A report on an industrial wastes survey of Shell Canada Limited. Corunna, Ontario. June 19th, 20, 1968.

By: Ontario. Ministry of the Environment.

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A

Report On

An Industrial Wastes Survey

of

SHELL CANADA LIMITED

Corunna, Ontario

June 19, 20, 1968

Division of Industrial Wastes

ONTARIO WATER RESOURCES COMMISSION

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REPORT

Ontario Water Resources Commission

Municipality: Moore Township, Ontario. Date of Inspection: June 19, 20, 1968.

Re: SHELL CANADA LIMITED

Field Inspection by: R. W. Hussain Report by: R. W. Hussain

An intensive investigation was conducted into the sources and characteristics of liquid wastes from the Sarnia refinery of Shell Canada Limited, located in the Township of Moore, on June 19th and 20th, 1968. The purpose of this investigation was:

a) To obtain comprehensive data for an overall appraisal of the status of pollution control in the oil refining industry in the Province of Ontario, and

b) To evaluate the effectiveness of waste segregation, control, treatment and disposal at this particular refinery.

SUMMARY

It was found during this survey that the Shell Canada Limited (Sarnia) refinery discharged wastes to Talford Creek which exceeded OWRC objectives for a discharge to a watercourse. The wastes to Talford Creek were made up of two effluent flows:

a) A clean water flow (26 million gallons per day) which exhibited phenolic concentrations in the range of 40 to 60 parts per billion and, therefore, exceeded the OWRC objective of 20 parts per billion, and

b) A combined flow of two circular gravity separator effluents, 18.2 million gallons per day, which showed phenolic concentrations in the range of 70 parts per billion to 120 parts per billion.

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It was also noted that the phenolic concentrations in the combined flow were significantly lower than concentrations found during previous OWRC surveys. This is indicative of better waste segregation, control and treatment measures that have been implemented at this refinery. On the other hand, it was found that dissolved solids and chloride concentrations increased over past results. This was later determined to have been caused by a brine solution overflow from some butane storage caverns to the storm drainage system. The industry is thinking in terms of rectifying this problem by installing brine handling facilities in the near future.

The waste phenolics and sulphides (as H_2S), daily loadings to the Deep Well Injection System, were calculated to be 240 pounds and 920 pounds respectively. This represents the disposal into the underground formations of approximately 90% and 95% of the water-borne phenolics and sulphides generated in this refinery.

The oil removal efficiency of the Oily Water Separator was calculated to be in the range of 95% and 99% during the course of this survey. Similar efficiencies are anticipated for the Potentially Oily Water Separator on account of the very low oil content found in the effluent from this separator. However, there are indications that during periods of heavy rainfall, as occurred on June 19, 1968, less efficient oil removal is effected in these separators. This would appear to be one cause of the deterioration of the aesthetic qualities of the banks and waters of Talford Creek by oil pollution.

This report recommends that phenolic and other solubles levels in the effluents from this refinery to Talford Creek be reduced. Phenolics can be reduced first by identification and in-plant control of contributory sources, followed by one or a combination of the following:

(i) disposal to the Deep Well Injection System

(ii) stripping and biological treatment, and (iii) chemical treatment.

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Ether solubles can be reduced by one or more of the following:

(i) better in-plant housekeeping practices

(ii) more intense surveillance at potential sources

(iii) extra oil-water separation capacity, or chemical treatment.

In addition it may be necessary, at some time in the future, to install an extended outfall to conduct these wastes into the St. Clair River if the aesthetic problems associated with Talford Creek are to be eliminated.

DETAILS OF SURVEY

Personnel Participating

Shell Canada Limited:

Mr. T. McIver	-	Technical Superintendent
Mr. T. Parry	-	Engineer
Mr. R. Sutherland	-	Engineer

Ontario Water Resources Commission:

Mr. S. W. Hussain	-	Engineer
Mr. R. A. Abbott	-	Technologist
Mr. M. V. Filey	-	Technologist
Mr. T. E. Wood	-	Technologist
Mr. R. VanSoest	-	Student
Mr. D. Harris	-	Student

Production and Operating Data

The refinery processes 45,000 barrels of Western Canadian crude oil daily to produce a broad range of refined petroleum products including gasoline, deisel fuel, furnace oil, stove oil, bunker fuel oil, liquified petroleum gases, aromatic solvents such as benzene and toluene and by-product elemental sulphur.

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The units involved in the manufacture of these products are as follows:

Crude Distillation Units (two)

Crude Oil Desalters (two)

Fluid Catalytic Cracking Unit (FCCU)

Hydrocracker (Isomax Unit)

Vis-breaker

Platformer (motor fuel platformer)

BTX Platformer and Udex Extraction Unit

Hydrodealkylation Unit (Hydeal)

Polymerisation Unit

Hydrodesulphurisation Unit (Unifiner)

Sulphur Recovery Unit

Liquified Petroleum Gas Recovery Unit

All of these units were in operation during this survey. Number one crude unit was processing high sulphur crude oil, whereas number two crude unit was processing crude oil with a low sulphur content.

The plant employs a total workforce of 350, of which 200 are production employees and 150 are administrative and clerical personnel.

Water Consumption and Distribution

All process water is obtained from the St. Clair River and the total usage varies seasonally between 44 and 58 million gallons per day with maximum usage occurring during the summer months when production and cooling requirements are greatest. There is little consumptive use of water in the refinery so that the peak waste flows shown in Table I are indicative of the distribution of water throughout the refinery.

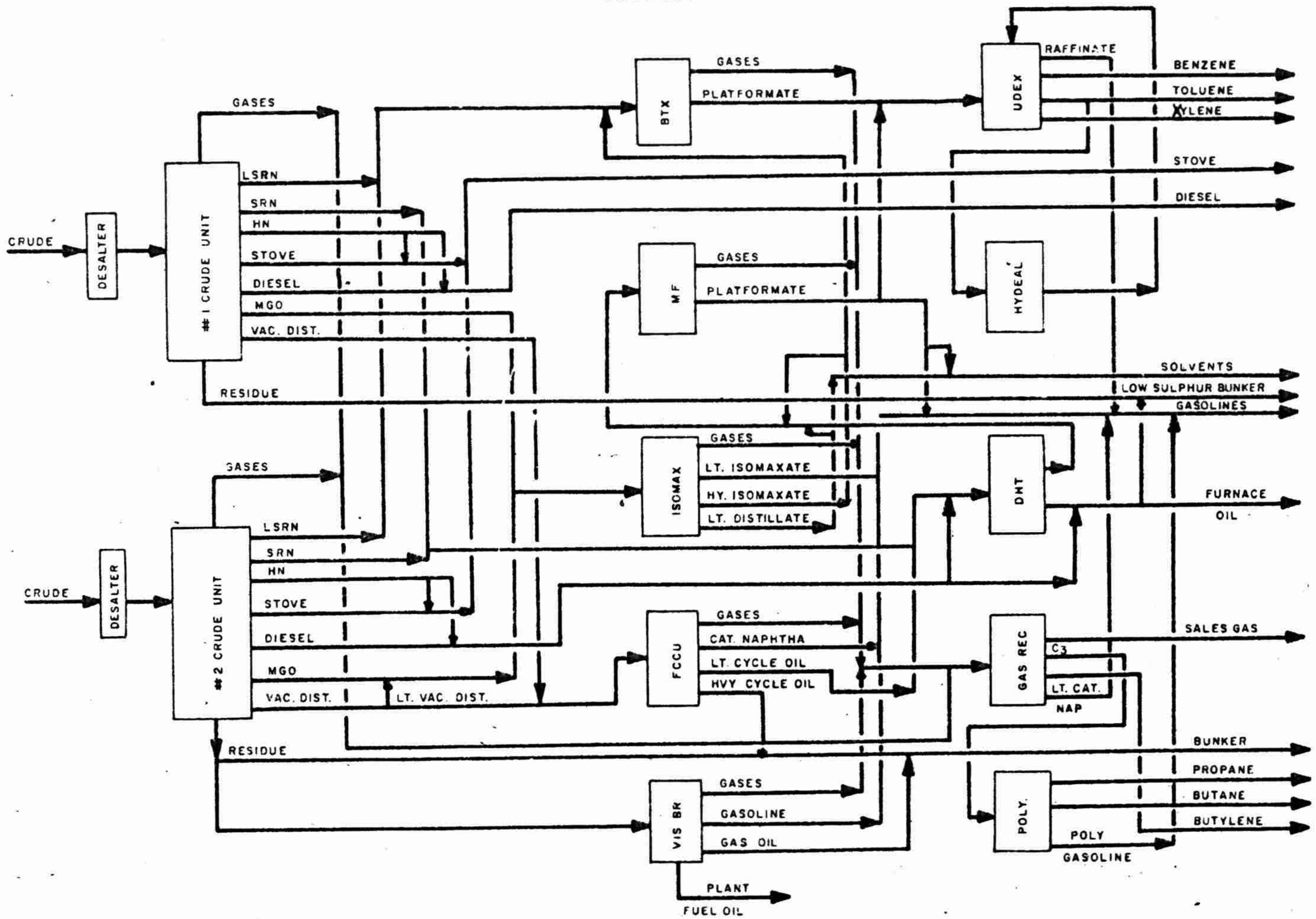
Average waste flow data gives the following approximate average distribution:

