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**TREATABILITY STUDIES**  
**for the**  
**INORGANIC CHEMICALS MANUFACTURING**  
**POINT SOURCE CATEGORY**

**Prepared for**

**Effluent Guidelines Division**  
**Office of Water and Waste Management**  
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# NOTICE

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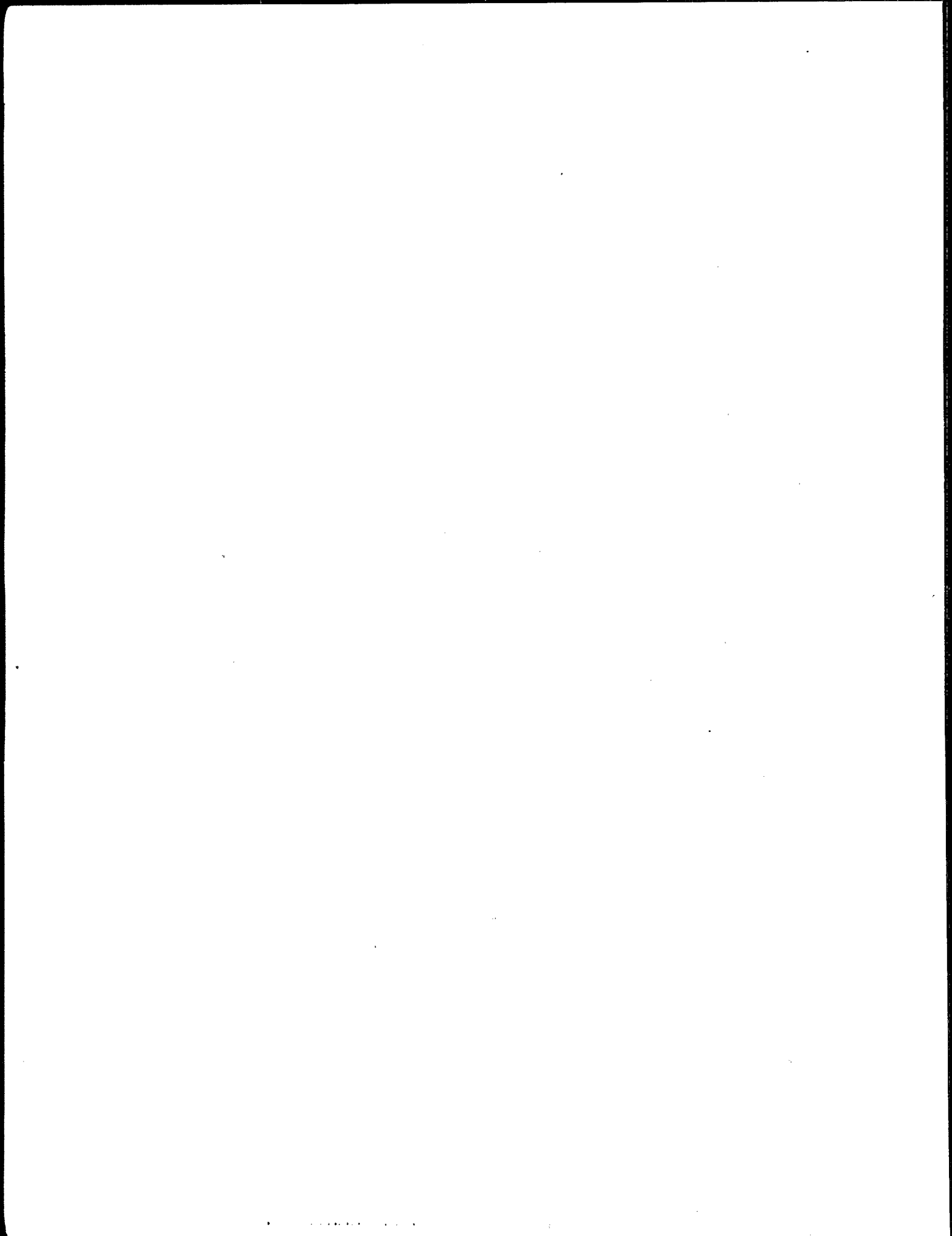
