



Site Remediation via Dispersion by Chemical Reaction (DCR)

Giles M. Marion, James R. Payne, and Gurdarshan S. Brar

August 1997

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OFFICE OF THE CHIEF OF ENGINEERS

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PREFACE

This report was prepared by Dr. Giles M. Marion, Research Physical Scientist, Geochemical Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory; James R. Payne of SOUND/Epic (formerly Sound Environmental Services); and Dr. Gurdarshan S. Brar, formerly of CRREL. This work was funded through U.S. Army Corps of Engineers CPAR (Construction Productivity Advancement Research) Project AC910260, *Site Remediation via Dispersion by Chemical Reaction (DCR)*, to evaluate DCR technologies for handling different types of contaminants at DOD facilities.

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EXECUTIVE SUMMARY

The DCR (Dispersion by Chemical Reaction) technologies are a group of patented waste treatment processes using CaO (quicklime) for the immobilization of heavily oiled sludges, oil-contaminated soils, acid-tars, and heavy metals in $\text{Ca}(\text{OH})_2$ and CaCO_3 matrices. The objectives of this project were to 1) evaluate the DCR process for remediating soils contaminated with pesticides, petroleum hydrocarbons (oils and fuels), and heavy metals in cold regions and 2) evaluate DCR-treated oil-contaminated soil as a non-frost-susceptible (NFS) construction material. Three major studies evaluated the DCR process to remediate 1) hydrocarbons at Eareckson Air Force Station on Shemya in the Aleutians, 2) pesticide-contaminated soils from Rocky Mt. Arsenal, and 3) heavy-metal contaminated soils from a former zinc smelter site at Palmerton, Pennsylvania.

The DCR process was originally developed for the immobilization of liquid hydrocarbons. The laboratory-scale tests on Shemya wastes were a test of the efficacy of the DCR process to immobilize liquid hydrocarbons. The DCR process caused a major decrease in TCLP-extractable hydrocarbons. Both volatilization and $\text{Ca}(\text{OH})_2$ encapsulation may have played a role in the disappearance of these organic constituents. The results were, however, not consistent between wastes, indicating that the specific nature of the wastes will play a major role in the efficacy of the DCR process to remediate the wastes.

We also examined two organic wastes that were solids at the prevailing temperature. One was the

asphalt tar from Shemya, and the other was the pesticides from Rocky Mt. Arsenal. In neither case was there a significant overall improvement in chemical properties due to the DCR treatment. It would appear that unless the hydrophobic CaO can readily disperse into the organic phase, the DCR process is not effective immobilizing organics.

On the other hand, the DCR process is strongly dehydrating. Application of the DCR process to the solid asphalt tar from Shemya produced a drier, more soil-like, material with hydrophobic properties. This would improve the physical properties for potential reuse as road subgrade or landfill covers.

The DCR treatment greatly reduced the mobility of Zn through greenhouse soil columns. Neutralization of acidity, and adsorption onto and precipitation as hydroxides and carbonates probably were responsible for reduced Zn mobility. Judging by the Zn concentrations in plant tissue and biomass production, the DCR treatment improved plant growth in the Zn-contaminated soil.

The DCR process was successful in stabilizing liquid organics and heavy metals in contaminated soils. The chemical properties of soils contaminated by solid organics (asphalt tar and pesticides) were not generally improved by the DCR process, but even in these cases, the physical properties were improved for potential reuse as construction materials. Following laboratory verification for a specific waste, we can recommend the DCR process for the field remediation of liquid organics and heavy-metal-contaminated materials.

Site Remediation via Dispersion By Chemical Reaction (DCR)

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INTRODUCTION

Lime-based technologies

Lime (CaO) is one of the oldest chemicals used on Earth (Wray 1991). Although history does not record its discovery, lime is mentioned in the Bible and in documents from ancient China as well as Egypt, dating back about 6000 years. Lime and its by-products used in the waste treatment industry are summarized in Table 1. Many lime products and by-products behave differently. Chemically these by-products are poorly defined, and their use in place of lime requires extensive analysis to determine the equivalent quantity of lime. Most common forms of lime used in waste treatment are quicklime or unslaked lime (CaO) and hydrated or slaked lime [Ca(OH)₂]. In 1989, more than 1.54×10^{10} kg (34 billion lb) of lime were produced in the United States (*Chemical and Engineering News*, 18 June 1990).

Lime is often used in water treatment to pre-

cipitate potentially toxic metals and neutralize acids (Lewis and Boynton 1976, Boynton 1980). Lime application for metal precipitation requires pH adjustment to produce lowest solubility. Most potentially toxic metals (e.g., cadmium, chromium, lead and nickel) are amphoteric, a process where metal hydroxides show increased solubility at very low and high pH values. Weeter and Jones (1987) concluded that a lime/fly ash additive significantly reduced the chromium (Cr) concentration of industrial sludge high in copper (Cu), nickel (Ni), and Cr. The concentrations of Cu and Ni were reduced by solidification. Furthermore, they stated that a lime/fly ash admixture is more cost effective than other agents such as portland cement, lime, or sodium silicate. On the other hand, Malone et al. (1987) found that the fly ash/lime additive produced a product which lowered the overall hydraulic conductivity of the leachate but did not significantly lower the losses

Table 1. Characteristics of major lime, limestone products, and by-products used in waste treatment (Malone and May 1991).

| <i>Reagent</i> | <i>Formula or composition</i> | <i>Bulk density (kg m⁻³)</i> | <i>pH</i> |
|----------------------------|--|---|-----------|
| High calcium quicklime | CaO | 769–1121 | 10.5–12.4 |
| Dolomitic quicklime | CaO–MgO | 790–1400 | 9.0 |
| High calcium hydrate | Ca(OH) ₂ | 400–641 | 10.5–12.4 |
| Normal dolomitic hydrate | Ca(OH) ₂ .Mg(OH) ₂ | 400–560 | 9.0 |
| Dolomitic pressure hydrate | Ca(OH) ₂ .Mg(OH) ₂ | 480–640 | 9.0 |
| High calcium limestone | CaCO ₃ | — | 6.5 |
| Dolomitic limestone | CaCO ₃ .MgCO ₃ | — | —* |
| Lime kiln dust | 10–15% lime | — | ~ 12.4 |
| Cement kiln dust | Lime varies | — | ~ 12.4 |
| Fly ash† | Lime varies | — | ~ 12.4 |
| Waste lime | Lime varies | — | ~ 12.4 |

* Nonreactive.

† High calcium fly ash may have up to 2.4% uncombined CaO.

of heavy metals. The process using soluble silicate and cement additives gave the best containment of the heavy metals.

Crawley et al. (1984) outlined techniques for using hydrated, high calcium lime to treat acidic sludges. Remedial action using hydrated lime injection proved very effective in preventing groundwater pollution under and around acid waste pits. Morgan et al. (1984) developed and tested a variety of lime and by-product mixtures in treating oil refinery sludges. Blacklock et al. (1982, 1984) described a technique for injecting a lime/fly ash grout into landfills. Francis (1984) reported an interesting application of hydrated lime and limestone (oyster shell) to a landfill cap to maintain alkaline conditions inside an industrial waste landfill.

In 1971, EIF (Ecology of France) developed lime based fixation technology to detoxify wastes rich in organic content (Separation and Recovery Systems 1987). The examples of organic wastes treated with the technology include crude oil, refinery intermediate or final products, halogenated chemicals (e.g., PCBs), pesticides, sludges, tars, painting wastes, and acid sludges. The permeability of the treated and compacted refinery impoundment sludge waste was less than $1.0 \times 10^{-12} \text{ cm s}^{-1}$.

In Dallas, Texas, Morgan et al. (1984) used several solidification agents to treat 19 million liters of 30-year-old refinery oil sludge. The best solidifying agent found was fresh and stale cement kiln dust. Furthermore, the kiln dust was also tested in combination with small amounts of sulfur, cement and lime. Excellent solidification was observed with cement and lime. Sulfur did not increase the strength significantly. The solidification process is simple, economical, and potentially applicable to other waste-disposal sites.

Zenobia and Turco (1985) studied the lime-based stabilization technique to remediate hazardous waste site containing basins of inorganic sludges, incineration residues, and spent biomass. They found that fly ash in combination with lime and lime kiln dust were the best stabilizing agents. In France, Such and Roux (1981) treated oil spills with quicklime and hydrophobic lime (Boelsing reagent, see *DCR Technologies*). They reported that the chemical reaction of dehydration occurred immediately in quicklime and relatively delayed with hydrophobic lime.

Koper et al. (1993) reported that CaO is an effective solid reagent for destruction of chlorocarbons (CCl_n). Furthermore, in a editorial note,

Rittenhouse (1993) wrote about CaO as an effective reagent for the destruction of CCl_4 . He discussed the work of O. Koper, Y.-Xi Li, and K.J. Klabunde at Kansas State University.

Soundararajan (1991) found a strong interaction between high calcium-fly ash and polychlorinated biphenyls (PCBs) resulting in the total destruction of PCBs. Although he concluded that a catalyst was probably responsible for the PCB destruction, the specific catalyst responsible is unknown. Einhaus et al. (1991) reported that PCB-contaminated soil treated with quicklime and water significantly reduced (60 to 80%) PCB concentrations after five hours of treatment. However, they concluded that use of reactive quicklime as an in-situ treatment may be counterproductive due to the potential for migration of PCBs as vapor or airborne particulates. Sediak et al. (1991) attributed most PCB losses to volatilization due to the high heat of reaction for the CaO hydration reaction. They concluded that the "quicklime" treatment, per se, was not an effective treatment for PCB-contaminated soil.

Lime and lime products are useful in the engineered disposal of nonhazardous and hazardous wastes. In some cases lime can be used to convert hazardous waste to nonhazardous waste. Malone (1984) reported that lime has great potential as a neutralizing and cementing agent in waste management. Furthermore, he suggested that application of lime in hazardous waste reduction processes should increase because new ideas of its use in liners, lime/fly ash grout injection, and enhancement of methane production have been evaluated and found safe and useful. Lime stimulates activity of anaerobic methane generating bacteria responsible for the decay of refuse. Methanogenic bacteria function best in the pH ranges of 6.4 to 7.4; however, some methane producers can operate at high pHs of 9.0 (Klass 1984). Lime in the form of quicklime is also used in drying semisolid wastes. The hydration reaction of quicklime eliminates water from the system and produces a dry product which is easy to handle.

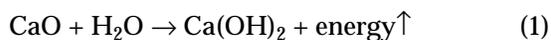
Malone and May (1991) found that the porosity and permeability of lime-amended soil were greatly reduced by precipitation of contaminants in intergranular spaces in the soil. Initially the amended soil had a permeability of $3.5 \times 10^{-6} \text{ cm s}^{-1}$; after 20 pore volumes of an acidic waste had passed the column, the permeability decreased to $4.0 \times 10^{-8} \text{ cm s}^{-1}$. In contrast, the permeability of the untreated soil ranged from $4.0 \times 10^{-6} \text{ cm s}^{-1}$ to $1.0 \times 10^{-6} \text{ cm s}^{-1}$ after contact with

24 volumes of acidic waste. The lime-amended soil decreased the permeability, reduced the amount of leachate passing through the liner, and reduced the total dissolved solvent content, trace metal, and radionuclide concentrations in the waste that moved through the liner. The lime-amended liner was considered to be a very successful method for reducing the discharge of pollutants from acid waste piles.

Quicklime mixed with clay soils has been used to produce hard, impervious soil liners in stock ponds, small earth dams and irrigation channels (Gutschick 1978). A compacted lime liner was constructed by BASF Corp. for a hazardous waste landfill on the Island of Flotzgrun near Speyer, Germany (BASF 1983).