Clean Water	-	26,000,000 gpd
Potentially Oily Water	-	16,000,000 "
Oily Water	-	2,200,000 "
Sanitary	-	10,000 "
TOTAL		44,210,000 gpd

Manufacturing Processes

Diagram I on page 6, outlines schematically the refining processes with respect to the separation and distribution of the component fractions of the crude petroleum. The primary separation achieved in the crude distillation units is followed by the up-grading of lighter components into gasoline-type fractions by polymerization and catalytic reforming processes and the catalytic and thermal cracking of heavier components into gases, gasolines and fuel oil feedstocks. Secondary refining processes include the catalytic hydrodesulphurization of furnace oils, deisel fuel and catalytic reforming feedstocks, the recovery of elemental sulphur from the resultant by-product hydrogen sulphide, the solvent extraction of catalytically reformed feedstocks (platformates) to obtain benzene, toluene and xylene petrochemicals and the hydrodealkylation of toluene to increase the yield of benzene.

DIAGRAM #1
PRODUCTION FLOW SHEET
SHELL CANADA LIMITED
CORUNNA



LEGEND

LSRN - LIGHT STRAIGHT RUN NAPHTHA
SRN - STRAIGHT RUN NAPHTHA
HN - HEAVY NAPHTHA
MGO - MIDDLE GAS OIL
VAC. DIST. - VACUUM DISTILLATE
ISOMAX - HYDRO CRACKER
B.T.X. - BENZENE TOLUENE XYLENE
MF - MOTOR FUEL REFORMING
FCCU - FLUID CATALYTIC CRACKER
VIS BR - VIS BREAKER
POLY. - POLYMERIZATION
GAS REC - GAS RECOVERY
D.H.T. - HYDROTREATER
HYDEAL - HYDRODEALKYLATION
UDEX - SOLVENT REFINING

Sources and Collection of Liquid Wastes

The liquid wastes encountered in the Shell Canada Limited (Sarnia) refinery are typical of oil refining operations — that is, the major portion is made up of once-through cooling waters from condensers and coolers, while the remainder is comprised of oily or potentially oily waste waters and chemical wastes.

The sewer system in this refinery is divided in such a way that the different types of wastes are segregated and conducted to their ultimate point of disposal by separate sewers. These separate sewers are:

(i) the oily water sewer

(ii) the potentially oily water sewer

(iii) the clean water sewer and five special sewer systems

(i) Oily Water Sewer:

This sewer system collects all waste waters which come into direct and continuous contact with oil, including those which are subject to emulsified oil contamination. These wastes include pump-gland cooling waters, barometric condenser waters, desalting waters, spills and equipment pad drains. The units contributing to the flow in this sewer are the two Crude Units, the Catalytic Cracker, the BTX and Udex, and the Motor Fuel Platformer. The total flow in this system is approximately 1,500 gallons per minute.

(ii) Potentially Oily Sewer:

This system handles cooling waters from processes and operations where there exists the possibility of the waters becoming contaminated with the products by leakage in exchangers, coolers, etc. This system services all the main units with the exception of the BTX, Udex and Motor Fuel Platforming Units. The total flow in this system is rated at between 12,000 and 18,000 gallons per minute, (according to the season).

(iii) Clean Water Sewer:

This system handles once-through cooling waters from condensers and coolers where the pressure on the water side is higher than the pressure on the product side. This system serves all the units in this refinery including the boiler house. The total flow in this system is estimated to be between 17,000 gallons per minute and 21,000 gallons per minute depending on the season.

Special Sewer or Collection Systems: There are individual systems in this refinery for handling:

a) Ballast-water from the docking facilities

b) Tank car interior washings

c) Storage tank bottom drainage

d) Storm water runoff from the entire refinery, and

e) High phenolic and sulphidic wastes from overhead accumulators (foul condensates) and washing operations

Diagram II on page 10, gives the general lay-out of the waste treatment and disposal system, while Diagram III on page 11, shows a more simplified picture of the individual waste effluent segregation systems in this refinery. In addition, a further breakdown on the various sewer flows according to the sources or units is presented in Table I.

TABLE I

Maximum Waste Flow Breakdown *

Sources or Units	MAXIMUM FLOWS (gpd) Clean Water	Potentially Oily	Oily Water
Sulphur Plant	-	-	-
Catalytic Cracker	15,200,000	5,530,000	650,000
#1 Crude Unit	6,480,000	5,190,000	435,000
Platformer	-	6,000,000	145,000
Isomax	1,725,000	1,450,000	100,000
#2 Crude Unit	2,420,000	1,550,000	510,000
Unifiner and Hydeal	-	5,660,000	-
BTX and Udex	4,020,000	-	525,000
Water Treatment	345,000	-	-
Storm Water	-	Variable	-
Ballast Water	-	Variable	-
Steam Plant	-	145,000	-
Tank Bottom Drainage	-	-	Variable
Tank Car Interior Washings	-	-	Variable
TOTAL FLOWS	30,190,000	25,525,000	2,365,000

* These flow figures were obtained from Shell Canada Limited and represent the maximum waste flows from the various units.

