

OIL SPILL CLEAN-UP SYSTEM USING HOT WATER*

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ABSTRACT

The process of hot water extraction of tar sand was modified and adapted for removal of heavy oil from bottom tank petroleum sludges, and was submitted to a laboratory feasibility study. This process can also be utilized to clean beach sands contaminated by accidental heavy oil spills. The process mainly consists of a hot-water extraction (digestion), extruding the oil particles from their support of sand or clay. In the case of oil contaminated sands, a single stage extraction yielded a total recovery of hydrocarbons of 99 percent and a clean sand (hardly containing 0.1% of hydrocarbons), thus safe to be returned to the environment. In the case of heavy oil from bottom tank petroleum sludges, it was necessary to proceed with a double stage extraction with the addition of wetting agents: the utilization of Na_2SiO_3 aqueous solution of 1 percent in weight was proven efficient, allowing a 82 percent recovery of hydrocarbons, with only 0.5 percent hydrocarbons in the solid residues.

The damage to the intertidal region resulting from an untreated, intact, cohesive layer of oil is visually apparent and particularly distressing. It encompasses both biological and property damage. The very large extent of the property damage is evident from the amount of the lawsuits following an oil spill undertaken by

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tourist interests, property owners, etc. In addition, the cleanup costs for a typical, large spill in a valued resort area can be several million dollars. This is also the most publicized aspect as can be readily appreciated from extensive magazine coverage (e.g., in *Life* [1, 2]). The Santa Barbara, Tampa Bay, San Francisco Bay, Gulf of Mexico, Valdez, and other spills have been publicized with the appropriate photographs of oil stained beaches and shore property.

The effects of untreated oil coming ashore was well documented in a scientific manner by Blumer et al. [3]. In September 1969, a spill of highly aromatic fuel oil from the barge Florida in Buzzards Bay was incorporated into the bottom sediment to at least 10 meters of water depth. This illustrates very well the wetting effect of untreated spilled oil and its ability to cling to shore surfaces. In this instance, the oil was physically dispersed by the heavy seas but retained its adhesive characteristics. It is postulated that the oil droplets came into contact with and wetted the sand particles that were temporarily suspended in the turbulent water column.

The problem of beach contamination becomes severe in the case of large accidental oil releases at sea, such as that of the Torrey Canyon [4] and Santa Barbara [5, 6] incidents, and the more recent grounding of the Exxon Valdez in Alaska. Complete removal or dispersal of the released oil at sea in these incidents was not possible, and very large oil slicks moved ashore, coating entire beaches up to the high-tide mark.

Once the oil comes ashore, serious economic and ecological consequences may result. Oil contamination has an obvious adverse effect on recreational uses of beaches. Since in many situations complete removal or dispersal of oil before it reaches the coast will be impossible, effective beach-restoration procedures are needed. In all major spills to date, containment of the oil spill at sea has been ineffective resulting in oil contamination of shorelines.

The policy in the United States is not to use dispersants to treat oil on the beaches except under special circumstances such as an acute fire hazard. Previous restoration methods have used excessive amounts of labor. The cleaning method recommended by Environment Canada [7, 8] for small spills is by hand. For larger spills, it is preferable to dig excavations or trenches serving as storage tanks. If large volumes of sediments have to be removed, they have to be replaced with sediments borrowed from a higher zone of the concerned beach. The choice of a restoration method depends upon the economical and recreational value of the area and surface conditions and topography of the shoreline. Although various types of earthmoving, construction, and agricultural equipment have been utilized in beach-restoration projects, the equipment does not appear to have been utilized either effectively or efficiently, and little has been done to mechanize or systematize beach cleanup operations.

Also, the method and equipment selected to restore a beach contaminated with oil will depend upon the manner in which the oil has been deposited onto the beach and the type of beach contaminated.

GOALS OF THIS ARTICLE

The present process focusses on the extraction of heavy oils from their particle support (clay, silt, sand) with hot water: this process has successfully been applied to the extraction of bitumen from “tar sands” (Utah in the United States and Athabasca in Canada). The goals of this hot water extraction process are two-fold [9]:

1. To clean the contaminated solids (sand, clay, silt) sufficiently so as to render them innocuous and to return them to the location from which they were removed; and
2. To recover the valuable heavy oils for recycle for energy generation.

BASIS FOR A HOT WATER PROCESSING SCHEME

The process of oil extraction with hot water originated from a very common observation: the washing of oily dishes with hot soapy water yielded oil particles floating at the surface of the water phase and cleaned dishes. From this down-to-earth matter of fact, K. A. Clark designed the “hot water washing” process for exploitation on Athabasca bituminous tar sands in Alberta, Canada [10-14]. These tar sands consist of viscous hydrocarbons (called bitumen) trapped in a matrix of clay and loosely consolidated sandstone. Hydrocarbon content ranges from about 3 to 18 percent [15-17].

Often, the term “hot water” was used instead of “steam” or “water vapor” because the operating temperature range was maintained near the boiling point of water without ever reaching it: a temperature around 90°C was the most commonly used [10]. Another essential factor was the necessity of adding a surface active agent (the soap in the example above) in aqueous solution, such as sodium hydroxide, sodium carbonate, sodium silicate, or other synthetic wetting agents commercially available. Although the explanation of the phenomenon underlying the process seems obvious with the help of the dish-washing illustration above, the mechanism of the displacement of oil particles is much more complex and combines approaches by superficial energy (surface charge) and free energy changes in interfacial area [18-20].

DESCRIPTION OF TREATMENT SYSTEM

The original “hot water washing” process (see Figure 1) as conceived and developed by K. A. Clark of the Research Council of Alberta consisted of four fundamental steps [12]: (I) Mixing; (II) Hot Water Contact; (III) Flooding; and (IV) Separation.

