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TREATMENT
OF
REFINERY CRUDE OIL TANK SLUDGE

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Abstract

The treatment and disposal of oil refinery tank sludge is a critical issue among oil refineries. This is because of the hazardous nature of the sludge due to high levels of oil and heavy metals, which must be removed prior to disposal. This study was carried out to investigate the removal of crude oil and heavy metals to allow the design of an appropriate disposal treatment that could meet the environmental regulations for this type of waste.

A typical emulsified crude oil tank sludge, produced from tank cleaning operations was characterised and was shown to contain approximately 41%, 16%, 25%, and 8% of solids (sand), oil, water and volatile materials, respectively. The sludge also contained high level of metals, of which more than 98% resided in the solids fraction. The heavy metals analysed were copper, nickel and zinc with average values of 3,955mg/kg, 443 mg/kg and 13,851 mg/kg of raw sludge, respectively.

The crude oil fraction of the sludge was removed by solvent washing with kerosene which resulted in emulsion breakdown. A model which optimises the removal of crude oil was developed and validated against experimental data. The model predictions agreed well with experimental trials using kerosene as the solvent. A 2:1 solvent to sludge ratio is adequate to remove the oil (> 98%) in the sludge after two washing stages. This resulted in oil-free/metal-rich solids. Kerosene washing reduced the volume by 76% and mass by 59 %, which allows easier handling and disposal.

Heavy metals reduction was achieved by acid washing using 8N nitric acid and a 10:4 mixture of 2.4N hydrochloric and 8N nitric acids. Approximately 99% of the metals were removed using a 10:1 acid to solids ratio, at pH <1 and ambient conditions, making the sludge suitable for land application and meeting the appropriate disposal guidelines for oil and metal levels.

The solvent washing process was shown to be industrially feasible for volume and mass reduction of the sludge. However, heavy metal reduction by acid washing requires further optimisation before it can be applied on an industrial scale.

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Nomenclature

δ_b	= bulk density of raw sludge [kg/m ³]
W_b	= bulk mass of raw sludge [kg]
V_b	= bulk volume of raw sludge [m ³]
δ_p	= particle density of washed solids [kg/m ³]
W_p	= mass of washed solids [kg]
V_k	= volume of kerosene at ambient temperature [m ³]
V_f	= final volume (kerosene + washed solids) [m ³]
x	= concentration of oil in raffinate/feed stream [kg oil/kg (oil + solvent)]
X	= concentration of oil in solvent/extract stream [kg oil/kg (oil + solvent)]
y	= concentration of solids in raffinate/feed stream [kg solids/kg (oil + solvent)]
Y	= concentration of solids in solvent/extract stream [kg solids/kg (oil + solvent)]
w	= concentration of water in raffinate/feed stream [kg water/kg (oil + solvent)]
W	= concentration of water in solvent/extract stream [kg water/kg (oil + solvent)]
R	= mass of raffinate/feed stream [kg (oil + solvent)]
S	= mass of solvent stream [kg (oil + solvent)]
E	= mass of extract stream [kg (oil + solvent)]
m	= mass of mixture [kg (oil + solvent)]
x_{mn}	= concentration of oil in mixture [kg oil/kg (oil + solvent)]
y_{mn}	= concentration of solids in mixture [kg solids/kg (oil + solvent)]
w_{mn}	= concentration of solids in mixture [kg water/kg (oil + solvent)]
C	= concentration of oil [kg oil/kg solvent]
RI	= refractive index [dimensionless]

Chapter 1

Introduction

1.1 Background of the problem

The New Zealand Refining Company Ltd. (NZRC) generates an average of 100 tonnes of crude oil tank sludge annually from tank maintenance operations. This sludge was found to contain heavy metals at levels exceeding those set out by Public Health Guidelines, (NZ Dept. of Health 1992) for disposal by land application. Heavy metals found in the sludge were mercury, chromium, cadmium, lead, nickel, zinc and copper. The type of sludge being produced by NZRC is an oil/water/sand emulsion that makes it difficult to handle (Gozan *et al.* 1996).

NZRC has been using landfarming as the mode for disposal of their oily refinery wastes. However, the adverse effect on the environment of heavy metals accumulation makes this practice unsustainable. Analysis of soil samples taken from the landfarming site (Gozan *et al.* 1996) has shown that it exceeded the heavy metal concentration set by the Public Health Guidelines (NZ Dept. of Health 1992). For this reason an alternative treatment methodology is required.

At present, NZRC sludge has been disposed through co - landfill. However, this system is recognised as a short-term solution and is subject to increasing restrictions and criticisms by regulatory authorities.

1.2 Objective of the study

This study is aimed at developing an alternative method of treatment that can be applied industrially to stabilise crude oil tank sludge. This method will be aimed at making the sludge suitable for land application. This study aims to:

- Remove the crude oil from NZRC tank sludge.
 - Reduce the heavy metal concentration in NZRC sludge.
-

- Investigate the feasibility of the method for industrial application.

Achieving these aims would provide the solution for treatment and disposal of oil refinery sludge and could be used in oil refineries globally.
