) must face an ever-expanding problem of how to handle and measure the harmful byproducts. Before contaminants can be removed or neutralized, they must be characterized for type and quantity. Field-Portable X-ray Fluorescence (FPXRF) instrumentation has been shown to be useful as a screening tool for heavy metals in soils at hazardous waste sites (1,2). Instruments are smaller than their laboratory counterparts, transportable by a single individual, hermetically sealed, and provide immediate data from analyses completed with little or no sample preparation. Analyses are either conducted in a field laboratory or in situ.

The Bunker Hill Superfund Site is located in the Coeur d'Alene mining district of northern Idaho. The site is 7 miles by 3 miles. Primary site contaminants are lead and zinc associated with the mining, beneficiation, smelting and refining of lead-zinc-silver ores. Lead smelting commenced in 1917 and zinc refining operations began in 1927. Operations ceased in 1981. Over the period of operation of these facilities, metals were emitted to the atmosphere from both point and fugitive sources. Tailings from the beneficiation operations were discharged to the Coeur d'Alene River prior to the construction and use of tailings impoundments. These emissions and discharges resulted in widespread contamination of area with metals (3).

The management of large, complex Superfund sites requires years of effort by many parties, and is composed of a series of individual projects and concurrent tasks. Each task requires development of its own quality assurance plan. Quality control within and between projects relating to the same site is an

important element of an overall quality assurance program. Due to the size of the site (21 square miles), the number of parties involved, and the length of time until remediation is complete, the use of Site Comparison Samples (SCS) as tools for applied quality control allow quality assurance of data between projects on the same site.

As a result, two requirements presented themselves simultaneously:

- (1) The need to develop large, homogenous volumes of heavily contaminated soils for treatability studies, and
- (2) The need to develop large homogenous samples of soils which should be processed as Site Comparison Samples ("SCS project").

Field screening using FPXRF technology was selected as the analytical tool to ensure that appropriate soils were developed for both of these purposes.

FIELD ACTIVITIES

Over 500 kilograms of soil was required for the site studies and the SCS project. The soils needed to be heavily contaminated and as dry as possible. Authorization to proceed was received in October 1987. Then current weather conditions in northern Idaho were unusually dry for that time of year; hence, any field effort had to be mobilized quickly or postponed until the following summer. Postponement was not acceptable. The high cost of the treatability studies and the critical nature of the SCS project to the long term quality control program at the site demanded that soils of known concentrations with known data quality be obtained; sample collection without concurrent analysis was not acceptable. Field activities needed to be supported, therefore, with instrumentation that could be mobilized quickly, be portable enough to be moved throughout a large site and be capable of providing analytical responses to field personnel on a "real-time" basis.

Equipment

The FPXRF used at Bunker Hill is the X-Met 840 manufactured by Columbia Scientific Industries Corporation. A technical description highlighting its applicability for use at hazardous waste sites is provided by Piorek and Rhodes (4). The X-Met 840 is a

self-contained, battery powered, microprocessor-based, multichannel X-ray fluorescence analyzer weighing 8.5 kg. The surface analysis probe is specially designed for field use. The X-Met 840 is hermetically sealed and can be decontaminated with soap and water. The probe includes a radioisotope source of Curium-244, a proportional counter and the associated electronics. The source is protected by an NRC-approved safety shutter.

The electronic unit has eight calibration memories called "models". Each model can be independently calibrated for as many as six elements each. These can be used to measure elements from aluminum up to uranium assuming two probes with the associated isotope sources are available. The unknown sample intensities are regressed against the calibration curves to yield concentrations. For the Bunker Hill site only lead and zinc were investigated and only two models were calibrated. Model 1 was calibrated from background up to 4980 mg/kg Pb and 9791 mg/kg Zn.

Reference Soil Standards for Quality Control and Standardization

The commercially available FPXRF systems use standards to establish calibration curves for comparison. Heretofore there has not been a demand for FPXRF systems in hazardous waste screening. Because of this low demand, there were no standards commercially available until recently. Columbia Scientific Industries Inc. (CSI) has produced the first set of commercially available standards designed specifically for hazardous wastes in soils. The primary calibration curves are based on these standards, which are listed in Table I as CSI. A description of a calibration technique for X-Ray Analyzers used in hazardous waste site screening is presented by Piorek and Rhodes (5).