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DIAGRAM # 2
REFINERY SEWER LAY-OUT
SHELL CANADA LIMITED
CORUNNA

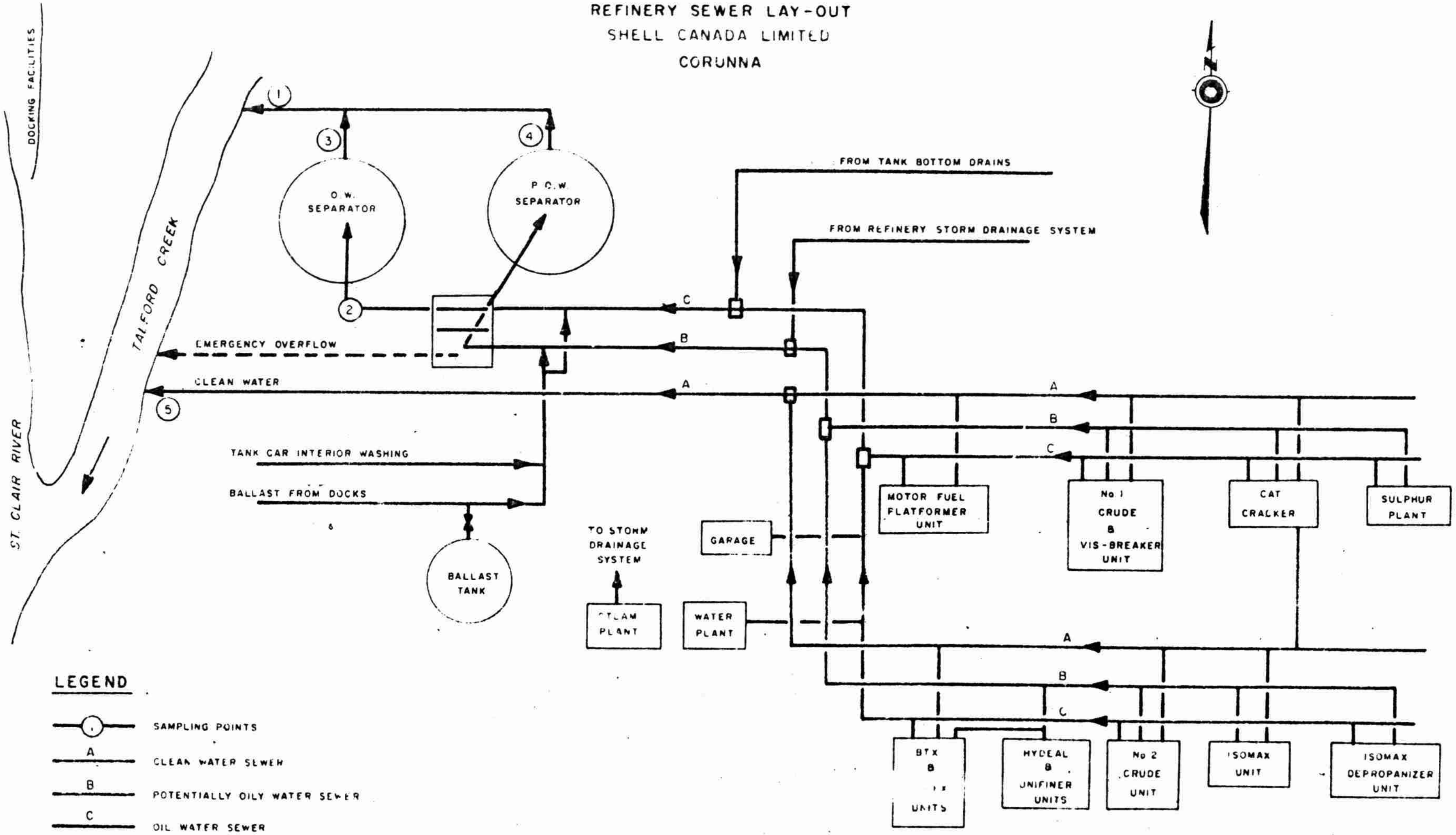
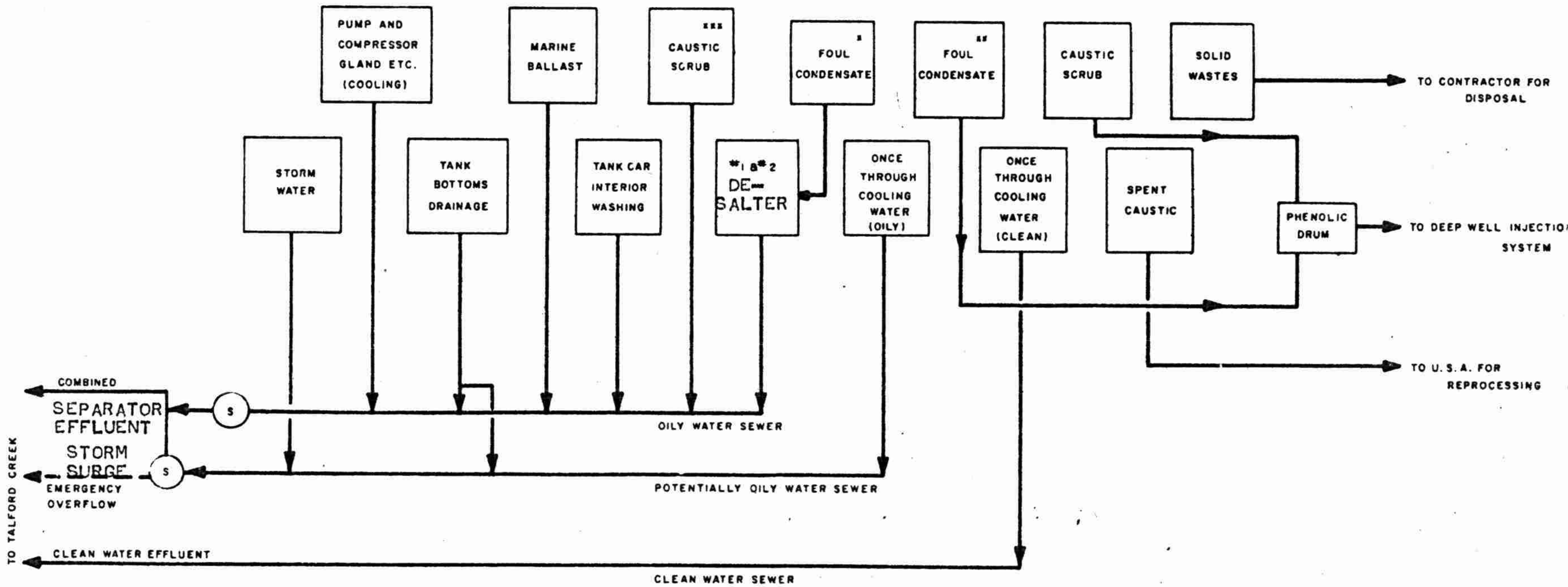


DIAGRAM # 3
INDIVIDUAL WASTE EFFLUENTS SEGREGRATION
SHELL CANADA LIMITED
CORUNNA



LEGEND

S — OIL SEPARATOR
* - #1 CRUDE ATM & VACUUM AND #2 CRUDE VACUUM OVERHEAD
** - VISBREAKER, CAT AND #1 CRUDE PRIMARY OVERHEAD
*** POLY GASOLINE SCRUB WATERS

<u>Waste Treatment and Disposal</u>

With the exception of the clean water system which discharges directly to Talford Creek, the wastes collected in the various sewer systems are subjected to oil-water separation in two circular gravity separators equipped with oil skimming facilities. The oily waters plus the tank bottom drainage and tank car interior washings are treated in one separator, while the potentially oily water and the storm drainage are combined and treated in the other separator. Ballast water can be treated in either of these two separator systems. The effluents from these two separators combine before entering Talford Creek. It should be noted that there is a by-pass at the inlet to the potentially oily separator which affords a direct discharge to the creek in times of heavy storm water runoff.

The concentrated phenolic wastes are disposed via a deep well injection system, while spent caustics, solvents, sludges and clays are either regenerated or disposed of outside the confines of the refinery.

Table II is presented in order to summarize the sources, volumes, characteristics, treatment and disposal of all wastes at the refinery.

