CHAPTER 4

CASE STUDIES

4.1 Case Study 1: Acid Clay Process

4.1.1 Process Description [2,8,24]

This process is the traditional re-refining process (Category 3.2.1 (A)). ULO is initially undergone filtration and dewatering (heating or stripping) to remove water, debris and other solid particles. Then it is contacted with 92 to 93 % sulfuric acid to extract metal salts, acids, aromatics, asphaltics and other impurities from the oil where these impurities form an acidic sludge that settles out of the oil.

Next, the slightly acidic oil is mixed with clay to remove mercaptans and other contaminants and to improve color. Approximately 0.4 lb of clay is required for every gallon of ULO. The final steps in the process are clay treatment and distillation, where the re-refined product oil is removed as overhead. Spent clay or clay sludge is removed from the bottom product by filtration. The block diagram for this process is shown in Figure 4.1, where Table 4.1 shows relative flow rates and the distribution of heavy metals in the process streams.

This process was the most widely applied re-refining process for many years, but the use of this process has drastically dropped recently due to high disposal cost of large volume of acid sludge and spent clay.

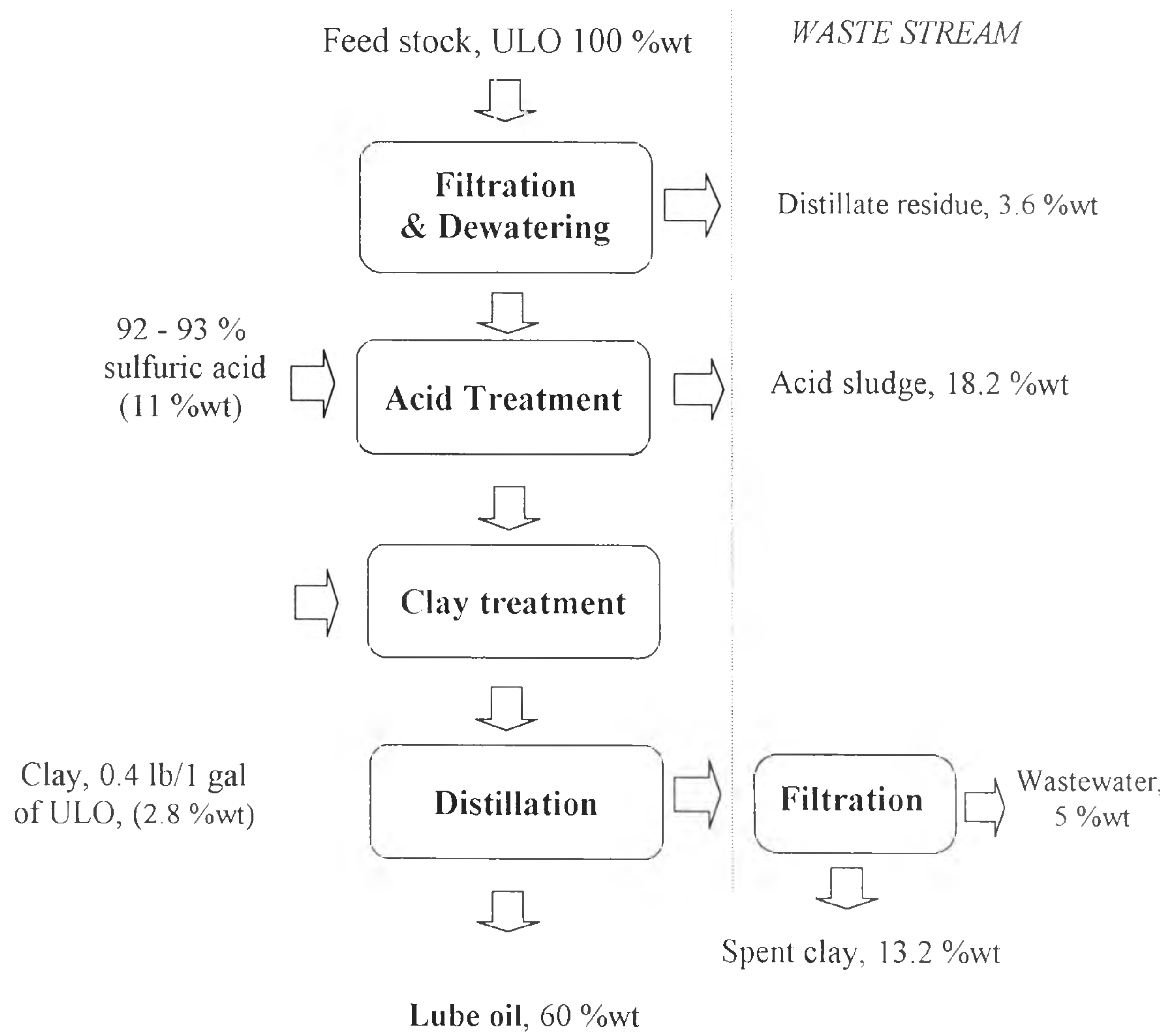

Figure 4.1 Block diagram of acid – clay process [8,24]

Table 4.1 Composition of process streams in an acid clay re-refinery [8]

	Feedstock	Acid sludge	Spent clay	Treated oil
Relative Flow rate, % by wt	100	19.2	13.2	60
Contaminant, ppm				
Aluminum	34	28	12	12
Arsenic	9.7	5.4	< 0.2	2
Barium	70	41	1.5	12
Cadmium	1.4	1.1	< 0.01	< 0.1
Calcium	1140	650	20	130
Chromium	9.5	75	< 0.01	0.4
Copper	36	41	0.04	0.2
Lead	1250	880	30	240
Iron	280	225	11	51
Zinc	820	630	3	9
PCB	43	3.4	10	2.7

4.1.2 Environmental Impact Assessment

The most significant problem associated with the acid clay process is the disposal of a large quantity of acid sludge and spent clay (which accounts for as much as 37.9 %wt of ULO feed).

Not only are large quantities of hazardous waste produced but these wastes also contain high proportion of metals. The constituents of waste streams in the process can be estimated based on their relative flow rates and concentrations in process streams as shown in Table 4.1. The following is an example of the calculation.

$$C_{ij} = \frac{W_{ULO} \times C_i \times m_{ij}}{W_j} \qquad 4.1$$

where C_{ij} = concentration of heavy metal i in waste j

W_{ULO} = weight of used lubricating oil feed stock

C_i = concentration of heavy metal i in ULO feed

m_{ij} = fraction of heavy metal i in waste j

W_j = weight of waste streams

The fraction of heavy metals (m_{ij}) in waste streams in Table 4.2 were calculated using Equation 4.1 and data in Table 4.1.

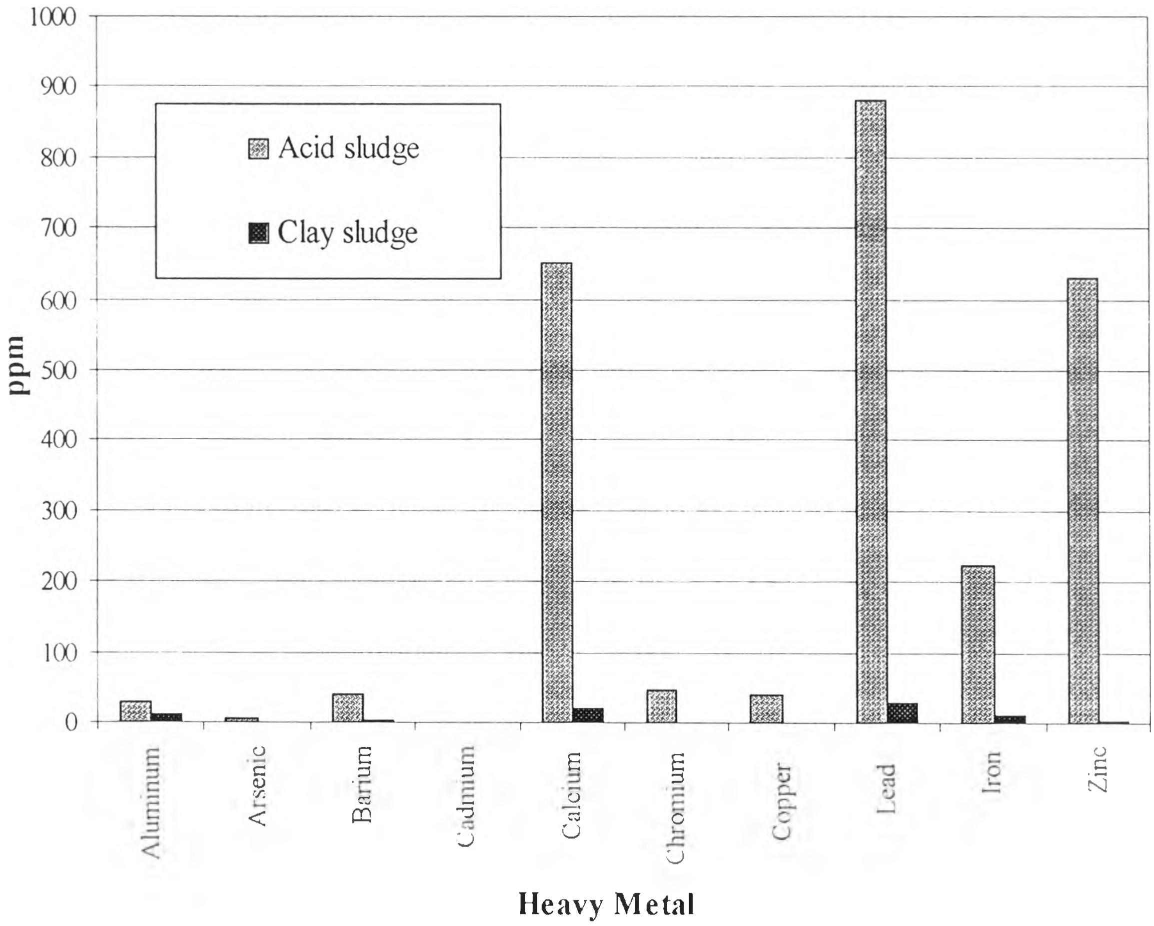

Figure 4.2 Concentration of heavy metals in acid sludge and spent clay from acid clay process

Table 4.2 Fraction of heavy metals in process streams from the acid sludge process *

Heavy metals	Acid sludge	Spent clay	Treated oil
Aluminum	0.165	0.0529	0.229
Arsenic	0.111	0.0031	0.134
Barium	0.117	0.0032	0.111
Cadmium	0.157	0.0011	0.046
Calcium	0.114	0.0026	0.074
Chromium	0.968**	0.0002	0.027
Copper	0.228	0.0002	0.004
Lead	0.141	0.0036	0.125
Iron	0.161	0.0059	0.118
Zinc	0.154	0.0005	0.007

* Based on feed ULO 100 unit (by weight), ** this value comes from mass balance of due to some error of the data.

Example; if 1 kg of ULO containing 1250 ppm of Pb was processed in the spent clay, Pb in spent clay can estimated from the following calculation:

1) 15 %wt of total weight becomes spent sludge of spent clay
2) 0.0036 is fraction value of Pb in spent clay from Table 4.2

Pb in spent clay = (1 kg x 1250 ppm) x 0.0036 / (15% x 1kg)
= 30 ppm.

Table 4.2 presents fraction of heavy metals in acid sludge, spent clay and treated oil, where it can be seen that each waste stream only contains slightly small amounts of metals. Hence, the remaining fraction should probably be in distillate residue and wastewater (see Figure 4.1)

Figure 4.2 represents the constituents in process stream products in the proposed re-refining technologies based on the characteristics of ULO in Table 4.1 and 100 %wt of ULO

The characteristics of acid sludge from this process is of high environmental concerns due to very high concentration of lead and zinc, which are 880 and 630 ppm respectively, and high quantity, 20% of feed stock.

Beside sulfuric acid, the acid sludge contains aromatic and asphaltics compounds, metals, polymers and acids removed from the ULO. Some of the characteristics of acid sludge streams are presented in Table 4.3. The high acid content requires that the sludge should be handled as carefully as the original acid As much as 30 to 42% of acid sludge can be combusted, where the remaining is left as a combustion residual. Lead content, believed to be approximately 2 to 10% by wt of the treated oil, primarily as sulfate, is another important factor to be considered prior to further processing.

Table 4.3 Characteristics of acid sludge from acid clay treatment [8].

Property	Used Lubricating Oil
Acid, %	40.8
pH	0.1
Sulfated ash, %	11.26
Viscosity, SUS (cSt)	14.1
75°F	4,000,000 (863,000)
105	457,000 (98,600)
125	150,000 (32,360)
Combustible, %	30 - 42

This is considered as a treatment step commonly employed to remove the final contaminants and to improve the color and odor of the final product. Processes using clay as a filtration media also generate waste stream with low concentration of heavy metals. This waste is generally known as "spent clay".

Acid sludge and spent clay are classified as hazardous waste group 4, i.e.chemical wastes containing heavy metals which are generated from industrial waste disposal operation according to the Notification of Ministry of Industry NO.6 [2540(1997)] [25]. Consequently both of them are treated as significant problems

To conclude this Section, Table 4.4 summarizes all significant environmental impacts from acid clay treatment process.

Table 4.4 Significant environmental impacts from acid clay treatment process

Waste Stream	(% wt)	Environmental impacts
Acid Sludge	18.2	✓
Spent Clay	13.2	✓
Distillate residue & Wastewater	8.6	✓

Remark: ✓ determine the significant environmental impact

4.1.3 Pollution Control approach

1) Treatment of acid sludge and spent clay

Acid sludge and spent clay from this process should be incinerated in a high-efficiency incinerator due to their high acid content, high concentration of heavy metal and possible PCB contamination [26], as of these pollutants can cause adverse effects to health and environment.

2) Treatment of wastewater and distillate residue

Wastewater and distillate residues from acid clay treatment contain high concentrations of heavy metals and oil & grease, which do not generally soluble in water. The treatment can be achieved by filtration of these contaminants, and precipitation of heavy metal by adjustment of the pH to the proper level (alkaline pH for hydroxide precipitation and acidic pH for sulfide precipitation) and then removal of the precipitated solid by coagulation and then gravity settling and/or filtration.

