NRC Publications Archive
Archives des publications du CNRC

# Concurrent removal of hydrocarbons and fixation of lead from a sample of invert drilling mud using the SESR process

Majid, Abdul; Toll, Floyd; Sparks, Bryan D.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

**Publisher's version / Version de l'éditeur:**

*Proceedings of the 18th Canadian Waste Management Conference, 1996, 1996*

**NRC Publications Record / Notice d'Archives des publications de CNRC:**
https://nrc-publications.canada.ca/eng/view/object/?id=e0ab598d-8043-4fd2-b18f-686aaedac126
https://publications-cnrc.canada.ca/fra/voir/objet/?id=e0ab598d-8043-4fd2-b18f-686aaedac126

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada
Canada

# CONCURRENT REMOVAL OF HYDROCARBONS AND FIXATION OF LEAD FROM A SAMPLE OF INVERT DRILLING MUD USING THE SESR PROCESS

Abdul Majid, Floyd Toll and Bryan D. Sparks

*National Research Council of Canada*
*Institute for Chemical Process & Environmental Technology*

## 1.0 INTRODUCTION

Contamination of soil by hazardous organic pollutants and/or heavy metals is a serious environmental problem facing the global community. Over time, these pollutants, trapped in the soil matrix, leach through inadequate holding facilities and migrate deep into the earth, finally making their way to groundwater aquifers. Once contaminated, these aquifers carry the toxins through the ecological system, bringing them into the food chain.

Typically, both heavy metals and hydrocarbon contaminants are associated with the finer particle fractions of soils and sediments. Most techniques for the removal of metals involve contacting the soil with an aqueous solution. Similarly, some processes remove hydrocarbon contaminants by aqueous washing methods. For fine textured, high clay soils these techniques tend to produce intractable sludges having poor solid-liquid separation characteristics. Other soil cleaning technologies, such as thermal desorption, are also poorly suited for treating fine textured top soils because of adverse effects on the associated humic matter or soil mineralogy. In such cases the treated soil may have to be land filled or used as subsoil because of impaired soil fertility.

At the National Research Council of Canada, liquid phase agglomeration techniques, in combination with solvent extraction, have been successfully used for the remediation of fine textured, organic contaminated soils. Agglomeration of fine and coarse particles greatly improves the efficiency of solids-liquid separation, required to achieve effective treatment. Typically, only a few extraction steps are required. As an extension of this work, metal binding materials have been incorporated into the soil agglomerates formed during the solvent extraction of organic contaminants. The combined process allows concurrent removal of organics and fixation of heavy metals. As a result, soil treatment should be more economical in terms of material handling and equipment costs, than methods which require separate extraction and leaching steps for organic contaminants and heavy metals.

In this work we present the results for tests in which the SESR process was used to treat a sample of invert drilling mud. The sample, containing 4.9 w/w% diesel fuel, was artificially contaminated with 680 ppm of leachable lead. Concurrent removal of the hydrocarbon and fixation of lead by incorporation of metal binding agents into the agglomerates was investigated. Fixation of lead was followed using the US EPA's Toxicity Characteristics Leaching Procedure (TLCP) on the dried agglomerates. The affect of these additives on the extraction efficiency of diesel was also studied.

## 2.0 EXPERIMENTAL METHODS

### 2.1 Materials

Soil - a used Diesel Invert Drilling Mud (DIDM) sample from Alberta, was used for this study. The sample was artificially contaminated by spiking with a solution of lead nitrate. The composition and properties of the contaminated sample are given in Table 1.

### 2.2 Estimation of Oil Content of Diesel Invert Drilling Mud (DIDM)

The amount of oil contained in DIDM was estimated by extracting the oil in toluene using the Dean and Stark Soxhlet method[1]; extraction was carried out for 20 hours. The extract was characterized and subsequently quantitated by GC.

### 2.3 Agglomeration Procedure

In a typical test a Waring Blendor Jar (500mL polypropylene) equipped with Teflon washers and a plastic cover was accurately weighed. To the jar were added: DIDM (100g), lead fixation reagent, additional water or sand if required, and solvent (250 mL). The jar was weighed at each stage in order to determine the amount of each ingredient added. The contents were agitated at high shear for 1 minute followed by 2 minutes at low shear. The solution was carefully drained through a preweighed glass filter paper and the filtrate collected in a preweighed 250 mL glass measuring flask. After the filtration was finished, the filter paper was reweighed in order to calculate the amount of solids and solution retained. The filter paper was dried at 110°C and the amount of solids lost on the filter paper determined; the amount of solution was calculated by difference. The flask containing the solution was also reweighed in order to obtain the amount of solution collected. The amount of agglomerates plus residual contaminant and solvent was obtained from the weight of jar plus contents after draining the solution. This completed

Syncrude analytical methods for oil and sand bitumen processing, J.T. Bulmer and J. Star Editors. Alberta ds Information Centre, Edmonton, AB, pp. 46-51 (1979).

stage 1. The process was repeated four more times with fresh solvent. In the subsequent stages the high shear agitation was maintained for 30 seconds instead of 1 minute as in stage 1. Total agitation time for stages 2 to 4 remained 2.5 minutes.