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TABLE II

SUMMARY OF WASTE SOURCES, VOLUMES, CHARACTERISTICS, TREATMENT AND DISPOSAL

SHELL CANADA LIMITED – CORUNNA

TYPE OF WASTE	SOURCES OF WASTE	VOLUME (GPD)	1968 WASTE CHARACTERISTICS *								POINT OF DISPOSAL	TREATMENT
			BOD	COD	SOLIDS TOTAL	SOLIDS SUSP.	PHENOLS (PPB)	ETHER SOLUBLES	FREE AMMONIA	OTHER		
CLEAN WATER	ALL UNITS	30,000,000 MAX.	15	20	246	13	40	2	0.05	53 CL^-	TALFORD CREEK	–
		26,000,000 AVG.	10	35	272	15	40	TRACE	0.25	53 CL^-		
			14	15	242	10	60	3	0.31	45 CL^-		
POTENTIALLY OILY WATER	ALL UNITS EXCEPT BTX, UDEX, AND PLATFORMER	25,000,000 MAX. 16,000,000 AVG.	NO SAMPLES TAKEN								POTENTIALLY OILY WATER SEPARATOR	OIL-WATER SEPARATION
OILY WATER	2 CRUDE UNITS	945,000	NO SAMPLES TAKEN								OILY WATER SEPARATOR	OIL-WATER SEPARATION
	CATALYTIC CRACKER	650,000										
	BTX AND UDEX	525,000										
	PLATFORMER	145,000										
	#1 DESALTER	50,750	–	1,790	4,894	11	10,000	35	6	550 H_2S		
	#2 DESALTER	63,000	–	2,250	3,458	89	4,000	810	19	56 H_2S		
	TANK BOTTOMS	100-900 LBS/WEEK	–	–	–	–	19.5-140** LBS/MONTH					
	BALLAST TANK WATER	1.7×10^6 BARRELS/YEAR	–	–	–	–	**20-300	2-50 **	–	–		
	TANK CAR INTERIOR WASHINGS	N.A.	–	–	–	–	–	–	–	–		

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TABLE II CONTINUED

TYPE OF WASTE	SOURCES OF WASTE	VOLUME (GPD)	1968 WASTE CHARACTERISTICS *							OTHER	POINT OF DISPOSAL	TREATMENT
			BOD	COD	SOLIDS		PHENOLS (PPB)	ETHER SOLUBLES	FREE AMMONIA			
					TOTAL	SUSP.						
	INFLUENT TO OILY WATER SEPARATOR	2,200,000	-	-	-	-	-	1,050	-	-	OILY WATER SEPARATOR	-
			-	-	-	-	-	740	-	-		
								786	-	-		
FOUL CONDENSATES	#1 CRUDE VACUUM TOWER CONDENSER	6,000	-	-	-	-	25,000**	-	-	-	DESALTERS	REUSE
	#2 CRUDE VACUUM TOWER CONDENSER	52,500	-	-	-	-	25,000**	-	-	-	DESALTERS	REUSE
	#1 CRUDE ATMOSPHERIC TOWER CONDENSER	27,500	-	-	-	-	60,000**	52**	-	-	DESALTERS	REUSE
	CATALYTIC CRACKER FRACTIONATOR OVERHEAD CONDENSER	47,000	-	-	-	-	525,000**	130**	-	-	PHENOLIC DRUM	OIL SKIM
	#1 CRUDE PRIMARY TOWER CONDENSER	2,500	-	-	-	-	10,000**	36**	-	-	PHENOLIC DRUM	OIL SKIM
	VISBREAKER TOWER CONDENSER	2,500	-	-			100,000**	82**	-	-	PHENOLIC DRUM	OIL SKIM

TABLE II CONTINUED

TYPE OF WASTE	SOURCES OF WASTE	VOLUME (GPD)	1968 WASTE CHARACTERISTICS *									POINT OF DISPOSAL	TREATMENT
			BOD	COD	SOLIDS TOTAL	SOLIDS SUSP.	PHENOLS (PPB)	ETHER SOLUBLES	FREE AMMONIA	OTHER			
WASH WATERS	CATALYTIC CRACKER OFF-GAS	12,000	-	-	-	-	41,000**	40**	-	-		PHENOLIC DRUM	OIL SKIM
	CATALYTIC CRACKED GASOLINE	16,800	-	-	-	-	450,000**	-	-	-		PHENOLIC DRUM	OIL SKIM
	CATALYTIC CRACKED NAPHTHA	7,200	-	-	-	-	500,000**	72**	-	-		PHENOLIC DRUM	OIL SKIM
	#1 CRUDE STOVE OIL	3,000	-	-	-	-	15,000**	250**	-	-		PHENOLIC DRUM	OIL SKIM
	POLY GASOLINE	N.A.	-	-	-	-	9**	-	-	-		OILY WATER SEPARATOR	OIL-WATER SEPARATION
STORM WATER	ENTIRE PLANT	VARIABLE	-	-	-	70**	5**	0-50**	-	-		POTENTIALLY WATER SEPARATOR	OIL-WATER SEPARATION
CHEMICAL WASTES	SOLVENTS	N.A.	NO DATA AVAILABLE									REGENERATION SYSTEM	REPROCESSED
	SPENT CAUSTIC	1,000	4.4% AND 16.5% CRESYLIC ACID									U. S. A.	REPROCESSED
PHENOLIC DRUM WASTES	ENTIRE PLANT	91,000	-	4,300	348	4	240,000	76	450	920 H_2S		DEEP WELL AND CATALYTIC CRACKER SPRAY WATER	-

TABLE II CONTINUED

TYPE OF WASTE	SOURCES OF WASTE	VOLUME (GPD)	1968 WASTE CHARACTERISTICS *								POINT OF DISCHARGE	TREATMENT
			BOD	COD	SOLIDS TOTAL	SOLIDS SUSP.	PHENOLS (PPB)	ETHER SOLUBLES	FREE AMMONIA	OTHER		
SEPARATOR EFFLUENTS	POTENTIALLY OILY WATER SEPARATOR	16,000,000 AVG.	15	35	1,924	16	100	0	0.61	588 CL^-	COMBINED SEWER	-
			22	48	1,234	45	50	1	0.50	606 CL^-		
			13	61	1,822	9	40	TRACE	0.71	674 CL^-		
	OILY WATER SEPARATOR	2,200,000	230	320	588	21	600	10	28.5	74 H_2S	COMBINED SEWER	-
			154	344	538	29	800	37	26.5	64 H_2S		
			138	270	464	16	800	26	25.5	70 H_2S		
	COMBINED SEWER	18,200,000 AVG.	26	54	1,830	34	70	8	3.8	374 CL^-	TALFORD CREEK	-
			39	54	1,196	56	120	9	25	573 CL^-		
			23	50	1,690	33	120	8	3.7	474 CL^-		

NOTE: N.A. STANDS FOR "NOT AVAILABLE"

* ALL ANALYSES REPORTED IN PARTS PER MILLION (PPM) EXCEPT PHENOLS

** DATA SUPPLIED BY SHELL CANADA LIMITED

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Sampling Programme and Analysis

The sampling programme conducted at the Shell Canada Limited (Sarnia) refinery on June 19, 20, 1968 is summarized in Table III.

The samples collected were divided into five portions. Those portions for cyanide, sulphide and phenol determinations were preserved with the appropriate chemicals, while separate portions were set aside for ether soluble determinations and chemical analysis.

