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Emerging Technology Summary

Simultaneous Destruction of Organics and Stabilization of Metals in Soils

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The Center for Hazardous Materials Research (CHMR), through a Cooperative Agreement with the U.S. Environmental Protection Agency's National Risk Management Research Laboratory, conducted a laboratory evaluation of the Sulchem Process for treatment of soils contaminated with organic hydrocarbons and heavy metals.

The Sulchem Process mixes the material being treated with elemental sulfur at elevated temperatures in an inert reactor system. Organic hydrocarbons react with the sulfur to form an inert fine solid of carbon and sulfur, hydrogen sulfide gas, and modest amounts of carbon disulfide. Heavy metals react to form sulfides or sulfide-coated particles which are less soluble. The acid gases formed may be scrubbed or treated to recover elemental sulfur using an auxiliary process unit.

At processing temperatures of 250° to 350°C, destruction and removal efficiencies for aromatic hydrocarbons from phenanthrene to benzopyrene were all in excess of 99%.

Using the EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), cadmium, copper, lead, nickel, and zinc were significantly reduced following treatment of the soil by the Sulchem process. Copper TCLP values were reduced most effectively; lead was reduced below regulatory targets when concentrations in the original soil were below about 10,000 ppm. Cadmium was reduced below TCLP limits when the concentration in the original soil was below several thousand ppm.

Process economics for remedial soil treatment were estimated to be in the range of $105 to $181/ton depending on the size of the site and the processing rate.

This Summary was developed by EPA's National Risk Management Research Laboratory, Cincinnati, OH, to annnounce key findings of the SITE Emerging Technology that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This research and development focussed on the application of the Sulchem Process to contaminated soils at Superfund sites to provide destruction of hazardous organics while stabilizing metals in contaminated soils. The Sulchem Process uses elemental sulfur, which reacts with the carbon in organic materials at moderately elevated temperatures to form an insoluble, inert carbon-sulfur amorphous solid ($CS_{0.56}$). The contained heavy metals are immobilized through formation of insoluble metal sulfides.

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The Sulchem Process's main process components include a pre-reaction mixer where the soil and sulfur are mixed; an externally heated rotating solids reactor; a vapor phase reactor where desorbed organics from the first reactor are further reacted with elemental sulfur; the off-gas handling system, which collects and treats condensable byproducts and scrubs acid gases from the effluent vapors; and a post-reaction treatment unit that recovers excess reagent and prepares the treated product to comply with on-site disposal requirements. A general block flow diagram for the Sulchem Process is shown in Figure 1.

The Sulchem Process, as applied to treatment of soils and sludges, consists of two reactors: one for treating the solid phase material and a second for treating the gases emitted from the first reactor, including desorbed organic vapors. The second reactor is required because, for the more volatile organic compounds, desorption effectively competes with reactions with liquid phase sulfur.

The feed soil, possibly after some dewatering, is fed into a pre-reaction mixer where elemental sulfur (and other reagents, if used) are added to the feed soil and lightly mixed. The feed mixture (soil and reagents) is next fed to the first reactor, which consists of an indirectly heated, rotary reactor. A controlled atmosphere is produced in the reactor with the flow of inert gases over the tumbling solids, which acts to exclude oxygen from the reactor and remove off-gases released by the process.

