

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT

EPA-330/2-80-025

EVALUATION OF PROCESS WASTEWATER SOURCES,
WASTE TREATMENT, AND DISPOSAL SYSTEMS

SCM GLIDDEN-DURKEE, ADRIAN-JOYCE WORKS

Baltimore, Maryland

July 1980

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
Denver, Colorado



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METRIC/ENGLISH CONVERSIONS

	<u>Metric Unit</u>	<u>multiplied by</u>	<u>English Unit</u>
Length	millimeters (mm)	0.0394 → ← 25.4	inches (in)
	centimeters (cm)	0.3937 → ← 2.54	inches (in)
	micrometers (um)	3.937×10^{-5} → ← 2.545×10^{-4}	inches (in)
	meters (m)	3.281 → ← 0.3048 1.0936 → ← 0.9144	feet (ft) yards (yd)
	kilometers (km)	0.6214 → ← 1.6093	miles (mi)
Area	square centimeters (cm ²)	0.155 → ← 6.452	square inches (in ²)
	square meters (m ²)	10.76 → ← 0.0929 1.196 → ← 0.8361	square feet (ft ²) square yards (yd ²)
	square kilometers (km ²)	0.3861 → ← 2.590 247.1 → ← 4.0469×10^{-3}	square miles (mi ²) acres
	hectares (ha)	2.471 → ← 0.4047	acres
	cubic centimeters (cm ³)	0.0610 → ← 16.39	cubic inches (in ³)
Volume	cubic meters (m ³)	35.31 → ← 0.0283 1.3079 → ← 0.7646	cubic feet (ft ³) cubic yards (yd ³)
	liters (l)	1.057 → ← 0.9461 0.2642 → ← 3.785 0.0353 → ← 28.32	quarts (qt) gallons (gal) cubic feet (ft ³)
	meters/second (m/sec)	3.281 → ← 0.3048 2.237 → ← 0.447	feet/second (ft/sec) miles/hour (mph)
	kilometers/hour (km/hr)	0.6214 → ← 1.609 0.5396 → ← 1.853	miles/hour (mph) knots (kn)
	cubic meters/second (m ³ /sec)	35.31 → ← 0.0283 1.585×10^4 → ← 6.31×10^{-5} 22.883 → ← 0.0437	cubic feet/second (cfs) gallons/minute (gpm) million gallons/day (mgd)
Flow	cubic meters/day (m ³ /day)	0.1835 → ← 5.4504 2.64×10^{-4} → ← 3785 4.086×10^{-4} → ← 2450 8.11×10^{-6} → ← 1230	gallons/minute (gpm) million gallons/day (mgd) cubic feet/second (cfs) acre-feet/day (afd)
	grams (g)	0.0353 → ← 28.3495 2.205×10^{-3} → ← 453.59	ounces (oz) pounds (lb)
Weight	metric tons (m tons)	1.102 → ← 0.9072 2205 → ← 4.535×10^{-4}	short tons (tons) pounds (lb)
	kilograms/sq centimeter (kg/cm ²)	14.22 → ← 0.0703	pounds/square inch (psi)
Temperature	° Celsius (°C)	$9/5 (°C) + 32$ → ← $5/9 (°F - 32)$ $9/5$ (absolute) → ← $5/9$ (absolute)	° Fahrenheit (°F)

I. INTRODUCTION

On January 22 to 25 and February 20 to 22, 1980, personnel from the National Enforcement Investigations Center (NEIC) and the State of Maryland Water Resources Administration conducted a plant inspection of process wastewater sources, wastewater treatment and disposal systems, and solid and hazardous waste disposal practices at the SCM Glidden-Durkee Adrian-Joyce Works near Baltimore, Maryland [Figure 1]. The Adrian-Joyce Works is operated by the Glidden Pigments Group of the Chemical and Metallurgical Division of SCM. The facility manufactures titanium dioxide (TiO_2) by the sulfate and chloride processes.

Titanium dioxide, a high-volume chemical ranking within the first fifty of all U.S. chemical production, is manufactured domestically by six companies in eleven plants [Table 1]. Over 50% of the TiO_2 produced is used in paints, varnishes, and lacquers. About one-third is used in the paper and plastics industries. Other uses are found in ceramic, ink, and rubber manufacturing.

Waste streams from the chloride process fall into two categories: (1) chlorination wastes composed of sludge from titanium tetrachloride production, and (2) wastes incurred during the oxidation process and milling of the TiO_2 product. The sulfate process has a very heavy water-borne waste load consisting of about 2,000 lbs of sulfuric acid and 1,000 lbs of metal sulfates per 1,000 lbs of product. Waste streams generated in the sulfate process include: (1) sludge from the digestion and subsequent filtration of the ore, (2) copperas, (3) strong acid cuts, (4) weak acid cuts, and (5) titanium dioxide losses. The sulfate process wastewater is the more difficult to treat due to impurities from the lower-grade ores and the volumes of sludge and gypsum produced in wastewater neutralization.

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TABLE 1
U.S. TITANIUM DIOXIDE PRODUCTION FACILITIES

Company	Location	Process
American Cyanamid Co.	Savannah, George	Sulfate and chloride
E.I. DuPont deNemours & Co. Inc.	Antioch, California	Chloride
	DeLisle, Mississippi	Chloride
	Edge Moor, Delaware	Chloride
	New Johnsonville, Tennessee	Chloride
Gulf & Western Industries, Inc.	Ashtabula, Ohio	Chloride
	Gloucester City, New Jersey	Sulfate
Kerr-McGee Corporation	Hamilton, Mississippi	Chloride
N.L. Industries, Inc.	Sayerville, New Jersey	Sulfate
SCM Corporation	Ashtabula, Ohio	Chloride
	Baltimore, Maryland	Sulfate and chloride

On March 12, 1974, effluent limitations for the Inorganic Chemicals Manufacturing Point Source Category were published in the Federal Register by the U.S. Environmental Protection Agency. Titanium dioxide effluent limitations were included as a subcategory [Table 2]. The American Cyanamid Company in Savannah, Georgia was the first TiO_2 manufacturer to build treatment facilities which produced an effluent that complied with the limitations. The treatment system produced gypsum as a byproduct of the neutralization step. White gypsum (contains very little impurities) is recovered in the first neutralization step (pH 4.5) and red gypsum (contains high levels of impurities) is recovered in the neutralization from pH 4.5 to 7. The red gypsum to date has no market value and presents a disposal problem. Although a market for white gypsum for use as wallboard was being developed, the cost of natural gypsum was so low as to suppress the synthetic gypsum market. Therefore, the white gypsum and red gypsum are being stockpiled onsite in Savannah. However, Cyanamid has recently made arrangements with Lemco, Inc. for the sale of the gypsum.*

On March 10, 1976, the United States Court of Appeals for the Fourth Circuit decided in *E.I. DuPont de Nemours and Company, et al v. Train* (No. 74-1261) to set aside and remand for reconsideration a number of general definitions and specific discharge regulations promulgated in 1974. The TiO_2 subcategory was included in the Court's remand.

N.L. Industries, Gulf & Western, and SCM Glidden-Durkee did not install best practicable control technology currently available (BPT) for the sulfate processes and missed the July 1, 1977 compliance date. To date, neither N.L. nor Gulf & Western have installed treatment systems. N.L. continues to barge process wastes from Sayerville, New Jersey to the ocean for disposal. Gulf & Western discharges raw wastes to a slip (which is subject to daily tidal flooding), then to the Delaware River. SCM Glidden-Durkee developed and installed a neutralization-filtration treatment system for the sulfate wastes, but Discharge Monitoring Reports (DMR's) submitted by the Company showed that the effluent was not in compliance with the NPDES permit limitations.

* Chemical Week Technology Newsletter, August 29, 1979.

Table 2
EFFLUENT LIMITATIONS FOR TITANIUM DIOXIDE INDUSTRY^a
March 12, 1974

	BPT ^b (lb/1,000 lb)	BAT ^c and NSPS ^d (lb/1,000 lb)
Chloride Process		
Total Suspended Solids	4.4	2.6
Iron	0.72	0.36
pH	within range 6.0 to 9.0	within range 6.0 to 9.0
Sulfate Process		
Total Suspended Solids	21	10.6
Iron	1.68	0.84
pH	within range 6.0 to 9.0	within range 6.0 to 9.0

a Remanded by the United States Court of Appeals for the Fourth Circuit, March 10, 1976.

b Best practicable control technology currently available.

c Best available technology economically achievable.

d New source performance standards.

In August 1978, the State of Georgia and American Cyanamid entered into a consent decree whereby the effluent limitations were relaxed and the Company agreed to pay the State \$500/day for each day the effluent total iron exceeds 510 lbs but does not exceed 60,000 lbs. If the total iron exceeds 60,000 lbs, the Company pays a surcharge based on the amount discharged. This consent decree was granted because American Cyanamid was the only Company meeting BPT and was absorbing unit wastewater costs that were significantly greater than those encountered by the other companies.

The long-term outlook for titanium dioxide is for modest growth, based mainly on its established uses as a pigment in paint and other coatings, paper, and plastics. TiO_2 prices are less than twice the level of 1970, despite soaring increases in all costs.*

The Director of the Enforcement Division of EPA Region III requested that NEIC investigate the process waste discharges from the Adrian-Joyce Works and determine what treatment technology is needed to meet the final permit limitations. The NPDES permit [Table 3] for this facility was based on best engineering judgment pursuant to Section 402 (a)(1) of the Federal Water Pollution Control Act PL 92-500 because there were no guidelines for the industry.

The specific objectives of the NEIC inspection were to:

1. Investigate processes to determine sources of process waste.
2. Evaluate the adequacy of wastewater treatment facilities to determine the capability of meeting the permit limitations.
3. Recommend effluent limitations for the second round NPDES permit.
4. Determine the treatment technology available to meet second round permit limitations.

* Chemical Week, May 21, 1980, page 25.