Sampling

Sampling was completed in two days. Formerly acquired metals data was reviewed to identify several potential areas for field screening. These were visited in an attempt to limit the number of areas actually screened with the FPXRF. Three areas ranging in size from less than one to greater than 10 acres appeared to be appropriate, i.e., existing data suggested heavy contamination at those locations, the soil matrix was typical of the area, the areas were accessible and dry, and samples processing could be accomplished without disrupting other activities.

FPXRF screening was accomplished in two steps. First, a series of stations were staked and located on site maps. A two-person crew was used, one to set stakes and one to map the sample locations using a Brunton compass and a 300 foot tape. Second, a two-person FPXRF crew completed on site screening at each station. One person operated the instrument and one served as data recorder.

FPXRF data was acquired at each of the three target areas at a rate which exceeded one data point per two minutes. The rate limiting factor at each target area was the time required to survey the sampling grid, not to operate the FPXRF instrument. It might have been possible to eliminate the second person on the FPXRF crew without compromising the data acquisition rate. More time was required to move between target areas than to sample once the team was in an area. Typical

FPXRF measurement times were 20 seconds per data point.

The levels of contamination as measured by the FPXRF for stations within the three areas ranged from 2300 to 70,000 mg/kg for lead, and 750 to 27,000 mg/kg for zinc. These values cannot be compared directly to contaminant values as obtained by standard SW 846 methods or CLP methods because they use partial digestions or extracts for analysis and FPXRF provides total elemental (or bulk) analyses.

Based on a review of these data, bulk soils were collected at two target areas between stations exhibiting the highest contamination levels. Sixteen samples, each with a field weight of at least 60 pounds was collected. Prior to shipping, each of these was analyzed in duplicate for lead and zinc by the FPXRF. Lead contamination in the samples ranged from 15,000 to 67,000 mg/kg. Zinc ranged from 1900 to 28,000 mg/kg. Samples with this level of contamination were adequate for both the SCS project and the treatability studies.

SCS DEVELOPMENT

As analytical instrumentation has moved into the field to complement laboratory instrumentation, so have the inherent problems of quality assurance and the application of field quality control to compare to data produced by established "conventional" methods of sample analysis. Given the problems of variability in results caused by selection of sampling points on a site, or by variability in relative large volume samples later analyzed by small aliquot "high sensitivity" methodologies, project officers and sample plan designers have turned to two recognized QC procedures to establish comparability; splitting samples between analytical facilities and increased use of Standard Reference Materials. With the increased use of contract laboratory facilities, the problems have increased disproportionately with each added analytical facility introduced in the larger multiple party sites. Cost and resource expenditure in time and logistics increase.

Definition

"A Site Comparison Sample (SCS) is a site specific reference material which is representative of the type of problems encountered when analyzing or treating materials from the site." SCS's:

- Contain key contaminants in the matrix of the site;
- Are available in sufficient numbers to satisfy numerous site management and QA/QC purposes;
- Exhibit the lowest possible coefficient of variation (cv);
- Are managed by an organization capable of being a depository of analytical results, providing a common management point for quality assurance, inter- and intra-laboratory studies.

SCS differ from Standard Reference Materials (SRM) by virtue of being site specific, and not produced under a protocol requiring the pre-release rigorous analytical method specific, statistically validated

characterization applied to SRMs. They also differ from Performance Evaluation (PE) samples used in studies to directly compare inter-laboratory results under a defined methodology. A SCS stock could conceivably provide the material for a SRM or PE, but would require those protocols to be applied before so identifying.

Quality assurance of data developed from multiple sources presents a complex situation. One major problem is the question of sample variability and comparability caused by distribution of compounds of interest on a site. A second is the variability inherent in, and between, analytical methods, particularly due to matrix interference effects. Two common techniques for dealing with these problems are the use of "split" samples and analyses of Standard Reference Materials. Splitting increases the risk of magnifying the problem due to distribution; standard reference materials seldom reflect the matrix effects present in "natural" site samples.