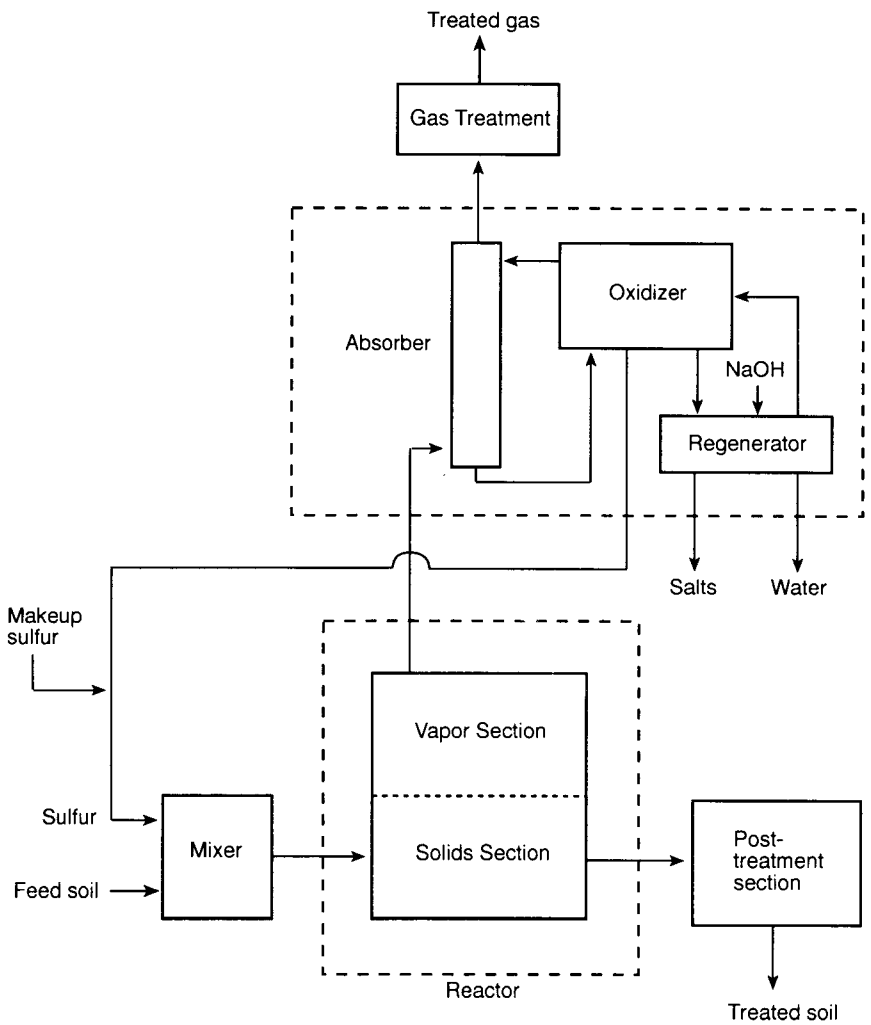

Figure 1. Sulchem process schematic.

Batch Reactor Experimental Procedures

Three different small batch test reactors were employed for the initial screening studies. Each was sized to heat batches of approximately 200g of soil in an inert atmosphere from ambient temperature to nominal reaction temperatures ranging from 250° to 450°C. For the initial tests, two unstirred reactors were employed. One of these was designated as the closed mode reactor (high pressure) and the other, the vented mode reactor (low pressure). These two reactors were heated by immersion in a heated fluidized sand bath. Subsequently, an autoclave was modified to provide an auger mixed reactor. The autoclave was heated with a cylindrical furnace jacket which could be lowered after the run for rapid cooling of the reactor.

Organics Destruction

The Sulchem Process is a two-stage process in which the soil reacts with sulfur in the first stage. Unreacted organics desorbed from the first stage react with sulfur in the vapor phase in the second stage. The purpose of these tests was (1) to establish the soil treatment temperatures and other process conditions necessary to achieve organic compound destruction in the soil reactor; (2) to estimate the boiling range of volatile organics that will be desorbed during the heatup of the soil reactor before reaction temperatures are reached; and (3) to evaluate process conditions for a second-stage vapor reactor to treat the volatile organics desorbed from the soil reactor.

Soil Batch Reactor Tests

In batch reactor tests of the reaction mixture, the soil and sulfur are heated, while mixing, from ambient temperature to the desired reaction temperature and then held at the run temperature for the desired time interval. The temperature at which significant reaction first occurs was estimated, based on small batch tests with mineral oils in the closed and vented mode reactors, to begin in the range of 200°C to 250°C for the more reactive saturated hydrocarbons. Therefore, the initial screening tests were run at temperatures of 250°C and higher.

A comparison of the boiling range of the organics in the feed soil with the boil-

ing range of the desorbed vapors collected in downstream traps and the scrubber (i.e., overhead) indicated the approximate temperature range over which desorption and reaction compete in the solids reactor. For example, those compounds with high recoveries in the overhead represent the boiling range where desorption takes place before any reaction occurs. Those compounds not found in the overhead represent the boiling range above the reaction temperature regime. An intermediate boiling point regime, where only partial recovery is found, represents the boiling range where reaction and desorption processes compete.

Several scoping tests were performed using a series of organic compounds of successively higher boiling points to 1) establish the boiling range where desorption occurred before reaction (thereby establishing the approximate threshold reaction temperature) and 2) provide an initial screening of the level of destruction and effect of process variables for the higher boiling components where desorption is not important.

