

# **Haz-Flote(TM): Ex-Situ Decontamination of Materials**

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## EXECUTIVE SUMMARY

Western Research Institute (WRI), in conjunction with the U.S. Department of Energy (DOE), Morgantown Energy Technology Center, is developing a soil remediation technique called Haz-Flote™. Initial tests were conducted for petroleum-contaminated materials employing a number of chemical combinations. The most promising chemicals used in this study showed about a 75% reduction in organic carbon content in the coarse fraction. This reduction demonstrates that the treatment can remove some petroleum contaminants from the coarse fraction. Tests were conducted using the fine fraction of the petroleum-contaminated soil. The preliminary results show that the process separates a portion of the hydrocarbons from the very fine soil fraction under less than optimum conditions. After separation, the organic carbon content of the fine size fraction was about 26% lower than that of the feed material. The material collected had a 54% increase in organic carbon content compared to that collected from the feed. Optimization of the equipment and the chemistry of the system should enhance these results significantly.

The bulk of the work on the Haz-Flote process has been focused on removing mercury from contaminated soil fines. A sample of mercury-contaminated soil was obtained, and the distribution of mercury within the various size fractions was determined. The -200 mesh (<75 um) material contains the majority of the mercury contaminant. For convenience, the sample was sieved through a 70 mesh screen. All of the testing was conducted on the -70 mesh (<212 um) fraction. This fraction contained on average 122 mg Hg/kg of dry soil before processing. Mercury concentrations after processing were reduced to as low as 0.95 mg Hg/kg of dry soil. This represents >99% mercury reduction for the fine fraction. Tests have removed >99.5% of the mercury from the system.

## INTRODUCTION

### **Background**

There are thousands of known contaminated sites in the United States, including Superfund sites, Resource Conservation Recovery Act (RCRA) corrective action sites, underground storage tanks, U.S. Department of Defense sites, U. S. Department of Energy sites, mining refuse piles, and numerous other hazardous metals and organic contamination sites. Only a small percentage of these sites have been cleaned up. At the present time, several technologies are available to remediate soil at these sites. Unfortunately, many of these technologies are only effective for materials coarser than approximately 200 mesh (>75  $\mu\text{m}$ ). The fine materials are disposed of or treated at considerable expense. As a result, the costs associated with the remediation of contaminated soils are often quite high.

Western Research Institute (WRI) is developing a technique for removing contaminants from fine-textured soils, sediments, and sludges. The capital investment and operating costs for the Haz-Flote™ process will be low, and the process will reduce the costs to dispose of the fine fraction at waste disposal sites. This process will extend the use of soil washing techniques to contaminated sites that are currently remediated using more costly technologies.

This interim topical report describes the work done to date using Haz-Flote to remove petroleum products (crude oil) and mercury from contaminated soil materials.

### **Anticipated Benefits**

The development of innovative technologies to handle the various cleanup problems on a national and international scale is commonplace. Many innovative soil washing technologies have been developed during the past few years that can effectively remediate contaminated materials. However, these technologies usually require considerable investment in equipment, and the cleanup costs of soil material are relatively high (in excess of \$140 to \$270 per  $\text{m}^3$ ). These costs result from the elaborate nature of the processes, the costs for power, and the chemical costs.

The Haz-Flote technology has numerous advantages over other ex-situ soil washing techniques. Capital investment and operating costs are low, and it results in high levels of re-emplacement of the cleaned material on site. Haz-Flote has is capable of cleaning the fine fraction (< 100 mesh) of the soil, resulting in the replacement of 95+% of the material back on-site and

reducing the costs of disposal. The Haz-Flote technology expands the application of soil washing technology to heavy soils (clay type soils) to which current soil washing practices are not applied. WRI is not aware of any other soil washing technologies that demonstrate this ability at the expected cost on a per ton basis. This technology is considered excellent for Superfund and other organic and inorganic contaminated sites.

## **OBJECTIVE**

The objective of this research is to develop a low-cost method for remediation of contaminated soil fines, sediments, and sludges. The process will be developed as an ex-situ treatment technology for the removal of organics and metals from contaminated soils and other materials. The emphasis will be on the cleanup of fine materials (i.e., < 100 mesh materials).