Figure 4.3 summarizes the pollution control approaches needed for the treatment of waste associated with this process

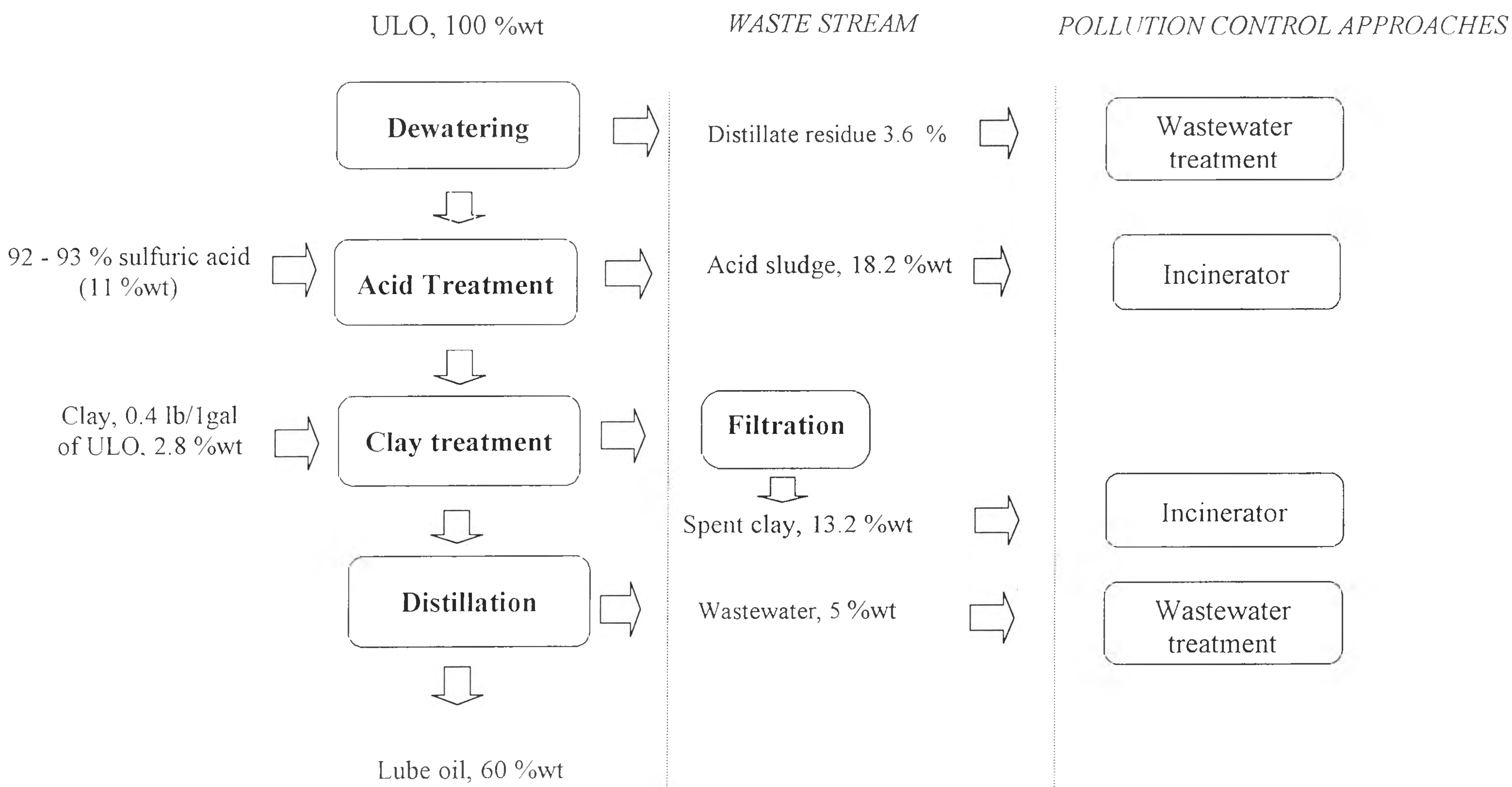

Figure 4.3 Schematic diagram of waste streams management approaches from acid clay

4.1.4 Economic Analysis [8,19,27-34]

Detailed economic studies are performed below according to the discussion in Section 3.3.2 (Eqs.3.1-3.4).

Assumption:

- Convert to updating cost by Marshall & Swift cost index [See detail in appendix]

- ULO consumption	=	100	ton/year
- Treatment efficiency	=	60 %	
- 1$	=	42.37	Bt
- Cost of ULO	=	2,000	Bt/ton
- Cost of fuel (natural gas)	=	150 Bt/million BTU	
- Cost of burning in incineration	=	98,000 Bt/ton waste	
- Cost of wastewater treatment	=	8,000 – 9,000	Bt/ton
- Treated oil price	=	88,000	Bt/ton
- Depreciation life	=	15	years

1) Investment Cost

Skid mounted acid clay unit	=	25,854,430	Bt

2) Operating cost

2.1) Cost of ULO	=	200,000	Bt
2.2) Cost of material processing	=	550,000– 660,000	Bt
2.3) Cost of fuel (natural gas)			
This process use fuel	=	352.8	MBTU
Cost of fuel = 352.8 x 150	=	52,920	Bt

2.4) Cost of pollution control (burning acid sludge, spent clay and wastewater)

Quantity of acid sludge and spent clay are produced	=	0.3 ton/input 1ton ULO	
Quantity of wastewater is produced	=	0.086 ton/input 1ton ULO	
Cost of burning in incinerator (30 x 98,000)	=	2,940,000	Bt
Wastewater treatment cost (8.6 x 6,600)	=	77,400	Bt
Cost of pollution control	=	3,017,400	Bt
∴ Total operating cost = (2.1)+ (2.2)+ (2.3) + (2.4)	=	3,930,320	Bt

3) Revenue

New lube oil price = 0.6 ton x 100 x 88,000	=	5,280,000	Bt

Cash flow analysis

Table 4.5 Cash flow analysis for acid clay treatment

Year	Investment Cost (Bath)	Operating Cost (Bath)	Total cost (Bath)	Quantity of ULO (ton)	Quantity of output (ton)	Revenue (Bath)	Benefit (Bath)
1	25,854,430	3,930,320	29,784,750	100	60	5,280,000	-24,504,750
2		3,930,320	3,930,320	100	60	5,280,000	1,349,680
3		3,930,320	3,930,320	100	60	5,280,000	1,349,680
4		3,930,320	3,930,320	100	60	5,280,000	1,349,680
5		3,930,320	3,930,320	100	60	5,280,000	1,349,680
6		3,930,320	3,930,320	100	60	5,280,000	1,349,680
7		3,930,320	3,930,320	100	60	5,280,000	1,349,680
8		3,930,320	3,930,320	100	60	5,280,000	1,349,680
9		3,930,320	3,930,320	100	60	5,280,000	1,349,680
10		3,930,320	3,930,320	100	60	5,280,000	1,349,680
11		3,930,320	3,930,320	100	60	5,280,000	1,349,680
12		3,930,320	3,930,320	100	60	5,280,000	1,349,680
13		3,930,320	3,930,320	100	60	5,280,000	1,349,680
14		3,930,320	3,930,320	100	60	5,280,000	1,349,680
15		3,930,320	3,930,320	100	60	5,280,000	1,349,680
Total	25,854,430	58,954,800	84,809,230	1,400	840	73,920,000	18,895,520
Present value			53,398,354	737	442	38,896,110	9,942,671

From Table 4.5, the summary of cost estimation are below:

Average cost of 1 ton ULO	=	72,486	Bath
Average revenue of 1 ton ULO	=	52,800	Bath
NPV	=	9,942,671	Bath
B/C ratio	=	0.73	

4.2 Case study 2: Chemical and Clay Treatment

4.2.1 Process Description [8,34-39]

This process is classified as a re-refining approach (Category 3.2.1 (A)) developed by the Phillips Re-refined Oil Process (PROP). Principally the ULO is treated by chemical demetallization with clay/hydrotreating as finishing step. ULO is initially heated and mixed with aqueous solution of ammonium salts which reacts with metal contaminants in the ULO to form metal phosphates. Due to the low solubility of these metal phosphates, they separate from both water and oil. Concentration of ammonium salts required in this process is about 30-95% of aqueous and ratio of solution per ULO is in a range from 0.002-0.05 %wt. This ammonium salts are selected from diammonium phosphate, ammonium bisulfate, ammonium phosphate etc.

Demetallization is conducted at temperature about 60-120°C, pressure range from 14.7-20 psig for 10-120 minutes, where metallic phosphates are formed and are subsequently removed by filtration. During the demetallization reactions, water and light ends are also formed; these are generally taken off as overheads.

Next, the remaining oil is heated, mixed with hydrogen, percolated through a bed of clay, and passed over a nickel molybdate catalyst (Ni/Mo) The overall objective of these series of operations is to remove sulfur, nitrogen, oxygen, chlorine and other trace inorganic compounds and to improve the oil's color. The treated oil is then flashed, cooled and distilled to strip off any remaining contaminants from the used lube oil. This process is depicted in Figure 4.4, where, Table 4.6 illustrates constituents in process stream product from this chemical and clay treatment process.

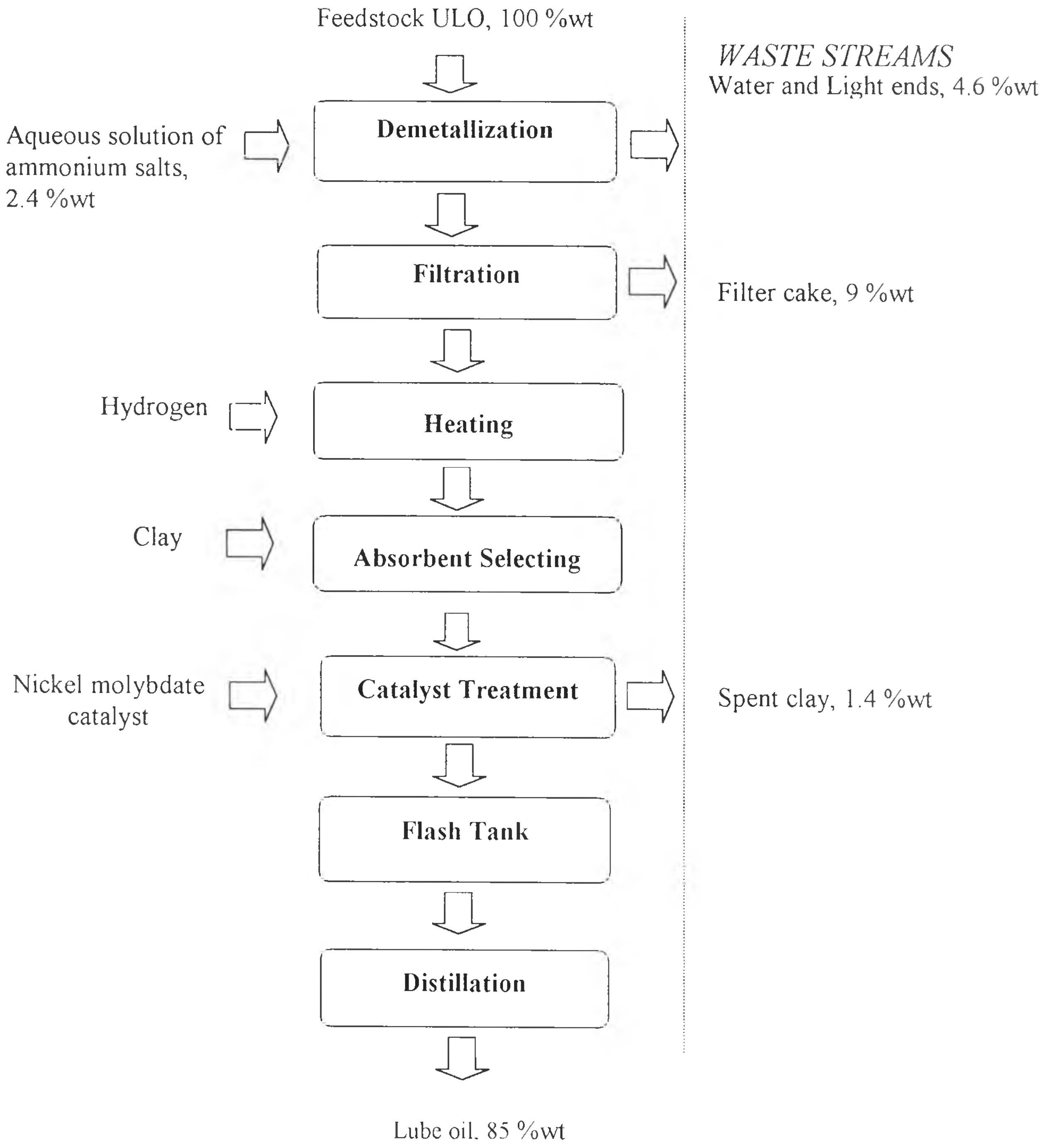

Figure 4.4 Block diagram of chemical and clay treatment process [8,36].

Table 4.6 Composition of process streams from chemical and clay treatment process [8]

Property	Feedstock	Water & Light ends	Spent Clay	Filter cake	Treated Oil
Relative Flow rate, %by wt	100	4.6	1.4	9	85
Contaminant, ppm					
Aluminum	34	< 0.01	260	37	< 0.1
Arsenic	9.7	< 0.03	1.8	9.2	< 0.5
Barium	70	<0.01	2.6	130	0.06
Cadmium	1.4	0.3	0.05	0.4	< 0.01
Calcium	1140	0.08	130	420	1.5
Chromium	9.5	< 0.01	1	3 1	< 0.06
Copper	36	0.03	6.7	4.6	< 0 03
Iron	280	0.1	180	250	2 6
Lead	1250	0 03	250	1300	3.5
Zinc	820	0.01	13	400	0.3
PCB	< 1	< 0.1	-	-	< 1

Among the disadvantages of the PROP process are its complexity and high cost (requires a $1 million royalty fee alone) [8]. The only functional PROP facility is in Mexico.

4.2.2 Environmental Impact Assessment

Waste streams in this process are water and light ends, filters cake and spent clay. The approximate amount of each waste stream is 4.6 , 9 and 1.4 % wt of the total ULO weight, respectively.

Table 4.6 represents the fraction of the remaining of heavy metals in waste stream from the chemical and clay treatment process according to the calculations, which is described previously in Equation 4.1.

Figure 4.5 represents the constituents of heavy metals in waste streams of chemical and clay treatment process, the high concentration of iron, and lead in filter cake are of most environmental concern and the same is apply to spent clay. The amounts of waste streams in this process are lower than the acid clay process, filter cake is amounted 9 %wt and spent clay is amount 1.4 %wt, which makes the total amount of 10.4 %wt (total amount of waste in Acid clay process 31.4 %wt). Fuel fraction (water and light ends) is the by-product can be used as fuel directly as it almost undetectable level of low concentration of heavy metals.

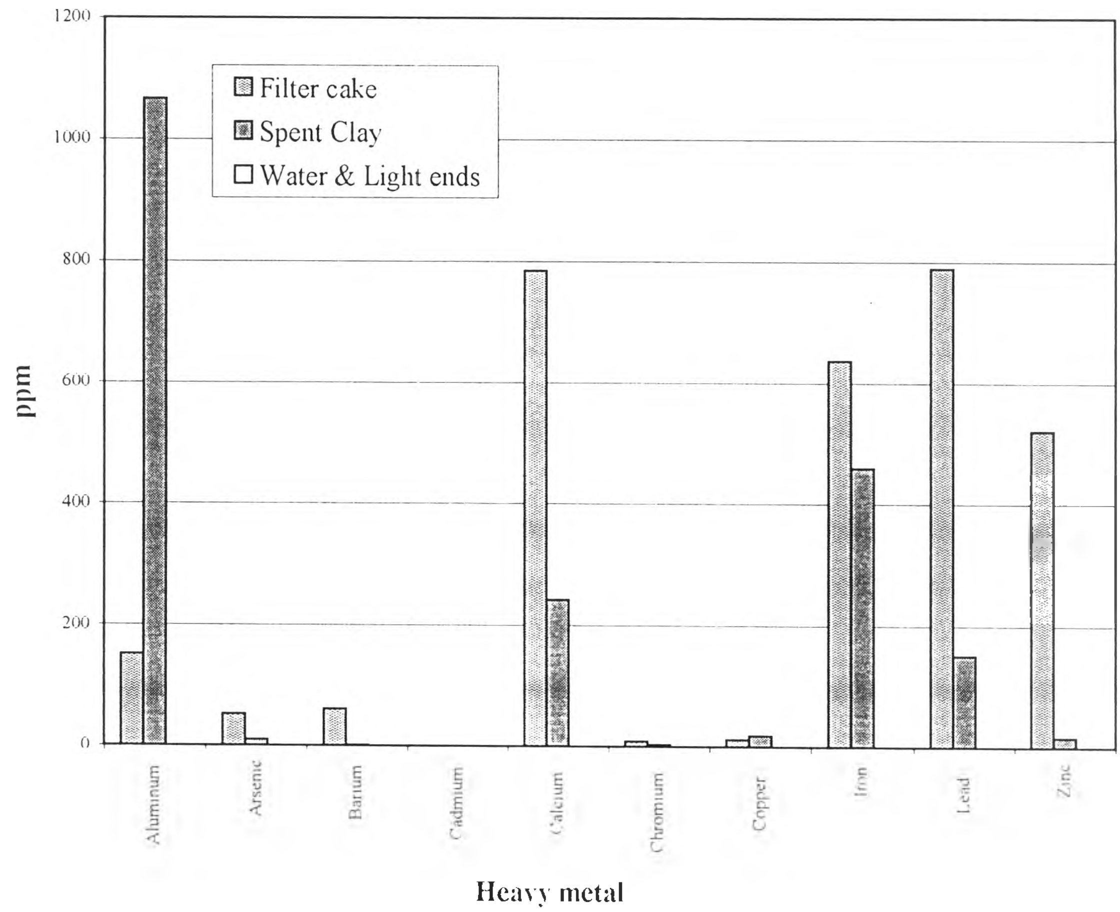

Figure 4.5 Concentration of remaining heavy metals in filter cake, spent clay and fuel fraction from chemical and clay treatment process

The fraction of heavy metals (m_{ij}) in waste streams in Table 4.7 were calculated using Equation 4.1 and data in Table 4.6.