These samples were shipped to the OWRC Toronto Laboratories for analysis for BOD_5, COD, solids, sulphates, chlorides, phosphates, total Kjeldahl nitrogen, free ammonia, cyanides, phenols, sulphides and ether solubles. These tests were carried out in accordance with the procedures outlined in "Standard Methods for the Examination of Water and Wastewater", Twelfth Edition.

The complete tabulation of the analytical results of samples taken on June 19th and 20th, 1968 are appended to this report.

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TABLE III

Summary of Sampling Programme

SAMPLE NUMBER*	SAMPLE LOCATION	DATE OF SAMPLING	SAMPLING SHIFT NO.	TIME OF SAMPLING	NATURE OF SAMPLE
1	Combined Sewer to Talford Creek	June 19/68	1	8 a.m. to 4 p.m.	eight-hour composites
		"	2	4 p.m. to midnight	"
		June 20/68	3	midnight to 8 a.m.	"
2	Inlet to Oily Water Separator	June 19/68	1	same as above	"
		"	2	"	"
		June 20/68	3	"	"
3	Effluent from Oily Water Separator	June 19/68	1	"	"
		"	2	"	"
		June 20/68	3	"	"
4	Effluent from Potentially Oil Water Separator	June 19/68	1	"	"
		"	2	"	"
		June 20/68	3	"	"
5	Clean Water Sewer Effluent to Talford Creek	June 19/68	1	"	"
		"	2	"	"
		June 20/68	3	"	"
-	#1 Desalter	June 19/68	1	2:30 p.m.	Grab
-	#2 Desalter	"	1	"	"
-	Contents of Phenolic Drum	"	1	"	"
-	Combined Sewer to Talford Creek	"	2	6:30 p.m.	Grab
-	Effluent from Oily Water Separator	"	2	"	"
-	Effluent from Potentially Oily Water Separator	"	2	"	"

* The numbers in this column refer to the corresponding numbers on the Refinery Sewer-Layout Diagram (Diagram #2 on page 10).

FUTURE CONSIDERATIONS AT THIS REFINERY

1) Production

The construction of a new ten million dollar catalytic reforming unit is planned at this refinery site.

2) Production Technology

The presence of such units as the hydrocracking unit, which improves overall refinery efficiency and allows considerable flexibility in choosing the end products, the vis-breaking unit and the hydrodealkylation unit for maximum benzene production, serve to bear out the fact that the new innovations in refining technology are being used at this refinery site.

3) Waste Treatment and Disposal

There have been recent discussions between Shell Canada Limited and the Ontario Water Resources Commission on the following considerations regarding waste treatment and disposal:

a) Reactivation of a stripping column and an activated sludge unit in case that there are any problems associated with the deep well injection system.

b) Improvement of the oil-water separator systems.

c) Construction of brine handling facilities to prevent any overflow of brine from storage caverns to the storm drainage system.

DISCUSSION OF FINDINGS

Effluent Characteristics

a) Oily and Potentially Oily Water Waste Streams:

The analytical results of the flows from the oily water separator and potentially oily water separator found during this survey are shown in Table IV. Also included in this table are the results of the combined separator effluent flow plus the results of a similar sample taken during the 1967 OWRC survey.

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TABLE IV

CHARACTERISTICS OF EFFLUENTS FROM CIRCULAR GRAVITY SEPARATORS

SEPARATOR EFFLUENT	VOLUME (GPD)	SAMPLING SHIFT NO.	WASTE CHARACTERISTICS *								
			BOD	SOLIDS TOTAL	SOLIDS SUSP.	COD	PHENOLS (PPB)	ETHER SOLUBLES	FREE AMMONIA	SULPHIDES	CHLORIDES
POTENTIALLY	16,000,000	1	15	1,924	16	35	100	0	0.61	0.02	588
OILY WATER	(AVERAGE)	2	22	1,234	45	48	50	1	0.50	0.03	606
SEPARATOR		3	13	1,822	9	61	40	TRACE	0.71	0	674
OILY WATER	2,200,000	1	230	588	21	320	600	10	28.5	74	275
SEPARATOR		2	154	538	29	344	800	37	26.5	64	242
		3	148	464	16	270	800	26	25.5	70	228
COMBINED FLOWS	18,200,000	1	26	1,830	34	54	70	8	3.8	0.18	374
FROM 2 SEPARATORS		2	39	1,196	56	54	120	9	25	0.08	573
(1968)		3	23	1,690	33	50	120	8	3.7	0.22	474
COMBINED FLOWS FROM 2 SEPARATORS (1967)	N.A.	-	45	210	25	-	400	9	4.92	-	89

NOTE: ALL ANALYSES, EXCEPT PHENOLS, ARE REPORTED IN PARTS PER MILLION (PPM); PHENOLS REPORTED FROM GIBB'S SCREENED TEST ARE REPORTED IN PARTS PER BILLION (PPB).

The OWRC objectives for a direct discharge to an open watercourse with regards to BOD_5, phenols and suspended solids are: 15 parts per million, 20 parts per billion and 15 parts per million respectively. As can be seen from Table IV, the concentrations of these waste parameters in the combined separator effluent flow to Talford Creek exceed the respective OWRC objectives. On the other hand, comparison with the 1967 results on a similar sample shows a marked decrease in the concentrations of phenols and, to a lesser extent, BOD_5.

Although BOD_5 levels exceed the Commission's effluent objective of 15 parts per million, the levels indicated should have no significant effect in reducing the dissolved oxygen concentration of any portion of the St. Clair River. However, they may affect the oxygen balance in Talford Creek depending on creek flow rates and rate of bio-degradation.

The phenolic content could arise from almost any section in this refinery, but it is suspected that the desalter effluents contribute significantly to the final loading to the creek. This point will be discussed at a greater length further on in this report.

A significant concentration of free ammonia (25 parts per million) was found in the combined flow to Talford Creek during the second shift of this sampling program, but one would tend to discount this high concentration on the grounds that there was no noticeable corresponding increase in the ammonia concentration in the two flows (i.e., Oily Water effluent and Potentially Oily Water effluent) making up this combined flow.

In the same vein, the phenolic concentration in the combined flow during the first sampling shift was 70 parts per billion, while the concentrations in the two flows making up the combined flow exhibited phenolics much higher than

70 parts per billion. The probable explanation for this discrepancy is that the portion of the sample of the combined effluent used for phenolic determination was not properly preserved with the $CuSO_4/H_3PO_4$ solution in order to prevent degradation and oxidation of the phenols prior to analysis.

Another noteworthy point borne out by the analytical results was the high total (mostly dissolved) solids concentration in the combined flow over the 1967 OWRC results, even though the suspended solids concentrations were in the same order of magnitude. The dissolved solids indicate the amount of chemicals in solution such as chlorides, sulphates, carbonates and bicarbonates of sodium and calcium. With a noticeable rise only in the chloride concentration (89 parts per million in 1967 versus 415 parts per million in 1968) as an indicator, one would suspect that an increased desalter flow, which contains very high dissolved solids and chlorides concentrations and which discharges into the Oily Water system, would in part, be responsible for the significant increase over the 1967 figures. However, a closer look at past and present analytical results reveals that marked increases in the dissolved solids and chlorides had also occurred in the effluent from the Potentially Oily Water separator. Since the increase in concentrations in the flow from this separator was more significant than that in the other separator effluent (which handles the desalter waters), it becomes evident that the solids and chlorides originate in this system. Although the exact units that caused this increase were not pin-pointed by this sampling programme, there could be a relationship to the operation of the butane storage caverns located in the salt formation underlying the refinery. This point was subsequently discussed with the refinery officials, and it was disclosed that there was a possibility of an overflow of brine solution to the storm drainage system from a butane storage cavern during the sampling programme.