## **TECHNICAL APPROACH**

Haz-Flote is an ex-situ treatment technology for organics- and metals-contaminated materials. The process incorporates the use of specifically designed chemical reagents with a novel separation approach. The evaluations were conducted on mercury-contaminated soils and on petroleum-contaminated soil materials. The chemicals were specifically optimized for each application through testing and experimentation. A range of chemicals were evaluated to determine their ability to remove the contaminant from the matrix. The conditioned materials are separated from the matrix using a novel concept. The cleaned matrix will be dewatered and available for return to the site.

Contaminated materials were characterized to determine their chemical and physical nature. The particle-size classification was determined for each material studied. In addition, the levels of contaminant were determined for each particle size class. It is anticipated that four (4) classes will be evaluated (< 325 mesh, 325 mesh to 200 mesh, 200 mesh to 60 mesh, and > 60 mesh). Also, dewatering of the treated materials and the physical nature of the materials following the removal of contaminants will be studied. These considerations are very important to the process and the use of decontaminated materials for backfill, plant growth medium, and other uses.

## RESULTS AND DISCUSSION

### **Activity I. Design and Construction of the Unit**

The initial work associated with this project dealt with the development of facilities to accommodate the research effort. Appropriate equipment was purchased, and the laboratory was modified for the placement of the equipment.

### **Activity IV. Tests for Soils Contaminated with Petroleum Hydrocarbons**

The objective of the chemical tests was to find a reagent or reagent combination capable of removing a hydrocarbon contaminant (crude oil) from a clay soil. The results in terms of carbon removal are summarized in Table 1. The reduction in carbon content is the percentage of carbon in the feed that was removed in the operation. The soil sample prepared in the laboratory contained some inorganic carbon. Therefore, accounting for the inorganic carbon will increase the apparent efficiency of the various chemicals but will not change their relative efficiencies.

### **Activity V. Characterization of Mercury-Contaminated Materials**

The use of Haz-Flote to remove mercury from contaminated materials was evaluated. Mercury-contaminated soils were sampled from sites associated with manometer locations along oil and gas pipelines in northeastern Canada. The samples have been characterized for total RCRA metals (Table 2). The analysis shows that the samples contain high levels of mercury and elevated levels of lead.

The levels of mercury associated with the various size fractions of materials have been determined (Table 3). The -200 mesh material contains about 86% of the mercury contaminant on a wet-sieve basis and about 76% on a dry-sieve basis. This difference is expected, as a wet-sieve analysis would separate fine particles that are attached to the coarse fraction, while the coarse fraction associated with the dry-sieve analysis would contain a portion of the fine size fraction attached.

Test variables included pulp density (weight of the feed/weight of the pulp), pH, reagents and reagent dosages, temperature, residence time, and rinse water volume. A soil sample collected from manometer sites along a gas pipeline was used for the testing. The only preparation for this material was sieving to -70 mesh. The tables of this report show some of the characteristics of this particular soil sample. Total organic carbon for the sample was 1.86 wt%, corresponding to 3.5-4.2% soil organic matter.

**Table 1. Summary of Chemical Tests**

Sample	Feed	Mixer	-C%
46-5	1	1	32
46-6	1	1	52
46-7	2	1	80
46-8	2	1	84
54-1	1	1	36
54-2	1	1	37
54-3	1	1	36
54-4	1	1	33
54-5	1	1	29
54-6	1	1	36
54-7	1	1	37
54-8	1	1	38
	2		83
	2		83
60-1	1	2	4
60-2	1	2	11
60-3	1	2	20
60-4	1	2	18
67-1	1	3	21
67-2	1	3	20
67-3	1	3	24
67-4	1	3	12
67-5	1	3	21
67-6	1	3	20
67-7	1	3	21
67-8	1	3	17
67-9	1	3	38
67-10	1		15
67-11	1	3	66
67-12	1	3	8
71-1	1	3	-70
71-2	1	3	4
71-3	1	3	-45
71-4	1	3	25
71-5	1	3	44
71-6	1	3	81
75-11	1	3	-70
75-12	1	3	-16
75-13	1	3	54
75-1	1	4	48
75-2	1	4	62
75-3	1	4	33
75-4	1	4	49
75-5	1	4	55
75-6	1	4	-25
	2		81
	2		82
	2		92

