DEVELOPMENT OF A PROCESS FOR OIL RECOVERY FROM WASTE OIL SLUDGES

FINAL REPORT

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DEVELOPMENT OF A PROCESS FOR OIL RECOVERY FROM WASTE OIL SLUDGES

By: Tricil Limited

For: Conservation and Protection
Environment Canada
and
Unsolicated Proposal Fund
Supply and Services Canada

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EXECUTIVE SUMMARY

Significant amounts of the waste oil sludges produced by Canadian industry are still disposed of to the land. Amid growing concerns of the environmental impact of such practices, a survey of potential oil recovery technologies was conducted. The objective was to identify a process to recover the oil from these sludges leaving an aqueous phase that would be easily treated for discharge and a solids phase acceptable for landfill. Six processes were identified and subjected to lab scale testing using samples of "light" (e.g. separator sludges) and "heavy" (e.g. tank bottoms) sludges collected largely from the refining industry. Three of the processes were successful in meeting the objective:

(a) An adaptation of conventional solvent extraction;

(b) Critical fluid extraction as demonstrated by CF Systems Corp; and

(c) The Basic Extractive Sludge Technology (B.E.S.T.^{TM}) process from Resources Conservation Co.

These processes all yielded oil phases of good quality (> 90% oil) and solids phases typically containing 2 to 10% residual oil and grease. Preliminary testing of the

aqueous phase from conventional solvent extraction indicates that it is amenable to biological treatment.

The "conventional" solvent extraction was conducted using toluene as the extractant. It was found that heating the toluene not only improved the extraction efficiency but greatly facilitated filtration of the extraction mixture. This process yielded high oil removal efficiencies (averaging >92%) and was also evaluated in a small non-integrated pilot plant. These results verified the lab scale performance.

Preliminary economics of the hot toluene process based on a 50,000 tonne/year fixed facility indicated a treatment cost of approximately $56/tonne (excluding disposal costs for the solids and aqueous phases and taking no credit for recovered oil). Information supplied from the other two manufacturers on a similar basis showed treatment costs of $60 to $80/tonne. These costs are based on information supplied in early 1987.

The recommendations from the project are:

° Monitor the implementation of the B.E.S.T.^{TM} process to confirm estimated costs and performance.

° Provide samples to CF Systems Corp. for pilot testing to confirm lab scale results and to assess operability.

- Based on the promising technical and economic results for the toluene extraction process, further development is recommended to establish the performance characteristics and costs of the key operations such as toluene recovery. The applicability to other organic sludges should also be evaluated. Successful completion of this work would form the basis for a demonstration scale facility.

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Funding for this project was provided by Environment Canada and Supply and Services Canada. The latter source included the Unsolicited Proposal Fund and the Federal Panel for Energy Research and Development (PERD).

ABBREVIATIONS

AOSTRA	Alberta Oil Sands Technology and Research Authority
RCC	Resources Conservation Company
L	Litre
mL	Millilitre
h	Hour
lb	Pound
g	Gram
mg	Milligram
kg	Kilogram
vol	Volume
B.E.S.T.^{TM}	Basic Extractive Sludge Technology
ORF	Ontario Research Foundation
MeCl	Methylene Chloride
MeOH	Methanol
TEA	Triethylamine
HSC	Heavy Sludge Composite
LSC	Light Sludge Composite
wt	Weight
EOR	Enhanced Oil Recovery
GC	Gas Chromatography
COD	Chemical Oxygen Demand
BOD_5	Biological Oxygen Demand (five day)
FCCU	Fluid Catalytic Cracking Unit
cP	Centipoise
MJ	Megajoule
GJ	Gigajoule
w/w	Values reported on a weight to weight basis
v/v	Values reported on a volume to volume basis
°C	Degree Celsius
psi	Pounds per square inch

ABBREVIATIONS (continued)

Igal	Imperial Gallon
ppm	Parts per Million
m	Metre
cm	Centimetre
yd	Yard
cal	Calorie
kWh	Kilowatt-hour
kPa	Kilopascal
Co	Cobalt
Zn	Zinc
Cd	Cadmium
B	Boron
Bi	Bismuth
P	Phosphorous
Be	Beryllium
Si	Silicon
Fe	Iron
Mn	Manganese
Ca	Calcium
Mg	Magnesium
Cu	Copper
Al	Aluminum
V	Vanadium
Mo	Molybdenum
Pb	Lead
Ni	Nickel
Cr	Chromium
Na	Sodium
Ba	Barium
Ag	Silver
As	Arsenic
Se	Selenium

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1.0 INTRODUCTION

Large volumes of waste oil sludges are generated each year throughout Canada. A large portion of these sludges is disposed of directly to land through the practices of land farming, land spreading and landfilling. Many jurisdictions, such as Quebec, are moving to restrict or prohibit these practices due to concerns about contaminant migration and the resultant environmental impacts. The land disposal option also fails to recover any potentially valuable materials in the sludges. The physical/chemical nature of the majority of these sludges precludes their disposal in a conventional fixed chamber, liquid injection incinerator. Rotary kiln incineration is feasible but such facilities are very expensive to construct and to operate and therefore disposal via this option is not practical. At present (1987), no commercial rotary kiln facilities exist in Canada.

This program addresses the above concerns by attempting to develop a process to separate waste oil sludges into their three major fractions:

1. An oil fraction which may be acceptable for (a) reprocessing,
    (b) direct combustion in boilers, or
    (c) burning in a stationary incinerator designed to destroy hazardous wastes;

2. An aqueous fraction suitable for discharge to a municipal treatment facility;

3. A reduced volume of solids acceptable for disposal in a landfill.

The original intent of this project was to review technologies used for recovering oil from oil sands for their applicability to waste oil sludges. After being altered to include only the most developed of these technologies, the Hot Water Process, the scope was subsequently broadened again to include a "paper" evaluation of other identified technologies with potential to treat waste oil sludges.

The program was begun in April 1986, took approximately 18 months to complete and was divided into three phases:

Phase One	- Waste Characterization and Process Selection
Phase Two	- Lab Scale Testing of Selected Process(es)
Phase Three	- Pilot Scale Testing

The literature review and detailed laboratory and pilot scale testing was performed by Ontario Research Foundation (ORF) under subcontract to Tricil Limited.

2.0 PROGRAM OBJECTIVE

The objective of the program is to develop a cost effective process for the separation of waste oil sludges into a recoverable or reuseable oil fraction, an aqueous sewerable fraction and a small volume of solids for landfill. More specific objectives were established for each phase and these are outlined in the appropriate sections. A chronology of the project scope is contained in the Terms of Reference in Appendix A.

3.0 WASTE CHARACTERIZATION & PROCESS EVALUATION

Broadly stated, the objectives of the first phase were:

a) to obtain samples of, and identify the characteristics of, "typical" wastes generated by the Canadian petro-refining and related industries, and

b) to determine from current development activity and the literature, processes having the potential to treat the wastes identified in (a) and to select the most promising process or processes for further investigation.

3.1 Sample Collection/Characterization

Oily sludges are generated by a number of industries with a high proportion of the volumes coming from the petroleum industry itself. Industries using oil products also generate a significant amount of waste sludges and others are produced from spills of oil products.

Twenty waste samples were received and characterized. With the exception of two which were from a large oil user, all samples came from the petroleum industry. The samples were divided into two general categories, namely 'light' sludges and 'heavy' sludges. The light sludges are typical of separator sludges. Compared to the heavy sludges they have lower viscosity, less organics and solids, and more water. The heavy sludges include materials such as tank bottoms and spill residues. Table 3.1 presents the analytical results for the light sludges and Table 3.2 gives the analysis for the heavy sludge samples.

Twenty element DC (directly coupled) plasma emission spectroscopy was performed on all of the samples with the exception of samples 3, 4 and 17 (sample number 14 was not received), and these results are presented in Table 3.3.

3.2 Process Evaluation

3.2.1 Process Identification

Potential processes were identified by searching the literature and by reviewing current activity in the waste treatment field and in the refining industry itself.

A computerized literature search was carried out using the facilities of the Ontario Research Foundation library which connects to all major North American databases. Databases searched in this program were chemical abstracts, pollution abstracts, energy line and Tulsa (U.S. oil sands, oil shale and petroleum industry) abstracts. The AOSTRA

TABLE 3.1

RAW WASTE CHARACTERIZATION, LIGHT SLUDGES

Analysis Parameter	Sample #1 Steel Mill, Separator Bottom Sludge	Sample #2 Refinery, Separator Bottom Sludge	Sample #3 Refinery, Slop Oil	Sample #4 Refinery, Slop Oil	Sample #8 Refinery, Separator Sludge
Organic Content* (%)	-	5	5	-	10
Organic Sludge* (%)	-	70	20	95	-
Aqueous* (%)	30	15	65	-	40
Solids* (%)	70	10	10	5	50
Aqueous** (% v/v)	62.0	73.8	-	-	62.7
Specific Gravity	-	1.006	0.991	1.029	1.110
Viscosity at 25°C (cP)	>10,000	<100	975	<100	770
Heating Value (MJ/kg)	14.5	5.63	10.9	5.38	5.66
Ash*** (%)	11.6	1.6	2.4	10.5	12.2
T-SO_4^{2} (% w/w)	2.95	3.54	2.70	7.32	1.20
R-Cl (% w/w)	-	-	-	-	<0.1
% Oil and Grease****	55.4	13.6	5.8	6.8	16.5
Appearance	-	-	-	-	Brown Sludge
Odour	-	-	-	-	Strong Sulphur
Flashpoint (°C)	>100	>100	>100	>100	>100
Total Solids @ 180°C (% w/w)	62.0	5.8	5.2	18.5	-
Pumpable @ 25°C (Yes/No)	No	Yes	Yes	Yes	Yes

*Spin results from lab centrifuge (% v/v)

**By distillation

***Ash = dry wt basis (@ 775°C)

****Petroleum ether extractable (includes Sulfur - % w/w)

TABLE 3.1 (continued)

RAW WASTE CHARACTERIZATION, LIGHT SLUDGES

Analysis Parameter	Sample #13 Treater & Tank Bottom Sludge, EOR Fireflood Production	Sample #16 Refinery, Slop Oil	Sample #20 Refinery, Separator Sludge	Sample #21 Steel Mill, Separator Bottom Sludge
Organic Content* (%)	20	-	-	-
Organic Sludge* (%)	25	-	-	-
Aqueous* (%)	40	-	-	-
Solids* (%)	15	-	-	-
Aqueous** (% v/v)	56	82.5	71.5	72.5
Specific Gravity	1.047	-	-	-
Viscosity at 25°C (cP)	<100	-	-	-
Heating Value (MJ/kg)	7.87	-	-	-
Ash*** (%)	23.7	15.8	-	10.0
T-SO_4^{2} (% w/w)	0.85	-	-	-
R-Cl (% w/w)	<0.1	-	-	-
% Oil and Grease****	17.2	2.8	2.0	5.7
Appearance	Brown Slurry	-	-	-
Odour	Slight Oil	-	-	-
Flashpoint (°C)	>100	-	-	-
Total Solids @ 180°C (% w/w)	-	24.6	16.4	20.6
Pumpable @ 25°C (Yes/No)	Yes	Yes	Yes	Yes

*Spin results from lab centrifuge (% v/v)

**By distillation

***Ash = dry wt basis (@ 775°C)
****Petroleum ether extractable (includes Sulfur - % w/w)

TABLE 3.2

RAW WASTE CHARACTERIZATION, HEAVY SLUDGES

Analysis Parameter	Sample #5 Refinery, Tank Bottom	Sample #6 Refinery, Residue from Bunker Distillation	Sample #7 Refinery, Residue From Spill	Sample #9 Refinery, FCCU Catalyst Residue	Sample #10 Refinery, Tank Bottom Heavy Fuel Oil
Organic Content* (%)	-	-	-	3	-
Organic Sludge* (%)	-	-	-	-	-
Aqueous* (%)	-	-	-	7	-
Solids* (%)	100	100	100	90	100
Aqueous** (% v/v)	0.88	17.8	0.8	27.5	7.5
Specific Gravity	-	1.593	1.830	1.494	1.462
Viscosity at 25°C (cP)	-	>10,000	>10,000	>10,000	>10,000
Heating Value (MJ/kg)	32.4	17.7	5.87	7.11	30.0
Ash*** (%)	3.4	37.2	55.4	52.2	4.7
T-SO_4^{-2} (% w/w)	12.0	6.78	0.26	<0.1	3.66
R-Cl (% w/w)	-	<0.1	<0.1	<0.1	<0.1
% Oil and Grease****	27.8	30.4	9.4	21.0	86.3
Appearance	-	Black Solid	Gravel + Oil	Grey Slurry	Black Solid
Odour	-	Moderate Sulfur	Moderate Sulfur	Slight Oil	Moderate Sulfur
Flashpoint (°C)	>100	>100	>100	>100	>100
Total Solids at 180°C (% w/w)	96.5	-	-	-	-
Pumpable @ 25°C (Yes/No)	No	No	No	No	No

*Spin results from lab centrifuge (% v/v)

**By distillation

***Ash = dry wt basis (@ 775°C)

****Petroleum ether extractable (includes Sulfur - % w/w)

TABLE 3.2 (continued)

RAW WASTE CHARACTERIZATION, HEAVY SLUDGES

Analysis Parameter	Sample #11 Refinery, Residue From Maintenance	Sample #12 Refinery, Residue From Maintenance	Sample #15 Refinery, Tank Bottom Tar/Coke	Sample #17 Refinery, Sludge Basin	Sample #18 Refinery, Tank Bottom High Sulphur Oil	Sample #19 Refinery, Tank Bottom Heavy Fuel Oil
Organic Content* (%)	-	-	-	-	-	-
Organic Sludge* (%)	-	-	-	-	-	-
Aqueous* (%)	-	-	-	-	-	-
Solids* (%)	100	100	-	100	-	-
Aqueous** (% v/v)	1.1	-	26.0	-	<0.1	28.0
Specific Gravity	1.429	1.430	-	1.29	-	-
Viscosity at 25°C (cP)	>10,000	>10,000	-	>10,000	-	-
Heating Value (MJ/kg)	35.30	32.56	-	71.5	-	-
Ash*** (%)	-	1.8	25.3	11.5	2.1	-
$T\text{-}SO_4^{-2}$ (% w/w)	4.28	3.65	-	1.45	-	-
R-Cl (% w/w)	<0.1	<0.1	-	<0.1	-	-
% Oil and Grease****	26.9	31.4	54.9	-	85.5	15.3
Appearance	Black Solid	Black Solid	Black Solid	Black Semi-solid	-	-
Odour	Moderate Sulfur	Moderate Sulfur	-	Moderate of Oil	-	-
Flashpoint (°C)	>100	>100	-	-	-	-
Total Solids @ 180°C (% w/w)	-	-	36.7	-	40.4	60.5
Pumpable @ 25°C (Yes/No)	No	No	No	No	No	No

*Spin results from lab centrifuge (% v/v)

**By distillation

***Ash = dry wt basis (@ 775°C)

****Petroleum ether extractable (includes Sulfur - % w/w)

TABLE 3.3

RAW WASTE METALS ANALYSIS

	Sample Number																
Element	1	2	5	6	7	8	9	10	11	12	13	15	16	18	19	20	21
Co	1.2	1.9	1.9	22	<2	8.3	16	11	<2	7.9	20	2.5	6.1	6.7	14	2.5	1.4
Zn	949	55	123	780	27	180	12	169	54	57	37	186	14	740	270	165	859
Cd	0.92	0.47	2.5	<4	<4	<4	<4	<4	<4	<4	<4	2.1	<0.25	0.32	3.4	0.62	<0.25
B	4.2	5.6	14	37	13	31	6.7	13	9.4	13	14	4.3	11	1.2	6.2	4.2	<0.5
Bi	<2	<2	<1	<40	<40	<40	<40	<40	<40	<40	<40	<5	<5	<1	<2	<2	<5
P	1460	92	67	<100	415	223	180	115	<100	<100	119	310	825	370	710	340	710
Be	<0.02	<0.02	<0.1	<0.4	0.58	<0.4	0.56	<0.4	<0.4	<0.4	<0.4	<.05	<0.05	<.01	0.08	0.036	<0.05
Si	505	158	468	49	65	73	78	49	77	29	64	129	42	39	430	250	40
Fe	12600	1470	4750	79800	9450	2540	3550	69400	3030	1630	4430	33,800	10,300	330	48,000	8,600	12,000
Mn	88	19	30	700	226	68	17	201	39	13	41	96	84	2.9	320	76	132
Ca	14700	1790	920	19100	217000	57400	353	1740	11000	1690	923	4840	15,100	970	19,000	16,500	19,900
Mg	150	284	169	3020	9790	5720	89	271	2770	627	911	681	2,960	81	3,200	1,600	705
Cu	155	25	81	339	33	25	25	106	45	59	10	138	266	17	210	62	119
Al	242	365	744	4960	3676	1340	57200	2050	1420	469	1040	316	4,860	41	19,000	4,100	78
V	3.7	4.3	92	74	149	29	162	56	84	112	28	2.1	73	.12	120	24	101
Mo	18	<6	10	<10	<10	<10	11	<10	<10	<10	<10	7.7	10	.97	13	7.8	11
Pb	113	34	36	160	29	44	59	1290	<4	21	37	72	76	500	410	415	58
Ni	28	5.8	79	122	35	26	77	63	49	67	36	73	52	1.1	120	40	28
Cr	171	63	132	792	16	379	58	32	9.5	8.2	9.7	100	313	1.9	68	275	54
Na	156	217	638	1540	<200	<200	<200	<200	299	510	18600	2260	224	710	750	84	160
Ba	21	34	87	60	72	59	16	101	38	33	789	-	-	-	-	-	-
Ag	0.18	0.06	<0.1	<4	<4	<4	<4	<4	<4	<4	<4	-	-	-	-	-	-
As	18	2.2	2.2	12	1.9	8.6	0.82	11	1.9	1.2	2.3	-	-	-	-	-	-
Se	0.047	0.38	0.57	0.18	0.28	<0.1	0.15	0.41	0.36	0.27	0.1	-	-	-	-	-	-

All concentrations in mg/kg.

(Alberta Oil Sands Technology and Research Authority) database has been thoroughly searched in connection with ongoing projects at Ontario Research and this literature was reviewed to identify processes useful to this project.

From these sources, several processes were identified as having potential for treating the types of oily wastes present in the market place. Nine processes were identified as worthy of further consideration / evaluation. These are:

- Kruyer Process (Oleophilic Sieve)
- Taciuk Process (Horizontal Rotary Kiln)
- Solvent Extraction ("Conventional")
- Hot Water Process
- Gulf-Lavalin Process (Pyrolytic Cracking)
- Supercritical Fluid Extraction
- Keane Solvent/Membrane Extraction Process
- Centrifugation
- B.E.S.T.™ (Basic Extractive Sludge Technology) Process

A brief description of each process is contained in Appendix B.

3.2.2 Evaluation Criteria

Although most of these processes had little or no available information regarding specific application to refinery based waste oil sludges, it was not in the scope of this study to develop such data (see Appendix A). However, information regarding costs and expected performance for a 7.7 tonne/h unit was solicited from the vendors of the proprietary technologies. This size of unit (50,000 tonnes annually) was selected since the original proposal for this project suggested this was the estimated yearly production of oily sludges in Ontario and Quebec. An example of the content of these requests for information is shown in Appendix C.

The information received was complimented by telephone discussions and, in some cases, meetings with representatives of the companies involved.

An example of one of the more detailed responses (letter from Taciuk without the attachments) is given in Appendix D.

The other technologies - conventional solvent extraction, hot water extraction and centrifugation - were evaluated from information gathered on current similar applications.

Detailed objectives were then established for this program by the project team - several representatives from ORF and Tricil. Each objective was given a weighting factor in terms of its relative importance - 10 being most important and 1 being least important. This weighting was performed by senior operating and technical personnel from Tricil. Each process was then subjectively rated by the project team on its expected ability to meet each specific objective - a score of 10 representing very high probability and 1 representing low probability. The product of the weighting factor of the objective multipled by the probability of the process meeting that objective was summed for all objectives yielding an overall rating or probability of success. As a check to ensure that a high overall score was not the result of scoring high in some areas but very low in others, the objectives were broken into five main categories and the performance for each category assessed separately. The objectives, grouped in the five main categories, along with the weighting factors used are listed in Table 3.4.

3.2.3 Results and Discussion

Due to the subjective nature of this analysis, small differences in overall rating or satisfaction were not considered significant. In terms of overall satisfaction the highest rating was achieved by centrifugation. Four processes with very similar ratings came next - Kruyer, hot water extraction, conventional solvent extraction and the B.E.S.T.^{TM} Process. The remaining four processes also had similar overall ratings, somewhat lower than the others.

TABLE 3.4

EVALUATION CRITERIA

OBJECTIVE	WEIGHTING FACTOR
1) Performance	
- process reliability	10
- sludge (solids) phase quality	10
- organic phase quality	8
- aqueous phase quality	8
- ability to handle feedstock fluctuations	6
2) Operability	
- ability to treat physically diverse sludges	9
- potential to make process transportable	8
- ability to treat chemically diverse sludges	7
- operating simplicity	7
- turndown ratio	6
- equipment reliability	5
- equipment simplicity	5
3) Safety/Environmental Impact	
- public acceptance	10
- air/odour emissions	8
- minimize liability	8
- maximize equipment and process safety	7

TABLE 3.4 (continued)

EVALUATION CRITERIA

OBJECTIVE	WEIGHTING FACTOR
4) Costs	
- minimize operating cost	8
- minimize capital cost	5
- minimize licence fees	4
5) Other	
- most advanced stage of development	8
- maximize plant life expectancy	3

This evaluation was conducted during the summer of 1986. Several of the processes involved were being actively developed at that time and have continued to be developed in the time since the evaluation. For example, UMATAC Industrial Processes (A Division of UMA Engineering) completed a project in 1988 entitled "Demonstration of the Taciuk Processor to Treat Heavy Oil Wastes, Emulsions, Sludges and Spills". Although the materials tested were not exactly the same as those focussed on in this program, the study represents further development of the process subsequent to this program. However, in order to proceed with this program according to the schedule established with Environment Canada, this evaluation only considered information available in the summer of 1986.

The overall evaluation is not necessarily the final word in process selection. Each process was reviewed regarding how well it met the objectives in each of the sub-groups. For example, if two processes were rated similarly in overall satisfaction but one scored substantially higher in the performance related objectives without being excessively lower in the other categories, it would be considered a more likely candidate for development. A brief summary of the considerations for each process is given below.

Centrifugation is a relatively simple, safe operation. Modified disc centrifuges are being used commercially in refinery lagoon clean-ups. Capital cost is comparatively low while operating costs will depend primarily on the requirement for feed dilution as would be necessary for the heavy sludges, pretreatment chemicals, and maintenance. The main concerns were the quality of the phases produced, in particular the sludge or solids phase. Despite these performance concerns, this technology was included in the program for further study.

The Kruyer oleophilic sieve process is being developed to recover oil from tar sands. Anticipated costs, both capital and operating, are relatively low and it rated highly on the safety/environmental objectives. Significantly lower ratings were achieved in the performance category and it is a process in an early stage of development. Samples were provided to Kruyer for their evaluation.