DCR technologies

The Dispersion by Chemical Reaction (DCR) technologies are a group of patented waste treatment processes developed by F. Boelsing (University of Hannover, Germany) over 18 years ago in Europe for the immobilization of heavily oiled sludges, water-in-oil emulsions, oil contaminated soil, industrial wastes such as acid-tars and heavy metals (Boelsing 1988, 1995, Payne et al. 1992). Hydrophobized CaO is used in the DCR process to remediate organic-contaminated materials. Calcium oxide, in its pure state, is hydrophilic. Hydrophobic and oleophilic lime is prepared by treating CaO with natural fatty acids. This process delays the hydration step and allows the fatty acid-coated CaO reagent to preferentially adsorb oils during a mixing step. The delayed hydration then produces calcium hydroxide [Ca(OH)₂], which is fractured into submicron sized particles (eq 1). This hydration reaction is highly exothermic. Hydrate particles are homogeneously charged throughout their internal and external cavities with the oil phase. The finely dispersed Ca(OH)₂ then slowly reacts with natural CO₂ to generate relatively insoluble CaCO₃ (eq 2):



Thus, the oil components are immobilized in a CaCO₃ matrix to levels passing EPA Toxic Characteristic Leaching Procedure (TCLP) requirements. Other physical properties of the DCR product that facilitate lower chemical leaching are the compactibility of the soil-like product,

which lowers the hydraulic conductivity, and the hydrophobicity of the product, which resists absorption of water. During the initial mixing step, other reagents can be added for specific reactions. For example, a hydrophobized nucleophilic reagent has been used for dehalogenation of PCBs (Payne et al. 1992). Remediation of heavy metals relies upon the formation of insoluble heavy metal hydroxides and carbonates; when used to remediate heavy metals, hydrophilic CaO is used as the primary reagent (Marion et al., in prep.).

The objectives of this project were to 1) evaluate the DCR process for remediating soils contaminated with pesticides, petroleum hydrocarbons (oils and fuels), and heavy metals in cold regions and 2) evaluate DCR-treated oil-contaminated soil as a non-frost-susceptible (NFS) construction material. These objectives were met with three major studies. We evaluated the DCR process to remediate 1) hydrocarbons at Eareckson AFS on Shemya in the Aleutians, 2) pesticide-contaminated soils from Rocky Mt. Arsenal, and 3) heavy-metal-contaminated soils from a former zinc smelter site at Palmerton, Pennsylvania.

METHODS AND MATERIALS

This final CPAR report will focus on the highlights of the three studies at Shemya, Rocky Mt. Arsenal, and the Palmerton zinc smelter site, with primary focus on the chemistry. Other physical and chemical testing beyond that described below and in the *Results and Discussion* were done at all these sites. For a complete description of the experimental work, refer to the following publications: Payne et al. (1994), Brar and Marion (1995), Marion et al. (1997), Payne and Marion (in press), Marion et al. (in prep.).

Shemya study

Shemya Island (5.6 × 2.4 km) is located at the western tip of the Aleutian Archipelago, 2400 km southwest of Anchorage. Historically Shemya has been uninhabited. The earliest written records of human activity were by Russians who introduced blue foxes on Shemya for the purposes of fur farming in 1775. In 1943, the U.S. Army's 4th Infantry and 18th Engineering Regiments developed Shemya and constructed a runway and aircraft hangers, which were used during World War II. Today, the U.S. Air Force occupies the entire island; the primary mission of the Eareckson Air Force Station is to monitor space and missile activities.

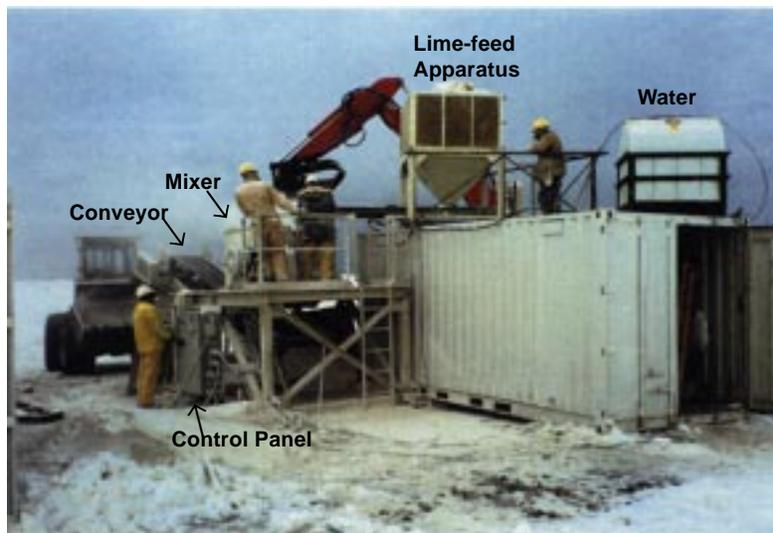


Figure 1. Transportable treatment unit used on the Shemya study.

Shemya Island is dominated by a persistent low pressure system known as the “Aleutian Low.” Frequent storms track across the north Pacific into the Aleutian Islands. The Aleutian low pressure cells are responsible for the relatively mild maritime climate of the Aleutian Islands. Summer fogs are severe and preclude any flying as often as one day in four. The persistent wind, fog, and salt spray are responsible for the highly corrosive and harsh conditions.

The mean annual temperature is 3.6°C. The minimum and maximum recorded temperatures are -13.9 and 17.2°C, respectively. The diurnal temperature variation rarely exceeds 6°C. Measurable winds are recorded 363 days yr⁻¹ with a mean annual wind velocity of 32 km hr⁻¹. Wind direction is evenly distributed without any true prevailing wind direction. Precipitation occurs more than 330 days yr⁻¹. Average annual precipitation is 79.5 cm. The average annual snowfall is 178 cm. Drifting snow and driving rain are common in winter because of strong wind velocities (CH2M Hill 1990).

Eareckson AFS has several types of soil contamination problems which are the result of historic and ongoing USAF operations. The primary focus of this study was on a site identified as the PS-9 Asphalt Tar Drum Storage Area. This site is contaminated as a result of leaked asphalt tar stored in 55-gal. drums. In addition, we examined, at the laboratory scale, the efficacy of the DCR process to remediate organic-contaminated soil from three sites identified as 1) Oil/Water Separator Pond Sediment, which is contaminated with oils and greases; 2) Cell 21 Oiled Peat, which

is contaminated with JP-4 and other volatile fuels; and 3) Fire Training Pit, which is contaminated with diesel residuals that were not volatilized or burned during fire training exercises.

SOUND Environmental Services (now known as SOUND/epic), Anchorage, Alaska, under contract with the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), demonstrated the DCR technology at Eareckson AFS, Shemya. To treat the asphalt tar waste, SOUND used a skid-mounted transportable treatment unit (Fig. 1). The transportable treatment unit consists of a control panel, mixer, lime-feed apparatus, water container, and conveyer assemblies. Asphalt tar was excavated with a Link-Belt excavator and stockpiled on the site. The excavated asphalt tar material and accompanying soil were added to the pug-mill mixer on a volumetric basis. Lime was metered into the mixer on a timed basis dependent on the volume of waste addition. Occasionally water was also added to the mixture at the discretion of the mixing overseer.

Two bulk soil samples (18 kg each) for laboratory physical tests were collected by mixing different batches of DCR-treated asphalt material in the field. These samples were air-freighted to CRREL without any special provisions for preservation. Three soil samples were used in the physical tests. Samples 1 and 2 were from the two separate buckets, and sample 3 was a composite sample from the two buckets.

ASTM Method D 5084-90 was used to determine the saturated hydraulic conductivity (permeability) of DCR-treated asphalt tar materials before and after one freeze-thaw cycle. Rocks

greater than 1.0 cm were excluded from the test samples. Four sets of hydraulic conductivity measurements were made on each sample. The test measures one-dimensional laminar flow of water within saturated porous materials. This test assumes hydraulic conductivity is unaffected by hydraulic gradient. The following procedures were used to freeze the samples. The compacted soil samples used to determine the hydraulic conductivity of unfrozen soil were placed in a cold-room. Two cold plates, one at the bottom and another at the top of the test sample, were positioned. Vermiculite was used as insulating material around the test sample. Temperatures of the test samples were kept at 3°C for one night. Temperatures of 0° and -6.1°C were maintained for the next 18 hr at the bottom and top of the sample, respectively. Then temperatures at the bottom and top of the specimen were maintained at 0°C and -10°C for an additional 5 hours. These temperatures at the bottom and top of the sample were further lowered to -3°C and -12°C, respectively, for an additional 24 hours. For thawing the samples, temperatures were raised to 3°C and 4°C at the bottom and top of the cell for 24 hours.

The gravimetric water content of DCR-treated asphalt tar samples was determined by heating at 105°C for 24 hours (ASTM Method D2216-90). These tests were performed in a field laboratory at the treatment site. Three soil samples were drawn from the untreated asphalt tar material, and four samples were drawn from different batches of field DCR-treated asphalt tar material. In addition, three replicate samples were taken from the laboratory DCR-treated batches.

Temperatures of the DCR-treated asphalt tar material were measured in the field with copper-constantan thermocouples that were fabricated and tested at CRREL. Four thermocouples, each separated by 30 cm, were attached to a wooden stick. Two wooden sticks with eight thermocouples were embedded horizontally into an untreated asphalt tar pile or a DCR-treated pile. Air temperatures were measured at a 2-m height above the ground with unshielded thermocouples. Data were logged every minute with a data-logger (model CR-10, Campbell Scientific).

Asphalt tar-soil samples for chemical analyses were collected in quality certified (QC) glass jars and stored outdoors (-5° to -1°C) until ready for shipment. Five untreated samples were collected around the excavated tar pile on 27 January 1994. Five treated samples were collected during the DCR operation on 27-28 January. These chemical

samples were air-freighted on "blue ice" in Igloo coolers from Shemya to Anchorage on 28 January, stored in a freezer overnight, and then shipped on 29 January via Federal Express to the U.S. Army Corps of Engineers Environmental Laboratory in Hubbardston, Massachusetts (henceforth to be called the Environmental Lab), where they arrived on 31 January. Total petroleum hydrocarbons (TPH) (as diesel) was determined using EPA Methods 3550/8015M (USEPA 1992). Toxic Characteristic Leaching Procedure (TCLP) extracts for TPH were done using EPA Methods 1311/8015M. Volatile organics were determined using EPA Method 8260. TCLP extracts for volatile organics were done using EPA Methods 1311/8260.

Samples from the Oil-Water Separator Pond Sediment, the Cell 21 Oiled Peat, and the Fire Training Pit were collected, DCR-treated in the portable field laboratory using an Eirich mixer, and analyzed by Commercial Testing & Engineering Company in Anchorage, Alaska. TPH (as diesel) was analyzed using EPA Methods 3510/3550/8100M; vapor phase hydrocarbons were analyzed using EPA Methods 5030/8015M/8020; and BTEX constituents (benzene, toluene, ethylbenzene, and xylenes) were analyzed using EPA Method 8020. TCLP extracts (EPA Method 1311) were used to measure the leachability of TPH and BTEX constituents.

Rocky Mt. Arsenal study

Four separate 15-gal. (56.7-L) drums containing representative soil samples were transported under full chain of custody to SOUND/epic. Upon initial receipt, each sample was further homogenized and examined to assess handling and physical characteristics. An aliquot of each was removed for hexane extraction and gravimetric determinations of oil and grease and total petroleum hydrocarbons (TPH). The extracts were then further characterized by flame ionization detector (FID) gas chromatography (GC) to determine total resolved hydrocarbons and the approximate molecular weight range (distillate cut fraction) of any petroleum-type constituents in the sample. Electron capture detector (ECD) GC was then used to screen for pesticides.

Based on the chromatograms of the four samples, we selected the most contaminated soil ("soil-amended Basin F sludge") for all subsequent work (Payne and Marion, in press). It was known that the majority of the contamination originated in the Basin F Liquid (Table 2), and for this reason as well, this sample was selected. In

Table 2. Descriptive chemical characterization of RMA Basin F liquid* (highest historical data).

| <i>Constituent</i> | <i>mg/L</i> |
|---|-------------|
| Water | 620,000 |
| Major metals | |
| Sodium (Na) | 65,000 |
| Copper (Cu) | 5,860 |
| Potassium (K) | 2,900 |
| Major inorganics | |
| Chloride (Cl ⁻) | 159,000 |
| Ammonia (NH ₃) | 60,900 |
| Sulfate (SO ₄ ⁼) | 27,000 |
| Total phosphorus | 16,200 |
| Nitrate (NO ₃ ⁻) | 1,300 |
| Additional components | |
| Urea | 143,000 |
| Dimethylmethylphosphonate | 2,000 |

* From R.F. Weston Document 1212WG.APA (12/17/90).

addition to significant levels of pesticides, the Basin F Liquid (later mixed with clean soil to yield the “soil-amended Basin F sludge”) contained very high concentrations of inorganic salts [e.g., NaCl, NH₄Cl, and (NH₄)₂SO₄] as well as 14% urea (Table 2).