Table 4.7 Fraction of remaining heavy metal in process stream from chemical and clay treatment process *

Property	Water & Light ends	Filter cake	Spent clay	Treated oil
Aluminum	6.02E-05	0.490	0.439	0.001
Arsenic	8.82E-04	0.595	0.015	0.025
Barium	3.3E-06	0.095	0.000	3.40E-04
Cadmium	0.019	0.055	0.001	0.011
Calcium	6.6E-06	0.076	0.003	2.1E-03
Chromium	1.5E-04	0.10	0.0041	0.015
Copper	1.2E-04	0.04	0.0072	2.0E-03
Iron	4.5E-05	0.25	0.0229	0.002
Lead	7.3E-07	0.07	0.0017	1.4E-03
Zinc	7.9E-07	0.07	0.0003	4.0E-04

* Based on feed ULO 100 unit (by weight)

To conclude in this Section, Table 4.8 summarized the significant environmental impact from chemical and clay treatment process.

Table 4.8 Significant environmental impacts on waste streams from chemical and clay treatment process.

Waste Stream	(% wt)	Environmental impacts
Water & Light ends	5	Use as fuel
Filter Cake	11	✓
Spent Clay	14	✓

Remark: ✓ Determine significant environmental impact

4.2.3 Pollution control approach

This process generated water and light ends, filter cake and spent clay, and their associated pollution control approaches depicted in Figure 4.6

Filter cake and spent clay from the PROP process can be safely disposed of by burning in cement kiln since they only contain low level of toxic heavy metal < 1% (lower than 1000 ppm) [8].

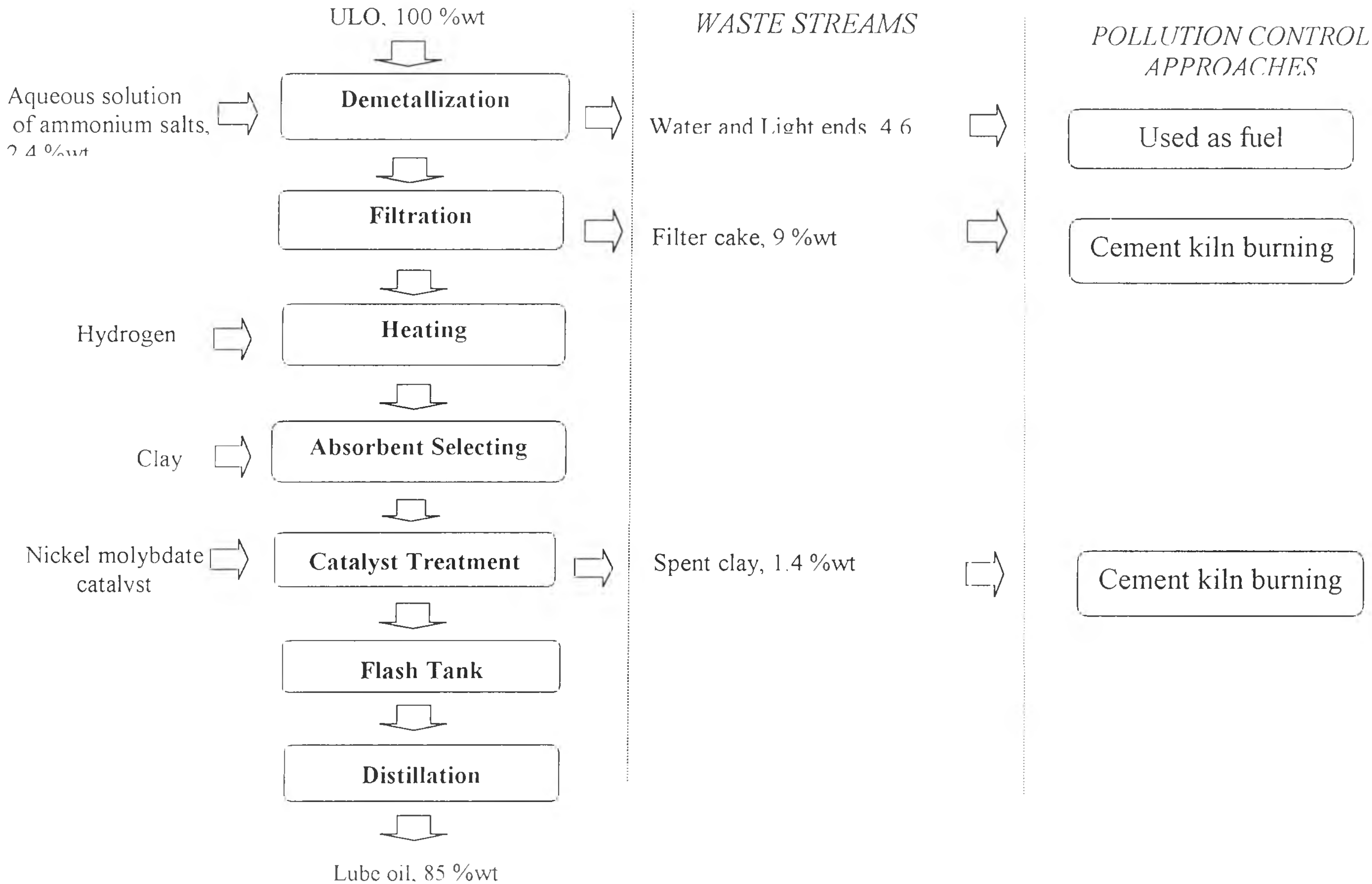

Figure 4.6 Schematic diagram of waste streams management approaches from chemical and clay treatment process

Figure 4.6 summarizes the pollution control approaches needed for the treatment of waste associated with chemical and clay treatment process.

4.2.4 Economic Analysis [8,19, 27-28, 31-33, 35,38]

Detailed economic studies are performed below according to the discussion in Section 3.3.2 (Eqs.3.1-3.4).

Assumption:

- Convert to updating cost by Marshall & Swift cost index [See detail in appendix]
- ULO consumption = 6,800 ton/year
- Treatment efficiency = 80 %
- 1$ = 42.37 Bt
- Cost of ULO = 2,000 Bt/ton
- Cost of fuel (natural gas) = 150 Bt/million BTU
- Cost of burning in cement kiln = 4,300 Bt/ton waste
- Cost of wastewater treatment = 8,000 – 9,000 Bt/ton
- Treated oil price = 88,000 Bt/ton
- Working time = 2,560 hr/year
- Depreciation life = 15 years

1) Investment Cost

Skid mounted acid clay unit	=	182,191,000	Bt
Royalty	=	42,370,000	Bt
	=	224,561,000	Bt

2) Operating cost

2.1) Cost of ULO	=	13,600,000	Bt
2.2) Cost of material processing	=	16,941,221	Bt
2.3) Utilities cost			
- 900 lb/h of 150-psi stream ($4.46/1000lb)	=	435,387	Bt
- 85 kwh/h of electricity ($ 0.0354/kwh)	=	326,378	Bt
- 300 gal/h cooling water ($0.055/1000gal)	=	1,790	Bt
- 0.85 million BTU/h fuel($3.5/million BTU)	=	322,690	Bt
	=	1,086,245	Bt
2.4) Working capital cost (20% investment cost)	=	36,438200	Bt

2.5) Cost of pollution control (burning filter cake and spent clay)

Quantity of filter cake and spent clay are produced = 0.14 ton/input 1ton ULO

Cost of burning in cement kiln (0.14 x 6,800 x 4,300) = 4,093,600 Bt

∴ Total operating cost = (2.1) + (2.2) + (2.3) + (2.4) + (2.5)

= 72,159,266 Bt

3) Revenue

New lube oil price = 0.8 ton x 6,800 x 88,000 = 478.72 million Bt

Cash flow analysis

Table 4.9 Cash flow analysis of chemical and clay treatment

Year	Investment Cost (Baht)	Operating Cost (Baht)	Total cost (Baht)	Quantity of ULO (ton)	Quantity of output (ton)	Revenue	Benefit
1	224,561,000	72,159,266	296,720,266	6,800	5,440	478,720,000	181,999,734
2		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
3		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
4		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
5		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
6		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
7		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
8		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
9		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
10		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
11		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
12		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
13		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
14		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
15		72,159,266	72,159,266	6,800	5,440	478,720,000	406,560,734
Total	224,561,000	1,082,388,984	1,306,949,984	102,000	81,600	7,180,800,000	5,873,850,016
Present value			752,995,475	51,721	41,377	3,641,182,381	2,888,186,907

From Table 4.9 ; the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	14,559	Baht
Average revenue of 1 ton ULO	=	70,400	Baht
NPV	=	2,888,186,907	Baht
B/C ratio	=	4.84	

4.3 Case Study 3: Solvent Extraction Technology

4.3.1 Process Description [8,26, 34,38-44]

This regeneration process is classified into a re-refining approach (Category 3.2.1 (A)). Principally the ULO is treated by solvent extraction, where solvent selectively extracts the base lube material from the ULO. Examples of solvents that can be used are aliphatic type such as butane, heptane or hexane, mixture of alcohol and ketone [40, 42-44]. This proposed process, developed by Bartlesville Energy Technology Center (BETC) or now called National Institute for Petroleum and Energy Research (NIPER) by use combine the solvent treatment and vacuum distillation in treating ULO.

As shown in Figure 4.7, the incoming ULO is first dehydrated and light hydrocarbon stripped off fraction are in the distillation column. The dehydrated sludge-containing oil is then treated with 1:3 mixture of oil mixed with solvents, in this case 267 %wt of solvent, which composed of butyl alcohol, isopropyl alcohol and methyl ethyl ketone (ratio 2:1:1) [38]. The solvent-used oil mixture is settled and the sludge is drown off the bottom of the tank or centrifuged to recover the oil and solvent. The solvent is next sent to a solvent recovery unit to recover and reuse the solvent Finally, the extracted oil is distilled in a vacuum distillation column followed by clay treatment or hydrotreatment of the distillate to remove color bodies and improve odor

In the original configuration of BETC process, clay contacting was used to produce a clean-finished base stock. However hydrotreatment has been evaluated as a substitute for the clay-contacting step to produce oils of superior color and clarity with acceptable viscosity and heteroatom content In addition, product yields may also be improved which eliminate the trouble of bulky clay disposal

Hydrotreatment or hydrofinishing is a process for stabilization of petroleum products or remove sulfur, nitrogen, oxygen, halides and metallic compounds from products or feedstock by reaction with hydrogen on catalyst. Operating conditions for hydrotreating are the temperature at 260 – 430 ^{o}C, pressure of 0.93-13.80 Mpa, with

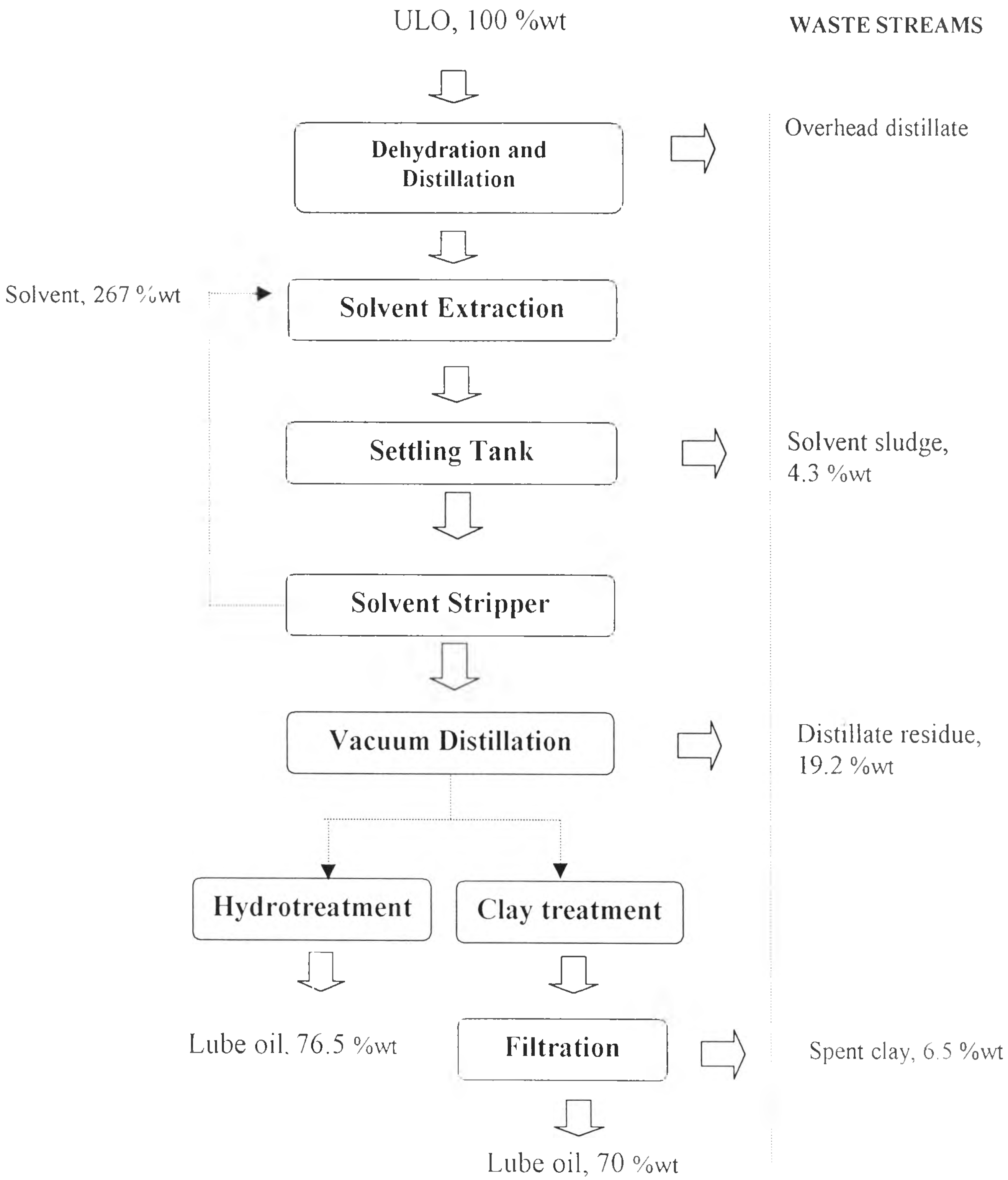

Figure 4.7 Block diagram of solvent extraction process

liquid space velocity ranging from 0.5 –2.5 h^{-1} and with gas flow rate 1 5-133.93 $kmol/m^3$ or gas to oil ratio 34-3000 vol gas/vol oil.[41]

Observation of interest in Table 4.10 is the efficiency of hydrofinishing in destroying PCBs. The hydrofinished solvent treatment-distillation product is superior to the final product obtained from acid – clay and chemical and clay treatment process .