Late in 1984 and early in 1985, the concept of manufacturing a homogenized bulk sample was developed to provide vendors of proprietary soil stabilization services uniform materials for evaluation. The use of screening techniques to define areas of concern on a site was directly applied to statistically choosing sources of material to provide a sample representative of the more highly contaminated material distributed in the matrix of the site. Mixing methods were investigated from the viewpoints of cost, available resources, and practicality. Separate elements of the methodology were tested on available materials at various sites. Protocols and standard operating procedures regarding from where to select the material, how to homogenize it, and how to fill the bulk sample containers in a manner that would reduce bias in the distribution of the material to the large bulk containers were developed.

The question of how to mix bulk samples of site matrix materials to achieve a relatively homogenized material had to be answered empirically. Because of the wide variety of particle sizes, moisture content, cohesive characteristics and distribution of contaminants, it was decided to thoroughly mix the material for the first 1400 pound sample by manually quarter piling through several cycles; and then do a multiple random fill of enough buckets (sixty-nine) to meet all projected needs. It was labor intensive, and took 4 people most of one day.

The sequence of events discussed in the creation of the bulk reference materials led logically to the concept of further treatment of the bulk material to provide a "Site Comparison Sample (SCS)" for each major site. Initially, approximately two dozen 8 oz. sample containers were "broken out" of a bucket, and used for comparative analyses to determine the degree of mixing achieved. Some pressure was felt to supply some of these for comparison analyses instead of splitting samples. At that time, resources were not available to so use the material; no statistically sound evaluation of the material existed to back up any results.

It cannot be emphasized too heavily that the SCS is not to be considered a sample that represents the actual concentration of a contaminant at any given point on a site. Also, it cannot initially be considered as a true SRM, although it may be possible to up-grade it's status if a large number of SCS are generated, and enough

analytical resources are available to utilize a portion of the banked samples for a statistically sound standardization analyses. The concept of the SCS is to produce a material that can be used in lieu of split samples, and provide a data bank for both continuing and retroactive analysis of variation due to differing methods of sample acquisition, handling, and analyses. As the discrete SCS will be archived in controlled storage, the effects of holding time can be demonstrated for each set by continuing characterization analyses. The more SCS analyzed, the stronger the statistical evaluation of all data generated by analyses becomes; not only of the SCS bank itself, but of the sample of record data and the laboratories producing the data.

In Statistics there is the "The Central Limit Theorem": It states:

"From an unknown distribution a random sample size n is obtained. If n is allowed to become larger, the sample mean will behave as if it came from a Normal distribution, regardless of what the parent distribution looked like."

John Webber, Statistician for EPA Office of Policy and Planning, had provided a table illustrating how Normality affects a sample population (Table II) taken from a universe, and reverse logic suggests that very low variances could be expected from discrete samples of n_h , especially if the discrete samples were produced by actually filling the randomly selected sample containers with a series of multiple portions selected at random from the bulk n_h material. (The "double random" referred to hereafter.)

Reasoning from this point, if n is sufficiently large, and then thoroughly mixed or homogenized, multiple random creation of n_h should result in a low variance that approaches the "true" value of the concentration of the mean of n . As the number of random selections used to create n_h increases, the coefficient of variation should decrease.

Through the balance of 1985 and into 1986, the analytical results from the stabilization tests made on the bulk materials were reviewed. Protocols were developed through experimentation to mix sludges of water, sediment and hydrocarbon products. A protocol for groundwater SCSs was developed.

Finally, in late 1986 an opportunity presented itself to produce an actual SCS for a large, established Superfund site. This dovetailed with the trial of the X-Met FPXRF equipment, and made it possible to more soundly screen the bulk "raw material" for both stabilization studies and two SCSs; one "high" range and one "low" range. A fairly ambitious design was proposed to produce between 300 and 500 8 oz. samples in each range.