The application of the Hot Water Process to these waste oil sluges appeared to have potential being rated quite highly in all categories except the performance based objectives. However, there were unanswered questions regarding the quality of phases from the process, in particular the aqueous and sludge. Further work in the form of lab scale testing was considered necessary to determine its suitability.

The conventional solvent extraction process and the B.E.S.T.^{TM} process appeared to hold promise based on expected good performance and operability at reasonable cost. The B.E.S.T.^{TM} process uses triethylamine as the extractant which introduces some additional environmental concerns. However, the process has been demonstrated at a Superfund site in Georgia treating oily wastes. Composite samples of the sludges from this program will be forwarded to the vendor for their evaluation. It was decided that the application of "conventional" solvent extraction should be pursued in a lab-scale investigation as part of this program.

CF Systems Corp. have performed lab and pilot scale tests on wastes similar to those from this program. Compared to conventional solvent extraction and B.E.S.T^{TM}, this process is at an earlier stage of development. Composite sludge samples were provided to CF Systems Corp. for their evaluation.

The other solvent based process, Keane, is being developed to extract oil from tar sands. The additional steps involved in this two solvent process raised concerns of its ability to handle the varying waste characteristics envisioned. This concern, combined with the very early stage of development of this process, led to its exclusion from the remainder of the program.

The Gulf-Lavalin process is a pyrolytic rotary kiln. The high temperatures in the kiln are used to crack the hydrocarbons. The process has been developed to the pilot scale on refinery wastes. Costs associated with kiln operation are expected to be quite high and the ability to use the pyrolytic gas generated would be an important factor. No further work was planned for this process.

The Taciuk process also uses a horizontal rotating reactor. This process is seen as having great potential for oil recovery from tar sands. This process rated highly in terms of quality of phases produced but overall process reliability and operability is likely to be lower than the solvent extraction processes due to increased process complexity. This technology would not lend itself to transportability as readily as centrifugation, Kruyer or the solvent extraction processes. The capital cost is expected to be high compared to solvent extraction (downstream gas handling equipment would be large in order to handle the wide range of water and organic concentrations) and operating costs are likely to be similar or higher. Pending the evaluation of the previously mentioned alternatives, this process will not be pursued further.

4.0 LAB SCALE EXPERIMENTAL PROGRAM

The objective of the experimental program was to verify, on laboratory scale, that those processes identified as having potential, would in fact produce the desired phase separation using waste oil sludges.

Based on the process evaluation conducted in Phase One, six processes were identified for further investigation. Two of these were evaluated on a lab scale through testing conducted under this contract.

- Hot Water Extraction
- "Conventional" Solvent Extraction

This evaluation involved an extensive testing program of more than 125 individual experiments. The results of the Hot Water Extraction tests can be found in Section 4.1.1. For conciseness, only the pertinent solvent extraction results are presented in the body of this report (Section 4.1.2). A summary of all lab scale extraction tests conducted is presented in Appendix E. The remaining four processes were evaluated at the laboratory scale by submitting composite waste samples to the companies involved and reviewing their test results:

- Critical Fluid Extraction (CF Systems Corp.)
- B.E.S.T.™ Process (Resources Conservation Co.)
- Kruyer Oleophilic Sieve (Oleophilic Sieve Development Co.)
- Centrifugation (Total Garap, Inc.)

At the conclusion of the lab scale program, all results were analyzed and one process was selected for pilot scale testing.

4.1 Lab Scale Testing Conducted Under This Program

Prior to conducting the lab scale experiments, a composite sample of both the light sludges and the heavy sludges was prepared using selected samples collected and characterized in Phase One. These composites were used both in the ORF testing as well as by the other process manufacturers. Pertinent analyses of the prepared samples were:

Component* (wt %)	Heavy Sludge Composite (HSC)	Light Sludge Composite (LSC)
Oil & Grease	41.0	7.5
Water	6.5	81.0
Solids	52.5	11.5

*Oil and Grease determined by Soxhlet extraction using petroleum ether(1). Water by toluene distillation(2). Solids by difference.

Testing, using either the hot water or solvent extraction techniques, was conducted using 50 to 100 g of sludge and diluting it with a quantity of solvent (i.e. water or petroleum solvent) to the appropriate solvent:sludge ratio (volume solvent:mass sludge). The solutions were then agitated in a beaker using a magnetic stirring bar apparatus for a set period of time (usually one hour) at the desired temperature, after which separation of the phases by filtration or centrifugation was effected. Oil removal efficiencies were calculated using the following formula:

$$\frac{\text{Wt. of Oil in Feed} - \text{Wt. of Oil in Solids}}{\text{Wt. of Oil in Feed}} \times 100$$

Provided that no significant amounts of the extracted oil remain in the aqueous phase, this is equivalent to oil recovery efficiency for practical purposes.

4.1.1 Hot Water Extraction

The hot water extraction process (or Clark process) is employed commercially to recover bitumen from water-wet oil sands at the two large mining facilities located in Fort McMurray, Alberta. Basically, the oil sludges are diluted to approximately 65% at 85°C, and sodium hydroxide is added to a pH of approximately 8.5. The solution is rigorously agitated for a set period of time, and then separation of the phases by filtration or centrifugation is effected.

In this research program, tests were conducted on both the heavy and light sludge composites. The feasibility of using surfactants instead of sodium hydroxide was also studied.

4.1.1.1 Heavy Sludge Composite (HSC)

Test conditions and results for hot water extraction of HSC are presented in Table 4.1. An attempt to reproduce the Clark process (65% water to solids, 85°C and pH approximately 8.5) resulted in the solid HSC phase absorbing most of the water and producing no real phase separation. The experiment was repeated using a ratio of water:HSC of 2:1 at 85°C and pH 8.5. When centrifuged hot, a three-layer phase separation took place. The top layer consisted of congealed oil and grease and had the texture of lubricating grease. The middle layer appeared to be largely unaltered water, and the bottom layer appeared to be somewhat coarser solids than the top layer. The same conditions were repeated only at 90°C using 50 g of waste. When the hot mixture was poured into the bottle for centrifugation, it almost immediately separated into water and an hour-glass shaped

TABLE 4.1

HOT WATER EXTRACTION

LAB SCALE TEST RESULTS, HEAVY SLUDGE COMPOSITE

Solvent (Water): Sludge Ratio *	Surfactant	Temperature (°C)	pH	Degree of Dispersion	Oil Removal Efficiency (%)	Comments
0.65:1	NaOH	85	8.5	None	-	Most of water absorbed - no phase separation.
2:1	NaOH	85	8.5	Fair	-	Three layers: Top - grease; middle - unchanged water; bottom - coarse solids.
2:1	NaOH	90	8.5	Fair	-	Three layers: Top, 24 g "grease"; middle, 95 cc water; bottom, 24 gm coarse solids. Starting material, 50 g sludge.
2:1	NaOH	95	9.5	Good	52.2	Three layers: Top, 11.41 g grease (dry) containing 86.5% oil & grease; middle, 191 g of unchanged water; bottom, 87.5 g solids (dry) containing 22.4% oil & grease.
2:1	1% SLS	80	-	Uniform/Good	-	Two layers: Top - unchanged water; bottom - black solids.
10:1	1% SLS	80	-	-	-	Two layers: Top - oil & solids; bottom - yellow water.
5:1	2% SLS	80	-	Even/Good	-	Three layers: Top - oil & grease; middle - unchanged water; bottom - small amount of solids.

*Solvent (grams) : waste (grams)
SLS - Sodium Lauryl Sulfate

oily globule. After centrifugation, three layers were observed; a top layer, approximately 24 g of heavy "grease"; a middle layer, approximately 95 mL of essentially unchanged water; and a bottom layer of approximately 22 g of coarse "solids" material. The experiment was repeated with 100 g HSC and 200 g water and a mass balance determined. Following extraction at approximately 95°C, pH 9.5, and centrifugation while hot, 200 mL of liquid weighing 191 g were recovered. The liquid was essentially unchanged water with a top layer of approximately 18 mL of congealed grease. The wet solids recovered from the centrifuge bottle weighed approximately 100 g, and appeared to be wet granules plus oil. A total recovery of 98% of the starting materials (3 g left in beaker) was achieved. After air drying overnight, the residual solids weighed 87.6 g and contained 22.3% oil and grease (19.6 g). The top grease layer lost weight from 12.1 g to 11.4 g (6.7%) after air drying and contained 86.5% oil and grease (9.9 g). Since HSC contained 41% oil and grease, 11.5 g of oil should be contained in the water layer. These analyses suggested an oil removal efficiency of 52.2%.

An anionic surfactant, sodium lauryl sulfate (SLS), was also evaluated. An experiment was performed in which 50 g HSC and 100 mL of 1% sodium lauryl sulfate in water were mixed and heated to 80°C with stirring. The effect of

SLS as a dispersing agent was confirmed since a uniform dispersion resulted (heating HSC with water alone at 5:1 does not effect a dispersion). The entire mixture was centrifuged hot. Two layers were formed: an upper layer of essentially unchanged water and a bottom layer of black solids. Changing the SLS concentration from 1% to 2% and the water:solids ratio from 2:1 to 5:1 and 10:1 were also examined. With 2% SLS at 5:1, when centrifuged, three layers are formed, top oil and grease, "unchanged" water and coarse solids on bottom.

4.1.1.2 Light Sludge Composite (LSC)

Test conditions and results for hot water extraction of LSC are presented in Table 4.2. An attempt to reproduce the Clark process (65% solids:water, 85°C, pH 8.5) produced much the same results as with HSC, i.e. most of the water was absorbed by the sludge and no real phase separation could be observed. As with HSC, a much better dispersion of solids in water is obtained by increasing the solvent:waste ratio to 2:1 at 85°C, pH 8.5. When centrifuged hot, this mixture gave two layers: an oil and water emulsion on top and black solids on bottom. Heating to 90°C with 2:1 water:sludge at pH 8.5 gave a fair dispersion which, when centrifuged hot, gave a liquid black emulsion and a layer of black solids. In an attempt

TABLE 4.2

HOT WATER EXTRACTION

LAB SCALE TEST RESULTS, LIGHT SLUDGE COMPOSITE

Solvent (Water): Sludge Ratio *	Surfactant	Temperature (°C)	pH	Degree of Dispersion	Comments
0.65:1	NaOH	85	8.5	-	No real phase separation.
2:1	NaOH	85	8.5	Better	Two layers: Top - oil/water emulsion, bottom - black solids.
2:1	NaOH	90	8.5	Fair	Two layers: Top - liquid black emulsion; bottom - black solids.
2:1	NaOH	85	9.5	Excellent	Two layers: Top, 97g of black liquid; bottom, 40.1 g solids (dry) containing 10.4% oil & grease. Starting material, 50 g sludge.
2:1	1% SLS	Room	-	Very Good	Cannot be filtered.
5:1	1% SLS	Room	-	Very Good	Cannot be filtered - H_2S evolved when acidified.
5:1	1% SLS	80	-	Very Good	After centrifugation: 23.91 g solids (dry) containing 20.4% oil & grease. Starting material - 50 g sludge.
10:1	1% SLS	80	-	Good	Very poor separation on centrifugation.
5:1	2% SLS	80	-	Excellent	Two layers: Top - dark material emulsion; bottom - greasy solids.
5:1	2% SLS	80	-	-	As above.
5:1	1% SAAS	Room	-	Very Good	Cannot be filtered - H_2S evolved when acidified.

*Solvent (grams) : waste (grams)
SLS - Sodium Lauryl Sulfate
SAAS - Sodium Alkyl Aryl Sulfonate

to break the emulsion, the emulsion layer from centrifugation was acidified to pH 2 and allowed to stand. The "oil" sank to the bottom, leaving essentially unchanged water on top. A mass balance experiment, in which 50 g of LSC and 100 g of water at pH 9.5 were heated to 85°C and centrifuged hot, was performed. When separated, the liquid layer yielded 97 g of black liquid and 40.05 g (from 50 g starting) of air-dried (overnight) solids containing 10.35% oil and grease, corresponding to a negligible overall oil extraction efficiency.

Experiments were performed with LSC using 1% and 2% sodium lauryl sulfate (SLS) and 1% sodium alkyl aryl sulfonate (SAAS), examples of anionic surfactants, both at room and elevated temperatures. At room temperature, good dispersions of LSC in the surfactant solutions were achieved at 2:1 and 5:1 water:waste ratios. None of the dispersions, however, could be filtered. When acidified to break the dispersion, hydrogen sulphide was evolved from the samples. At temperatures of 80-85°C and water:waste ratios of 5:1 to 10:1, excellent dispersions of the LSC were formed. When centrifuged (hot), rather poor separations resulted, giving a top layer of black liquid and a bottom layer of wet solids. A mass balance experiment, in which 50 g of starting LSC was mixed with 250 mL of 1% SLS in water, yielded, after centrifugation, 23.91 g of "dry" solids (air-dried overnight) containing 20.41% oil and grease.

Experiments were conducted using medium (e.g. Percol 728) and high strength (e.g. Percol 757) cationic surfactants. Tests were performed at approximately 85°C and at a 5:1 water:LSC ratio. Surfactant concentrations ranged from 10 ppm to 1,000 ppm. In all cases, a very viscous solution was created, which was very difficult and time consuming to filter.

4.1.1.3 Hot Water Extraction Summary

It was observed for both the HSC and LSC samples, that a dispersion could be created by heating and addition of caustic or surfactant. However, the difficulty of the ultimate separation of the phases still remains. The dispersion effected is probably oil:solids globules being agitated in a continuous water phase. In other words, the caustic or surfactant did not actually penetrate the outer oil layer to the oil:solid interface, at which a real extraction could only occur.

4.1.2 "Conventional" Solvent Extraction

Three-different solvents were tested in this program:

- Toluene (an aromatic solvent)
- Petroleum Ether (an aliphatic solvent blend)
- Methylene Chloride - MeCl (a chlorinated hydrocarbon solvent)

The first set of experiments was conducted using a 10:1 solvent to sludge ratio (mL solvent to grams of sludge). Good dispersions were created in all cases and the filtered solids were observed to be relatively free of oil and grease. It was then decided to lower the solvent:waste ratio to 5:1, which would then represent a base case for test condition comparisons. When the agitation time of the sludge/solvent mixture was completed, filtration of the solution was attempted. In many cases, however, filtration could not be performed due to incomplete dispersion and/or excessive solution viscosities. Tests were then repeated at similar conditions, and the solutions were centrifuged.

Experimental results of selected conventional solvent extraction trials on both HSC and LSC are presented in Table 4.3. It is readily apparent from this table that higher extraction efficiencies were obtained with the HSC than with the LSC. Both methylene chloride and toluene extracted over 95% of the oil from the HSC. However, on LSC, methylene chloride extracted just over 80% of the oil, while the efficiency with toluene was approximately 68%.

TABLE 4.3

"CONVENTIONAL" SOLVENT EXTRACTION

SELECTED LAB SCALE TEST RESULTS

Room Temperature

Sludge Type	Solvent	Solvent:Waste Ratio*	Oil Removal Efficiency (%)	Comments
HSC	Toluene	5:1	95.3	Cannot filter, therefore centrifuged
HSC	MeCl	5:1	97.1	Cannot filter, therefore centrifuged
HSC	Petroleum Ether	5:1	84.0	Filtered moderately well
LSC	Toluene	5:1	67.6	Very slow filtration
LSC	MeCl	5:1	81.5	Cannot filter, therefore centrifuged
LSC	Petroleum Ether	5:1	80.5	Slow filtration

*Vol Solvent (mL):mass waste (g)

Even though the toluene extractions of HSC were excellent, severe handling problems were evident, due to the high solution viscosity. Since toluene has a higher boiling point (111°C) than either petroleum ether (approximately 60°C) or methylene chloride (40°C), experiments could be conducted at elevated temperatures to reduce the solution viscosity. The results of increasing the extraction temperature to 80°C were significant, as filtration could be effected rapidly, and oil removal efficiency was recorded at over 99%. A comparison of a few tests using toluene at elevated temperatures is given in Table 4.4.

It was felt that the major reason for low oil removal efficiencies with LSC was that the high water content was limiting penetration by the solvent by creating a boundary layer encapsulating the oil-wetted solid particles. A number of tests were then conducted using various pretreatment methods for water removal. Those methods considered and tested were:

- Pressure Filtration
- Methanol (MeOH) Extraction
- Thermal Drying
- Vacuum Evaporation

Pressure filtration proved to be far less successful than either methanol extraction, vacuum evaporation or thermal drying.

TABLE 4.4

TOLUENE EXTRACTION

SELECTED LAB SCALE TEST RESULTS, HEAVY SLUDGE COMPOSITE

Solvent	Solvent:Waste Ratio*	Oil Removal Efficiency (%)	Comments
Toluene (at room temperature)	5:1	95.3	Very slow filtering due to high viscosity of slurry
Hot Toluene (@ 80°C)	5:1	99.8	Rapid filtering
Hot Toluene (@ 80°C)	3.5:1	97.7	Slower filtering than @ 5:1
Hot Toluene (@ 80°C)	5:1	98.6	5 minute residence time in solvent
Hot Toluene (@ 80°C)	5:1	91.8	Individual tank bottom sample, filters rapidly

*Vol. Solv. (mL):Mass waste (g)

Therefore, only results from the latter three dehydration techniques will be discussed.

The procedure during a test was basically to "dry" the LSC, filter the solution in the case of MeOH extraction, and subject the "dry" solids to solvent extraction in a manner similar to that discussed previously. Although petroleum ether, methylene chloride and room temperature toluene were employed for extraction in a number of tests, emphasis was focussed on using hot toluene. Selected test results comparing the three approaches are given in Table 4.5. The drying pretreatment was found to be very effective in improving the subsequent extraction of oil from the LSC. Both the oven drying and methanol extraction techniques yielded similar results, which were higher than that recorded for vacuum evaporation. However the vacuum evaporation test was performed on an individual separator sludge sample, not on the composite sample. Also the water content was not quite as low (26% vs. 20%).

Rigorous tests were conducted using light sludges to determine mass balances around the process for: i) thermal drying to 20% water; ii) thermal drying to 40% water; and iii) drying using methanol extraction. This information was used to compare the economics of the different drying techniques (see Section 4.3).

TABLE 4.5

HOT TOLUENE EXTRACTION

LAB SCALE TEST RESULTS USING

"DRYING" PRETREATMENT, LIGHT SLUDGE COMPOSITE

Drying Technique	Solvent Extraction	Oil Removal Efficiency (%)
MeOH @ 5:1 (to approx. 20% moisture)	Toluene, 80°C, 5:1*	89.2
Oven Drying (to 20% moisture)	Toluene, 80°C, 5:1	89.5
Vacuum Evaporation (to 26% moisture)	Toluene, 80°C, 5:1	82.0**

* 5:1 represents Solvent (mLs) to waste (g) ratio
**Not LSC, individual separator sludge sample

4.2 Lab Scale Testing Conducted by Others

In order to evaluate the proprietary technologies, samples of both the heavy sludge composite and the light sludge composite were forwarded to each of the companies involved for lab scale testing. All four companies agreed to perform, at no charge, initial screening tests on the samples to assess whether or not their process demonstrated enough promise to justify further work. Discussions were held with each company to relay the overall objective of the work. Each proponent was asked to supply information regarding the conditions under which tests were conducted and the results i.e. analysis of each phase generated. It was also requested that samples of the products generated be returned for evaluation.

4.2.1 Oleophilic Sieve Development Co.

The basis of the Kruyer process is a sieve made from oleophilic materials which allows water and the hydrophilic solids to pass through the apertures while the oil phase adheres to the sieve surfaces. The sieve used is in the form of a moving conveyor that prevents the oil from blinding the sieve because of its motion.

Samples of HSC and LSC were tested using the Oleophilic Sieve. Dr. J. Kruyer, President, reported verbally that no separation could be achieved, eliminating the possibility of using this technology for refinery wastes.

4.2.2 CF Systems Corp.

Supercritical fluid extraction is a solvent extraction conducted at conditions at or above the critical point of the extractant. Under these conditions the extractant exhibits some of the beneficial properties of both a liquid (ability to dissolve significant amounts of organics) and a gas (high transfer rates).

Samples of each of HSC and LSC were tested by CF Sytems Corp. in a small batch scale critical fluid extraction system. Conditions for these tests were:

Temperature:	Ambient
Pressure:	1000 kilopascals (150 psi)
Solvent:	Propane
Extraction Residence Time	20 minutes

These conditions are not quite the critical conditions for propane. An additional advantage of using an extractant that is a gas at ambient conditions is that subsequent recovery of the solvent for re-use is facilitated.

(i) Heavy Sludge Composite

A high quality extract was recovered from the CF Systems process which was analyzed to contain over 96% oil and grease. The raffinate was found to be 11.7% oil and grease. On a mass balance basis, the extract was approximately 35% of the feed weight, and the raffinate about 65%. The overall oil extraction efficiency was calculated to be in the order of 83%.

(ii) Light Sludge Composite

As observed for the HSC, a fairly high quality extract was produced from the CF Systems test. The raffinate (solids and water) contained about 0.49% oil and grease. The filtered solids were analysed at 6.17% oil and grease. The overall extraction efficiency was determined to be approximately 78%.

4.2.3 Resources Conservation Co. (RCC)

RCC market the Basic Extractive Sludge Technology (B.E.S.T.^{TM}) process, which employs triethylamine as the extracting solvent, for recovering oils from waste sludges. The first commercial scale unit operated successfully during 1986 and early 1987 at a Superfund clean-up site in

Savannah, Georgia. This transportable unit treated about 3,700 tons of acidic, oily sludge.

RCC conducted batch scale tests of both the HSC and LSC samples submitted to them. The extraction procedure used involved "solids washing" - essentially re-extraction of the solids. A summary of the results from the extraction of HSC and LSC was provided by RCC and is presented in Tables 4.6 and 4.7 respectively. Residual oil and grease contents in the extracted solids (dried @ 105°C)were good, being 6.9% and 3.3% for HSC and LSC respectively. These analytical measurements were obtained using methylene chloride extraction. Since weights of the recovered solid phase were not provided, overall oil removal efficiencies could not be calculated.

4.2.4 Total Garap, Inc.

A modification of the conventional disc centrifuge is being used to treat some oily wastes. This modification includes an outer scroll, rotating at a slightly different speed than the disc stack, designed to facilitate movement of the solids to the discharge ports.

Samples of LSC were submitted to Total Garap, Inc. to evaluate the effectiveness of a modified disc type centrifuge. Mr. Gerry McFadden of Total Garap reported verbally after a bench top test that their centrifuge could not process the LSC. He indicated that the solids content was too high and excessive pretreatment steps would be required prior to treatment.

4.3 Lab Scale Program Discussion

The results of the research program suggested no potential for using hot water, with or without caustic or surfactant addition, as a process for recovering oil from refinery generated sludges.

Conversely, any of the three hydrocarbon solvents tested could be used for the extraction, provided sufficient solvent:waste ratios could be employed. Toluene and methylene chloride yielded the greatest extraction efficiencies, but the solutions were quite viscous at reasonable solvent:waste ratios (i.e. 5:1). Advantage was taken of the relatively high boiling point of toluene to increase the extraction temperature to reduce the solution viscosity. This modification yielded improved oil removal efficiency and a dramatic improvement in handling properties (i.e. filtration).