TABLE 3
NPDES PERMIT LIMITATIONS
Total Discharge for Outfalls 001 Plus 002
SCM GLIDDEN-DURKEE
ADRIAN-JOYCE WORKS
July 1, 1977 - June 27, 1979

Effluent Characteristic	Discharge Limitations				Monitoring Requirements	
	kg/day (lb/day)		Other Units		Measurement Frequency	Sample Type
	Daily Avg	Daily Max	Daily Avg	Daily Max		
Flow - m ³ /day (mgd)	N/A	N/A	N/A	N/A	Continuous	Recorded
Total Suspended Solids	1,960 (4,320)	2,948 (6,500)	N/A	N/A	1/2 day	24-hr Comp.
Total Iron	550 (1,212)	825 (1,818)	N/A	N/A	1/2 day	24-hr Comp.
Temperature	N/A	N/A	N/A	110°F	Continuous	Recorded

The pH shall not be less than 6.0 standard units nor greater than 9.0 standard units and shall be monitored continuously and recorded.

II. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

On January 22 to 25 and February 20 to 22, 1980, personnel from the NEIC and State of Maryland Water Resources Administration conducted an investigation of the SCM Glidden-Durkee Adrian-Joyce Works operations. The investigation consisted of discussing processes and waste disposal practices with Company representatives and verifying the information by touring the plant, treatment facilities, and disposal areas. The information developed was used to provide the rationale for limitations for the second round NPDES permit, and to determine treatment needs to bring the wastewater effluents into compliance with these limitations.

CONCLUSIONS

The acid-bearing wastewater from the sulfate process can be effectively treated by neutralization and clarification in the PWAN/SWAN* facility provided that the system is not overloaded due to increased production. The effluent quality deteriorates with high production. There is insufficient capacity in the batch attack lagoon (flow equalization pond) to control flow to the PWAN/SWAN reactors and final clarifier. If high production is intermittent, an acceptable effluent can be produced if the batch attack lagoon capacity is increased. If high production becomes continuous, then the PWAN/SWAN reactors and clarifier systems must be expanded.

The wastewaters discharged from Outfall 001 will not comply with effluent limitations without treatment. The discharge in itself exceeds

* Primary Waste Acid Neutralization/Secondary Waste Acid Neutralization.

the allowable load for iron and TSS for all effluents. The only treatment provided is pH adjustment which is not always effective. Due to the high concentrations of iron and TSS contributed by processes and runoff, compliance cannot be achieved without either removing and treating all contaminated waste streams discharged to the Outfall 001 line or by treating the entire flow discharged from 001. The iron must be oxidized to the ferric form and removed with the solids prior to discharge. The existing baffled, concrete basin through which the 001 waste stream flows does not provide adequate sedimentation. Therefore, iron oxidation is necessary and either a clarifier must be installed or the effluent must be rerouted to the 002 lagoon system for sedimentation. Better pH control is also required to meet limitations and to promote the oxidation of the iron.

Outfall 002 contains all the process wastewaters from the chloride area plus additional flows from the sulfate finishing area. The acidic chloride process wastewaters are partially neutralized in a pit containing aragonite, then flow through two lagoons (upper and lower lagoons) prior to discharge. Between the lagoons, caustic is added for pH control. The lower lagoon has recently been partially dredged and is being used for clarification. However, the data submitted by the Company after dredging of the lagoons indicate that sedimentation alone will not bring the effluent into compliance. The iron concentrations are excessive (210 mg/l average). Because the pH frequently is less than 6.0, oxidation of iron was significantly impaired. The pH must be kept above 6.5. If iron oxidation is not adequate through pH adjustment, chemical removal or aeration will be required to reduce the concentration.

The solids load can be reduced by recovering coke and ore from the chloride process waste streams. The Company has indicated that this can be done, but wants to determine if the lagoon system can reduce the load significantly to achieve compliance.

According to an EIMCO study for the Company, solids settle well if a polymer is added to the wastewater. Since the lower lagoon provides sufficient surface area for sedimentation, the effluent from 002 should meet limitations if treatment systems are operated properly.

The Company has developed a treatment system for the process wastewater from the sulfate operations. However, the other wastewaters have not received the same effort in developing adequate treatment. The Company cannot consider the other waste streams as inconsequential and only provide minimal treatment. Outfalls 001 and 002 waste streams contain high concentrations of iron and solids, are low in pH, and cannot be discharged without treatment if compliance is to be achieved.

RECOMMENDATIONS

The second round NPDES permit should be based on the EPA's Effluent Guidelines for the titanium dioxide industry. These limitations were proposed in the Federal Register in June 1980. The SCM Glidden-Durkee Adrian-Joyce Works can achieve compliance with these limitations if the wastewaters from Outfall 001 and 002 are neutralized and clarified.

Based on these limitations, the allowable net loads for the total of Outfalls 001 and 002, and the effluent from PWAN/SWAN should be the following:

	30-Day Average lb/day	Daily Maximum lb/day
Total Suspended Solids	9,510	34,800
Total Iron	380	1,300
pH	6.0 - 9.0	

The average limitations correspond to TSS and iron concentrations of 57 mg/l and 2.3 mg/l, respectively, on a net basis with the current wastewater flows. Based on data supplied by the Company, the gross concentrations of TSS and iron in the effluent would average 97 mg/l and 10.3 mg/l, respectively.

III. PROCESS DESCRIPTION, WASTEWATER SOURCES, AND TREATMENT

CHRONOLOGY OF COMPANY'S TiO₂ PRODUCTION

In 1933 the American Zirconium Corporation was formed through a joint venture between Glidden Company and Metal & Thermit to produce titanium dioxide pigment. Glidden assumed responsibility for the operations, management, and sales of the joint effort. Metal & Thermit provided a portion of the investment and participated in policy formulation. In the early 1940s, Glidden purchased Metal & Thermit's interest in the joint venture and began operating it as the St. Helena pigment plant of the Glidden Company.

The initial rated capacity of the St. Helena plant was 6,000 tons of TiO₂ annually. Incremental expansion resulted in a capacity of 18,000 tons by 1950. By 1956, a completely new production facility was brought on-stream because of the need for additional capacity and due to technological improvements made in the industry. The new facility (the Adrian-Joyce Works) [Figure 1], which occupies 135 acres, was the last sulfate process TiO₂ plant built in the United States and had a rated annual capacity of 15,000 tons. Soon after startup of the new facility, the St. Helena facilities were phased out and capacity at the Adrian-Joyce Works was expanded. Production of TiO₂ at St. Helena ceased after 1958; by that time the annual capacity at the Adrian-Joyce Works had reached 35,000 tons. In 1962, another expansion raised the rated capacity to 48,000 tons/yr.

The chloride process for producing TiO₂ was gaining acceptance by the industry because of the pollution control problems associated with the sulfate process. In the late 1960s, Glidden purchased the chloride process technology from the Kerr-McGee Corporation and started construction of a second plant at the Adrian-Joyce Works. The new chloride facility went on-stream in 1969.

In October 1974, the Sherwin-Williams TiO_2 plant in Ashtabula, Ohio was purchased by Glidden. It was built in 1969 using DuPont's chloride process technology, and produces only rutile TiO_2 pigment. This was the only license granted by DuPont for the use of their chloride process.

The DuPont oxidation process was incorporated into the chloride process at the Adrian-Joyce Works in the mid 1970s and the Kerr-McGee oxidation process was phased out. However, the Kerr-McGee chlorination process is still used.

SCM Glidden-Durkee's planned addition of 10,000 tons/yr of chloride process titanium dioxide in Baltimore will enhance its second place standing among U.S. producers. The additional capacity, to be completed around July 1981, will raise the Company's chloride process capacity to 84,000 tons/yr, and increase its total capacity to 135,000 tons/yr. The sulfate and chloride TiO_2 capacities at Baltimore are currently 51,000 and 32,000 tons/yr, respectively. The Ashtabula plant has a chloride TiO_2 capacity of 42,000 tons/yr.*

Because SMC Glidden-Durkee officials requested that detailed process descriptions and wastewater treatment methods be considered CONFIDENTIAL, the processes are described in general to define where waste streams originate. The treatment of the sulfate process wastewater streams is also discussed in general terms. The Company officials answered all questions concerning waste sources, treatment processes, and provided data to NEIC personnel.

Titanium Dioxide Production

Titanium dioxide occurs naturally in three crystalline forms; anatase, brookite, and rutile. These crystals are substantially pure titanium dioxide but usually contain impurities, such as iron, which give them a

* Chemical Week, May 21, 1980, page 25.

dark color. Brookite is rare and the crystalline structure is orthorhombic (three unequal axes at right angles to each other). Anatase and rutile are tetragonal (three axes at right angles and the two lateral axes equal), but are not isomorphous (identical or like form). Rutile forms slender, prismatic crystals, and anatase usually occurs in near-regular octahedra.

Titanium dioxide pigments are manufactured by the sulfate and chloride processes. In the sulfate process, the essential step is hydrolysis, under carefully controlled conditions, of an acid solution of titanyl sulfate, followed by calcination and milling of the hydrous precipitate. In the chloride process, the essential step is the burning of titanium tetrachloride in oxygen to yield titanium dioxide and chlorine.

The raw material for the sulfate process is ilmenite ore or ferrous titanate ($\text{FeO} \cdot \text{TiO}_2$) or Quebec Iron and Titanium Corporation (QIT) slag. The ilmenite ore contains around 60% TiO_2 and the QIT slag contains about 72% TiO_2 . The raw material for manufacturing titanium tetrachloride is mineral rutile which is essentially pure titanium dioxide. The relative abundance of ilmenite compared with rutile makes beneficiation of the former attractive. Beneficiation is the removal of part of all of the iron from the ilmenite, leaving a product soluble in sulfuric acid, or which can be chlorinated economically.

