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Sparks, B. D.; Meadus, F. W.; Majid, A.; McNabb, D. H.; Guo, I.

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PREPRINT EXTENDED ABSTRACT  
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SESR - A Novel Canadian Technology for Remediating Petroleum and Heavy Metal Contaminated Soil

B.D. Sparks\*, F.W. Meadus\*, A. Majid\*, D.H. McNabb\*\* and I. Guo\*\*

\* National Research Council of Canada  
Institute for Environmental Chemistry  
Ottawa, Ontario, K1A 0R9, Canada

\*\* Alberta Environment Centre  
P. O. Bag 4000  
Vegreville, Alberta, T9B 1T4, Canada

INTRODUCTION

Spills of crude oil and petroleum products from the vast network of collection, processing, transportation and marketing facilities in North America pose a major risk to the environment. Tens of thousands of kilometres of pipelines and thousands of hectares of well-sites and facilities are needed to collect and process crude oil. Although reported losses of liquid hydrocarbons from these facilities average less than 0.01 percent of production, spills in Alberta have exceeded  $5 \times 10^6 \text{ m}^3$  annually in the 1980's (Energy Resource Conservation Board, 1991, Environment Information System, unpublished document, Calgary, Alberta). Gasoline, fuel oil and jet fuel represent 90 percent of the hazardous materials (3.6 billion tons) transported in the United States annually and account for 25 percent of the reported spills<sup>1</sup>. The United States Environmental Protection Agency estimates that 35 percent, or 840,000, of the underground fuel storage tanks are leaking<sup>2</sup>. Also, another 100,000 to 400,000 tanks, used to store other liquid petroleum and chemical substances, may be or have been leaking.

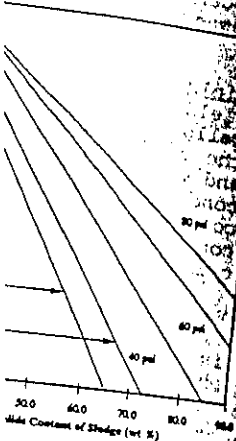
Existing technologies for clean-up of petrochemical spills have limitations with respect to costs, contaminant type and soil properties. Landfarming and landfilling, are being reduced or abandoned because of environmental concerns. New technologies are poorly suited for treating fine textured soils without adversely affecting the associated humic matter or soil mineralogy. Except for solid phase bioremediation these technologies require that the treated soil be landfilled because of impaired soil fertility. Other solvent extraction methods have been described.<sup>3</sup> In general, these processes work well with coarse material but have trouble with fine textured soils.

The Solvent Extraction Soil Remediation (SESR) process, followed by on-site biotreatment, resolves the limitations posed by many single remediation technologies. In the SESR process solvent extraction of the contaminants occurs concurrently with disaggregation and then agglomeration of the dispersed soil particles. The agglomeration process is based on the principle of immiscible liquid wetting. Soil is initially mixed with a bulk liquid phase which must be a good solvent for the contaminant but be non-wetting with respect to the particulate surfaces. A minor amount of a second liquid is required to be immiscible with the suspending phase but preferentially wet the soil particles. For the remediation of petroleum contaminated soil the two liquids of choice are a hydrocarbon solvent and water respectively. During mixing of the soil with solvent and water a slurry is formed, the contaminant is dissolved and the water wet particles are bound together by bonds formed through the wetting liquid phase. The strength of the bonds is governed by interfacial tension, the particle size and the contact angle of the wetting phase with respect to the solids. Under appropriate conditions, the solids

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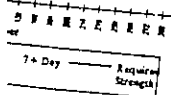
FIGURE 2

Slurry Requirements per UCS Strength Level



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Time of De-watered Sludges



will form spheroidal agglomerates the size of which can be controlled, within a selected range, by process adjustments.

A sample of high clay, petroleum contaminated soil has been successfully treated by this process. Currently, this technology is being developed to the stage whereby it could be adapted to the remediation of soil contaminated by both petroleum and heavy metals.

## MATERIALS

A brine and crude oil contaminated soil from near Erskine, Alberta was used. The soil was a black Chernozem; only the surface horizons had been contaminated with a mixture of brine and crude oil during a pipeline break between the well-site and the battery. The excavated soil was thoroughly mixed with a Rototiller before sampling, analysis indicated 5.6% hydrocarbons and 4.2% natural organic matter. Non-contaminated soil from the same site was a silty, clay loam, containing 39% sand (50-2000µm), 27% silt (2-50µm) and 34% clay (< 2µm)<sup>4</sup>.

## METHODS

A series of small scale batch tests were carried out to determine the suitability of the SESR process for treating Erskine soil. Prior to the laboratory tests the samples were delumped to remove small stones. Several solvents were compared and different combinations of washings and dispersion/agglomeration treatments were tested<sup>5</sup>.