Table 4.10 Composition of process streams from the Bartlesville Energy Technology Center Re-refining Process [8].

Property	Feedstock ULO	Solvent sludge	Distillate residue	Spent clay*	Hydro-Treatment Product	Clay treatment Product
Relative Flow rate, % by wt	100	4.3	19.2	6.5	76.5	70
Contaminant, ppm						
Aluminum	34	13	16	4	1.2	0.4
Arsenic	9.7	4.8	3.3	< 0.8	< 0.7	< 0.7
Barium	70	22	42	< 0.8	<0.07	<0.07
Cadmium	1.4	0.6	0.5	< 0.8	< 0.7	< 0.7
Calcium	1140	300	700	0.1	1.5	0.4
Chromium	9.5	4.6	5.2	0.2	< 0.07	< 0.07
Copper	36	16	13	26	1.4	< 0.07
Lead	1250	530	420	0.3	< 0.3	< 0.07
Iron	280	80	210	1.0	5.1	1.2
Zinc	820	320	340	34	1.6	1.3
PCBs	43	0.6	<1	24	<1	20

* The spent clay comes from clay treatment process

4.3.2 Environmental Impact

Waste streams from solvent extraction process are solvent sludge, distillate residue and spent clay. The approximate amount of each waste streams is 4.3,19.2 and 6.5% wt of the total ULO weight, respectively.

Figure 4.8 presents relative flow rates and the concentrations of heavy metals in process stream of the solvent extraction process. Concentrations of calcium, lead, iron and zinc are of the most environmental concerns. Small amount of spent clay (6.5% weight) with trace concentration of heavy metal is relatively significant.

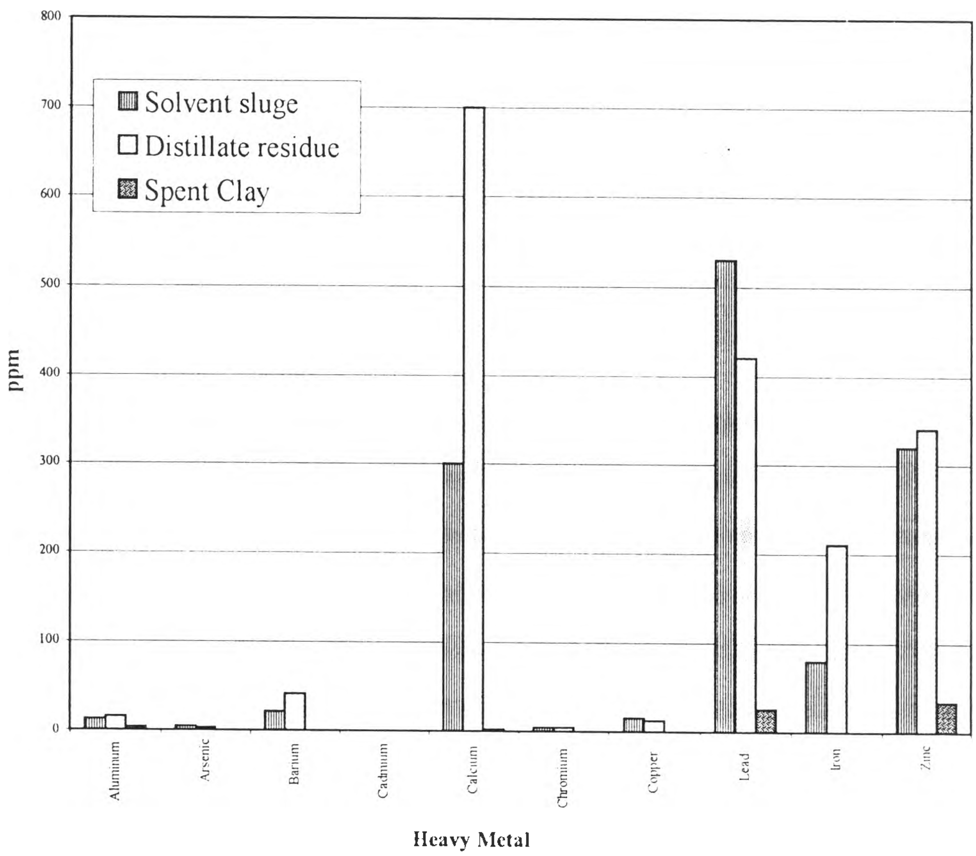

Figure 4.8 Concentration of heavy metals in solvent sludge, distillate residue and spent clay from the solvent extraction process

Equation 4.1 is used to show fraction of remaining heavy metals in process streams from solvent extraction process in Table 4.11.

Table 4.11 Fraction of heavy metal ratio in process stream from the solvent extraction process *

Property	Distillate residue	Solvent sludge	Hydrofinished Product	Clay finished Product	Spent Clay
Aluminum	0.090	0.016	0.025	0.008	0.008
Arsenic	0.065	0.021	0.051	0.051	0.005
Barium	0.115	0.014	0.001	0.001	0.0001
Cadmium	0.069	0.018	0.350	0.350	0.037
Calcium	0.118	0.011	0.001	0.0002	0.000
Chromium	0.105	0.021	0.005	0.005	0.001
Copper	0.069	0.019	0.027	0.001	0.0004
Lead	0.065	0.018	0.000	0.00004	0.001
Iron	0.144	0.012	0.013	0.003	0.0001
Zinc	0.080	0.017	0.001	0.001	0.003

* Based on feed ULO 100 unit (by weight)

Solvent sludge contains high concentrated stream of metal, high ash, high non-volatile residue, high heat content, low solvent insoluble and low sulfur. Distillate residue from distillation process is contains significantly larger quantities of ash, sulfur, nitrogen and oxygen than the feed oil. For example, ash content may range between 10 to 25% and lead content approaches 1.5 %, depending upon the composition of the ULO and extent of pretreatment prior to distillation [8]

Table 4.12 summarized the significant environmental impact from solvent extraction process.

Table 4.12 The pollution control approaches for significant environmental impacts on waste streams from solvent extraction process.

Waste Stream	(% wt)	Environmental impacts
Over head distillate	trace	
Solvent sludge	19.2	✓
Distillation residue	4.3	✓
Spent Clay	6.5	✓

Remark: ✓ determine significant environmental impact

4.3.3 Pollution Control approach

Since distillate residue and solvent sludge from solvent extraction process have an acceptable level of heavy metal concentration, both of them can be burnt as fuel in cement kiln However, spent clay contains a high level of PCB (24 ppm), it should be disposed of by incinerator [26].

Figure 4.9 summarizes the pollution control of waste streams from solvent extraction process.

4.3.4 Economic Analysis [19, 27-28, 31-33, 38, 44-45,]

Detailed economic studies are performed below according to the discussion in Section 3.3.2 (Eqs.3.1-3.4).

Assumption:

- Convert to updating cost by Marshall & Swift cost index [See detail in appendix]

- ULO consumption	=	3,400	ton or 1Mgal/year
- Treatment efficiency	=	70 %	
- 1$	=	42.37	Bt
- Cost of ULO	=	2,000	Bt/ton
- Cost of fuel (natural gas)	=	150	Bt/million BTU
- Cost of burning in cement kiln	=	4,300	Bt/ton waste
- Cost of burning in incinerator	=	98,000	Bt/ton waste
- Treated oil price	=	88,000	Bt/ton
- Working time	=	2,560	hr/year
- Depreciation life	=	15	years

1) Investment Cost

Skid mounted acid clay unit	=	97,761,024	Bt

2) Operating cost

2.1) Cost of ULO	=	6,800,000	Bt
2.2) Cost of material processing			
- methyl ethyl ketone ($0.5/gal)	=	14,193,950	Bt
- iso propyl alcohol ($2.85/gal)	=	80,905,515	Bt

- butyl alcohol ($3.5/gal)	=	197,232,350	Bt
	=	292,331,815	Bt

Note : Solvent can recovered for 3 years

2.3) Utilities cost

- 400 lb/h of 150-psi stream ($4.46/1000lb)	=	193,505	Bt
- 70 kwh/h of electricity ($ 0.54/kwh)	=	4,100,060	Bt
- 120 gal/h cooling water ($0.055/1000gal)	=	716	Bt
- 1.62 million BTU/h fuel($3.5/million BTU)	=	615,009	Bt
	=	4,909,290	Bt

2.4) Cost of pollution control (burning filter cake and spent clay)

Quantity of solvent sludge and distillate residue are produced = 0.235 ton/input 1ton ULO

Quantity of spent clay are produced = 0.065 ton/input 1ton ULO

Cost of burning in cement kiln (0.235 x 3,400 x 4,300)	=	3,435,700	Bt
Cost of burning in incinerator (0.065 x 3,400 x 98,000)	=	21,658,000	Bt
Cost of pollution control	=	25,093,700	Bt
∴ Total operating cost (2.1)+(2.2)+(2.3)+(2.4)	=	329,134,806	Bt

3) Revenue

New lube oil price = 0.7 ton x 34,000 x 88,000 = 209,440,000 Bt/year

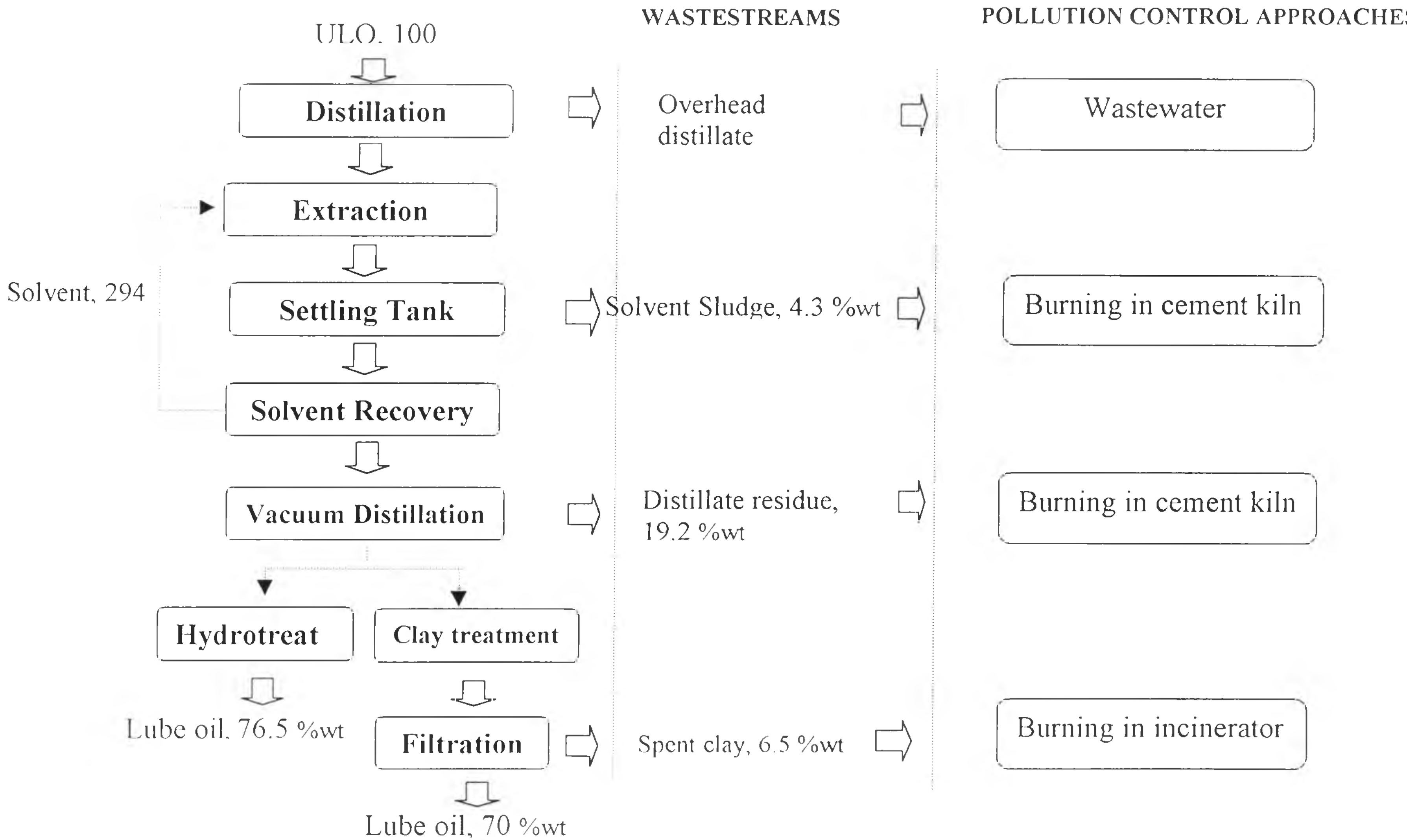

Figure 4.9 Schematic diagram of waste streams management approaches from solvent extraction process

Cash flow analysis

Table 4.13 Cash flow analysis of solvent extraction process

Year	Investment Cost (Baht)	Operating Cost (Baht)	Total cost (Baht)	Quantity of ULO (ton)	Quantity of output (ton)	Revenue (Baht)	Benefit (Baht)
1	97,761,024	329,134,806	426,895,830	3,400	2,380	209,440,000	- 217,455,830
2		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
3		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
4		329,134,806	329,134,806	3,400	2,380	209,440,000	- 119,694,806
5		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
6		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
7		329,134,806	329,134,806	3,400	2,380	209,440,000	- 119,694,806
8		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
9		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
10		329,134,806	329,134,806	3,400	2,380	209,440,000	- 119,694,806
11		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
12		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
13		329,134,806	329,134,806	3,400	2,380	209,440,000	- 119,694,806
14		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
15		36,802,991	36,802,991	3,400	2,380	209,440,000	172,637,009
Total	97,761,024	2,013,703,933	2,111,464,958	51,000	35,700	3,141,600,000	1,030,135,042
Present value			1,181,620,017	25,861	18,102	1,593,017,292	411,397,275

From Table 4.13, the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	45,692	Baht
Average revenue of 1 ton ULO	=	61,600	Baht
NPV	=	411,397,275	Baht
B/C ratio	=	1.35	

4.4 Case Study 4: Distillation – Clay Filtration Process

4.4.1 Process description [8,26, 34-35, 38-39]

Distillation process is the currently re-refining technology approach (Category 3.2.1 (A)). There are six distinct and separate unit operations comprising this simple re-refining process. Figure 4.7 illustrate this system which these include the following: pretreatment, dehydration, stripping, distillation, clay treatment and filtration. Usually pretreatment will be used for a given ULO depending upon its source and extent of contamination, normally settling and centrifugation are provided. The clean oil is then dehydrated by being heated to flash off the water at 150 °C. The wastewater from dehydrator is pumped to wastewater treatment plant while the oil is sent to the distillation section.