PROCESS DESCRIPTION AND WASTEWATER SOURCES

Sulfate Process [Figure 2]

Raw material is stored outside behind a wooden wind screen. Runoff from the storage area and adjacent plant grounds is collected in drainage channels and discharged through Outfall 001. The ore or slag is dried in driers fueled by No. 2 fuel oil and then ground in ball mills. The gas stream from the driers passes through baghouses (one baghouse for each drier); recovered material is returned to the driers. Coarse material from the ball mills is returned to the feed end of the mills and the fines are digested in the batch attack vessels (digesters) with sulfuric acid. The

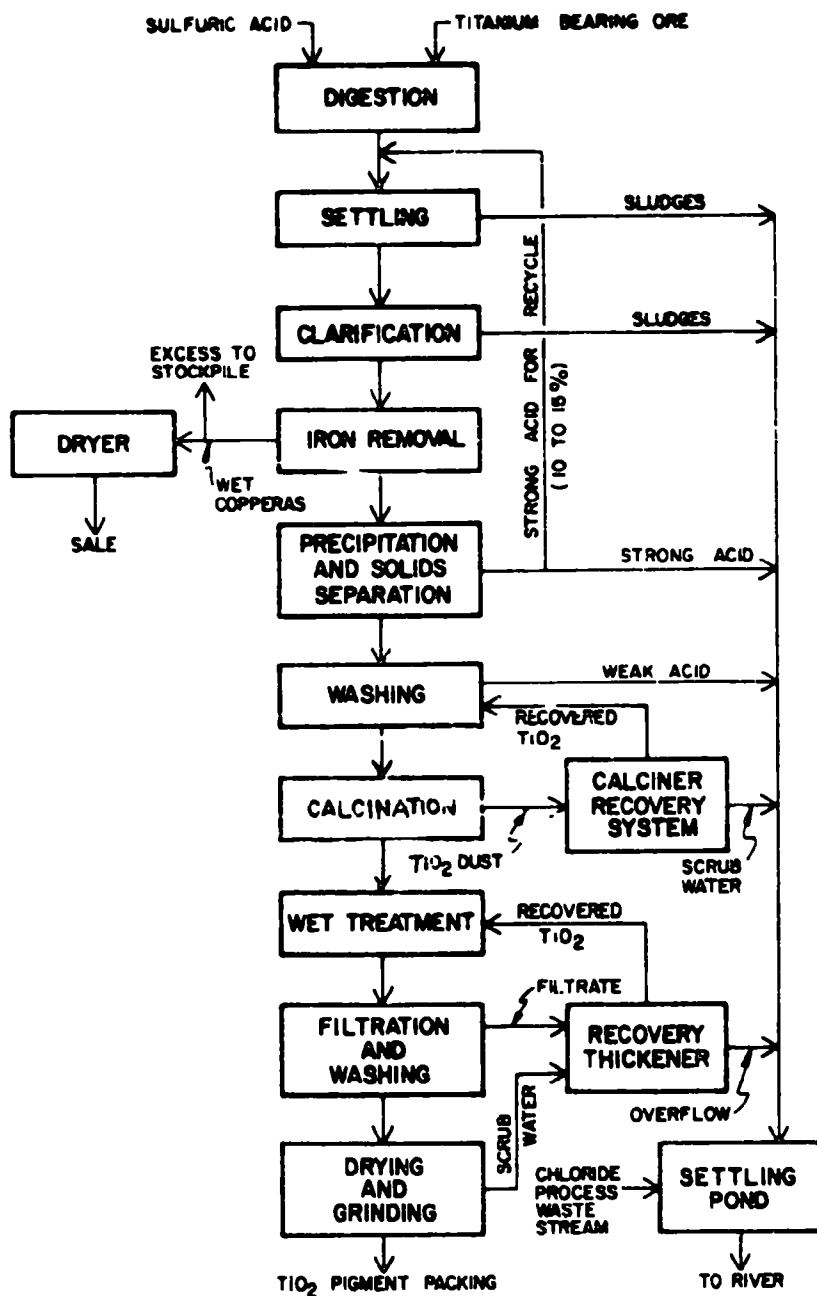


Figure 2.
Typical Sulfate Process Flow Diagram
For TiO_2 Industry

mixture of ground ore and sulfuric acid is agitated by an air stream, with live steam blown in. When the temperature reaches about 160°C (320°F), a violent exothermic reaction occurs and the mixture is converted to a porous cake containing ferric, ferrous, and titanium sulfates. The digesters are vented through a manifold system to one of two scrubbers, operated in parallel. Each scrubber uses river water on a once-through basis. The scrubbers are manually turned on for the critical exothermic reaction period which lasts about 30 minutes. About 6,000 gal/min of river water is pumped into the scrubber during the critical reaction; this flow rate currently causes a hydraulic problem as the pumping capacity cannot maintain the high pumping rate. The scrubber water is discharged from Outfall 001 for a period of 15 to 30 minutes. The Company plans to install a 28,000 gal holding tank to recycle the scrubber water.

The porous cake is extracted with water or dilute sulfuric acid and the ferric iron in solution is reduced to ferrous by means of scrap iron. Reduction is carried to the point where some trivalent titanium is present in order that all the iron is kept in the ferrous state during subsequent handling of the liquor.

Sedimentation then follows in covered clarifiers to remove insoluble residues remaining after digestion. In the clarification process, hydrogen sulfide (H_2S) is liberated and collected in a manifold system vented to a low-rate continuous scrubber. Sodium hydroxide (NaOH) is used for scrubbing and is recycled through the scrubber; the bleed-off is discharged to Outfall 001. The "bottom mud" or underflow from the clarifiers is washed and dewatered on precoated rotary filters. The filter solids (gangue solids) are landfilled on Company-owned land, about 3 miles from the plant site. The filtrate is sent to the feed tank for the vacuum crystallizers along with the "black solution" or clarifier overflow. Spills from the clarification process flow to the batch attack lagoon.

Much of the iron present in the black solution is removed by crystallization as copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in the vacuum crystallizers; the solution is chilled to approximately 10°C. A steam jet booster evacuator

pulls a vacuum on the crystallizer. The condensate is discharged to Outfall 001. After crystallization, the black solution is washed and filtered; the filter cake is copperas which is stored on a pad onsite until shipped. Drainage from the pad is collected in a sump and pumped to the batch attack lagoon.

Water is removed from the black solution (copperas filtrate) in three Struthers-Wells Concentrators which use steam jet evacuators; the condensate is discharged to Outfall 001. After concentration, the black solution is filtered in pressure filters; the filter residue is combined with the gangue solids and sent to the landfill.

The next stage, precipitation of the titanium as hydrous titanium dioxide by hydrolysis, is the most critical one in the entire process. Ferric iron cannot be present in solution. The precipitation is accomplished under controlled conditions so that the precipitate can be readily filtered and washed and, upon subsequent calcination, give crystals of the correct type and dimensions. Steam is circulated through coils in the lined hydrolysis tanks; fresh water is added to replace water lost in boiling to maintain a uniform solution level. All TiO_2 precipitated is in the anatase form.

The precipitate is then filtered and washed in the first Moore Filter sequence. There are two first Moore Filter lines, operated in parallel. The precipitate is picked up on the precoated filter leaves in the pickup tank. The vacuum on the filters pulls the acid solution through the filter leaves and the precoat and pigment are retained. The first 45 minutes of filtration produces a strong acid (or mother liquor) which is either recycled to the digesters or discharged as wastewater to the batch attack lagoon. The filter frame is transferred by overhead crane to the Moore wash tank; city water is used to wash impurities out of the pigment. The wash water or weak acid is discharged to the batch attack lagoon. After washing, the filter frame is transferred to the stripper tank; the pigment is stripped from the filter and dropped into a repulp tank. Sulfuric acid and aluminum powder are added to bleach the precipitated pulp under reducing conditions to remove iron. The repulped precipitate is then filtered

in the second Moore Filter sequence. There are two parallel second Moore Filter lines. Filtrate from the second Moore pickup tanks and wash tanks is recycled to the first Moore wash step; filtrate which is not recycled is discharged to the batch attack lagoon. After washing, the pigment is stripped from the second Moore filter frame and placed in tanks for pre-calcination treatment.

The pretreated pigment is filtered on rotary vacuum filters, repulped, and screw conveyed to the three calciners. The filtrate from the vacuum filters is sent to filter receivers, then to Dorr tanks. The underflow from the Dorr tanks is sprayed on the rotary vacuum filters. The Dorr tank overflows are discharged to the upper lagoon.

Calcination occurs in gas-fired inclined rotary kilns. As it travels through the kiln, the wet pulp is first dried, then water and SO_3 are driven off (7 to 8% SO_3 is strongly adsorbed by the precipitated pulp and cannot be removed by washing). Conversion to rutile and crystalline growth to pigmentary size only occur in the last few feet of the kiln. The conversion to rutile is governed primarily by the amount of rutile seed or nuclei added to the nucleation stage. After calcination, the pigment is cooled in drum-type barrel coolers on the exit side of the kilns. The cooled pigment is then conveyed to storage bins.

Each calciner has its own air emission scrubber system. The calciner exhaust gas passes through a cyclone and scrubber. Recovered particulate is sent to the filter Dorr tank. The Dorr tank underflow is returned to the rotary vacuum filters which feed the calciner repulp screw. Cyclone exhaust gas is scrubbed in a slot scrubber and then a venturi scrubber. The slot scrubber water is recycled from the scrubber Dorr tank. Overflow from the filter Dorr tank is sent to the scrubber Dorr tank. The scrubber water for the venturi scrubber is recycled from the "recover tank." Fresh water is added to the recover tank as makeup; bleed-off from the venturi scrubber is sent to the scrubber Dorr tank. Overflow from the scrubber Dorr tank is discharged to the batch attack lagoon. The underflow from the scrubber Dorr tank is returned to the hydrolysis tank.

The scrubber on the sulfate process calciner is manually removed from service every Thursday for inspection. The gas stream from the slot scrubber is routed through an electrostatic precipitator (ESP) and separate stack.

The anatase pigment is then prepared for shipment by either milling in a roller mill, or steam-jet mills (micronizers). The rutile pigment is wet milled, surface treated, filtered, dried and packaged for shipment. Wash waters from the surface treatment and filtering operations are collected in Dorr tanks (grade specific). Underflow from the Dorr tanks is returned to the finishing process and the overflow is discharged to the upper lagoon. Steam condensate from the jet mills is sent to the Dorr tanks.

The wastewater, air emission, and solid waste sources from the sulfate process are summarized in Table 4.