The process to recovery oil which we have developed consists of four main steps (I to IV), and are depicted in Figure 2. In cases where the content of fine clay particles was high, two supplementary steps were added: the oily clay solids

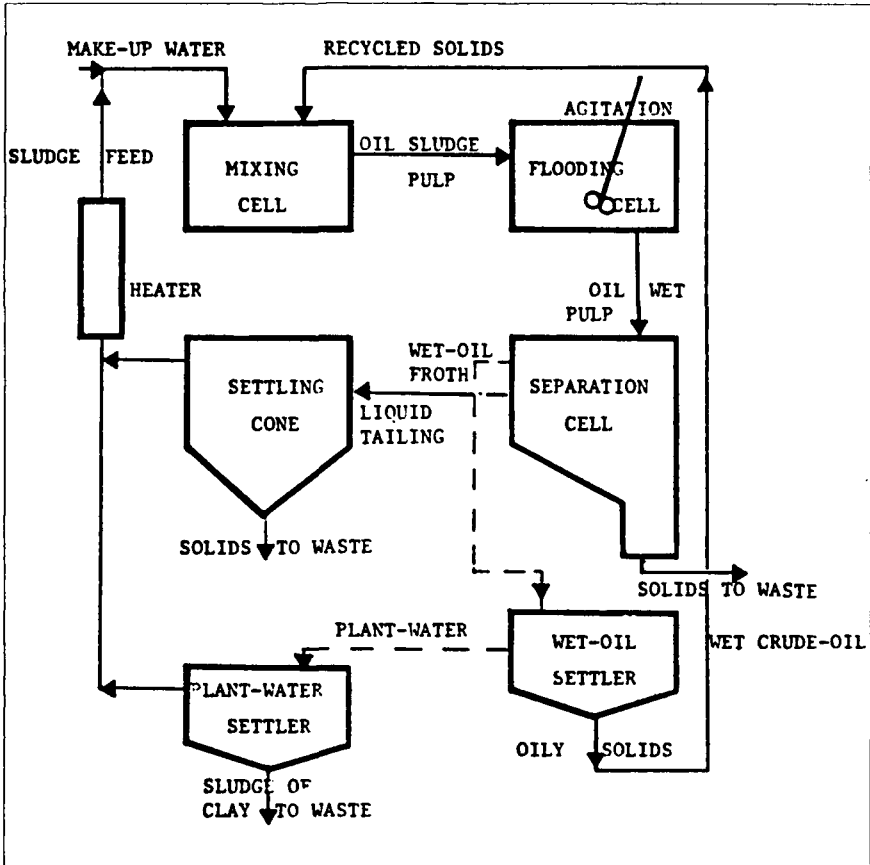


Figure 1. Flow diagram of hot water extraction process for tar sands.

contact hot water for a second time (step V), and the bubbles forming the froth layer are separated from the clay particles (step VI). Clark and Pasternak explained the necessity of these two extra-steps due to the fact that tiny oil flakes have a settling rate comparable to that of clay [13]. In a later section, we will point out how the present hot water process needs also to include these two extra-steps in the case of petroleum sludges.

I. Screening and Mixing

Oil Contaminated Sands (OCS sludge) or Crude Oil Sludge (COS sludge) is passed through a 6.5 mm mesh screen, where big rock particles are removed. The resulting sludge shows a porous structure, from which emanates a strong bitumen odor; the oil content can oscillate from 8 to 14 percent in weight. One kg of

