Job Report

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Investigation of Delhi-Taylor Refinery's Effluent and Disposal Area

Abstract: Delhi-Taylor Refinery's waste is harmful or fatal to fish by the presence of a toxic amount of phenolic compounds and sulfides in the wastes. The waste also contains a high oxygen consuming sludge that depletes the dissolved oxygen in the water to such an extent that asphyxiation may result.

The median tolerance limit of phenols to aquatic life was found to be 14.5 parts per million (Job No. F-1, 1959). The phenol concentration was never below 19.0 ppm. at Station 3, but decreased rapidly after entering the harbor. Sulfides reduced the tolerance significantly at Station 1, but aeration by agitation in the ditch prior to disposal reduced the sulfides to an average of 0.8 ppm. before entering the harbor. The concentration was always less than 1.0 ppm. in the harbor.

Oil globules collect to suspended particles in the API separators obtaining a specific gravity nearly equal to water. The stringy, flocculent, emulsified sludge is not retained in the separators and flows out with the cooling water. This agglomerate waste tends to settle within 25 yards of the disposal area, presenting a threat to aquatic life by decreasing the dissolved oxygen content and covering the bottom with oil.

An area diked off in the harbor at the disposal site and used as a retention pond would retain this agglomerate waste. It would also restrict the contaminants in the water from dispersing in the harbor and provide suitable dilution of the waste. In this way the toxicity would be reduced.

Objectives: To detect, measure and evaluate Delhi-Taylor Refinery's waste for toxic components. Data gathered will be used to promote a pollution abatement program.

Procedure: Four stations were established in the disposal area and effluent route as follows: Station 1 was in the effluent route after leaving the API separators; Station 2 was midway between the API pits and the disposal entrance into the harbor; Station 3 was in the effluent route prior to disposal into the harbor; and Station 4 was 25 yards from the effluent outfall into Corpus Christi harbor. These stations were sampled twice a month, in 250 milliliter glass containers, preserved and chemically analyzed in the laboratory for phenols (4-aminoantipyrine method), sulfides, oil and oxygen consumed according to Standard Methods for the Examination of Water, Sewage and Industrial Waste, 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 concentration was conducted by the Rideal-Stewart modification of Winkler Method.

Toxicity studies were conducted on the effluent using bay water as the dilution medium. Samples of the effluent were collected in five gallon, polyethylene containers and stored in the laboratory until the samples 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 container 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 added and observed for 48 hours. A median tolerance limit (TLm), the concentration in which 50 per cent of a marine index (Pinfish) can survive for a 48-hour period, was then determined by plotting on semilog graph paper the dilution strength on the logarithmic scale 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 from a cylinder at the rate of 30 to 180 bubbles per minute.

Bottom samples of the disposal area were collected, weighed and placed in 10-liter containers of bay water with a known oxygen content. Dissolved oxygen tests were made after a 15- and 30-minute period to determine the oxygen consumption value of the sludge.

Samples of the waste oil sludge were collected, agitated for 30 minutes and analyzed for oil content.

Information on plant operations, production and waste disposal, were obtained from plant personnel and from personal observation.

Findings and Discussion: Delhi-Taylor Refinery processes 45,000 barrels a day of sweet and sour crude petroleum to produce butane, premium and regular grade gasoline, jet fuel, kerosene, diesel and hearing oils, carbon black, benzene, toulene, xylene and aromatic solvents. The process wastes are treated in two API separators. Sanitary wastes are treated separately and are confluent with the process waste. The combined wastes consist primarily of emulsified hydrocarbons and chemical wastes not separated by gravity.

Phenolic compounds are produced in the waste by decomposition of naphthenic acid in the catalytic cracker condensate. Sulfides occur in the waste from the sulfur present in sour crude petroleum. Caustic washes and steam strippers remove most of the phenols and sulfides from the cracked gasoline. The spent caustic is then given to a neighboring industry for the sulfide content.

The combined wastes flow through an open ditch for one mile before emptying into Corpus Christi harbor.

The largest concentration of toxic components occurs at Station 1. Phenols averaged 31.9 ppm. and ranged from 16.0 to 45.0 ppm. (Table 1). The pH was alkaline at 8.9. Sulfides were exceptionally high, averaging 14.1 ppm. and ranging from 9.0 to 33.0 ppm. Oil concentration averaged 32.9 ppm. This average does not include the concentration in November when one of the separator units was closed for repairs. This caused an overload on the other unit increasing the oil content to 181.0 ppm. The chemical oxygen demand (C.O.D.) average was 482 ppm. and the dissolved oxygen readings were consistently 0.0 ppm.

The waste water is black and turbid and has a pungent hydrocarbon odor. Stringy, flocculent sludge particles saturate the banks with oily deposits.

Samples collected at Station 2 contained an average of 25.0 ppm. phenols ranging from 2.0 to 34.0 ppm., 7.3 ppm. sulfides ranging from 5.0 to 14.0 ppm., 23.2 ppm. oil, 432.0 ppm., C.O.D. and 0.8 dissolved oxygen. The pH remained alkaline at 8.9.

The waste at this station flows over a mass of rocks added to the creek to reduce erosion and agitate the waste. This excessive aeration oxidizes the toxic chemicals with air and reduces their concentration. The water remains black and turbid and the pungent smell is enhanced by the agitation which releases some of the sulfides present.

At Station 3, the waste flows through a wide, shallow cement culvert for 50 yards prior to disposal. The waste is diluted with bay water by tidal fluctuation, reducing the toxic components to an average of 26.8 ppm. phenols, 16.7 ppm. oil and 286 ppm. C.O.D. The dissolved oxygen content was increased to an average of 3.0 ppm.