## 2.4 Determination of Diesel

The extract was analyzed employing a Varian Model 3300 GC equipped with an FID detector and a temperature gradient program. The column used was a DB-5, megabore, capillary column, 30 meters in length with a 0.53 mm internal diameter and a 1.5 micron film thickness (J & W Scientific). The initial operating temperature was 50 degrees Celcius with an initial hold-time of 5 minutes. The temperature was then increased at the rate of 10 degrees per minute to a final temperature of 300 degrees Celcius and held for 5 minutes. Calibration curves were prepared using a sample of Diesel Fuel #2, from a local gas station.

## 2.5 Mass Balance Calculations for Diesel

Agglomerates obtained from stage 5, after removal of contaminant, were extracted by the Dean and Stark method to determine residual contaminant for mass balance purposes. These results are shown in Table 2.

## 2.6 Drying Tests

The agglomerated soil was dried in a vacuum oven at various temperatures with subsequent recovery of residual solvent by condensing in a dry ice trap.

## 2.7 Recovery and estimation of residual solvent in dried agglomerates

The residual solvent (toluene) in the dried agglomerates was estimated using three independent techniques:

1. **Supercritical Fluid Extraction (SFE).** Toluene was first extracted by a Supercritical Fluid Extraction (SFE) method using an ISCO SFX-210 extraction unit with $CO_2$ (SFE grade, air products) and an ISCO Model 260D syringe pump operating at 5000 psi. The quantitative estimation of the residual toluene in the SFE extracts was carried out by GC/FID.

2. **Methanol Extraction.** Dried agglomerates (10 g) were weighed into a tared 20-mL vial, using a top-loading balance. Ten mL of HPLC grade methanol was added quickly to

the vial, which was then capped and shaken by hand for two minutes[2]. The contents were centrifuged and an aliquot of the extract analyzed by GC.

**3. Headspace GC.** Dried agglomerates (1 g) were weighed into a tared 10 mL glass vial, which was then sealed using a Teflon coated silicon rubber septum and aluminum cap. The vials were thermostated at 60 °C for two hours in an aluminum block heater. An aliquot of the headspace was then analyzed by GC.

### 2.8 Leaching Tests

The TCLP extractions were performed according to the methods described in the US Federal Register[3] and specified in SW-846[4].

### 2.9 Analysis of Lead

Lead was analyzed by Inductively Coupled Plasma Spectroscopic Analysis (ICP). Mass balances for total lead were carried out by analyzing leached as well as unleached samples of blank spiked soil and soil-additive mixtures. Screening tests for lead were carried out using Hatch Colorimeteric methods.

### 2.10 Carbon analysis of dry solids

Total carbon was determined using a Leco CR12 carbon analyzer. Organic carbon was determined after decomposing carbonate carbon with dilute hydrochloric acid; carbonate carbon was then determined by difference.

## 3.0 RESULTS AND DISCUSSION

Contaminated soils pose a significant challenge for characterization and remediation programs. The first challenge in the evaluation of any remediation process for oily wastes is the reliable estimation of the total oil content of the contaminated material. This number is essential in order to evaluate the contaminant removal efficiency of the process. Dean &

---

J. L. P. G. Walters and M. Hoffman, "Sampling and Analysis of Soils for Gasoline Range Organics", Hydrocarbon Contaminated and Groundwater, **1**, 105-132 (1991), American Chemical Society, Washington DC.

US EPA Federal Register. **51**, (142), March 1990, Office of Solid Waste, Washington DC.

US EPA - "Test Methods for Evaluation of Solid Waste: Physical/Chemical Methods", SW-846, 3rd Ed., Office of Solid Waste a rgency Response, Washington DC, Nov. 1986.

Stark extraction is the most used method for this purpose[5]. Quantitative estimation of the extent of contamination in the Diesel Invert Mud (DIM) sample used in the present investigation was carried out using this method coupled with the determination of the total diesel in the toluene and methylene chloride extracts by GC. As shown in Table 1, in the mass balance experiments we were able to account for 99.94% of the total constituents (oil, water and solids). All calculations regarding the extraction efficiency of diesel from DIM by the Solvent Extraction Soil Remediation (SESR) process are based on the amount of diesel extractable by Dean and Stark method.