Tests of Desorption Versus Boiling Range

Nine aromatic compounds (2000 ppm each, except pyrene at 1000 ppm) with boiling points from 165° to 393°C were mixed into a 75/25 Synthetic Soil Matrix (SSM) topsoil blend. Several series of three sets of runs were carried out at 250°C, 350°C, and 440°C for 2 hours with 200g soil and 30g sulfur. Analysis of the recovered samples for the spiked organic compounds was compared with a sample of the original spiked soil. The results are

Table 1. Effect of Boiling Point on Destruction and Removal

Compound	BP	Charge (mg)	Reactor Residual	Recovery in Ice Trap	Recovery in Scrubber	Total	Percent Recovered	Percent Destroyed	Destruction and Removal Efficiency (%)
1a. Reactor run at 250°C and 2 Hour Residence Time									
mesitylene	165	276.9	0.15	225.5	0.35	226	81.6	18.4	99.9
durene	197	276.2	0.15	249.3	0.08	249.53	90.3	9.7	99.9
naphthalene	218	343.7	0.65	287.9	0.17	288.72	83.8	16.0	99.8
2-Me Naphthalene	241	353	1.07	276.9	0.06	278.03	78.5	21.2	99.7
biphenyl	254	368.5	3.11	295.8	0.06	298.97	80.3	18.9	99.2
bibenzyl	285	356.8	3.87	229.2	0.00	233.07	64.2	34.7	98.9
hexachlorobenzene	322	327.5	8.60	204.4	0.36	213.36	62.5	34.9	97.4
anthracene	340	306.1	7.32	64.0	0.00	71.32	20.9	76.7	97.6
pyrene	393	175	2.56	6.9	0.00	9.46	3.9	94.6	98.5
1b. Reactor run at 350°C and 2 Hour Residence Time									
mesitylene	165	276.9	1.13	220.3	2.98	224.41	80.6	19.0	99.6
durene	197	276.2	0.27	245.6	5.09	250.96	90.8	9.1	99.9
naphthalene	218	343.7	0.2	296.3	8.25	304.75	88.6	11.3	99.9
2-Me Naphthalene	241	353	0.15	281.8	7.24	289.19	81.9	18.1	>99.9
biphenyl	254	368.5	0.32	298.4	7.68	306.4	83.1	16.9	99.9
bibenzyl	285	356.8	0.28	221.5	4.67	226.45	63.4	36.5	99.9
hexachlorobenzene	322	327.5	17.66	96.5	2.11	116.27	30.1	64.5	94.6
anthracene	340	306.1	9.15	23.3	0.59	33.04	7.8	89.2	97.0
pyrene	393	175	2.71	2.3	0.04	5.05	1.3	97.1	98.5
1c. Reactor run at 440°C and 2 Hour Residence Time									
mesitylene	165	276.9	0.27	243.8	4.24	248.31	89.6	10.3	99.9
durene	197	276.2	0.08	245.8	10.15	256.03	92.7	7.3	>99.9
naphthalene	218	343.7	0.09	280.2	12.48	292.77	85.2	14.8	>99.9
2-Me Naphthalene	241	353	0.08	269.2	8.22	277.5	78.6	21.4	>99.9
biphenyl	254	368.5	0.15	282.5	7.64	290.29	78.7	21.2	>99.9
bibenzyl	285	356.8	0.08	228.8	4.87	233.75	65.5	34.5	>99.9
hexachlorobenzene	322	327.5	0.49	205.4	3.56	209.45	63.8	36.0	99.9
anthracene	340	306.1	0.35	69.0	1.22	70.57	22.9	76.9	99.9
pyrene	393	175	0.67	12.7	0.14	13.51	7.3	92.3	99.6

presented in Table 1. Surrogate recoveries for all recovered fractions were in the 60 to 90% range.

The combined recovery from the product fractions was compared with the analytical results from the extraction of the feed soil (based on a 200g charge that nominally contains 400mg of each compound except pyrene which was loaded at 200mg) to arrive at a total recovery for each compound. This procedure corrects for losses in the experiment, sampling, and analysis. Absolute recoveries of mesitylene and durene in both the soil charge and the product analyses were about 70% and below the values of 85 to 90% observed for the higher boiling compounds spiked in the soil. These compounds are technically not semivolatile organics (defined as BP > 200°C) and are outside the method range for the Soxhlet extraction (Method 3540) used for the sample workup; therefore recoveries were lower.

Table 1 shows three different measures of process performance: recovery from the overhead, destruction, and destruction and removal efficiency (DRE) of the treated soil. These measures are discussed further.