Chloride Process [Figure 3]

Pigments manufactured by the chloride process were first introduced commercially in the U.S. by DuPont in 1958. The process produces pigment by the oxidation of titanium tetrachloride (TiCl_4) which is obtained from the mineral rutile by chlorination in the presence of carbon. There are two methods by which TiO_2 can be produced from TiCl_4 in the vapor phase: by hydrolysis, and by oxidation. Hydrolysis was initially used at the Adrian-Joyce Works, but was replaced by the DuPont oxidation process because the chlorine produced as a co-product can be recycled, thereby reducing waste products and because less process equipment is required.

The chloride process uses rutile or upgraded ilmenite ores and coke as raw material. The ore and coke are dried and then reacted with chlorine to form TiCl_4 at a temperature between 800° and 1000°C (1472° and 1832°F) in a fluidized bed reactor. The chlorinator is cooled by cascading water over the exterior; this cooling water is recycled. The cooling water is bled off to the upper lagoon after it has been neutralized.

TABLE 4
SUMMARY OF WASTE SOURCES
Sulfate Process
SCM GLIDDEN-DURKEE
ADRIAN-JOYCE WORKS

Waste Source and Type	Treatment	Disposal
Runoff from raw ore storage area	Sedimentation/Neutralization in concrete basin	Patapsco river (001)
Gas stream from ore driers	Collected in baghouse, fines returned to drier	Baghouse vented to atmosphere
Dust from ball mill grinding of ore	Collected in cyclone and baghouse; coarse returned to ball mill	Cyclone and baghouse vented to process
Fumes from batch attack digesters	Collected in scrubber during critical reaction	Scrubber vented to atmosphere
Scrubber water for digester scrubber	Once through river water discharged to 001 sewer; ineffective neutralization with caustic in concrete basin	Patapsco river (001)
H ₂ S gas liberated in settling tanks	Collected in scrubber	Scrubber vented to atmosphere
H ₂ S scrubber water	Recycled through scrubber; bleed-off neutralized with caustic in concrete basin	Patapsco river (001)
Batch attack mud or gangue solids	Dewatered on rotary filter; filtrate returned to process	Landfilled at Designated Hazardous Substance (DHS) Site
Spills from digester settling tanks	Sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
Condensate from vacuum crystallizers steam evactors	Sedimentation/Neutralization in concrete basin	Patapsco river (001)

Table 4 (Cont'd)
SUMMARY OF WASTE SOURCES
Sulfate Process
SCM GLIDDEN-DURKEE
ADRIAN-JOYCE WORKS

Waste Source and Type	Treatment	Disposal
Drainage from copperas process	Sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
Residue solids from concentrator filters	Collected on cartridges	Landfilled at DHS
First Moore Filter strong acid	Recycled to process or sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
First Moore Filter weak acid	Sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
Second Moore Filter acids	Recycled to First Moore or sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
Rotary Filter (preceding calciner) filtrate	Collected in Dorr tank; tank overflow discharged to upper lagoon	Patapsco river (002)
Gases from calciners	Collected in venturi scrubber system	Scrubber vented to atmosphere
Venturi scrubber water	Recycled through scrubber; bleed-off sent to batch attack lagoon and neutralized at PWAN/SWAN	Patapsco river (002)
Finishing process rotary filter filtrate	Collected in Dorr tanks; tank overflows discharged to upper lagoon	Patapsco river (002)

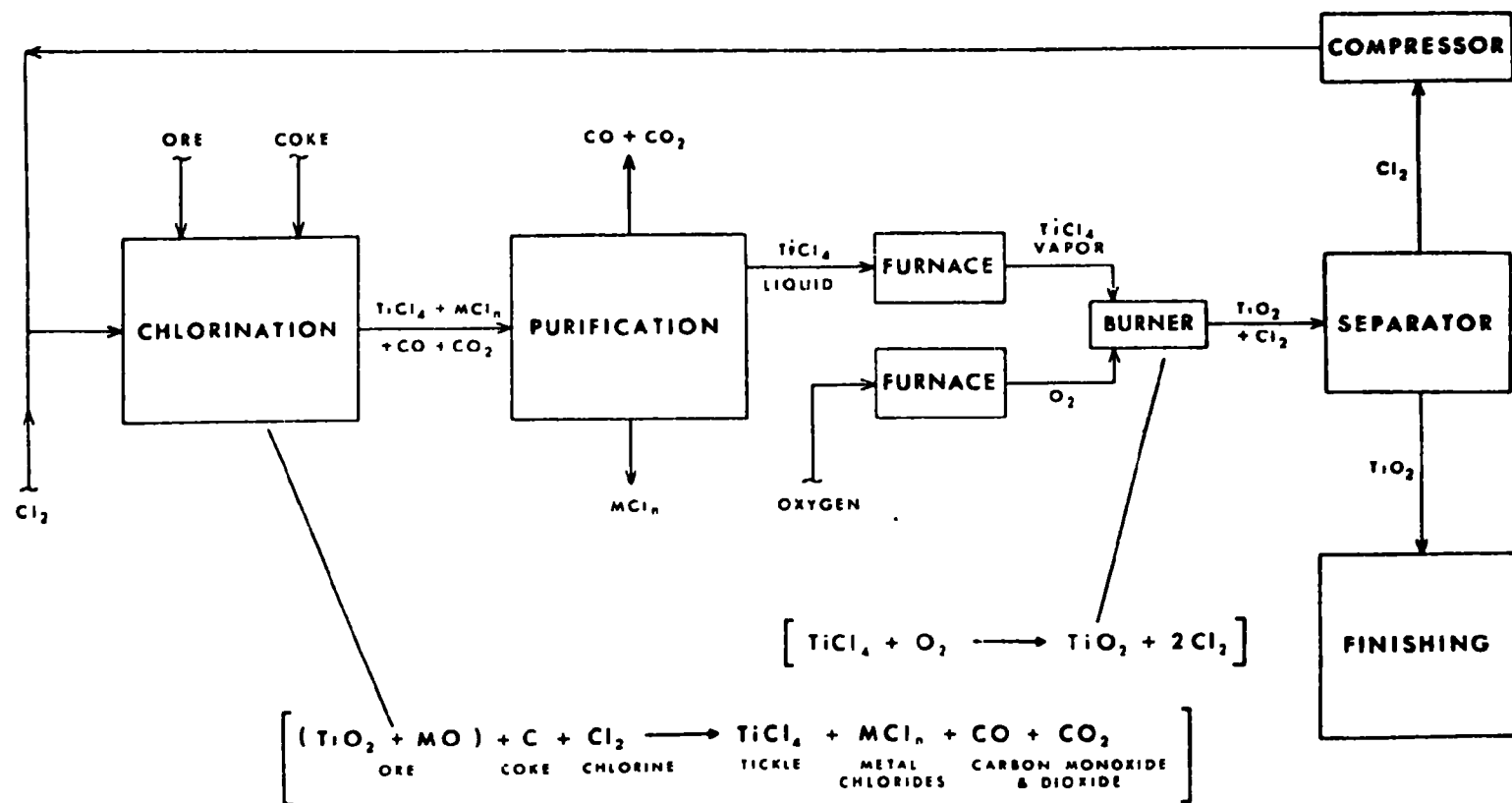


Figure 3.
 TiO_2 Chloride Process

The product gases leaving the chlorinator consist of TiCl_4 , unreacted chlorine, carbon dioxide, carbon monoxide, and minor amounts of heavy metal chlorides. The gases are cooled initially to 250°C (482°F) with liquified titanium tetrachloride to remove impurities. The impurities are collected in the two waste solid pits along with the chlorinator cooling water bleed-off. Prior to discharge to the upper lagoon, the effluents from the pits flow through a neutralization pit; aragonite (a mineral composed of calcium carbonate) is used to neutralize the waste stream.

After cooling and impurity removal, the gas is condensed. Cooling water is recycled to a cooling tower; blow-down from the cooling tower is discharged to the upper lagoon.

In the chlorination-condensation sequence, the only air emission is controlled by a venturi water scrubber. The water is continually recycled; the bleed-off is done at a controlled rate to maintain an acid concentration of 20%. The bleed-off is discharged to the acid storage system, then to the aragonite neutralization pit.

The liquified TiCl_4 contains impurities such as aluminum chloride, silicon tetrachloride, etc., which are removed by distillation. Non-contact steam condensate from distillation is discharged to the upper lagoon. The distillate, or purified TiCl_4 , is oxidized by a process patented by DuPont. The TiO_2 passes through two layers of serpentine pipe inside a concrete basin. The cooling water in the basin is recycled through an indirect heat exchanger. The overflow from the cooling basin is discharged to the upper lagoon. After cooling, the TiO_2 solids and chlorine gas stream are separated in a baghouse. The chlorine is recycled to the chlorination process and the TiO_2 is sent to the finishing operation.

In the finishing operation, the TiO_2 is ground, filtered, dried and milled. Filtrates and wash waters are collected in grade-specific Dorr tanks (primary and secondary). The Dorr tanks underflows and the secondary Dorr tank overflows are recycled. The overflows from the primary Dorr

tanks are discharged to the upper lagoon. All floor washings, spills, etc., in the finishing process are collected in a sump. A Hydrosieve is used to separate trash from the wastewater; the screenings are landfilled and the wastewater is sent to the primary Dorr tank.

After milling, the TiO_2 is sent to a baghouse. The product from the baghouse is sent to packaging and stored for shipment. The baghouse gas passes through a steam-barometric condenser. Condensate from the hot well is discharged to either the secondary Dorr tanks or directly to the filters.

The wastewater, air emissions, and solid waste sources for the chloride process are summarized in Table 5.

WASTEWATER TREATMENT [Figure 4]

PWAN/SWAN

The Primary Waste Acid Neutralization (PWAN) and Secondary Waste Acid Neutralization (SWAN) systems are proprietary wastewater treatment operations developed by the Company to comply with the effluent limitations for the sulfate process wastewaters.

Strong and weak acidic wastewaters from the sulfate process are discharged to the batch attack lagoon. The waste acid is pumped from the lagoon and mixed with aragonite to neutralize the free acid. In the neutralization process, primary synthetic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is produced as a wet slurry. The slurry is dewatered on a vacuum filter and stockpiled onsite or on adjacent Company-owned property used for hazardous waste disposal. The Company has developed a market for the primary gypsum and currently sells some of the material.