Poorer extraction efficiencies were observed for LSC as compared to HSC. It was theorized that the high water content of LSC was inhibiting solvent penetration to the

TABLE 4.6

B.E.S.T.™ LAB SCALE TEST RESULTS*

HEAVY SLUDGE COMPOSITE

		Feed	Products	
			Solids**	Oil
Oil & Grease	(wt %)	43	6.9	
Solids	(wt %)	52		
Water	(wt %)	5		1.1
TEA (triethylamine)	(mg/kg)	-	1,300	< 120
Metals	(mg/kg)			
Silver			< 4	< 1
Arsenic			< 31	< 50
Barium			120	4
Cadmium			< 3	< 1
Chromium			160	20
Copper			110	-
Lead			370	< 40
Nickel			38	26
Zinc			300	60
Selenium			32	-
Vanadium			-	73

*Provided by Resources Conservation Co.
**Results are for filtered solids following drying @ 105°C to evaporate TEA.

Note: Insufficient water phase recovered for analysis.

TABLE 4.7

B.E.S.T.™ LAB SCALE TEST RESULTS*

LIGHT SLUDGE COMPOSITE

		Feed	Products		
			Solids**	Water	Oil
Oil & Grease	(wt %)	10	3.3	0.017	-
Solids	(wt %)	15	-	-	-
Water	(wt %)	75	-	-	5.8
TEA (triethylamine)	(mg/kg)		1,700	66	< 110
Metals	(mg/kg)				
Silver			< 1	0.03	< 1.0
Arsenic			160	< 0.5	< 5.0
Barium			130	0.6	0.3
Cadmium			13	< 0.01	< 1.0
Chromium			950	0.75	150
Copper			1,300	0.19	-
Lead			960	< 0.2	2.0
Nickel			240	0.3	20
Zinc			280	0.38	12
Selenium			92	< 0.5	-
Vanadium			-	-	40
Total Organic Carbon	(mg/L)		-	1,800	-
Total Dissolved Solids	(mg/L)		-	14,000	-
Total Suspended Solids	(mg/L)		-	110	-

*Provided by Resources Conservation Co.

**Results are for filtered solids following drying @ 105°C to evaporate TEA.

oil:solid interface. Various dehydration pretreatments were tested and it was found that either methanol extraction or thermal drying of the LSC, prior to hot toluene extraction, significantly improved the potential oil recoveries.

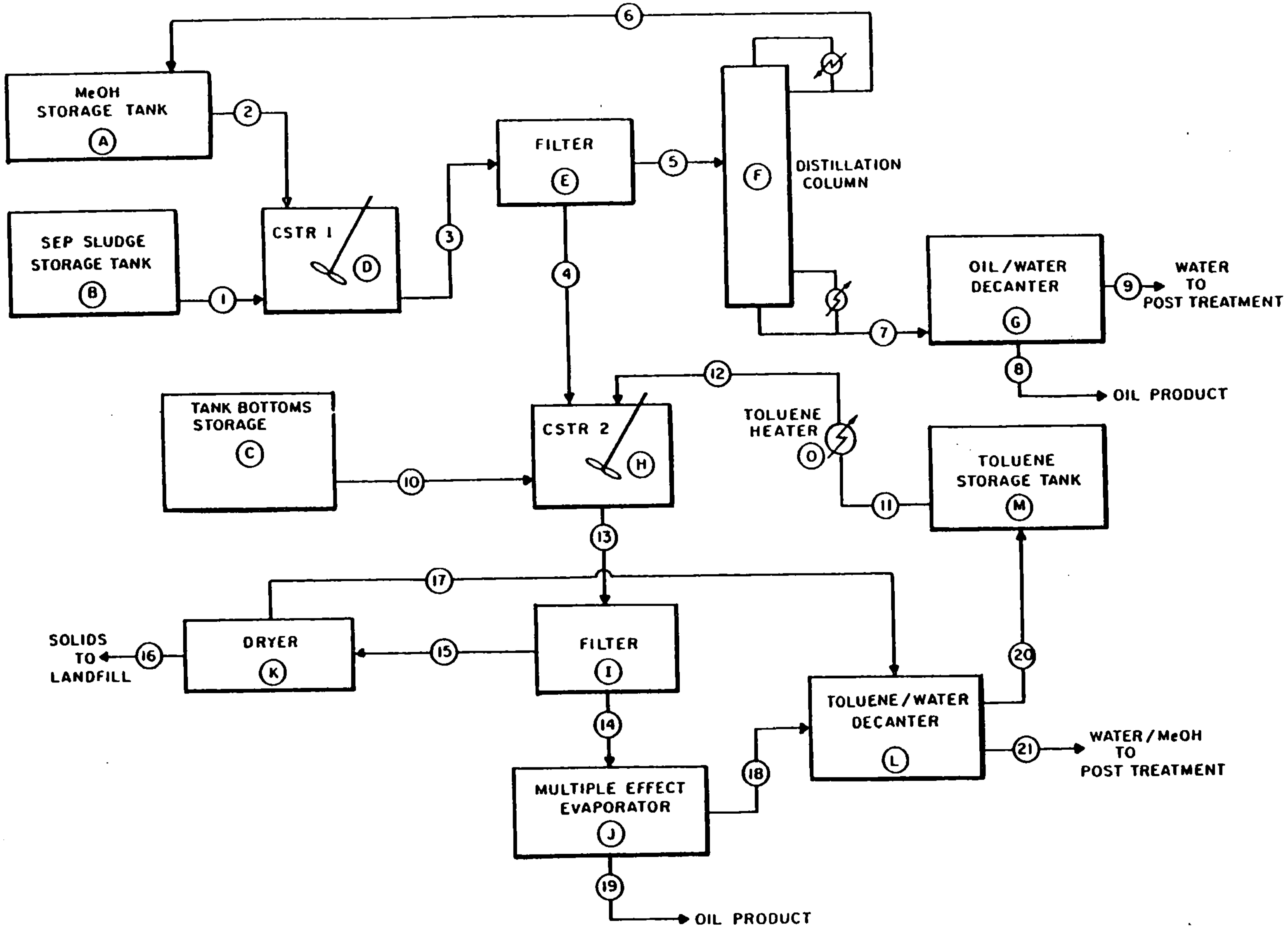
Therefore, two significant findings were arrived at during this research:

* Toluene heated to 80°C was a very effective oil extraction solvent which exhibited good filtration characteristics and handling properties.

* Pretreatment to remove a portion of the water from light sludges improves considerably the ability of a solvent to extract oil from the "dried" sludge.

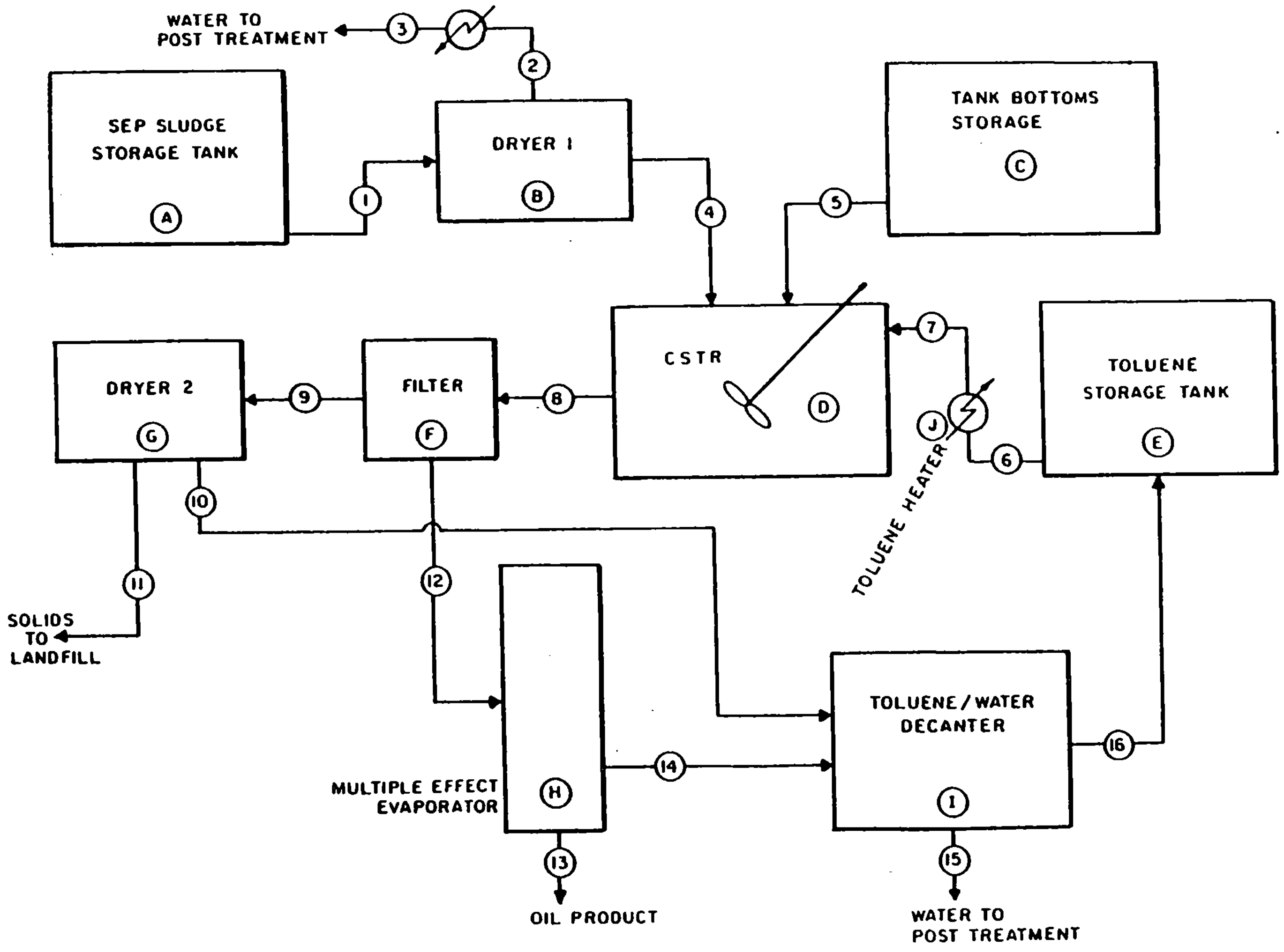
These findings led to the conceptual development of two processes, differing only in the manner in which water was removed from the light (separator) sludges. Figure 4.1 illustrates a system using a methanol extraction dehydration step, while a system using thermal drying of light sludges is presented in Figure 4.2.

Bench scale mass balance trials were performed using the two different concepts. Using the results of these experiments, an order of magnitude economic assessment was conducted. The objective of the comparison



MeOH/HOT·TOL EXTRACTION PROCESS

FIGURE 4.1



DRYER / HOT-TOL EXTRACTION PROCESS

FIGURE 4.2

was to select the most feasible system for pilot scale study. This evaluation, based on the above mentioned flow diagrams, assumed a plant capable of processing 50,000 tonnes per year of a feedstock evenly split between light sludges and heavy sludges. Stream flowrates were estimated from the data gathered during mass balance tests and this was used to size the major equipment. Capital costs were determined for this equipment and a factor applied to yield an estimate of total plant cost. All equipment costs were updated to third quarter 1986. This was done using the Chemical Engineering Plant Cost Index(3). Due to the additional equipment required for filtration and distillation, the process using methanol extraction for drying had a higher capital cost.

Major operating costs (direct labour, chemicals, utilities and maintenance) were then assessed for each option. Labour costs were assumed to be the same for both processes. Chemical costs were estimated using current pricing in the Chemical Marketing Reporter(4). Drying by methanol extraction was estimated to have higher chemical and energy requirements. It also had higher estimated maintenance cost since this was assumed to be a percentage of equipment cost (4%).

Combining the capital (assuming depreciation over 10 years) and the operating costs, the order of magnitude sludge treatment costs are as follows:

MeOH Extraction - Hot Toluene Extraction	$105/tonne sludge
Thermal Drying to 20% Moisture followed by Hot Toluene Extraction	$50/tonne sludge
Thermal Drying to 40% Moisture followed by Hot Toluene Extraction	$47/tonne sludge

Neither solids disposal costs nor credit for recovered oil was considered since these are likely to be similar for both approaches.

The economic benefit to using an oven drying dehydration step compared to methanol extraction was obvious. It was, therefore, decided to pursue the process utilizing thermal drying of light sludges followed by hot toluene extraction of mixed heavy sludges and dried light sludges on a pilot scale.

It was also found in the program that both the CF Systems Corp. critical fluid extraction process, and the RCC B.E.S.T.™ system are viable oil extraction processes. It is important to understand some of the differences in the way the tests were conducted and the analyses performed for the three different processes. As mentioned RCC performed multiple extractions of the sample. The residual oil and grease levels

(3.3 wt % on LSC and 6.9 wt % on HSC) reported by RCC were performed on filtered solids after drying at 105°C to evaporate triethylamine. By contrast, the hot toluene tests were single stage extractions (re-extraction is discussed in Section 5.3). Residual oil levels on wet filtered solids were 3.2 wt % for LSC and 1.2 wt % for HSC (values for air dried filter cakes are reported for the pilot scale tests in Section 5.3). CF Systems results indicate 6.1 wt % oil and grease on the wet solids from the LSC trial. The 11.7 wt % oil and grease reported for the HSC trial was for the water and solids combined before filtering. Since these tests were conducted, CF Systems Corp. have made improvements to their process. They now claim (unsupported) that they can get oil and grease contents on the solids consistently below 1% w/w.

5.0 Pilot Scale Experimental Program

As discussed in Section 4.3, a promising method of recovering oil from refinery generated light sludges and heavy sludges (e.g. tank bottoms) was conceptualized. Besides the technical merits of realizing high oil removel efficiencies, an economic analysis indicated that the net treatment costs of the concept were also attractive. To confirm results generated in the bench scale experimentation, and to assess potential practical problems of the system, it was decided to test the process in a small non-integrated pilot plant. More than twenty pilot tests were conducted.

5.1 Pilot Plant Description

The pilot plant was housed in a small room that was equipped with explosion proof electrical equipment including an exhaust fan effecting one air change per minute. Where possible, remote actuators were used for valves to minimize the requirement for entering the room during a test. Key temperatures were also displayed outside the room. A schematic of the unit operations for the pilot plant - as originally specified - is given in Figure 5.1.

Each trial utilized approximately 10 kg of waste feed. This represents a scale-up factor of 200 times from the lab-scale testing.

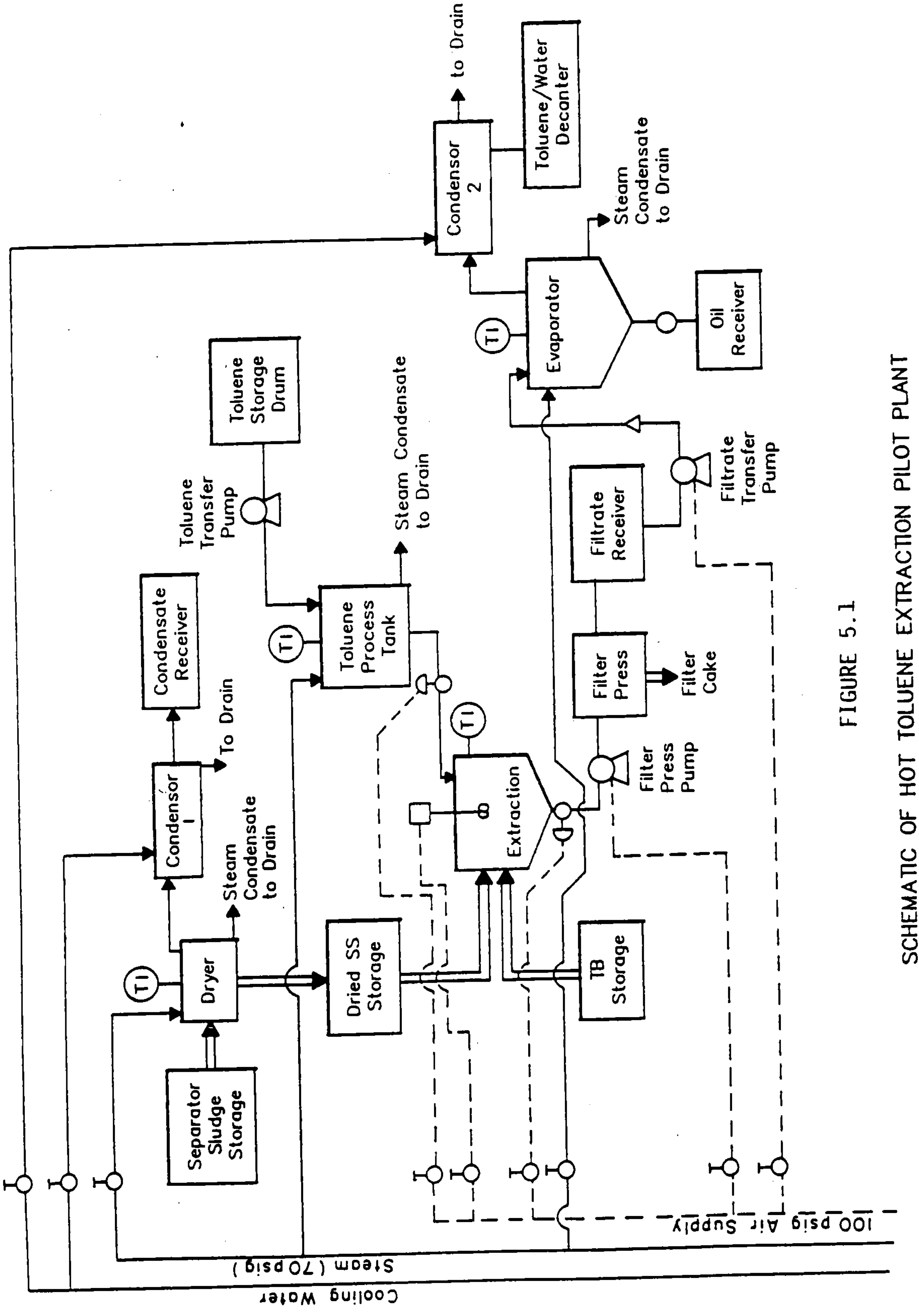


FIGURE 5.1

SCHEMATIC OF HOT TOLUENE EXTRACTION PILOT PLANT
(AS ORIGINALLY DESIGNED)

Operational problems before and during the test program resulted in a significant change in the operation and appearance of the process as depicted in Figure 5.1. The two major problems were:

- The dryer manufacturer from whom rental of the light sludge dryer had been arranged, could not deliver the unit, due to mechanical problems which could not be rectified in time. Attempts at securing another dryer from other manufacturers were unsuccessful, due to long lead times on equipment delivery.

- The slurry created during extraction of the toluene and sludge could not be pumped to the filter press. Various pumps were tried, and failed due to plugging. This appeared to be caused by the precipitation of the fine, albeit heavy, solids in the relatively low viscosity extraction solution.

The only available solution to the dryer problem was to dry small quantities of the light sludges in a laboratory oven.

Although some test results (i.e. oil and grease in filtered solids) were obtained using the pump-filter press arrangement, it was recognized that the planned mass balance experiments would be totally impractical. Therefore, both the pump and the filter press were abandoned in favour of a "drum vacuum filter" constructed for the duty. Basically, the lid of a 70 L drum was perforated and fitted with a 325 mesh size stainless steel screen. A vacuum was then applied to the drum to improve filtration rate.

A description of the steps involved in conducting a pilot scale test is contained in Appendix F.

5.2 Waste Description

Several barrels of tank bottoms and separator sludges were received from refineries located in Ontario and Quebec. In addition, one sample was obtained from an oil user rather than an oil refiner. Portions of each of these were mixed together to create two composite samples, one for heavy sludges (largely tank bottom wastes) and one for light sludges. The classification of "heavy" or "light" was made based on the sample's origin and water content. Less than 30% water content samples were heavy, and greater than 30% water content were light sludges. Pertinent analyses of the composite samples are given below and compared to the lab scale composites:

Component* (wt %)	HSC Pilot	 Lab	LSC Pilot	 Lab
Oil & Grease	40.9	41.0	8.0	7.5
Water	13.2	6.5	67.1	81.0
Solids	45.9	52.5	24.9	11.5

*Oil and grease determined by Soxhlet extraction using petroleum ether (1). Water by toluene distillation (2). Solids by difference.

5.3 Pilot Scale Test Results

Most of the experiments were devoted to analyzing only the oil and grease content of the filtered solids. By so doing, a greater spectrum of variables could be examined than if exhaustive mass balances were conducted on every test. For the pilot scale tests the solvent to sludge ratio is a weight to weight ratio.

The range of conditions tested in the pilot unit were:

Sludges:	HSC, LSC, Dried LSC, Mixed HSC/LSC
Solvent:Sludge Ratio:	3:1, 5:1
Temperature:	40°C, 80°C
Extraction Time:	10 minutes all tests
Re-extracting Solvents:	Toluene, petroleum ether

The pilot plant test results for the different waste sludges tested are given in Table 5.1.

TABLE 5.1

HOT TOLUENE EXTRACTION

PILOT SCALE TEST RESULTS

Waste	Solvent: Sludge Ratio*	Temp. (°C)	Oil & Grease (wt. %) Feed	Oil & Grease (wt. %) Air Dried Filter Cake	Oil Removal Efficiency (%)	Comments
HSC	5:1	80	53.7	4.3	95.1	Average of 2 tests
HSC	5:1	40	51.0	6.8	94.1	Average of 2 tests
HSC	3:1	80	58.7	7.8	95.8	
HSC	3:1	40	41.6	4.7	94.7	Average of 3 tests
LSC	5:1	80	7.7	3.0	83.9	Average of 2 tests
LSC	3:1	40	8.6	6.4	79.5	
LSC Dry**	5:1	80	25.8	1.0	97.5	
LSC Dry**	3:1	40	27.5	4.0	90.4	
LSC/HSC 1:1	5:1	80	32.0	3.3	96.1	
LSC/HSC 1:1	5:1	40	26.8	3.0	95.7	
LSC/HSC 1:1	3:1	80	20.6	4.1	90.5	Average of 2 tests
LSC/HSC 1:1	3:1	40	29.3	2.3	97.5	Average of 3 tests

* Solvent (kg):waste (kg)
**Water content = 11-12%

Detailed mass balance experiments were also conducted on three waste types. A summary of the outcome of these individual experiments, plus the averaged results of the three trials, are presented in Table 5.2. Additional analyses were conducted on the various streams resulting from these mass balance trials. For all three tests, the toluene recovered from the evaporator had a measured water content of < 0.1% w/w. The water recovered from the evaporator in the HSC trial was analyzed by gas chromatography (GC) and indicated 110 ppm of toluene plus traces (low ppm levels) of hydrocarbon oils. The chemical oxygen demand (COD) of this water was 1220 mg/L and the five day biological oxygen demand (BOD_5) was 136 mg/L. The water from the mass balance trial of the mixed HSC/LSC showed 78 ppm of toluene and low ppm concentrations of other hydrocarbons. The COD of the water was measured as 1210 mg/L and the BOD_5 was 139 mg/L. Similar analyses for the LSC trial yielded a toluene concentration of 120 ppm and low ppm levels of hydrocarbon type oils. The COD was 1100 mg/L and the BOD_5 was 236 mg/L. In conducting the biological oxygen demand for this sample, it was diluted 3:1 to overcome some toxic effects exhibited in the raw form and at 1:1 dilution.