It was determined that the high levels of sulfate (and possibly urea) in the waste (Table 2) were interfering with the CaO hydration inherent to the DCR process. As a result, uneconomically high levels of CaO reagent were required to obtain an acceptable product. To circumvent this problem, additional tests were undertaken to see if the waste could be pretreated with lime milk [hydrated Ca(OH)₂] to tie up the sulfate (for example as gypsum, CaSO₄·2H₂O) and also remove the urea. These tests were very successful, and it was found that addition of 30% lime milk slurry in H₂O [Ca(OH)₂ at approximately 10–13% of contaminated soil weight] was sufficient to tie up all the sulfate as gypsum. Then with subsequent addition of dry CaO for the DCR reaction, it proceeded without delay and at economically feasible reagent addition levels. The lime milk pretreatment also proved to be an excellent way to remove ammonia by volatilizing any ammonium originally present as ammonium sulfate and catalyzing the hydrolysis of urea to CO₂ and ammonia. In field applications, this approach could be used to release and reclaim ammonia through a specially designed emissions control capture system on the transportable treatment unit prior to DCR processing.

The DCR process (unlike other pozzolan-based

stabilization approaches) achieves its greatest technological advantage with wastes containing very high (> 10–30%) levels of organics (e.g., diesel oil residuals and waste oils) because such materials facilitate transfer of the contaminants of concern onto the hydrophobic CaO reagent before the dispersion by chemical reaction takes place. It was apparent that there would not be sufficient free organic (oily) phase in the sludge/soil matrix for optimum DCR processing. It was determined in a wettability study that addition of a benign food additive (Archer Daniels Midland [ADM] regular soy oil soap stock) at 10% of soil weight significantly improved the water repellency of the resultant product, so its addition was implemented as a standard procedure for all further tests.

Following the initial scoping studies completed in the first week after sample receipt, 0.7-kg scale batch preparations were undertaken to generate sufficient DCR-treated material for independent, third-party laboratory testing. The initial DCR product prepared for outside laboratory analyses was generated from 55% CaO addition to lime-milk pretreated soil plus 10% ADM soy oil. The total CaO reagent requirement (including that used to generate the lime milk slurry) for this sample was 64.7%. This material and a sample of the raw untreated waste soil were packaged for shipment and transferred under chain of custody to the Environmental Lab. The following analyses were performed: FID GC (*Diesel Range Total Petroleum Hydrocarbon Screening*, EPA Method 8015M), ECD GC (EPA Method 8081, *Pesticide and PCB Analyses*), GC/MS (EPA Method 8270, *Total Waste Analyses*), TCLP (EPA Method 1311 *Extraction for Pesticides*, EPA Method 8081).

Subsequent to sample shipment, several additional larger-scale (1.5 kg) scoping experiments were completed with SOUND/epic’s high intensity Eirich Mixer. Through these later determinations, it was found that at the larger batch size and with more aggressive mixing, an acceptable product could be obtained with only a 23% CaO addition to lime-milk pretreated soil (total CaO addition, including preparation of lime milk was 27.4%). Because the 27.4% CaO addition is more representative of what might be utilized in field applications, samples of this DCR-treated material were compacted into a Proctor cylinder for physical testing. A portion of this compacted cylinder was allowed to cure and was set aside for additional chemical analyses to assess the effects of lower DCR reagent utilization and sample

compaction on pesticide sequestering and leachability. This compacted cylinder sample was shipped via Federal Express under chain of custody to the Environmental Lab. The same suite of analyses used for the raw untreated soil sample and loose (uncompacted) 64.7% DCR-treated material was requested, with the proviso that the cylinder be crushed to the minimum extent necessary to pass through the 9.5-mm sieve (specified in the TCLP test) before leaching.

Palmerton zinc smelter study

Palmerton is in Carbon County, Pennsylvania, just north of the Lehigh Water Gap. Current vegetation on the Blue Mountain site is depauperate with many areas completely barren; common species on these sites include *Sassafras albidum*, *Nyssa sylvatica*, and *Arenaria patula* (Buchauer 1973). The soils on top of Blue Mountain are Dekalb very stony loams, formed on periglacially worked, acid, gray sandstone (Fisher et al. 1962). The soil is classified as a loamy-skeletal, mixed, mesic Typic Dystrochrept. These soils are strongly acidic, well drained, and contain many stones.

The contaminated soil was collected in plastic bags at the Palmerton site about midslope on the north aspect of Blue Mountain and shipped in metal drums to CRREL. The “clean” soil was a Charlton silty sand and was collected locally. These soil samples were air-dried on large tarps and sieved to pass a 2-mm screen.

The air-dried and sieved soils were DCR-treated at the SOUND/epic laboratory in Carlsbad, California, in August 1995. Contaminated soil and CaO (10% w/w) were mixed in an Eirich mixer with sufficient water to assure proper hydration (eq 1). The resultant product was a dry, dusty, soil-like material.

Total, TCLP extractable, and water soluble heavy metals were measured by the Environmental Lab. Total soil analyses for Ag, Be, Cd, Cr, Cu, Ni, Sb, and Zn were done using EPA Methods 3051 (digestion) and 6010 (ICP); for As, Methods 3051 and 7060 (AA) were used; for Pb, Methods 3051 and 7421 (AA) were used; for Se and Tl, Methods 3051 and 7740 were used; and for Hg, Method 7471 (AA) was used (USEPA 1992). TCLP extractions and analyses for Ag, Be, Cd, Cr, Co, Ni, Sb, Zn, As, Pb, and Se were done using EPA Methods 1311 (extraction) and 6010 (ICP); TCLP extractions and analyses for Hg were done using EPA Methods 1311 and 7470 (AA) (USEPA 1992). The TCLP tests used acetic acid extraction fluid no. 2 (USEPA 1992) for all samples because of the

alkalinity of the DCR-treated soils. The water soluble tests were identical to the TCLP tests except that water was used as the extraction fluid.

The CRREL greenhouse column experiments were designed to assess the efficacy of the DCR process to stabilize heavy metals against leaching losses and plant uptake. The clear acrylic columns were 60 cm in length and 5 cm in inside diameter. These columns were split longitudinally to facilitate root sampling at the conclusion of the study. The tubes were placed in a dark box with each tube inclined 15° from the vertical to facilitate root growth observations. Each tube was divided into three sections. On the bottom was a 14-cm sand zone; on top of this layer was a 20-cm experimental soil zone; and the surface 25-cm zone consisted of a clean (i.e., uncontaminated) soil.

The four experimental soils were 1) a Charlton silty sand (clean soil), 2) a Palmerton silt (contaminated soil), 3) a DCR-treated Palmerton soil, and 4) a compacted DCR-treated Palmerton soil. The compacted treatment was designed to assess whether plant roots would grow around the DCR-treated soil if given an opportunity. The compacted samples were 4.0 cm in diameter and 20 cm in length and were prepared by dropping a weight 10 times on the soil encased in a plastic tube. The final density of these cores was $2.02 \pm 0.05 \text{ g cm}^{-3}$. The core was then placed in the center of the column and clean soil was filled in around the core.

The two plant species were Pennfine perennial ryegrass (*Lolium perenne*) and Pixie tall fescue (*Festuca arundinacea*). These two grasses were chosen because tall fescue shows promise for heavy metal tolerance, while perennial ryegrass has little tolerance for heavy metals (Chaney 1993). There were four replicates of each treatment for a total of 32 columns (4 soils \times 2 plant species \times 4 replicates).

The experimental columns were prepared on 7 December 1995. Unfortunately the greenhouse heating system broke down shortly thereafter, which caused the columns to freeze. Problems with the heating system and other factors delayed planting with tall fescue and perennial ryegrass until 19 January 1996. Seeds were germinated on filter paper, planted 1.0 cm deep in the tubes, and after emergence and early growth, thinned to four plants/tube. Plants were watered as needed with half-strength, pH-neutral Hoagland's nutrient solution (minus Zn) (Johnson et al. 1957). Every third watering was with distilled

water to reduce salt accumulation. Ten times during the experiments leachates were collected and analyzed for pH and heavy metals. The plants were harvested on 23 April 1996, rinsed in deionized water, and separated into shoots, crowns, and three root samples from the three soil zones. The plant material was frozen until ready for analyses.

Leachates were analyzed for Zn, Pb, Cu, Cd, and pH. Samples were refrigerated after sampling, but were not filtered. There was no visual evidence for any significant movement of suspended material or organics as judged by settling out of suspension or discolored solutions. Working standards for heavy metals were prepared from 1000-ppm Fisher primary standards. A Perkin-Elmer Model 5000 atomic absorption spectrophotometer (AAS) was used for the heavy metal analyses. The pH meter was calibrated with Fisher standards at $\text{pH} = 10.00 \pm 0.02$ and $\text{pH} = 7.00 \pm 0.01$.

The plant material was dried in an oven at 80°C , then ground in a stainless steel Wiley mill to pass a 20-mesh screen. Subsequent plant processing for heavy metal analyses closely followed the procedures used by Brown et al. (1994). Briefly, plants were ashed at 480°C for 16 hours, digested with 5 mL of concentrated HNO_3 , evaporated to dryness, taken up in 5 mL of 3 M HCl, and then diluted to volume (25 mL) with 1 M HCl. Blanks were carried through the identical process. These solutions were analyzed on a Perkin-Elmer model 5000 AAS. Working standards were prepared from primary standards (Fisher, 1000 mg L^{-1}) and contained the same HCl concentrations as the samples to assure a similar sample matrix.

RESULTS AND DISCUSSION

Shemya study

This study involved more physical testing of the treated material than the subsequent studies, because there was interest in possibly using this material for either road subgrade or in a landfill cover in an area subject to freeze-thaw cycles.

The water content of untreated asphalt tar was around 30% by weight; both laboratory and field DCR-treated asphalt tar material contained significantly less moisture (Fig. 2). This dehydration of the treated material is partly due to formation of $\text{Ca}(\text{OH})_2$ and partly due to release of steam in the exothermic reaction (eq 1). The laboratory treated material contained significantly higher water compared to field treated material.

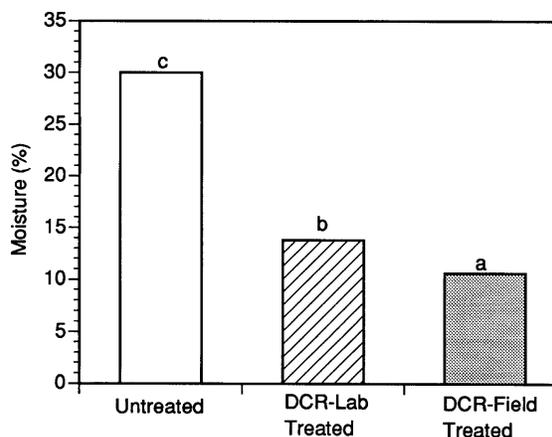


Figure 2. Water content of untreated soil-asphalt tar and laboratory and field DCR-treated material.