Recovery from Overhead

The percentage recovered from overhead is a measure of the amount of a compound that is desorbed from the soil rather than reacted. It is calculated as the ratio between the total amount of the compound recovered in the ice traps and scrubber to the amount originally present in the soil.

Destruction

The percentage destroyed is a measure of the effectiveness of the sulfur in the reactor. The percentage destroyed was calculated simply as the difference between the amount originally present in the soil and the amount recovered both in the overhead and soil fractions, divided by the amount originally present in the soil.

Destruction and Removal Efficiency

The DRE is a measure of overall removal of each compound from the soil. The DRE is calculated by subtracting the ratio of the amount of residual compound left in the soil to the amount originally present from one. For the lower boiling point compounds, it reflects primarily the effect of desorption. For the higher boiling compounds, it reflects reaction efficiency.

Reaction temperature does not greatly affect the recoveries as the desorption step removes the compound from further opportunity to react in the simple batch reactor system. The residual content of the treated soil is nonetheless greatly reduced, corresponding to DRE values of better than 99% at the higher reaction temperatures.

Metals Stabilization

A series of batch screening runs were made on several soil blends containing various heavy metals. The purpose of these initial tests was to find how well each of the various heavy metals responded to the sulfur treatment of the Sulchem Process. A priori one might expect that the stabilization mechanism might be the formation of metal sulfides as an insoluble coating. If this is the case, then the heavy metals whose sulfides are soluble in acid (e.g., chromium, cobalt, iron, nickel, and zinc) might not be rendered immobile as much as other metals (e.g., lead) with the Sulchem treatment since the TCLP test leaches the sample with a buffered acetic acid solution. It was for the purpose of examining this premise that the initial metal screening tests were made.

For the screening studies to compare the behavior of different heavy metals reported here, the process parameters were sulfur-to-soil ratio, reaction temperature, and reaction time. Generally one sulfur-to-soil ratio was used (typically 0.15), a range of reaction temperatures were used (i.e., 250°C, 300°C, and 350°C), and the reaction time was typically one-half hour.

The initial metal screening tests were done on soil samples of Standard Analytical Reference Matrix (SARM-III) and prepared blends of metals spiked in either Synthetic Soil Mixture (SSM) or a 75/25 blend of SSM and horticultural topsoil. The SARM samples had been prepared with arsenic trioxide (As_2O_3), cadmium sulfate ($CdSO_4$), chromium nitrate ($Cr(NO_3)_3$), copper sulfate ($CuSO_4$), lead sulfate ($PbSO_4$), nickel nitrate ($Ni(NO_3)_2$), and zinc oxide (ZnO).

Screening studies of various metals were made with a series of closed-mode reaction runs made on five separate metal/SSM mixtures. These individual blends were made using lead oxide (PbO), cadmium oxide (CdO), arsenic oxide (As_2O_3), chromium (III) oxide (Cr_2O_3), and nickel hydroxide ($Ni(OH)_2$) to contain 1000 ppm of each of the metals. TCLP analyses were made of the soil blend as well as the three raw reactor products from each processing temperature. Two-hour reaction runs were used in these tests, which were conducted in the closed mode unstirred reactor. These data are listed in Table 2. It was concluded that both lead and cadmium responded to the treatment, the latter more at elevated temperatures. The results on the arsenic and nickel were inconclusive.

Tests using SARM-III were conducted to evaluate the performance of the different contained heavy metals. These runs were carried out in the stirred reactor autoclave to ensure that adequate mixing was used. Since the objective was to determine metals stabilization, no analyses were made on these runs for the contained organic compounds also present in the SARM-III.

Table 3 shows the results for the SARM-III feed. For the main metals present in the SARM-III TCLP leachate (i.e., all but arsenic and chromium), copper responds the most effectively to the Sulchem Process, decreasing the TCLP value 100-fold at the mildest conditions and to the detection limit at the highest temperature, presumably because of insoluble sulfide formation. A continuous reduction of TCLP nickel leachate levels for the treated soils is shown at successively higher temperatures. The results for cadmium, lead, and zinc also demonstrate some temperature effect, but not as extensive as observed for nickel.

Based on these results, additional test blends were prepared using the oxides or hydroxides of lead, cadmium, nickel, and zinc to further evaluate the process conditions necessary to improve the TCLP results. The objective was to evaluate the stabilization of these metals in soils with a higher organic carbon content than those employed in the previous tests. Therefore, the next series of tests used the 75/25 SSM/top soil blend.