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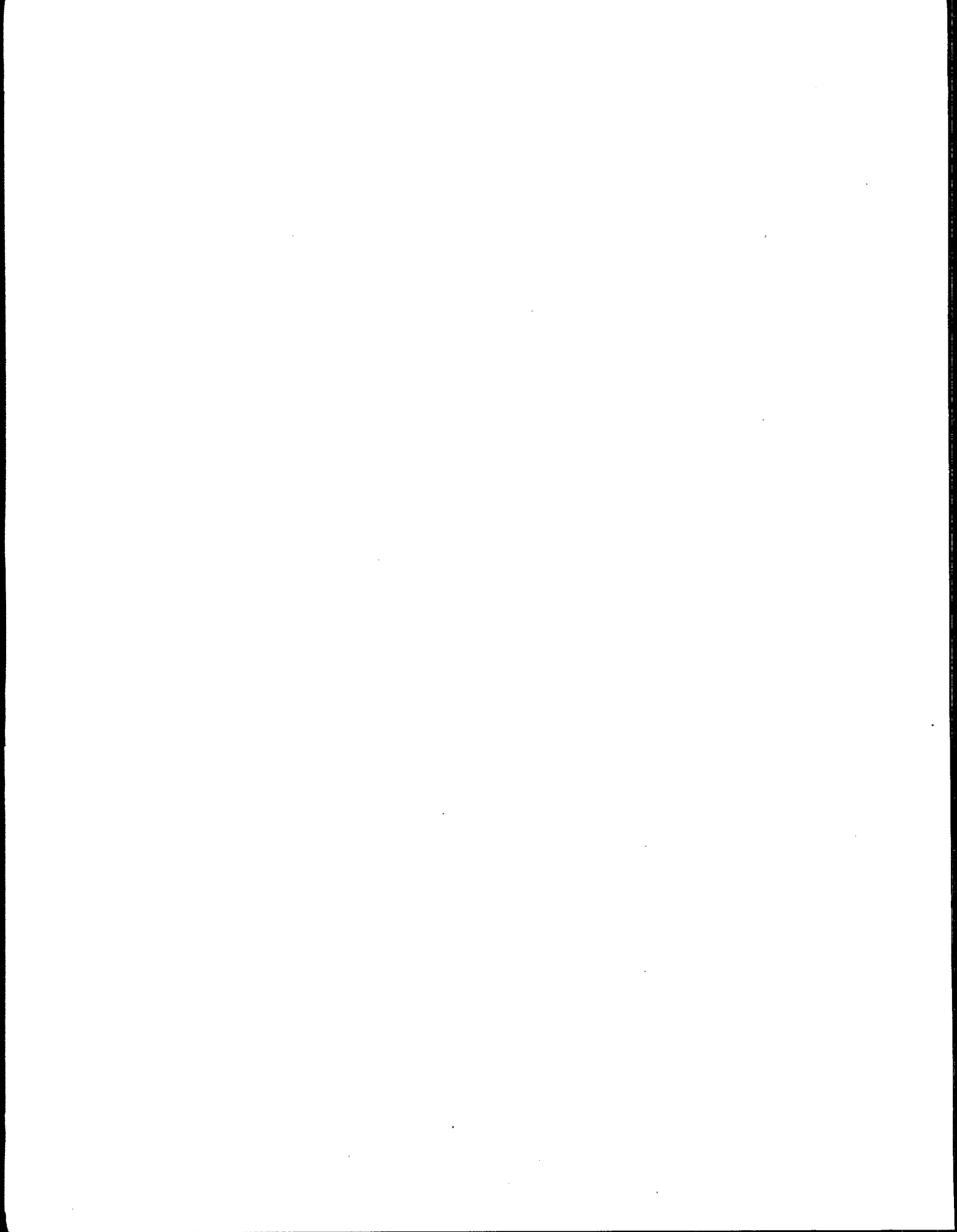
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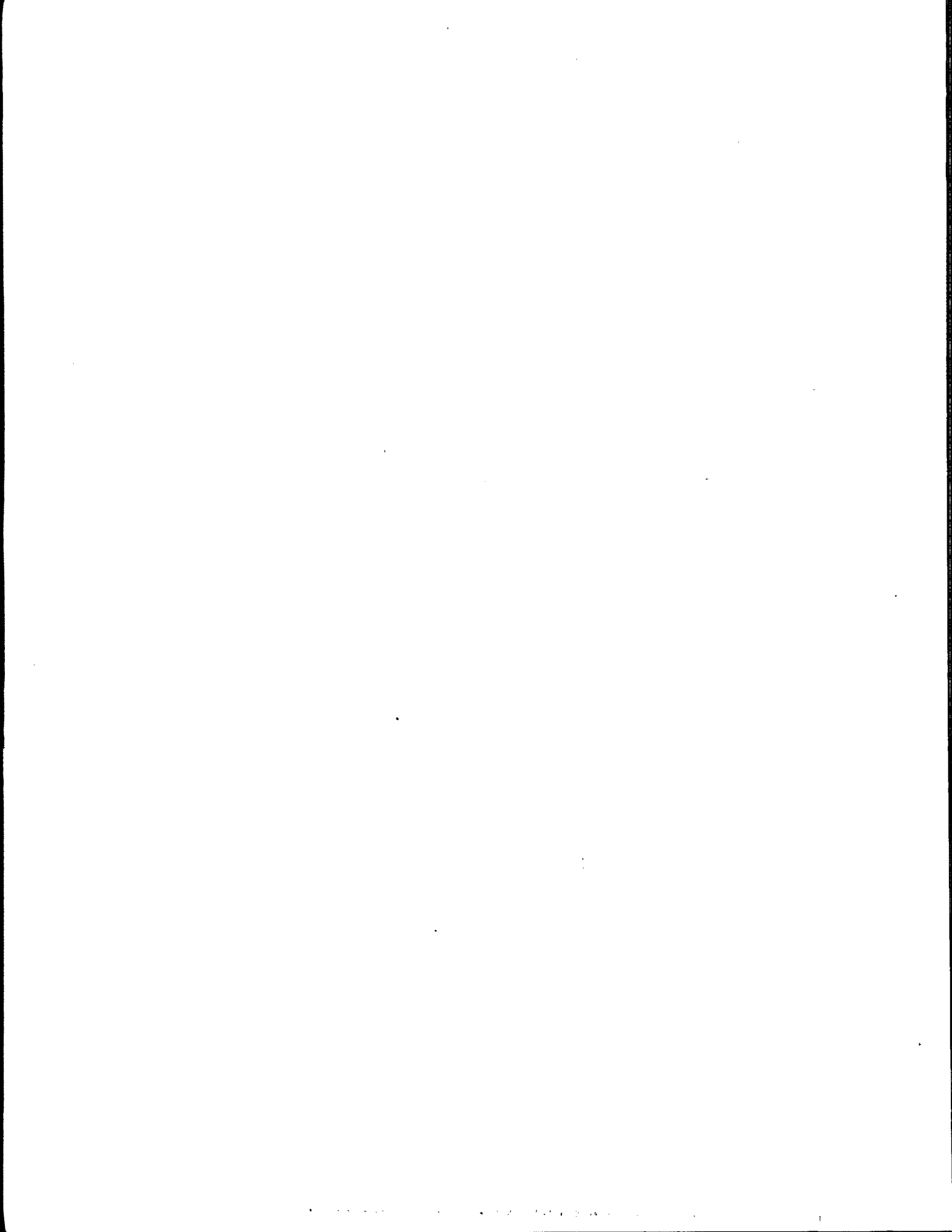


