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PART III: Arsenic

Chapter 4

TREATING ARSENIC-CONTAMINATED SOIL AT A FORMER HERBICIDE BLENDING FACILITY

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Abstract: Arsenic-contaminated soil at a Superfund site in Missouri was treated during 2005 using a ferric sulfate-based additive. Initial testing indicated that 20 percent Portland cement was needed to treat the soil; in contrast, only around 2 percent of the ferric sulfate additive was required. The exact dosage depended on the arsenic content of the soil. Arsenic screening using X-ray fluorescence (XRF) was used for the in-field determination of the dose required for each batch of soil. Varying levels of available iron in the soil was an additional factor in selecting the dose of treatment chemical. More than 70,000 tons were successfully treated and disposed, at an average chemical dose of 2 percent. The correlation of XRF arsenic data with wet compositional analysis, the relationship of available iron to arsenic ratio with TCLP-arsenic analysis, and the dosage-response for chemical treatment of soil comparing the bench-scale and full-scale treatment data are discussed.

1. INTRODUCTION

Arsenic is a known carcinogen and is one of the most commonly reported contaminants at U.S. EPA Superfund sites (USEPA, 2002). In the past, the most frequently used technology for remediating arsenic-contaminated soil at Superfund sites has been solidification/stabilization (S/S) with Portland cement (USEPA, 2002). Cement treatment gained an early endorsement from the USEPA because it physically binds the contaminants within a solid stabilized mass and reduces the hazard potential of the waste by limiting the solubility and mobility of the contaminants. A major disadvantage of the cement treatment process, however, is that it adds a lot of weight and bulk because of the relatively high additive dosages that are normally needed to solidify the waste. This additional weight results in higher handling and disposal cost. In recent years, a more cost-effective approach for remediating arsenic-contaminated soil has been chemical stabilization, in which the leaching and mobility potential of the contaminants are greatly reduced by the addition of pH control and adsorption/coprecipitation agents. Chemical stabilization uses much less additive dosage than cement treatment, which reduces disposal cost. In this instance, a proprietary, ferric sulfate-based chemical stabilization chemistry was used for soil stabilization at the subject site. In-field XRF arsenic analysis of the soil was used for dosage determination. Additionally, the additive dosage had to be controlled for a certain molar ratio of iron to arsenic for effective treatment. A case study on chemical stabilization of arsenic-contaminated soil using the ferric sulfate-based chemistry is presented in this paper.

2. SITE HISTORY/BACKGROUND

A herbicide manufacturing/blending plant operated in North Kansas City, Missouri from the 1920s until 1986, when numerous chemical releases to the soil and groundwater occurred. The USEPA placed the site on the Superfund list (USEPA, 1999) with the focus on remediating the arsenic present in soil at concentrations exceeding 10,000 mg/kg. The contamination extended to 18 feet below ground surface (bgs), some of which was below the water table (14-20 feet bgs). Anthropogenic fill material was present up to a depth of about 5 feet bgs. The underlying native materials consisted of soft to medium-stiff silty clay to depths of up to 23 feet bgs.

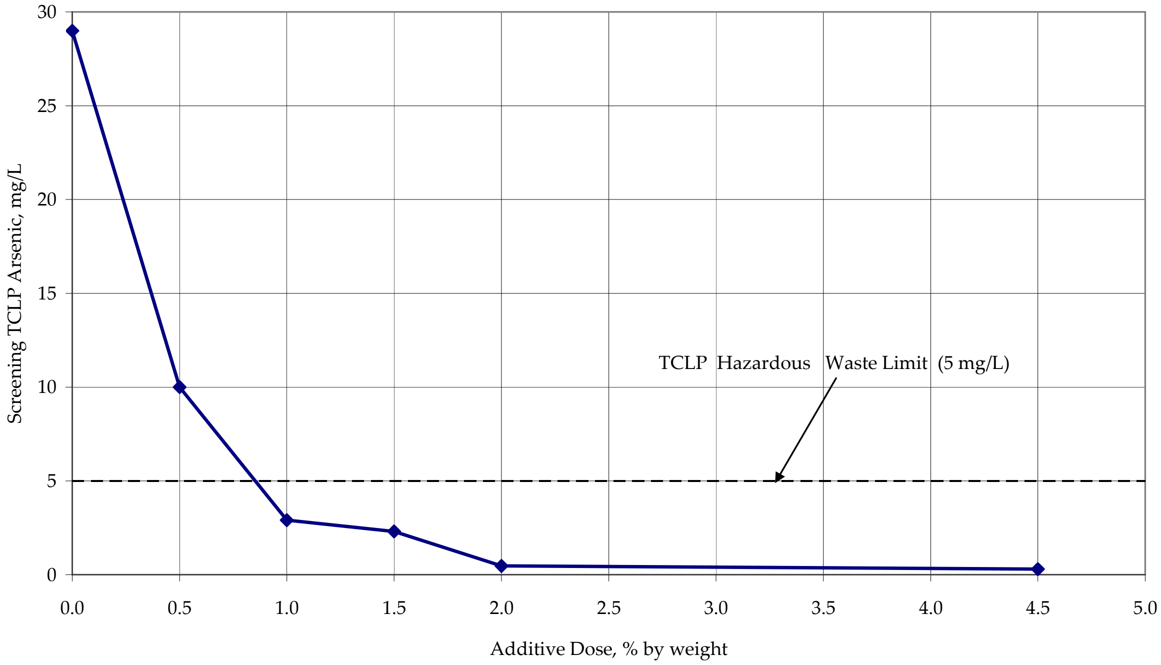
When the U.S. EPA Region VII ordered the removal of the contaminated soil, much of the soil had to be stabilized because it exceeded the Toxicity Characteristic Leaching Procedure (TCLP) hazardous waste criterion of 5 mg/L for arsenic. To further reduce long-term risk, an additional regulatory requirement was added. The treatment chemistry had to demonstrate in bench testing that it could pass the U.S. EPA Multiple Extraction Procedure (MEP) for arsenic.