Sample	Feed	Mixer	-C%
89-1	1	4	0
89-2	1	4	18
89-3	1	4	20
89-4	1	4	12
89-5	1	4	23
89-6	1	4	19
89-7	1	4	19
89-8	1	4	17
89-9	1	4	25
89-10	1	4	34
89-11	1	4	5
89-12	1	4	10
89-13	1	4	-3
89-14	1	4	-9
89-15	1	4	-34
89-16	1	4	-53
89-17	1	4	-62
89-18	1	4	-33
93-1	3	4	4
93-2	3	4	48
93-3	3	4	63
93-4	3	4	75
93-5	3	4	75
93-6	3	4	82
93-7	3	4	25
93-8	3	4	46
93-9	3	4	64
93-10	3	4	75
93-11	3	4	79
93-12	3	4	85
93-13	3	4	N.A.
93-14	3	4	-24
93-15	3	4	-55
93-16	3	4	-60
93-17	3	4	-64
93-18	3	4	-154
93-19	3	4	-85
93-20	3	4	-28
93-21	3	4	-27
93-22	3	4	49
93-23	3	4	97
93-24	3	4	79
95-1	3	4	-62
95-2	3	4	16
95-3	3	4	30
95-4	3	4	45
95-5	3	4	45
95-6	3	4	38

Sample	Feed	Mixer	-C%
103-1	3	4	74
103-2	3	4	83
103-3	3	4	-27
103-5	3	4	12
103-4	3	4	-79
103-6	3	4	-38
103-7	3	4	-24
103-8	3	4	-36
103-9	3	4	17
103-10	3	4	-46
103-11	3	4	-52
103-15	3	4	77
103-12	3	4	74
105-1	3	4	-67
105-2	3	4	-67
105-3	3	4	72
105-4	3	4	70
105-5	3	4	76
105-6	3	4	77

Sample	Feed	Mixer	-C%
15-16	3	4	-51
15-17	3	4	-30
15-18	3	4	-37
15-19	3	4	-1
15-6	3	4	28
15-7	3	4	41
15-8	3	4	53
15-9	3	4	20

**Feed:**

1. Soil sample preparation—pulverized, screened to -100 mesh and saturated with Shannon crude oil
2. Soil as above but without crude oil containment
3. Oily soil from Kaycee, Wyoming

**Table 2. Total Concentrations of RCRA Metals Found in the Mercury-Contaminated Soil**

Element	Total Concentration (mg/kg)
arsenic	2.26
barium	61.5
cadmium	1.89
chromium	50
lead	132
mercury	52.4
selenium	<0.1
silver	0.68

**Table 3. Total Concentrations of Mercury in the Contaminated Soil by Particle Size Fraction Using Dry-Sieve and Wet-Sieve Separation Techniques**

Sieve Size	Dry Sieve Hg (mg/kg)	Wet Sieve Hg (mg/kg)	Dry Sieve Wt - g (g)	Wet Sieve Wt of Soil (g)	Tot-Hg dry (mg)	Tot-Hg wet (mg)
10 Mesh	14	10	49.7	35.4	0.6958	0.354
20 Mesh	14	8.2	139.2	128.5	1.9488	1.0537
70 Mesh	23	9.8	546.7	450	12.5741	4.41
200 Mesh	47	8.8	335.5	273.9	15.7685	2.41032
325 Mesh	200	80	60.4	29.3	12.08	2.344
400 Mesh	220	110	15.6	6.3	3.432	0.693
-400 Mesh	220	250	73.3	128.9	16.126	32.225

#### **Activity VI. Health and Safety Plan**

Prior to the initiation of the work plan for the evaluations, a complete health and safety plan was developed. Implementation of this plan has been initiated.

#### **Activity VII. Tests for Soils Contaminated with Mercury**

The objective of these tests was to find a reagent or reagent combination capable of removing mercury contamination from a fine soil. After suitable reagents were identified, further testing was conducted to reduce reagent consumption while maintaining or increasing mercury removal efficiency.

#### **Procedures**

For a typical test, a sample of contaminated soil was mixed with water and the test reagents. After mixing, the liquid was decanted from the surface of the settled solids. The solids were then rinsed by mixing with clean water and centrifuged again. Solids and liquids from the test were analyzed to determine mercury concentrations. Quadruplicate analyses were conducted on the solids samples, and the results were averaged to provide a single value for each sample. All solids analyses were converted to a dry basis for comparison with the feed values. A mercury balance was calculated for each test to verify the analytical results.