### 3.1 Contaminant Removal Efficiency under Optimum Conditions of Agglomeration

Several metal binding agents were incorporated into the agglomerates during processing in order to fix lead in the spiked DIM sample. Coarse sand was used to reduce the water content of soil samples spiked with lead nitrate solutions in order to produce agglomerates in the 1-2 mm size range. The effect of these additives on the efficiency of diesel removal by the SESR process was investigated. Results from batch tests using hexane as a solvent, are summarized in Table 3 and graphically represented in Figure 1.

Under optimum conditions of agglomeration, close to 100% contaminant can be removed in a five stage extraction step. Over 90% of the contaminant is removed during the first two stages and the rest in the last three stages.

Whereas sand and additive-C did not affect the basic extraction efficiency of SESR process, compared to the blank, two of the other additives used in this study appear to have a beneficial effect. Best recoveries were achieved in presence of additive-B. In this case over 90% recovery was achieved in the first stage and almost 100% recovery was obtained by the second stage. Subsequent stages did not extract much more of the contaminant. Although overall recovery of the contaminant was almost independent of the amount of additive-B, initial recovery was much better with smaller amounts. With additive-A, overall contaminant removal efficiency was comparable to the case of additive-B, but recovery during the initial stages was considerably lower than in other tests.

### 3.2 Lead Fixation

---

P. Y. P. Yeoug, R. L. Johnson and S. N. Acharya, "An Improved Procedure for Determining Oil Content in Wet Soil Samples". ysis of Soil Contaminated with Petroleum Constituents, ASTM STP, 1221, Tracey A. O'Shay and Keith B. Hoddinott,Eds., Ameri ety for Testing and Materials, Philadelphia, 1994.

The extracted dried soil samples were leached using US EPA leaching procedure (TCLP) at pH 2.9 ± 0.1 to evaluate the lead fixation capacity of these additives. The results are summarized in Table 4. The data shown in this Table suggests that of all the additives tested, additive-A is the most effective reagent for lead fixation. One hundred % lead fixation was achieved with only 1w/w% of this additive. Additive-B also appears to have excellent lead binding capacity. Lead fixation capacities for peat and additive-C sample tested were much lower than additive-A and B, suggesting that considerably more of these materials will be required for complete fixation of lead.

## 4.0 CONCLUSIONS

It has been demonstrated that a fine textured, petroleum contaminated soil can be successfully remediated by concurrent removal of organics and fixation of lead to produce an agglomerated product with a similar size distribution to natural aggregates. Up to 100% contaminant removal could be achieved under optimum conditions of agglomeration. Two of the additives incorporated into the soil agglomerates as metal binding agents, appear to have a beneficial effect on the extraction efficiency of process. Results from the US EPA's Toxicity Characteristics Leaching Procedure (TLCP) on the dried agglomerates suggest 100% lead fixation.

## ACKNOWLEDGMENT

The authors are grateful to J. R. Woods, R. D. Coleman and V. Boyko for technical help.

**Table 1. Composition of Diesel Invert Drilling Mud (DIDM)**

| | | |
|---|---|---|
| Total Solids, w/w% (by Dean & Stark) | | 82.9 ± 0.3 |
| Water, w/w% (by Dean & Stark) | | 12.2 ± 0.4 |
| Organics, w/w% (by GC of the Dean & Stark extract) | | 4.84 ± 0.1 |
| Mass Balance (Total of solids + water + organics) | | 99.94 |
| Total carbon of dried toluene extracted solids, w/w% | | 2.1 |
| Organic carbon content of dried toluene extracted solids, w/w% | | 1.1 ± 0.1 |
| Carbonate carbon content of dried toluene extracted solids, w/w% | | 1.0 ± 0.1 |
| Clay plus silt content (<45μm), w/w% of dried solids | | 72.6 |
| TCLP leachable heavy metals (mg/kg of sample): | Pb | ND |
| | Cd | 1.2 |
| | Cr | 2.0 |
| | As | ND |
| | Se | ND |