The PWAN effluent is neutralized with more aragonite to convert ferrous iron to ferric hydroxide and remaining acid to secondary gypsum. The secondary gypsum is also dewatered on a vacuum filter and stockpiled at the hazardous waste site.

TABLE 5
SUMMARY OF WASTE SOURCES
CHLORIDE PROCESS
SCM GLIDDEN-DURKEE
ADRIAN-JOYCE WORKS

Waste Source and Type	Treatment	Disposal
Non-contact cooling water (NCCW) from chlorinator	Neutralized and sent to upper lagoon	Patapsco river (002)
Waste solids from chlorination process	Collected and slurried through aragonite neutralization pit to upper lagoon	Patapsco river (002)
NCCW from condensation sequence	Recycled to cooling tower; bleed-off sent to upper lagoon	Patapsco river (002)
Gas stream after condensation of $TiCl_4$	Collected in venturi scrubber system	Scrubber vented to atmosphere
Venturi scrubber water	Sent through aragonite neutralization pit to upper lagoon	Patapsco river (002)
Condensate from distillation sequence	Sent to upper lagoon	Patapsco river (002)
NCCW from oxidizer cooling pond	Sent to upper lagoon	Patapsco river (002)
Filtrate from rotary filters in finishing sequence	Collected in Dorr tanks; overflow discharged to upper lagoon	Patapsco river (002)
Waste acid and base from regeneration of ion exchange resins	Sent to upper lagoon	Patapsco river (002)

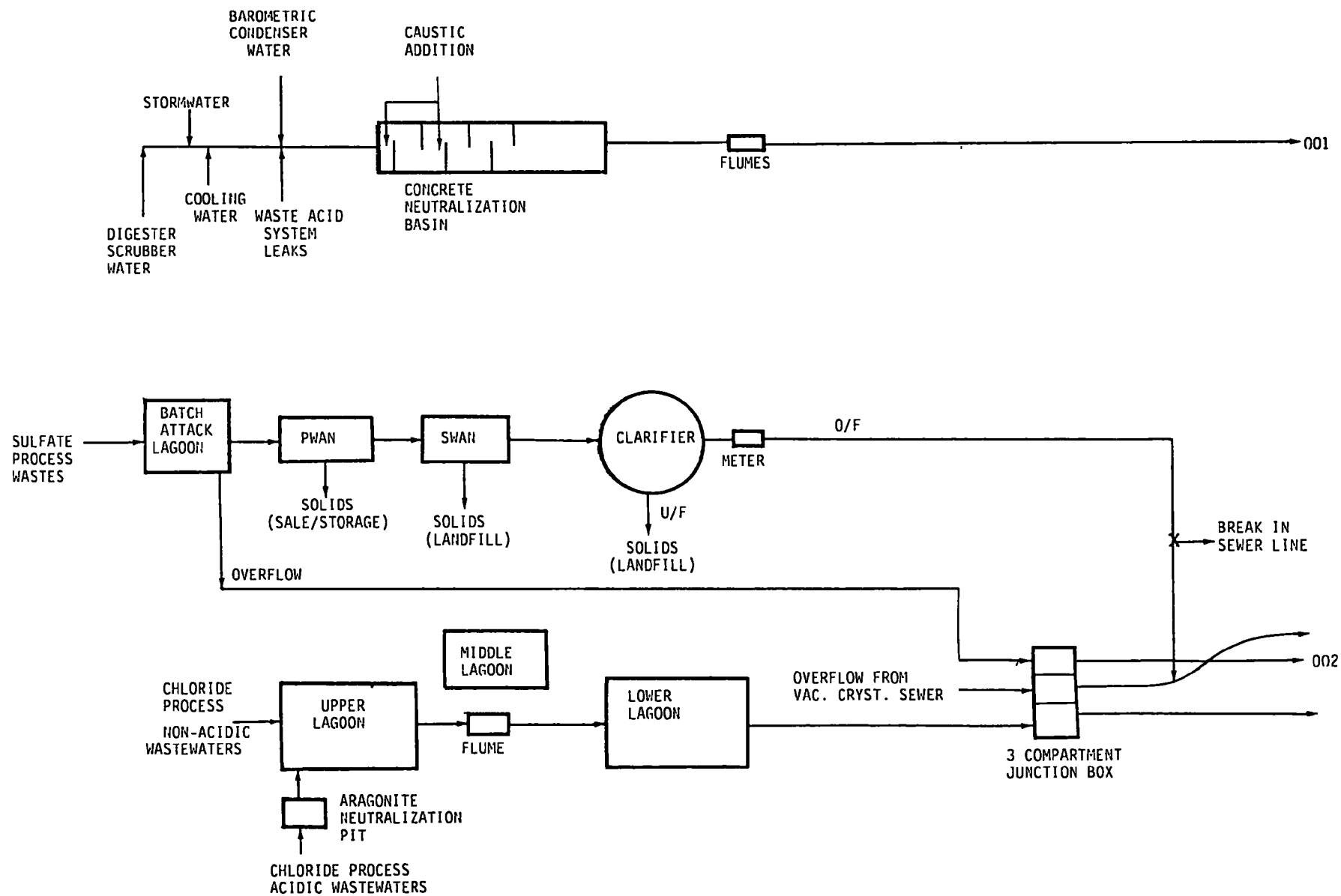


Figure 4
Wastewater Treatment Schematic
SCM Glidden-Durkee
Adrian Joyce Works
Baltimore, Maryland

The SWAN effluent and the gypsum filtrates from PWAN/SWAN are sent to a 60 ft diameter x 16 ft SWD flat bottom clarifier. Bottom rakes are positioned at a 30° angle to provide a false cone effect for the clarifier. The rake mechanism continually removes solids from the clarifier to a drum filter. The dried filter cake, or gel mud, is landfilled at the hazardous waste disposal site.

The clarifier rake mechanism has been a problem. The rake shaft has been fitted with a torque indicator which raises the rake off the bottom whenever the torque reaches a specified level. A broken bearing in the shaft resulted in operational problems which increased the effluent solids level.

The effluent from the clarifier is pumped to the Patapsco River. The flow normally combines with other effluents downstream of a three-compartment junction box. The junction box receives the effluent from the lower lagoon, overflow from the batch attack lagoon, and an excess overflow from the vacuum crystallizer building (sulfate process). The junction box splits the flow into three pipes which are designated Outfall 002. However, the effluent pipe from the clarifier has been broken along the river bank and the effluent flows into the river at this location. The Company would like to have this discharge designated Outfall 003.

Lagoon System

There are four lagoons used for wastewater treatment [Figure 1]. The surface areas of each lagoon, estimated from Company drawings, are as follows:

	Surface Area	Depth
batch attack lagoon	14 acres	26 ft
upper lagoon	13.5 acres	26 ft
middle lagoon	7.1 acres	26 ft
lower lagoon	24.7 acres	26 ft

The batch attack lagoon receives sulfate process wastewaters prior to neutralization in PWAN/SWAN. During periods of high rainfall, etc., the batch attack lagoon will overflow to the junction box at Outfall 002. The three remaining lagoons are filled with solids from the processing operations. The Company currently discharges process wastewaters from the chloride process to the upper lagoon which connects to the lower lagoon. The flow is measured in a 36-in Parshall Flume located between the upper and lower lagoons. The middle lagoon is by-passed and receives no waste material. Because of the deposited solids, the wastewater in the upper and lower lagoons is channeled directly to the junction box at Outfall 002. Company personnel estimated that more solids are leaving the lower lagoon than are currently being deposited.

The acidic effluent from the chloride process enters the upper lagoon after it is neutralized; a small pit estimated to be 8 ft x 8 ft deep is used for neutralization. Coarse aragonite is periodically placed in the pit and the acidic wastewaters flow through the pit into the upper lagoon. Non-acid wastewaters (finishing processes, demineralizer regeneration backwash, and cooling water) enter the lagoon at other locations.

The Company has hired contractors to dredge the lower lagoon to provide settling for the chloride process solids. Until recently, the contractors have not been able to dredge the lagoons because the equipment would remove too much water and insufficient quantities of solids. However, the current contractor is using a dredge with a pump that can handle solids concentrations of 200 gram/l and has been able to successfully dredge the solids.

The dredged solids will be stockpiled in the middle lagoon and allowed to dewater before being landfilled offsite. If the dredging operation is successful, the Company intends to divide the lower lagoon into two cells; once the first cell is full, flow will be diverted to the second cell, and the solids will be dredged from the first cell.

The chloride process wastewaters contain coke, ore, metal chlorides, and TiO_2 solids from finishing. The Company personnel estimated that the load to the lagoons ranges between 15 and 30 tons/day which must be removed to comply with the effluent limitations. Company in-house laboratory tests indicate that the coke and ore solids could be recovered and recycled, reducing the solids load to the Outfall 002 lagoons by 40 to 50%.

Non-Process and Other Wastewaters

Wastewaters not treated in PWAN/SWAN or collected in the upper and lower lagoons are discharged from Outfall 001. These include: (1) storm water runoff from the plant processing site (except for the chloride processing area, the runoff flows to the upper and lower lagoons); the raw material storage areas, and PWAN and SWAN treatment area; (2) river water used for cooling and barometric condensers; (3) scrubber water from the digester scrubbers; and (4) leaks in the sewers serving the waste acid system in the finishing area, even though a major portion of the sewer has been replaced.

With the exception of some storm water runoff, these wastewaters are collected in a concrete basin about 100 ft long x 20 ft wide x 10 ft deep. The basin is partially subdivided by six concrete baffles which direct the flow around the baffles in a serpentine route. The pH of the wastewater is measured immediately upstream of the concrete basin, however, this measurement is only used as an indicator by the operators whenever they are in the area. The wastewater is neutralized in the basin with sodium hydroxide which is controlled by pH probes in the first, third, and fourth chambers created by the baffles. The caustic can be added to either the first or third chambers.

The system is supposed to control the basin effluent pH at 7, however, due to the 6,000 gal/min flow from the digester scrubbers over a 30-minute period four or five times/day, the pH drops to levels below 6.0 (permit limit). Sufficient sodium hydroxide cannot be added to neutralize the highly-acid scrubber water. The effluent from the basin flows through two

parallel pipes into two Palmer-Bowles flumes, and then to the concrete headwall into the Pataspco River (Outfall 001). Flow is measured in one flume and then doubled for the total flow.