The oil phase from the pilot scale mass balance trials (after toluene was removed by

TABLE 5.2

HOT TOLUENE EXTRACTION

PILOT SCALE, MASS BALANCE TEST RESULTS

	Input Materials		Output Products						
Sludge Type	Feed Sludge wt	Toluene In wt	Filter Cake Wt		Evaporator Condensate wt	Evaporator Bottoms wt	Weight Recovery (%)	Toluene Recovery (%)	Oil Removal (%)
			Wet	Air Dry					
HSC	5.18	15.60	3.70	3.00	13.24	2.10	91.60	91.10	91.70
HSC/LSC	5.50	16.50	3.00	2.13	14.50	2.02	88.70	88.70	94.40
LSC	5.08	15.24	3.58	1.06	17.80	0.92	109.70	102.70	91.30
Average of above 3 tests	5.25	15.78	3.40	2.06	15.17	1.73	96.70	93.50	92.60

All weights in kg.

vacuum evaporation) was determined to have a high heating value (approximately 39 MJ/kg) and relatively low ash content (approximately 1%). The concentration of metallic elements was measured and is shown in Table 5.3. The sulfur content was measured and found to be 8.3% (compared to approximately 4% for a high sulphur No. 6 fuel oil). It is important to remember that the types of materials fed to the process determine to a large extent what the make up of the products will be. For example, the high sulfur content in the oil originates primarily from one of the constituent streams of the heavy sludge composite which was from a high sulfur oil storage tank.

The air dried filter cakes from each of the mass balance runs was subjected to a leachate extraction procedure according to Ontario Regulation 309. The leachate was then analyzed for the metals of concern. These results, along with the limits for each metal prescribed under the regulation, are presented in Table 5.4. Based on these results none of the filter cakes would be considered leachate toxic under this regulation.

In addition to the single step extractions described in the foregoing, a number of trials were conducted whereby successive solvent extractions were performed. Two different methods of secondary extraction were employed:

TABLE 5.3

HOT TOLUENE EXTRACTION

METALS ANALYSIS OF RECOVERED OIL

Element	Concentration mg/kg
Co	0.6
Zn	95
Cd	<0.5
B	0.8
Bi	<5
P	211
Be	<0.05
Si	81
Fe	2,020
Mn	17
Ca	1,140
Mg	131
Cu	87
Al	248
V	37
Mo	1.4
Pb	133
Ni	19
Cr	46
Na	71

TABLE 5.4

HOT TOLUENE EXTRACTION
LEACHATE METALS ANALYSIS
ON AIR DRIED SOLIDS*

		LSC:HSC	HSC	LSC	Schedule 4 Criteria**
Arsenic	mg/L	0.0024	0.0024	0.0037	0.05
Barium	mg/L	1.2	0.43	1.9	1.0
Cadmium	mg/L	< 0.002	< 0.002	< 0.002	0.005
Boron	mg/L	0.16	0.23	0.17	5.0
Chromium	mg/L	0.01	< 0.01	0.01	0.05
Lead	mg/L	0.07	< 0.02	< 0.02	0.05
Mercury	mg/L	< 0.0001	< 0.0001	< 0.0001	0.001
Selenium	mg/L	< 0.001	< 0.001	< 0.001	0.01
Silver	mg/L	< 0.005	< 0.005	< 0.005	0.05

* Leachate extraction procedure conducted according to Ontario Regulation 309.

**If leachate levels exceed these criteria by more than one hundred times, the waste is leachate toxic. If leachate levels exceed these criteria by between ten and one hundred times, the waste is leachate sensitive.

(1) The filter cakes produced by the primary extraction were "washed" with a known volume of fresh toluene during the final stages of filtration; and

(2) The filter cakes produced by the primary extraction were physically subjected to a second extraction cycle using fresh solvent.

Procedure (1) above was tried on the filter solids from a dried LSC test. Using a 1:1 ratio of wash toluene (80°C) to filter solids, an oil and grease removal efficiency of 18.6% was achieved. The same procedure was employed on the filter solids from an HSC test. Hot toluene (80°C) at a 2:1 ratio was used for the wash and an oil removal efficiency of 18.5% was measured.

Method (2) gave substantially better performance in a secondary extraction. The wet filter cake from a HSC:LSC (1:1) trial was used. First of all, a small portion was re-extracted in the laboratory with a 5:1 ratio of petroleum ether at approximately 40°C. The balance of the filter solids was re-extracted in the pilot plant using a 3:1 ratio of toluene @ 40°C. In both cases the oil removal efficiency in the second extraction was approximately 80% and the measured oil content on the final air dried cake was 1.7% w/w (from 5.5% on the starting wet filter cake).

At the request of Environment Canada, a pilot scale test was conducted on sample Number Thirteen - treater and tank bottom sludge from an enhanced oil recovery (EOR) fireflood production operation. This test was conducted at 40°C, with a toluene to sludge ratio of 3:1. The overall oil removal efficiency was determined to be >95%. Residual oil and grease on the air dried solids was 5.2% w/w. This sample does not appear to be significantly different from the other light sludges.

5.4 Pilot Plant Program Discussion

5.4.1 Comparison with Lab Scale

Gathering of homogenous samples of sludges for the pilot scale test was very difficult. The raw prepared composites could not practically be stirred and there were inevitable variations in the compositions of "aliquots" for individual experiments. Despite the operational problems, duplicate experiments did indicate consistent trends of oil removal efficiencies and results generally confirmed the lab scale experiments. Important differences included:

- Increasing the severity of test conditions (for example, from 3:1 toluene:sludge at 40°C, to 5:1 toluene sludge) did not improve extraction efficiencies as much as was expected, based on lab scale testing. For this reason, the mass balance experiments were conducted using the more moderate operating conditions.

- Reducing the moisture content of the light sludges prior to toluene extraction did improve oil removal efficiency, but was not as significant as was anticipated. On the lab scale, the extraction efficiency using hot toluene improved from the 65 - 70% range to almost 90% when dried. By comparison, the improvement during pilot testing was from approximately 80% to 90% (at 3:1 toluene:sludge, 40°C).

It is believed the major reason for the above differences is that agitation in the pilot plant extractor was much more severe than that in the bench scale tests - a turbine agitator vs a magnetic stirrer. The shear effects in the pilot unit evidently contributed to greater removal efficiencies at less favourable conditions. It should also be noted that the water concentration in the LSC was lower in the pilot scale than it was for the lab scale (67.1% vs 81.0%).

Since the increase in oil removal efficiency as a result of drying light sludges was small and since these raw sludges were found to contain less than 10% oil and grease (compared to over 40% for heavy sludges), it was concluded that the added complexity and cost of predrying could not be justified. To illustrate, consider a plant treating 25,000 tonnes per year of both light and heavy sludges. The quantity of oil recovered from the heavy sludges (at 40% oil in the feed and 90% recovery) would be 9,000 tonnes per year. Without drying, the oil recovered from the light sludges (at 8% oil in the feed and 80% recovery) is 1,600 tonnes. Predrying would recover an additional 200 tonnes/year of oil. Thus, the drying step would increase the recovered oil by less than 2%.

5.4.2 Operational Considerations

One of the objectives of running the pilot plant program was to ascertain what operational problems could be expected on a large scale process. Pumping the extraction mixture to the filter press was one of these problems. The pump supplied with the filter press, an air operated diaphragm pump, had rubber components which swelled after exposure to the toluene. Since time did not permit the securing of another similar pump but with teflon based internals, this type of pump was abandoned. A progressive cavity pump was also unsuccessful, probably due to settling of the fine solids in the suction housing. A piston type pump was also tried and it plugged before the bulk of the extraction mixture could be transferred. These problems were deemed attributable to the relative density difference between the solids and the hot toluene solution and to the mixture's very low viscosity. On a larger scale, it is believed that a centrifugal type trash pump could be employed since high velocities in both the pump housing and line would ensure minimum precipitation of solids.

As a direct result of this pumping problem, it was not possible to establish the filtration rates in the filter press. Indeed, it is not known whether this type of filter would be most suitable for the application, or if, perhaps, another filter type would be the preferred method of solids separation. It may be best and most cost effective to take advantage of the density difference between the solids and the solution, and utilize a centrifuge or simple clarification to obtain the needed separation.

The average weight recovery (Table 5.2) during the mass balance experiments was calculated to be about 97% although there were considerable differences between the individual trials. The major reason for the erratic recovery during the tests was attributed to the high surface area of the evaporator (heating coils, walls). The evaporator was drained for a relatively short time period for the HSC and HSC/LSC runs. The evaporator surfaces were still coated with a relatively large quantity of oil/water/toluene, which came out of the unit in the final LSC trial when a much longer drainage period was used.

The batch type evaporator used also presented another problem. The toluene content averaged about 38% in the evaporator bottoms, attributable to the fact that the steam coils were not totally immersed in the bottoms after the majority of the toluene and water had been evaporated away. It is recommended that a larger scale system use a continuous type evaporator, preferably with wiped surfaces, to maintain heat transfer efficiency and minimize fouling.

6.0 CONCEPTUAL DESIGN AND ECONOMIC ASSESSMENT

The results of the laboratory and pilot scale evaluation of the "Hot Toluene" extraction process would suggest that its performance is comparable, if not superior, to any of the processes reviewed. With this in mind a conceptual design of a full scale extraction plant, using the information learned during this research was developed. This enabled a preliminary economic analysis of the process to be carried out.

6.1 Conceptual Process Design

The conceptual design (see Fig. 6.1) assumed a plant capable of processing 50,000 tonnes per year based on a 24 hour/day, seven days per week operation. Assuming 300 operating days per year, this translates to a waste processing rate of approximately 125 kg/minute. The feedstock is assumed to be 50% light sludges and 50% heavy sludges, by weight. This assumption is made only to fix the overall compositions of feed and products. Perfomance of the process is not substantially effected whether the feed at any given time is heavy sludge, light sludge, or a combination of both. Because the pilot scale testing indicated only a marginal increase in oil recovery (see Section 5.4.1) as a result of drying the light sludges prior to extraction, this step is not included in the design. The extraction is to be

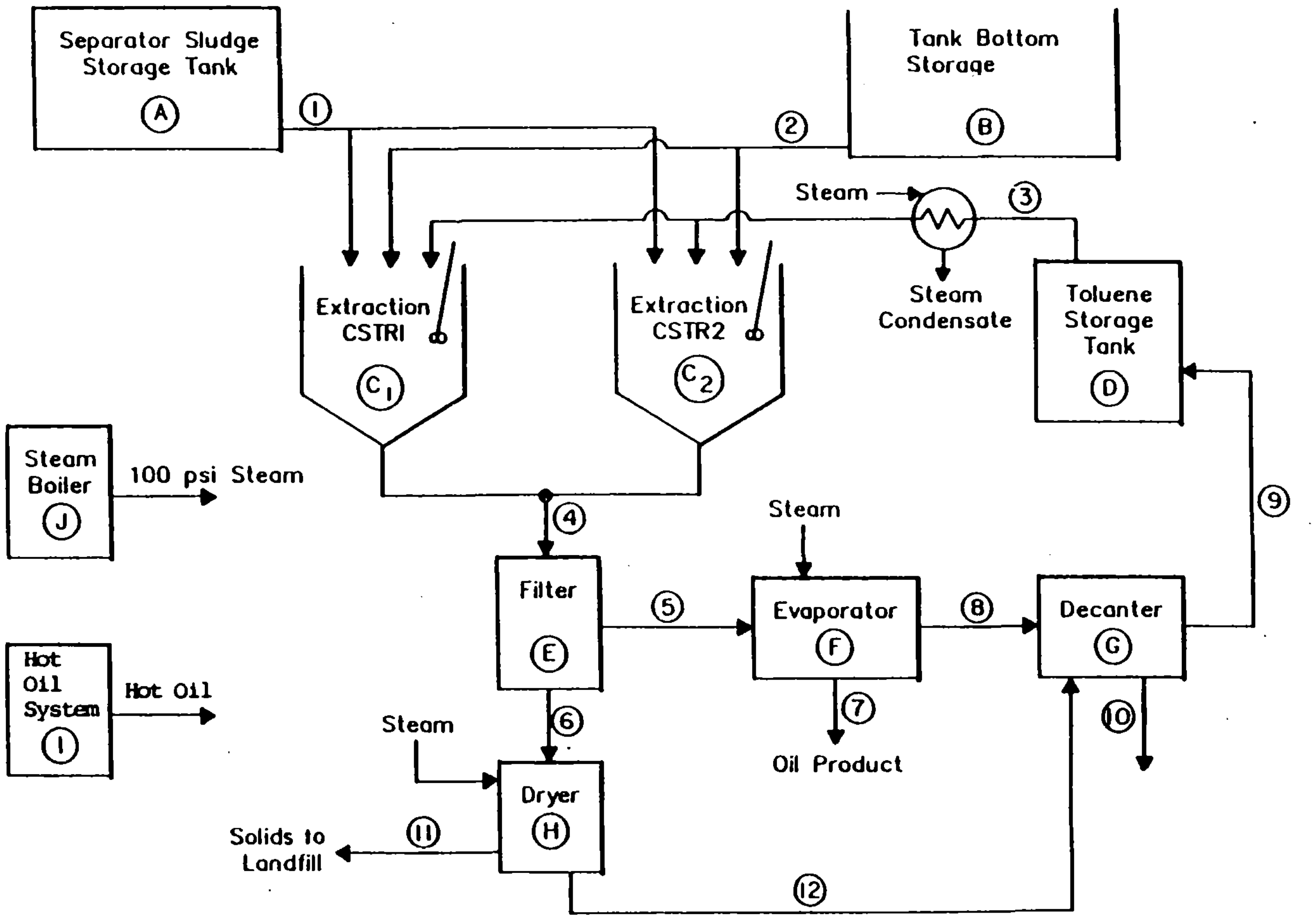


Figure 6.1

HOT TOLUENE EXTRACTION PROCESS - CONCEPTUAL DESIGN performed in a batch mode - two extraction vessels are supplied with a designed cycle time of 30 minutes. A 3:1 solvent to sludge ratio has been assumed and an extraction temperature of 40°C.

A listing of the major equipment is provided in Table 6.1 along with the basis for equipment sizing. Suitable storage must be provided for incoming wastes - a tank for pumpable material and a pit for non-pumpables. The latter will require slurrying prior to the extraction step. The extraction will take place in one of two steam heated, agitated vessels. At the end of the extraction, the mixture in the extractor would be transferred to an equalization vessel prior to phase separation. The design is based on using a vacuum filter although certain operational advantages would arise if a centrifuge could be used. The solids from the filter would be dried in a heated, screw type dryer prior to disposal. Vapours driven off in the dryer would be condensed and pumped to a decanter. The filtrate from the filter enters a 3 effect evaporator from which the product oil is recovered. The vapour from the evaporator is condensed and allowed to phase separate in the decanter (along with the condensed vapours from the solids dryer). The water from the decanter will require post treatment. The toluene is returned to

TABLE 6.1

HOT TOLUENE EXTRACTION

EQUIPMENT SELECTION

Item	Description	Size	Basis for Sizing	Comments
A	LS Storage Tank	900 m^3	10 day holding capacity	Carbon Steel
B	HS Storage	900 m^3	10 day holding capacity	
C1,C2	Extraction Vessel	20 m^3	30 minute cycle time each extractor	Carbon Steel, Agitated
D	Toluene Storage	45 m^3	10 day holding capacity at 0.5% toluene losses	Carbon Steel
E	Vacuum Filter	6.1 m^2	Filter rate 5.6 $m^3/m^2/h$	
F	Evaporator	55 m^2	Duty = 16 GJ/h	Overall U = 0.027 $cal/sec/cm^2/°C$, 3 effect
G	Decanter	150 m^3	5 hour residence time	
H	Dryer	Scaled from Holoflyt(6)	Duty = 4.0 GJ/h	
I	Heating Oil System			
J	Boiler	1,100 kg/h		700 kilopascals

toluene storage for re-use. Energy is supplied by steam and a hot oil heating system. Fugitive emissions from the process would be collected, condensed and the residual scrubbed (e.g. carbon adsorption).

Estimation of the flow rates of the various streams was made using the following basis:

- Sludge characteristics, flow rates, and oil removal efficiency were based on the average of the three pilot scale mass balance experiments, corrected to give 100% weight recovery (Table 5.2).
- All toluene and water entering the commercial scale, continuous evaporator will exit as overhead (this did not occur during pilot scale program due to batch mode of operation and inefficient heat transfer surfaces).
- Oil exiting as bottoms from evaporator is the difference between the oil contained in the feed sludges minus that contained in the filter cake.
- Because of the difficulties in the toluene recovery step encountered in the pilot scale program, it was difficult to assess what the actual toluene losses would be. Very little toluene was measured in the aqueous phase recovered from the evaporator. For the solids

phase, residual toluene would have to be less than 2% w/w for disposal in a secure landfill in Canada and even lower if disposal in a sanitary landfill is to be considered (flash point >60°C in Ontario). The target residual toluene level for the oil will depend on the use to be made of this phase. If it is to be returned as a refinery feedstock then removal to extremely low levels may not be required. An overall loss of toluene of 0.5% of the amount supplied to the extraction has been assumed. For the wastes tested, this would allow for approximately 2% w/w toluene in both the solids and oil phases.

The mass flowrates to and from the individual operations are presented in Table 6.2.

6.2 Economic Analysis

Based on the system presented in Section 6.1, an order of magnitude estimate was made of the capital cost of a permanent facility. Since any proposed process will require raw waste storage and most (if not all) will require post treatment of the water phase, these items have not been included in the estimate. The cost of supplying auxiliary facilities such as utilities (electricity, water, air, etc.) and services (roads, walks, fire protection systems, etc.) is very dependent upon the specific site. For this

TABLE 6.2

HOT TOLUENE EXTRACTION PROCESS MASS BALANCE

Stream No.	Description	Flowrate (kg/hour)				
		Total	Oil	Water	Solids	Toluene
1	LS to Extraction	3,860				
2	HS to Extraction	3,860				
1 + 2	Mixture to Extraction	7,720	2,000	3,230	2,490	-
3	Toluene to Extraction	23,200	-	-	-	23,200
4	Extracted Solution to Filter	30,900	2,000	3,230	2,490	23,200
5	Filtrate	25,900	1,850	1,500	-	22,500
6	Filter Cake to Dryer	5,000	149	1,730	2,490	633
7	Oil from Evaporator	1,850	1,850	-	-	-
8	Toluene/Water from Evaporator	24,000	-	1,500	-	22,500
9	Recycle Toluene	23,000	-	-	-	23,000
10	Water to Treatment	2,970	-	2,970	-	-
11	Dry Solids to Landfill	3,030	149	265	2,490	127
12	Toluene/Water from Dryer	1,970	-	1,470	-	506

reason, and since these costs are likely to be similar for any of the proposed processes, these costs have also been excluded except for the cost of a boiler for steam supply and a hot oil heating system. In addition the following items were also excluded from the capital estimate:

- land cost
- laboratory facilities
- cost of permitting
- process development costs
- contingency

Due to the level of information available at this stage of the project, a factoring technique was used to prepare the estimate. The accuracy of such an estimate is considered to be ± 50%. Within this framework, the capital cost of the plant is estimated to be 4.9 million dollars (Canadian) based on equipment costs from the second quarter of 1987. Engineering, procurement and construction management costs will depend on how the project is executed. These functions alone would add at least 25% to the capital, bringing the cost to approximately 6.1 million dollars (Canadian).

To operate such a facility the major costs incurred annually would be (based on prices as of the second quarter of 1987):

i)	Depreciation of Capital (Assume 10 year amortization period)	$610,000
ii)	Labour - 8 people (2/shift)	320,000
iii)	Toluene Make-up (from Chemical Marketing Reporter (5))	310,000
iv)	Steam	135,000
v)	Natural Gas	1,100,000
vi)	Electricity	75,000
vii)	Maintenance (4% of estimated direct costs)	200,000
viii)	Miscellaneous	150,000
Estimated Annual Operating Costs		$2,800,000

The assumptions used in estimating these costs are shown in Appendix G.

These costs translate to a treatment cost of approximately $56/tonne. This cost does not include the disposal cost of waste solids (i.e. landfill), costs for wastewater treatment, nor credit for oil products recovered, since these costs will vary with the application. Based on the analyses of the samples used in this program, a measure of the relative impact can be obtained.

Approximately 25% of the feed volume to the plant would be recoverable oil and grease - 12,500 tonnes per year. Similarily, approximately 35% of the feed volume is solids - 17,500 tonnes per year. If the oil can be sold to a reclaimer for $.022/L ($.10/Igal) this would approximately offset the disposal cost of the solids assuming that the cost of sanitary landfill would not be more than $\$15.70/m^3$ ($\$12/yd^3$).

For purposes of comparison, Resources Conservation Company (RCC) and CF Systems Corp. were asked to submit their estimated treatment costs for a 50,000 tonne/year plant based on the type of wastes tested in this program. The information from RCC was adjusted to delete the disposal cost for solids and the revenue from recovered oil. The treatment cost was estimated to be approximatley $60/tonne. CF Systems Corp. provided information based on a lease arrangement, for a transportable unit, and a charge per unit volume processed. This cost did not include disposal costs (or revenue) for any of the phases. It was also conditional on being provided with working space, utilities, solvent make-up and operating labour. After including these items, the estimated treatment cost is between $60 - $80/tonne. Both of these estimated treatment costs are higher than that estimated for the hot toluene process. This is in part due to the inclusion of a royalty fee or a processing fee. For this price, a client would gain the benefit of the respective company's experience and know-how.

7.0 IMPLICATIONS OF THE DEVELOPMENT PROGRAM

Based on the results of this program, the solvent extraction type processes - conventional solvent extraction, critical fluid extraction and the B.E.S.T.™ process - appeared to offer the most cost effective approach. Some of the factors which effect implementation of this type of technology are discussed below.

7.1 Regulatory Considerations

The products from these solvent extraction processes are an aqueous phase, an organic phase and a solids phase. The successful application of any of these processes hinges on re-use or low cost disposal options for the phases generated.

The organic phase produced in the pilot scale testing of the hot toluene process was considered to be of good quality - high heating value and low ash. Based on the lab scale work performed using B.E.S.T.™ and critical fluid extraction, similar characteristics could be expected. Ideally, this phase could be re-used e.g. as a refinery feedstock. If this was not possible, it could be used as a fuel in an industrial boiler. This raises the regulatory question of what requirements must be met for burning the recovered oil in an industrial boiler i.e. what permitting requirements and emission regulations will be placed on boilers burning waste derived fuel? This issue is currently being discussed in Ontario and Quebec. Existing regulations in Ontario would identify the incoming wastes to a central facility as a hauled liquid industrial waste. The waste would be considered hazardous if it was from a listed source or if it satisfied one or more of the hazardous characteristics e.g. ignitability, corrosivity, etc. If it was classified as hazardous, then the oil product generated through extraction might also be defined as hazardous-either because it exhibits a hazardous characteristic or because the regulatory body deems it hazardous due to its origin-and would have to be disposed of at a properly licenced facility. A portion of the recovered oil could be re-used at the treatment facility - e.g. as a fuel to the steam boiler and hot oil system required for the extraction process. This use would consume approximately 35% of the total oil recovered. Similar comments would apply to the other two phases if the waste was classified as hazardous when received. This would add significantly to the cost of operation. Although most jurisdictions provide for a 'delisting' procedure, it is often an involved exercise requiring considerable time and effort. No delistings have yet been granted in Ontario.