The hydraulic conductivity was determined on three DCR-treated asphalt tar samples subjected to a single freeze-thaw cycle. Although the hydraulic conductivity increased with a single freeze thaw cycle, the difference was not significant (Table 3). Because of the high levels of sand and gravel in the raw waste, the DCR-treated tar material was coarse-textured. As a consequence, the hydraulic conductivity was high (Table 3). Reduction of hydraulic conductivity to a regulatory limit of $1.0 \times 10^{-5} \text{ cm s}^{-1}$ for some applications (e.g., landfill covers) will necessitate mixing of the treated material with finer-textured silts

Table 3. Changes in hydraulic conductivity after one freeze-thaw cycle.

| Sample no. | Dry density (g cm^{-3}) | Hydraulic conductivity (cm sec^{-1}) | | |
|------------|------------------------------------|---|-----------------------|-------|
| | | 0 | 1 | Ratio |
| 1 | 1.41 | 1.03×10^{-3} | 1.12×10^{-3} | 1.09 |
| 2 | 1.36 | 5.76×10^{-4} | 9.85×10^{-4} | 1.71 |
| 3 | 1.37 | 2.06×10^{-4} | 2.67×10^{-4} | 1.30 |
| Mean | 1.38 | 6.04×10^{-4} | 7.91×10^{-4} | 1.37 |

and clays. A single freeze-thaw cycle increased the hydraulic conductivity by 37% (Table 3), which agrees with Chamberlain (1994) who found that the hydraulic conductivity of most compacted clays increased significantly after freezing and thawing. Chamberlain (1994) reported that freeze-thaw cycles are the major problem affecting the design and performance of landfill containment structures and surface impoundment systems in cold regions. The coarse texture and high hydraulic conductivity of this DCR-treated tar-soil mixture may limit potential reuse.

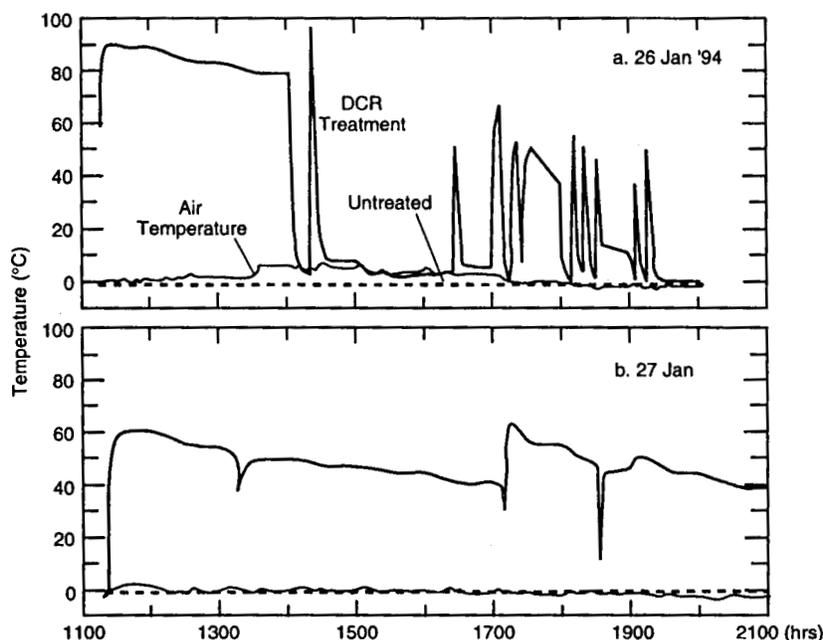


Figure 3. Changes in air, stockpiled untreated, and DCR-treated material temperatures.

Fifteen peaks of elevated temperatures for various DCR-treated batches were recorded on 26–27 January 1994 (Fig. 3). Sharp temperature peaks were the result of placing the probes in a batch for short periods. Plateaus and steady declines in temperature were the result of leaving the probes in a given batch for extended periods. The temperature of treated material increased to between 35° and 95°C. The temperature of untreated material was close to 0°C, and no change was observed on either sampling day. On 26 January, air temperatures started increasing after 1130 hours and reached a maximum of 6°C in an unshielded position.

The DCR reaction was both highly exothermic and dehydrating. The high temperatures (> 90°C,

Fig. 3) could potentially have an adverse effect on soil microorganisms. On the other hand, the dehydration produced a drier soil material, which should facilitate its reuse. The original tar-soil mixture was very dark and consisted of many large tar masses, some weighing 2–5 kg. The end-product was more soil-like, drier, with only a few small (0.5-kg) tar balls. The DCR process, overall, improved the physical properties of this asphalt tar material for reuse.

Many of the volatile organics in the asphalt tar-soil were below the limits of detection (Brar and Marion 1995). Statistically significant differences between untreated and DCR-treated soils were only found for acetone, 2-butanone, 4-methyl-2-pentanone, and total xylenes (Table 4). With the

Table 4. Total extractable concentrations of TPH and volatile organics in asphalt-tar samples (mean \pm 1 SE).

| Compound | Units | Minimum detectable limit | Untreated | Treated |
|----------------------|-----------------------|--------------------------|-----------------|-----------------|
| Acetone* | $\mu\text{g kg}^{-1}$ | — | 66 \pm 14a | 466 \pm 14b |
| 2-Butanone | $\mu\text{g kg}^{-1}$ | 2.3 | 11 \pm 5a | 226 \pm 12b |
| Benzene | $\mu\text{g kg}^{-1}$ | 1.0 | 0.5 \pm 0.0a | 3.9 \pm 2.1a |
| 4-Methyl-2-pentanone | $\mu\text{g kg}^{-1}$ | 2.3 | 1.2 \pm 0.0a | 21 \pm 2b |
| Toluene | $\mu\text{g kg}^{-1}$ | 0.58 | 7.1 \pm 1.8a | 4.8 \pm 1.6a |
| 2-Hexanone | $\mu\text{g kg}^{-1}$ | 1.9 | 30 \pm 23a | 49 \pm 13a |
| Ethylbenzene | $\mu\text{g kg}^{-1}$ | 0.56 | 6.7 \pm 1.4a | 6.5 \pm 1.5a |
| Total xylenes | $\mu\text{g kg}^{-1}$ | 1.1 | 64 \pm 13a | 31 \pm 3b |
| TPH | mg kg^{-1} | — | 2602 \pm 621a | 2160 \pm 254a |

* Also detected in method blanks run with with samples.

Statistically significant differences are designated by different lower-case letters.

exception of total xylenes, volatile organic concentrations were higher in treated than in untreated samples. Elevated levels of ketones may be the result of in-situ oxidation of corresponding alcohols present, but not analyzed for, in the starting material.

Increasing organic concentrations runs counter to the basic principle of the DCR process that is designed to encapsulate organics rendering them less available. We believe that this outcome was caused by two factors. One, the mixing process broke up the tar masses greatly increasing contact surface areas for the extracting solutions. Two, the hydrophobic CaO never properly dispersed into the asphalt tar because at the prevailing field temperatures (< 0°C), the asphalt tar was a solid. The heat of mixing was insufficient for a proper CaO dispersion into the organic phase prior to the hydration reaction. Under cold climates, heating the asphalt tar prior to mixing would probably lead to a better DCR product.

Most constituents were either not detected in the TCLP extracts or were present at levels that were just above the detection limits (Table 5). There was no leachable benzene detected; when other leachable aromatics were detected, they were four orders of magnitude below applicable drinking water standards. The most water-soluble constituents, notably acetone and 2-butanone, were generally only present at low ppb levels, three to four orders of magnitude below the regulatory limit for 2-butanone, the only ketone for which limits exist.

The TPH in the solid raw and DCR-treated tar samples is quite variable, and no doubt reflects differing amounts of small tar flakes in the soil/

tar samples (Table 4). Because of the variability, there is no statistically significant difference in the samples before and after treatment. Conversely, when the TCLP results are examined, there is a slight increase in the total leachable TPH in the samples after treatment (Table 5). Here again, the increase in leachability is believed to be due to the increase in surface area associated with the finely dispersed DCR product compared to the hard and almost intractable obsidian-like tar lumps in the starting material. This leachability would be significantly lower in hard compacted DCR soil bodies, as in subgrade for parking areas or road construction, compared to the loose, fine product subjected to TCLP testing in the laboratory.

In contrast to the solid asphalt tar, the other contaminants evaluated at the laboratory scale generally led to large decreases in organic concentrations following DCR treatment (Tables 6 and 7). There were at least two reasons for this contrast. One, the other organics were present in the liquid state (e.g., oils, greases, JP-4, diesel) at these sites which facilitates proper adsorption of the organic phase onto the hydrophobic CaO before the DCR reaction. Two, the other organics were present at much higher concentrations initially for these three sites (Tables 6 and 7) compared to the asphalt tar site (Tables 4 and 5).

There was a dramatic reduction in the extractable TPH after DCR treatment for the Oil/Water Separator Pond Sediments, and this presumably reflects a combination of volatilization and Ca(OH)₂ encapsulation of intermediate- and higher-molecular-weight hydrocarbons associated with the oils and greases released to the pond (Table 6). The total lower-molecular-weight (gasol-

Table 5. Total extractable concentrations of TPH and volatile organics in TCLP extracts of asphalt-tar samples (mean±1 SE).

| <i>Compound</i> | <i>Units</i> | <i>Minimum detectable limit</i> | <i>Untreated</i> | <i>Treated</i> | <i>Alaska or Federal standard</i> |
|----------------------|--------------------|---------------------------------|------------------|----------------|-----------------------------------|
| Acetone* | µg L ⁻¹ | — | 23 ± 14a | 156 ± 111a | n.a.† |
| 2-Butanone | µg L ⁻¹ | 1.6 | 1.4 ± 0.4a | 6.4 ± 1.1b | 200,000 |
| Benzene | µg L ⁻¹ | 0.63 | 0.3 ± 0.0a | 0.3 ± 0.0a | 5 |
| 4-Methyl-2-pentanone | µg L ⁻¹ | 1.5 | 1.3 ± 0.2a | 2.2 ± 0.4a | n.a. |
| Toluene | µg L ⁻¹ | 0.58 | 0.37 ± 0.08a | 0.40 ± 0.11a | 1,000 |
| 2-Hexanone | µg L ⁻¹ | 1.2 | 0.6 ± 0.0a | 1.7 ± 0.1b | n.a. |
| Ethylbenzene | µg L ⁻¹ | 0.56 | 0.28 ± 0.00a | 0.56 ± 0.18a | 700 |
| Total xylenes | µg L ⁻¹ | 1.1 | 1.2 ± 0.1a | 2.4 ± 0.4b | 10,000 |
| TPH | mg L ⁻¹ | — | 0.73 ± 0.02a | 1.24 ± 0.07b | n.a. |

* Also detected in method blanks run with these samples.

† n.a. = no applicable State or Federal standard is set.

Statistically significant differences are designated by different lower-case letters.

Table 6. Total extractable concentrations of TPH and BTEX constituents in organic-contaminated soils.

| Compound | Units | Oil/water sep. pond | | Cell 21 oiled peat | | Fire training pit | |
|-----------------------------|-----------------------|---------------------|----------|--------------------|----------|-------------------|----------|
| | | Untreated | Treated | Untreated | Treated | Untreated | Treated |
| Benzene | $\mu\text{g kg}^{-1}$ | n.d.(20)* | n.d.(20) | 7030 | n.d.(54) | 621 | n.d.(25) |
| Toluene | $\mu\text{g kg}^{-1}$ | 43 | 115 | 121,000 | 713 | 8040 | 25 |
| Ethylbenzene | $\mu\text{g kg}^{-1}$ | 39 | 27 | 138,000 | 2,290 | 7010 | n.d.(25) |
| Total xylenes | $\mu\text{g kg}^{-1}$ | 185 | 360 | 584,000 | 11,500 | 29,500 | 62 |
| Total volatile hydrocarbons | mg kg^{-1} | 8.25 | 6.66 | 10,600 | 164 | 518 | 2.8 |
| TPH | mg kg^{-1} | 39,600 | 4,870 | 111,000 | 39,000 | 35,500 | 38,700 |

* n.d. = not detected at the stated minimum laboratory reported level in parentheses.