Tables 4-7 show runs on various blends of Cd, Pb, Ni, and Zn as a function of temperature. The first three test blends, listed in Tables 4-6, contained a relatively high loading of metals to evaluate possible process limits for reduction of the leachate to TCLP limits. The cadmium results demonstrate the previously observed effect of process temperature on the reduction of TCLP, although the effect of process temperature is much less for lead in this case. Substituting the more soluble nitrate at the same lead loading demonstrates how the more soluble form can prevent reaching the TCLP regulatory limit of 5 mg/L in this case. Although somewhat higher TCLP levels are observed for the starting soil blend using more soluble salts, the response of the soil to the Sulchem treatment shows comparable reduction in TCLP values. The nickel- and zinc-spiked SSM topsoil blend did not demonstrate as great an effect from process temperature that was previously noted for

Table 2. Tests of Various Metals vs. Reaction Temperature

Temp °C	Sulfur/ Soil	Pb TCLP (mg/L)	Cd TCLP (mg/L)	As TCLP (mg/L)	Cr TCLP (mg/L)	Ni TCLP (mg/L)
	0/1.0*	14.4	38.9	3.07	<0.05	1.51
250	.25/.75	0.69	8.34	5.97	<0.05	0.89
300	.25/.75	0.58	4.43	8.23	<0.05	1.21
350	.25/.75	0.20	0.62	11.7	<0.05	1.16

* Denotes untreated SSM.

Table 3. Metal Treatment Results with SARM-III Soil*

Untreated Soil		Run Numbers 27-77		Run Numbers 27-78		Run Numbers 27-79		Run Numbers 27-84		Run Numbers 27-92	
Metal/ Concen-tration (ppm)	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
AS/500	0.21	250	0.16	300	0.23	350	0.37	400	0.21	440	<0.05
Cd/1,000	36.8	250	22.5	300	15.1	350	12.4	400	6.02	440	3.66
Cr/1,500	<0.05	250	0.07	300	0.12	350	<0.05	400	<0.05	440	<0.05
Pb/14,000	35.5	250	25.5	300	22.7	350	21.2	400	16.1	440	12.2
Ni/1,000	22.2	250	17.3	300	6.71	350	3.72	400	0.72	440	0.4
Cu/9,500	153	250	1.13	300	0.05	350	0.03	400	0.03	440	<0.01
Zn/22,500	791	250	628	300	361	350	162	400	58.1	440	32.4

*All test runs were 0.5-hr. duration with 13% sulfur content in the feed soil.

Table 4. Metal Treatment Results with 75/25 SSM/Topsoil Blend*

Untreated Soil			Run Numbers 27-69		Run Numbers 27-71		Run Numbers 27-70		Run Numbers 27-76		Run Numbers 27-91	
Metal/ Concen-tration (ppm)	Salt Added	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
Cd/5000	CdO	144	250	28.3	300	42.0	350	22.4	400	4.41	440	0.54
Pb/10,000	PbO	61.7	250	4.08	300	1.22	350	1.21	400	2.21	440	2.03

*All tests were 0.5-hr. duration with 13% sulfur content in the feed soil.

Table 5. Metal Treatment Results with 75/25 SSM/Topsoil Blend*

Untreated Soil				Run Numbers 33-40		Run Numbers 33-41	
Metal	Salt Added	Metal Concen-tration (ppm)	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
Cd	$CdCl_2$	1,000	30.1	250	4.98	440	0.31
Pb	$Pb(NO_3)_2$	10,000	96.4	250	29.2	440	7.61

*All tests were 0.5-hr. duration with 13% sulfur content in the feed soil.

Table 6. Metal Treatment Results with 75/25 SSM/Topsoil Blend*

	Untreated Soil			Run Numbers 27-95		Run Numbers 27-96		Run Numbers 27-97	
Metal	Salt Added	Metal Concentration (ppm)	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
Ni	$Ni(OH)_2$	2,000	0.54	250	1.95	300	2.5	350	4.7
Zn	ZnO	2,000	36.3	250	25.6	300	22.6	350	24.8

*All tests were 0.5-hr. duration with 13% sulfur content in the feed soil.