An initial treatability study evaluated soil stabilization using Portland cement. The recommended minimum dosage was 20 percent by volume cement to pass the TCLP and MEP criteria. Later, RMT, Inc. (RMT) of Madison, Wisconsin, tested its alternative EnviroBlend® ferric sulfate based treatment chemistry and found it to be more cost-effective.

3. BENCH-SCALE EVALUATION OF ENVIROBLEND® CHEMISTRY

Using site soil samples, RMT conducted a bench-scale treatability study using various mix ratios and dosages of the EnviroBlend® chemistry. A dose-response plot for bench-scale stabilization of the arsenic-contaminated soil is shown on Figure 1. The untreated soil contained 15,000 mg/kg total arsenic, with a TCLP arsenic concentration of 29 mg/L. EnviroBlend® dosages starting at 1 percent by weight treated the soil below the 5 mg/L TCLP-arsenic threshold concentration. On the basis of this bench-scale study, an average 2 percent by weight dosage was recommended for on-site soil stabilization to satisfy both the TCLP and the MEP criteria for arsenic.

Figure 1
Bench-scale Treatability Study Dosage Response



4. REMEDIATION APPROACH

The EnviroBlend® treatment chemistry was easier to implement compared to Portland cement in the highly visible and cramped quarters of the Armour Road site. EnviroBlend's low dust characteristics allowed it to be stored on the ground and handled and mixed with a backhoe. The cement alternative would have required a big footprint pugmill/silo system that would needed to be moved at least twice.

The overall approach for full-scale remediation at the site included the following steps:

- Stockpile approximately 500 cubic yards (approximately 700 tons) of contaminated soil in a working area.
- Screen the soil in the field using XRF. Subject the untreated soil to the TCLP.
- Determine the EnviroBlend® dosage.
- Add and mix the treatment additives with the soil using an excavator.
- Subject the treated soil to the TCLP, to confirm treatment effectiveness.
- Add and mix more treatment chemicals, if needed, and retest.

The stabilized soil was hauled to a Subtitle D landfill while the excavation was backfilled with clean fill material.

5. FULL-SCALE TREATMENT RESULTS AND DISCUSSION

Soil treatment started with little variation in chemical dosage during the first phase of the soil remediation. On the basis of initial field data and the bench-scale treatability data, EnviroBlend® dosages were modified somewhat to reflect the variability of the arsenic concentration in soil as shown below:

Soil Arsenic Concentration, mg/kg	EnviroBlend® Dosage, weight %
<2,000	1.15
2,000-5,000	1.75
5,000-15,000	2.3

Approximately 11,000 cubic yards of soil were initially treated at dosages ranging from 0.75 to 2.3 percent by weight. Table 1 provides a summary of full-scale treatability data on the initial soil stockpiles.