Table 7. Total extractable concentrations of TPH and BTEX constituents in TCLP extracts of organic-contaminated soils.

| Compound | Units | Oil/water sep. pond | | Cell 21 oiled peat | | Fire training pit | |
|-----------------------------|----------------------|---------------------|---------|--------------------|---------|-------------------|---------|
| | | Untreated | Treated | Untreated | Treated | Untreated | Treated |
| Benzene | $\mu\text{g L}^{-1}$ | n.d.(1) † | n.d.(1) | n.d.(1) | n.d.(1) | 110 | n.d.(1) |
| Toluene | $\mu\text{g L}^{-1}$ | 3.6 | 4.9 | 5.6 | 11 | 97 | 6.2 |
| Ethylbenzene | $\mu\text{g L}^{-1}$ | n.d.(1) | n.d.(1) | 64 | 8.3 | 33 | n.d.(1) |
| Total xylenes | $\mu\text{g L}^{-1}$ | n.d.(1) | n.d.(1) | 308 | 54 | 183 | 1.7 |
| Total volatile hydrocarbons | mg L^{-1} | 0.183 | 0.026 | 1.93 | 0.446 | 1.00 | 0.169 |
| TPH | mg L^{-1} | 2.93 | 1.06 | 0.718 | 2.72 | 1.92 | 1.93 |

* n.d. = not detected at the stated minimum laboratory reported level in parentheses.

line and diesel range) volatile hydrocarbons in these samples were not present at very high concentrations to begin with (those constituents would have long since been lost from the soil/water separator pond), and as such, there was not a large reduction in the total volatiles for these samples. As shown by the BTEX values, there is no benzene either before or after DCR treatment, and it appears that the toluene and total xylenes may have been slightly liberated by the increased surface area of the dry, finely dispersed product compared to the wet pond sludge that originally made up the sample. TPH in TCLP extracts was reduced by a factor of three, and total volatile hydrocarbons were reduced by a factor of six (Table 7). The individual BTEX constituents were either not detected or just at the limit of detection, both before and after DCR treatment.

The Cell 21 oiled peat was heavily contaminated with JP-4 and other volatile fuels. There was a dramatic reduction in both the extractable TPH and total volatile hydrocarbons after DCR treatment (Table 6). Benzene and toluene were reduced by over two orders of magnitude, and the other volatile constituents were reduced by a factor of 50 to 60. The TCLP data for these samples were somewhat more variable (Table 7). TPH in TCLP extracts appeared to increase slightly; this

is presumably due to the increased surface area of the dry, finely dispersed product compared to the wet peat sample, which would be more difficult to leach. The leachable total volatile hydrocarbons were reduced as were ethylbenzene and total xylenes (Table 7).

For the Fire Training Pit samples, the majority (>98 %) of the hydrocarbon contamination would come from higher-molecular-weight diesel residuals which had not been volatilized or burned off during fire training exercises. Therefore, the total extractable TPH constituents remaining in the soil/tar would not be expected to be altered significantly by the DCR process (Table 6). The DCR process is designed to convert liquid (mobile) hydrocarbons into a solid nonmobile phase, which will resist all natural forms of migration (i.e., surface runoff and groundwater), but not necessarily extraction by organic solvents such as methylene chloride. Therefore, it is not surprising to see the high extractable TPH values both before and after treatment in this instance. Those volatiles that were still present in the sample at 518 ppm were reduced to less than 3 ppm during the exothermic reaction; this was also reflected in the significant reductions of BTEX constituents to nearly nondetectable levels. For these Fire Training Pit samples, there was essentially no change

in the leachable TPH (Table 7), a very significant reduction was observed in the total volatile hydrocarbons, and one to two orders of magnitude reductions were observed for the individual BTEX constituents.

Both volatilization and $\text{Ca}(\text{OH})_2$ encapsulation may have played a role in the disappearance of organic constituents. Lower-molecular-weight volatile constituents such as BTEX are no doubt lost to volatilization; however, intermediate- and higher-molecular-weight petroleum hydrocarbons are probably largely sequestered into the newly formed $\text{Ca}(\text{OH})_2$ matrix.

Comparison of TCLP extract organic concentrations to Federal Drinking Water Standards (Table 5) helps place these concentrations in perspective. The benzene concentration from the Fire Training Pit before DCR treatment (Table 7) was the only case where a measured concentration ($110 \mu\text{g L}^{-1}$) exceeded the Federal Drinking Water Standard ($5 \mu\text{g L}^{-1}$); after DCR treatment, benzene was not detectable. In all other cases, the organic concentrations were well below drinking water standards and therefore pose minimal pollution danger for surface or groundwaters.

Rocky Mt. Arsenal study

Two basic analytical approaches are currently utilized by the U.S. EPA to evaluate reduction in contaminant mobility and total constituent concentrations. These are Total Waste Analyses (organic solvent extraction followed by GC or GC/MS analyses) and leachability usually by the TCLP test. The volatile lower molecular weight alkylated- and chlorinated-benzenes in the RMA soil sample were essentially eliminated during the DCR Process. This is due to volatilization or

steam stripping during the exothermic hydration of CaO to $\text{Ca}(\text{OH})_2$, and in field implementation these constituents can be captured using transportable treatment units equipped with modular emissions control systems. Their removal is important in that they constitute the more water-soluble constituents, which can contribute to leachate or groundwater contamination if not otherwise controlled.

With regard to the pesticides and semivolatile organics in the RMA soils, it should be emphasized again that the DCR Process is not a destructive technology. Any liquid (or solubilized) organic wastes treated by the DCR process are homogeneously dispersed into very fine (submicron sized), hydrophobic particles. Since the pesticides present in the RMA soil samples are for the most part solids under ambient-temperature conditions, the ADM soy oils were added in an effort to partially "solubilize" them and facilitate transfer to the CaO before hydration. Therefore, the slight increase in the gravimetric oil and grease value (Table 8) for the 64.7% reagent addition is no doubt due to the addition of the ADM soy oil. This increase is partially offset by oil sequestration/adsorption (even against organic solvent extraction) into the voids, cracks, and fissures of the newly formed $\text{Ca}(\text{OH})_2$ generated during the DCR Process. More importantly, there is a significant decrease in the total resolved pesticides in the 64.7% reagent addition as measured by ECD GC at SOUND/epic, and this is also reflected in the individual pesticides reported by the Environmental Lab. These reductions in total and individual pesticide concentrations are believed to be due primarily to simple dilution from DCR reagent addition. Similar reductions are noted for

Table 8. Summary of selected constituent analyses of RMA Basin F soil sample no. 24216 at different levels of DCR reagent addition with and without compaction.

| <i>Waste constituent</i> | <i>Raw waste before treatment</i> | <i>64.7% DCR reagent addition (loose)</i> | <i>27.4% DCR reagent addition (loose)</i> | <i>27.4% DCR reagent addition (compacted)</i> |
|--|-----------------------------------|---|---|---|
| Gravimetric oil & grease ¹ (mg/kg dry wt) | 10,700 | 12,900 | 41,800 | 15,200 |
| Total resolved pesticides ¹ | | | | |
| ECD GC (mg/kg dry wt.) | 3,270 | 2,150 | 2,110 | 1,110 |
| Aldrin (ng/g dry wt.) | 390,000 | 270,000 | N.A. | 350,000 |
| Dieldrin (ng/g dry wt.) | 260,000 | 180,000 | N.A. | 220,000 |
| Endrin (ng/g dry wt.) | 140,000 | 100,000 | N.A. | 120,000 |
| 1,2,4-Trichlorobenzene (ng/g dry wt.) | 210 | 120 | N.A. | < 16 |
| Hexachlorobutadiene (ng/g dry wt.) | 6,900 | 630 | N.A. | 750 |

Analyses denoted by superscript one (1) completed by SOUND/epic, all others by U.S. Army Corps of Engineers Environmental Laboratory, Hubbardston, Massachusetts.
N.A. – Not analyzed.

Table 9. Summary of TCLP leachable constituent analyses on RMA Basin F soil sample no. 24216 before and after DCR treatment.

| Waste constituent | Raw waste before treatment (µg/L) | 64.7% DCR | 27.4% DCR | 27.4% DCR | CA STLC regulatory limit (µg/L) |
|------------------------|-----------------------------------|---------------------------------|---------------------------------|-------------------------------------|---------------------------------|
| | | reagent addition (loose) (µg/L) | reagent addition (loose) (µg/L) | reagent addition (compacted) (µg/L) | |
| | | | Rep. 1 | Rep. 2 | |
| Aldrin | 52 | 30 | 4.0 | 4.8 | n.a. |
| Dieldrin | 90 | 51 | 31 | 42 | n.a. |
| Endrin | 74 | 44 | 20 | 28 | 20 |
| 1,2,4-Trichlorobenzene | < 1.9 | < 1.9 | N.A. | | n.a. |
| Hexachlorobutadiene | 3.4 J | < 1.8 | N.A. | 500 | n.a. |

CA STLC – State of California soluble threshold limit concentration.

J – Estimated value; less than the practical quantitation limit.

n.a. – Not applicable.

N.A. – Not analyzed.

most of the semivolatile constituents with an order of magnitude decrease in hexachlorobutadiene (presumably from volatilization).

In the low-reagent case (27.4%), the gravimetric oil and grease concentration increased more than was the case for the high-reagent addition (Table 8). This is particularly true with the loose 27.4% product before compaction, and reflects the fact that less CaO was added, so there would be less sequestering of the soy oil against organic solvent extraction. With subsequent compaction, however, it is more difficult to extract the “oil and grease” with organic solvents, and a concomitant decrease in gravimetric oil and grease content is observed. As noted with the higher DCR reagent additions, significant reductions in total resolved pesticides by ECD GC are observed, and this reduction is further improved with compaction. No individual pesticide data are available for the loose 27.4% DCR-treated product, but with the compacted product, individual constituent concentrations are reduced, as expected, to an intermediate value between those observed in the raw soil and the 64.7% DCR-treated material (Table 8). The reductions of aldrin, dieldrin, and endrin can be accounted for by a simple dilution with reagent CaO. The reduction of total resolved pesticides in the compacted sample, however, cannot be due entirely to dilution and implies some sequestration against solvent extraction due to either microencapsulation or macroencapsulation.

The TCLP test is carried out using an acidic leaching solution to mimic an acidic landfill environment. Table 9 presents the results obtained on the “soil-amended Basin F sludge” sample before and after DCR treatment. These are worst-case data, in that all TCLP testing on treated waste

material was performed on the powdered DCR product in a noncompacted state. There were no volatile constituents identified in the leachate of the DCR-treated soil. The TCLP leachable pesticide data show an even more significant improvement with DCR-treated sample compaction. Significant reductions in leachable aldrin, dieldrin, and endrin were observed after the initial DCR treatment at 64.7% reagent addition (Table 9). When the reagent addition was dropped to 27.4% and the sample was compacted, even further reductions in leachable pesticides were observed. In contrast to the 64.7% reagent addition, these reductions at the low reagent addition cannot be attributed solely to reagent dilution of the soil. Because of the interest in pesticide leachability, these later tests were run in duplicate, and in one case, the leachable endrin was measured right at the RCRA limit of 20 ppb. In the other replicate, endrin was just slightly higher at 28 ppb.