This would, in essence, explain the high rise in dissolved solids and chlorides concentrations found in the Potentially Oily Water system and the combined flow to Talford Creek.

The concentrations of sulphides, cyanides and phosphates in the combined flow to Talford Creek were well within acceptable levels for discharge to a watercourse. It is also interesting to note using a sulphur (S) mass balance on the Potentially Oily, Oily, and Combined waste flows, that the sulphides in the Oily waste flow were apparently oxidized to sulphates.

The ether soluble results reported for the Potentially Oily Water separator indicate very good control on this waste stream under normal refinery operations. The results for the Oily Water Separator effluent exceed Commission effluent objectives. This could be due to exceeding the design capacity of the separator or could be caused by the presence of emulsified oils. The combined separator effluents comply with the Commission's objective of 15 parts per million ether solubles. However, the effluent was not acceptable in terms of its effects on the aesthetic quality of the receiving stream. That is, oil was evident on the surface of Talford Creek and the banks were highly discoloured due to deposition of oil.

b) Clean Water Effluent:

The other effluent to Talford Creek is the clean water or once-through cooling water flow. The quality of this flow, as indicated by the analytical results in Table V, is considered to be acceptable for direct discharge to a watercourse with one notable exception — the phenol concentrations (range 40 to 60 parts per billion) are in excess of the OWRC objective. The levels would not appear to be critical from a pollution standpoint, but are of such magnitude that investigations as to the origin, or origins, should be made by Shell Canada

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Limited. It is possible that minor leakage and spillage of process waste had occurred during these sampling periods, or that some contaminated cooling waters were inadvertently or intentionally diverted from the Potentially Oily Water system to this system at one or more processing units. In addition, these levels may be partially attributable to the presence of phenolics in the refinery service water. Normally phenolic concentrations in this water vary from 5 to 10 parts per billion, however, higher values could be experienced.

TABLE V

Characteristics of Clean Water Effluent

DATE OF SAMPLING	VOLUME (GPD)	SAMPLING SHIFT NO.	WASTE CHARACTERISTICS * BOD$_5$	SOLIDS Tot.	SOLIDS Susp.	COD	Phenols (ppb)	Ether Solubles	CHLORIDES
June/68	26,000,000 (average)	1	15	246	13	20	40	2	53
		2	10	272	15	35	40	trace	53
		3	14	242	10	15	60	3	45
March/67	N.A.	-	4.4	136	36	22	0	4	43

* All analyses reported in parts per million (ppm) except phenols

Waste Loadings

The gross daily waste loadings from this refinery discharged to Talford Creek were calculated by totalling shift loadings determined using one-third the daily effluent flows and the analytical results of the three eight-hour composite samples. These are given and totalled in Table VI.

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TABLE VI

DAILY GROSS WASTE LOADING TO TALFORD CREEK

WASTE FLOW	FLOW (GPD)	SAMPLING SHIFT NO.	BOD		COD		TOTAL SOLIDS		SUSPENDED SOLIDS		PHENOLS		ETHER SOLUBLES		FREE AMMONIA		CHLORIDES	
			(PPM)	(LBS)	(PPM)	(LBS)	(PPM)	(LBS)	(PPM)	(LBS)	(PPB)	(LBS)	(PPM)	(LBS)	(PPM)	(LBS)	(PPM)	(LBS)
CLEAN WATER	26,000,000	1	15	1,300	20	1,730	246	21,300	13	1,130	40	3.5	2	175	0.05	4	53	4,600
	(AVERAGE)	2	10	870	35	3,000	272	23,600	15	1,300	40	3.5	TRACE	10	0.25	22	53	4,600
		3	14	1,220	15	1,300	242	21,000	10	870	60	5.2	3	260	0.31	27	45	3,900
COMBINE SEPARATOR EFFLUENTS	18,200,000 (AVERAGE)	1	26	1,580	54	3,240	1,830	112,000	34	2,060	70**	4.2**	8	500	3.8	230	374	22,700
		2	39	2,360	54	3,240	1,196	72,600	56	3,400	120	7.3	9	550	25*	1,500*	573	34,900
		3	23	1,400	50	3,000	1,690	103,000	33	2,000	120	7.3	8	500	3.7	220	474	28,700
TOTAL DISCHARGE TO TALFORD CREEK	44,200,000	--	-	8,730	-	15,600	-	353,500	-	10,760	-	31	-	2,000	-	2,000*	-	99,400

* VERY HIGH FIGURE - NOT REALISTIC BASED ON OTHER SAMPLES COLLECTED.

** QUESTIONABLE AND MAY BE LOW ACCORDING TO RESULTS OF OTHER SAMPLES COLLECTED.

As mentioned previously, a discrepancy arose regarding the phenolic mass balance on the effluents from the two separators and the combined flow to the creek. According to Table VI, the phenolic loading in the combined flow to Talford Creek was 18.8 pounds per day. However, if the loadings from the separators are individually calculated and added the total phenolic loading would be 26 pounds per day. This discrepancy would appear to be due to the phenolic result of 70 parts per billion obtained on the combined separator flow for the first sampling period which was considerably lower than the results obtained on either of the contributing waste streams for the same period. If a phenolic concentration of 160 parts per billion, obtained by waste concentrations - volumes ratios on the two separator effluents, is used for waste loading calculations instead of the 70 parts per billion, then the phenolic loading in the combined flow to Talford Creek is figured to be 24 pounds per day. This would mean that the total phenolic loading to Talford Creek is 36 pounds per day as opposed to 31 pounds per day.

Effectiveness of Waste Treatment and Disposal

Composite samples were obtained on the influent to the Oily Water Separator for the purpose of determining the oil removal efficiency of this particular unit. The analytical results on these samples (T-1396-7-8 on the analyses sheets which are appended) showed an ether solubles content of 1052 parts per million, 740 parts per million and 786 parts per million for sampling shift numbers 1, 2 and 3 respectively in the inlet to this separator, and 10 parts per million, 37 parts per million and 26 parts per million in the outlet for the corresponding sampling periods. This represents an oil removal efficiency in the range of 95 to 99 per cent. A similar oil removal efficiency range is expected at the Potentially Oily Water Separator where very low (0 to 3 parts per million) ether solubles concentrations were found in the effluent.

The phenolic and sulphidic concentrations in the waste flow to the deep well injection system (T-1407) were found to be 240,000 parts per billion and 920 parts per million respectively. Based on an average daily flow of approximately 100,000 gallons of high phenolic waste waters to this system, 240 pounds of phenolics and 920 pounds of sulphides are pumped to the underground strata daily. This represents a removal of about 90% and 97% respectively of the water-borne phenolic and sulphide waste loadings generated in this refinery.

Improvements in Waste Treatment and Disposal Systems

Phenolic concentrations were lower in the combined separator flow compared to past (1966 and 1967) OWRC surveys, which would suggest that either there has been an overall improvement in the waste segregation and disposal practices in this refinery or that good housekeeping practices were optimized during the period of this survey. In this regard, it should be noted that certain batch operations such as drainage of tank bottoms and ballast water would not necessarily have to be carried out during this survey. Naturally, effluent quality would be dependent to some extent on whether these operations were being carried out or not. Regardless of the apparent improvement, the analytical results suggest that the phenolic concentrations could be further reduced.

First, the Clean Water Sewer should not contain phenolic concentrations in the range of 40 to 60 parts per billion simply because of the fact that the flow in this sewer is supposed to be once-through cooling waters and should not be contaminated by process fluids.