If the waste to be treated was not classified hazardous as received, then the products from the process would be evaluated individually to determine if they exhibited any of the characteristics which would make them hazardous.

For the organic phase, the characteristic of concern is likely to be ignitability. Assuming that the recovered organic is not flammable, the source would be the extracting solvent i.e. for hot toluene extraction, the step removing toluene from the organic must be efficient enough to leave the recovered organic phase with a closed cup flashpoint of >60°C (according to current Ontario regulations).

The aqueous phase is not likely to posses any of the characteristics that could classify it as hazardous.

For the solids phase, the characteristics of concern are ignitability and leachate toxicity. Again, if the recovered organic is not flammable then the efficiency of removal of the extractant (if flammable) becomes the main criteria. Since solvent extraction does not chemically alter any of the constituents of the waste but will tend to concentrate the metals in the solids phase, leachate toxicity is likely to be a significant concern. Although the filter cakes from the composites tested with the hot toluene were not found to be leachate toxic, this may not always be the case depending on feed characteristics and current regulations.

A solution to overcome some of the above problems would be to operate transportable treatment units. In this way, the raw waste would not be taken off-site. The water phase could be directed to the client's treatment facility, the oil phase could be returned for processing into saleable oil, and the solids would then probably be disposed of in a sanitary landfill. Therefore, the added cost of a transportable system over a centralized facility would likely be justified, considering lower costs for disposal of the water, and a real credit for the oil phase. Although not considered in the economic assessment, the overall capital cost of a transportable treatment system for 50,000 tonnes/year capacity would likely be higher than for a stationary plant. The primary reason for this is that in order to trailer mount the process, restrictions on vessel sizes would probably limit the practical maximum throughput to 25,000 tonnes/year. A comparison of fixed versus transportable options at the 25,000 tonnes/year rate would likely yield similar capital costs. Additional equipment required for the movable system would include trailers to haul the system and, perhaps, excavation machinery for pit clean-outs. To offset these expenses, the tank bottoms and separator sludge storage tanks would be much smaller, if required at all. Some operating costs would increase, primarily due to longer downtimes, since provision must be made for travelling time and set-up / set-down. In addition, labour associated costs (i.e. supervision, secretary, accomodations) would be greater than for a stationary plant. A final consideration in the transportable vs. stationary plant debate is that wastes must be transported to a stationary facility. This not only implies an economic penalty, but liability to the shipping party.

7.2 Process Considerations

The solvent extraction processes share some common requirements. First of all, the feed materials must be pumpable. This raises the question of front end materials handling. Many of the materials received were not readily pumpable, especially at lower temperatures. A system to handle these materials and transfer them to the extraction vessel must be supplied. In addition, some form of screening will be required to protect the processing equipment.

Secondly, the aqueous phase is likely to require post treatment. Initial information from this program using hot toluene extraction, indicates that the aqueous phase is treatable by biological oxidation provided that acclimitization is allowed. More detailed studies would be required for specific applications.

By comparison, the oil removal efficiencies achieved by CF Systems were somewhat lower than those obtained using the hot toluene process. The critical fluid extraction process for this application would use a mixed vessel as the extractor and propane as the extractant. This system has been developed over the last couple of years and a demonstration unit was just started up at the end of 1987. The process is more developed than the hot toluene process and the efficiency may be better than that which was achieved a year ago on the samples from this program. The system has the advantage that it uses relatively simple equipment which is compact (can easily be made transportable). However, the process has not been proven on a commercial scale.

The B.E.S.T.^{TM} process has been demonstated on waste oil sludges from an abandoned oil re-refining facility. The unit was rated at 100 tons/day capacity and was transportable although many trailers were required. Performance, based on our samples, was similar to that achieved by the hot toluene process. This process is somewhat more complicated than either of the other two. The use of triethylamine as extractant necessitates nitrogen blanketting and a comprehensive site monitoring system.

8.0 CONCLUSIONS

Following a literature survey and a review of current activity in the waste management and petroleum refining fields, six potential processes were identified as the most likely to satisfy the objectives of this program and worthy of lab scale testing. Four of the proesses - B.E.S.T.^{TM}, critical fluid extraction, Kruyer and the modified disc centrifuge were evaluated by supplying samples to the vendors of the technology. The other two - hot toluene extraction and the Hot Water Process were lab tested as part of this program. The significant findings of this phase of the program are as follows:

- The Kruyer process, marketed by the Oleophilic Sieve Development Co. is not effective at separating the oil from these sludges.
- The modified disc centrifuge is not suitable for phase separating these refinery sludges due to their high solids content and high viscosity.
- The hot water extraction process, as modified with other surfactants and at higher solvent to sludge ratios than are used in the bitumen recovery application from the Canadian Oil Sands, is marginally successful in separating the oil from refinery sludges but the removal efficiency is low.

- The B.E.S.T.^{TM} process, using triethylamine as the extracting solvent, demonstrated good performance with low residual oil levels on the dried solids for both light (3.3 % w/w) and heavy (6.9% w/w) sludges, based on lab scale tests by Resources Conservation Co.

- The critical fluid extraction process, using propane as the extracting solvent, demonstrated good oil removal efficiencies for both light (78%) and heavy (83%) sludges, based on lab scale tests by CF Systems Corp.

- Hydrocarbon solvents studied in this program (toluene, methylene chloride and petroleum ether) all produced good dispersions and good oil removal efficiencies provided a sufficiently high solvent: sludge ratio is employed. However, materials handling problems were encountered with the extraction mixture.

- Performing the extraction at higher temperatures (40-80°C) was tried with toluene and this significantly improved the materials handling characteristics of the extraction mixture and produced a modest improvement in oil removal efficiency. Residual oil levels on the wet solids were 3.2% w/w for light sludges and 1.2% w/w for heavy sludges.

- Lower removal efficiencies were achieved with the light sludges (higher water content) than with the heavy sludges. Reducing the water content of these sludges (by thermal drying, methanol extraction, or vacuum evaporation) prior to extraction with toluene, significantly improved overall oil removal efficiency.

Based on the lab scale results, a small non-integrated pilot plant of the hot toluene extraction process was constructed. Tests were conducted using waste materials similar to those used in the lab scale testing. The significant findings may be summarized as follows:

- Oil removal efficiencies using hot toluene extraction in the pilot plant were similar to those achieved in the lab testing with the exception that less severe conditions were required i.e. 3:1 solvent:sludge ratio and 40°C yielded efficiencies only slightly lower than tests conducted at 5:1 solvent:sludge and 80°C. It is postulated that the improved mixing in the pilot extractor (high shear turbine impeller) compared to that used in the lab scale (magnetic stirrer) caused this result.

- Washing of the filter cakes with fresh toluene during filtration effected only a marginal reduction in oil content on the filtered solids.

- Re-extraction of the filter cake using either hot toluene or petroleum ether significantly reduced the residual oil on the filtered solids.

- In the pilot scale, evaporation of the filtrate yielded a condensate which readily separated into toluene and aqueous phases. The decanted toluene contained <0.1% w/w water. The aqueous phase typically contained 100 ppm of toluene and traces (low ppm levels) of other hydrocarbons and had a chemical oxygen demand of 1000 ppm. Preliminary screening tests indicate that the aqueous phase is amenable to aerobic biological treatment.

- The oil phase recovered typically was a high heat value, low ash material suitable for re-use or as a waste fuel.

- The solids phase must be "dried" to remove residual toluene. This will ensure that the solids will not be classified as ignitable.

An economic analysis was conducted for a fixed commercial facility capable of treating 50,000 tonnes per year evenly split between light and heavy sludges. For hot toluene extraction, the analysis was based on the results of the pilot scale testing. For the B.E.S.T.™ process and critical fluid extraction, information supplied by the vendors formed the basis of the evaluation. The costs for disposal of the solids and aqueous phases and any credit for recovered oil were excluded. The outcome of the analysis yielded the following:

- Estimated operating cost (including capital depreciation) for the hot toluene extraction process is \$56/tonne of sludge treated (based on pricing from the second quarter of 1987).

- On a similar basis, estimated costs for the B.E.S.T.^{TM} process are \$60/tonne treated and for critical fluid extraction \$60-\$80/tonne treated. These costs are based on information provided in early 1987.

- Capital costs for a trailer mounted hot toluene extraction process are likely to be similar to a fixed unit up to a processing capacity of 25,000 tonnes/year - the practical limit for a trailer mounted unit. Operating costs will be higher due to decreased utilization.

9.0 RECOMMENDATIONS

Three processes have been identified which meet the original objective of the program. Specific recommendations for each are:

1) B.E.S.T.^{TM} Process

This is the most developed of the three processes and is already being used at a demonstration scale (100 tons/day). Predicted costs are competitive but no major operational benefits were identified for this process over the other two. It is recommended that its development be monitored to confirm current cost estimates and performance.

2) Critical Fluid Extraction

Costs are estimated to be similar to the B.E.S.T.^{TM} process but potential advantages include process simplicity and compactness (more easily made transportable). CF Systems Corp. has developed a pilot scale unit for testing. It is recommended that samples be supplied for processing through this unit to confirm results obtained at the lab scale and to assess operability.

3) Hot Toluene Extraction

The costs for this process are estimated to be very competitive with the other two although it is at an earlier stage of development. The technical aspects of performance and operability are also promising. Based on these factors, it is recommended that development of this process be continued in order to evaluate in more detail the costs and performance characteristics of the key operations, in particular, the recovery of the toluene from both the filtrate and the filter cake. Potential application to other organic sludges should also be evaluated in this step since this could impact significantly on the commercial viability of the system. Successful completion of this study, including an economic analysis, would form the basis for the development of a suitably integrated demonstration plant.

REFERENCES

1. Standard Methods for The Examination of Water & Wastewater, 13th Edition, 1971, prepared and published jointly by: American Public Health Association; American Water Works Association; Water Pollution Control Federation.

2. Annual Book of ASTM Standards, 1985, Vol. 05.01, 06.01, 06.03, Test Method D-95-83.

3. Chemical Engineering, McGraw-Hill Inc., Vol. 93, No. 23, 1986.

4. Chemical Marketing Reporter, Schell Publishing Company, Vol. 230, No. 25, 1986.

5. Chemical Marketing Reporter, Schell Publishing Company, August 31, 1987.

6. Personal Communication: J.W. Patterson Associates Ltd., 1986/87.

BIBLIOGRAPHY

1. Sauerwein, S., "Bitumen Recovery from Tailings Ponds May Mean High Profits", Canadian Petroleum, March, 1983.

2. Camp, F.W., "Processing Athabasca Tar Sands - Tailings Disposal", Presented at the 26th Canadian Chemical Engineering Conference, October 6, 1976, Toronto.

3. Krishnan, R., and Hlavin, R., "Alternatives for Hazardous Waste Management in the Petroleum Refining Industry", Report to the U.S. EPA No. EPA/530/SW-172C, 1979, Available as NTIS Report PB81-113417.

4. Davitt, H.J., U.S. Patent 3,963,599 (1976) and Canadian Patents 975,696, 975,697, 975,699 and 975,700 (1975).

5. Refinery Sludge Upgrading: Gulf Demonstration Unit, Montreal East Refinery - Preliminary Engineering Project 35550-0002-0010, April, 1983, by Andre Marsan et Associes Inc.

APPENDIX A

TERMS OF REFERENCE

DEVELOPMENT OF A PROCESS FOR OIL RECOVERY FROM WASTE OIL SLUDGES

Background

In 1984, a joint proposal was submitted to the federal government by Tricil Limited and Ontario Research Foundation entitled "Investigation of Methods for the Separation of Oil from Oil Sludges". The objective of this proposal was to develop a simple, reliable, cost effective process for the separation of waste oil sludges into three component streams: oil, water, and dry solids. The program involved two phases:

i) Initial Screening
  - literature review
  - waste collection/characterization
  - process selection and preliminary economic assessment

ii) Laboratory and Pilot Scale Investigation
  - laboratory trials (up to 5 processes)
  - pilot trials (1 or 2 processes)

A third phase - Commercial Demonstration - was mentioned as part of a separate proposal. The amount of funding requested was $200,000.

Based on comments received from the federal government, the scope of the proposal was changed to investigate a single process - hot water extraction - in detail at the laboratory scale (including post treatment options) and to confirm lab scale performance in a small pilot plant. Commercial demonstration remained part of a separate proposal and the cost was $200,000. This rewritten proposal was submitted in October 1984 by Tricil Limited and was entitled "Development of a Process for Oil Recovery from Waste Oil Sludges."

A meeting was held in December of 1985 with the scientific advisor, Trevor Bridle of the Canada Centre for Inland Waters. He raised two issues to be addressed before he would support the proposal. First of all, he expressed a concern at focusing on a single technology and asked if an evaluation of the various processes mentioned in the proposal could be incorporated into the program. This review would be done on the basis of current literature and would not involve any testing. Tricil agreed that this request could be accommodated recognizing that in most cases such an evaluation would be based on process performance on significantly different feed materials than are involved in this proposal. Secondly, for the process tested at pilot scale, consideration be given to its environmental impact opposite specific analyses e.g. metals. Tricil agreed to this request as well.

Following a review of the changes in scope and the change in charge rates as a result of the time taken for approval, Tricil committed to executing the project while maintaining the solicited amount at $200,000. The contract was signed in March of 1986. The update of March 4, 1986 on the original proposal referred to in the contract basically summarizes the above commitment and includes the appropriate charge rates.

Scope of Work

Detailed work statements were established for all three phases of the project and were discussed and reviewed by the Scientific Authority from Environment Canada prior to implementation.

Phase One:

Because the scope of this phase was significantly different than that contained in the proposal, the entire work statement is presented in Attachment One.

Phase Two:

Two composite samples to be prepared (light and heavy sludges) consisting of equal volumes of 3 - 4 typical samples.

i) Solvent Extraction Testing

- Test on lab scale an aliphatic solvent such as petroleum ether, an aromatic solvent such as toluene and a chlorinated hydrocarbon solvent such as methylene chloride.

- Initial examination to be at room temperature.
- Initially, a high solvent to waste ratio, e.g. 10:1, to be used to extract the composite and selected wastes (first tier of testing).
- Crude measurement of extraction efficiency to be made using separatory funnel procedure.
- Crude measurement of solvent recovery efficiency to be made by evaporating the solvent phase from the separatory funnel extraction on a rotary vacuum evaporator.
- Centrifugation may be employed to enhance phase separation of the extracted materials.
- Selecting the most efficient solvent(s) as identified by tier 1, tier 2 testing will evaluate lower solvent:waste ratios.
- If a solvent does not prove successful in tier 1 tests, the experiment will be repeated at a higher temperature.

- Extraction efficiencies in tier 2 tests will be determined as in the tier 1 program.

- Depending on the results achieved in tiers 1 and 2 testing, further tier(s) of testing to be undertaken.

- In the final test stages, a more complete assessment of the phases produced by the extraction process will be undertaken (i.e. % oil and grease in solvent, ash content, solvent loss in solids, solvent recovery efficiency, heating value of rich phase after solvent recovery, etc.)

ii) Hot Water Extraction Testing

- Initial experiments on a laboratory scale will be performed on the composite samples, duplicating as closely as possible the Clark Hot Water Process.

- Variation of pH will be evaluated (other parameters kept constant).

- Effect of surfactant, i.e. type and concentration, will be examined (other parameters kept constant).

- Effect of temperature will be examined.

- Effect of dilution will be examined.

- Effect of centrifugation on separated phases (to enhance phase separation) will be examined.

- Based on the above, the best combination of variables to effect maximum separation of the selected wastes will be implemented and tested. A more complete assessment (similar to that for final solvent extraction) will be carried out at this stage.

iii) Testing At Other Laboratories

- Critical Fluid Extraction: A 1 gallon (max) sample of each of the two composites will be submitted to CF Systems Corp. This initial evaluation is free. We may witness the tests.

- B.E.S.T.^{TM}: Resources Conservation Co. in Seattle will be sent at least one gallon of each composite sample for an initial 'shake and bake' test. We may witness the tests. Both tests will be free, although analytical data will not be provided.

- Kruyer: A 1 gallon sample of both composites will be sent to Oleophilic Sieve Development Co. for an initial assessment. This will confirm the potential of this system to treat the sludges in question. Again this will be free, although no analysis will be provided.

These tests will be done to confirm, or otherwise, the potential of each process to treat the oil sludges in question. Once this potential has been confirmed, then the need for subsequent bench scale testing under more controlled conditions will be assessed. This phase will involve expenditure in all three cases.

Phase Three:

Pilot scale testing of the hot toluene extraction process.

- Construction of a small pilot scale test facility to confirm the results obtained during the lab scale testing.
- Each trial will utilize approximately 10 kg of waste.
- Unit to be housed in a room currently available at ORF.
- Approximately 30 tests will be conducted to evaluate parameters such as:
  - effect of water content,
  - effect of temperature,
  - effect of residence time,
  - effect of varying ratios of light and heavy sludges.
- Update economic evaluation.

ATTACHMENT ONE

Revised Work Statement - Phase One
(Tasks 6.1.1 and 6.1.2)

1. Characterization of Sludges

As stated in the original proposal, essentially 55% of oil sludges generated in Canada are attributable to the following three sludge types:

API Separator Sludge
Tank Bottoms
Oil Spills

Tricil Limited will then select 3 - 5 sources for each of these sludges which they feel best represent these waste types. Tricil will obtain approximately one gallon samples of 12 wastes (an average of 4 of each type). These will be delivered to Ontario Research for characterization.

At this stage of the programme, we will be trying to characterize the sludges for their handling characteristics and gross make-up, viz. proportions of oil, water and solids. The parameters which we will examine will be:

° Physical characteristics at various temperatures, i.e. is the material solid or liquid, at what temperature is the material pumpable?

- Water content
- Oil content
- Ash content
- Calorific value
- Chlorine and sulphur content
- Semi quantitative metals scan

From the data generated for each oil sludge type, one sample will be chosen which can best be described as "typical" of the type. Or, alternatively, it may be more appropriate to collect several samples and mix together to form an industry-wide composite sample. Larger quantities of these three chosen waste oily sludges will be obtained by Tricil for use for the duration of the project.

With all of the data in hand, a meeting between Tricil, ORF and Environment Canada will be convened to choose one of the waste types for initial experimentation. Our proposed approach will be to develop and optimize a procedure for separation of oil, water and solids on one waste sample, and then subject the other two "typical" or composite waste type samples to the same procedure to confirm its universal applicability.

2. Selection of Separation Process

A number of approaches to the separation of oils, water and solids, based on technologies developed for the oilsand industry, were briefly described in Section 3 of the proposal. An updated literature review will be conducted on these processes and other methods which might be applicable to separation of oils from oily sludges. The information gathered will be critically reviewed and approaches compared on the basis of:

- Oil recovery efficiency
- Simplicity and operability
- Preliminary economic feasibility
- Environmental acceptability of product streams not destined for reuse
- Stage of development
- Reusability of the recovered oil

Our original contention was that the Clark hot water process or a modification thereof would be the preferred route for oil sludge treatment. This task will compare alternatives against the hot water process to prove or disprove this initial choice.

Ontario Research would take the lead in this task to gather and review the information available in the literature and through personal contacts.

Ontario Research would rely on Tricil's expertise in operation of waste treatment processes to review and comment on the information pertaining to:

- Simplicity and operability
- Preliminary economic feasibility
- Stage of development

The output from this task will be a recommendation to proceed to a laboratory investigation of oil sludge separability based upon the approach which is apparently most promising.

APPENDIX B

PROCESS DESCRIPTIONS

B.1 SOLVENT EXTRACTION

Solvent extraction is a well established technology. Commercial operations for the solvent extraction of hops, caffeine, spices, vegetable oils, etc., have existed for over 40 years. Solvent extraction of oil from tar sands has been investigated thoroughly in recent years.

Process Description

Solvent extraction consists of three basic unit operations, i.e. extraction, distillation and drying. A typical solvent extraction flow diagram is presented in Figure 1. The material to be extracted is mixed with the solvent of choice in an agitated vessel or in a countercurrent column. Solvent:residue ratios may vary considerably, depending on the nature of the "solid" material, solvent and process in question. High water content sludges, for instance, may be so wet as to resist penetration of the oil-coated solids by most oleophilic (and, consequently, hydrophobic) solvents. In such cases, thermal conditioning or pretreatment with a solvent to reduce or remove the water content would be necessary prior to separation of the oil/grease and solids particles. After extraction, the mixture may be centrifuged or filtered to separate the solids and extracted liquid phase. The damp solids are dried in a drier operating above the solvent boiling point. This ensures the production of a dry solid for disposal (e.g. landfill). The solvent is recovered from the extract by distillation, evaporation or simple decantation, if phases are immiscible.

B.2 HOT WATER EXTRACTION PROCESS

The Hot Water Process for extraction of bitumen from oil sands was first described by Dr. Carl A. Clark in the 1930s and 1940s. Clark discovered that sand in the ore is water-wet and that the oil is essentially isolated from it by a thin film of water. Bitumen extraction using this process is practised at the only two oil sands mining facilities in the world - Suncor and Syncrude in Alberta.

Process Description

In this process, the mined tar sands are mixed in large rotating conditioning drums with steam, hot water and sodium hydroxide at approximately 80°C. Lumps are reduced to slurry by ablation. Sodium hydroxide or other base is critical to the process and apparently acts to alter interfacial tensions, which results in more efficient separation of bitumen. Other important parameters in this process are the oil sand to water ratio, temperature, residence time and mechanical energy input.

Effluent from the conditioning drum is screened to remove undigested material, additional water is added and the mixture is fed to the primary separation cell. This cell is a gravity settler where the solids sink and the bitumen rises to the top. A third output, middlings, which consists of bitumen, solids and water, is withdrawn and fed to air flotation cells which are effective in scavenging the bitumen. The resultant froth is cleaned, de-aerated and combined with the primary cell froth and further de-aerated to yield the hot water process froth. This is subjected to further bitumen extraction through the addition of naphtha (approximately 5%) and centrifugation in a two-stage operation, each stage consisting of multiple centrifuges of conventional design installed in parallel. The purified bitumen is withdrawn and the naphtha recovered and recycled. The bitumen then passes on for upgrading (see Figure 2).

In practice, on a large scale, a major concern of the Hot Water Process is the volume of tailings produced, which exceed considerably the amount of material actually mined. The presence of trace amounts of a clay, montmirillonite, make separation of the water and solids extremely difficult. The anticipated tank bottoms and separator sludges to be treated for Tricil may not behave in the same manner as oil sands, which depend on a monomolecular layer of water on the sand particle for bitumen removal, which the solids in the anticipated wastes may not have. On the other hand, should the oil/grease be removed by the Hot Water Process, the solids may be of such a nature as to settle rapidly from the water, thus making a tailings pond unnecessary.

B.3. KRUYER PROCESS (Oleophilic Sieve)

The Kruyer process was developed in 1975 by Dr. Jan Kruyer. The process is based on the discovery that, when a mixture of oil phase and aqueous phase (i.e. an emulsion) is passed through a sieve made from oleophilic materials, the aqueous phase and the hydrophilic solids contained in that phase will pass through the sieve apertures but the oil will adhere to the sieve surface on contact. The oil does not have to float to be recovered and the mixture does not necessarily have to be warm or hot to be separated. The sieve is in the form of a moving conveyor that runs fast enough to prevent blinding of the sieve by the adhering oil phase while the aqueous phase passes through the sieve.