Palmerton zinc smelter study

Table 10 summarizes the total, TCLP-extractable, and water-extractable heavy metal concentrations for the clean soil, the contaminated Palmerton soil, and the DCR-treated Palmerton soil. The clean soil was, in fact, much cleaner with respect to total heavy metals than the Palmerton soil. Normal metal ranges for uncontaminated soils are as follows: Zn = 10–300 µg g⁻¹, Pb = 2–200 µg g⁻¹, Cu = 2–100 µg g⁻¹, and Cd = 0.01 to 0.70 µg g⁻¹ (Lindsay 1979). By these standards, the clean soil is a normal uncontaminated soil, and the Palmerton soil is grossly contaminated. There were no differences in total heavy metals between the Palmerton soil and the DCR-treated Palmerton soil. This is because the DCR treat-

Table 10. A summary of the soil analyses for the Palmerton zinc smelter study (mean \pm 1 SD; $n = 4$).

| Element | Total metals ($\mu\text{g/g}$) | | | TCLP extracts ($\mu\text{g/mL}$) | | | Water extracts ($\mu\text{g/mL}$) | | |
|-----------|----------------------------------|-----------------|-----------------|------------------------------------|-----------------------|-----------------------|-------------------------------------|-----------------|-----------------|
| | Clean* | Contam. | DCR | Clean | Contam. | DCR | Clean | Contam. | DCR |
| Zinc | 31 \pm 1 | 29000 \pm 816 | 29500 \pm 577 | 0.21 \pm 0.11 | 588 \pm 29 | 1.9 \pm 0.8 | 0.066 \pm 0.014 | 16 \pm 2 | 1.2 \pm 0.8 |
| Lead | 5.6 \pm 0.1 | 1850 \pm 58 | 1900 \pm 82 | <0.31 | 8.0 \pm 0.6 | 2.2 \pm 0.3 | <0.30 | <0.30 | 2.4 \pm 0.7 |
| Copper | 16 \pm 1 | 248 \pm 10 | 252 \pm 10 | <0.012 | 0.72 \pm 0.04 | 0.26 \pm 0.07 | 0.014 \pm 0.017 | <0.012 | 0.54 \pm 0.08 |
| Cadmium | <0.51 | 155 \pm 6 | 160 \pm 0 | <0.0042 | 4.0 \pm 0.2 | <0.0041 | <0.0041 | 0.29 \pm 0.03 | <0.0041 |
| Silver | <1.7 | 7.0 \pm 1.5 | 6.4 \pm 0.1 | <0.014 | <0.014 | <0.014 | <0.014 | <0.014 | <0.014 |
| Arsenic | 5.2 \pm 0.4 | 78 \pm 5 | 85 \pm 4 | <0.45 | <0.45 | <0.45 | <0.45 | <0.45 | <0.45 |
| Beryllium | 0.22 \pm 0.01 | 1.01 \pm 0.06 | 0.94 \pm 0.03 | <0.00045 | 0.00053 \pm 0.00005 | 0.00098 \pm 0.00015 | <0.00045 | <0.00045 | <0.00045 |
| Chromium | 13 \pm 1 | 24 \pm 3 | 21 \pm 2 | <0.015 | <0.015 | <0.015 | <0.015 | <0.015 | <0.015 |
| Mercury | 0.015 \pm 0.006 | 1.5 \pm 0.1 | 1.5 \pm 0.1 | <0.0002 | <0.0002 | <0.0002 | <0.0002 | <0.0002 | <0.0002 |
| Nickel | 14 \pm 0 | 29 \pm 1 | 26 \pm 1 | <0.017 | 0.12 \pm 0.01 | <0.017 | <0.017 | <0.017 | <0.017 |
| Antimony | <34 | <36 | <37 | <0.30 | <0.30 | <0.30 | <0.30 | <0.30 | <0.30 |
| Selenium | <0.95 | 8.6 \pm 0.4 | 9.2 \pm 0.4 | <0.90 | 7.0 \pm 0.4 | <0.90 | <0.90 | <0.90 | <0.90 |
| Thallium | <0.38 | 0.42 \pm 0.06 | 0.52 \pm 0.06 | n.a. [†] | n.a. | n.a. | n.a. | n.a. | n.a. |

* The soils analyzed were a Charlton silty sand (the clean soil), the Palmerton site soil (contaminated), and the DCR-treated Palmerton site soil.

[†] Not analyzed.

ment immobilizes heavy metals but does not physically remove them from the soil. The average total Zn, Pb, and Cd concentrations in the Palmerton soil of 29,000, 1900, and 160 $\mu\text{g g}^{-1}$ are somewhat lower than those cited by Sopper (1989) of 31,000, 5200, and 1250 $\mu\text{g g}^{-1}$, respectively. Distance from the smelter and specific location on Blue Mountain are both critical factors with respect to soil contamination at Palmerton (Buchauer 1973, Sopper 1989).

For the TCLP extracts, the Palmerton soil had higher concentrations of Zn, Pb, Cu, Cd, Ni, and Se than either the clean soil or the DCR-treated Palmerton soil. The Palmerton soil exceeded TCLP regulatory limits for Pb (5.0 $\mu\text{g mL}^{-1}$), Cd (1.0 $\mu\text{g mL}^{-1}$), and Se (5.0 $\mu\text{g mL}^{-1}$); this soil passed regulatory limits for Ag (5.0 $\mu\text{g mL}^{-1}$), As (5.0 $\mu\text{g mL}^{-1}$), Cr (5.0 $\mu\text{g mL}^{-1}$), and Hg (0.2 $\mu\text{g mL}^{-1}$); regulatory levels have not been established for Zn, Cu, Be, Ni, Sb, and Tl (*Federal Register*, 29 March 1990). The DCR treatment lowered TCLP concentrations of Zn, Pb, Cu, Cd, and Se; in all cases, the DCR-treated soil passed TCLP standard for regulated heavy metals (Pb, Cd, Ag, As, Cr, Hg, and Se).

The Palmerton soil had higher levels of water soluble Zn and Cd than the DCR-treated Palmerton soil (Table 10). On the other hand, water-soluble Pb and Cu concentrations were higher in the DCR-treated Palmerton soil than in the contaminated Palmerton soil. The DCR extracts had comparable levels of heavy metals in the TCLP and water extracts (Table 10). This suggests that the alkalinity of the DCR treatment neutralized the acetic acid used in the TCLP test. During laboratory TCLP tests, it was clear that the aromatic bite of acetic acid was missing from the DCR-treatments. The real comparison between the TCLP and the

water extractions for the DCR-treated soil is probably between a calcium acetate extraction and a water extraction, which apparently extract similar quantities of heavy metals.

Because Zn is the dominant heavy metal in these soils (Table 10), the following discussion will focus on Zn chemistry. In another report, we also discuss Cu, Pb, and Cd chemistry in leachates and plants (Marion et al., in prep.).

The DCR-treatment leachates were alkaline from the beginning of the experiments, and became progressively more alkaline with time, reaching pHs in the 11–12 range by the conclusion of the experiments (Fig. 4). The compacted core was slower in reaching high pH, indicating some vertical movement of water around the core. The clean soil and the Palmerton soil had similar pHs, in the range 6.2–7.4, until day 61 when the Palmerton soil became more acidic (pH < 6.0).

Zinc concentrations also showed a sharp increase for all treatments on day 61 (Fig. 5). This was most striking for the Palmerton soil, which reached 200 mg L^{-1} . In contrast, the levels in the other treatments were always less than 1 mg L^{-1} . The DCR treatments were effective in immobilizing Zn in the Palmerton soil.

There were no apparent differences between plant species with respect to pH (Fig. 4) or Zn (Fig. 5). The responses of perennial ryegrass and tall fescue were quite similar. Plant roots reached the experimental soil level by day 50 in all treatments, approximately 30 days after planting. Shortly thereafter, there was a sharp drop in pH in the Palmerton soil (Fig. 4) and a sharp increase in Zn leaching in all the treatments (Fig. 5). The plant roots probably acidified the soil increasing the mobility of Zn, especially in the contaminated

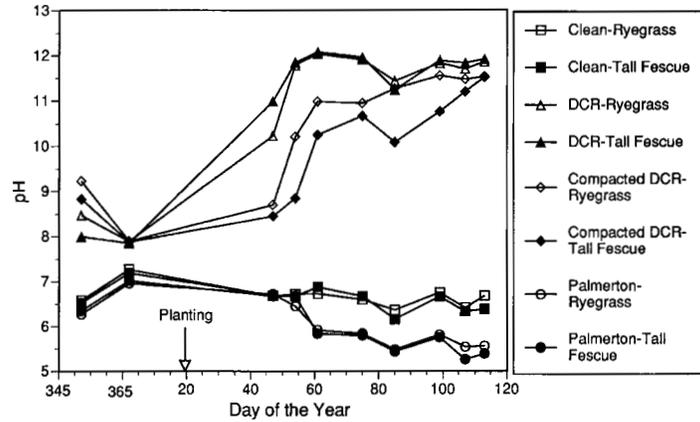


Figure 4. Leachate pH as affected by soil treatment, plant species, and time.

Palmerton soil. The alkalinity of the DCR treatments neutralized this acidity greatly reducing the mobility of Zn.

The plant root and shoot properties were analyzed using a two factorial experimental design with soil treatment (clean, Palmerton, DCR, DCR-compacted) and plant species (perennial ryegrass and tall fescue) as the main factors. In these analyses, the soil treatment-plant species interaction term was never statistically signifi-

cant. Therefore, results of these analyses will be presented by comparisons of the main factors.

Plant shoot, crown, root, and total biomass/tube were never statistically different among soil treatments or between plant species (Fig. 6). Despite this lack of statistical significance, there were clear patterns in both the soil treatments and plant species. The Palmerton treatment (contaminated) always produced the lowest biomass with respect to the other three soil treatments.

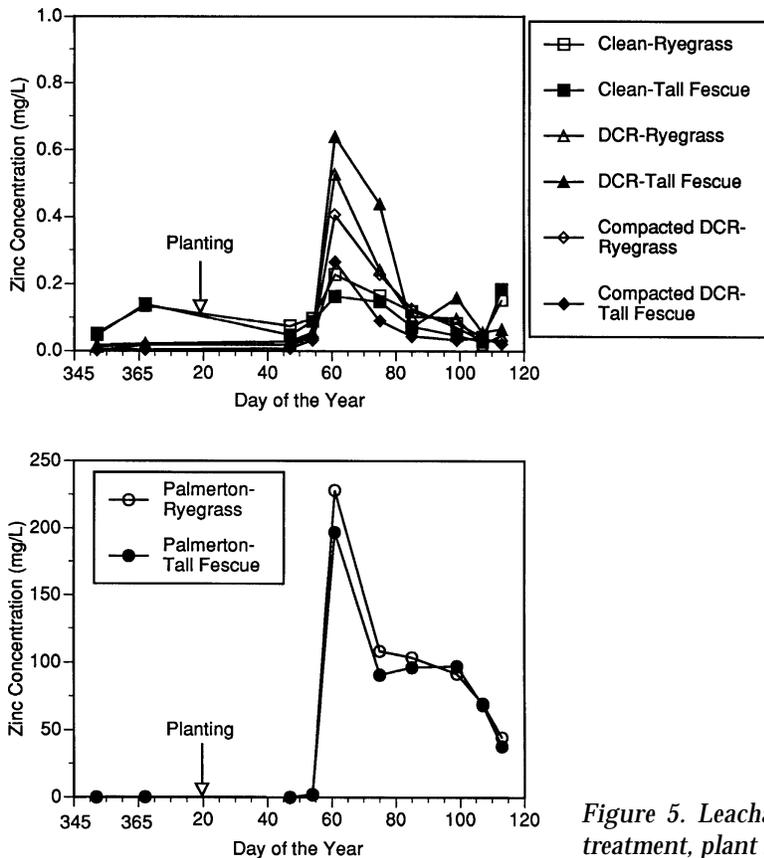


Figure 5. Leachate Zn concentration as affected by soil treatment, plant species, and time.

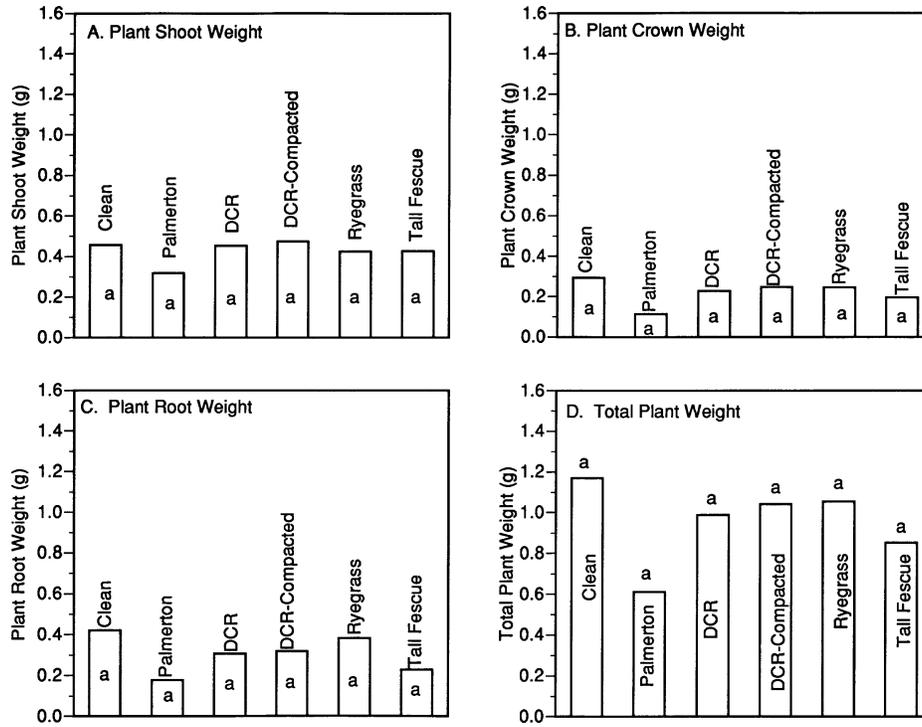


Figure 6. Plant biomass/tube as affected by soil treatment and plant species. A different lower-case letter within the four soil treatments or the two plant species implies a statistically significant difference within soil treatments or plant species, respectively.