Test variables included pulp density (weight of the feed/weight of the pulp), pH, reagents and reagent dosages, temperature, residence time, multiple stage washing, and rinse water volume. A soil sample collected from manometer sites along a gas pipeline was used for the testing. The only preparation for this material was sieving to -70 mesh. Total organic carbon for the sample was 1.86 wt%, corresponding to 3.5-4.2% soil organic matter.

Samples were analyzed using the flameless atomic adsorption technique developed by Hatch and Ott (1968). A BUCK model 400 Mercury Analyzer System, which measures adsorption at 253.7 nm, was used for the mercury analyses. Solids samples were digested following the method detailed in Methods of Soil Analysis (Page, 1982). Liquid samples were digested in accordance with a WRI standard operating procedure. Solid samples were divided into eight subsamples, four of these were used for mercury determination, and four were dried to determine the moisture content of the sample.

## **Results**

The results of the tests in terms of mercury removal are summarized in Table 4. The reduction in mercury content was calculated by subtracting the mercury content of the cleaned soil from that of the feed material and dividing by the mercury content of the feed. This result was multiplied by 100 to give percentage mercury reduction. The results of four samples were averaged. Entries of OR indicate samples that were out of range for the analyzer. Entries of NA indicate the first stage of a two-stage test in which the sample was treated with partially spent reagent from a previous test.

**Table 4. Summary of Scrubber Tests**

Test	Reagent		Efficiency %	Amt/Reag. gal/ton	Cost \$/ton
	ml	ml/g			
1-C	120	4.69	93.2	1123.6	\$ 337
1-1	120	5.04	85.6	1208.6	\$ 363
1-2	60	2.32	90.5	555.3	\$ 167
1-3	120	5.11	85.5	1224.0	\$ 367
1-4	120	4.98	84.4	1193.5	\$ 358
1-5	60	2.62	93.6	628.0	\$ 188
2-C	120	4.49	93.9	1077.3	\$ 323
2-1	60	2.20	90.5	526.8	\$ 158
2-2	120	5.31	96.8	1272.7	\$ 382
2-3	60	2.06	93.0	494.2	\$ 148
2-4	120	4.41	OR	1057.5	\$ 317
2-5	60	2.45	97.1	587.0	\$ 176
3-1	60	1.65	84.0	395.1	\$ 119
3-2	110	3.67	94.6	878.9	\$ 264
3-3	150	6.25	95.9	1498.1	\$ 449
3-4	40	0.89	83.4	212.6	\$ 64
3-5	73.3	1.88	94.7	450.5	\$ 135
3-6	100	3.03	96.9	726.4	\$ 218
4-1	60	2.30	92.1	551.0	\$ 165
4-2	30	1.36	90.0	326.9	\$ 98
4-3	15	0.57	84.1	137.2	\$ 41
4-4	60	2.40	97.7	575.3	\$ 173
4-5	30	1.34	97.0	321.0	\$ 96
4-6	15	0.54	89.0	128.4	\$ 39
7-C	120	4.38	94.7	1049.8	\$ 315
7-1	15	0.72	OR	173.7	\$ 52
7-2	15	0.66	OR	158.4	\$ 48
7-3	30	1.31	93.9	314.0	\$ 94
7-4	30	1.12	93.1	267.3	\$ 80
7-5	30	1.18	93.3	282.0	\$ 85