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## SECTION 1.0

### INTRODUCTION

#### 1.1 OBJECTIVES

The major purpose underlying this Treatability Study is to evaluate the achievable performance of proposed Best Available Technologies (BAT) for the treatment and control of pollutant discharges, and to provide empirical treatment system performance information applicable to selected inorganic chemical subcategories. The study specifically concentrated on those subcategories in the Inorganic Chemicals Industry for which analytical data on raw waste waters and treated effluents either do not exist or are deficient, and for which data are needed for purposes of comparison with proposed effluent limitations currently being proposed by the Effluent Guidelines Division of the Environmental Protection Agency (1).

This study focuses on available treatment technologies which have been selected as the basis for the proposed BAT regulations. The majority of plants in the particular industries under study practice the BPT level of treatment in accordance with existing or previous regulations. In most cases, the BAT level of treatment can be achieved by adding onto the BPT systems a final polishing step designed to remove additional toxic metals and other pollutants of concern from the process waste streams. Although BAT treatment is generally known and practiced to some extent in the Inorganic Chemicals Industry, its application in the particular product subcategories under study represents a transfer of technology within the industry. For this reason, a demonstration of applicability and an evaluation of performance with regard to the treatment of these particular waste streams are required in the regulation development process.

- (1) U.S. Environmental Protection Agency. Development Document for Proposed Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Inorganic Chemicals Manufacturing Point Source Category. June 1980.

## 1.2 SCOPE OF TREATABILITY STUDIES

Table 1-1 outlines the inorganic chemical subcategories studied, treatment technologies tested, and pollutants evaluated in each subcategory.

TABLE 1-1. INORGANIC CHEMICAL INDUSTRY SUBCATEGORIES  
EVALUATED BY TREATABILITY TESTS

Subcategory	Pollutants of Concern	Treatments Tested
Hydrofluoric Acid/ Aluminum Fluoride	TSS, F, Ni, Zn, Cr(T)	Lime plus filtration
Chlor-Alkali (Diaphragm Cell with graphite anodes)	TSS, Pb, Cr(T), Ni	Lime followed by iron sulfide plus filtration.
Chrome Pigments	TSS, Cr(T), Pb, Zn, Cd	Treatment by FeS to precipitate residual metals. (Cr had already been removed by reduction with SO <sub>2</sub> followed by precipi- tation as Cr(OH) <sub>3</sub> .)
Sodium Dichromate	TSS, Cr(T), Ni	a) Simultaneous chro- mate reduction and precipitation by Na <sub>2</sub> S followed by alkaline precipita- tion plus dual media filtration.* b) Chromate reduction by ferrous chloride, then precipitation by lime; dual media filtration.
Nickel Sulfate	TSS, Ni	a) Caustic soda plus filtration. b) Lime plus filtration.

\*Originally proposed treatment although modified to alternate b during the treatability investigations.

TABLE 1-1 - continued

Subcategory	Pollutants of Concern	Treatments Tested
Copper Sulfate	TSS, Cu, Ni, Se	a)Caustic soda plus filtration. b)Lime plus filtration.
Sodium Bisulfite	TSS, COD, Zn	Aeration.
Sodium Hydrosulfite	TSS, COD, Cr(T), Zn	Aeration plus filtration.
Titanium Dioxide (Chloride Process)	TSS, CR(T), Fe, Ni, Zn	Lime plus filtration.