Experience with the homogenization of the original stability samples suggested that it would be desirable to utilize more efficient methods of mixing the bulk sample material. Accordingly, a "drum roller" was obtained, and 55 gal O.T. steel drums were modified with two interior deflection vanes similar to those used in industrial dry mixing of materials. The bulk sample material was batched through this drum and then spread out in a distribution box for the double random selection of the SCS samples. The available quantity of material dictated that only a single SCS be produced, so the "high" and "low" bulk retains were incorporated into

a single batch for processing.

The 600 aliquots have been "banked", and a master random distribution list prepared. From the bank, an initial set of 10 SCS (the first block on the list) were supplied to the USEPA Environmental Monitoring Services Laboratory, Las Vegas, NV. for preliminary characterization analyses. At the same time, a principle contractor was issued the next 30 samples for release to their contract laboratories for the same purpose. All analytical data results are to be reported to Region 10, and a running control chart of results developed.

As the number of samples analyzed increases, the data will become progressively more refined, and amenable to other statistical analyses to more closely define the sources of variability, from laboratory, to method, and to a certain extent, the effects of holding time. Data currently available are presented in Figures 1 and 2. Although the number of data points are limited, there is a suggestion that inter-laboratory differences may be important (Figure 1), and that overall cv's are low (less than 30%).

As related, this is an ongoing developmental effort. Preliminary data indicate the approach is sound. For middle to large site hazardous waste operations, and for long term ambient monitoring projects, the economies of scale would apply. For improved data quality and scientific credibility the concept is entirely appropriate and defensible. The practical application awaits resources and initiatives on the part of the user programs.

REFERENCES

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- (2) Raab, G. A., D. Cardenas, and S. J. Simon, "Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening," EPA/600/4-87/021, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.
- (3) Gulf Resources and Chemical Corporation, "Bunker Hill Site Remedial Investigation/Feasibility Study for Unpopulated Areas," April 24, 1987.
- (4) Piorek, S., Rhodes, J. R., "Hazardous Waste Screening Using a Portable X-ray Analyzer," Symposium on Waste Minimization and Environmental Programs within DOD, American Defense Preparedness Association, Long Beach, California, April 1987.
- (5) Piorek, S., Rhodes, J. R., "A New Calibration Technique for X-Ray Analyzers Used in Hazardous Waste Screening"

Table I
Concentrations of Standards

Standard Elements: Name		Pb	Zn	Cu	As
		(All values are in mg/kg)			
1	CSI 1B	0	4790	4790	6970
2	CSI 2B	0	0	0	11,340
3	CSI 3B	4980	0	0	0
4	CSI 5B	240	240	8160	7740
5	CSI 6B	484	482	6300	5590
6	CSI 7B	4760	4900	3810	11,070
7	CSI 8B	1474	983	2950	4530
8	CSI 9B	1990	2970	982	3390
9	CSI 10B	2930	3910	1960	2250
10	CSI 11B	2440	6360	490	1140
11	CSI 12B	3405	8270	243	565
12	CSI 13B	4126	9791	96	224
13	CSI 14B	0	0	4950	0
14	CSI 15B	0	4950	0	0

Table II

Illustration of How Normality Affects Samples

Let us phrase the question "How many samples do I need to be within Q sigma "s" (Standard Deviations) of the true value?":

Q Sigma "s"	Confidence 90%		Confidence 95%		Confidence 99%	
	Normal	Worst Case	Normal	Worst Case	Normal	Worst Case
2s	1	3	1	5	2	25
1s	3	10	4	20	6	100
0.75s	5	18	7	36	10	178
0.5s	11	40	16	80	22	400
0.4s	17	63	25	125	34	625
0.3s	31	112	43	223	61	1112
0.2s	68	250	97	500	136	2500
0.1s	271	1000	385	2000	543	10000

from: "Statistical Considerations in Sampling Hazardous Waste Sites", John Warren,
E.P.A./O.P.R.M.