Effluent Quality

The characteristics of the effluents discharged from Outfalls 001 and 002, and the PWAN/SWAN treatment system are summarized from Discharge Monitoring Reports in Table 6. The river water intake averages 15 mgd with a total suspended solids concentration of 200 mg/l. The Company personnel do not know how much river water flows into the 001 or 002 drainage systems. Through in-plant process flow estimates, they estimated that between 25,000 and 50,000 gal/day of river water is discharged from Outfall 002; the rest is discharged from Outfall 001. The amount of water pumped from the river is measured. The amount of water purchased is also measured. Company personnel have estimated that 0.5 mgd is discharged from 001, the rest through 002. Storm water runoff is computed for the area drained, the number of days/month that rain occurred, and a factor for the amount that would run off. The flow from the clarifier is measured. These data are put into a computer and the flows and net loads are calculated. The basic flow formulae for each outfall are as follows:

$$\text{Outfall 001 Flow (mgd)} = 0.5 \text{ mgd} + (\text{River Water Intake Flow} - 0.05 \text{ mgd}) + \text{Runoff}$$

$$\text{Outfall 002 Flow (mgd)} = \text{River Water Intake Flow of } 0.05 \text{ mgd} + \text{Runoff} + \text{SWAN effluent flow} + (\text{Purchased Water} - 0.5 \text{ mgd}).$$

Samples for permit parameters are collected once/week over a 24-hour period and composited on an equal-volume basis.

TABLE 6
EFFLUENT QUALITY^a
SCM GLIDDEN-DURKEE
ADRIAN JOYCE WORKS

Characteristic	Outfall 001	Outfall 002	PWAN/SWAN Clarifier
Flow m ³ /day	39,500	15,100	5,450
mgd	10.45	4	1.44
pH	0.0 to 14	0.0 to 10	7.2 to 7.5
TSS mg/l	65	960	20 ^b
kg/day	2,600	14,500	108
lb/day	5,700	32,000	240
Iron mg/l	65	790	6 ^b
kg/day	1,100	12,000	32
lb/day	2,400	26,400	72

a 1978-1979 Discharge Monitoring Reports.

b Best results obtained.

IV. HAZARDOUS WASTE DISPOSAL

Land space for solid and hazardous waste disposal is not available at the main plant site. The Company owns a 51-acre site on Quarantine Road, about 2 miles from the main plant. The Quarantine Road site, or the Designated Hazardous Substance (DHS) area, is part of a larger tract of land used for landfilling municipal refuse by Browning-Ferris, Inc., (BFI). The entire site was owned by DuPont and was used for waste disposal from their Curtis Bay sulfate plant. BFI purchased the tract from DuPont, except for the 51 acres purchased by SCM. SCM negotiated a contract with BFI to operate the DHS area for them. However, SCM could not obtain a permit from the State for disposal of the process solids, therefore, BFI could not accept the SCM wastes. Access to the BFI site is across the DHS area, SCM has denied access to BFI, therefore, the BFI landfill is inactive.

SCM currently hauls the digester gangue solids, the SWAN gel mud, and excess copperas to the DHS area for burial. The SWAN gypsum is being stored above ground near the burial cells; excess PWAN gypsum is also stored at the DHS site, but away from the burial cells.

SCM has retained the consulting firm of Harrington and Lacey to design a landfill which will comply with State and Federal regulations for hazardous waste disposal. The site is being developed currently. A leachate collection, monitoring, and treatment facility is being designed by Industrial Pollution Control; samples for design parameters are still being collected in a temporary pit.

The State has issued a draft disposal permit for the DHS site. If the digester gangue solids, gel mud, and copperas are the only materials required to be landfilled, SCM estimates that the expected life of the site will be 8 years.

The SWAN gypsum contains high concentrations of impurities including priority pollutant metals such as zinc and chrome. According to Company personnel, the State maintains that the SWAN gypsum must be considered hazardous and must be landfilled in the DHS site. The Company's position is that if the SWAN gypsum is landfilled, the effective life of the DAS site will be less than one year. Disposal costs will increase rapidly if the solid wastes have to be landfilled at an offsite location after the DHS site is closed. The alternatives for the Company are to develop a market for the SWAN gypsum or to demonstrate that the gypsum does not fall under EPA's criteria as a hazardous waste. Preliminary data from the Extraction Procedures (EP)* indicate that the extract from the SWAN gypsum does not contain levels of hazardous materials exceeding those listed. The EP test was conducted by a consultant laboratory.

* Federal Register, "Hazardous Waste and Consolidated Permit Regulations"; Monday, May 19, 1980, Part III, Subpart C Section E, pages 33110 to 33112.

V. TREATMENT NEEDS AND PERMIT LIMITATIONS

TREATMENT NEEDS

The NPDES permit limits the discharge of pollutants to the Patapsco River from Outfalls 001 and 002. After the permit had been issued, the sewer conveying the PWAN/SWAN treated wastewater failed and the wastewater is discharged directly to the river instead of combining with the wastewater discharged from Outfall 002. SCM, therefore, has three separate waste streams; 001, 002, and PWAN/SWAN.

Although the Company had been submitting monitoring data as required by the permit, NEIC personnel requested that the Company monitor each discharge and the salt water intake on a daily basis to determine daily fluctuations.

Outfall 001

The waste stream discharged from Outfall 001 is composed of storm water runoff, river water from the sulfate process vacuum crystallizers and evaporators, intermittent discharges of once-through scrubbing water from the sulfate process digester scrubbers, and waste acid and ammonia overflow from the sewer carrying the wastewater to Outfall 002. Caustic is added to the wastewater in the baffled, concrete basin for neutralization. Due to velocities and basin design, adequate sedimentation is not achieved in the basin.

The DMR data for 1978 and 1979 are summarized in Table 7, and the daily monitoring data for March 7 to May 5, 1980, are summarized in Table 8. During the NEIC inspection, the total suspended solids concentration

TABLE 7
 SUMMARY OF EFFLUENT DATA
 Discharge Monitoring Reports
 SCM GLIDDEN-DURKEE
 ADRIAN-JOYCE WORKS
 January 1978 to September 1979

Parameter	Outfall 001		Outfall 002 ^a	
	Average	Range	Average	Range
Flow, mgd ^b	10.45	4.89-18.45	8.78	4.99-15.94
Total Iron, lb/day	2,420	470-16,250	32,000	6,400-51,000
TSS, lb/day	5,170	300-21,590	26,400	2,800-173,000
pH, S.U.	-	0.04-14	-	1-10
pH reported each month	≤2.7	-	≤1.4	-

a Includes PWAN/SWAN effluent.

b Flows for June 1978 to September 1979.

TABLE 8
60-DAY CONTINUOUS MONITORING DATA - OUTFALL 001
SCM GLIDDEN-DURKEE - ADRIAN-JOYCE WORKS
March 7 - May 5, 1980

Date	Iron				TSS		
	pH S U	Gross Conc. mg/l	Process ^a Conc. mg/l	Net Load ^b lb/day	Gross Conc. mg/l	Process ^a Conc. mg/l	Net Load ^b lb/day
3/7	6.2	27	20	2,335	16	0	0
8	7.2	12	7	825	12	6	708
9	6.9	27	19	2,226	78	68	7,914
10	5.1	53	17	2,068	96	65	7,506
11	6.4	9	7	817	10	0	0
12	7.6	12	1	141	78	25	2,927
13	6.2	62	57	6,621	206	194	22,534
14	6.9	12	5	600	20	0	0
15	8.1	10	6	708	34	0	0
16	6.0	18	8	950	54	32	3,769
17	3.0	336	308	35,795	100	62	7,289
18	6.7	50	49	5,687	34	0	0
19	6.5	10	0	0	0	12	0
20	7.0	13	0	0	56	0	0
21	7.2	38	29	3,386	264	222	25,862
22	8.1	46	22	2,618	204	122	14,136
23	8.2	5	0	0	100	29	3,436
24	8.4	22	20	2,326	116	79	9,148
25	7.3	20	15	1,751	76	38	4,503
26	6.3	36	34	3,953	106	100	11,617
27	6.1	25	23	2,668	106	86	9,999
28	5.7	8	6	700	36	34	3,953
29	6.3	35	33	3,911	16	<1	41
30	7.0	40	32	3,736	116	102	11,867
31	3.0	34	27	3,152	48	0	0
4/1	5.3	23	15	1,759	80	27	3,160
2	6.8	60	54	6,280	166	104	12,093
3	5.3	26	19	2,218	70	34	4,036
4	7.5	45	40	4,663	152	138	16,046
5	7.2	29	21	2,460	70	44	5,170
6	7.2	25	15	1,349	104	75	6,605
7	6.5	59	35	3,051	166	129	11,389
8	4.6	79	65	5,689	276	144	12,704
9	7.5	32	29	2,565	154	129	11,358
10	6.2	95	90	7,951	292	263	23,188
11	7.3	4	0	0	8	6	534
12	7.5	4	0	0	2	0	0
13	7.5	5	<1	13	12	0	0
14	7.2	5	0	0	10	0	0
15	7.5	6	1	101	38	22	1,982
16	7.0	3	<1	8	34	11	945
17	7.3	4	0	0	46	19	1,661
18	6.8	12	10	887	20	16	1,421
19	7.0	12	12 ^c	1,058	74	74 ^c	6,527
20	7.5	14	12	1,063	66	45	3,938
21	7.3	6	4	358	86	37	3,306
22	7.4	7	0	0	76	0	0
23	7.0	9	0	0	88	0	0
24	7.0	12	12	887	78	31	2,772
25	7.2	3	3 ^c	264	16	16 ^c	1,411
26	6.4	25	25 ^c	2,205	166	166 ^c	14,642
27	6.5	64	64 ^c	5,645	334	334 ^c	29,460
28	7.6	28	24	2,127	182	141	12,458
29	6.9	26	20	1,779	64	31	2,735
30	7.1	32	29	2,565	130	113	9,926
5/1	6.6	35	29	2,573	192	126	11,115
2	7.0	17	14	1,242	64	54	4,789
3	7.2	12	10	887	70	66	5,832
4	7.3	18	7	646	122	110	9,733
5	7.4	17	15	1,328	158	55	4,864
AVG	6.8	30	24	2,510	94	64	6,383

a Process concentration equals amount added to background levels to produce net load

b Flow = 13.594 mgd of river water + 0.314 mgd of added water = 13.908 mgd for March 7 to April 15. Flow = 10.262 mgd of river water + 0.314 mgd of added water = 10.516 mgd for April 6 to May 5

c No sample collected of river water

in the wastewater discharged from Outfall 001 seemed, by appearance, to be less than the concentrations reported in the 1978 to 1979 DMR's. Company representatives were not aware that the effluent was, by itself, exceeding the permit limitations for the total of all plant effluents. It was their opinion that sampling and/or analytical procedures were in error. However, the data for March 7 to May 5, 1980, verifies that both TSS and iron levels discharged from Outfall 001 exceed the existing permits total allowable load for the three outfalls. The pH control is not acceptable as the composite pH was less than 6.0 on seven days.