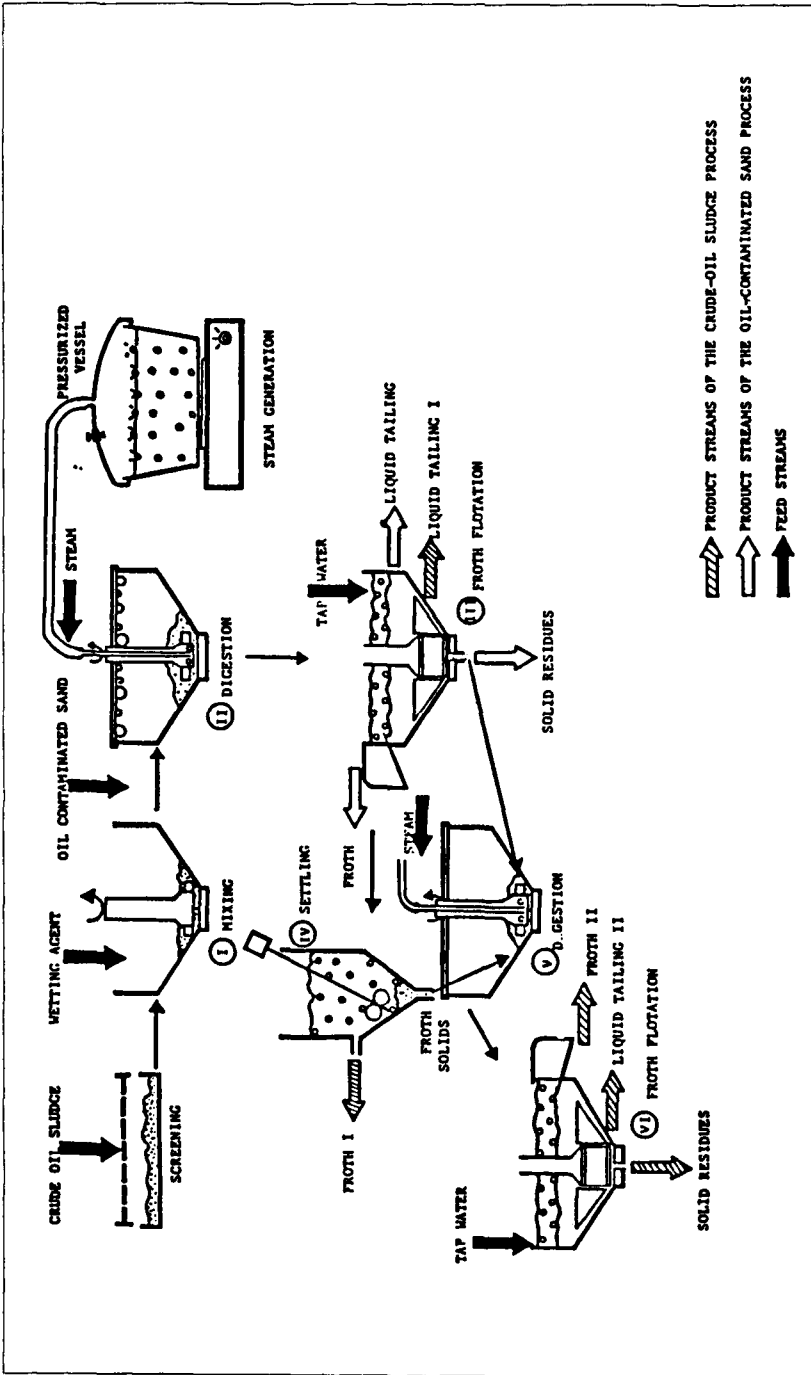


Figure 2. Flow diagram of the hot water extraction process of oil.

sample is poured and slowly agitated in a Wemco's cell used as mixer, digester, and frother (see Figure 3). With the introduction of the solution of wetting agent, the agitation is gradually increased to 1050 RPM for a good contact to be achieved. Often, the oil contaminated sand process does not have to go through this first step.

II. First Stage Digestion

A heated pressurized vessel containing boiling water provides an average hot water rate of 1.3 L/min, measured at hose exit conditions of pressure and temperature. The completely enclosed Wemco cell (see Figure 3) starts operating as a high temperature and continuously stirred digester. Big droplets of hot water can be observed on the cover topping the cell. The hot water goes down through the hose, down into the hollow agitation shaft (see Figure 4). The average agitation level distributes the hot water in the form of small jets that penetrate into the porous structure of the wetted sludge. The alkaline wetting agent helps in freeing the oil particles from their solid support (sand, clay, or silt), and in suspending them in the hot water phase. Usually, a digestion of 20 min. is necessary for a good-oil recovery.

III. First Stage Froth Flotation

At the end of the digestion period, the top cover is removed, tap water at 15°C is added to float the oil particles in the form of a froth. The hot water feed hose is disconnected, and the air feed valve closed. A very mild air stream is drawn into the digested floating sludge from ambient atmosphere. The agitation is set at a lower level. A thick froth starts to build up due to the specifically designed triangular baffles, that favor turbulent agitation. Water is added until the froth reaches the level of the spout: this facilitates froth removal. The total volume of this slurry mixture is 4-5 L.

IV. Froth Solids Settling and Recycle

A 5 L clarifier is used to collapse the froth phase with the help of a mild mechanical mixing. Part of the solids settle at the bottom. This amount will be incorporated into the coarser solids, which have previously settled at the bottom of the cell. The Liquid Tailing (I) was withdrawn (by gravity) beforehand (see Figure 2).

V. Second Stage Digestion

This second digestion is intended to extract the rest of the oil from the solid residues left in the cell. This latter is sealed and fed with hot water (agitation is resumed at a mild level). Conditions of operation (agitation, temperature) duplicate those of the first stage digestion, with the exception that no wetting agent is added.