With the exception of shoot weight, the perennial ryegrass had higher biomass than tall fescue.

Because of the consistent patterns among soil treatments (Fig. 6), we also evaluated these treatment means using “contrasts” (Steel and Torrie 1980). For example, we tested the following hypotheses:

Hypothesis 1

$$H_0: (T_1 + T_3 + T_4)/3 - T_2 = 0 \quad (3)$$

Hypothesis 2

$$H_0: (T_3 + T_4)/2 - T_2 = 0 \quad (4)$$

where T_1 is the clean treatment mean, T_2 is the Palmerton mean, T_3 is the DCR mean, and T_4 is the compacted DCR mean.

Hypothesis 1 is a test of whether the Palmerton mean is significantly different from the other treatment means. For crown weight, we rejected the null hypothesis at the 5% level of a Type I error. Relaxing the standard to the 10% level, then Hypothesis 1 would be rejected for all tested plant properties (Fig. 6). The contaminated Palmerton treatment was significantly worse than the average of the other treatments.

Hypothesis 2 is a test of whether the DCR treat-

ments are significantly different from the Palmerton treatment. For this hypothesis, none of the biomass categories were significant at the 5% level. If the statistical criterion is relaxed to the 20% level, then all null hypotheses are rejected for all four plant properties (Fig. 6).

Overall there were distinct patterns for plant growth. The perennial ryegrass grew better than the tall fescue. Growth of plants in the contaminated Palmerton treatment was poorest, and growth of plants was improved in the DCR-treated Palmerton soil.

Zn concentrations in plant shoots, crowns, and roots were always highest in the Palmerton soil and lowest in the clean soil; the DCR treatments fell between the latter two treatments (Fig. 7). There were no significant differences in Zn concentrations attributable to plant species. For Zn, there was a trend in relative concentrations that fell in the following order: roots > crowns > shoots.

Element contents in plant compartments (uptake) are a product of biomass and element concentration. For Zn, there were no significant differences in Zn uptake attributable either to soil treatment or plant species (Fig. 8). Treatments that were high in Zn concentrations, such as the

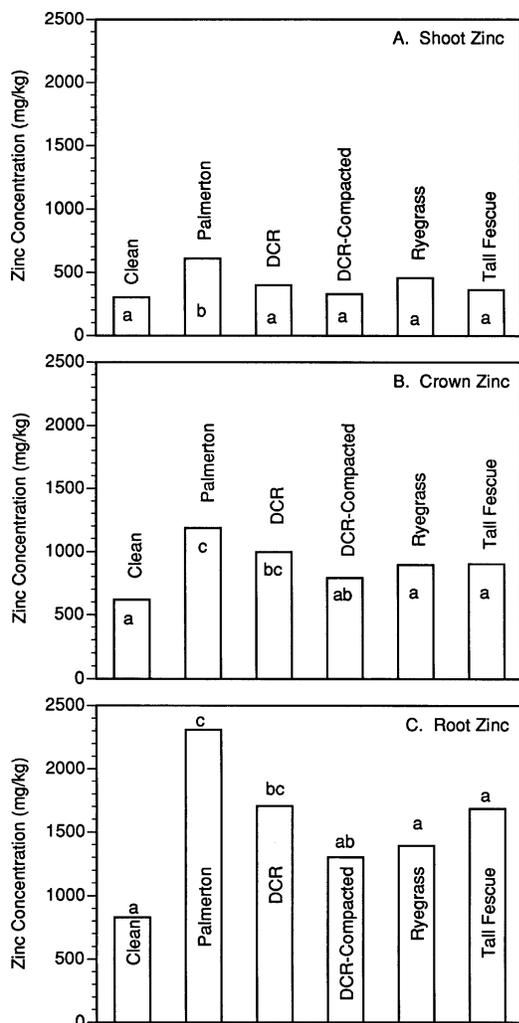


Figure 7. Plant Zn concentrations as affected by soil treatment and plant species. A different lower-case letter within the four soil treatments or the two plant species implies a statistically significant difference within soil treatments or plant species, respectively.

Palmerton soil (Fig. 7), were low in biomass (Fig. 6). Conversely, the clean soil was high in biomass but low in Zn concentrations. The consequence of this inverse relationship between biomass and Zn concentrations are Zn uptakes that are independent of soil treatment or plant species.

CONCLUSIONS

The DCR process was originally developed for the immobilization of heavily oiled sludges, water-in-oil emulsions, oil-contaminated wastes, and industrial wastes such as acid-tars (Boelsing 1988, 1995). All of these wastes contain liquid hydrocarbons. Only the three laboratory-scale tests on Shemya wastes were tests of the efficacy of the DCR process to stabilize liquid hydrocarbons. The DCR process caused a major decrease in many monitored hydrocarbons (Table 6). Both volatilization and $\text{Ca}(\text{OH})_2$ encapsulation may have played a role in the disappearance of these

organic constituents. Lower-molecular-weight volatile constituents, such as BTEX, are no doubt lost to volatilization; however, intermediate- and higher-molecular-weight petroleum hydrocarbons are probably largely sequestered into the newly formed $\text{Ca}(\text{OH})_2$ matrix. The results were, however, not consistent between wastes, indicating that the specific nature of the wastes will play a major role in the efficacy of the DCR process to remediate the wastes.

We also examined two organic wastes that were solids at the prevailing temperature. One was the asphalt tar from Shemya, and the other was the pesticides from Rocky Mt. Arsenal. In neither case was there a significant overall improvement in chemical properties due to the DCR treatment (Tables 4, 5, 8, 9). In some cases, there were actual increases in organic concentrations; in other cases, reductions in organic concentrations could be accounted for primarily as a dilution effect. It would appear that unless the hydro-

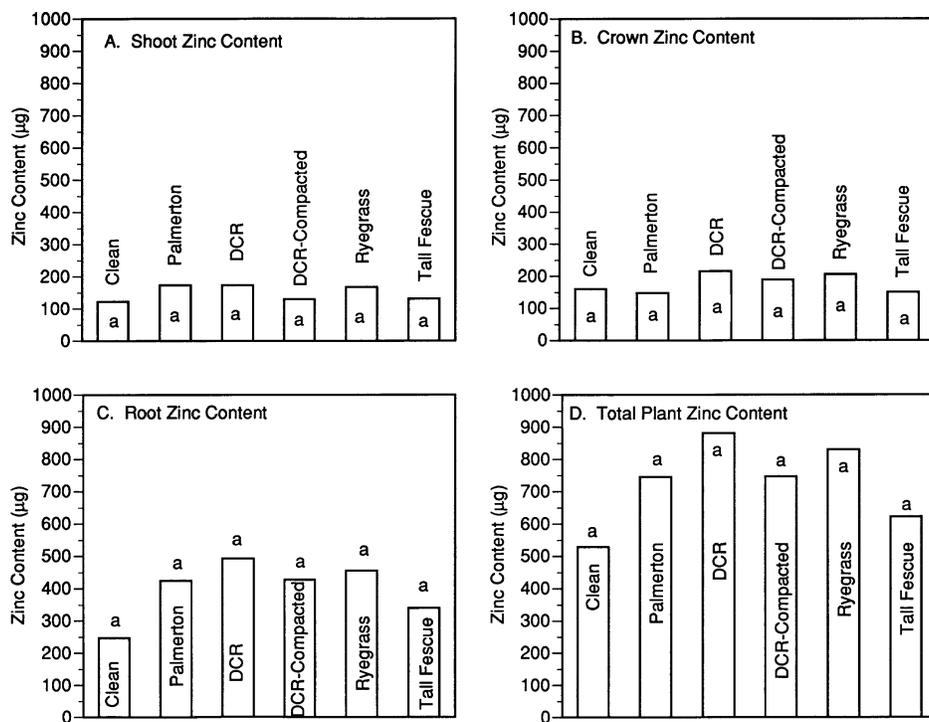


Figure 8. Plant Zn contents/tube as affected by soil treatment and plant species. A different lower-case letter within the four soil treatments or the two plant species implies a statistically significant difference within soil treatments or plant species, respectively.

phobic CaO can readily disperse into the organic phase, the DCR process is not effective in stabilization of organics.

On the other hand, the DCR process is strongly dehydrating. Application of the DCR process to the solid asphalt tar from Shemya produced a drier, more soil-like, material with hydrophobic properties. This improved the physical properties for potential reuse as road subgrade or landfill covers.

Heavy metal immobilization would seem a natural application of the DCR technology because many heavy metals form insoluble hydroxides and carbonates (Lindsay 1979). In fact, the DCR treatment greatly reduced the mobility of Zn through greenhouse soil columns (Fig. 5). The acidification of the soil presumably due to root growth was neutralized by the alkaline DCR treatment, which greatly reduced Zn mobility. Adsorption of Zn onto the $\text{Ca}(\text{OH})_2$ and CaCO_3 and precipitation of Zn hydroxides and carbonates may also have played a role in immobilizing Zn.

Zn concentrations in plant shoots, crowns, and roots were always highest in the contaminated Palmerton soil and lowest in the clean soil; the DCR treatments fell between the latter two treat-

ments (Fig. 6). No significant differences were apparent in Zn concentrations attributable to plant species. For Zn, there was a trend in relative concentrations that fell in the following order: roots > crowns > shoots. Distinct patterns for plant growth (biomass production) were present in the heavy metal experiments. The perennial ryegrass produced more biomass than the tall fescue. Growth of plants in the contaminated Palmerton treatment was poorest, and growth of plants was improved in the DCR-treated Palmerton soil. Judging by the Zn concentrations in plant tissue and biomass production, we consider that the DCR treatment improved plant growth.

RECOMMENDATIONS

Overall the DCR process was successful in stabilizing liquid organics and heavy metals but not solid-phase organics. Stabilization of liquid organics and heavy metals have been demonstrated but not under the rigorous experimental design and statistical testing that were used in our studies. There was an inconsistency between wastes in the efficacy of the DCR process. This, however, should not be a serious impediment for the utilization of the DCR process because the efficacy of

the DCR process for a specific waste is always ascertained at the laboratory scale prior to field implementation. If the DCR process is ineffective in remediating a specific waste at the laboratory scale, then field implementation should not be undertaken.

This work also demonstrated a favorable influence on plant growth of the DCR treatment of heavy metal contaminated soil. The high alkalinity of the DCR product helped neutralize the heavy metal mobility, which led to improved plant growth. This work demonstrated that the DCR product is compatible with revegetation of contaminated sites and can be used for the remediation of severely contaminated soils, where several technologies may be necessary to fully remediate a site.

Following laboratory verification for a specific waste, we can recommend the DCR process for the field remediation of liquid organics and heavy metal contaminated materials.

COMMERCIALIZATION/TECHNOLOGY TRANSFER

The DCR technologies are patented processes. SOUND/epic has an exclusive license to market the DCR technology in the United States. Companies or agencies interested in using this technology should contact Richard W. McManus, Executive Vice President, at SOUND/epic (214-393-6965).

