

Job Report

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Investigation of Southwestern Oil and Refinery's
Effluent and Disposal Area

Abstract: Southwestern Oil and Refinery, located at Corpus Christi, has a toxic waste present in its cooling water waste. The phenols, sulfides and oxygen demanding sludge are not sufficiently reduced by plant treatment methods to a concentration which can be tolerated by aquatic organisms. However, the waste flows through a series of earthen pits which allow additional oxidation of the chemicals, thereby decreasing the concentration of toxic compounds and increasing the median tolerance limit of the waste to 85 per cent. The toxic materials are reduced further by mixing with basin water in a retention pond in the harbor waste and the final waste is non-toxic to marine life in Corpus Christi harbor.

The API gravity separators in the plant do not retain waste oil efficiently. An emulsified oil, with a specific gravity approximately equal to water, forms by oil globules attaching to suspended solids in the water. This emulsion forms a heavy, oily sludge that flows out of the API separators, through the earthen pits and into the basin. This sludge has a high oxygen consuming value which reduces the dissolved oxygen content to a range of 0.0 ppm. to 2.9 ppm. at Station 2.

The company plans to reduce this oily sludge by saturating the effluent with oxygen in air tanks and releasing it through a perforated line into the earthen pits. This oxygen saturated waste will float the emulsified oil to the surface thereby increasing the skimming capacity of the pits.

Objective: To detect, measure and evaluate the toxic conditions of Southwestern Refinery's effluent and promote a better pollution abatement program.

Procedure: Four sampling stations were established as follows: Station 1 was the site where the effluent left the API separators; Station 2 was at the earthen skimming pits; Station 3 was the disposal area in the retention pond; and Station 4 was the entrance point into Corpus Christi harbor. The stations were sampled monthly and chemically analyzed in the laboratory for phenols, sulfides, oil and oxygen consumed. The analysis methods used are given in Standard Methods for the Examination of Water, Sewage and Industrial Wastes, Eleventh Edition. Dissolved oxygen and pH measurements were made in the field. Hydrogen ion concentration measurements were made with a Beckman, Model G, glass electrode meter. Since organic contaminants were known to be present, dissolved oxygen measurements were made by the Rideal Stewart Modification of Winkler Method.

Toxicity tests were made on the effluent, using bay water as the dilution medium. Samples of the effluent were collected in 5-gallon, polyethylene containers and stored until the sample reached room temperature. Test concentrations of effluent were mixed in 10-liter glass containers in a logarithmic series of 100, 32, 10 and 3.2 per cent. After an acclimatization period of 24 hours, five pinfish (Lagodon rhomboides) were placed in each of the containers and observed for a 24-hour period. When the per cent strength was established for 100 per cent deaths and no deaths, this range was reduced on a logarithmic scale, five fish were added and observed for 48 hours. A median tolerance limit (TLm), the concentration in which 50 per cent of a marine index species can survive for a 48-hour period, was then determined by plotting the dilution strength on the logarithmic scale of semi-log graph paper and the per cent of deaths on the arithmetic scale. A straight line was drawn through the maximal concentration (100 per cent deaths) and minimal concentration (no deaths), interpolating the TLm at the 50 per cent death level.

Aeration was supplied in the form of pure oxygen at the rate of 30 to 180 bubbles per minute so as not to release volatile substances present in the waste.

Bottom samples were collected, agitated, digested by blending, filtered and analyzed for toxic components.

Information on plant operations, production and waste disposal, was obtained from plant personnel.

Findings and

Discussion: Southwestern Oil and Refinery fractionates from 37,000 to 52,000 barrels of sweet and sour crude oil daily to produce fuels. Water, used in the process for cooling purposes, is obtained from the city. During refining operations, this cooling water collects some chemical components and is discharged at the rate of 250 gallons per minute into Corpus Christi harbor.

This cooling tower waste goes through two standard API design gravity separators. The waste continues flowing through a 24-inch line into a series of ten earthen skimming pits. After two hours in the pits, the waste flows into a three-acre retention pond formed in the harbor by a rock and earth wall. After mixing with basin water, the contents then flow into Corpus Christi harbor through a narrow opening in the retention pond wall.