ND = Not detected

**Table 2. Mass Balance Calculations for the Extraction of Diesel from Diesel Invert Mud**

| Test No. | Solvent | Recovery by SESR* | | Recovery of residual diesel from agglomerates*** | | Total Diesel** | |
|---|---|---|---|---|---|---|---|
| | | (g) | (%)** | (g) | (ppm)**** | (g) | (%) |
| 1 | Hexane | 4.22 | 87.2 | 0.55 | 5500 | 4.77 | 98.7 |
| 2 | Hexane | 4.55 | 94.0 | 0.16 | 1600 | 4.71 | 97.3 |
| 3 | Toluene | 5.05 | 104.3 | 0.019 | 19 | 5.169 | 106.8 |
| 4 | Toluene | 4.83 | 99.8 | 0.004 | 4 | 4.834 | 99.9 |
| 5 | Trichloroethylene | 4.82 | 99.6 | 0 | 0 | 4.82 | 99.6 |
| 6 | Trichloroethylene | 4.80 | 99.2 | 0.01 | 1 | 4.81 | 99.4 |
| 7 | Trichloroethylene | 4.24 | 87.6 | 0.14 | 1400 | 4.38 | 90.5 |

* Based on 100g wet sample
** Based on analysis of original sample
*** By soxhlet
**** Based on the weight of wet sample

**Table 3. The Effect of Additives on the Extraction Efficiency of Diesel from DIM (Solvent: HPLC grade Hexane)**

Total amount of water (including original amount present in DIM), w/w% of dry solids: 22-28%
Size of agglomerates: 0.5-2mm
Wt. of sample: 100 g wet
Solids:Solvent ratio, w/w basis: 0.65 ± 0.05
Agitation: Waring Blendor , 1L plastic jar, stage 1:1minute high shear, 2 minutes low shear; stage 2-4: 0.5 minute high shear, 2 minutes low shear

| **Test No.** | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Additive | None | Sand | A | B | B | C |
| Amount of the additive, w/w% of wet solids | - | 5 | 1 | 5 | 1 | 5 |
| % Extraction, S- 1 | 61.3 ± 2.2 | 66.1 ± 0.8 | 56.6 ± 2.8 | 69.1 ± 4.0 | 93.1 ± 1.6 | 80.5 ± 0.2 |
| % Extraction, S- 2 | 81.6 ± 1.8 | 83.8 ± 1.2 | 77.2 ± 1.9 | 93.4 ± 5.0 | 100.7 ± 0.2 | 87.9 ± 0.8 |
| % Extraction, S- 3 | 88.2 ± 1.2 | 86.2 ± 2.2 | 84.2 ± 3.7 | 98.5 ± 4.2 | 101.7 ± 0.1 | 89.3 ± 0.1 |
| % Extraction, S- 4 | 89.5 ± 1.0 | 87.0 ± 2.1 | 91.6 ± 7.1 | 99.6 ± 3.4 | 102.0 ± 0.1 | 90.6 ± 0.9 |
| % Extraction, S- 5 | 89.7 ± 1.0 | 87.2 ± 2.0 | 103.0 ± 6.4 | 100.5 ± 2.4 | 102.5 ± 0.3 | 91.2 ± 1.3 |

**Table 4. Summary Results for Concurrent Extraction of Diesel and Fixation of Lead from Diesel Invert Mud (MID)**

| Test No | Solvent | Additive (w/w% of wet DIM) | Amount of Diesel Extracted, (w/w% of total)* | Organic C, of Extracted dried solids (w/w% ) | TCLP Extractable Lead (% fixed))*** |
|---|---|---|---|---|---|
| 1 | Toluene | None | 100** | 1.0 ± 0.1 | 0 |
| 2 | Toluene | None | 94.8 ± 7.9 | 1.1 ± 0.1 | 0 |
| 3 | Toluene | A (1) | 104.5 ± 9.5 | 1.0 ± 0.1 | 100 |
| 4 | Toluene | B (5) | 102.9 ± 3.0 | 1.0 ± 0.1 | 83.2 |
| 5 | Hexane | None | 89.7 ± 0.9 | 1.0 ± 0.1 | 0 |
| 6 | Hexane | Sand (5) | 87.2 ± 2 | 1.2 ± 0.1 | 2.4 |
| 7 | Hexane | A (1) | 103.0 ± 4.5 | 1.0 ± 0.1 | 100 |
| 8 | Hexane | C (5) | 91.2 ± 1.2 | 1.2 ± 0.1 | 59.4 |
| 9 | Trichloroethylene | Peat (5) | 91.4 | - | 60.9 |

* Based on the Soxhlet extractable amount in original sample using toluene; determined by GC;

** By soxhlet extraction

*** As determined using US EPA Toxicity Characteristics Leaching Procedure, based on the amount in original sample (680 mgs/kg of dry solids)

Figure 1. Contaminant Removal Efficiency in Hexane:
The effect of metal binding agents