Table 7. Metal Treatment Results with 75/25 SSM/Topsoil Blend*

	Untreated Soil			Run Numbers 33-12		Run Numbers 33-13		Run Numbers 33-14		Run Numbers 33-15	
Metal	Salt Added	Metal Concentration (ppm)	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
Cd	CdO	200	2.37	250	0.33	300	0.17	350	<0.01	400	<0.01
Pb	PbO	2,000	2.40	250	0.38	300	0.41	350	<0.10	400	<0.10
Ni	$Ni(OH)_2$	500	0.097	250	0.28	300	0.35	350	0.08	400	<0.01
Zn	ZnO	500	6.76	250	3.49	300	4.60	350	0.80	400	0.11

*All tests were 0.5-hr. duration with 13% sulfur content in the feed soil.

these metals in the SARM blend (Table 3).

Based on the results from these three tests with high levels of added metals in the 75/25 SSM/topsoil blend, a fourth blend was prepared at intermediate concentrations of Cd, Pb, Ni, and Zn and run at various temperatures. This blend was prepared to more fully challenge the process at the highest concentrations possible and yet still achieve a passing TCLP for the treated soils.

However, the results in Table 7 show that the fourth blend did not adequately challenge the process for all of the metals. These experiments demonstrate significant reduction of TCLP values for the treated soils for lead and, at elevated temperatures, for cadmium. Zinc was not greatly reduced and the nickel results were inconclusive due to a too-low TCLP value for the starting soil. Tests of additional blends with higher metal contents are needed to arrive at a more suitable demonstration test mixture.

Finally in Table 8, a soil blend was then spiked to 10,000 ppm by weight of cobaltous (II) oxide and run at several temperatures. In contrast with the other metals, lower treatment temperatures actually enhanced the leachability of the cobalt from the added cobaltous oxide. This may be due to formation of a more acid soluble surface on the particles.

Summary of Metals Tests

Preliminary results of the screening tests on different spiked soil mixtures provide the opportunity to assess the response of the different heavy metals to stabilization by the Sulchem Process. Each metal responds differently, but in general there will be a maximum metal content that can be processed to achieve passing TCLP leachate values. The maximum metal content that can be reduced to the TCLP regulatory limit by the process will vary somewhat, based on the reaction temperature, reaction time, sulfur stoichiometry, or organic content of the soil. In general, however, a batch screening test at 250°C, using sulfur content on the order of 10 to 15% and reaction time of one half hour will define an approximate upper limit of the content of each metal that can be processed. Higher levels of metals can be processed to give passing TCLP values by increasing the temperature and/or adding soluble sulfide, particularly for cadmium, nickel, cobalt, and zinc. Increasing the stoichiometry or reaction time provides only a marginal improvement.

Recognizing that actual soil composition will affect the results, treatability studies are required to more precisely define the metal concentration that can be processed for a particular soil to give acceptable TCLP leachate values. Based on the very limited tests to date, lead limits of approximately 10,000 ppm and cadmium of several thousand ppm would seem to

Table 8. Metal Treatment Results with 75/25 SSM/Topsoil Blend

	Untreated Soil			Run Numbers 23-40		Run Numbers 23-42	
Metal	Salt Added	Metal concentration (ppm)	TCLP mg/L	Temp °C	TCLP mg/L	Temp °C	TCLP mg/L
Co	CoO	10,000	15.0	350	65.8	440	11.3

*All tests were 0.5 hr. duration with 13% sulfur content in the feed soil.

be generally feasible. Copper responds very well and nickel and zinc appear to be processed although the results are mixed. No definitive information on arsenic or chromium could be developed from the SARM-III tests.

Rotary Soil Reactor Tests

CHMR conducted six tests for organic compound destruction using a rotary soil reactor. The tests were conducted using manufactured gas plant (MGP) site soils. The MGP sample was selected for the larger-scale rotary soil reactor runs because 1) these soils typically have high levels of higher boiling aromatic hydrocarbons but very few VOCs and 2) there are over 1500 MGP sites across the United States. Approximately 15 gallons of the material was obtained from the site. Table 9 summarizes the characterization of the MGP sample.

The objectives of the tests were to demonstrate organic destruction at a larger scale using Superfund soil and the Sulchem configuration present in the rotary reactor, and to determine the appropriate process conditions for optimal destruction. Four runs were conducted using the soil as it was obtained from the site. Two runs were conducted with soil that was dried to reduce the moisture content and thereby reduce the vapor flow rate.

Runs were made at 300° and 350°C at reaction times of 0.5 and 1.0 hours. A one-hour residence time at reaction temperature was used initially because it was thought to provide sufficient time for the reaction to proceed completely. A half-hour residence time was used for two of the six runs to determine whether a half hour was sufficient for the reaction to proceed.