Table 1 contains bi-monthly analytical values of the waste. The following observations are based on these values.

Samples collected at Station 1 contained an average of 36.0 parts per million (ppm.) oil. Bottom and surface scrapers in the API separators do not retain an emulsified, oily sludge which forms when oil globules in the pits attach to suspended solids in the water and obtain a specific gravity approximately equal to water. This agglomerate waste flows through the separators into the earthen skimming pits. The oil in waste samples collected at Station 2 averaged 25.0 ppm. Only 28 per cent of the oil leaving the API separators was skimmed by the earthen pits. The emulsified sludge flows through the earthen pits, covers the bottom of the retention pond and releases pools of oil upon agitation. This oily sludge has a high oxygen consuming demand and depletes the dissolved oxygen content in the water to a level below the survival limit of 4.0 ppm. The dissolved oxygen content at Station 2 ranged from 0 to 2.9 ppm. and from 1.8 to 3.4 ppm. at Station 3. When sludge collected at Station 3 was added at the rate of 2.0 grams per liter to bay water, with a dissolved oxygen content of 6.0 ppm., the dissolved oxygen content was reduced 15 per cent within 30 minutes (Table 2).

Southwestern plans to reduce this oily sludge by air flotation. In this method the waste waters and air are drawn into a centrifugal pump, which raises the pressure on the water to about 30 psi and forces the air into solution. The waste waters then pass directly to the flotation tank. The extremely fine air bubbles, caused by a frictional resistance of the most of the pressure of the psi, floats oil to the surface, where some type of skimmer collects and moves the oil to a discharge pit.

Phenols occur in the waste from decomposition of naphthenic acid in the catalytic cracker. Caustic washes are used to remove most of the phenols from the condensate but this method is not 100 per cent effective since concentrations ranging from 10 to 76 ppm. phenols were present in the effluent at Station 1. The concentration was reduced to an average of 20 ppm. at Station 2. This reduction may be attributed to biological treatment or oxidation by air in the earthen pits. Sheets, et al, reported that phenol resistant microorganisms were responsible for the destruction of phenols.

Sulfides are formed in the waste water when the sulfide ion in sour crude oil unites with the hydrogen ion in water. According to Water Quality Criteria, they are in the form of H_2S or HS and the proportion of each depends on the pH value. Thus, at pH 9 about 90 per cent of the sulfides present are in the form of HS . At pH 7 the sulfides are equally divided between the two forms. At pH 5, less than one per cent of the sulfides are present as HS . Consequently, aeration will allow H_2S to escape in the air.

The sulfides are stripped from the water with a steam stripper and caustic washes. The spent caustic is reclaimed and given to Columbia Southern Chemical Corporation for the sulfide content. Samples collected at Station 1 contained an average of 21.0 ppm. sulfides. The pH, ranging from 6.4 to 7.0, indicates the majority of sulfides were present in the H_2S form. The sulfide content was reduced to 3.0 ppm. at Station 2 and 0.0 ppm. at Station 3. This reduction is attributed to the retention time in the earthen pits allowing the excess sulfides to escape into the air.

Toxicity studies made of samples collected at Station 1 indicated the waste to be toxic to marine organisms. The average 48-hour TLm was 28 per cent. The toxicity of this waste is attributed to phenols, sulfides and Chemical Oxygen demand, being above the optimum concentration that is safe to aquatic life.

Oxidation of the toxic components and possibly biological treatment in the earthen pits reduced the average 48-hour TLm at Station 2 to 64 per cent.

The average 48-hour TLm at Station 3 was 85 per cent. However, this limit was determined in a laboratory study inducing oxygen into the test water. The dissolved oxygen content at the station was below the survival limit of 4.0 ppm. consistently. This low content is attributed to the oxygen consuming sludge from the plant that settles to the bottom within 25 yards of the outfall.

Excessive agitation and dilution of the waste with basin water increased the median tolerance limit to 100 per cent at Station 4.