The waste dissipates rapidly upon entering the harbor. Station 4 was set up to measure the dispersion distance. Phenols were restricted to within 25 yards of the outfall, with a maximum concentration of 5.0 ppm. Sulfides decreased rapidly to 0.8 ppm., within 10 yards from the outfall. The pH averaged 7.5, the C.O.D. averaged 262 ppm. and the dissolved oxygen averaged 3.4 ppm.

Laboratory studies of bottom samples collected in the area of disposal showed a 23 per cent decrease in dissolved oxygen when added to bay water which has 5.8 ppm. dissolved oxygen (Table 2). The dissolved oxygen readings of the water at Station 4 showed a 46 per cent reduction as compared to readings away from contamination.

Pools of oil were released to the surface while collecting the bottom samples. The stringy, flocculent waste seemed to settle out of the water within 25 yards of the outfall. Ten grams of the emulsified oil agglomerate agitated in one liter of bay water for 30 minutes showed 21.0 ppm. oil present.

Bio-assay studies at Station 3 indicate the waste to be toxic to aquatic organisms. The increase and decrease in TLm values coincide with the increase and decrease in all chemical components. However, the most notable fluctuation in the tolerance is compared with phenol concentration. Table 1 shows that in August the phenol content was 36.0 and the 48-hour TLm was 30 per cent. In January and June the 48-hour TLm increased to 75 and 55 per cent and the phenol content was 19 and 16.0 ppm., respectively. Comparable to this fluctuation are the TLm values and the sulfide content at Station 1. In May the sulfide content was 33.0 ppm. and the 48-hour TLm value was 35 per cent. In October when the sulfide content was 9.0 ppm., the 48-hour TLm value was 70 per cent.

The area of contamination in the harbor seems to be restricted to a distance of 25 yards. Bottom contamination may exceed this distance since samples were not collected beyond this point because of water depth. A rock or earth wall enclosing this area would retain the oily sludge and dilute the chemical wastes sufficiently to render the waste non-toxic.

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Table 1
Refinery Waste Water Analytical Data

Month	Phenols (ppm)	Sulfides (ppm)	Oil (ppm)	C.O.D. (ppm)	Dissolved Oxygen (ppm)	pH	48hrTLm (%)
Station 1							
January	31.0	14.0	35.0	494	0.0	8.9	25
February	----	12.0	29.0	---	0.0	8.9	--
March	45.0	----	28.0	---	0.0	8.7	--
April	----	----	36.0	---	0.0	---	--
May	34.0	33.0	42.0	481	0.0	8.8	35
June	16.0	----	19.0	---	0.0	---	55
July	29.0	14.0	24.0	---	---	---	--
August	36.0	9.0	26.0	---	---	---	30
September	----	12.0	62.0	472	---	8.7	--
October	21.0	9.0	28.0	---	0.0	---	70
November	43.0	10.0	181.0	---	0.0	---	--
Average	31.9	14.1	32.9	482			
Station 2							
January	24.0	8.0	29.0	429	0.8	8.8	65
February	----	9.0	21.0	---	0.9	8.8	--
March	29.0	----	18.0	---	1.2	8.5	--
April	----	----	25.0	---	0.6	---	--
May	32.0	14.0	34.0	419	0.9	8.4	50
June	12.0	----	10.0	---	0.6	---	45
July	12.0	----	10.0	---	0.6	---	45
August	31.0	7.0	20.0	---	---	---	--
September	----	10.0	48.0	450	---	8.9	--
October	25.0	5.0	15.0	---	0.5	---	60
November	34.0	8.0	160.0	---	0.8	---	--
Average	25.0	7.3	23.2	432			
Station 3							
January	19.0	1.0	28.0	296	2.8	7.6	75
February	24.0	1.0	15.0	---	2.9	7.7	--
March	27.0	----	21.0	---	3.0	7.5	--
April	25.0	----	24.0	220	3.1	---	60
May	31.0	0.9	26.0	---	2.9	7.8	--
June	16.0	----	10.0	---	2.4	---	55
July	30.0	5.0	9.0	331	---	---	--
August	36.0	3.0	14.0	---	---	7.4	30
September	24.0	1.0	8.0	---	---	---	85
October	36.0	2.0	12.0	296	3.9	---	--
November	27.0	0.6	100.0	---	---	---	--
Average	26.8	1.8	16.7	286			
Station 4							
January	3.0	0.5	12.0	---	4.0	7.3	100
February	----	0.8	9.0	321	3.9	7.1	100

Table 1--Continued

Station 4

Month	Phenols (ppm)	Sulfides (ppm)	Oil (ppm)	C.O.D. (ppm)	Dissolved Oxygen (ppm)	pH	48hrTLm (%)
March	----	---	9.0	---	3.5	---	100
April	4.0	---	---	246	3.4	---	--
May	5.0	0.0	---	---	---	---	--
June	2.0	0.0	0.0	---	3.1	7.5	--
July	----	---	0.0	---	3.0	---	--
August	----	---	---	---	---	---	--
September	6.0	0.5	---	219	2.9	7.4	100
October	----	0.0	---	---	---	---	--
November	----	---	95.0	---	---	---	--
Average	4.0	0.6	10.0	262			

Table 2
Oxygen Consumed by Bottom Sludge

Concentration (gie)	Dissolved Oxygen Values Before Add.(ppm)	After Add.(ppm)	Time (minutes)
0.5	5.8	5.7	15
0.5	5.8	5.4	30
1.0	5.8	5.1	15
1.0	5.8	4.9	30
2.0	5.8	4.5	15
2.0	5.8	4.1	30

Figure 1
Bio-Assay of Pinfish in a Phenol Solution