The sulfur/soil ratio was generally 10%, but runs were also conducted at 6 and 20%. Four of the runs were conducted with the soil as it was obtained from the site. Before conducting two of the runs, the soil was dried to reduce the moisture content and thereby reduce the vapor flow rate.

Analyses were conducted using EPA Methods 3550, 3660, and 8100 which involve extraction with methylene chloride, followed by analysis using gas chromatographic methods. The GC/FID results were quantitated by calibrating for four major constituents (2-methyl naphthalene, acenaphthene, phenanthrene, and pyrene) which covered the boiling point range for the contaminants in the soil. In addition to quantifying the recovery of these compounds, semi-quantitative recoveries for other constituents in the GC (which had been identified by GC/MS) could also be determined from the ratio of GC/FID peak areas for both the starting soil and the product fractions based on their relative quantities and dilutions as were done for the four compounds that were quantitated. These other constituents showed similar behavior of recovery as a function of boiling point.

Table 9. Characterization of MGP Sample

Moisture Content		20.1%
Total Extractable Organics		2.8%
Particle Size Distribution	<4 mesh	51.1%
	4-10 mesh	20.7%
	10-20 mesh	14.7%
	20-60 mesh	11.2%
	>60 mesh	2.2%
Organic Compound Types		
Napthalene, and C_1-,C_2-, C_3-substituted		1253 µg/g
Dibenzothiophene, and C_1-,C_2-, C_3-substituted		423 µg/g
Fluorene, and C_1-,C_2-, C_3-substituted		623 µg/g
Phenanthrene, and C_1-,C_2-, C_3-substituted		1626 µg/g
Pyrene, and C_1-, and C_2-substituted		1343 µg/g
Chrysene, and C_1-, and C_2-substituted		605 µg/g
Dibenzoanthracene		30 µg/g
Benzopyrenes and Benzofluoranthenes		543 µg/g
Pristane		366 µg/g
Phythane		256 µg/g

Quantitative Results

Table 10 shows the run conditions and quantitative results from the experimental runs, including individual product fractions. Several of the caustic traps were also extracted for organics, but very low quantities were found. Therefore the summary table only lists the reactor solids, condensate trap (trap #1), and the ice trap (trap #2). The percent recovered from the overhead, percent destroyed, and DRE for six compounds are given. The results for the two highest boiling compounds are based on initial concentrations measured by GC/MS analysis.

The lowest boiling compounds (methyl naphthalenes) showed very little destruction, although the ratio of 1-methyl naphthalene to 2-methyl naphthalene decreased by a factor of two to three. In addition, naphthalene, not found in the original soil, was produced in the process, presumably by partial reaction of higher homologs. Differences in reaction rates are also observed for the intermediate boiling aromatics (dimethyl naphthalenes, acenaphthene, fluorene, phenanthrene, in the boiling point range between 260° and 340°C.) These compounds show destructions ranging from about 50 to over 90%, whereas some of the saturated hydrocarbons in the same boiling range (pristane and phytane) are generally present in the products at about 50% of the feed content.

Higher boiling aromatic hydrocarbons (pyrene, chrysene, benzopyrene, etc., with BP>340°C) are nearly completely destroyed with only very low levels, or non-detect levels, observed in any of the product fractions. This indicates that the process works well for the high boiling point compounds, even at temperatures below their boiling points.

The recoveries of the four compounds that were quantified by the analytical method are representative of the yields observed semi-quantitatively for the other hydrocarbons with similar boiling ranges in the test soil. The effect of boiling range on the fate of the hydrocarbon contaminant in the soil, whether desorbed into the overhead, chemically destroyed, or left as trace residuals on the treated soil, are similar to the initial screening studies on the effect of boiling range on the fate of contaminants in the process.