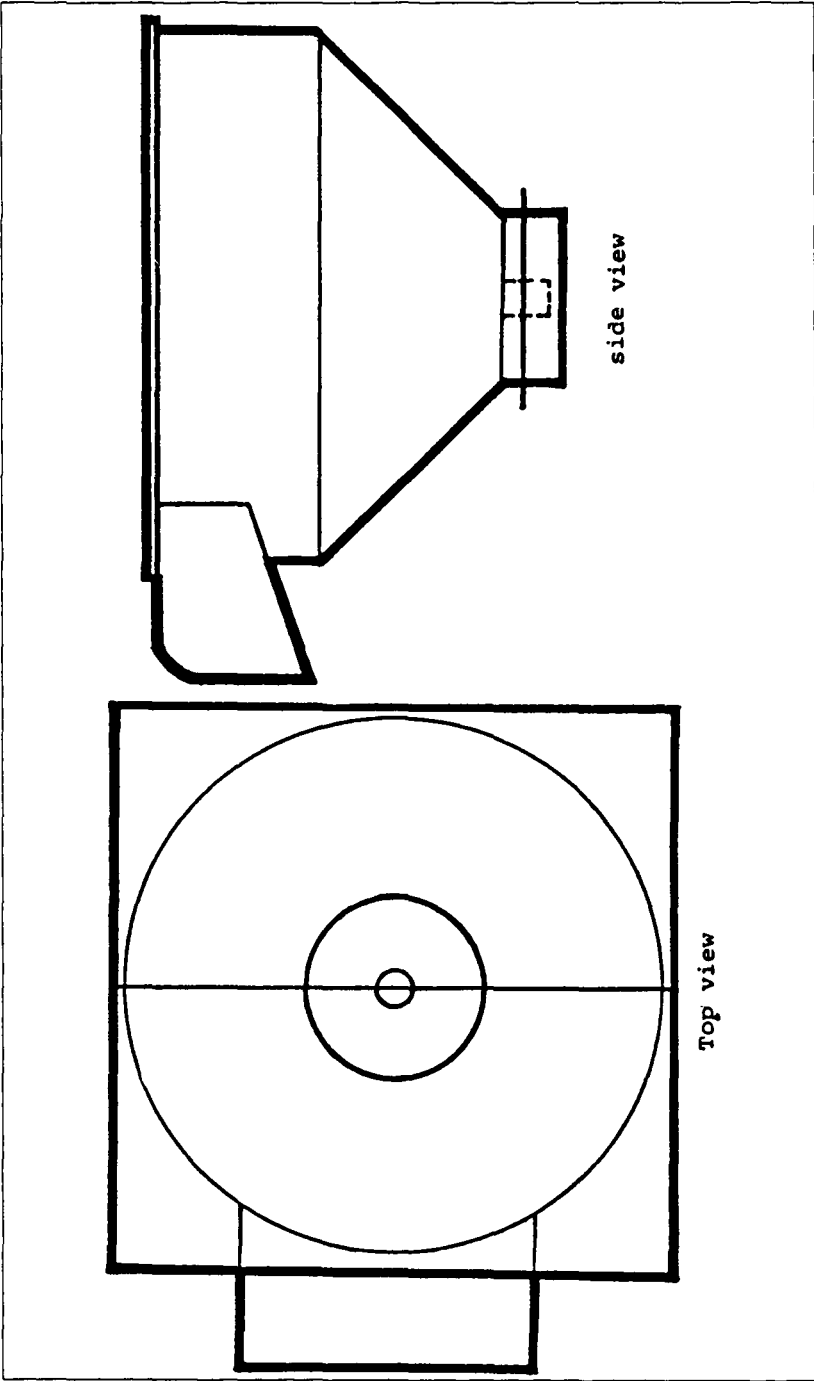


Figure 3. Schematic of digestion/froth flotation cell: side and top views.

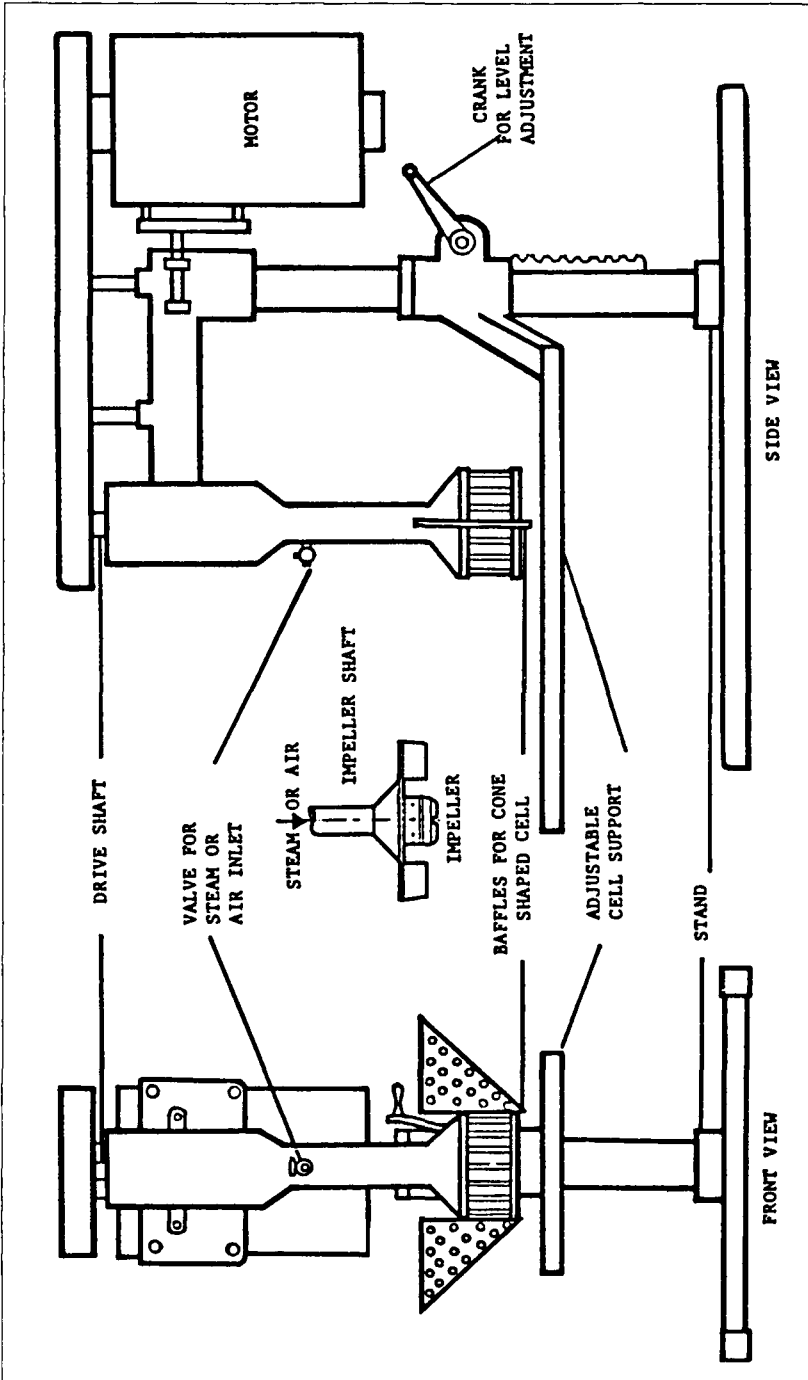


Figure 4. Schematic of Wemco's mixing and frothing units: side and front views.

VI. Second Stage Froth Flotation

As in the first stage flotation, tap water is added and agitation increased to 2300 RPM. Froth collected in (II) is mixed with froth (I) previously separated. Similarly, Liquid Tailing (II) is incorporated to Liquid Tailing (I). One sample of each product stream (striped arrow in Figure 2) is sent for composition analysis.

ANALYTIC TECHNIQUES

Feed Mixture

COS sludge comes from Gulf Oil Company's oil tank deposit. It has been delivered to us on three different occasions of one U.S. gallon each. OCS sludge is made up by mixing bunker C oil with standard beach sand collected from riverbank, on Varennes Route, at a spot located between electric poles 10 and 20 of Hydro-Québec, Province of Québec, Canada.

Samples Composition Determination

Samples of the feed, froth, liquid tailings, and solid residues of each experimental hot water extraction run were analyzed to determine their composition with respect to hydrocarbon, solids, and water.