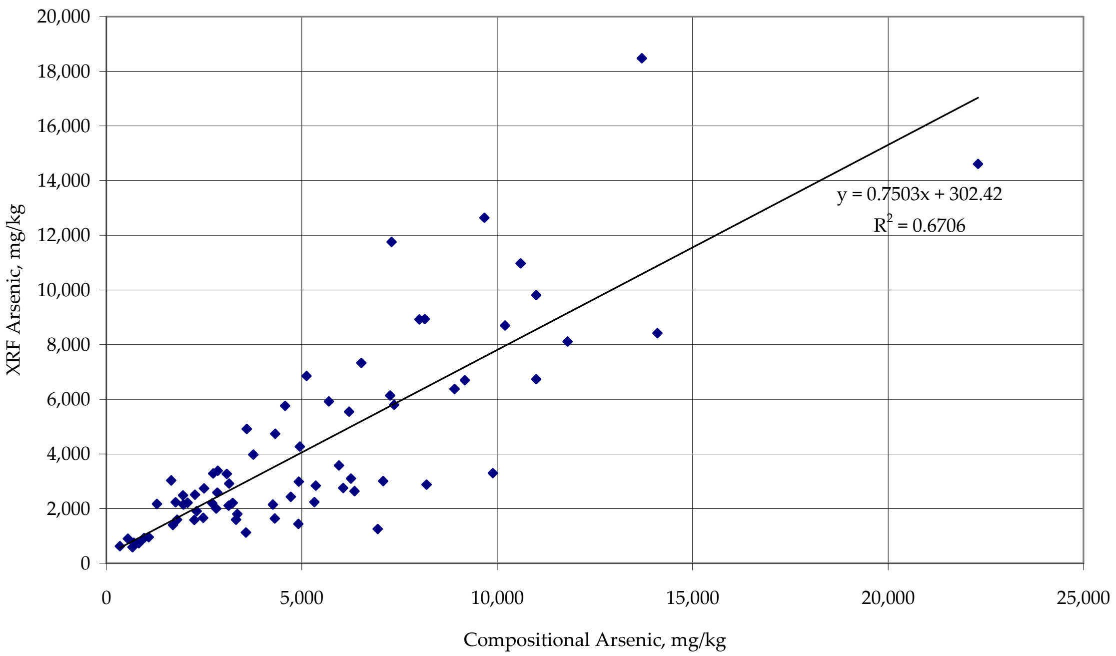
Table 1. Initial Full-scale Treatability Data Summary

		Pre Treatment		Post Treatment
	Dose	**Total Arsenic**	**TCLP Arsenic**	**TCLP Arsenic**
Range	0.75% - 2.30%	1,700 – 10,600	1.7 – 63.6	0.28 – 2.90
Median	1.25%	5,220	15.1	1.20
Mean	1.53%	5,450	20.7	1.32

Notes: Number of samples included in this data set = 20

XRF analysis of the soil for arsenic proved to be a key cost-saving step in calculating the treatment dosage rates for each individual soil stockpile. To help ensure that the XRF analysis correlated reasonably well with the actual arsenic concentrations, the XRF field data were compared with the total arsenic data obtained using standard analytical methods by an off-site certified lab. Figure 2 presents a correlation of the in-field XRF data with the laboratory total arsenic data. The XRF data correlated well (correlation coefficient of 0.82) with the total arsenic data.