Figure 1

BETWEEN LABORATORY COMPARISON

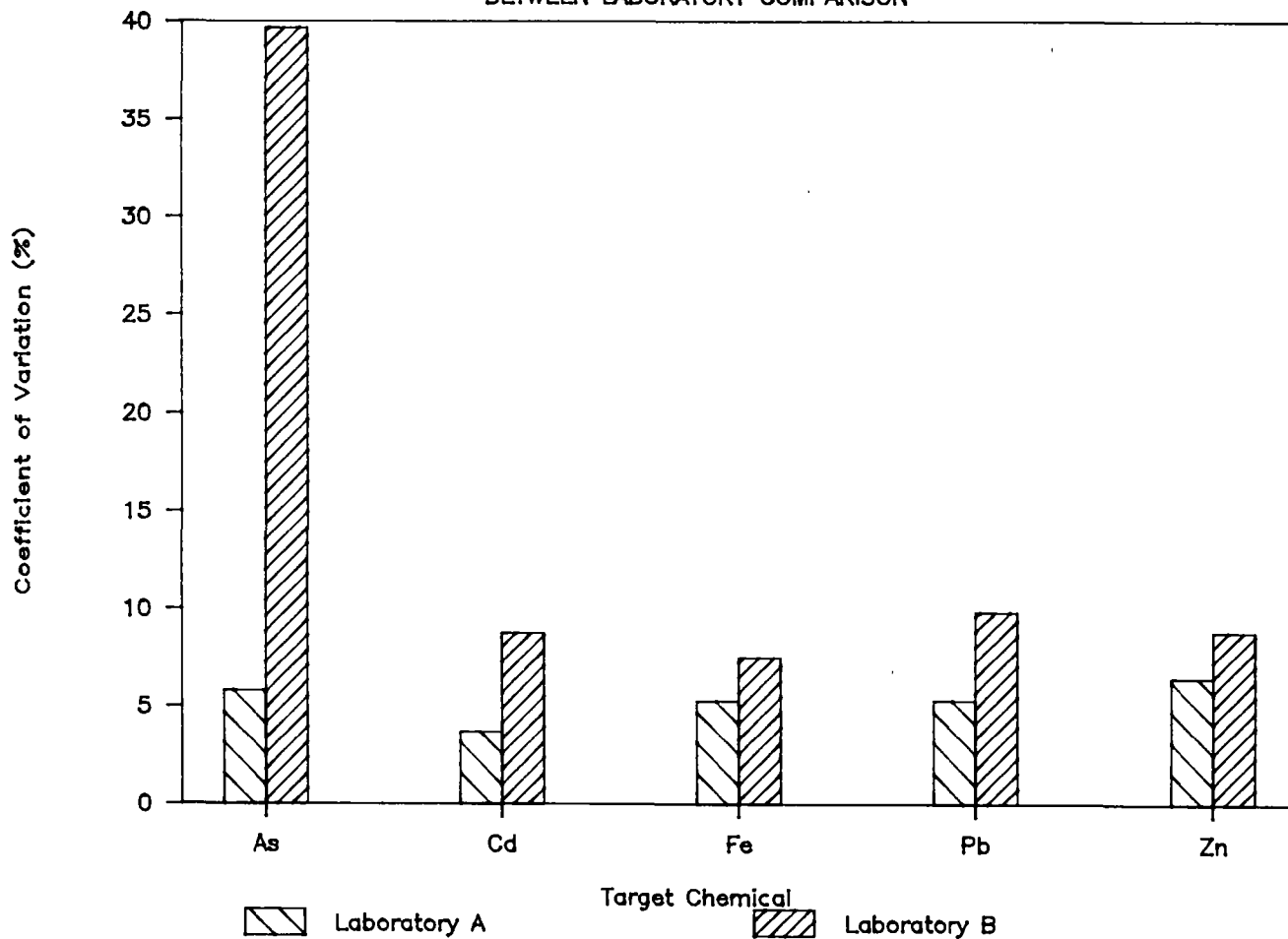
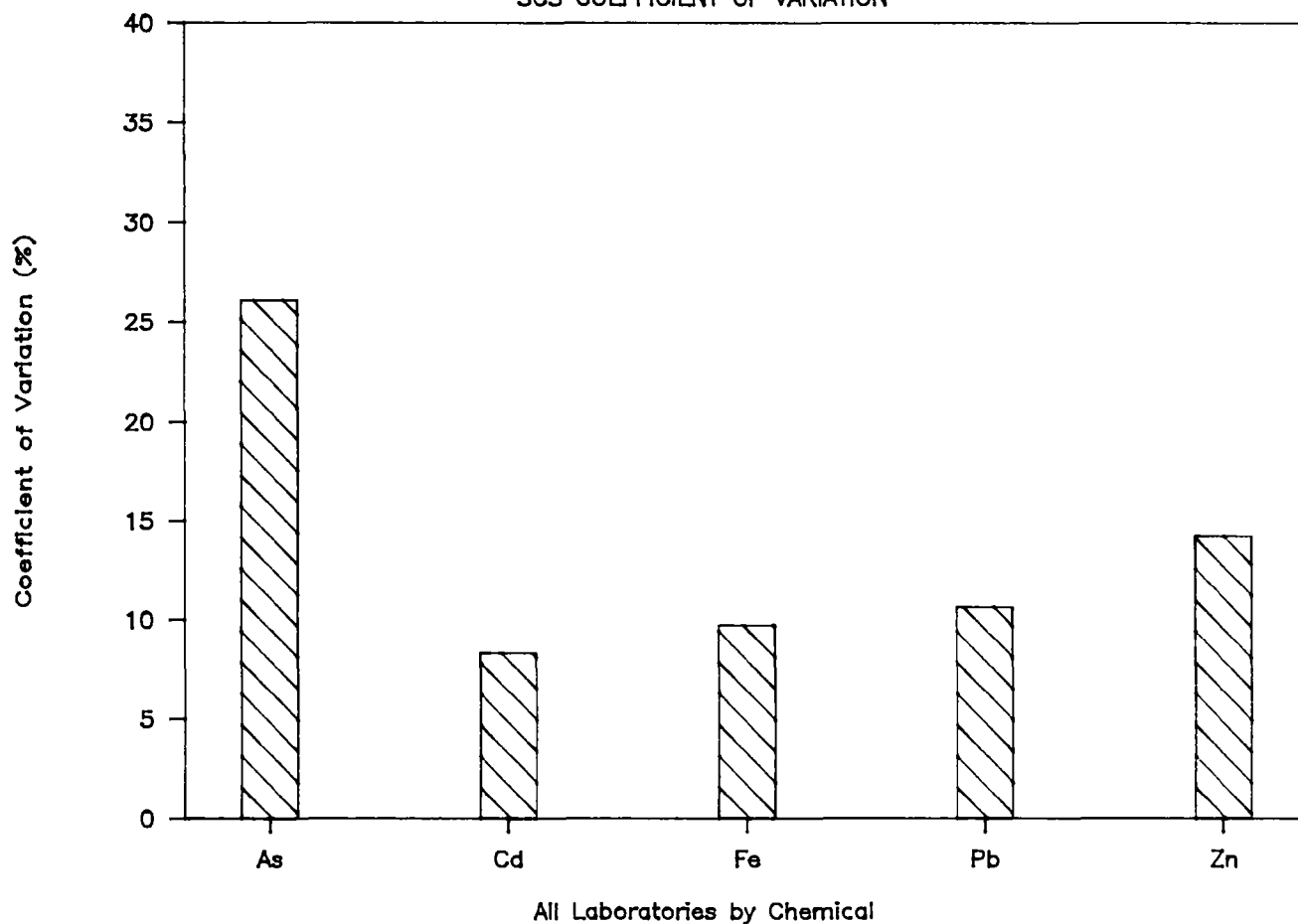


Figure 2

SCS COEFFICIENT OF VARIATION



DISCUSSION

HAROLD VINCENT: How were you going to apply the zeolites to the problem?

JOHN BARICH: Our first step was to determine whether or not the zeolites would be a useful soil amendment. If the answer to that was a strong yes, then the application technique would have been the next thing we would have looked at.

HAROLD VINCENT: That's in place of removal?

JOHN BARICH: In place of removal, yes. We had literally many square miles of land whose condition needed to be improved. There was just not enough secure landfill capacity, to do anything other than *in situ*