EXTRACTION AND MEASUREMENT OF OIL CONTENT IN MINERAL FINES (SLUDGE)

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ABSTRACT

Oil production, processing and transport result in accidental spills in a wide range of environments. The choice of land reclamation procedures in these cases depends upon an analysis of oil content throughout the soil profile. Conventional methods for extracting and determining oil content in mineral and organic soils were reviewed and found unsatisfactory for measuring bitumen residues in mineral fines (sludge) resulting from oil sand processing. Common solvents, like toluene and methylene chloride, may not penetrate water-oil films associated with saturated fines. Pretreatment, by drying the sludge at 40°C, greatly improves the efficiency of oil extraction by methylene chloride. Drying an oil contaminated soil sample at higher temperature before oil extraction is not recommended due to loss of oil by volatilization. The chemical and physical properties of the oil-free sample are unaffected by the proposed extraction procedure, thus permitting further analytical measurements on previously contaminated samples.

INTRODUCTION

A method of extracting oil from soils and unweathered geological materials is needed to measure the level of contamination and to evaluate alternative reclamation procedures. Crude oil is soluble in a variety of organic solvents. Some organic solvents used in oil extraction methods for soils and water include methylene chloride (McGill and Rowell, 1980; Law, 1978), toluene (Patel, 1974), benzene, hexane and chloroform (Walker *et al.*, 1975), trichlorotrifluoroethane and carbon tetrachloride (Gruenfeld, 1973).

The most highly recommended method for oil extraction from soils now is probably methylene chloride (McGill and Rowell, 1980). However, the method needs modification for samples containing large amounts of water where oil-in-water emulsions can drastically reduce extraction efficiency. Furthermore, methylene chloride has low extraction efficiency in soils containing "untopped" or unaerated oil.

The reclamation of the solids portion (sludge) of tailings ponds associated with Alberta's oil sand industry requires a measurement of bitumen content and the elimination of residual bitumen from the sample to facilitate further analytical measurements. The existing methods cannot be used without modification because sludge contains large amounts of water (70-80% by weight) and a viscous, unaerated species of oil residue (Scott *et al.*, 1985).

This paper reports on the refinement of an oil extraction method which can be used on soils or unweathered geological materials containing any amount of moisture and oil in any state of oxidation. It compares the extraction efficiency of methylene chloride and toluene and defines a pretreatment suitable for a wide range of soil materials which does not change their inherent physical and chemical properties.

MATERIALS AND METHODS

Sludge and Soil

The oil-contaminated sludge used in this study is a by-product of oil production from oil sands. It is disposed of in huge tailings ponds near Ft. McMurray and consists of a thixotropic mixture of very fine mineral particles and process water (Table 1). There is approximately four percent residual bitumen in the sludge, left over from an incomplete extraction by the Clark hot water process. The residual bitumen represents lost product for the operating company and influences the choice of reclamation procedures of the unconsolidated sludge. The tailings pond environment is aqueous, highly alkaline and extremely sodic. The level of soluble salts is elevated but not extreme (Table 2).

The soil used in the evaluation of oil recovery procedures is the A horizon material from the Malmo series, Black Solod (Table 3). Oil-free samples of this surface soil were spiked with a

Table 1: Particle Sizes of Sludge

Particle size (μm)	% less than
88	99.2
44	95.0
22	88.5
11	75.2

Table 2: Properties of the Oil Sand Sludge

Sludge Properties	Measured values
Solids (%)	26
Water (%)	70
Bitumen (%)	4
pH	9.1
E.C. (mS/cm)	2.9
SO_4 (ppm)	384
Cl (ppm)	332
SAR	61

Table 3: Properties of Malmo Soil (A horizon)

Soil Properties	Measured values
pH	8.4
E.C. (mS/cm)	2.1
Saturation percentage	78.6
SAR	2.7
Sand (%)	27
Silt (%)	41
Clay (%)	32
Textural class	CL

known amount of "untopped" (unaerated) oil and extracted with both solvents. Selected chemical and physical properties of spiked and unspiked soil samples were measured to evaluate the effect of the solvent. All laboratory analyses, except as detailed in this paper, follow standard procedures (McKeague, 1978; Richards, 1954).