Secondly, it is felt that the phenolic concentration in the combined flow from the separators would be lowered by segregating several relatively

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high strength phenolic waste waters for alternate treatment and/or disposal. The waste flows from the desalters for instance, showed concentrations of 4,000 and 10,000 parts per billion and a total daily phenolic loading of approximately 8 pounds. The water used in the desalters is made up of approximately 86,000 gallons per day of foul condensates from the #1 Crude Vacuum and Atmospheric Towers and #2 Crude Vacuum Tower, and 28,000 gallons per day of service water. According to the Company's data on these foul condensates, approximately 27 pounds of phenolics enter the desalters, which would mean that there is about a 70% phenolic reduction in these units. It must be recognized, however, that the desalter effluents contribute 8 pounds or approximately 22% of the phenolics found in the waste waters to the Talford Creek. Therefore, some other form of treatment and/or disposal may have to be considered in the future if the Company is to further reduce phenolic concentrations and loadings to the creek.

The most obvious remedial action for the desalter effluents is the disposal of these waste waters to the deep well injection system. However, this would mean the collection and diversion of 114,000 gallons per day to this system which would essentially double the present flow. Whether this form of disposal is feasible on account of the increased waste flow, is now not known. Nevertheless, if it is not feasible, then some other form of treatment and/or disposal may have to be considered at a future date. This may take the form of chemical treatment or stripping followed by biological treatment.

Phenolics may also arise in this refinery from leaks, spills and accidental or intentional dumpings of high phenolic waste waters to the various systems leading to Talford Creek. It is felt that tighter in-plant control at these sources may help minimize the levels of phenolics in the waste waters. Furthermore, if these waste waters can be segregated on a practical basis, then more advanced treatment, as discussed for the desalter effluents, should be considered for future waste reduction programmes.

Another point of note brought out by the results of this survey was the relatively higher concentrations of ether solubles and phenolics found in the samples of the two separator effluents following a heavy rainfall (T14C8-9-10). It was reported by OWRC personnel, sampling during this occurrence, that waste oil sprayed onto the area surrounding some storage tanks had been washed into the separator systems by the storm flow, thus resulting in high waste concentrations in the effluents. It is felt that extra capacity should be made available to handle these sudden surges of potentially oily water flows without hydraulically overloading the present facilities.

In spite of the high degree of oil removal in the two circular separators, the effects of the combined separator effluents on the aesthetic quality of Talford Creek and its banks makes improved control of oil arising from day-to-day operations and batch dumps in this refinery a necessity. The day-to-day oil contamination could be alleviated by tighter in-plant control measures followed by more advanced or improved waste treatment and/or disposal techniques such as chemical treatment, and disposal to the St. Clair River via an extended outfall. It must be remembered that the use of an extended outfall is not a substitute for adequate waste treatment, however, considering the environmental conditions surrounding the disposal of waste waters at this refinery, this procedure may ultimately be necessary. Batch dumps of oil caused by infrequent leaks, spills and accidental or intentional losses can be controlled by better in-plant housekeeping practices and more intense surveillance of potential oil pollution sources. However, in an operation as large and complex as is the case here, it is reasonable to assume that batch discharges or spills could reach the receiving watercourse unless adequate facilities are provided to in-

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tercept and treat such wastes regardless of source.

The question of high concentrations of chlorides and dissolved solids in the Potentially Oily Water system appears to be resolved since the Company has since indicated its intention to construct brine handling facilities which would, in effect, prevent any further overflow of brine solution from the storage caverns to the Potentially Oily Water system via the storm drainage system.

CONCLUSIONS AND RECOMMENDATIONS

The results of the industrial waste survey conducted at the Shell Canada Limited (Sarnia) refinery on June 19 and 20, 1968 showed that:

1) During the three sampling periods, the phenolic concentrations in the combined Circular Gravity Separator flows to Talford Creek exceeded the OWRC phenolic objective for a discharge to an open watercourse.

2) The phenolic and, to a lesser degree, the BOD_5 concentrations in this same flow were found to be significantly lower than the corresponding concentrations found during the 1967 OWRC sampling. This is probably due to tighter in-plant control and/or waste segregation measures. On the other hand, dissolved solids and chloride concentrations were found to have increased over the past results. This was later determined to have been caused by an overflow of brine from the butane storage caverns via the storm drainage system and separator systems to Talford Creek. Plans are underway to rectify this situation.

3) The clean water flow to Talford Creek also exhibited high concentrations (40 to 60 parts per billion) of phenolics. This flow is supposed to be comprised entirely of once-through cooling waters with an absolute minimum possibility of being contaminated by process fluids so that concentrations of phenolics in the 40 to 60 parts per billion range are of some concern.

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4) Daily gross waste loadings emanating from this refinery to Talford Creek were calculated by using volumes and characteristics of the two flows into the creek. These were 8,730 pounds BOD_5, 15,600 pounds COD, 353,500 pounds total solids, 10,760 pounds suspended solids, 2,000 pounds ether solubles and 99,400 pounds chlorides, in a waste flow of 44.2 million gallons per day. The phenolic loading was calculated to be 31 pounds per day, but there is some evidence to suggest that this figure could be as high as 36 pounds per day.

5) The oil removal efficiency at the Oily Water Separator was found to vary from 95 to 99% during this survey. A similar efficiency range is expected for the Potentially Oily Water Separator because very low concentrations of ether solubles were found in the effluent from this separator.

6) The phenolic and sulphide (as H_2S) daily loadings to the Deep Well Injection system were 240 pounds and 920 pounds respectively. This represents the disposal into the underground formations of approximately 90% of the water-borne phenolics and approximately 95% of the water-borne sulphides (as H_2S) in this refinery.

7) During periods of heavy rainfall, there is a distinct possibility of less efficient oil removal in the circular gravity separators. This is evidenced by the higher ether solubles concentrations found in the effluents from the two separators immediately following a heavy rainfall during the second sampling shift. This could be one cause of the deterioration of the aesthetic qualities of the banks and waters of Talford Creek.

Since phenolics and ether solubles were determined as the most signiificant pollutants emanating from this refinery to Talford Creek, it is recommended that corrective measures be undertaken to reduce the amounts of these materials reaching the creek.

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The first steps for the reduction of phenolic levels emanating from this refinery should be the identification and in-plant control of the contributory sources. Following this, one or a combination of the following measures should be considered:

a) Disposal to the Deep Well Injection system

b) Stripping followed by biological treatment, and

c) Chemical treatment

Even though ether solubles removal in the circular gravity separators is of a high standard, a further reduction of ether solubles is necessary to bring about an improvement in the aesthetic qualities of the banks and waters of Talford Creek. It is therefore recommended that the Company consider the following:

a) Extra oil-water separation capacity for handling sudden surges of potentially oily wastewater caused by heavy rainfalls.

b) Tighter in-plant control measures followed by more advanced or improved waste treatment and/or disposal techniques, such as chemical treatment, and the use of an extended outfall to the St. Clair River, for the day-to-day control of oil contamination in the waste waters, and

c) Better in-plant housekeeping practices and more intense surveillance of potential oil pollution sources.

Prepared by:

for ....
R. W. Hussain, B.A.Sc.,
Division of Industrial Wastes.

Approved by:

....
R. M. Cotts, P. Eng.,
District Engineer,
Division of Industrial Wastes.

ONTARIO WATER RESOURCES COMMISSION
CHEMICAL LABORATORIES

INDUSTRIAL WASTE ANALYSIS

All analyses except pH reported in p.p.m. unless otherwise indicated

1 p.p.m. = 1 mgm. / litre = 1 lb./100,000 Imp. Gals.