In non-liquid samples – A Soxhlet tube assembly is used for this case (Figure 5). A sample of 10 g of solid material is ground with 50-80 g of anhydrous sodium sulfate and 20 g of Ottawa sand by using a mortar and a pestle. The dry free flowing powder is then introduced into a cellulose extraction thimble and refluxed for four hours at a rate of twenty cycles per hour with petroleum ether which dissolves all the vegetable oils, fats, and hydrocarbons contained in the sample. The extract is then well mixed with silica gel and filtered. Petroleum ether is separated by rotational evaporation. The residue, hydrocarbons, is weighed for subsequent mass balance calculations.

In liquid samples – In a separation funnel, the sample is well mixed with petroleum ether, which dissolves all greases, oils, fats, and hydrocarbons. The organic layer, separated from the aqueous layer by means of a phase-separating (P/S) filter paper, is well mixed with silica gel and filtered. Petroleum ether is evacuated by evaporation and the residue is separated and removed.

Solids contents – A weighed sample is mixed with petroleum ether, which dissolves its content of oils, fats, and hydrocarbons. The solids are separated by centrifugation, and then dried at 105°C to free the rest of water and organic traces. The final dry solids weight allows the calculation of solids percentage of the sample.

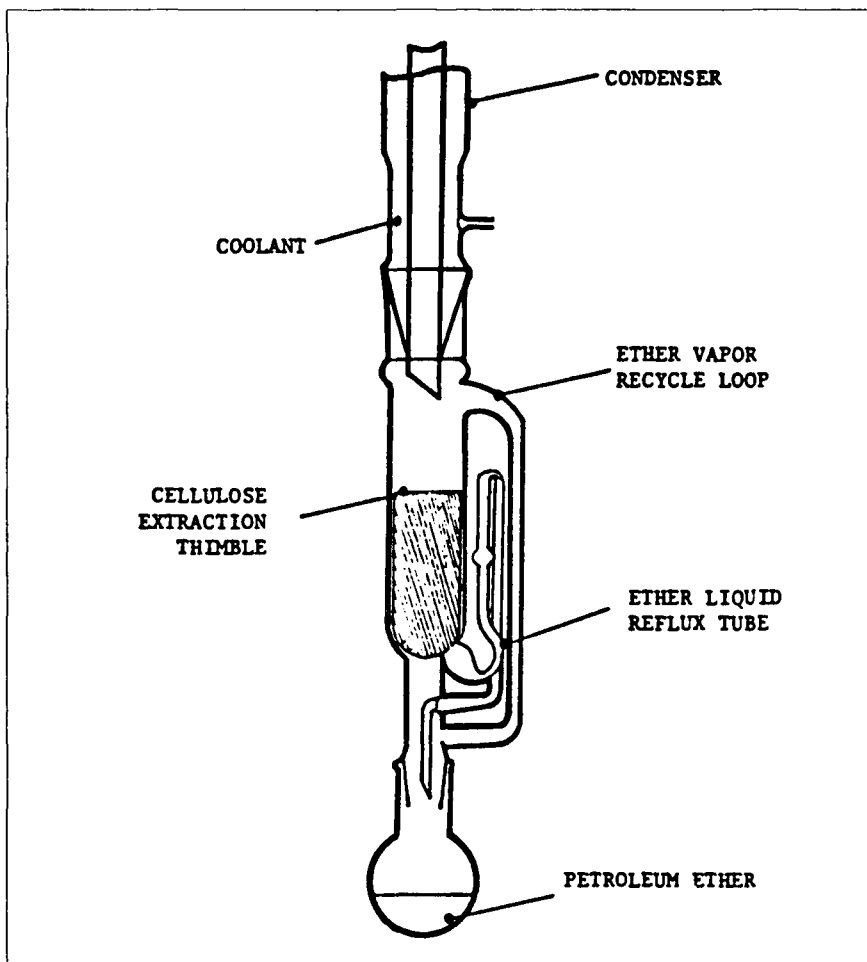


Figure 5. Soxhlet tube assembly used for hydrocarbons content analysis.

Water content – The percentage of water is obtained by difference after those of hydrocarbons and solids are known.

Flocculation and Settling Properties Determination

Froth and liquid tailings collected separately in the hot water extraction process were subjected to the following tests:

- Flocculation tests: optimization of the amount of alum de-emulsifier to be added in order to form flocs that readily settle;

- Cylinder tests of the flocculated solutions, that allow calculation of SVI (Sludge Volume Index) which defines the settleability of the sample; and
- Buchner funnel tests that quantify the filterability of the flocculated solutions.

Laboratory flocculator – The main item consists of a bank of stirrers with a variable speed drive (Figure 6). The speed of rotation will depend on the sample size (0.5L or 1 L and maintained preferably at the level of 60-100 RPM). The most important factor is to guarantee the reproducibility of the speeds. The paddles should be located near the base of the beaker to prevent settling and the beaker should be located centrally under the shaft. Quality of the flocs can be evaluated through comparison with a floc comparator chart: medium and large flocs yield a good settleable sludge corresponding to an SVI (Sludge Volume Index) well under 100 (value showing good ability to settle) [21] .

Cylinder test – Figure 7 depicts a cylinder test set-up. Flocculated froth is transferred to a one liter cylinder where a triangular shaped stirrer moves the cylinder content at a speed of 1 RPM. Interface height (in mL) is recorded along with time elapsed. This curve provides data for calculation of Sludge Volume Index (SVI) and gravity clarifier retention time.