Solid state <sup>13</sup>C NMR was used to characterize the organic material in samples of treated, contaminated and uncontaminated soils. Cross polarization (CP/MAS) and Bloch decay techniques were used for solid organics (humics) and mobile, liquid organics (contaminants) respectively.

Agglomerated, treated soil was placed in bottom drained pots and leached to remove brine. Plant growth tests were carried out in a controlled environment chamber, after the soil had been inoculated with 1% uncontaminated earth in order to restore the natural micro-organism population.

## RESULTS AND DISCUSSION

The soil agglomerates produced in the batch tests had size distributions similar to natural soil aggregates but were three times more stable; solvent type had no effect on these properties. After recovery of residual solvent, the extracted soil aggregates contained approximately 0.1-0.4% hydrocarbon; this corresponded to 95-98% recovery of the contaminant<sup>5</sup>. As expected highly aromatic solvents were the most effective for heavy oil removal<sup>6</sup>.

The retention of a resident organic pool, in unchanged form, most likely contributed to the excellent stability of the agglomerates produced from the extracted soil. Maintenance of stable aggregates is crucial to the uptake of soil quality and its stability to support crop production. NMR spectra for a) untreated and b) treated soil are shown on Figure 1. The Bloch decay method gave two broad peaks corresponding to aromatics (75-150ppm) and aliphatic (0-30ppm) species. This spectrum is typical for Alberta crude oils. Remediated soil (spectrum b) showed no evidence of residual liquid organic contaminants. The CP/MAS <sup>13</sup>C NMR spectra for treated and untreated soil are shown superimposed on Figure 2c). The spectra were remarkably similar and are typical of soil humic matter<sup>7</sup>.

The tilth of the remediated soil was evaluated by growing a crop of field peas. After six weeks the plants growing in the restored soil were nearly as large as those growing in the uncontaminated earth;

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germination was 100% in both cases. Despite nearly optimum growing conditions only one pea seed germinated in the contaminated soil.

## REMEDIATION OF HEAVY METAL CONTAMINATED SOILS

Often soil is contaminated with different types of materials each requiring a different remediation approach. For example petroleum contaminated soil may also contain heavy metals which represent more of a hazard than the petroleum itself. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. The SESR process in its present state will not separate heavy metals unless they are directly associated with the oily material. Although agglomerated soil has been demonstrated to be ideal for a subsequent leaching step to remove soluble inorganic components this additional treatment would represent a major increase in process costs. Recently, a number of reagents have been used successfully for the extraction of non-ferrous metals from metal finishing wastes<sup>8</sup>. These materials are also soluble in solvents suitable for extraction of oily contaminants. Further test work will be carried out to determine the efficiency of extraction of heavy metals, dissolved in the soils connate water, concurrently with oil dissolution.

## CONCLUSIONS

It has been demonstrated that a fine textured, petroleum contaminated soil can be successfully remediated to produce an agglomerated product with a similar size distribution to natural aggregates but with three times the stability. Up to 98% contaminant removal could be achieved by selecting the most appropriate solvent. The humic matter in the soil was largely unchanged by the treatment. After six weeks growth, there was little difference in the size of field pea plants grown in both treated and uncontaminated soils. Currently, the process is being developed to the stage whereby it could be adopted to the remediation of soil contaminated by both petroleum and heavy metals by incorporating organic soluble chelating agents into the solvent extraction step of the process.

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SOIL

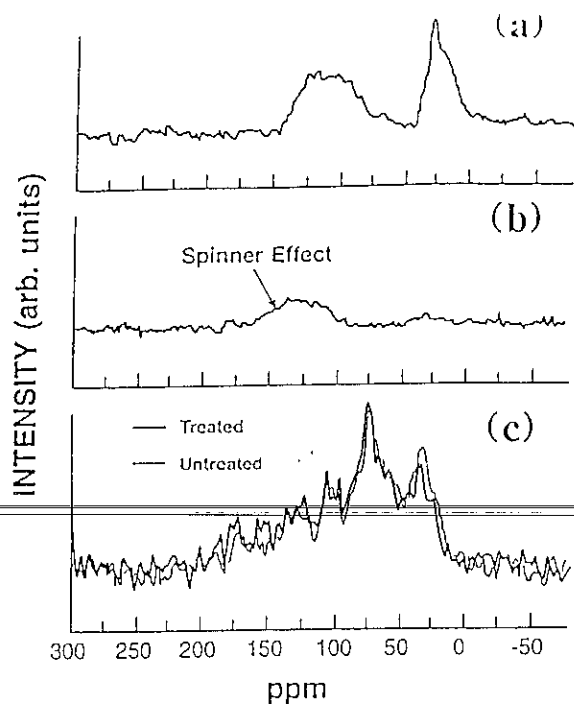


Figure 1: Bloch Decay  $^{13}\text{C}$  NMR Spectra for a) Untreated, b) Treated Soil Samples and c) CP/MAS  $^{13}\text{C}$  NMR Spectra of Humic Matter in Treated and Untreated Soils

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