Process Description

The Kruyer process consists of an endless oleophilic sieve mesh belt wrapped around a revolving apertured drum (separation zone) at one end and a set of three steam heated rollers (bitumen recovery zone) at the other end (see Figure 3). The apertured drum is charged with oleophilic free bodies (steel balls). Sludge containing dispersed bitumen is fed into the apertured drum through a rotary seal mounted in the drum axis.

When the drum is rotated, the free bodies attract and agglomerate the bitumen particles. A layer of bitumen that builds up on the free bodies ultimately sloughs off and is extruded through the walls of the apertured drum and onto the oleophilic sieve belt. The belt permits the water and the hydrophilic minerals in the sludge to pass through its apertures whilst capturing the oleophilic bitumen and minerals. The tailings are collected directly below the apertured drum. The belt conveys the captured bitumen and the entrapped minerals to the steam heated rollers. The steam rollers reduce the viscosity of the bitumen and allow it to collect as a warm, free-flowing bitumen product in the recovery zone.

B.4 SUPERCRITICAL FLUID EXTRACTION (SFE)

This process exploits the unique properties of a fluid at or near its critical point. Such a fluid behaves like a liquid organic solvent in that it can dissolve significant amounts of oil or other organic solvents. But, at the same time, it behaves like a gas in that its extraction is much higher - typically 50 to 100% - than the separation rate achieved by other technologies.

Process Description

It was discovered in 1960 that fluids under supercritical conditions were potentially excellent solvents for high boiling substances. The density and the dielectric constant of an organic compound are important factors which determine solvent power. SFE can be performed under either isobaric or isothermal conditions (see Figure 4). The oil sand and solvents are mixed in the reactor under high temperature and pressure. The extraction pressure should be above the critical pressure and may be in the range of 500 to 10,000 psi, though preferably as low as possible. Temperatures can range from 25°C to 600°C. Following extraction, the extract and extractant are separated with the extractant being recovered for further use. The solvent/oil sand ratio ranges between 1:1 and 10:1. Suitable solvents include aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene and isopropyl benzene. Critical Fluid Systems Inc. employ propane as the solvent in its continuous extraction process for separator sludges and tank bottoms.

Up to 99+% of the organics is dissolved out into the organic solvent, leaving a water/solids mixture which is subsequently removed from the reactor and separated by filtration or centrifugation.

B.5 B.E.S.T.^{TM} SOLVENT EXTRACTION PROCESS

The B.E.S.T.^{TM} system, developed by Resource Conservtion Company, uses a vertical countercurrent extractor and was developed initially to recover oil from municipal sludges. It has been tested recently for the recovery of oil from API separator sludge (pilot scale) and is currently being used to recover oil at a Superfund site in Georgia using a 100 tonnes per day 'mobile' plant. A process flow diagram is shown in Figure 5.

Process Description

The success of the extraction depends on a unique property of triethylamine, the solvent employed in the B.E.S.T.™ process. At temperatures below 18.7°C, triethylamine is completely miscible with water, allowing it to penetrate the solids and dissolve the oils/greases. At temperatures above 18.7°C, the solvent becomes only very slightly soluble in water. The sludge/solvent is mixed cold and then centrifuged for liquid/solid separation. The liquid is then heated above 18.7°C, whereupon the oil/grease laden solvent separates from the water almost completely. The solvent is recovered from the oil/grease by steam stripping. A more complete description of the process mechanics follows:

Sludge is continuously metered into the system and mixed with recirculated cold solvent in varying ratios (claimed to go as low as 1:1). The sludge/solvent mixture is then cetrifuged for liquid/solid separation.

Ninety-eight percent or more of the system solids feed is captured by the centrifuge and discharged as a solvent-wet cake. Up to 90 percent of the water is removed mechanically, without a phase change, and does not enter the dryer. The wet cake enters the continuously operating dryer which yields a cake dried to 95 percent solids at temperatures between 121°C and 160°C. Solvent and water vapour from the dryer are then condensed and returned to the system.

Most of the oil contained in the sludge feed is taken into solution with the solvent and is part of the liquid fraction (centrate) leaving the centrifuge at 4°C. The temperature of the centrate, composed of solvent, water and oil, is raised to 60°C and separated into solvent and water fractions in the decanter. Colloidal solids, not initially captured in the centrifuge, agglomerate at the solvent/water interface in the decanter and are drawn off, cooled and returned to the centrifuge for removal.

The separated water in the decanter is continuously pumped to a water still where any residual solvent is steam stripped and returned to the system. The water in the still bottoms is cooled and available for return to the headwaters of the wastewater sewage treatment plant for discharge.

The separated solvent from the decanter is cooled to -9°C by recuperative and refrigerative heat exchangers and is recirculated to be mixed with the incoming sludge. A portion of the recirculated solvent is continuously bypassed to a solvent still where the oil is removed by steam stripping. The bypass rate is controlled to maintain a desired oil concentration in the recirculated solvent.

The mixture of oil and water remaining in the solvent still bottom is separated. The water is cooled and returned to the wastewater treatment plant or disposal with the water from the water still, and the separated oil is recovered for use.

B.6 CENTRIFUGATION

Centrifugation is a well-understood and developed technology and effects liquids-solids or liquid-liquid separations by means of centrifugal force. There are several types of centrifuge design available for sludge dewatering; decanter, basket and nozzle disc. The most common type employed for sludge separation is a modified disc centrifuge.

Process Description

There can be many variations to an oil sludge recovery process based on the centrifugation unit operation. The process flow diagram presented in Figure 6 shows the use of a modified disc centrifuge to treat waste oil sludges. In general, the waste oil is pumped from a storage tank through a filter where some of the solids are removed. Chemical addition may be used at this point. It is then passed through a heat exchanger where it is heated prior to centrifugation. Three streams are generated at the centrifuge: oil which goes to storage; water which goes back into the system for re-processing; and sludge which may require further processing prior to ultimate disposal.

Many modifications to this basic process are possible. Dilution with either water or solvent prior to centrifugation may be advantageous. Passing the feed through more than one centrifuge might be another option. Work in Japan by Mitsubishi Heavy Industries Ltd. involved the extraction of oil from sludge, followed by two centrifugation steps. The first was for liquid/solid separation and the second for oil/water separation.

B.7 KEANE SOLVENT/MEMBRANE EXTRACTION PROCESS

This process was developed and patented by James Keane initially for tar sands extraction, although some work has been done very recently on oil refinery residues.

Process Description

This is essentially a solvent extraction process, depending upon the formation of an interfacial membrane created by a mixture of dissimilar materials and stabilized temporarily by electrostatic forces. No chemical reaction occurs at the interface. It is preferable to add solvent first. Also, by reducing the solvent and displacing liquid temperature prior to mixing, interfacial tension can be increased.

Figure 7 shows a flow diagram for the process and the following describes the essential features of the process.

First Stage Mixer: To reduce any lumps to grain size and thoroughly wet the oil covering the sand grains to achieve the greatest amount of oil in solution in the solvent.

Second Stage Mixer/Grinder: The displacing liquid is added. This mixer provides the grain to grain contact and liquid contact opportunities which permit the displacing liquid to contact the surface of the sand grains and spread.

Rake Clarifier: Oil solutions and displacing liquid are separated off, while the bottoms consisting of sand with solvent and liquid residues are fed to the sand separator.

Sand Separator: Sand bed is fluidized with both the solvent and displacing liquid, with fine bubbles of air introduced to generate turbulent mixing in order to free the entrained globules of oil solution.

Gravity Separator Column: Mechanical vibrator aids globule break-up.

First Stage Solvent Recovery: Oil laden solvent distiller - solvent returned to storage.

Second Stage Solvent Recovery: Partly distilled mixture moved by adding second solvent (high boiling point) for fluidity.

Recovery Levels:
100% oil
Sand residue which will not contaminate
No tailings ponds
6%:25% oil (wt)
Claimed to be applicable to asphalt paving
No surfactants

Solvents: Methylene chloride, trichloroethylene, perchloroethylene, FREON, FREON TF, etc.

Displaced Liquids: Water, ethanol, etc.

The process is claimed to recover 99+% oil from feeds containing 6% to 25% by weight oil, and to produce an essentially oil-free sand residue. No tailings ponds are required and the process employs no surfactants. It is claimed to be applicable to recovering bitumens from asphalt paving media.

B.8 GULF-LAVALIN PROCESS

This process was developed to upgrade oil residues produced in refining petroleum by Andre Marsan et Associes Inc. in conjunction with Universite de Sherbrooke.

Process Description

The Gulf-Lavalin process recovers hydrocarbons from oil residues generated by petroleum refineries (see Figure 8). The residues are thickened with an inert solid (which is a product of pyrolysis) if the oil content exceeds 25%, and then heated to high temperatures (760°C to 980°C) to crack the hydrocarbons. The kiln is heated indirectly by the combustion of recycled reaction gases. The process operates in an inert atmosphere and at atmospheric pressure. The high temperatures in the kiln permit the production of light hydrocarbons (C_3 and lower) which are recovered as gases (56.6% of products). The gases are high in energy and clean. A portion of the gases is returned to the kiln as fuel, thus making the process energy self-sufficient.

A typical distribution of the products of pyrolysis of oil residues gives the following values:

Solids:	10% (wt/wt)
Gas:	56.6%
Oil:	22.8%
Unaccounted:	10.6%

B.9 TACIUK PROCESS

This process is being developed by UMATAC Industrial Processes Ltd., and AOSTRA to recover the bitumen fraction from oil sands. A 5 ton/hour pilot plant has been built for trial runs. UMATAC are showing increasing interest in applying the Taciuk process to recover oil from oil sludges, and have done some testing on such wastes recently.

Process Description

The Taciuk process recovers hydrocarbons from tar sands in a horizontal rotating reactor. The reactor consists of four zones:

- Pre-heating zone
- Reaction zone
- Combustion zone
- Cooling zone

Feedstock passes through the preheat zone where water is evaporated off (see Figure 9). It then passes to the reaction zone where it is mixed with incandescent cinders, recycled from the combustion zone. Heat in the reaction zone cracks the hydrocarbons contained in the oil sand (or oil sludge) and organic vapours are evolved. These vapours will yield gases and liquids. Fine solids are removed from the vapour in a cyclone and a fractionating tower separates the different fractions for further processing. The remaining sand is covered with a thin layer of coke. The coated sand passes to the combustion zone where air is supplied to burn most of the coke. The inert hot solids are transferred to the cooling zone. Heat evolved as the solids cool serves to indirectly heat the preheating zone. The sand leaving the reactor is further cooled and recycled. Combustion gases pass through a cyclone and wet scrubber for solids and SO_2 removal.

Under steady state conditions, coke coated sand is the principal source of combustion (81%). Three supplementary fuels can also be used:

- Material from the bottom of the fractionation tower
- Reaction gases (C_3 and lower)
- Gases from an external source

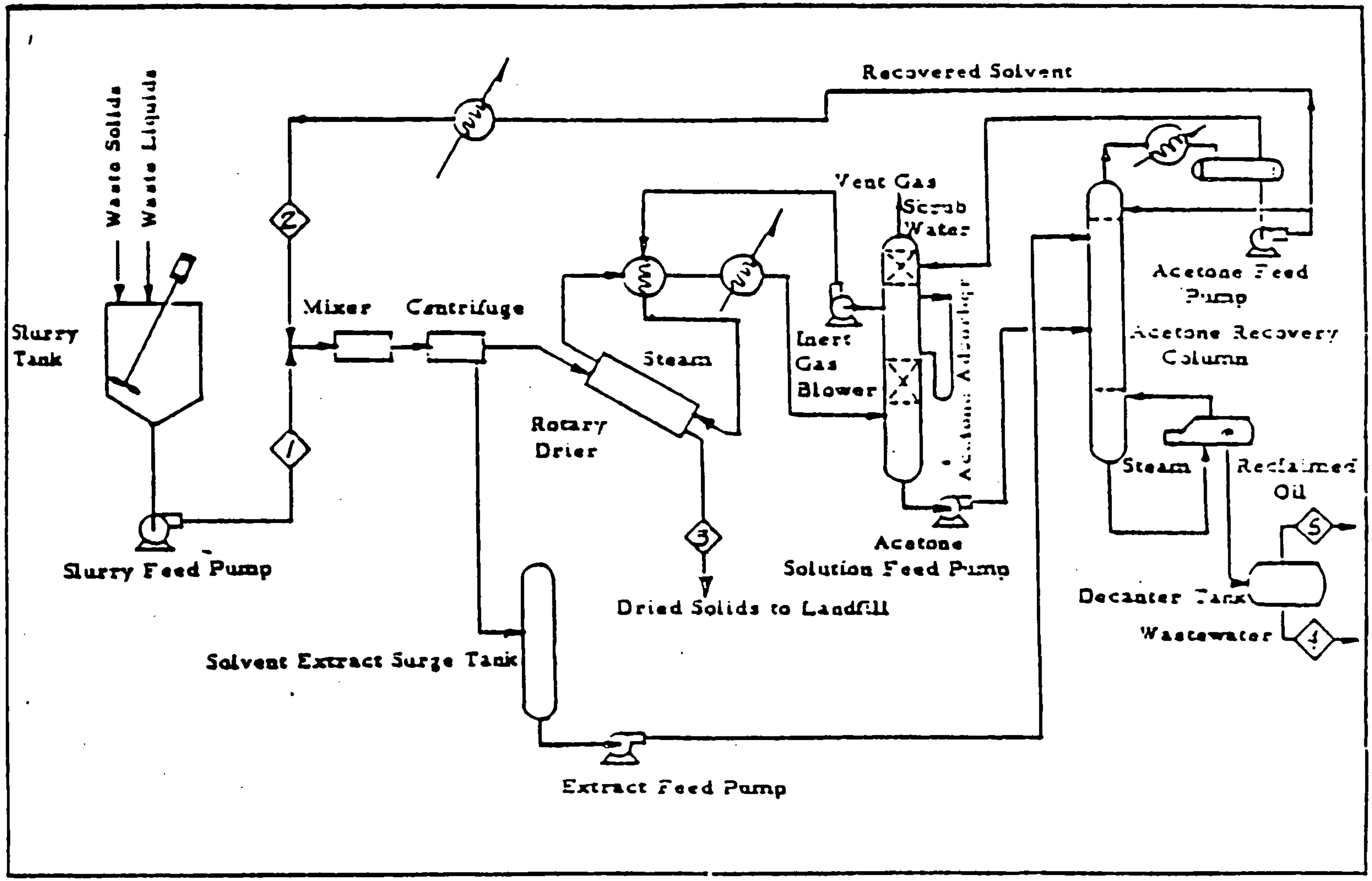


FIGURE 1 - Solvent Extraction Process Flow Diagram

Reference: "Alternatives for Hazardous Waste Management in the Petroleum Industry" by Jacobs Engineering Co., Pasadena, CA, for the United States Environmental Protection Agency, Washington, D.C., 1979