The dehydrated oil is next heated before being fed into a flash tank. As the heated oil enters the flash tank, the low boiling point fractions of oil are flashed off as vapor, condensed, collected in a receiver, and pumped to a temporary storage. Meanwhile, the higher boiling point oil is circulated to the thin film evaporator. By adjusting the level of vacuum, differing amounts of light ends can be removed during this processing step.

The oil flows continuously from the fuel-stripping step to the thin film evaporator. The temperature of this thin film evaporator and the internal vacuum are controlled to allow a wide range of products to be generated. Two condensers in series operating at two different temperatures condense the oil vapors. This differential provides partial condensation of the distillate vapor so that oils with differing product characteristics as heavy and light lube oil. Final step in operation of the distillation, clay filtration process consists of adding clay in the correct proportions. The slurry is then pumped through a filter press to remove the clay and any other impurities. The block diagram of this process is shown in Figure 4.10, where Table 4.14 shows relative flow rates and the distribution of heavy metals in the process streams.

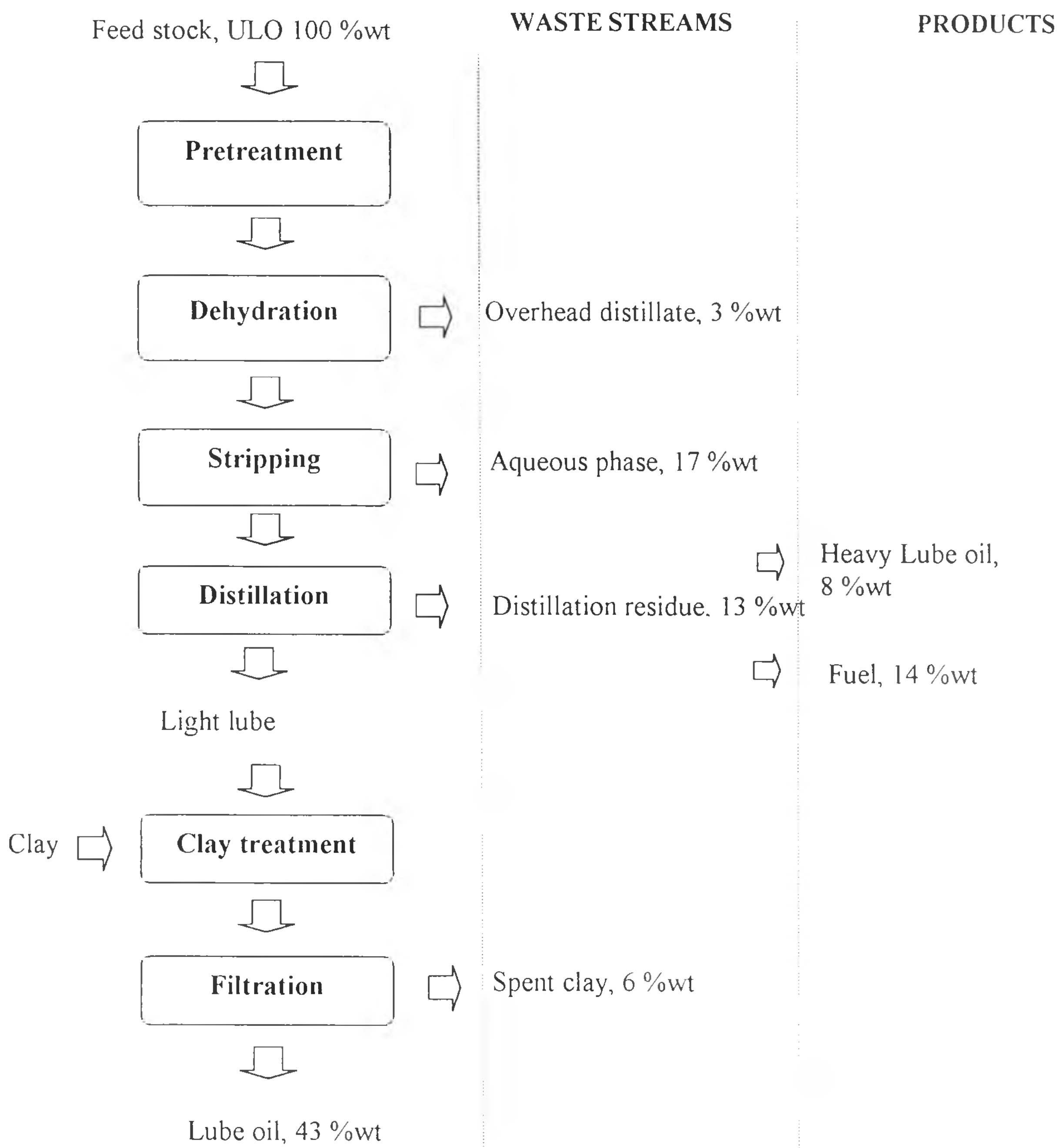

Figure 4.10 Schematics of Distillation – Clay Filtration Process [8,44]

Table 4.14 Composition of process streams from distillation clay filtration re-refining process [8].

	Feedstock ULO	Overhead distillate	Aqueous Phase	Fuel	Distillation residue	Heavy Lube	Spent clay	Light Product
Relative Flow Rate, by %wt	100	3	17	10	13	8	6	43
Contaminant (ppm)								
Aluminum	650	100	0.8	32	670	2.4	2.08	1.4
Arsenic	4.5	0.4	0.03	0.7	8.3	0.7	0.4	0.7
Barium	84	12	0.2	7	14	0.3	140	0.07
Cadmium	1	0.1	0.001	0.1	5.7	0.02	0.5	0.02
Calcium	1.3	24	22	83	3480	4.2	7730	0.7
Chromium	18	3	0.004	1.7	35	0.1	18	0.07
Copper	130	20	0.1	9.3	265	2.6	14	0.9
Lead	350	56	1.5	57	2090	7.4	0.4	2.7
Iron	1300	220	3.5	120	1600	6.8	7120	1.7
Zinc	340	19	4.4	47	2960	4.6	140	0.5
PCB	18	< 11	< 10	< 19	< 21	< 11	< 8	< 14

At present, this process is being used commercially in the United States of America, e.g. for 1 company in New York (5 million gallon/year) in a fully automated, continuous mode and other one in Indiana.

4.4.3 Environmental Impact

As same as the previous three processes, Equation 4.1 is employed compute to the fraction of remaining heavy metals in waste streams, and the results are presented in Table 4.15. Figure 4.11 represents the result from the concentration of heavy metal in waste streams.

With respect to environmental characteristics, no major problems are expected from a distillation clay filtration re-refinery. Odor and wastewater problems are not believed to be any more serious when compared with acid –clay process. From Table 4 14 composition of process streams show that the most of the elements in ULO feedstock end up in the bottom residue from the distillation unit, and some in wastewater from dehydration process

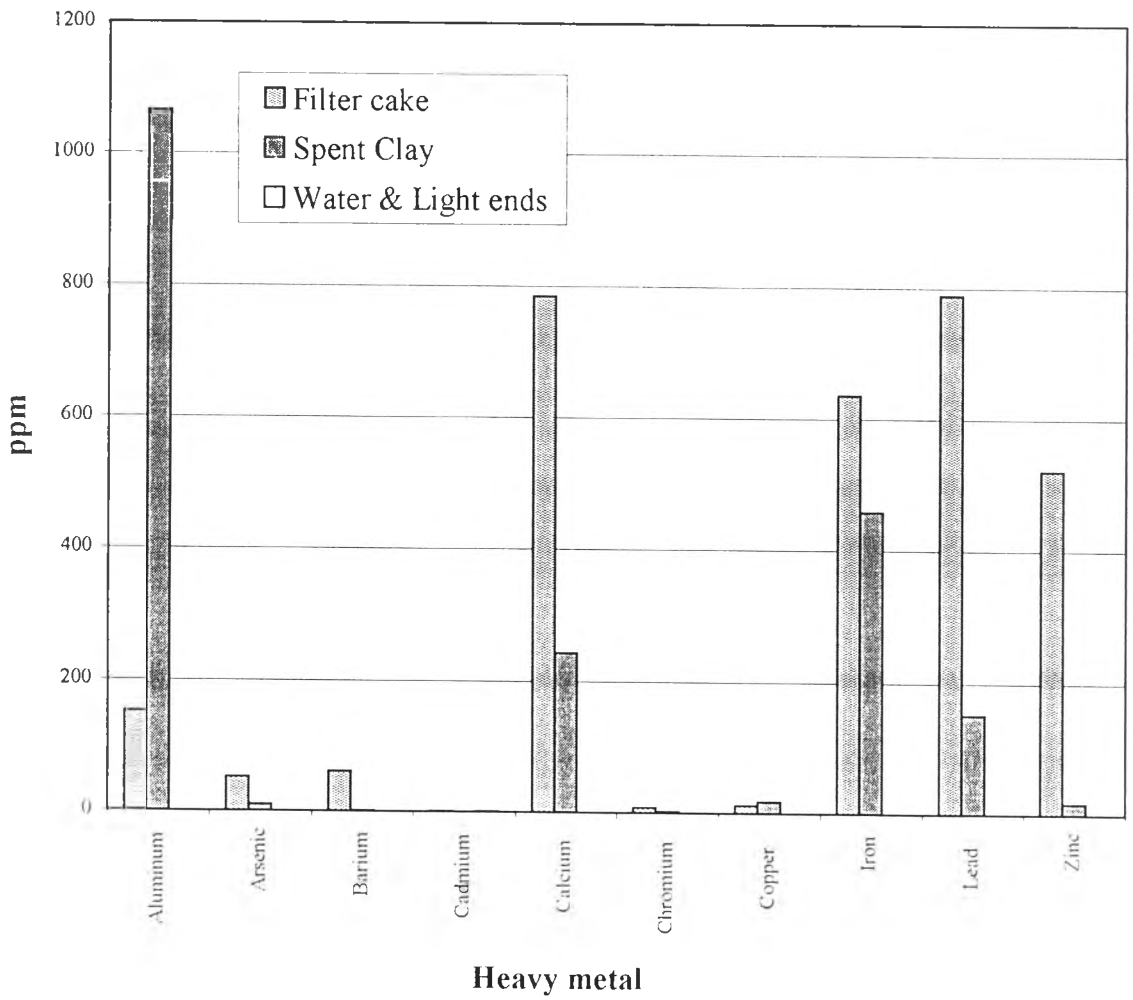

Figure 4.11 Concentration of heavy metals in filter cake, spent clay and fuel fraction from chemical and clay treatment process.

Table 4.15 Fraction of heavy metal ratio in process stream from the distillation clay filtration re-refining process*

Heavy metal	Organic	Aqueous Phase	Fuel	distillation residue	Heavy Lube	Spent clay	Treated oil
Aluminum	0.0046	0.0002	0.0069	0.134	0.0003	0.0002	0.0009
Arsenic	0.0027	0.0011	0.022	0.240	0.012	0.005	0.067
Barium	0.0043	0.0004	0.012	0.02	0.0003	0.1	0.0004
Calcium	0.0007	0.0036	0.011	0.44	0.0003	0.45	0.0003
Cadmium	0.003	0.0002	0.014	0.741	0.0016	0.03	0.009
Chromium	0.005	3.8E-05	0.0132	0.2528	0.0004	0.06	0.002
Copper	0.0046	0.0001	0.0100	0.265	0.0016	0.0065	0.003
Iron	0.0051	0.0005	0.0129	0.16	0.0004	0.3286	0.001
Lead	0.0048	0.0007	0.0228	0.78	0.0017	6.86E-05	0.003
Zinc	0.0017	0.0022	0.0194	1.13	0.0011	0.025	0.001

* Based on feed ULO 100 unit (by weight)

Figure 4.11 represents the various compositions of heavy metals in waste streams from distillation - clay filtration process. Spent clay and bottom residues are of the most environmental concern in this process due to high concentration iron and lead.

Table 4.16 summarized the significant environmental impact from this process

Table 4.16 Significant environmental impacts on waste streams from distillation clay filtration process.

Waste Stream	(% wt)	Environmental impacts
Aqueous phase	17	
Overhead distillate	3	✓
Fuel	10	
Heavy Lube oil		
Distillate bottom	13	✓
Spent clay	6	✓

Remark: ✓ determine significant environmental impact

4.4.3 Pollution Control approach

There are three approaches to managed waste streams in distillation – clay filtration;

1) Treatment of organic and aqueous phase

Liquid effluent in this process contains trace metals remained in the oil which is not settle out from the wastewater. On the other hand, chlorinated and aromatic solvents show fairly high concentrations in the wastewater, but not significantly different from those found in ULO [8].

The treatment steps for this wastewater is discussed. Initially, wastewater is transferred through coarse filter, which removes free and mechanically emulsified oil. The water then flows to neutralization for pH adjustment. After that flocculating agents are added to aid the coagulation and flocculation of settable solid. Finally, wastewater is treated by a combination of dissolved air flotation and clarifier [13].

2) Treatment of bottom residue and spent clay

Bottom residue from distillation step contains high boiling point and other nonvolatile materials, generated by distillation processes. Typically, it contains significantly larger quantities of ash, sulfur, nitrogen than the feed ULO [8]. Consequently, burning bottom residue in cement kiln is not suitable in this case, as it can produce particulate, SO_2 and other air pollutants.

Distillation bottoms are commonly used as asphalt extenders, and if not, they are usually disposed of in landfill [8]

Small amount of spent clay in this process (6 wt % of feed ULO) are generated by processes using clay as filtration media. As shown in Figure 4.10, heavy metals contents of spent clay vary widely. Other common contaminants in spent clay include negligible quantities of chlorinated and aromatic solvents are present.

In this approach, bottom residue and spent clay are ordinarily disposed of in a landfill [8].

Figure 4.12 summarized the pollution control approaches needed for the treatment of waste associated with this process.

4.4.4 Economic Analysis [19,27-28,31-33, 44,46]

Detailed economic studies are performed below according to the discussion in Section 3.3.2 (Eqs.3.1-3.4).