Figure 2
In-field XRF vs. Compositional Arsenic Analysis

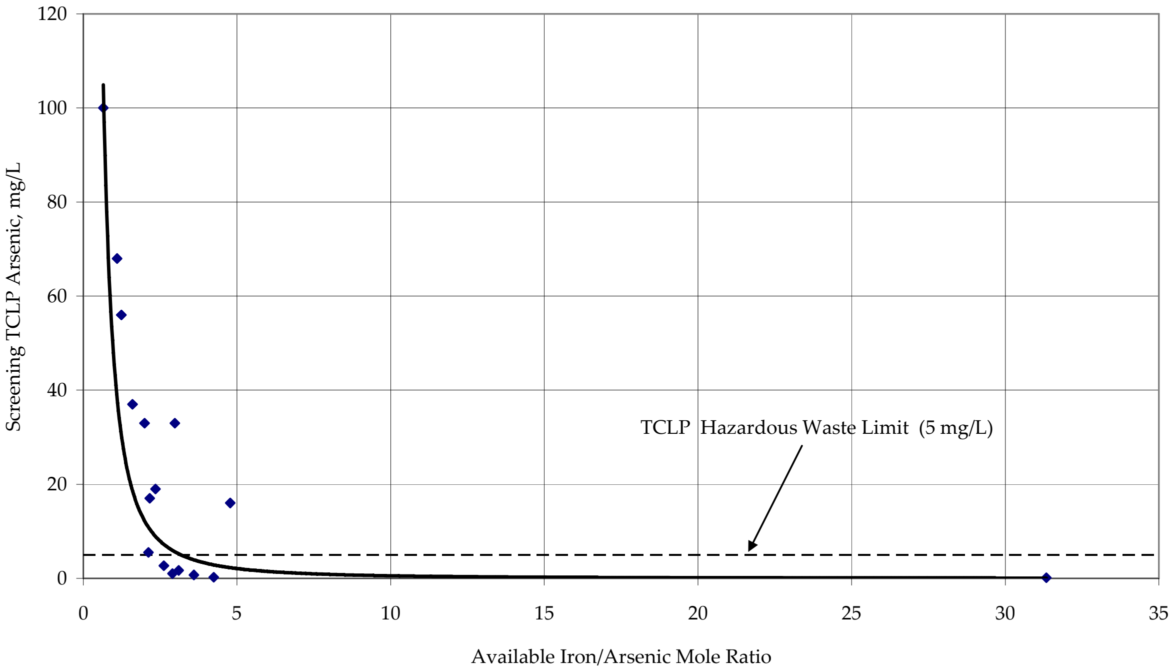


After the first 11,000 cubic yards of soil were treated and disposed, different soil/fill materials were encountered with higher total and TCLP-arsenic concentrations. Scaling up the treatment chemical dosage did not produce predictable results. Several of the stockpiles failed the TCLP after repeated additions of chemicals. Contributing to the problem was some material suspected of having high concentration of herbicides, which had TCLP arsenic levels of 520 mg/L. These values were an order of magnitude higher than the concentrations observed during the initial periods of remediation and required chemical dosages that were almost an order of magnitude higher, as well. However, mixing the hot spot materials with the other site soils with lower arsenic levels made it more amenable to the stabilization treatment. The blended soil types could be treated with an overall chemical dosage that was lower than the combined additive requirements if the samples were treated separately.

To further investigate the potential synergistic effects of the strategic mixing of the remaining untreated site soils, several grab soil samples from different areas of the site were analyzed for "available" iron (using a cold acid digestion procedure developed by RMT). The data on available iron and total arsenic showed that most of the samples that were TCLP toxic for arsenic had an available iron to arsenic (Fe/As) mole ratio of 0.65 to 2.14. Additionally, the available iron content of most of the site soils was not high enough to serve as a source of iron to supplement the treatment additive.

A strong correlation was observed between the Fe/As mole ratio and the TCLP arsenic concentration of the site soils. Figure 3 shows a plot of the Fe/As mole ratio versus the soil TCLP arsenic concentration. Generally, an Fe/As mole ratio in the range of 3 to 4 or higher is needed for TCLP arsenic concentrations to be below the 5 mg/L threshold. These data agree well with published literature (Krause et al., 1985; Pappasiopi, et al., 1988) on the influence of Fe/As mole ratio and pH versus arsenic solubility for providing a robust environmentally safe chemistry for arsenic stabilization.

Figure 3
Effect of Available Iron/Arsenic Ratio on Soil TCLP Arsenic



The on-site remediation activities continued with the additive dosage being controlled for adjustment of Fe/As mole ratio in the soil to treat material with a higher arsenic concentration material. An additive dosage of up to 13 percent by weight was needed to stabilize some of the higher arsenic soil stockpiles. A summary of the continued full-scale remediation treatability data is provided in Table 2. A total of approximately 70,000 tons of arsenic-contaminated soil were effectively stabilized using an approximate average additive dosage of 2.2 percent by weight.

Table 2. Continued Full-scale Treatability Data Summary

		Pre Treatment		Post Treatment
	Dose	**Total Arsenic**	**TCLP Arsenic**	**TCLP Arsenic**
Range	1.25% - 13.00%	965 – 22,300	2.0 – 126.0	0.02 – 4.35
Median	3.00%	4,950	23.6	0.65
Mean	3.42%	6,0.71	36.7	1.29

Notes: Number of samples included in this data set = 20

6. CONCLUSIONS

1. Arsenic-contaminated soil was effectively treated to render it non-TCLP toxic for arsenic using an average EnviroBlend® dosage of 2.2 percent by weight.
2. The available iron to arsenic ratio was a key factor in scaling up EnviroBlend® dosages with increased total arsenic concentrations in soil stockpiles. An Fe/As mole ratio of higher than 3-4 was essential for effectively stabilizing arsenic in soil.
3. In-field XRF arsenic analysis correlated well with total arsenic concentrations measured by standard laboratory analysis. The XRF analysis was very effective in delineating soil arsenic levels in soil stockpiles and in expediting chemical dosage optimization during on-site remediation.

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