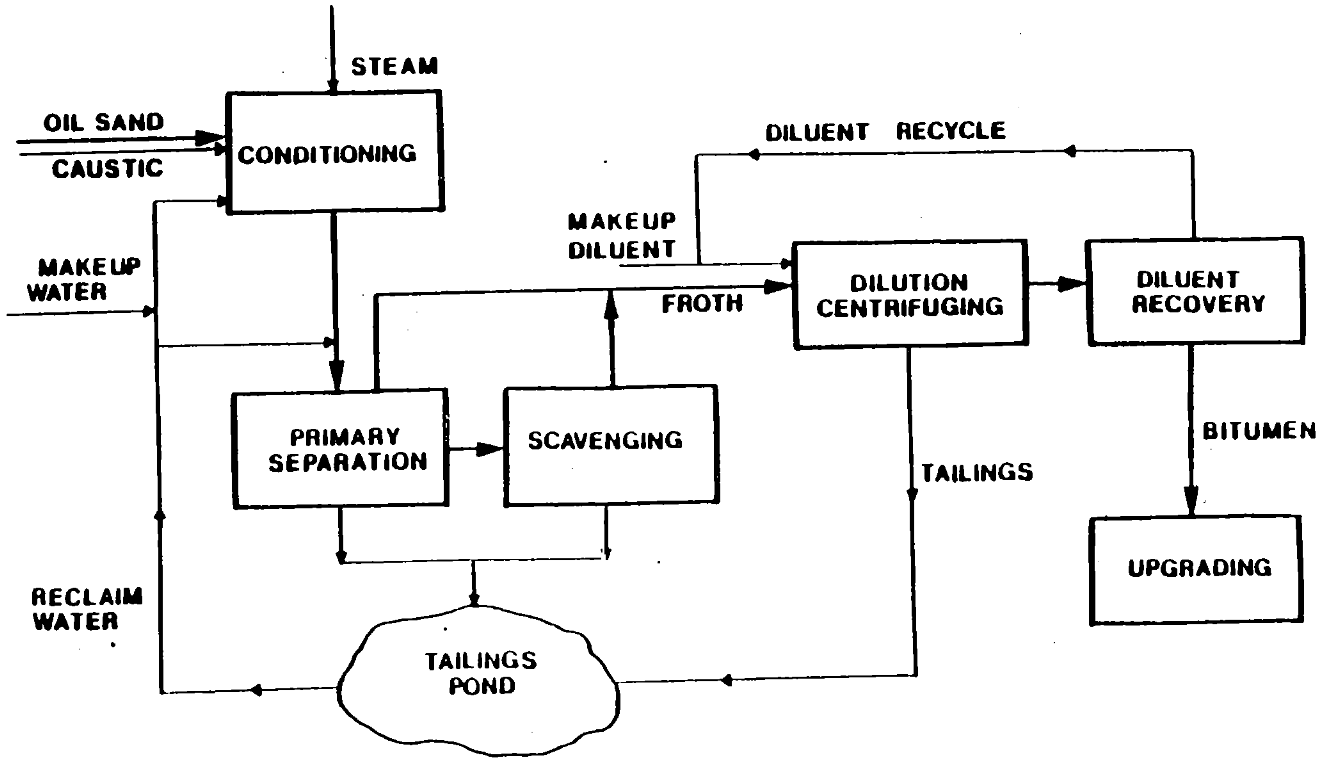


FIGURE 2 - Process Flow Diagram for Hot Water Extraction Process

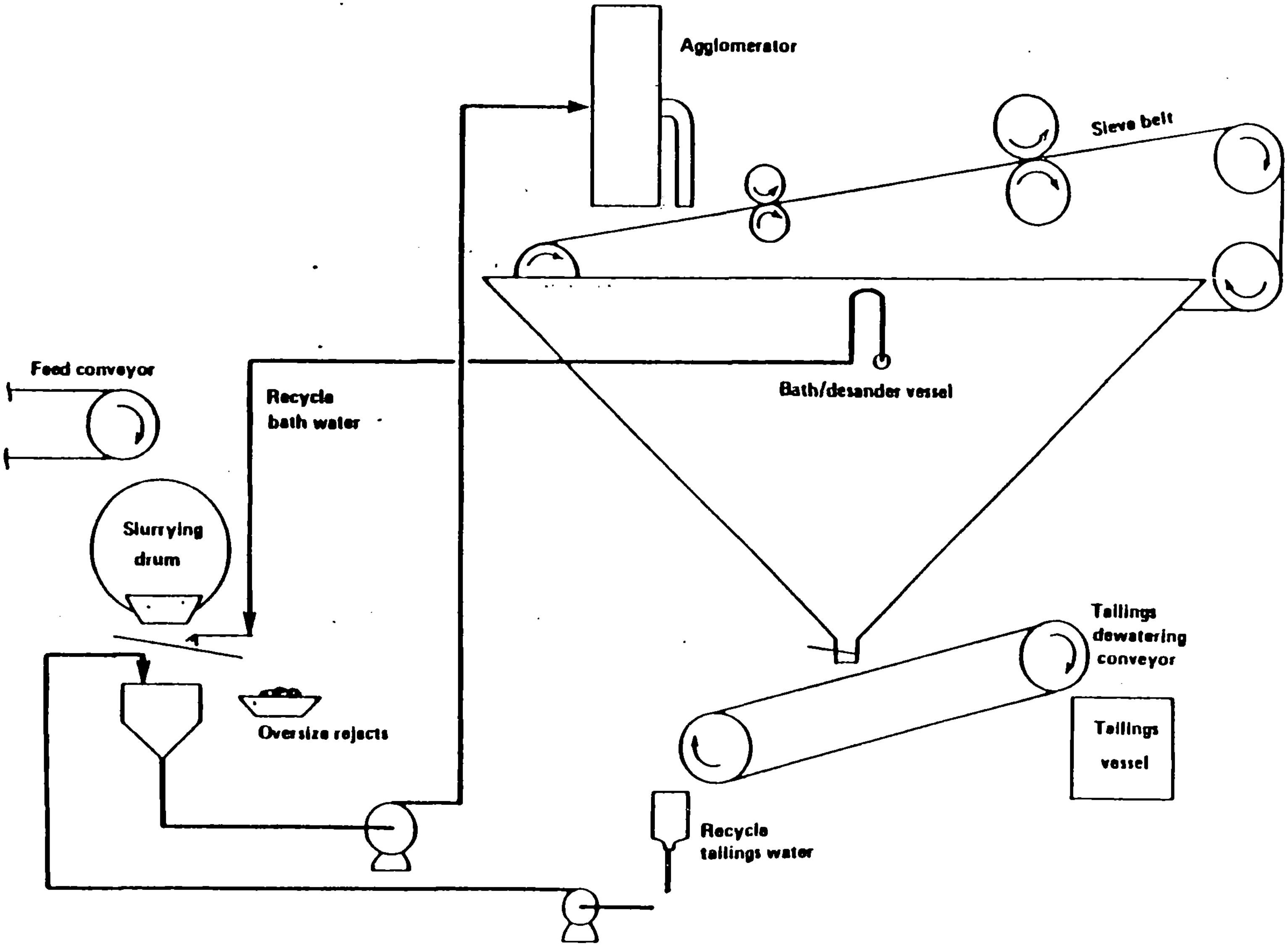


FIGURE 3 - Kruyer Process Flow Diagram

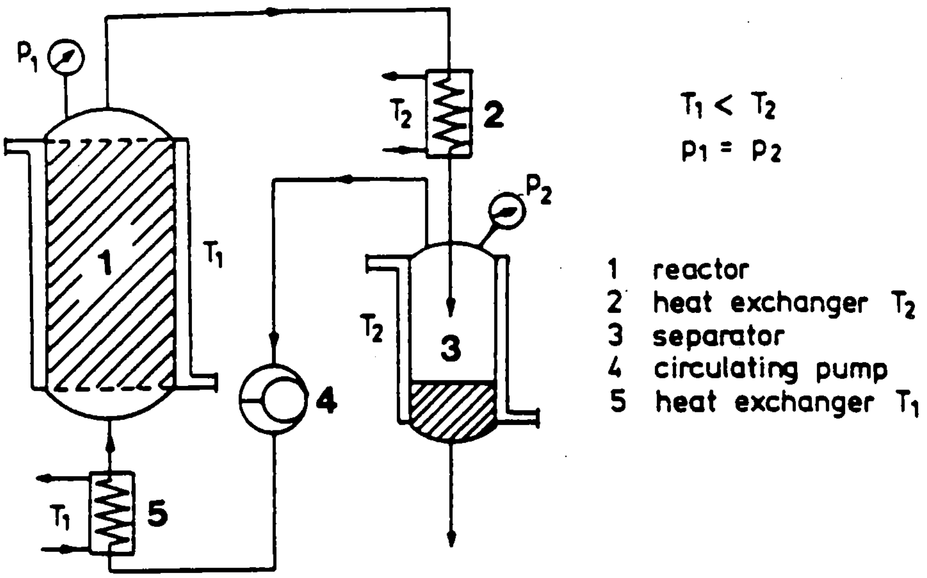


FIGURE 4(a)- Flow Diagram of Isobaric SCF Extraction

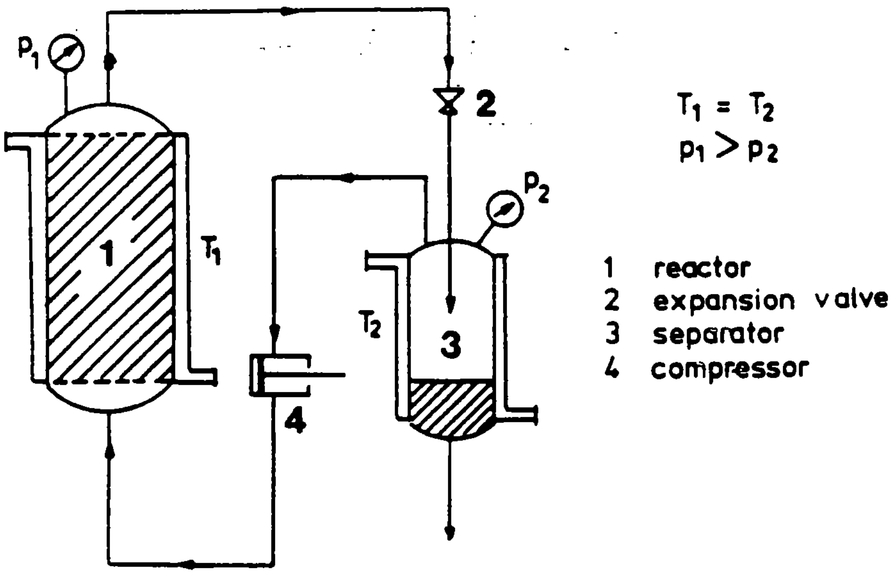


FIGURE 4(b) - Flow Diagram of Isothermal SCF Extraction

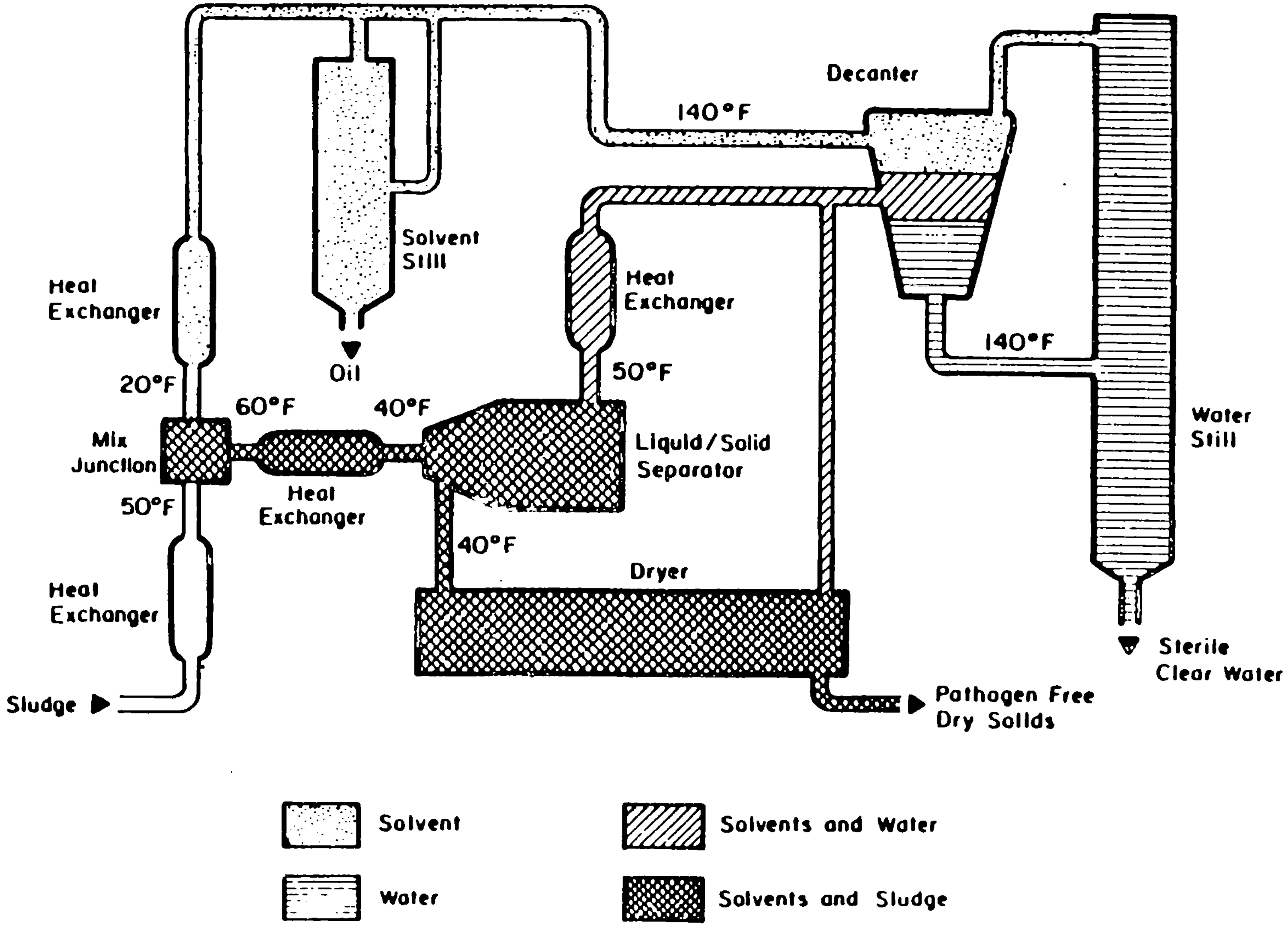


FIGURE 5 - B.E.S.T. Process Flow Diagram

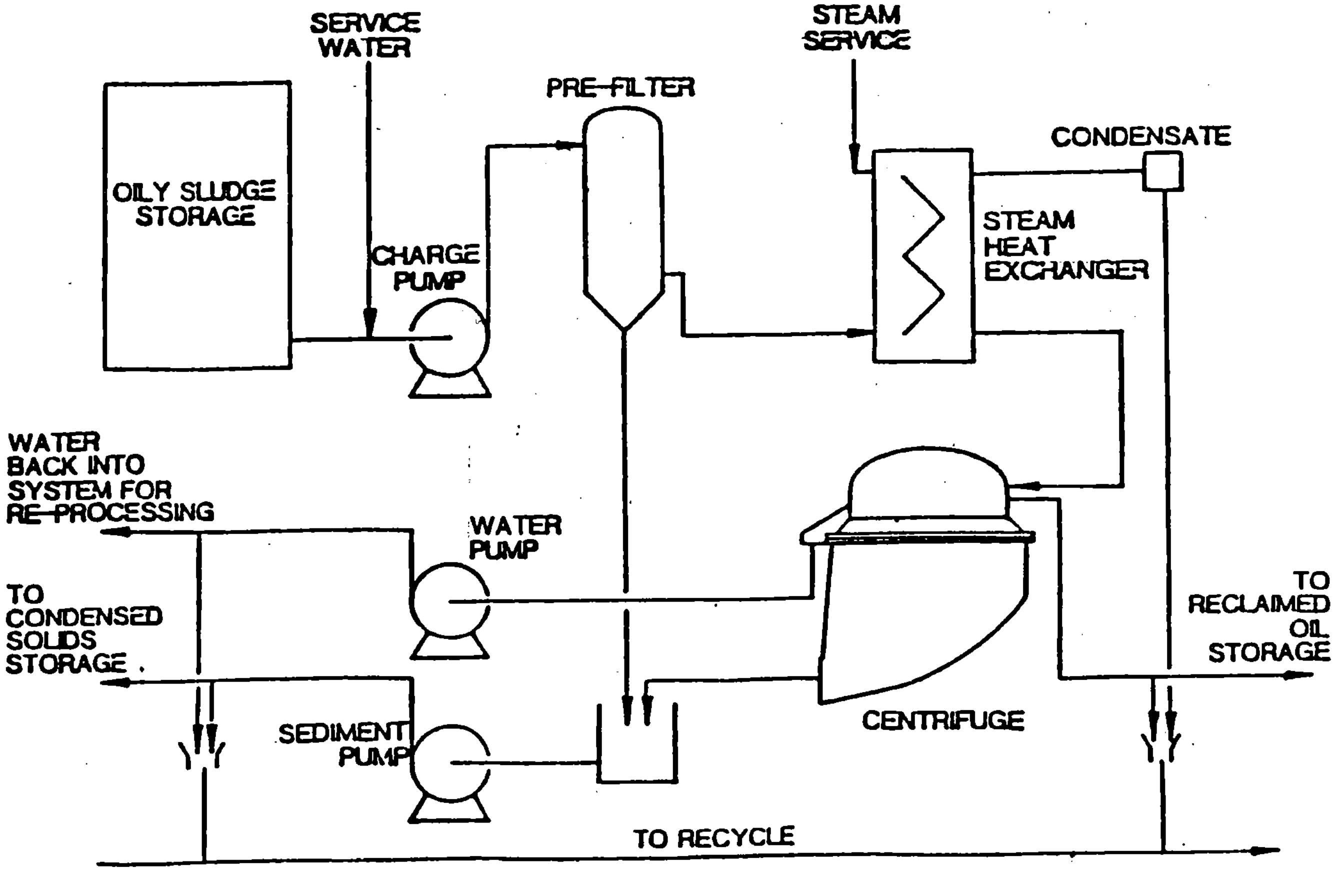


FIGURE 6 - Centrifugation Process Flow Diagram

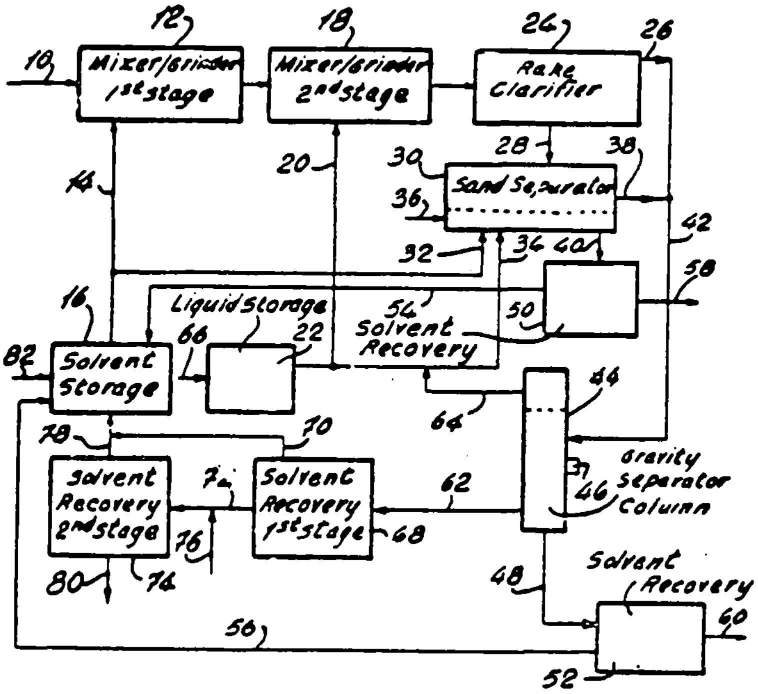


FIGURE 7 - Keane Solvent/Membrane Extraction Process Flow Diagram

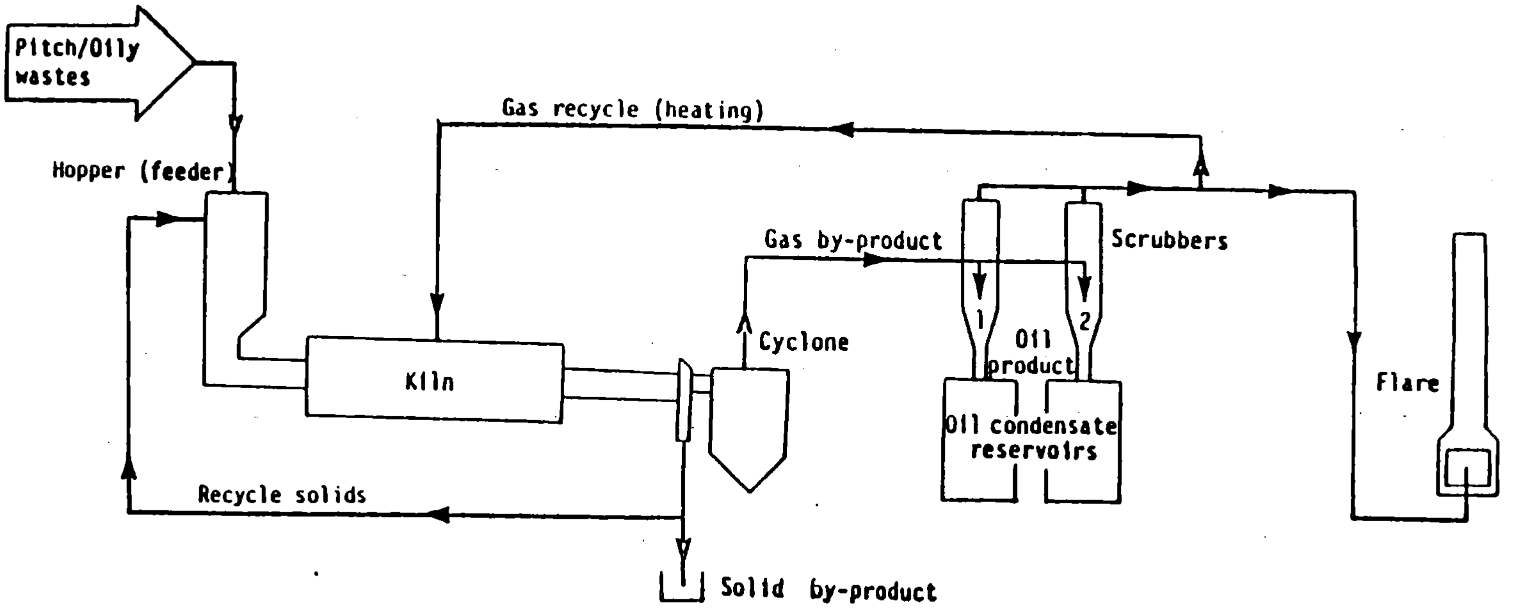


FIGURE 8 - Gulf-Lavalin Process Flow Diagram

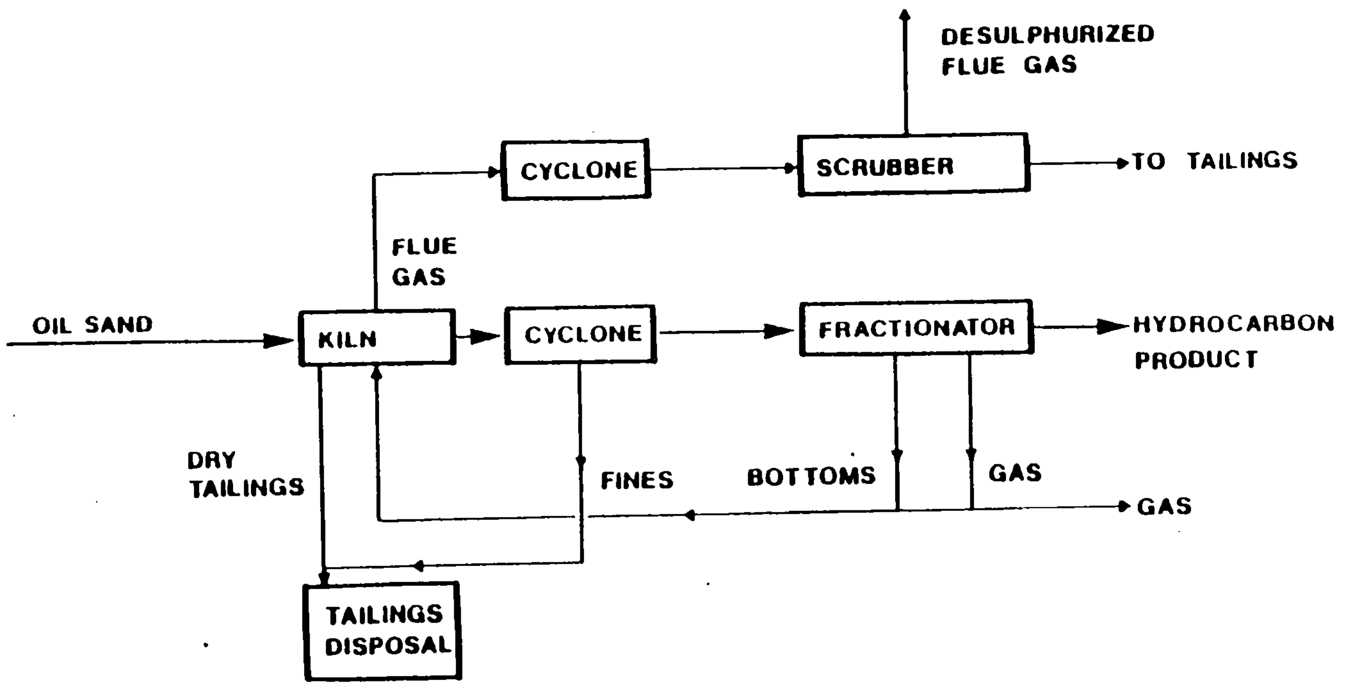


FIGURE 9 - Taciuk Process Flow Diagram

APPENDIX C

TYPICAL REQUEST FOR INFORMATION

June 23, 1986

TO: Bob Ritcey, P.Eng
Manager, Demonstration Operations
Umatac Industrial Processes
Calgary, Alberta

Bob,

As we have discussed, please provide the following information on the application of the Taciuk Process to treatment of waste oil sludges:

1) Capital cost for 17,000 lb/hr unit

2) Operating costs - Labour
   - Utilities
   - Chemicals

3) Process flow sheet

4) Results achieved on test using similar materials i.e. quality of products

5) Any process limitations
   e.g. Can solid materials be handled?
   Can unit be made mobile?
   Air pollution problems?

Main materials requiring treatment are API separator sludges and tank bottoms. Expected compositions are:

	Oil (%)	Water (%)	Solids (%)
API Sludge	5 - 10	60 - 85	10 - 30
Tank Bottoms	50 - 80	0 - 10	20 - 50

Would like to receive information by July 4/86. Please contact me if you have any questions.

Regards,

Jim Suddaby

Tricil Ltd.

APPENDIX D

INFORMATION RECEIVED FROM TACIUK

uma
UMATAC Industrial Processes
A Division of UMA Engineering Ltd.
210-2880 Glenmore Trail, Calgary, Alberta, Canada T2C 2E7 Telephone (403) 279-8080

File: 4538-012-08 A.1
June 30, 1986.

TRICIL Ltd.,
89 Queensway West,
Mississauga, Ontario L5B 2V2

ATTENTION: Mr. Jim Suddaby, P. Eng.,
Senior Process Engineer.

Dear Sir:

RE: Taciuk Processor Use for Tank Bottoms and API Separator Sludges.

UMATAC has completed a preliminary process design and estimate for blended sludge treatment.

On average, the analysis of the blend feed is assumed to be:

Water - 29%
Hydrocarbon - 40%
Inert Solids - 31%

The batch retort tests and Taciuk Processor yields from oil sands were used to predict process yields as follows:

Oil Product - 68%
C_3^- Gas - 9%
Coke - 23%

A light oil is produced and the flue gas and solids effluents are of a nature suitable for conventional treatment and disposal of by-products.

Operating cost estimates are for continuous plant operation, located on an existing site, and operated for a period of ten years during which time 558,000 tons of feed has been processed.

This basic cost estimate does not include costs associated with liability insurance, long-term environmental liability obligations, research and development sunk cost recovery (13 million dollars to date), environmental assessments, research testing and laboratory analysis prior to processor detail design, legal and contract negotiation costs, travel costs and other indirect cost components.

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UMA Gr [illegible]

The range for estimated costs associated with this Project are as follows:

Capital Cost (with interest)	- Total	- 11 to 14 million dollars.
	- Unit	- 20 to 25 dollars per ton.
Operating Cost	- Annual	- 2 to 3 million dollars per year
	- Unit	- 36 to 54 dollars per ton.
Excluded Item Costs (Guess)	- Total	- 2 to 6 million dollars.
	- Unit	- 4 to 11 dollars per ton.

No allowance has been included for credit value of the oil products, or for costs of transporting the materials.

Using this data, the minimum cost would be 60 dollars per ton and the maximum cost would be 90 dollars per ton with a probable cost of 70 to 72 dollars per ton.

Oil product sales could reduce unit costs by 15 to 20 dollars per ton.

The following comments are included as answers to specific questions raised in your teletype of June 23 to Mr. Bob Ritcey.

Item 1 Capital Costs - covered elsewhere.

Item 2 Operating Costs - covered elsewhere. Chemicals are not necessary unless specific problems associated with corrosion, emulsions, etc. are identified with particular feed stocks.

NOTE: The estimates do not allow for sulfur dioxide removal from the flue gases. If this is required, the system capital costs would be approximately 500,000 dollars, and the annual reagent cost for limestone, or lime, would be in the range of 50,000 to 200,000 dollars per year (this is dependent on quantity of sulfur removed and reagent transportation costs).

Item 3 Process Flow Sheet - See enclosed UMATAC Drawing A-01-101, titled, "Taciuk Processor Portable Unit - General Equipment and Flow Diagram". This provides the major equipment requirements and general process flows. The actual flow rates, thermal balances, material balances, etc., cannot be set until a specific feed material is identified and tested to determine feed and product properties.

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Item 4 Results from Tests Using Similar Materials - UMATAC has tested a wide range of feed materials including oil sands, oil shales, bitumens, heavy oil, bottom residuum materials, refinery waste dump and coal tar creosoting sludges. We have assumed that the tank bottoms and API sludges are similar to conventional heavy oil and bottoms sources. These feeds produce a dry carbon-coke material, an off-gas rich in methane, ethane, propane, etc., and a light oil product with an API of approximately 23 points, which is similar to conventional fluid coker oil products. For infromation purposes only, we are including typical analyses from products of oil sand processing.

These sheets are:

1. Pages 12 through 17 from UMATAC documents prepared as a study basis for Partec Lavelin. This study was to determine commercial oil sands plant comparative economics.

2. Pages 18 and 20 from test result summary document for Suncor oil sand feed.

3. Pilot Plant flowsheet with sample stream identification.

4. Core Laboratory Analysis sheet - D-48 - Solids Samples.
   C-1 - Water Analysis.
   C-2 - Water Analysis.

This data is from oil sands operation **NOT** from tests performed on feeds from TRICIL.

Item 5 Process Limitations - These are generally discussed in enclosed documents. Solids can be handled but trash and tramp rocks in excess of approximately 3" x 3" x 6" could collect in the reactor and plug off the sand recycle assembly. Material such as chains, cables, long rods, etc. would have to be separated prior to feeding into the unit.