Assumption:

- Convert to updating cost by Marshall & Swift cost index [See detail in appendix]			
- ULO consumption	=	8,500	ton or 1Mgal/year
- Treatment efficiency ; new lube oil	=	43 %	
heavy lube oil	=	8%	
fuel	=	14%	
- 1$	=	42.37	Bt
- Cost of ULO	=	2,000	Bt/ton
- Cost of fuel (natural gas)	=	150	Bt/million BTU
- Cost of burning in cement kiln	=	4,300	Bt/ton waste
- Cost of landfill	=	8,400 – 10,000	Bt/ton waste
- Wastewater treatment cost	=	8,000-9,000	Bt/ton waste
- Treated oil price	=	88,000	Bt/ton
- Heavy lube oil price	=	6,000	Bt/ton
- Fuel price	=	7,000	Bt/ton
- Depreciation life	=	15	years

1) Investment Cost

Skid mounted acid clay unit	=	259,214,837	Bt
Royalty	=	42,370,000	Bt
	=	301,584,837	Bt

2) Operating cost

2.1) Cost of ULO	=	18,707,483	Bt
2.2) Utilities cost			
- 11 lb/gal ULO of 100-psi stream ($4.46/1000lb)	=	1,039,336	Bt
- 0.246 kw/gal ULO of electricity ($ 0.54/kwh)	=	2,814,215	Bt
- 10,825 BTU/gal ULO($3.5/million BTU)	=	802,647	Bt
	=	4,656,198	Bt

2.3) Cost of pollution control (burning filter cake and spent clay)

Quantity of bottom is produced	=	0.13 ton/ton ULO
Quantity of spent clay is produced	=	0.06 ton/ton ULO
Quantity of wastewater is produced	=	0.20 ton/ton ULO

Cost of burning in cement kiln (0.13 x 8,500 x 4,300)	=	5,102,041	Bt
Cost of landfill (0.06 x 8,500 x 10,000)	=	5,178,197	Bt
Wastewater treatment cost (0.2 x 8,500 x 9,000)	=	15,306,122	Bt
Cost of pollution control	=	25,526,361	Bt
∴ Total operating cost (2.1)+(2.2)+(2.3)	=	48,890,042	Bt

3) Revenue

New lube oil revenue	= 0.43 ton x 8,500 x 88,000	=	321,768,707	Bt
Heavy lube oil	= 0.08 x 8,500 x 6,000	=	4,081,633	Bt
Fuel revenue	= 0.14 x 8,500 x 7,000	=	8,333,333	Bt
		=	334,183,673	Bt

Cash flow analysis

Table 4.17 Cash flow analysis of distillation clay filtration process

Year	Investment Cost (I)	Operating Cost (O)	Total cost	Quantity of input (ULO)	Quantity of output (ton)	Revenue	Benefit
1	301,584,837	48,890,042	350,474,879.12	8,503	5,527	334,183,673	- 16,291,206
2		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
3		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
4		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
5		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
6		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
7		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
8		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
9		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
10		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
11		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
12		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
13		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
14		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
15		48,890,042	48,890,042	8,503	5,527	334,183,673	285,293,632
Total	301,584,837	733,350,626	1,034,935,463	127,551	82,908	5,012,755,102	3,977,819,639
Present value			646,029,578	64,678	42,040	2,541,827,590	1,895,798,012

From Table 4.17, the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	9,988	Bt
Average revenue of 1 ton ULO	=	39,300	Bt
NPV	=	1,895,798,012	Bt
B/C ratio	=	3.93	

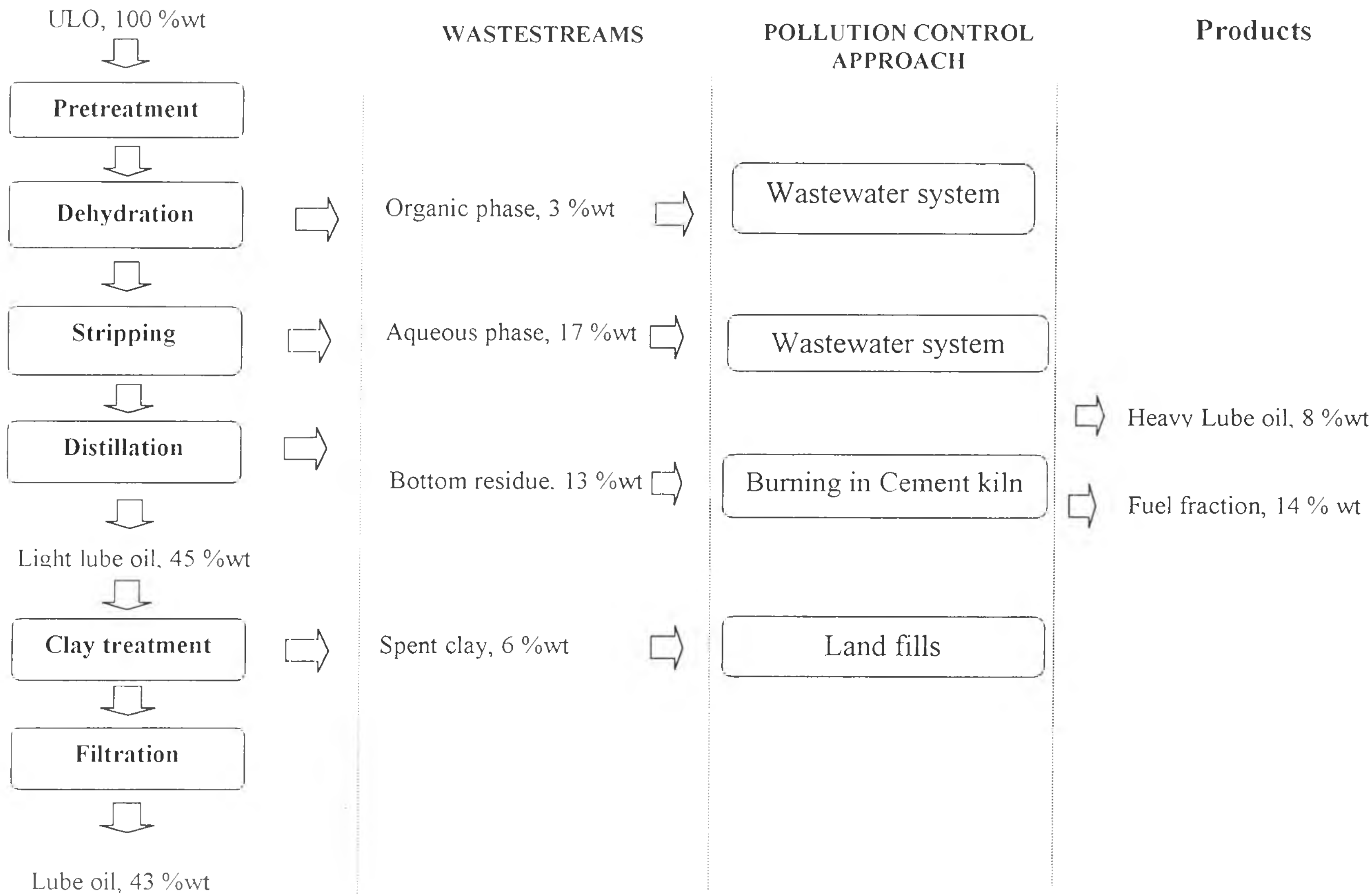

Figure 4.12 Schematics diagram of waste streams management approaches from dillation – clay filtration process

4.5 Case study 5: Membrane Technology

4.5.1. Process Description [39,47-48]

This process is the new by developed physical technology for the regeneration of ULO (Category 3.21 (B)). In this process, ultrafiltration membrane separates solutes from a solvent on the basis of molecular size and shape by passing the solution through a membrane module, where pressure difference is maintained across the membrane. Water and small molecules move through the membrane to the lower pressure side, while the membrane retains the larger molecules. The solutes with molecular weight greater than about 500 and less than 500,000 can be separated from solution.

Tabular ceramic membranes with a 300 kDa cuttoff and a 10.8 x 10 $^{-3}$ m hydraulic diameter were use in this study. Process procedure entered with set of experiments was conducted with an approximate 600 kg.h^{-1} flow rate inside the membrane (6 ms^{-1}), under various CO_2 pressures (0 MPa < P_{CO2} < 18 MPa) and transmembrane pressure (0 MPa < P < 1 Mpa). The temperature was set to 353 °K (80 °C) during the filtration runs and to 393 °K (120 °C)during the concentration run.

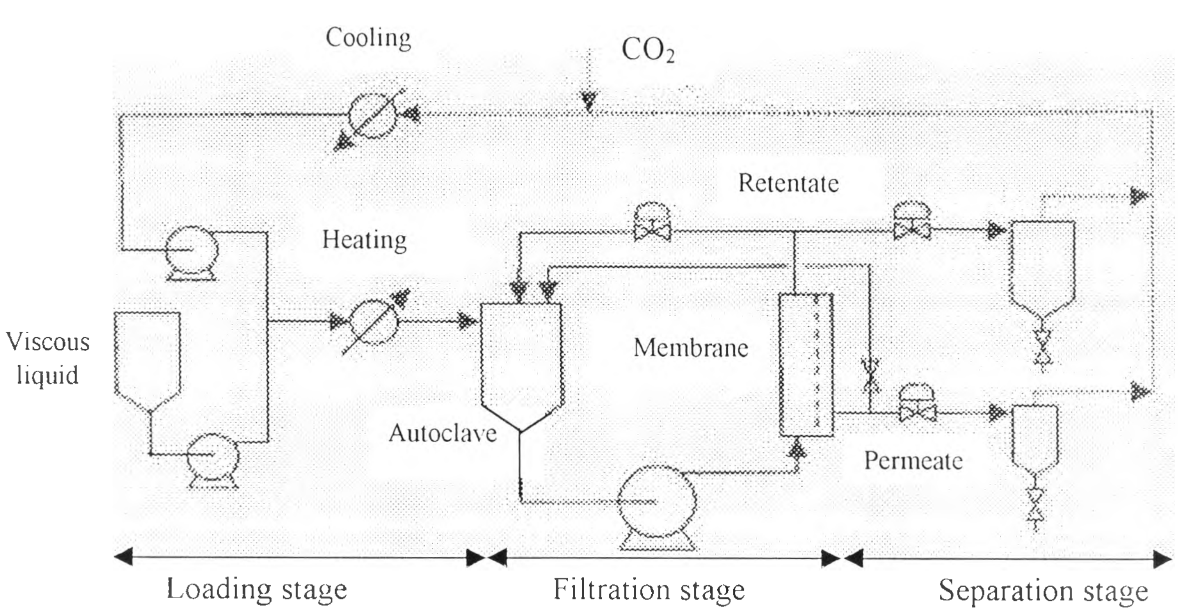

Figure 4.13 Schematic diagram of ULO regeneration by Ultrafiltration membrane[46]

As show in Figure 4.13 the membrane process is divided to 3 stages: loading, filtration and separation stage. In the loading stage, both liquid CO_2 and oil are pump to the membrane at the required pressure. For filtration zone, mixing and preheating are carried out just before entering the autoclave. The mixture (oil saturated with supercritical CO_2) is circulated through the membrane module In the membrane module, the solution is separated into two phases. Permeate, which is light compound riched phase, and retentate, which is riched with the heavy compounds.

In separation zone (not in the membrane) the membrane, an isothermal pressure release of each phase takes place. This leads, for both of them, to liquid (concentrate or filtrate) and gas streams at the exits of cyclone separators. The CO_2 in the Gas State can be recycled at the top of the process.

It appears that this process possible generates 96 % in mass of ULO and 4.13 % in mass of residue. The measured permeate flux as a function of transmembrane pressure are concluded in Table 4.18 and when plotted these data to be in a chart, it can applied to measured permeate oil equations with various CO_2 pressure as present in Table 4.19.

Table 4.18 Measured Permeate Flux for ULO with various Mpa CO_2 pressures [47]

Pco2/ Mpa	J/kg.h-1.m-2									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
0	8.76	11.15	11.45	12.3	13.72	14.66	14.82	15.38	15.5	15.6
12	25.28	31.78	36.24	37.06	37.65	38.04	38.44	38.9	39.08	39.26
15	32.32	39.85	42.26	42.5	44.78	46.16	47.86	48.21	49.68	50.83
18	33.15	42.14	44.85	48.08	49.12	50.02	50.72	51.24	52.03	53.72

Tables 4.19 Measured permeate flue of ULO, $kg.h^{-1}.m^{-2}$ with various Carbon dioxide Pressure

Transmembrane Pressure (Mpa)	Equation
1	y = 1.421x + 8.8912
2	y = 1.7793x + 11.213
3	y = 1.9255x + 12.039
4	y = 1.9991x + 12.495
5	y = 1.9993x + 13.825
6	y = 2.0053x + 14.71
7	y = 2.0402x + 15.232
8	y = 2.0473x + 15.641
9	y = 2.1426x + 15.731
10	y = 2.1803x + 15.324

Remark: x = CO_2 pressure (0-1 Mpa), y = permeate,$kg.h^{-1}.m^{-2}$

Table 4.20 shows relative flow rates and the distribution of heavy metals in ultrafiltration membrane process streams

Table 4.20 Composition of process stream in ultrafiltration membrane process.

Composition	ULO	Residue	Treated oil
Relative flow rate, % by wt	100	4.13	96
Contaminant, ppm			
Aluminium	34	244.92	0
Barium	70	329.15	0.0642
Calcium	1,140	6638.50	0.1589
Chromium	9.5	72.85	0.3208
Copper	36	264.12	0
Iron	280	1643.39	0.3995
Lead	1,250	9164.65	0.0055
Zinc	820	4489.15	0.0089

4.5.2 Environmental Impact Assessment

The potential problem is involved with the concentrations of heavy metals in residue or retentate Which the calculation as the same concept according to the Equation 4.1 for investigate the concentration of heavy metals in residue.

In using membrane, it was shown that the residue and could be detailed as in Table 4.21.

Table 4.21 Fraction of heavy metals in process streams from ultrafiltration membrane process.

Composition	Residue (retentate)	Treated oil (permeate)
Alumineum	0.298	0
Barium	0.194	4.67
Calcium	0.241	188.22
Chromium	0.317	3.17
Copper	0.303	0
Iron	0.242	116.23
Lead	0.303	7.14
Zinc	0.226	7.58

Figure 4.14 presents the constituents in process stream products in the proposed regeneration approach based on the characteristics of ULO in Table 4.11 (with basis of 100 % wt of ULO.)

3.5.3 Pollution Control Approach

Characteristics of residue from ultrafiltration membrane process to be like residue from re-refining process but smaller quantity. This waste should be only be disposed of in land fill, since the concentrations of heavy metals 9,000 ppm lead , 6600 ppm calcium and 4400 ppm zinc) exceed the maximum allowance of the cement kiln (must < 1%, about 100 ppm).