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Reference

Water Quality Criteria, State Water Pollution Control Board, 1952, Sacramento, California.

Sheets, Waldron D., M. K. Hamby and H. H. Weiser, "Microbiological Studies on the Treatment of Petroleum Refinery Phenolic Wastes." Sewage and Industrial Waste, Vol. 26, No. 7.

Table 1
Chemical Analysis of Southwestern Oil and Refinery's Effluent

<u>Date</u>	<u>Station</u>	<u>Phenols</u> ppm	<u>Sulfides</u> ppm	<u>pH</u>	<u>Oil</u> ppm	<u>C. O. D.</u> ppm	<u>D. O.</u> ppm	<u>TLm</u> O/O
Jan.	1	43	26	6.8	40.8	360	0.0	35
	2	26	5	7.1	28.6	-	1.5	55
	3	5	0	7.3	15.7	-	2.9	90
	4	0	0	7.5	5.6	-	5.1	100
Feb.	1	84	18	6.4	23.5	489	0.0	31
	2	39	1	6.9	19.4	-	2.3	50
	3	9	0	7.1	18.6	-	3.4	85
	4	0	0	7.4	-	-	-	100
March	1	29	15	7.3	35.8	561	0.8	22
	2	11	4	7.2	22.6	472	2.9	65
	3	-	0	7.5	19.5	-	3.1	90
	4	-	0	7.5	0.0	-	-	100
April	1	40	29	6.6	20.4	-	1.1	14
	2	29	3	6.9	12.1	-	0.9	75
	3	-	0	7.2	10.9	-	2.8	100
	4	-	0	7.4	-	-	5.5	100
May	1	31	36	6.9	29.3	379	0.0	22
	2	14	2	6.9	14.5	-	0.0	80
	3	0	0	7.3	21.2	-	2.5	100
	4	0	0	7.5	-	-	-	100
June	1	38	24	6.4	31.6	561	0.0	30
	2	21	1	6.9	20.4	-	0.8	65
	3	6	0	7.1	15.1	-	2.3	85
	4	-	0	7.5	3.9	-	-	100
July	1	76	22	7.0	45.9	-	0.0	10
	2	41	3	7.2	30.8	-	2.1	85
	3	10	0	7.4	27.2	-	3.0	100
	4	-	0	7.4	-	-	5.9	100
Aug.	1	51	17	6.8	56.5	349	0.0	21
	2	28	2	7.1	42.4	-	0.0	75
	3	-	0	7.2	31.5	-	1.7	80
	4	-	0	7.4	4.8	-	5.0	100
Sept.	1	27	23	6.7	51.2	-	0.0	25
	2	8	5	6.9	42.9	-	1.5	60
	3	0	0	7.2	30.6	-	2.9	65
	4	0	0	7.4	-	-	-	100

Table 1--Continued

<u>Date</u>	<u>Station</u>	<u>Phenols ppm</u>	<u>Sulfides ppm</u>	<u>pH</u>	<u>Oil ppm</u>	<u>C.O.D. ppm</u>	<u>D.O. ppm</u>	<u>TLm O/O</u>
Oct.	1	10	19	6.9	26.5	419	0.0	52
	2	0	4	7.1	15.6	-	1.9	40
	3	-	0	7.3	14.9	-	3.1	65
	4	-	0	7.3	-	-	-	100
Nov.	1	18	20	6.8	35.4	-	0.0	46
	2	3	3	7.1	25.8	-	2.0	55
	3	0	0	7.3	21.2	-	3.4	75
	4	-	0	7.5	-	-	-	100

Table 2
Oxygen Consumed by Bottom Sludge

<u>Concentration g/l</u>	<u>Dissolved Oxygen Values</u>		<u>Time (Minutes)</u>
	<u>Before Add.(ppm)</u>	<u>After Add.(ppm)</u>	
0.5	6.0	6.0	15
0.5	6.0	5.8	30
1.0	6.0	5.4	15
1.0	6.0	5.4	30
2.0	6.0	5.3	15
2.0	6.0	5.1	30