Measurement of Chemical and Physical Properties of Extracted Soils

One of the essential requirements of the proposed extraction method is that the properties of the extracted materials remain unaffected by the extraction procedure so that further analytical measurements can be carried out. Five treatments were used to evaluate the effects of solvent extraction on the properties of Malmo soils. Each treatment was replicated three times.

T1 = oil-free soil extracted with toluene
T2 = oil-free soil extracted with methylene chloride
T3 = oil-affected soil extracted by toluene
T4 = oil-affected soil extracted by methylene chloride
T5 = no extraction (control)

Extractants

Toluene and methylene chloride are compared as oil extractants because of their ready availability, low toxicity and common use in analytical labs measuring oil content of soil or water (Patel, 1974; Hilpert *et al.*, 1978; Law, 1978; McGill and Rowell, 1980).

Sample Pretreatment

Often salt and acids are used as additives to organic solvents to improve extraction efficiency (Grunfeld, 1973). The development of a method for oil sand sludges precludes the use of additives because of sample contamination after extraction. Pretreatment by drying, as originally proposed by McGill and Rowell (1980) for organic soils only, seems a viable alternative. Malmo soil was wetted to field capacity (-33 kPa) and spiked with 5% (by dry weight) crude oil. The soil samples were then air-dried ($22^{o}C$) for 7 days or oven-dried at $40^{o}C$ or $105^{o}C$ for 16 hours. Methylene chloride was used as the test extractant. Moist samples (-33 kPa), spiked with equal amounts of oil and not dried, were used as controls.

RESULTS AND DISCUSSION

Effect of Oil Extraction on Soil Properties

The investigation of the effect of different solvents on the properties of the extracted materials is a preliminary test to evaluate the effectiveness of the method for future oil extraction and measurement of mineral fines. Any change in properties of the tested materials by the extraction method will negate the usefulness of measuring the oil content.

Results of the tests indicate that neither the use of solvent nor the addition and extraction of oil affects chemical properties of Malmo soil prepared in a saturated paste (Table 4). In addition, soil particle size analysis is not affected by solvent or oil addition and solvent extraction (Table 5). The results allow further determination of the choice of solvent.

Choice of Solvents

Methylene chloride and toluene were both tested as potential solvents of crude oil. Both were capable of recovering more than 75% of the crude oil added to a Malmo soil (Table 6). This is in agreement with results obtained in the experiment conducted by McGill and Rowell (1980) in which between 29 and 30% of untopped (unaerated) oil was not recovered by methylene chloride extraction from different soils. The slightly higher recovery efficiency of toluene was not statistically different than methylene chloride. However, methylene chloride requires only one-third the time of extraction of toluene. This is perhaps due to the lower boiling point of methylene chloride (40°C) than toluene (110°C). Walker *et al.* (1975) compared extraction efficiency of benzene, hexane and chloroform from oil-contaminated sediments, but 12-24 hours of extraction time was required. As a consequence of the large differences in extraction time, methylene chloride was used as the extractant of choice for further testing.

Effect of Pretreatment on Oil Extract Efficiency

In the case of soil, water content, drying temperature and drying time do not affect the relative oil extraction efficiency of methylene chloride. McGill and Rowell (1980) used methylene chloride to extract mineral soils and also found no differences in oil recovery whether the soil samples were moist (at field capacity) or air-dried. However, no attempt was made to oven-dry soil samples at 105°C. In our study, samples left to air-dry for seven days yielded the same oil recovery as soil samples which were oven-dried at 40°C or 105°C for less than one day.

Pretreatment of sludge samples is needed because extraction by conventional methods without modification were proven unsatisfactory (authors' unpublished results).

Sludge samples contain much higher clay content, large amounts of sodium and water, and differ greatly in their response to solvent extraction efficiency (Table 7). When no drying pretreatment is imposed (control) and moisture content equals 70% by weight, oil extraction efficiency is only 2% of that achieved by seven days of air drying. The sharp increase in extraction efficiency after drying can be explained by the elimination of the oil-in-water emulsions that cause extraction difficulty (McGill and Rowell, 1980).