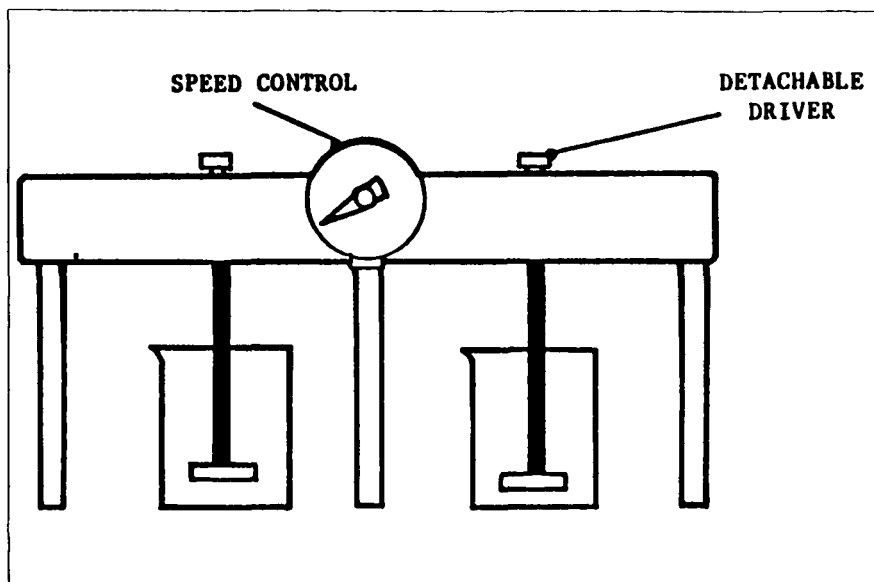


Figure 6. Flocculation test.

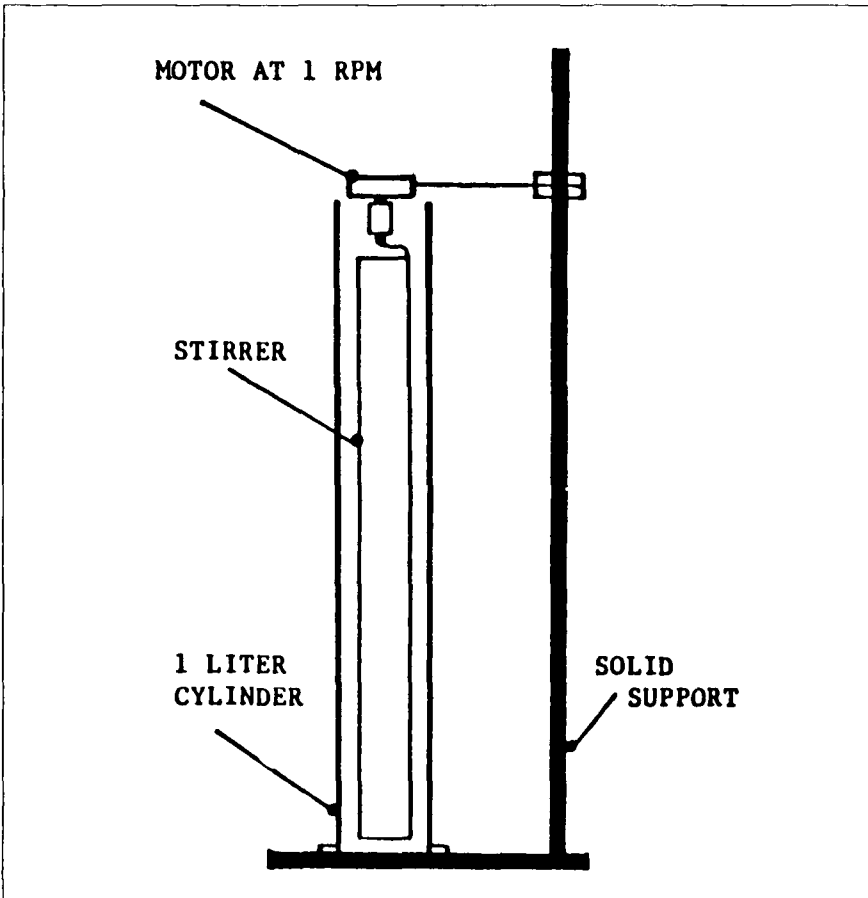


Figure 7. Sludge Volume Index (SVI) settling test.

Buchner funnel test – A simplified Buchner funnel laboratory set-up is used (Figure 8). The pressure is 49 kPa or 369 mm Hg. Volume of filtrate collected is recorded along with time of filtration. The slope of the line obtained by plotting time/volume (sec/mL) vs. volume will allow the determination of specific resistance to filtration, which is a measure of the filterability of the flocculated sludge.

RESULTS AND DISCUSSION

The efficiency of the hot water extraction process is shown in Tables 1 and 2 for two representative runs. The experimental conditions governing each run are summarized on the top of each table.

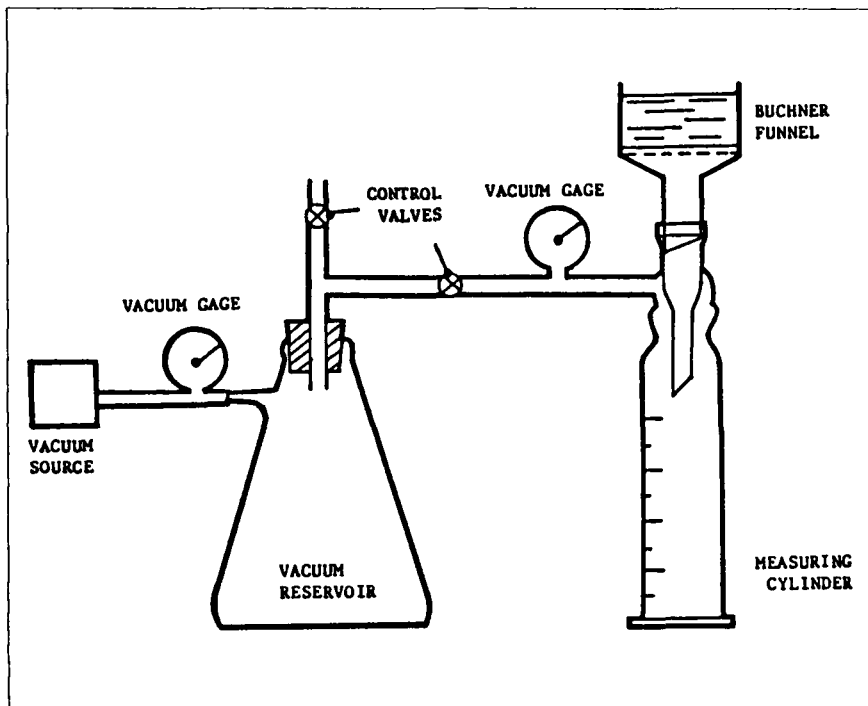


Figure 8. Buchner funnel test apparatus.