Municipality: Corunna

Report to: R. Hussain London Lab.

c.c.Chem. Lab.*

Source: Shell Canada Limited

Date Sampled: June 19/68 by:

Lab. No.	5-Day B.O.D.	Solids Total	Solids Susp.	Solids Diss.	Free Ammonia as NH_3	Phosphate as PO_4							
?-1406					19.0	1.6							
?-1407					450	9.0							
?-1408					—	—							
?-1409					—	—							
?-1410					—	—							

SEE NEXT PAGE FOR DESCRIPTION .....

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Shell Canada Limited June 19, 20, 1968.

ONTARIO WATER RESOURCES COMMISSION
CHEMICAL LABORATORIES

INDUSTRIAL WASTE ANALYSIS

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Municipality: Corunna

Report to: R. Hussain * London Lab.

c.c. Chem. Lab. *

Source: Shell Canada Limited

Date Sampled: June 19/68 by:

Lab. No.	5-Day B.O.D.	Solids Total	Solids Susp.	Solids Diss.	COD	Sulphate as SO_4	Chloride as Cl	PHENOLS (ppb) Gibbs Screened	PHENOLS (ppb) Dist.	Sulphide as H_2S	Cyanide as HCN	Ether Solubles	Total Kjeldahl as N
T-1406		3458	89	3369	2230	93	600	4000	4000	56.0	0.0	810	17.8
T-1407		348	4	344	4300	36	0	240000	200000	920	0.70	76	650.
T-1408		—	—	—	—	—	—	600	—	—	—	20	—
T-1409		—	—	—	—	—	—	600	—	—	—	67	—
T-1410		—	—	—	—	—	—	320	—	—	—	12	—

Lab. No.		Description	Sample
T-1406	25	#2 Crude Unit Desalter Wastewater	Grab 2:30 p.m.
T-1407	26	Phenolic Drum Wastewater to Deep Well	" " "
T-1408	27	Combined Separator Effluent	" 6:30 p.m.
T-1409	28	Oily Process Separator Effluent	" " "
T-1410	29	Potentially Oily Separator Effluent	" " "

Shell Canada Limited

June 19, 20, 1968.

ONTARIO WATER RESOURCES COMMISSION
CHEMICAL LABORATORIES

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INDUSTRIAL WASTE ANALYSIS

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Municipality: Corunna

Report to: R. Hussain * London Lab.

c.c. Chem. Lab. *

Source: Shell Canada Limited

Date Sampled: June 19-20/64 by:

Lab. No.	5-Day B.O.D.	Solids			Total Kjeldahl as N	Free Ammonia as N	Phosphate as PO_4						
		Total	Susp.	Diss.									
T-1390					4.1	3.8	0.9						
T-1391					30.	25.	0.9						
T-1392					9.8	3.7	0.9						
T-1393					35.	28.5	0.9						
T-1394					34.	26.5	0.9						
T-1395					27.	23.5	1.8						
T-1396					—	—	—						
T-1397					—	—	—						

SEE NEXT PAGE FOR DESCRIPTION .....

Shell Canada Limited

June 19, 20, 1964.

ONTARIO WATER RESOURCES COMMISSION
CHEMICAL LABORATORIES

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INDUSTRIAL WASTE ANALYSIS

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Municipality: Corunna

Report to: R. Hussain * London Lab.

c.c. Chem. Lab. *

Source: Shell Canada Limited

Date Sampled: June 19-20/68 by:

Lab. No.	5-Day B.O.D.	Solids Total	Solids Susp.	Solids Diss.	COD	Sulphates as SO_4	Chloride as Cl	PHENOLS (ppb) Gibbs Screened	PHENOLS (ppb) Gibbs Dist.	Sulphide as H_2S	Cyanide as HCN	Ether Solubles
T-1390	26	1830	34	1796	54	59	374	70	60	0.18	0.0	8
T-1391	39	1196	56	1140	54	47	573	120	120	0.08	0.0	9
T-1392	23	1690	33	1657	50	56	474	120	120	0.22	0.01	8
T-1393	230	588	21	567	320	30	275	600	800	74.	0.0	10
T-1394	194	538	29	509	344	30	242	800	900	64.	0.01	37
T-1395	148	464	16	448	270	27	228	800	900	70.	0.01	26
T-1396	—	—	—	—	—	—	—	—	—	—	—	1050
T-1397	—	—	—	—	—	—	—	—	—	—	—	740

Lab. No.		Description	Shift
T-1390	9	Combined Separator Effluent Composite	Shift 1
T-1391	10	" " " "	Shift 2
T-1392	11	" " " "	Shift 3
T-1393	12	Oily Process Separator Composite	Shift 1
T-1394	13	" " " "	Shift 2
T-1395	14	" " " "	Shift 3
T-1396	15	Inlet to Oily Process Separator Composite	Shift 1
T-1397	16.	" " " " " "	Shift 2

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ONTARIO WATER RESOURCES COMMISSION
CHEMICAL LABORATORIES

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INDUSTRIAL WASTE ANALYSIS

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Municipality: Corunna

Report to: R. Hussain * London Lab.

c.c. Chem. Lab. *

Source: Shell Canada Limited

Date Sampled: June 19-20/68 by:

Lab. No.	5-Day B.O.D.	Solids			Total Kjeldahl as N	Free Ammonia as N	Phosphate as PO_4
		Total	Susp.	Diss.			
T-1398					—	—	—
T-1399					11.2	0.05	1.10
T-1400					8.0	0.25	0.60
T-1401					2.2	0.31	0.9
T-1402					3.0	0.61	0.3
T-1403					4.1	0.50	1.7
T-1404					2.6	0.71	0.9
T-1405					7.8	6.0	1.1

SEE NEXT PAGE FOR DESCRIPTION .....

Shell Canada Limited

June 19, 20, 1968.

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Municipality: Corunna
Source: Shell Canada Limited
Date Sampled: June 19-20/68 by:

Report to: R. Hussain * London Lab.

c.c. Chem. Lab. *

Lab. No.	5-Day B.O.D.	Solids Total	Solids Susp.	Solids Diss.	COD	Sulphate as SO_4	Chloride as Cl	PHENOLS (ppb) Gibbs Screened	PHENOLS (ppb) Dist.	Sulphides as H_2S	Cyanides as HCN		Ether Solubles
T-1398	—	—	—	—	—	—	—	—	—	—	—		786
T-1399	15	246	13	233	20	21	53	40	45	—	—		2
T-1400	10	272	15	257	35	24	53	40	35	—	—		trace
T-1401	14	242	10	232	15	21	45	60	60	—	—		3
T-1402	15	1924	16	1908	35	40	588	100	120	0.02	0.0		0
T-1403	22	1234	45	1189	48	38	606	50	70	0.03	0.01		1
T-1404	13	1822	9	1813	61	40	674	40	60	0.0	0.0		trace
T-1405	—	4894	11	4883	1790	56	22	10000	8000	550.	0.0		35

T-1398	17	Inlet to Oily Process Separator	Composite	Shift 3
T-1399	18	Cooling Water Effluent to Creek	"	Shift 1
T-1400	19	" " " " "	"	Shift 2
T-1401	20	" " " " "	"	Shift 3
T-1402	21	Potentially Oily Separator Effluent	"	Shift 1
T-1403	22	" " " "	"	Shift 2
T-1404	23	" " " "	"	Shift 3
T-1405	24	#1 Crude Unit Desalter Wastewater	Grab	2:30 p.m. June 19

Shell Canada Limited
June 19, 20, 1968.