The river water discharged from Outfall 001 is 98% of the total flow; the river water iron and total suspended solids concentrations averaged 8 mg/l and 40 mg/l, respectively. After correcting for the raw intake concentrations, the process effluent iron and TSS concentrations averaged 24 mg/l and 64 mg/l, respectively.

The method used by the Company for computing flows and net loads is questionable. On nine of the 60 days, the net iron load was zero and the net TSS load was zero on 13 days. Based on the data submitted, it is not reasonable that a zero value would occur on any day.

Due to the high concentrations of iron and total suspended solids contributed by processes and runoff, the Company cannot achieve compliance with effluent limitations without either removing and treating all contaminated waste streams from the 001 waste stream or by treating the entire wastewater prior to discharge. The elimination of the once-through scrubber water from the sulfate process digesters from the 001 waste stream should reduce the pollutant load, however, the scrubber water bleed-off will have to be treated before discharge. Additional sources of wastewater will have to be isolated and removed from the 001 waste stream and treated to comply with effluent limitations.

If the Company prefers to treat the entire wastewater flow, the iron will have to be oxidized to the ferric form and removed with the solids by sedimentation. After iron oxidation, the wastewater could be routed

through the Outfall 002 lagoon system for sedimentation or a clarifier could be installed and the effluent discharged through Outfall 001.

It is impossible to determine the amount of iron and TSS contributed by runoff because the Company does not monitor individual waste sources. The 60-day data do not indicate runoff was present, therefore, runoff could increase the TSS load significantly.

Outfall 002

The wastewaters discharged from Outfall 002 includes process waste streams from the chloride process, about 50,000 gpd of river water from the sulfate process, process wastewater from the sulfate finishing area, the waste acid and base from the regeneration of ion exchange resins, floor drain wash waters and spills except those collected in the recovery systems, leakage from the copperas vacuum crystallizers and evaporators, and sanitary wastes from the chloride processing areas.

The acidic process wastewaters from the chloride process pass through an 8 ft x 8 ft chamber containing unground aragonite. The aragonite supplies about 85% of the alkaline demand. The wastewater from the chamber then passes through the upper lagoon and through the Parshall flume to the lower lagoon. Caustic is added to the wastewater as it leaves the flume to adjust the pH to the 6 to 9 range. The valves which supply the caustic have been sticking and the pH was not above 6.0 for 31 of the 60 days.

During the NEIC inspections, both lagoons were completely full of settled material and the wastewaters were conveyed through the lagoons in shallow channels without sedimentation. The Company reported that previously settled solids were scoured and carried over into the effluent.

The lower lagoon was recently dredged successfully and the Company representatives believed that the solids would be removed prior to discharge. The TSS load reported in the 1978 to 1979 DMRs [Table 7] averaged 32,000 lb/day; this included the PWAN/SWAN effluent. After dredging, the

TSS load discharged March 7 to May 5, 1980, [Table 9] averaged 4,241 lb/day. Over the same 60-day period, the solids from PWAN/SWAN averaged 538 lb/day [Table 10]. However, the total iron discharged from March 7 to May 5 averaged 11,425 lb/day from the lagoons, and 97 lb/day from PWAN/ SWAN. The high iron levels discharged from the lagoons are partially due to poor pH control. For the first 30 days, the pH never exceeded 5.5 and averaged 3.1. The iron load for March 7 to April 5 averaged 11,400 lb/day. The data for April 6 to May 5 showed that the average iron load decreased to 7,750 lb/day, which includes very high iron loads for days when the pH was less than 6.0 (April 27 to May 5). The iron load for the days the pH was 6.0 or greater averaged 2,150 lb/day. At low pH levels, the iron will be in the soluble ferrous form and will not be removed. For effective treatment, the pH must be maintained above 6.5 to effectively convert the ferrous iron to ferric which will precipitate and be removed with the solids. At pH levels less than 6.5, the rate of oxidation is very slow. The Company must ensure that effective pH adjustment is maintained to enhance treatment and comply with effluent limitations.

A study of the settleability of the solids in the 002 waste stream was conducted for the Company by the EIMCO Process Machinery Division.* The study showed that the solids settled well if a polymer is added, and that the settled solids can be dewatered to 25 to 45% solids in either a vacuum or pressure filter. The area required for sedimentation to produce an effluent containing less than 15 mg/l TSS would be 1,800 ft², considerably less than the 12.4 acres that will be available when the lower lagoon is dredged and divided into two compartments.

The preliminary data (March 7 to May 5) indicate that effective sedimentation occurred, but additional treatment such as polymer addition may be required to reduce TSS levels. Iron removal should improve with pH control. However, the Company should initiate treatability studies if the TSS and iron concentrations are not reduced to permitted levels by sedimentation and precipitation in the lower lagoon. In addition, the Company

* "Water Clarification and Solids Dewatering for Glidden Plants, Inc. SCM Corporation, Baltimore, Maryland", September 1979.

TABLE 9
OUTFALL 002
60-DAY CONTINUOUS MONITORING DATA
SCM GLIDDEN-DURKEE - ADRIAN-JOYCE WORKS
MARCH 7 - May 5, 1980

Date	Iron				TSS		
	pH S.U.	Gross Conc mg/l	Process ^a Conc mg/l	Net Load ^b lb/day	Gross Conc. mg/l	Process ^a Conc mg/l	Net Load ^b lb/day
3/7	3.4	300	300	11,859	16	14	567
8	4.2	277	277	10,950	152	152	6,004
9	4.8	303	303	11,976	34	34	1,326
10	3.1	351	349	13,819	86	84	3,336
11	2.5	555	555	21,967	76	75	2,977
12	1.4	890	890	35,203	68	65	2,577
13	1.5	995	995	39,373	58	57	2,268
14	2.9	225	225	8,890	42	39	1,559
15	3.0	179	179	7,080	40	37	1,476
16	3.1	151	151	5,954	36	35	1,376
17	3.0	138	137	5,404	36	34	1,342
18	2.7	135	135	5,337	34	32	1,267
19	1.8	108	107	4,253	8	5	200
20	2.7	122	121	4,795	26	21	834
21	2.4	219	218	8,648	110	108	4,270
22	1.2	1,140	1,140	45,069	90	86	3,386
23	3.4	110	110	4,336	18	14	558
24	3.4	154	154	6,088	48	46	1,818
25	2.7	163	163	6,438	58	56	2,218
26	2.7	164	164	6,496	72	72	2,835
27	3.1	112	112	4,428	90	89	3,519
28	3.6	73	73	2,885	26	26	1,025
29	2.7	170	169	6,697	22	21	834
30	3.1	173	173	6,830	58	57	2,268
31	3.0	352	352	13,919	66	63	2,493
4/1	2.7	352	352	13,919	38	35	1,392
2	3.0	308	308	12,176	34	33	1,317
3	5.5	162	162	6,396	66	64	2,535
4	5.3	215	215	8,498	64	64	2,522
5	5.5	80	80	3,152	30	29	1,134
6	6.6	32	28	1,696	140	129	7,732
7	6.0	35	27	1,651	176	162	9,714
8	6.3	102	96	5,788	180	129	7,742
9	5.8	186	185	11,104	138	128	7,702
10	6.8	74	72	4,332	74	63	3,767
11	7.1	23	21	1,246	12	11	675
12	7.0	15	13	765	10	0	0
13	7.5	8	6	368	38	29	1,741
14	6.9	22	28	1,073	6	0	0
15	7.7	6	4	247	32	26	1,561
16	8.1	1	0	0	20	11	660
17	8.3	20	18	1,066	22	11	689
18	8.0	11	10	615	46	44	2,672
19	7.6	23	23	1,381	164	164	9,850
20	6.9	27	26	1,576	82	74	4,429
21	7.1	29	28	1,697	108	89	5,358
22	6.9	53	48	2,867	182	119	7,140
23	6.8	26	20	1,200	130	76	4,559
24	6.3	113	112	6,742	204	186	11,170
25	6.9	14	14	841	68	68	4,084
26	6.0	132	132	7,928	124	124	7,448
27	5.1	237	237	14,235	76	76	4,565
28	4.7	265	264	15,827	26	10	614
29	6.0	191	189	11,337	18	5	314
30	5.8	252	251	15,068	190	183	11,006
5/1	5.9	268	251	15,962	158	132	7,956
2	5.9	198	197	11,825	34	30	1,816
3	5.6	300	299	17,974	234	233	13,965
4	4.1	827	823	49,425	294	289	17,388
5	5.6	445	444	26,683	654	614	36,890
AVG	4.8	210	209	9,598	87	79	4,241

a Process concentration equals amount added to background levels to produce net load.

b Flow = 0.25 mgd of river water + 4.496 mgd of added water = 4.746 mgd for March 7 to April 5
Flow = 2.706 mgd of river water + 4.496 mgd of water added = 7.202 mgd for April 6 to May 5

TABLE 10
 SUMMARY OF EFFLUENT DATA
 PWAN/SWAN Neutralization Plant
 SCM GLIDDEN-DURKEE
 ADRIAN-JOYCE WORKS
 March to June 1979

Date	Flow mgd	Total Iron		TSS	
		mg/l	lb/day	mg/l	lb/day
March 1979	1.46	144	1,762	247	3,017
April	1.35	54	612	219	2,476
May	1.34	46	518	52	577
June	<u>1.39</u>	<u>36</u>	<u>423</u>	<u>59</u>	<u>687</u>
Average	1.39	72	829	146	1,689

should implement in-plant recovery of the coke and ore solids which are currently discharged in the effluent. Company data indicate that these solids comprise 40 to 55% of the solids discharged and that they are recoverable. Recovery will extend the period between dredging of the lower lagoon cells, reduce the volume of dredged solids to be dewatered and landfilled, and reduce the load on a new clarification system if the lagoon does not reduce the solids load.