Table 10. Rotary Reactor Tests-Recoveries

	BP °C	Fraction mg/kg feed	Reactor	Trap 1	Trap 2	Overhead Recovery	Destruction %	DRE %
Run 46-6: 350°C, 1 hour, 6.9% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	0.09	49.03	6.84	94.8	5.0	99.8
acenaphthalene	278	257.9	0.00	19.87	0.74	8.0	92.0	>99.9
phenanthrene	340	380.0	0.09	46.09	5.30	13.5	86.5	>99.9
pyrene	393	633.6	0.08	3.90	0.00	0.6	99.4	>99.9
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9
Run 46-10: 350°C, 1 hour, 20% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	0.00	24.96	0.30	42.9	57.1	>99.9
acenaphthalene	278	257.9	0.00	9.79	0.05	3.8	96.2	>99.9
phenanthrene	340	380.0	0.00	13.54	0.34	3.7	96.3	>99.9
pyrene	393	633.6	0.08	0.00	0.00	0.0	>99.9	>99.9
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9
Run 46-14: 300°C, 1 hour, 11% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	0.00	71.08	1.04	122.4	-22.4	>99.9
acenaphthalene	278	257.9	0.44	21.91	0.15	8.6	91.3	99.8
phenanthrene	340	380.0	1.07	60.50	2.37	16.5	83.2	99.7
pyrene	393	633.6	0.58	0.00	0.00	0.0	>99.9	>99.9
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9
Run 46-18 350°C, 1 hour, 9.1% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	1.90	18.00	0.79	31.9	64.9	96.8
acenaphthalene	278	257.9	1.56	11.20	0.00	4.3	95.1	99.4
phenanthrene	340	380.0	5.74	50.22	2.12	13.8	84.7	98.5
pyrene	393	633.6	1.99	0.00	0.00	0.0	99.7	99.7
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9
Run 46-22 300°C, 0.5 hour, 9.1% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	0.88	115.57	1.93	199.4	-100.9	98.5
acenaphthalene	278	257.9	0.00	0.00	0.00	0.0	>99.9	>99.9
phenanthrene	340	380.0	0.89	59.09	2.99	16.3	83.4	99.8
pyrene	393	633.6	0.00	0.00	0.00	0.0	>99.9	>99.9
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9
Run 46-26 350°C, 0.5 hour, 11.1% Sulfur, mg recovered/kg feed								
2-methyl naphthalene	241	58.9	0.69	106.71	2.47	183.5	-86.4	98.8
acenaphthalene	278	257.9	0.38	16.69	0.00	6.5	93.4	99.9
phenanthrene	340	380.0	0.96	165.34	7.64	45.5	54.2	99.7
pyrene	393	633.6	0.55	6.53	0.00	1.0	98.9	>99.9
chrysene	448	323	0.00	0.00	0.00	0.0	>99.9	>99.9
benzopyrene/benzofluoranthene	>450	680	0.00	0.00	0.00	0.0	>99.9	>99.9

The soil reactor showed nearly complete conversion for chrysene and benzopyrene, two compounds with boiling points above 400°C, and 99% conversion for pyrene. For lower boiling compounds, as anticipated, the soil reactor showed the effects of competition between reactions with sulfur, and desorption for the organic compounds.

Conclusions and Recommendations

The Sulchem process was shown to destroy certain polynuclear aromatic compounds in soil (particularly higher boiling compounds such as pyrene, chrysene and benzopyrene) in a reactor when operated at temperatures between 300° and 350°C. However, a reactor configuration capable of efficient destruction of a broader range of compounds was not obtained. This limitation may have been due more to limitations of the laboratory study, rather than inherent limitations of the technology. Specific conclusions from this laboratory study of the Sulchem Process are as follows:

- Destruction within the soil reactor was strongly correlated with compound boiling point:
  - Organic compounds with boiling points above 350°C are essentially completely destroyed in the process (destruction > 99.5%);
  - Organic compounds with boiling points in the range of 250° to 350°C are partially destroyed. However, a significant quantity volatilize before destruction occurs;
  - Organic compounds with boiling points below about 250°C primarily volatilize from the soil reactor before reaction can occur;
- A second stage sulfur/vapor reactor was shown to destroy a significant percentage of the organics desorbed from the soil reactor, thereby requiring subsequent treatment of the condensate produced;
- Metal stabilization in the treated soil (as measured by TCLP) is achievable for certain metals (particularly lead, cadmium, zinc, copper, and nickel) due to sulfide formation, with performance limits depending on the chemical form and concentration (e.g., typically lead below 10,000 mg/kg, cadmium below 1000 mg/kg).

Remediation costs employing the Sulchem Process are estimated at $105 to $183/ton based on site size, reactor configuration, and processing rate.

Only very limited testing of reactor configurations or techniques to destroy volatilized organics was employed. CHMR recommends additional testing of vapor-phase organic reactors at higher temperatures (400°C or higher) and longer residence times. From this, the destruction efficiency (and its limits) can be determined for an integrated soil/vapor reactor system.

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The complete SITE Emerging Technology report, entitled "Simultaneous Destruction of Organics and Stabilization of Metals in Soils," (Order No. PB98-133150, Cost: $25.00, subject to change) will be available only from

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