In general, the processor requires a sand charge which recycles inside the unit to provide a heat carrier and sealing material. If there was a shortage of suitable solids in the feed, this would be provided from a coarse sand feed hopper. We would anticipate using a coarse silica sand in the 4 to 14 mesh size range for this purpose.

General - The yield of products and heat balance is sensitive to quantity and type of liquids in the feed. If sufficient hydrocarbons are present at all

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times, there is further potential for heat recovery by burning excess coke and off-gas to provide auxiliary heat or steam for other facilities. These would tend to reduce the operator's overall site cost.

This information should provide you with the general data required for your study.

Please contact Mr. B. Ritcey, or the undersigned, if any further explanations or data is required. The plant size and feed rate can be varied up or down from the 20 ton per hour capacity used for this study, so that other alternatives are possible.

Yours very truly,

W. Taciuk,
Executive Vice-President.

Encls.

WT/dm(165)

cc: B. Turner, AOSTRA
D. Cote, UMA Group
A. Pasini, UMA Group
B. Ritcey
R. Caple

APPENDIX E

SUMMARY OF LAB SCALE TESTS

"CONVENTIONAL" SOLVENT EXTRACTION

TANK BOTTOMS - LAB SCALE TESTS

NO.	SOLVENTS	RAT	WEIGHT SLUDGE (g)	F/C (?)	SOLIDS PHASE RECOVERY (g)	SOLIDS PHASE RECOVERY (%)	OIL IN SOLIDS (%)	OIL IN SOLIDS (g)	OIL EXTRACT (%)	COMMENTS
9	TOL	5:1	50.00	C	30.38	60.76	3.18	0.97	95.29	CANT FILTER
11	MECL	5:1	50.00	C	19.76	39.52	3.00	0.59	97.11	" "
13	PE	2:1	50.00	F	44.70	89.40	14.90	6.66	67.51	GOOD DISP,4 Hr FILTER
15	PE	5:1	50.00	F	31.85	63.70	6.79	2.16	89.45	CAKE EXT'D WITH MEOH (~3:1)
G	PE	5:1	50.00	C	45.00	90.00	32.40	14.58	28.88	EST'D SOLIDS REC
6	PE	5:1	50.00	F	45.00	90.00	9.80	4.41	78.49	EST'D SOLIDS REC
26	PE	5:1	50.00	F	32.70	65.40	9.80	3.20	84.37	
27	PE/MEOH	5:1	50.00	F	33.90	67.80	14.00	4.75	76.85	FILTERS SLOWLY, PHASE SEPN
32	TOL	5:1	50.00	C	35.46	70.92	5.86	2.08	89.86	SAME AS No.9, EXCEPT DIFF CENTRIF.
34	TOL	5:1	50.00	F	28.19	56.38	0.13	0.04	99.82	SOLIDS FROM No32 EXTD 5:1 W. TOL.
35	PE	5:1	50.00	F	29.43	58.86	1.32	0.39	98.10	SOLIDS FROM No.26 EXTD 5:1 W. PE.
36	TOL	5:1	50.00	F	29.00	58.00	0.15	0.04	99.79	80 C, RAPID FILT;100 % TOT REC;
37	TOL	5:1	50.00	F	29.00	58.00	0.58	0.17	99.18	80 C SAME TEST & COMMENTS AS No.36
38	TOL	3.5:1	50.00	F	29.65	59.30	1.57	0.47	97.73	80 C SAME COMMENTS AS No. 36
39	TOL	5:1	50.00	F	32.41	64.82	2.34	0.76	96.30	50 C, SLOWER FILT THAN AT 80 C
42	TOL	5:1	50.00	F	33.30	66.60	4.27	1.42	93.06	30 C, 6 HRS TO FILT
43	TOL	2:1	50.00	F	29.04	58.08	1.05	0.30	98.51	80 C, RAPID FILT
44	TOL	2:1	50.00	C	39.64	79.28	5.51	2.18	89.35	ROOM T
45	TOL	3.5:1	50.00	C	39.66	79.32	6.27	2.49	87.87	ROOM T
46	TOL	5:1	50.00	C	40.59	81.18	3.68	1.49	92.71	ROOM T
47	PE	2:1	50.00	F	30.84	61.68	2.64	0.81	96.03	CAKE EXT'D AGAIN WITH 2:1 PE; BOTH FILT SLOW
54	TOL	5:1	50.00	C	37.85	75.70	1.89	0.72	96.51	HOT TOLUENE
55	TOL	2:1	50.00	C	39.73	79.46	4.36	1.73	91.55	HOT TOLUENE
56	PE	5:1	50.00	C	39.27	78.54	23.51	9.23	54.96	
57*	TOL	2:1	50.00	F	35.50	71.00	3.30	1.17	88.84	SAMPLE # 9 - HOT TOL,FILTERS RAPIDLY
58*	TOL	2:1	50.00	F	34.59	69.18	2.49	0.86	91.80	SAMPLE # 9 - HOT TOL,FILTERS RAPIDLY
63*	TOL	5:1	50.00	F	32.88	65.76	3.02	0.99	91.73	MIXED TBC:SSC 1:1,FILTERS MODERATELY WELL
83*	TOL	5:1	50.00	F	36.11	72.22	2.56	0.92	92.42	1:1 MIX OF VAC.EVPD.SAMPLE # 17 SOLIDS:TBC.,POOR DISP.,SLOW FILT.
84*	TOL	2:1	50.00	F	34.88	69.76	4.14	1.44	88.16	AS No.83
81*	TOL	5:1	50.00	F	35.10	70.20	9.77	3.43	83.11	1:1 MIX OF VAC.EVPD. SAMPLE # 1 SOLIDS (76):TBC.GOOD DISP.,SLOW FILT.
82*	TOL	2:1	50.00	F	35.54	71.08	9.93	3.53	82.62	AS No.81.FAIR DISP.LUMPY (SAMPLE # 1)
78	TOL	2:1	50.00	F	32.00	64.00	3.79	1.21	94.08	DISP.WELL,FILT.MOD/SLOW
79	TOL	1:1	50.00	F	33.43	66.86	6.50	2.17	89.40	DISP.NOT AS GOOD AS AT 5:1;FILT.SLOW.
86	TOL	5:1	50.00	F	29.31	58.62	0.99	0.29	98.58	5 MIN AT 80C;DISP.EXC.,FILT.,V.RAPID.
87	TOL	5:1	50.00	F	29.32	58.64	1.19	0.35	98.30	15 MIN AT 80C;DISP.EXC.,FILT.,V.RAPID.
88	TOL	5:1	50.00	F	30.37	60.74	1.42	0.43	97.90	30 MIN AT 80C;DISP.,EXC.,FILT.,V.RAPID.
109A	TOL	5:1	50.00	F	29.55	59.10	1.50	0.44	97.84	H.S.BLENDED 2 MIN.AT 80C,REHEAT TO 80C & FILT;DISP.SUPER,FILT.RAPID.
109B	TOL	5:1	50.00	F	30.81	61.62	1.80	0.55	97.29	AS 109A,EXCEPT HELD AT 80C 5MIN AFTER H.S.BLEND
110	TOL	5:1	50.00	F	31.51	63.02	1.92	0.60	97.05	AS 109 EXCEPT HELD AT 80C 15 MIN AFTER H.S.BLEND.
111	TOL	5:1	50.00	F	27.01	54.02	2.10	0.57	97.23	AS 109,EXCEPT HELD AT 80C FOR 30 MIN AFTER H.S.BLEND.
112	TOL	5:1	50.00	F	32.31	64.62	2.06	0.67	96.75	AS109,EXCEPT HELD AT 80C FOR 60 MIN AFTER H.S.BLEND.
114	TOL/TOL	2:1/1:1	50.00	F	30.69	61.38	3.46	1.06	94.82	STAGED WASH;2:1 W. H.TOL,THEN 1:1 W H.TOL,GOOD DISP.,RAPID FILT.
115	TOL	5:1	50.00	F	30.22	60.44	2.42	0.73	96.43	TOL HTD TO 90C,POUR OVER TBC,HEAT BACK TO 80C-5MIN & FILT,GOOD DISP, RAPID FILT.
108	TOL	5:1	50.00	F	29.91	59.82	1.38	0.41	97.99	MASS BAL. GOOD DISP,SLOW FILT,IMPINGER USED,93.06%OVERALL RECOVERY

SEPARATOR SLUDGES - LAB SCALE TESTS

NO.	SOLVENTS	RAT	WEIGHT SLUDGE (g)	F/C (?)	SOLIDS PHASE RECOVERY (g)	(%)	OIL IN SOLIDS (%)	(g)	OIL EXTRACT (%)	COMMENTS
10	TOL	5:1	50.00	C	42.44	84.88	2.85	1.21	67.75	CAN'T FILTER
12	MECL	5:1	50.00	C	29.22	58.44	2.37	0.69	81.53	CAN'T FILTER
14	PE	5:1	50.00	F	29.40	58.80	2.49	0.73	80.48	SLOW FILTER
19	MEOH	5:1	50.00	F	17.00	34.00	18.34	3.12	16.86	GOOD DISP AND FILTER
20	MECL+MEOH MIX	5:1	50.00	F	10.00	20.00	9.39	0.94	74.96	SOLVENT MIX;FILT GOOD-SOLVENT PHASE SEPN
21	PE+MEOH,MIX	5:1	50.00	F	11.20	22.40	6.33	0.71	81.09	SIMILAR TO No.20
22	MEOH/PE	5:1/5:1	50.00	F	14.20	28.40	1.11	0.16	95.80	CAKE EXT'D WITH PE (~5:1)
23	MECL	5:1	50.00	C	22.52	45.04	2.64	0.59	84.15	DONE TWICE-SIMILIAR SOLIDS RECOVERY
24	MECL/MEOH	5:1/5:1	50.00	C	7.50	15.00	4.00	0.30	92.00	SOLIDS FROM No. 23 EXT'D W 5:1 MEOH AND FILT.
25	PE+MEOH MIX	5:1	50.00	F	10.00	20.00	8.72	0.87	76.75	REPEAT OF 21
28	MEOH/PE	5:1/5:1	50.00	F	10.23	20.46	2.55	0.26	93.04	" " 22
29	MEOH/PE	2:1/2:1	50.00	F	16.40	32.80	6.14	1.01	73.15	CAKE EXT'D WITH PE (2:1)
31	MEOH/TOL	5:1/5:1	50.00	F	9.60	19.20	2.09	0.20	94.65	CAKE EXT'D WITH TOLUENE (~5:1) STAGED RINSING
33	MEOH/TOL	2:1/2:1	50.00	F	13.90	27.80	2.53	0.35	90.62	CAKE EXT'D W TOL (2:1), SLOW FILT @ ROOM T
40	PE	5:1	50.00	F	23.36	46.72	5.74	1.34	64.24	VISUALLY POOR O & G EXT'D;POOR DISP/FILT
41	TOL	5:1	50.00	F	21.84	43.68	3.31	0.72	80.72	POOR DISP
50	MEOH/HTOL	5:1/5:1	50.00	F	9.18	18.36	4.41	0.40	89.20	SOLIDS + HOT TOL 5:1,FILT.
51	MEOH/HTOL	2:1/5:1	50.00	F	9.21	18.42	4.18	0.38	89.73	SOLIDS + HOT TOL 2:1,FILT
52	MEOH/HTOL	5:1/2:1	50.00	F	9.70	19.40	7.24	0.70	81.27	FILTERS WELL W MEOH;2:1 HOT TOL ON SOLIDS,FILTERS SLOWLY
53	"	2:1/5:1	50.00	F	9.43	18.86	9.12	0.86	77.07	SAME AS No.52
61*	MEOH/HTOL	5:1/5:1	50.00	F	2.24	4.48	13.05	0.29	93.60	SAMPLE # 3, SOLIDS+5:1 HOT TOL,FILTERS WELL
62*	HTOL	5:1	50.00	F		0.00		0.00	100.00	SAMPLE # 3 - CANNOT BE FILTERED
64A	OVENDRIED	-	200.00	-	50.18	25.09	27.50	13.80	N/A	OVEN-DRIED SSC AT 103C
64	OVENDRY/HTOL	5:1	79.71	F	18.74	23.51	3.35	0.63	89.50	OVEN-DRIED SSC EXTD W.5:1 HOT TOL
65	"	2:1	79.71	F	18.23	22.87	6.43	1.17	80.39	OVEN-DRIED SSC EXTD.W.2:1 HOT TOL.
75A	OVENDRIED	-	100.00	-	36.50	36.50	33.00	12.05	N/A	SSC,OVEN-DRIED TO 48% H2O
75	OVENDRY/HTOL	5:1	55.00	F	15.55	28.27	7.09	1.10	73.27	20 GM SOLIDS FROM 75A EXTD.W.5:1 HOT TOLUENE
91	HTOL	5:1	50.00	F	42.83	85.66	3.15	1.35	64.02	VERY POOR DISP;VERY SLOW FILT.
104	MEOH/HTOL	5:1/5:1	50.00	F	13.28	26.56	6.80	0.90	75.92	5MIN MEOH RETENTION,DISP EX.,FILT.RAPID.TOL.5:1,DISP.GOOD,FILT.FAST
105	"	"	50.00	F	12.26	24.52	7.90	0.97	74.17	15 MIN MEOH RETENTION.OTHER COMMENTS AS 104
106	"	"	50.00	F	12.14	24.28	4.48	0.54	85.50	30 MIN MEOH RETENTION.OTHER COMMENTS AS 104.
59*	TOL	2:1	50.00	F	42.12	84.24	1.89	0.80	79.32	SAMPLE # 17 - HOT TOL,FILTERS SLOWLY
60*	TOL	5:1	50.00	F	44.53	89.06	2.08	0.93	75.94	AS No.59
66*	MEOH/HTOL	2:1/5:1	50.00	F	13.48	26.96	4.03	0.54	85.89	SAMPLE # 17 - MEOH DISP.EX.FILT.MOD.,SOLIDS 5:1 H TOL.,DISP.GOOD,FILT.MOD.
67*	MEOH/HTOL	5:1/5:1	50.00	F	10.00	20.00	5.27	0.53	86.31	SAMPLE # 17 - MEOH DISP.GOOD,FILT RAPID;SOLIDS 5:1 H TOL.DISP.V.GOOD,FILT.RAPID
90*	"	"	50.00	F	5.63	11.26	5.73	0.32	91.62	SAMPLE # 17 - MEOH DISP.EX.FILT.SLOW;SOLIDS 5:1 H TOL.DISP.EX.,FILT.MOD
95*	"	2:1/5:1	50.00	F	5.05	10.10	11.15	0.56	85.37	SAMPLE # 17 - MEOH DISP.GOOD.FILT.FAIR;SOLIDS 5:1 H TOL.DISP.POOR,FILT.SLOW
103*	"	"	50.00	C	1.64	3.28		0.00	100.00	SAMPLE # 17 - SOLIDS 5:1 H TOL.DISPV.GOOD,FILT.MOD/RAP.
98A*	O-DRIED	-	400.00	-	71.37	17.84	34.50	24.62	N/A	SAMPLE # 17 OVEN-DRIED AT 105C
98*	OVENDRY/HTOL	5:1	112.00	F	17.39	15.53	6.42	1.12	87.05	20 GM OVEN-DRIED SOLIDS EXTD 5:1 H TOL.DISP.FAIR,FILT.RAPID
77R*	VAC EVAP	-	400.00	-	174.68	43.67	19.71	34.43	N/A	SAMPLE # 17 - VACUUM EVAP.
85*	TOL	2:1	45.80	F	14.47	31.59	4.32	0.63	82.27	20 GM SAMPLE # 17 SOLIDS (77) EXTD W.2:1 H TOL.
89*	MEOH/TOL	5:1/5:1	50.00	F	21.92	43.84	12.29	2.69	86.63	SAMPLE # 1 - MEOH DISP.POOR,FILT.RAPID;TOL DISP.EXC.,FILT SLOW.
94*	MEOH/TOL	2:1/5:1	50.00	F	26.00	52.00	9.24	2.40	88.08	SAMPLE # 1 - POOR MEOH DISP.,FILT.RAPID.TOL DISP.EXC.,FILT.SLOW
102	MEOH/TOL	2:1/5:1	50.00	C		0.00	0.00	0.00	100.00	SAMPLE # 1 - MEOH DISP.POOR;TOL DISP.V.GOOD,FILT.SLOW
97A	O-DRIED	-	200.00	-	15.48	7.74	48.22	7.46	90.74	SAMPLE # 1 - OVEN DRIED
97	TOL	5:1	129.00	F	7.75	6.01	9.80	0.76	98.54	10.00 GM OVEN-DRIED SAMPLE # 1 EXTD.W.H TOL. DISP.EXC.,FILT.SLOW
76A*	VAC EVAP	-	271.30	-	149.65	55.16	49.59	74.21	N/A	SAMPLE # 1 VACUUM EVAPORATED
76*	TOL	5:1	36.30	F	15.00	41.32	17.96	2.69	81.57	SAMPLE # 1 VAC EVAP SOLIDS,20 GM,EXTD W.5:1 H.TOL.
80*	TOL	2:1	36.30	F	18.00	49.59	24.51	4.41	69.81	AS No.76,EXCEPT 2:1 H.TOL.
92*	MEOH/TOL	5:1/5:1	50.00	F	1.65	3.30	10.17	0.00	100.00	SAMPLE # 3 - MEOH DISP.GOOD,FILT.MODERATE;TOL DISP.GOOD,FILT.GOOD
93*	MEOH/TOL	2:1/5:1	50.00	F	1.44	2.88	9.42	0.14	97.03	SAMPLE # 3 - MEOH DISP.GOOD,FILT.SLOW;TOL DISP.GOOD,FILT.SLOW
100*	MEOH/TOL	5:1/5:1	50.00	C	3.16	6.32		0.00	100.00	SAMPLE # 3 - CENTRIFUGED W.MEOH;TOL DISP.V.GOOD,FILT.MODERATE

SEPARATOR SLUDGES - LAB SCALE TESTS

NO.	SOLVENTS	RAT	WEIGHT SLUDGE	F/C (?)	SOLIDS PHASE RECOVERY		OIL IN SOLIDS		OIL EXTRACT	COMMENTS
			(g)		(g)	(%)	(%)	(g)	(%)	
101*	MEOH/TOL	2:1/5:1	50.00	C	16.12	32.24	12.88	2.08	54.57	SAMPLE # 3 - CENTRIFUGED W.MEOH;TOL DISP.FAIR,LUMPY,FILT.MOD/RAPID
68A*	O-DRIED	-	200.00	-	13.05	6.53	40.00	5.22	N/A	OVEN-DRIED SAMPLE # 3
68*	TOL	5:1	153.00	F	8.90	5.82	7.86	0.70	95.00	10 GM OVEN-DRIED SAMPLE # 3 SOLIDS EXTD. W. 5:1 HOT TOL.
99A*	O-DRIED	-	200.00	-	105.61	52.81	62.22	65.71	*******	SAMPLE # 3 OVEN-DRIED
99*	TOL	5:1	20.00	F	-	-	-	-	-	CANNOT BE FILTERED
96A*	VAC EVAP	-	250.00	-	44.13	17.65	36.70	16.20	29.12	SAMPLE # 3 VACUUM EVAPD;GET 174 CC H2O/28 CC HYDROCARBON FROM 250 GM.
96*	TOL	5:1	85.00	F	4.20	4.94	2.83	0.12	98.47	15 GM SOLIDS FROM 96A,EXTD 5:1 H.TOL.DISP.EXC.,FILT.SLOW.
121A	O-DRIED	-	187.50	-	100.00	53.33	21.26	21.26	N/A	SSC O-DRIED AT 105C TO 37.5% H2O;CONTAINS 21.26% O&G.
121	TOL	2:1	65.83	F	57.32	87.07	6.06	3.47	75.0	15.83G SOLIDS FROM 121A:50G TBC(1:1 EQUIV)EXTD 2:1 W.H-TOL.
121	CONTD	-	-	-	-	-	-	-	-	DISP.V.GOOD,FILT VERY SLOW.RECOVER 65.3/112.6G TOL & 17.85G O&G(EVAP).
121	CONTD	-	-	-	-	-	-	-	-	APPROX 8.0% H2O IN TOLUENE EXTD SOLIDS.
113	TOL	5:1	100.00	F	43.00	43.00	3.10	1.33	82.23	SSC DRIED@105C TO 60% H2O,POOR DISP,SLOW FILT
116	MEOH/TOL	5:1/5:1	50.00	F	8.50	17.00	5.97	0.51	86.47	MEOH:DISP-GOOD,FILT SLOW;TOL DISP-GOOD,FILT RAPID, 60 MIN IN MEOH
117	MEOH	5:1	106.50	F	43.00	40.38	23.13	9.95	-24.52	MEOH MASS BAL,GOOD DISP,SLOW FILT,SSC DRIED TO 76% H2O
118	MEOH/TOL	5:1/5:1	106.50	F	22.56	21.18	6.37	1.44	82.01	MASS BAL;CO2 IMPINGER USED BOTH FILTRATIONS,MEOH DISP V GOOD,FILT SLOW
118	CONTD									TOL DISP EXC,FILT RAPID;"DRY" SOLIDS 20% H2O
119A	OVEN DRIED	N/A								SSC OVEN DRIED TO 20-22% H2O-(CAN'T BE FURTHER DRIED @105C)
119	TOL	5:1	168.30	F	50.00	29.71	4.29	2.15	83.01	DRY SOLIDS 119A,EXTD W/ H TOL,14% H2O LEFT IN SOLIDS AFTER H TOL
120	MEOH	5:1	53.30	F						WET SOLIDS FROM MEOH (33.35G) EXTD DEAN&STARK = 66%

APPENDIX F

HOT TOLUENE EXTRACTION

PILOT PLANT TEST PROCEDURE

HOT TOLUENE EXTRACTION

PILOT PLANT TEST PROCEDURE

1) Pump desired quantity of toluene from supplied 180 L drum to Toluene Process Tank.

2) Apply steam to coils in Toluene Process Tank to desired extraction temperature, plus 5-10°C.

3) Manually load desired weight of sludge (heavy sludge, light sludge, dried light sludge, etc.) into extraction vessel. Seal cover.

4) Open pneumatic activated outlet valve on Toluene Process Tank and allow it to drain into extraction vessel.

5) Turn agitator on and agitate for desired time.

6) Open manual valve on extraction vessel and drain into bucket.

7) Turn water on to create vacuum in filter.

8) Manually pour extraction solution onto filter screen.

9) Continue filtering until complete and release vacuum.

10) Turn on evaporator steam and condenser cooling water.

11) Pump filtrate to evaporator.

12) Continue heating until condensate flow stops (visual observation).

13) Collect evaporator bottoms in glass jars.

14) Sample the products as appropriate.

APPENDIX G

HOT TOLUENE EXTRACTION

BASIS FOR OPERATING COSTS

HOT TOLUENE EXTRACTION

BASIS FOR OPERATING COSTS

It is assumed that the plant will be staffed continuously - 24 h/day, 7 days/week. Actual operation has been estimated at 300 days/year (7200 operating hours).

1) LABOUR	
Operations - $16/h direct wages + 25% benefits	$20/h
2) CHEMICALS	
Toluene	$0.37/kg
3) UTILITIES	
a) 690 kPa(g) Saturated Steam	$17.60/1000 kg
b) Electricity	$0.06/kWh
c) Natural Gas	$0.14/m^3
4) MAINTENANCE	
Annual requirement	4% of direct capital