**Table 4. Summary of Scrubber Tests, Cont.**

Test	Reagent		Efficiency %	Amt/Reag. lb/ton	Cost \$/ton
	ml	ml/g			
5-C			94.5		
5-1	6	0.26	87.8	518.4	\$ 492.4
5-2	6	0.26	97.7	519.0	\$ 493.1
5-3	6	0.22	92.8	444.0	\$ 421.8
5-4	6	0.23	95.9	457.1	\$ 434.3
5-5	6	0.22	95.7	432.0	\$ 410.4
6-C			94		
6-1	5.88	0.25	97.1	492.3	\$ 467.6
6-2	6.04	0.23	96.3	455.7	\$ 432.9
6-3	2.97	0.12	91.9	233.5	\$ 221.8
6-4	3.05	0.14	97.9	274.7	\$ 260.9
8-C	3.1	0.12	95.2	237.8	\$ 225.9
8-1	2.12	0.07	95.2	148.9	\$ 141.5
8-2	0.99	0.04	95.3	77.9	\$ 74.0
8-3	0.55	0.02	OR	39.2	\$ 37.2
8-4	0.89	0.03	95.8	66.7	\$ 63.4
8-5	0.96	0.03	92.8	68.8	\$ 65.4
9-C	1.13	0.04	94.6	83.6	\$ 79.5
9-1	1.01	0.04	95.4	77.3	\$ 73.4
9-2	1.14	0.04	91.8	83.5	\$ 79.4
9-3	0.51	0.02	OR	37.0	\$ 35.2
9-4	0.54	0.02	OR	40.1	\$ 38.1
9-5	0.5	0.02	92.1	41.6	\$ 39.5
10-1	0.77	0.034	93.0	67.5	\$ 64.1
10-2	0.74	0.032	89.7	63.4	\$ 60.2
10-3	0.74	0.030	92.0	59.4	\$ 56.5
10-4	0.49	0.019	93.9	38.1	\$ 36.2
10-5	0.49	0.019	96.1	38.0	\$ 36.1
10-6	0.56	0.023	94.6	45.4	\$ 43.1
11-1	0.75	0.031	93.9	61.0	\$ 58.0
11-2	0.75	0.030	93.0	59.8	\$ 56.8
11-3	0.75	0.029	96.1	57.1	\$ 54.3
11-4	0.5	0.020	90.2	39.1	\$ 37.2
11-5	0.5	0.018	90.7	36.7	\$ 34.9
11-6	0.5	0.020	93.9	39.9	\$ 37.9

**Table 4. Summary of Scrubber Tests, Cont.**

Test	Reagent		Efficiency %	Amt/Reag. lb/ton	Cost \$/ton
	ml	ml/g			
12-1	0.81	0.023	92.1	46.7	\$ 44.4
12-2	0.82	0.032	95.0	64.8	\$ 61.5
12-3	0.81	0.032	96.1	64.3	\$ 61.1
12-4	0.55	0.022	93.4	44.3	\$ 42.1
12-5	0.52	0.022	93.1	44.2	\$ 42.0
12-6	0.59	0.026	94.1	51.3	\$ 48.8
13-C	0.68	0.027	94.6	53.0	\$ 50.4
13-1	0.61	0.022	86.8	44.7	\$ 42.5
13-2	0.61	0.023	83.3	46.8	\$ 44.5
13-3	0.4	0.016	92.1	31.7	\$ 30.2
13-4	0.44	0.020	82.0	39.4	\$ 37.5
13-5	0.43	0.019	83.7	37.3	\$ 35.5
14-1	1.44	0.030	94.3	60.4	\$ 57.4
14-2	0.71	0.056	>98.2	112.0	\$ 106.4
14-3	1.05	0.021	90.0	42.5	\$ 40.4
14-4	0.54	0.037	97.9	74.0	\$ 70.3
14-5	0.77	0.030	94.3	60.9	\$ 57.8
14-6	0.24	0.009	72.0	18.3	\$ 17.4
15-1	1.51	0.031	92.7	62.9	\$ 59.8
15-2	0.74	0.057	98.6	114.0	\$ 108.3
15-3	1.01	0.021	93.5	42.1	\$ 40.0
15-4	0.47	0.036	98.1	72.0	\$ 68.4
15-5	0.7	0.033	97.4	66.4	\$ 63.1
15-6	0.18	0.007	73.3	15.0	\$ 14.2
16-1	2.8	0.058	98.6	116.7	\$ 110.9
16-2	NA		77.6	NA	NA
16-3	0.69	0.023	98.1	46.9	\$ 44.6
16-4	0.67	0.028	97.1	56.5	\$ 53.7
17-1	2	0.041	98.8	82.5	\$ 78.3
17-2	NA		81.4	NA	NA
17-3	0.49	0.018	97.0	35.5	\$ 33.7
17-4	0.49	0.020	96.0	40.1	\$ 38.1
18-1	1.46	0.061	99.2	121.3	\$ 115.2
18-2	0.75	0.030	98.5	59.9	\$ 56.9
18-3	1.01	0.040	98.6	79.7	\$ 75.8
18-4	1.00	0.042	99.0	84.1	\$ 79.9
18-5	0.76	0.030	96.7	60.9	\$ 57.8

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