Our approach in this CPAR project has been to rigorously test the efficacy of these technologies and to publicize our results through presentations, publications, and a video. Below is a list of these products emanating from the CPAR project. Copies of the publications and the video are available from Giles M. Marion (603-646-4676). The video demonstrates a small-scale field implementation of the DCR process. Although this particular demonstration was not successful because of the solid state of the contaminant, it does demonstrate how contaminated soils are processed in the field. Two presentations of this project (1994 and 1997) were made at the annual Hazardous Toxic and Radioactive Waste (HTRW) Innovative Technology Transfer Workshops. These workshops are designed to introduce innovative technologies for environmental clean-up within the U.S. Army Corps of Engineers. The presentation at the 1994 Soil Science Society of America meeting and the ASA Special Publication resulting from this meeting are especially noteworthy for DOD. This was a Symposium on DOD Cleanup of Contaminated

Sites organized by Dr. C.R. Lee of the Waterways Experiment Station. This publication should receive wide circulation within DOD at all management levels dealing with cleanup of contaminated sites.

Typically DCR stabilization involves either a direct mixing of reagents and contaminated soil in-situ (landfarming) or an ex-situ treatment followed by return of the DCR product to the field, covering with topsoil, and finally, revegetation. The latter was the process that we simulated in the greenhouse heavy metal study. The USACE guidance specifications most relevant to the DCR process are *Bioremediation using Landfarming Systems* (CEGS-02287) and *Solidification/Stabilization of Contaminated Material* (CEGS-02445). However, neither of these guidance documents speaks directly to the way in which the DCR process is generally implemented. Nevertheless, the bioremediation guidance requires that the pH be maintained in the range from 5.0 to 8.0. This specification may preclude direct landfarming because of the high alkalinity of the DCR product and leachate (Fig. 4). The alternative, ex-situ treatment and covering with topsoil, was compatible with plant growth (Fig. 6) and presumably microbial activity. Other than pH, the DCR process is compatible with USACE guidance specifications.

LIST OF PRESENTATIONS, PUBLICATIONS, AND VIDEOS

Presentations

Dispersion by chemical reaction treatment of asphalt tar. Contributed paper, Fourth HTRW Innovative Technology Transfer Workshop. Omaha, Nebraska. July 1994.

Dispersion by chemical reaction treatment of asphalt tar, Eareckson Air Force Station, Shemya, Alaska. Contributed paper, Soil Science Society of America annual meeting, Seattle, Washington. November 1994.

Site remediation via dispersion by chemical reaction (DCR). Contributed paper, Seventh HTRW Innovative Technology Transfer Workshop. Las Vegas, Nevada. March 1997.

Heavy metal remediation via the dispersion by chemical reaction process. Contributed paper, Fourth International Conference on the Biochemistry of Trace Elements. Berkeley, California. June 1997.

Publications

Brar, G.S., and G.M. Marion (1995) Dispersion by chemical reaction technology to stabilize asphalt tar, Eareckson Air Force Station, Shemya, Alaska.

USA Cold Regions Research and Engineering Laboratory, Special Report 95-11.

Marion, G.M., G.S. Brar, J.R. Payne, and M.A. Stanka (1997) Dispersion by chemical reaction technology to stabilize organic-contaminated soils, Shemya, Alaska. ASA Special Publication.

Marion, G.M., G.S. Brar, D.K. Pelton, A.J. Palazzo, and J.R. Payne (in preparation) Heavy metal remediation via the dispersion by chemical reaction process. *Journal of Environmental Quality*.

Marion, G.M., J.R. Payne, and G.S. Brar (1997) Site remediation via dispersion by chemical reaction (DCR). USA Cold Regions Research and Engineering Laboratory, Special Report 97-18.

Payne, J.R., E.C. Cronick, J.P. Bowman, S.K. Fitzhugh, and J. Bayliss (1994) Dispersion by chemical reaction (DCR) treatment of asphalt tar: Results of pilot-scale demonstrations at Eareckson Air Force Station, Shemya, Alaska. USA Cold Regions Research and Engineering Laboratory, Internal Report No. 1148.

Payne, J.R., and G.M. Marion (1997) Dispersion by chemical reaction testing of Rocky Mountain Arsenal Basin F waste soils. USA Cold Regions Research and Engineering Laboratory, Special Report 97-3.

Video

DCR Technology in the Aleutians. 11 minutes. USA Cold Regions Research and Engineering Laboratory.

LITERATURE CITED

BASF Corporation (1983) A green hill by the year 2000 (Public Affairs Information). BASF Aktiengesellschaft, West Germany. p. 4.

Blacklock, J.R., R.C. Joshi, and P.J. Wright (1982) Pressure injection grouting of landfills using lime and fly ash. In *Proceedings of Conference on Grouting in Geotechnical Engineering*. 10-12 February, New Orleans, Louisiana.

Blacklock, J.R., R.C. Joshi, and P.J. Wright (1984) Pressure injection grouting of landfills. *Public Works*. May, p. 4.

Boelsing, F. (1988) *Remediation of Toxic Waste Sites. DCR Technology in the Field of Immobilization and Fixation of Hazardous Compounds*. Hannover, Germany: Ministry of Economics, Technology and Traffic.

Boelsing, F. (1995) DCR technology in the field of environmental remediation. In *Remediation of Hazardous Waste Contaminated Soils*. New York: Marcel Dekker, Inc., p. 869-923.

Boynton, R.S. (1980) *Chemistry and Technology of*

Lime and Limestone. 2nd ed., New York: John Wiley and Sons.

Brar, G.S., and G.M. Marion (1995) Dispersion by chemical reaction technology to stabilize asphalt tar, Eareckson Air Force Station, Shemya, Alaska. USA Cold Regions Research and Engineering Laboratory, Special Report 95-11.

Brown, S.L., R.L. Chaney, J.S. Angle, and A.J.M. Baker (1994) Phytoremediation potential of *Thlaspi caerulescens* and bladder campion for zinc- and cadmium-contaminated soil. *Journal of Environmental Quality*, **23**: 1151-1157.

Buchauer, M.J. (1973) Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper, and lead. *Environmental Science & Technology*, **7**: 131-135.

Chamberlain, E.J. (1994) Frost effects on geotechnical waste containment systems. In *Proceedings of Symposium on Practical Application of Soil Barrier Technology*, 9 February, University of Maine, Augusta. New York: American Society of Civil Engineers.

Chaney, R.L. (1993) Zinc phytotoxicity. In *Zinc in Soils and Plants. Proceedings of International Symposium*, University of Western Australia. Dordrecht: Kluwer Academic Publ., p. 135-150.

CH2M Hill (1990) Installation restoration plan. Stage 2. Shemya Air Force Base, Shemya, Alaska. Final work plan. Report prepared for the U.S. Air Force by CH2M Hill, Anchorage, Alaska.

Crawley, W., K.W. Brown, and D. Anderson (1984) Inplace closure of previously backfilled and active surface impoundments. In *Proceedings of 5th National Conference on Management of Uncontrolled Hazardous Waste Sites*, 7-9 November 1981, Washington, D.C.

Einhaus, R.L., I. Honarkhah, and P. Erickson (1991) Fate of polychlorinated biphenyls (PCBs) in soil following stabilization with quicklime. U.S. Environmental Protection Agency, EPA/600/2-91/052.

Fisher, G., R. Mattern, R. McCombs, J. Norgren, A. Rebert (1962) *Soil Survey of Carbon County, Pennsylvania*. Washington, D.C.: USDA Soil Conservation Service.

Francis, G.Z. (1984) *Pollution Engineering*. September, p. 37-39.

Gutschick, K.A. (1978) Lime stabilization under hydraulic conditions. In *Proceedings of 4th International Lime Congress*, 21-22 September, Hershey, Pennsylvania, p. 20.

Johnson, C.M., P.R. Stout, T.C. Broyer, and A.B. Carlton (1957) Comparative chlorine requirement of different plant species. *Plant and Soil*, **8**: 337-353.

Klass, D.L. (1984) Methane from anaerobic fermentation. *Science* **223**: 1021-1033.

- Koper, O., Y-Xi Li, and K.J. Klabunde** (1993) Destructive adsorption of chlorinated hydrocarbons on ultrafine (nanoscale) particles of calcium oxide. *Chemistry of Materials*. 5: 500–505.
- Lewis, C.J., and R.J. Boynton** (1976) Acid neutralization with lime for environmental control and manufacturing processes. *National Lime Association Bulletin*, p. 216.
- Lindsay, W.L.** (1979) *Chemical Equilibria in Soils*. New York: John Wiley.
- Malone, P.G.** (1984) Role of lime industry in waste management. *National Lime Association Meeting, 17–18 May, Charleston, South Carolina*.
- Malone, P.G., and J.H. May** (1991) Use of lime in the design of landfills for waste disposal. *National Lime Association Meeting, 22–24 April, San Diego, California*.
- Malone, P.G., L.W. Jones, R.A. Shafer, and R.J. Larson** (1987) Estimation of pollution potential of industrial waste from small-scale leaching studies. *National Lime Association Meeting, 9–10 April, Phoenix, Arizona*.
- Marion, G.M., G.S. Brar, J.R. Payne, and M.A. Stanka** (1997) Dispersion by chemical reaction technology to stabilize organic-contaminated soils, Shemya, Alaska. American Society of Agronomy Special Publication.
- Marion, G.M., G.S. Brar, D.K. Pelton, A.J. Palazzo, and J.R. Payne** (in preparation) Heavy metal remediation via the dispersion by chemical reaction process. *Journal of Environmental Quality*.
- Morgan, D.C., A.M. Asce, J.I. Novoa, and A.H. Halff** (1984) Oil sludge solidification using cement kiln dust. *Journal of Environmental Engineering*, 110: 935–947.
- Payne, J.R., E.C. Cronick, J.P. Bowman, S.K. Fitzhugh, and J. Bayliss** (1994) Dispersion by chemical reaction (DCR™) treatment of asphalt tar: Results of pilot-scale demonstrations at Eareckson Air Force Station, Shemya, Alaska. USA Cold Regions Research and Engineering Laboratory, Internal Report 1148 (unpublished).
- Payne, J.R., and G.M. Marion** (1997) Dispersion by chemical reaction testing of Rocky Mountain Arsenal Basin F waste soils. USA Cold Regions Research and Engineering Laboratory, Special Report 97-3
- Payne, J.R., R.W. McManus, and F. Boelsing** (1992) DCR treatment of oily wastes and oil-contaminated soils. In *Proceedings National Research & Development Conference on the Control of Hazardous Materials, February 1992, San Francisco, California*, p. 297–304.
- Rittenhouse, R.C.** (1993) Lime as antidote for PCBs is far from dead. *Power Engineering*. August.
- Sediak, D.L., K.E. Dean, D.E. Armstrong, and A.W. Andren** (1991) Interaction of quicklime with polychlorobiphenyl-contaminated solids. *Environmental Science and Technology* 25: 1936–1940.
- Separation and Recovery Systems** (1987) The SRS/EIF oily sludge fixation processes. Separation and Recovery Systems, Inc., Irvine, California.
- Sopper, W.E.** (1989) Revegetation of a contaminated zinc smelter site. *Landscape and Urban Planning*. 17: 241–250.
- Soundararajan, R.** (1991) Final report on the “disappearing PCBs project.” West Plains, Missouri: Environmental and Analytical Laboratories.
- Steel, R.G.D., and J.H. Torrie** (1980) *Principles and Procedures of Statistics. A Biometrical Approach*. 2nd ed. New York: McGraw-Hill.
- Such, C., and C.L. Roux** (1981) Treatment of wastes from oil spills. *Environmental Technology Letters*. 2: 161–170.
- U.S. Environmental Protection Agency** (1992) Test methods for evaluating solid waste. Third Edition, Final update I. Washington, D.C.: U.S. Department of Commerce, Report No. EPA/SW-846.
- Weeter, D.W., and L.W. Jones** (1987) Hazardous waste management utilizing lime. *National Lime Association Meeting, 9–10 April, Phoenix, Arizona*.
- Wray, T.K.** (1991) Lime. *Hazmat World*, June.
- Zenobia, K.E., and M.A. Turco** (1985) Lime—A hazardous waste stabilization agent. *ASTM Symposium on Lime for Environmental Uses, 23–28 June, Los Angeles, California*.

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