Table 1 gives the results obtained in the case of the OCS sludge process. Specificity of this case is that no addition of a wetting agent is necessary. Data are presented according to the three phases separated at the end of the extraction process: froth, solid residues, and liquid tailings. The first two columns show the pH and percentages of weight respectively. The next three columns deal with the composition (or grade) of each phase according to the three components—solids, hydrocarbons, and water—as obtained through analytical results (in this case, 800 g of beach-sand, 200 g of Bunker C oil, and 4000 g of water).

With the knowledge of initial amounts of materials introduced at the beginning of the process, one may calculate the percentages of recovery of each component in each phase, shown on the last two columns. In the case presented in Table 1, 95 percent of the recovered solids were found in the solid residues, and 99 percent of all the recovered hydrocarbons were found in the froth phase, compared to hardly 0.2 percent left in the liquid tailings. An overall mass balance based on final amounts recovered for each component revealed that no loss was incurred (during the process) as regarding the solids overall recovery percentage (last row in Table 1), compared to 53 percent for hydrocarbons.

Table 1. Hot Water Extraction of OCS Sludge

<i>EXPERIMENTAL CONDITIONS</i>							
Sample	800 g of beach sand						
Preparation	200 g of bunker C oil		1 kg of OCS sludge				
	Minimum age: 48 hours						
Digestion	Wetting agent		Nothing				
	Temperature range		90-98° C				
	Hot water rate		1.0-1.5 L/min. measured at the operating conditions				
	Hot water/sludge		1 kg/1 kg				
	Duration		20 min.				
	Agitation		1780 RPM				
Froth	Tap water addition		2 L/1 kg of OCS sludge				
Flotation	Agitation		2330 RPM				
<i>RESULTS</i>							
	<i>pH</i>	<i>Weight (Percent)</i>	<i>Grade (Percent)</i>			<i>Recovery (Percent)</i>	
			<i>Solids</i>	<i>Hydrocarbons</i>	<i>Water</i>	<i>Solids</i>	<i>Hydrocarbons</i>
Froth	8.7	5.0	10.8	40.2	49.0	3.5	99.0
Solid Residues	9.0	18.6	78.4	0.08	21.5	95.0	0.8
Liquid Tailings	8.8	76.4	0.3	0.005	99.7	1.5	0.2
Overall recovery from the initial 1 kg of OCS sludge (Percent):							
			of hydrocarbons in total:		52.8		
			of solids in total:		100.0		

Table 2 summarizes the results obtained with COS sludges from Gulf Oil Company. In the case considered here, 10 g of Na_2SiO_3 per kg of sludge was added as wetting agent. Composition of the initial amount of sludge (1000 g sample) is given on the first row of the table. Final amounts of each phase left at the end of the entire process were: 2235 g of froth, 423.2 g of solid residues, and 4000 g of liquid tailings, respectively. Data presented under the headings "percentage of grade" and "percentage of recovery" give the level of extraction efficiency of the process as was explained for Table 1 above. Overall percentages of recovery, shown on the last two rows, reveal that in this case of petroleum sludge, 88 percent of the initial hydrocarbons entrapped have been recovered compared to 98 percent of solids.

Heavy metal analysis (results given in Table 3) has shown that their level in the solid residues is very close to that of standard beach sand. Leaching tests which should be performed on these residues will tell whether land disposal could be safely applied. For the COS sludge, the following heavy metals have partly migrated from the sludge to the liquid tailings: Cu, Zn, Ni, and Cd. High levels of Cu and Ni in the liquid tailings exceed by 1 ppm the accepted critical level of 4 and 7 ppm, respectively. According to the above findings, it is

Table 2. Hot Water Extraction of COS Sludge

<i>EXPERIMENTAL CONDITIONS</i>							
<i>(Same for first and second stages unless otherwise specified)</i>							
Initial Composition	9.4% in hydrocarbons						
	77.0% in solids						
	13.6% in water						
Digestion	Wetting agent	10 g of Na ₂ SiO ₃ /1 kg of COS sludge only in the first stage					
	Temperature range	90-98°C					
	Hot water rate	1.0-1.5 L/min. measured at the operating conditions					
	Hot water/sludge	1 kg/1 kg					
	Duration	20 min.					
	Agitation	1780 RPM					
Froth	Tap water addition	2 L/1 kg of COS sludge: first stage 1 L/1 kg of COS sludge: second stage					
Flotation	Agitation	2330 RPM					
<i>RESULTS</i>							
	pH	Weight (Percent)	Grade (Percent)			Recovery (Percent)	
			Solids	Hydrocarbons	Water	Solids	Hydrocarbons
Froth	7.9	33.6	14.5	3.1	82.4	43.0	82.2
Solid Residues	7.9	6.4	82.6	0.7	16.7	46.4	3.6
Liquid Tailings	7.8	60.0	2.0	0.3	97.7	10.6	14.2
Overall recovery from the initial 1 kg of COS sludge (Percent):							
of hydrocarbons in total:				87.7			
of solids in total:				97.7			

recommended not to discard it to the environment, but to reuse it in the process for froth flotation flushing (in place of tap water). Non-recycled liquid should be filtered through heavy metal scavenger equipment, such as a suitable sand filter system before discharge to the environment.