3.5.4 Economic Analysis [19,27-28,31-33,47]

Detailed economic studies according to discussion in category 3.3.2 (Eq.3.1-3.4). the summary of cost estimation is below [46]:

<u>Assumption</u>

- ULO consumption = 313 ton year
- Treatment efficiency = 96 %
- 1 $ = 42.37 Bt
- Cost of ULO = 2,000 Bt/ton
- Cost of landfill = 8,400 – 10,000 Bt/ton waste

- Treated oil price	=	88,000	Bt/ton
- Depreciation life	=	8	years

1) Investment Cost

Skid mounted acid clay unit	=	4,740,144	Bt
Membrane (2 year)	=	466,070	Bt
	=	5,206,214	Bt

2) Operating cost

2.1) Cost of ULO	=	625,000	Bt
2.2) Cost of processing			
- Refrigeration of fluid	=	15,677	Bt
- CO_2	=	63,555	Bt
- Eliminate residue	=	91,096	Bt
- Energy consumption	=	137,703	Bt
- Working capital cost	=	1,041,243	Bt
	=	1,211,571	Bt

2.3) Cost of pollution control (residue)

Quantity of residue is produced = 0.043 ton/ton ULO

Cost of landfill (0.043 x 313 x 10,000)	=	134,375	Bt
∴ Total operating cost (2.1)+(2.2)+(2.3)	=	2,471,148	Bt

3) Revenue

New lube oil price = 0.96 ton x 313 x 88,000 = 26,400,000 Bt/year

Cash flow analysis

Table 4.22 Cash flow analysis of membrane technology

Year	Investment Cost (Baht)	Operating Cost (Baht)	Total cost (Baht)	Quantity of ULO (ton)	Quantity of output (ton)	Revenue (Baht)	Benefit (Baht)
1	5,206,214	2,108,648	7,314,861	313	300	26,400,000	19,085,139
2		2,108,648	2,108,648	313	300	26,400,000	24,291,352
3	466,070	2,108,648	2,574,718	313	300	26,400,000	23,825,282
4		2,108,648	2,108,648	313	300	26,400,000	24,291,352
5	466,070	2,108,648	2,574,718	313	300	26,400,000	23,825,282
6		2,108,648	2,108,648	313	300	26,400,000	24,291,352
7	466,070	2,108,648	2,574,718	313	300	26,400,000	23,825,282
8		2,108,648	2,108,648	313	300	26,400,000	24,291,352
Total	6,604,424	16,869,181	23,473,605	2,500	300	26,400,000	23,825,282
Present value			16,861,127	1,667	1,600	140,842,052	123,980,925

From Table 4.22, the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	10,114	Baht
Average revenue of 1 ton ULO	=	84,480	Baht
NPV	=	123,980,925	Baht
B/C ratio	=	8.35	

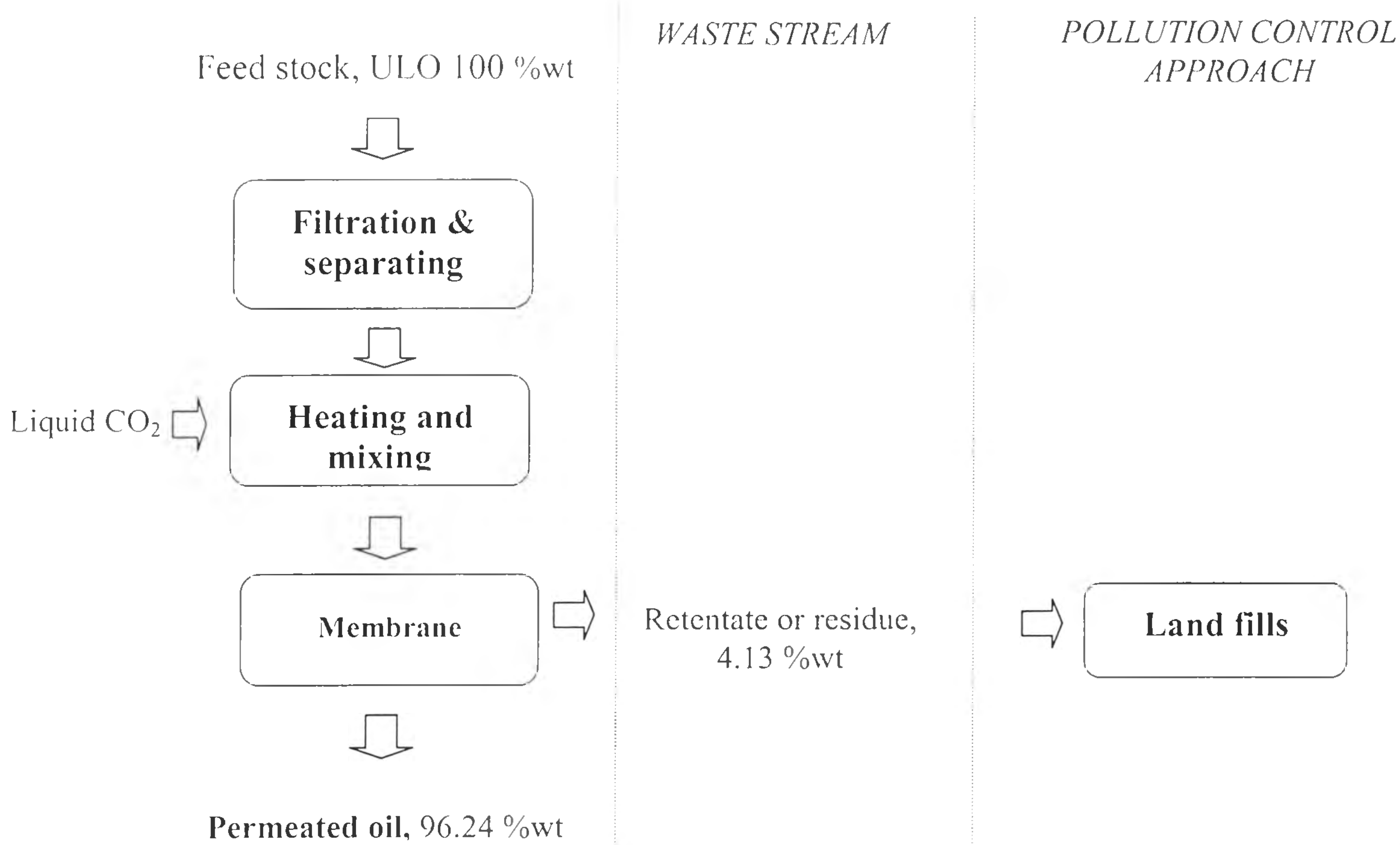

Figure 4.14 Block diagram of waste streams management approaches from ultrafiltration membrane

4.6 Case Studv 6: Combustion of ULO for fuel in Boiler

4.6.1 Process Description [26, 34, 39, 49, 50]

There are varieties of combustion systems for burning ULO as fuel e.g. industrial boilers, space heater, asphalt plant and waste oil furnace etc. In this case study, the combustion of ULO as fuel in boiler will be discussed in detail.

ULO is brought to cofiring with conventional fuels in boilers. The amount of waste inputs could be up to 10 to 25 %by wt of total fuel requirement. The constraints on the quantity of wastes to be cofired may arise because certain constituents, such as chlorine, heavy metals, or suspended solid can promote corrosion and fouling of boiler tubes [34, 36].

Specific design details of the retrofitting of an existing boiler or specifying a new boiler for waste cofiring are discussed below [26]:

1) Waste storage and transport

Raw waste containing large percentages of free water or undissolved solids should be treated by settling and decanting prior to introduction to the waste cofiring system Most non-homogeneous waste should be continually mixed by agitators or recirculation pumps. Where continual recirculation is used, strainers are usually installed to reduce solids, thus protecting pumps and downstream burner and boiler components. Strainers are usually effective in minimizing solids greater than about 40μm. Additionally, if the waste is viscous, steam-heat coils may be required in tanks to maintain pump capability and atomization in the burner.

2) Burners

Burner design and operation for cofiring is directed at achieving atomization and mixing to obtain a stable flame with good carbon burnout and high waste destruction. Waste nozzles are usually air or steam atomized, with steam more common for lower-quality waste with suspended solids.

3) Boiler Operation

The principal operating concerns are to minimize the effects of waste firing on boiler materials, maintenance and unit efficiency. Materials and maintenance problems arise mainly from inorganic materials, such as ash, materials and chlorine containing in ULO. Ash and metal deposited and/or condensed on walls in the furnace and on convective section of heat exchanger tubing.

4) Safety

Hazardous waste cofiring may require special safety precautions in addition to normally procedure. Example of procedures for routine maintenance are changing strainers, cleaning atomizer tips and cleaning the boiler's heat transfer surfaces. Containment or capture of fugitive emissions from tank vents, pump seals and valves also needs to be practiced.

The primary boiler modification is to retrofit the existing burners for waste firing [26].

Option1: Complete burner system, including forced – draft blowers and burner controls for regulation of the fuel – air mixture and flame safeguard.

Option2: Complete waste oil or ULO gas dual- fuel burner assemblies, including pilot, spark ignition and dampers.

Option 3: Simplest case, where only waste –atomizer nozzles are required.

4.6.1 Environmental Impact

Combustion is defined as the reaction of a substance with oxygen to produce the following set of specified substances: carbon dioxide, liquid or gaseous water and sulfur dioxide and nitrogen if the origin substance has any sulfur in it [50].

AP- 42 documentation [51] provides emission factors and emission factor rating from uncontrolled small boilers combusting ULO. All of the sources having acceptable test data for both blended and unblended ULO fuel.

Emission from ULO burning reflects the compositional variations of the ULO. Potential pollutants include carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulate matter (PM), particles less than 10 micrometers in size (PM-10), hydrogen chloride, organic compounds and toxic metals.

The emission factors for pollutants and toxic metals from ULO combustion in small boiler and space heater are presented in Tables 4.23 and 4.24 respectively.

Table 4.23 Emission factors for various air pollutants from ULO combustion [51]

Source Category	PM	PM-10	Pb	NO_x	SO_x	CO	TOC	HCl	CO_2
Small boilers	64A	51A	55L	19	147S	5	1	66 Cl	22,000
Space heaters* : vaporizing burner	2.8A	ND	0.41L	11	100S	1.7	1	ND	22,000
Space heaters* : Atomizing burner	66A	57A	50L	16	107S	2.1	1	ND	22,000

Remark: Unit = lb of pollutant/10^3 gallons of blended waste oil burned

A= % wt of ash in fuel, S= % wt of sulfur in fuel, ND = no data,

L = % wt of lead in fuel, Cl = % wt of chlorine in fuel

* space heater = small combustion unit generally less than 70 kw or 250,000 – 280,000 Btu/h.

Table 4.24 Emission factor for toxic metals from ULO combustors. [51]

Pollutant	Small Boilers	Space heaters : Vaporizing burner	Space heaters : Atomizing burner
Arsenic	0.11	0.0025	0.06
Cadmium	0.0093	0.00015	0.012
Chromium	0.02	0.19000	0.18
Manganese	0.068	0.0022	0.05
Nickel	0.011	0.005	0.16

Remark: Unit = lb of pollutant/10^3 gallons of blended waste oil burned

Potential significant air pollutants are discussed below [49,51]:

Particulate Matter (PM and PM-10)

Ash and trace element levels in ULO are normally present in much higher concentrations than those found in virgin fuel oils. Without air pollution controls, higher concentrations of ash and trace metals in the waste fuel translate to higher emission levels of PM and trace metal.

Sulfur Oxides

Emissions of SO_x are a function of the sulfur content of the fuel. The sulfur content varies but some data suggest that uncontrolled SO_x emissions will increase when ULO is substituted for a distillate oil but will decreases when residual oil is replace.

Table 4.25 shows the average results for the stack emission testing

Table 4.25 Average results for the stack emission testing [49].

Emission rate (mg/min)	**As**	**Cd**	**Cr**	**Pb**	**HCl**	**PM**
High	<0.05	<0.19	0.33	3.83	68.9	667
Average	<0.03	<0.08	0.17	2.09	34.6	466
Low	<0.02	<0.03	0.09	1.32	14.6	333

The ambient air impact can be calculated based on the following formula:

Ambient impact = emission rate (mg/min) x (4597) x (scaling factor) x (capacity factor)

where; Emission rate = emission rate from Table 4.25

Scaling factor = 0.4 for 24 hr standard. (HCl, PM_{10}); 0.15 for 3 month standard (lead); and 0.1 for annual standard (PM_{10}, As, Cd, Cr)

Capacity factor = no factor, assume value of 1, for 24 hr standard;

= (3000 gal)/ [(BTU/hr rating of unit) (2190 hrs) / (140,000 BTU/gal] for 3 month standard

= (3000 gal)/ [(BTU/hr rating of unit) (8760 hrs) / (140,000 BTU/gal] for annual standard

4597 is the value of ambient impact from US.EPA model based on unit emission rate of 1g/sec.

Example Ambient impact of HCl = 34.6 mg/min x 1g/mg x 1 min/60 x 4597 x 0.4 x 1

= 1.06 g/s

∴ Ambient impact of HCl is 1.06 g/s for 24 h standard

The results of ambient air impact from combustion ULO in waste oil furnace presented in Table 4.26.

Table 4.26 Comparison ambient air impact to the Hazardous Ambient Air Standard (HAAS) under the Vermont Air Pollution Control Regulations

Emission rate, g/s	As	Cd	Cr	Pb	HCl	PM*
Average	<0.000050	<0.00012	0.000262	0.02	1.06	0.8 / 14.3
HAAS	0.000230	<0.00057	0.000085	2.09	16.7	50 / 150

Remark: * The values in the left and right side represent annual and 24 hour impacts.

The results of ambient air impacts from Table 4.26, can be easily complied with the respective state in HAAS. In Thailand on the other hand, there is no emission-loading standard consequently in this case. Hence, it is proposed to use the Hazardous Ambient Air Standard (HAAS) be used instead.

Nevertheless, the results from this formula do not include any existing background concentrations for pollutants. When available, existing background concentration of the respective pollutant must be added to the predicted impact for comparison to the ambient standard.

To conclude this Section from above descriptions, Table 4.27 summarizes potential significant environmental impacts from combustion of ULO as fuel in boiler.

Table 4.27 Potential significant air pollutants from combustion of ULO as fuel in boiler

Air pollutants	Environmental impacts
Particulate Matter (PM and PM-10)	✓
Oxides of nitrogen	
Sulfur Oxides	✓
Chlorinated Organics	
Carbon monoxide	
Carbon dioxide	
Total organic carbon	
Heavy metals (Pb, Ar, Cd, Cr, Mg, Ni)	

Remark: ✓ Determine potential significant air pollutants

4.6.3 Pollution control approach

This case particulate matter (PM and PM-10), sulfur dioxide are the potential significance air pollutants. The pollution control approaches for both of them are described below:

1. Particulate matter control treatment

Wet scrubber is selected from a variety of method due to many advantages e.g. absorbs gas phase emissions, efficient through wide loading range, low capital, operating and maintenance cost [50].

However, wet scrubbers typically use water as the cleaning liquid, water usage and wastewater disposal requirements are important factors in the evaluation of a scrubber alternative.

2. Sulfur Oxides control treatment

The overall control strategy for SO_2 emissions is to convert the sulfur to $CaSO_4$ (or $CaSO_4 \cdot 2H_2O$) and return it to the ground in some kind of landfill. The most widely used device to deal with these problems is the limestone-wet scrubber [52].

4.6.4 Economic analysis [19, 26, 27, 32, 53]

The primary boiler modification is retrofit of the existing burners for ULO as waste firing. Consequently, in this case economic estimation will determine specified on primary capital cost, maintenance cost and pollution control approach cost

Assumption:

- 1$ = 42.37 Bt
- Characteristic of ULO in this case ; contain 5% ash, 4% sulfur
- Emission factor:

  PM = 51x %ash in ULO lb/1000 gallon ULO blended

  SO_x = 147 x % sulfur in ULO lb/1000 gallon ULO blended

- @ density 09 g/cm^3 ULO 294 gallon = 1 ton ULO

- This case use ULO input 15%wt of ULO blended 1 million gallon/year

So ULO consumption	=	150,000 gallon or 510 ton	
- Price of fuel oil	=	3,300 Bt/ton	
- Cost of PM treatment	=	484,628	Bt/ton PM
- Cost of SO_x treatment	=	722,705	Bt/ton SO_x
- Conversion factor lb/ton	=	50,000	

- Saving fuel oil:

From ULO = 9,783 Kcal/kg , fuel oil = 10,125 Kcal/kg

So 1 ton of ULO can instead of fuel oil = 0.97 ton

- Depreciation life = 10 years

1) Investment Cost

Feed pumps	=	84,740	Bt
Piping and filter	=	296,590	Bt
	=	381,330	Bt

2) Operating cost

2.1) Maintenance cost = 38,133 Bt

2.2) Cost of pollution control (PM and SO_x)

Quantity of PM	=	51 x 5 x 1000= 255,000 lb
	=	0.51 ton PM
Quantity of SO_x	=	147 x 4 x 1000= 588.000 lb
	=	1.176 ton SO_x

Cost of treatment air pollutants

PM	=	5.1 x 484,628	=	2,471,600	Bt
SO_x	=	11.76 x 722,705	=	8,499,010	Bt
			=	10,970,610	Bt

∴ Total operating cost (2.1)+(2.2) = 11,008,748 Bt

3) Saving cost

Saving fuel oil	=	0.97 x 51	=	493 ton fuel oil	
Saving cost	=	49.3 x 3,300	=	1,621,803	Bt/year

Cash flow analysis

Table 4.28 Cash flow analysis of combustion ULO for fuel in boiler

Year	Investment Cost (Baht)	Operating Cost (Baht)	Total cost (Baht)	Quantity of input (ULO)	Quantity of output (ton)	Revenue (Baht)	Benefit (Baht)
1	381,330	11,008,748	11,390,078	510	493	1,626,803	- 9,763,275
2		11,008.748	11,008.748	510	493	1,626,803	- 9,381.945
3		11,008,748	11,008,748	510	493	1,626,803	- 9,381,945
4		11,008,748	11,008,748	510	493	1,626.803	- 9,381.945
5		11,008,748	11,008.748	510	493	1,626,803	- 9,381,945
6		11,008.748	11.008.748	510	493	1,626,803	- 9,381,945
7		11,008,748	11,008.748	510	493	1,626,803	- 9,381,945
8		11,008,748	11,008,748	510	493	1,626,803	- 9,381,945
9		11,008,748	11,008,748	510	493	1,626,803	- 9,381,945
10		11,008,748	11,008,748	510	493	1,626,803	- 9,381,945
Total	381,330	110,087,480	110,468,810	5,102	4,930	16,268,027	-94,200,782
Present value			67,990,654	3,135	3,029	9,995,998	- 57,994,656

From Table 4.28, the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	21,688	Baht
Average revenue of 1 ton ULO	=	3,189	Baht
NPV	=	-57,994,656	Baht
B/C ratio	=	0.15	

4.7 Case Study 7: Direct burning in cement kiln

4.7.1 Process Description [26, 54-62]

The use of combustible hazardous waste as fuel in cement kilns has been common in the early 1970s. Cement kilns can accommodate a wide variety of fuels, and their very high operating temperature (1,400-1,500 °C) assure virtually complete destruction of the organic constituents in the fuels [26].