PWAN/SWAN Neutralization Plant Effluent

The PWAN/SWAN plant, which treats the combined strong and weak acid wastewaters from the sulfate process, is a two-stage neutralization and sedimentation process. The effluent data for March to June 1979 and March 7 to May 5, 1980, are summarized in Tables 10 and 11, respectively.

The 1979 data indicate that, although iron was being removed by treatment, the concentrations were still high. The 60-day monitoring data in 1980 show that the iron can be removed to very low levels. The total suspended solids in 1980 were also reduced significantly from 1979. However, further reduction of solids can be achieved by using the existing 25-ft diameter sand filter for polishing the clarifier effluent. The sand filter was not being used during the NEIC inspection and Company representatives stated that there are no plans for using the filter.

Use of the sand filter may not be required if the Company can effectively treat and remove the solids from the effluents discharged from Outfalls 001 and 002. The average iron and TSS loads discharged from the neutralization facility during March 7 to May 5, 1980 were only 8 and 12% of the 30-day average limitations in the existing permit, respectively.

The Company must solve the serious problem of overloading the PWAN/SWAN system. At high production rates, the batch attack lagoon, which is used for flow equalization, cannot contain the flows and the neutralization systems and clarifier cannot be operated efficiently. If high production is periodic, then increased flow equalization would be required. However,

TABLE 11
SUMMARY OF EFFLUENT DATA
PWAN/SWAN Neutralization Process
SCM GLIDDEN-DURKEE - ADRIAN-JOYCE WORKS
March 7 to May 5, 1980

Date	pH S.U.	Iron		TSS	
		mg/l	lb/day	mg/l	lb/day
3/7	7.7	2	21	10	104
8	7.3	3	31	24	249
9	7.4	11	114	14	145
10	7.9	1	5	26	270
11	7.6	5	52	20	208
12	7.8	15	156	32	332
13	7.7	3	31	36	374
14	7.0	7	73	40	415
15	7.1	5	52	42	436
16	7.0	9	93	56	581
17	7.2	14	145	50	520
18	6.8	7	73	32	332
19	7.0	6	63	8	83
20	7.1	8	83	52	540
21	7.6	2	21	68	706
22	7.7	6	63	84	872
23	7.6	1	10	42	436
24	7.8	18	187	80	831
25	7.6	49	509	240	2,492
26	7.4	53	550	174	1,806
27	7.8	16	166	126	1,308
28	7.0	3	31	200	2,077
29	7.6	17	177	102	1,059
30	7.5	3	31	84	872
31	7.5	8	83	40	415
4/1	7.6	6	63	24	249
2	7.6	7	73	76	789
3	7.5	1	10	4	42
4	7.6	6	63	6	63
5	7.4	8	83	28	291
6	7.5	10	115	8	92
7	7.4	2	23	28	324
8	7.5	2	23	26	300
9	7.4	1	12	62	717
10	6.8	14	161	54	624
11	6.8	8	92	6	70
12	6.6	25	289	46	531
13	6.3	74	855	16	185
14	7.0	8	92	12	139
15	7.0	3	35	26	301
16	7.6	3	34	46	532
17	6.7	4	46	32	370
18	7.4	7	81	51	601
19	7.5	2	23	6	69
20	7.5	4	46	34	393
21	7.7	7	81	58	670
22	7.8	5	57	34	393
23	7.8	2	23	48	555
24	7.7	3	35	32	370
25	6.9	5	58	20	231
26	7.5	6	69	18	208
27	7.6	2	23	76	879
28	7.7	2	23	46	531
29	7.5	16	185	104	1,202
30	7.5	5	57	46	532
5/1	7.6	8	93	84	971
2	7.1	2	23	14	162
3	7.4	2	24	16	185
4	7.5	2	23	34	393
5	7.7	2	23	72	832
AVG	7.4	10	97	49	538

Flow = 1,245 mgd for March 7 to April 5 and 1,386 mgd for April 6 to May 5.

if production schedules dictate extended periods of high production, the Company must increase flow equalization and install additional neutralization and clarification systems to produce an acceptable effluent.

PERMIT LIMITATIONS

Existing Permit

The existing NPDES permit limits the TSS and total iron loads on a total plant basis, i.e., the summation of the loads discharged from Outfalls 001 and 002, and "break" in the pipe for PWAN/SWAN cannot exceed 4,320 lb/day and 1,212 lbs/day, respectively (30-day average). At the existing flow rate of 19.90 mgd,* the allowable concentrations of TSS and iron are 26 mg/l and 7 mg/l, respectively, on a net basis.

The existing permit limitations were based on best engineering judgment, the remanded 1974 Effluent Guidelines and from data submitted by SCM Glidden-Durkee and the TiO_2 industry. SCM reported a process wastewater flow of 4 mgd from the production of 150 tons/day by the sulfate process, and 50 tons/day by the chloride process. The Company also reported that 1.95 mgd of the total flow was from the sulfate process Moore filters, one-third of which was strong acid and the rest weak acid.

Two-stage neutralization was the treatment operation selected by industry to reduce iron from the sulfate process strong acid waste streams to 5 mg/l with a final pH ranging between 7 and 8. The weak acid waste streams were to be neutralized to a pH 4 to 5 resulting in a final iron concentration of 100 mg/l. The final iron load for the chloride process was calculated to be 0.62 lb/ton based on a concentration of 5 mg/l and a flow of 15,000 gal/ton (9,000 gal/ton from milling and 6,000 gal/ton from other process wastes). The chloride production was assumed to be 100 tons/day based on SCM projections. Calculations of the final effluent iron load were as follows:

* 13.908 mgd (001) + 4.746 mgd (002) + 1.245 mgd (PWAN/SWAN).

Sulfate Process

$$\text{a) Strong acid: } \frac{1.95 \text{ mgd} \times 8.34 \times 5 \text{ mg/l}}{3} = 27 \text{ lb/day}$$

$$\text{b) Weak acid: } 1.95 \text{ mgd} \times \frac{2}{3} \times 8.34 \times 100 \text{ mg/l} = 1,084 \text{ lb/day}$$

$$\text{Total} = 1,111 \text{ lb/day}$$

$$\text{Roundoff} = 1,150 \text{ lb/day}$$

$$\text{Chloride Process: } 0.62 \text{ lb/ton} \times 100 \text{ tons/day} = 62 \text{ lb/day}$$

$$30 \text{ Day Average Total} = 1,212 \text{ lb/day}$$

$$\text{Daily Max} = 1 \frac{1}{2} \text{ Daily Ave} = 1,818 \text{ lb/day}$$

At the production capacity of 200 tons/day and total wastewater flows of 4 mgd, approximately 2.05 mgd would be milling wastes. At the increased production level of 250 tons/day, the milling wastes flow would be 2.56 mgd. The TSS concentration in the milling wastes was assumed to be 50 mg/l and 200 mg/l in the mixed acid waste after treatment. The TSS load was calculated as follows:

$$\text{Milling wastes: } 2.56 \text{ mgd} \times 8.34 \times 50 \text{ mg/l} = 1,067 \text{ lb/day}$$

$$\text{Mixed acid wastes: } 1.95 \text{ mgd} \times 8.23 \times 200 \text{ mg/l} = \underline{3,252 \text{ lb/day}}$$

$$\text{Total} = 4,319 \text{ lb/day}$$

$$30\text{-Day Average} = 4,320 \text{ lb/day}$$

$$\text{Daily Max} = 1 \frac{1}{2} \text{ Daily Average} = 6,500 \text{ lb/day}$$

Second Round Permit Limitations

The Effluent Guidelines Division has published the "Development Document for Effluent Limitations Guidelines and Standards the Inorganic Chemicals Manufacturing Point Source Category", June 1980 (proposed). Base level performance for Best Practicable Control Technology (BPT) currently available for the sulfate process has been identified as multiple-stage neutralization of acid wastes with limestone and lime, aeration for removal of ferrous iron, and settling. The Adrian-Joyce Works uses a multiple-stage neutralization system followed by clarification. Data supplied by the Company demonstrate that the treatment system can

produce an acceptable effluent and will meet the proposed effluent limitations. The sulfate process base level effluent concentrations for TSS and iron are 64 mg/l and 2.5 mg/l, respectively, on a net basis.

The chloride process base-level treatment consists of neutralization, final clarification, and ponding. This is the system used by the Company; however, neutralization achieved in the aragonite pit is questionable. The base-level effluent concentrations for TSS and iron from the chloride process are 64 mg/l and 2.5 mg/l, respectively, on a net basis. The Company can achieve the TSS and iron concentrations if they commit themselves to treatment rather than considering the wastewaters as an environmental stream with minimal treatment.

Based on the Development Document, the total wastewater load discharged from the PWAN/SWAN system and Outfalls 001 and 002 should not exceed the following on a net basis:

	<u>30-Day Average</u> lb/day	<u>Daily Maximum</u> lb/day
Total Suspended Solids	9,510	34,500
Iron	380	1,300
pH	6.0 - 9.0	

Based on the current flow rates provided by the Company, the TSS and iron concentrations in the entire plant load average 57 mg/l and 2.3 mg/l, respectively. Using the data submitted to NEIC by the Company for March 7 to May 5, 1980, river water TSS and iron concentrations averaged 40 mg/l and 8 mg/l, respectively. The allowable effluent concentrations on a gross basis would be 97 mg/l for TSS and 10.3 mg/l for iron.