With COS sludge, comparison of results obtained with and without addition of a wetting agent has shown that this latter prevents the fine soil particles (mostly clay) from being trapped in the froth. Table 4 shows that without wetting agent, the recovery of solids in the froth reaches the level of 57 percent compared to less than 16 percent with suitable wetting agent addition. A higher solids and oil recovery is obtained in the solid residues with the addition to a wetting agent (Na₂SiO₃, NaOH, and TWEEN 80).

A higher dose of Na₂SiO₃ (10%) or NaOH (20%) may result in higher hydrocarbons recovery in the froth and higher solids recovery in the solid residues. However, the slightly better quality of product streams does not justify the additional economical burden (ten times more in wetting agent cost). Several

Table 3. Heavy Metals Content

<i>Overall Metal Content</i>						
<i>Heavy Metals</i>	<i>OCS Sludge</i> $\mu\text{g/g}$	<i>Detoxified Sand</i> $\mu\text{g/g}$	<i>COS Sludge</i> $\mu\text{g/g}$	<i>Detoxified Sludge</i> $\mu\text{g/g}$	<i>Sand Liquid</i> $\mu\text{g/mL}$	<i>Sludge Tailings</i> $\mu\text{g/mL}$
Cd	1.5	1.2	9.9	4.2	0.0	0.01
Cu	40.9	4.7	305.8	73.2	0.4	3.9
Ni	8.6	8.7	131.7	73.9	0.1	6.7
Pb	7.5	3.5	28.8	17.3	0.3	0.1
V	5.1	5.3	16.7	19.7	0.2	0.2
Zn	37.7	19.6	499.6	147.8	0.6	0.4

<i>Detailed Mineral Content of COS Sludge Sample with 11.2% Moisture</i>											
<i>Minerals</i>	<i>Na</i>	<i>Ca</i>	<i>Mg</i>	<i>Fe</i>	<i>Cr</i>	<i>Cu</i>	<i>Pb</i>	<i>Cd</i>	<i>Zn</i>	<i>Co</i>	<i>Mn</i>
Composition ($\mu\text{g/g}$ dry)	370	1.3×10^5	7 500	17 100	590	233	81	5.8	380	22.5	210

Table 4. Effect of Additives on Recovery of COS Sludge Extraction

<i>COS Sludge</i> + <i>Additives</i>	<i>Recovery (Percent)</i>			
	<i>Solids In</i>		<i>Hydrocarbons In</i>	
	<i>Froth</i>	<i>Solid Residues</i>	<i>Froth</i>	<i>Solid Residues</i>
1% $\text{Na}_2\text{SiO}_3^a$	43.0	46.4	82.2	3.6
1% Na_2SiO_3 (Duplicata) ^a	22.0	74.2	76.4	3.4
10% Na_2SiO_3	49.9	43.4	70.0	13.1
2% NaOH	12.7	53.0	34.1	2.7
20% NaOH	15.3	79.0	64.7	6.1
1% TWEEN 80	15.8	76.7	62.1	0.5
COS Sludge with no additive	56.8	33.6	57.1	3.7

^a Different batches of sludge samples.

runs were then performed to minimize the amount of wetting agent spent to yield acceptably good recoveries. Three combinations have been found almost equally effective:

- 10 g of Na_2SiO_3 / 1 kg of COS sludge, i.e., 1% Na_2SiO_3 ;
- 20 g of NaOH / 1 kg of COS sludge, i.e., 2% NaOH; and
- 10 g of TWEEN 80 / 1 kg of COS sludge, i.e., 1% TWEEN 80.

The use of 2 percent NaOH solutions is the least expensive. It is also the least efficient among the three for high recovery of hydrocarbons in the froth and high recovery of solids in the solid residues. The 1 percent Na_2SiO_3 combination is recommended. Sodium silicate in bulk costs (1982) in the range of 0.30\$ to 0.40\$ CAN. per kg. The cost (1982) of silicate to treat 1,000 kg of crude-oil sludge will be: 3.00\$ CAN., which is economically sound and acceptable. Cost for 2 percent NaOH would be slightly lower. Cost for TWEEN 80 addition cannot be estimated as only one run was made, and thus an effective level cannot be determined. It is anticipated that with all parameters optimized, the results reported here could be improved upon significantly.

Among the many flocculants which have been tested, such as Alchem's 7715, 7725, 7726, 8102, and Dow Separan MG200, several gave efficient separation of solids. Alchem's 7726 gave the best results at a concentration of 0.1 percent in weight. Alum was also tested, but did not yield good flocculation. In the case of the duplicate runs with 1 percent Na_2SiO_3 as wetting agent, to settle 1.4 kg of froth obtained from 1 kg of sludge, 1.4×10^{-3} kg of de-emulsifier is required. The cost (at 3.5\$/kg) is then 0.5¢ per kg of crude oil sludge of 5\$/metric ton. The SVI (Sludge Volume Index) test gave data well below 100, which means an easy-to-settle sludge [21].

CONCLUSION AND RECOMMENDATIONS

The laboratory feasibility study has shown that the sand and sludge decontamination process is highly recommendable as a mobile lab process to clean accidental oil spills on the spot and return the decontaminated soil to its original location.

As regarding the OCS sludge, no screening is required as in the case of COS sludge. It was also found that the total recovery of oil can be completed without any wetting agent addition. The whole extraction process in this case comprises only three steps (I to III).

In the case of crude oil sludge, the laboratory results have shown that the following modifications have to be brought to the process:

- Provide for the feeding of a wetting agent before the first stage of digestion;

- Either add a second-stage of digestion (or hot water contacting kiln) or provide for a recycle of the first stage flotation solids residues; and
- Provide for the feeding of a flocculant to settle the solids in the froth and the liquid tailings.

Further optimization of wetting agent feeding ratio and of flocculant amount to be added is recommended.

Based on the laboratory results, which have not fully optimized all parameters, it is estimated that a high recovery of decontaminated solids (perhaps up to 90% recovery with less than 2% hydrocarbons) should be attainable.

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