The temperature of the drying treatment also affects the relative extraction efficiency in sludge. Sample drying at 40°C for 16 hours yields the same oil recovery as seven days of air drying. When sludge is dried at 105°C, however, extraction efficiency drops to 54% of the air-dried value. This is probably due to the loss of oil by volatilization.

Table 4: Chemical Properties of Soil With and Without Oil After Extraction With Two Solvents.

Treatment	pH*	E.C. (mS/cm)	Soluble Cations (meq/L) Na	K	Ca	Mg
T	8.2	2.3	6.5	1.7	7.4	5.7
MC	8.3	2.3	6.6	1.7	7.4	5.6
OIL + T	8.5	2.4	7.3	1.8	7.4	5.8
OIL + MC	8.4	2.3	7.1	1.7	7.5	5.8
CONTROL	8.4	2.1	6.5	1.6	6.3	5.0

* Saturated paste

Values are averages of 3 replicates and are not statistically different.

T = toluene extraction
MC = methylene chloride extraction
OIL = oil-spiked
CONTROL = no extraction

Table 5: Soil Particle Size Analysis of Soils With and Without Oil After Extraction With Methylene Chloride.

Treatment	Sand (%)	Silt (%)	Clay (%)	Textural Class
T	31	38	31	CL
MC	31	37	32	CL
OIL + T	27	43	30	CL
OIL + MC	28	43	29	CL
CONTROL	27	41	32	CL

Values are averages of 3 replicates and are not statistically different.

T = toluene extraction
MC = methylene chloride extraction
OIL = oil-spiked
CONTROL = no extraction

Table 6: Oil Extraction Efficiency and Duration of Two Solvents in Malmo Soil.

Solvents	Oil recovery (%)*	Time (hr) required to complete extraction
Toluene	80	3
Methylene chloride	76	1

* Values are averages of 3 replicates and are not stastically different

Table 7: Effects of Drying at Various Temperatures on the Relative Extraction Efficiency of Methylene Chloride on Oil-spiked Malmo Soil and Mineral Fines (sludge).

Treatment	Relative Extraction Efficiency (%)	
	Malmo Soil	Sludge
Air dry for 7 days	100 a	100 a
Oven dry at 40°C for 16 hrs	99.8 a	98.9 a
Oven dry at 105°C for 16 hrs	95.3 a	54.2 b
Control* (no drying)	91.2 a	2.1 c

* Moisture content of Malmo soil and tailing sludge without drying equals 30% and 70% respectively.

For any column, values are statistically different if followed by different letters.

CONCLUSION

An oil extraction method for mineral fines using methylene chloride and pretreatment by mild oven drying at 40°C for 16 hours was developed. Results obtained in this study indicate that moisture in mineral fines significantly affects extraction efficiency. The amount of oil recovered was greatly reduced if sludge samples were extracted in a saturated condition. Oven drying at 105 °C is not recommended due to decrease in extraction efficiency. Both chemical and physical properties of the extracted samples were not altered so that future characterization of the previously contaminated materials is possible.

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FOREWORD

The British Columbia Chapter of the Canadian Land Reclamation Association was formed in 1985 to provide a local public forum for the exchange of information and experience in land rehabilitation. Comprised of professionals from a wide range of backgrounds and interests, this organization pulled together quickly to host the 1986 Annual Meeting. The diverse membership in the B.C. Chapter was realized in a program that expanded the scope of the conference to include many fields that have not been represented in past programs. The quality of presentations and range of topics kept audience participation at a spirited level. It is our hope that we have initiated a trend to widen the scope of the annual meetings so as to not focus on traditional mining or energy development issues.

I wish to thank all speakers and attendees for making this first formal function of the B.C. Chapter a success. The enthusiastic support of chapter members in the planning and administration of the conference demonstrated a strong desire for a quality meeting. This drive bodes well for the future of our chapter.

A great deal of effort went into the publication of the proceedings of the 1986 Annual Meeting. Care was taken to accurately reproducce all papers, however minor errors may have escaped the review process. We hope that this will not detract from the information presented by the authors.

May the CLRA and all local chapters continue to grow and function as a focal point for land rehabilitation.