Many studies of air emissions from cement kilns burning hazardous waste have been conducted. Comparative emission tests on kiln burning conventional fuels and hazardous waste fuel show that there is no significant change in air emissions when hazardous waste fuel is properly used to replace conventional fuels specially lignite. This is due to the reasons below:[54]

- Complete combustion at high temperature (1450 °C) and long continuous combusting time (10 -12 seconds).
- Organic compounds, which contaminated the ULO and residue from finally become the part of the clinker product and concrete
- Chloride and sulfur compounds are neutralized and adsorbed by limestone and alkaline in boiler

In Thailand, Siam Cement Industry CO., LTD (SCC) [55-57] has created the combination of mixing waste and conventional fuel pilot project. The major constituent (70-80 % by wt) of liquid waste in this study is used lubricating oil The other constituents (20-30 %wt) are solvent or chemical liquid wastes. The pilot project mixed liquid waste with conventional fuel before injecting to the kiln at about 3-4 ton/hour. Figure 4.15 presented the injected ULO position in Portland cement process

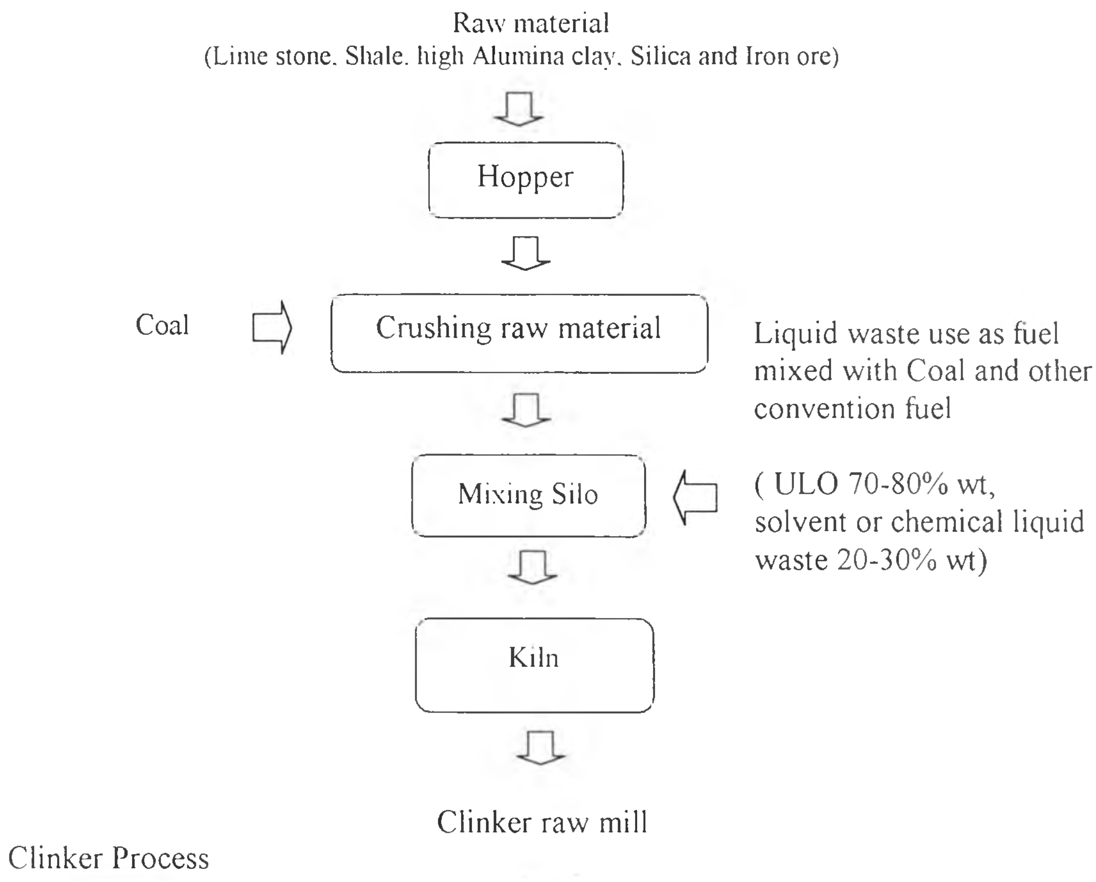

Figure 4.15 The injected liquid waste position in Clinker Process of Cement Portland [55,58].

There are four types of fuel use in SCC. Those are lignite, fuel oil, diesel and coal. The main fuel is lignite, 71% of total fuel and 29% for the others When use ULO mixing with conventional fuel (not higher than 10% of total fuel), it can replace lignite 521,142 ton/year (the quantity reduced from 1,163,942 to 642,800 ton/year) or 45% of lignite quantity [55].

Moreover, GENCO (General Environmental Conservation Public Company Limited) is the representative organization that receives hazardous waste and used lubricating oil and produces synthetic fuel used in industrial boilers or cement kilns. The composition of synthetic fuel varies depending on the type of characteristics of waste as shown in Table 4.29

Table 4.29 Organic Waste Categories for fuel blending in GENCO [59]

Parameter		Unit	FB1	FB2	FB3	FB4	FB5	FB6
PH		-	4 to 10	4 to 10	4 to 10	<4	-	-
Flash Point		Celcius	>60	>60	>60	>60	-	-
Viscosity	(max.)	CP	417	563	1000	>1000	Solid	-
Solid Content	(max.)	Wt%	17	25	50	>50	100	-
Ash Content	(max.)	Wt%	16	24	46	>46	-	-
Heat Content	(min.)	Kcal/Kg	7000	5750	2000	<2000	-	-
TOX	(max.)	Wt%	1	1.1	2.1	2.77	4.1	> 4.1
Sulphur	(max.)	Wt%	3	3.2	5.2	6.53	9.2	> 9.2
Antimony	(max.)	Ppm	883	1325	2650	3533	5300	> 5300
Arsenic	(max.)	Ppm	883	1325	2650	3533	5300	> 5300
Cadmium	(max.)	Ppm	1483	225	4450	5933	900	> 8900
Chromium	(max.)	Ppm	2493	3735	7460	9943	14910	> 14910
Copper	(max.)	Ppm	15000	22500	45000	60000	90000	> 90000
Laed	(max.)	Ppm	14150	20725	40450	53600	79900	> 79900
Mercury	(max.)	Ppm	217	325	650	867	1300	> 1300
Thalium	(max.)	Ppm	80	118	230	305	455	> 455
Zinc	(max.)	Ppm	14333	21000	41000	54333	81000	> 81000
ULO/ Waste ratio		% weight	1 - 40	41 - 60	60 - 80	80 - 93	85 – 93	93 – 98

FB1-FB6 in Table 4.29 are the various types of hazardous waste characteristics, where ULO is mixed according to some fixed ratio.

The fuel blending facility itself consists of bulk liquid unloading equipment, drummed liquids and solids emptying equipment, liquids and solids mixing equipment. The step of process is shown in Figure 4.16

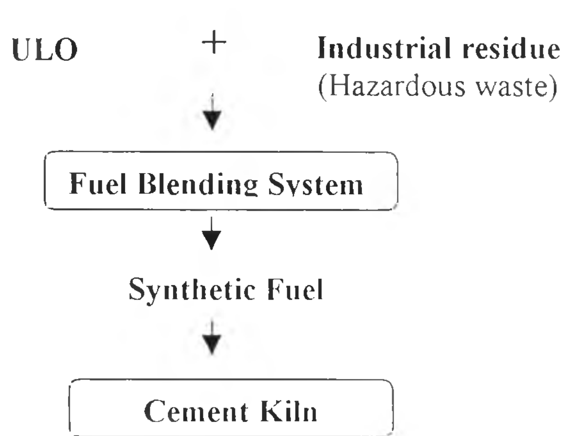

Figure 4.16 Steps of blending synthetic fuel process

4.7.2 Environmental impact

Recovery as fuels in cement kilns and boilers, the potential environmental impact is air pollution problem The pollutants of concerns are particular matter (PM), sulfur dioxide (SO_x), oxides of Nitrogen (NO_x), and heavy metals.

Tables 4.30 Concentration of pollutants from the 2 types of fuel in cement kiln: lignite and lignite mix with ULO in 1998 – 1999 [60-61].

Parameter	Unit	Standard [a]	Lignite		Lignite +ULO [c]	
			Range	Avg.	Range	Avg.
Particulate	mg/m^3	200 [b]	46 - 202	105.6	46-86	66
Oxide of Nitrogen	ppm	200	68.8–437.5	235.8	243-441	328.5
Sulfur dioxide	ppm	-	ND - 2.8	*	ND-14	*
Carbon monoxide	ppm	870	370	370	**	**
Copper	ppm	30	0.002-0.004	0.003	0.02	0.02
Zinc	ppm	-	0.042-0 172	0.107	2.24	2.24
Chromium	ppm	-	0.004-0.013	0.008	0 004	0.004
Nickel	ppm	-	0.001-0.026	0.013	0.063	0.063
Lead	mg/m^3	30	ND	ND	0.059	0.059
Cadmium	mg/m^3	10	0-0.001	0.0005	ND	ND
Arsenic	mg/m^3	20	ND	ND	ND	ND
Mercury	mg/m^3	3	ND-0.43	*	0.004	0.004

Remark: [a] Notification of the Ministry of Industry No.2, B.E. 2536 (1993) and No 9 B.E.2538 (1995)

[b] Recommendation from the Environmental Impact Assessment Committee in Industrial Project. Kaeng Koi Expansion Project(Kiln 1 and 2)April 1, 1994

[c] Rang of mixing ratio not much than 10%

* Cannot find average value, ** Not monitoring measurement, ND: no data

Table 4.30 indicates that the emission from the use of a mixture between ULO and lignite leads to even lower concentrations of particular matter, copper, chromium, cadmium, arsenic and mercury than that obtained from the used of alone. Also the concentrations of these pollutants are lower than the standard values. lignite and standard value. The oxides of nitrogen, sulfur dioxide, zinc, nickel and lead concentration are found to be higher than those from lignite but still not exceeds standard values. The significant pollutant is the oxide of nitrogen (NO_x) due to its only high concentration

4.7.3. Pollution Control Approach

In this case NO_x is the significant air pollutants. There are two possible approaches in controlling NO_x [52].

1.Nitrogen Oxide Control by Combustion Modification

This modification scheme involves mixing part of the combustion air with the fuel, burning as much of the fuel as that amount of air will burn, transferring some of the heat from the flames to whatever is being heated, then adding the remaining air and finishing the combustion. This scheme is often called " reburning or two-stage combustion". In the first stage the maximum temperature is reached when all oxygen has been used up, so that there is not enough oxygen to form NO. In the second stage enough of the heat in the first stage has been removed that maximum temperature reached in the presence of excess oxygen is low enough that the formation of NO is small.

2. Nitrogen Oxide Control by Post – Flame Treatment

This approach, post flame treatment processes add a reducing agent to the combustion gas stream to take oxygen away from NO. This is particularly elegant because pollutants are turned into two non-pollutants. This process is commonly used in the engine technology, where careful control of the engine is needed to produce NO and CO in the proper ratio. In modern auto engines the reaction is

$$2NO + 2CO \xrightarrow{\text{Platinum-rhodium catalyst}} N_2 + 2CO_2$$

In power plants and other large furnace a variety of reducing agents are used, the most popular appears to be ammonia.

4.7.4 Economic Analysis [19, 32, 46,53, 57]

Detailed economic studies are performed below according to the discussion in Section 3.3.2 (Eqs.3.1-3.4).

Assumption:

- No cost of ULO (disposal waste)
- Price of lignite = 750 Bt/ton
- Assume ULO molecular formula is C_8H_{17}, use O_2 burn 30% access air @ temp (145 C°). Balancing molecular equation found that use air to combusted = 22.57 m^3, which determined quantity of NO_x as follow:

  From Table 4.24, concentration of NO_x is 328 ppm, which means:

  Air 1 m^3 contain NO_x = 328 mg so if

  Air 22.57 m^3 contain NO_x = 0.0074 ton NO_x
- Cost of treatment NO_x = 820,029 Bt/ton NO_x
- Saving fuel oil:

  From ULO = 9,783 Kcal/kg , fuel oil = 10,125 Kcal/kg

  So 1 ton of ULO can instead of fuel oil = 0.97 ton of fuel oil
- Depreciation life = 10 years

1) Investment Cost = 10 million Bt
2) Operating cost

   Cost of maintenance (10% of investment) = 1,000,000 Bt

   Cost of treatment NO_x = 0.0074 x 820,029 = 6,068 Bt

   Operating cost = 1,006,068 Bt
3) Saving cost

   ULO mixing with conventional fuel can replace lignite 15,000 ton/year

   Saving lignite cost = 15,000 x 750

   = 11,250,000 Bt/year

Cash flow analysis

Table 4.31 Cash flow analysis of direct burning in cement kiln

Year	Investment Cost (Baht)	Operating Cost (Baht)	Total cost (Baht)	Quantity of input (ton)	Quantity of output (ton)	Revenue (Baht)	Benefit (Baht)
1	10,000,000	1,006,068	11,006,068	16,986	15,000	11,250,000	243,932
2		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
3		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
4		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
5		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
6		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
7		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
8		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
9		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
10		1,006,068	1,006,068	16,986	15,000	11,250,000	10,243,932
Total	10,000,000	10,060,682	20,060,682	169,860	150,000	112,500,000	92,439,318
Present value			15,272,763	104,372	92,169	69,126,380	53,853,617

From Table 4.31; the summaries of cost estimation are below:

Average cost of 1 ton ULO	=	146	Bt
Average revenue of 1 ton ULO	=	662	Bt
NPV	=	53,853,617	Bt
B/C ratio	=	4 53	