## SECTION 2.0

### DESCRIPTION OF CONTROL TECHNOLOGIES

#### 2.1 GENERAL CONSIDERATIONS

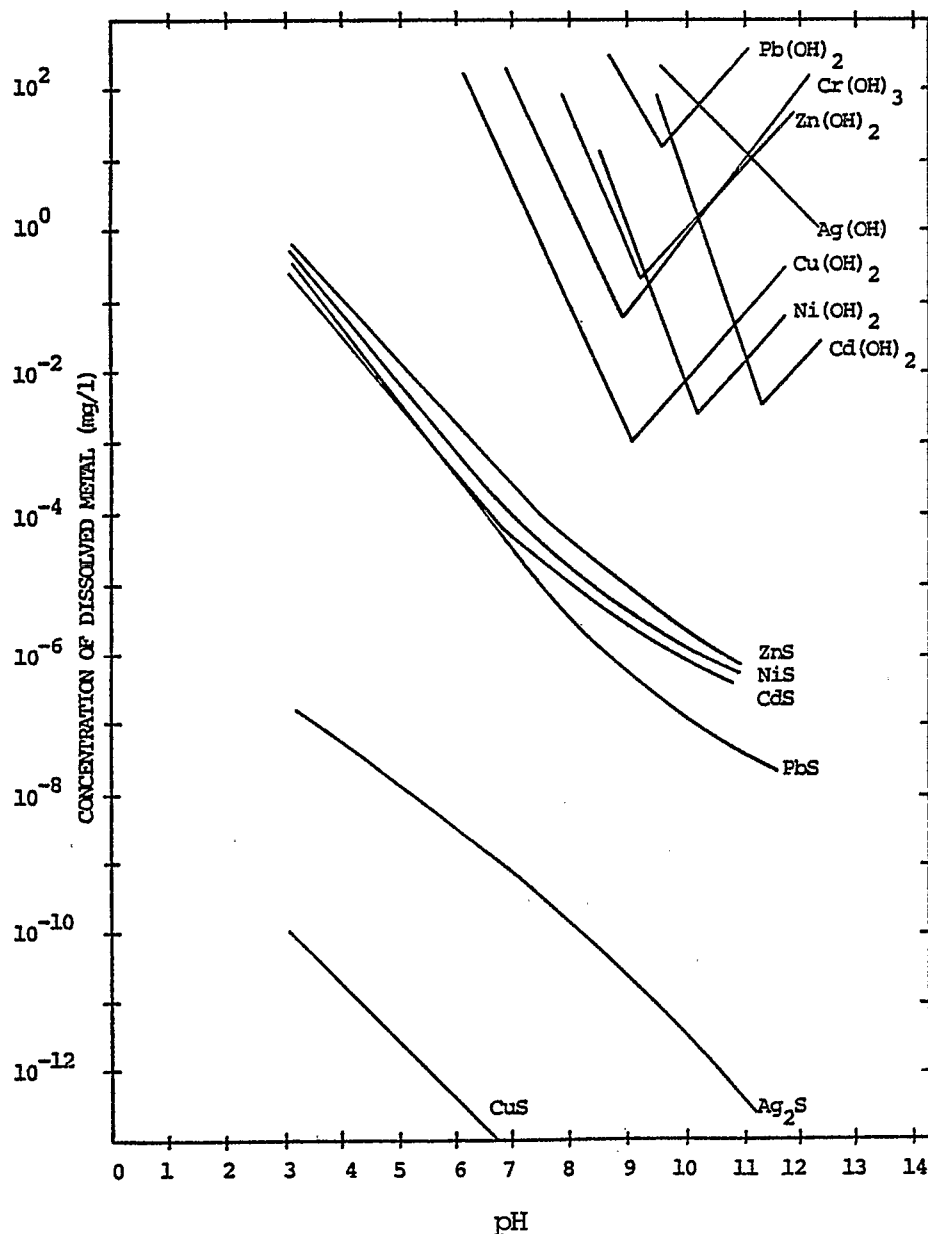
The treatment technologies applied in the treatability tests consisted of well established unit processes. These processes include removal of heavy metals by precipitation as hydroxides and/or sulfides, reduction of chromate, precipitation of fluorides with lime, separation of solids by settling and dual media filtration, and oxidation by aeration. The primary chemical unit processes are discussed below.

#### 2.2 PRECIPITATION OF HYDROXIDES

The most widely used treatment technology for the removal of most metals from chemical wastes is their precipitation as hydroxides. Caustic soda ( $\text{NaOH}$ ) and slaked lime ( $\text{Ca(OH)}_2$ ) are the two precipitants most commonly used for this purpose.

The amount of a metal ion, as for example,  $\text{Zn}^{++}$ , that can remain in solution diminishes with increasing pH, but a point is reached at which the metal can be in solution as a negative ion, as for example,  $\text{ZnO}_2^-$ . The amount of this ion that can be in solution increases with increase of pH. Thus, there is, for any metal showing this "amphoteric" character, a pH at which the solubility is minimal. This is often called the isoelectric point. Figure 2-1 shows this behavior of the hydroxides. The figure is illustrative and relative, and must not be considered as a representation of quantitative information.

The normal isoelectric pH of a metal is not always the optimal point for its removal, because other components, especially complexing agents, may have major effects. For any particular type of waste water, the optimal pH needs to be found by trial.



NOTE:

1. Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," Industrial Water Engineering, Page 31, (Jan./Feb. 1973).
2. Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

Figure 2-1. Comparative solubilities of metal hydroxides and sulfide as a function of pH.



### 2.3 PRECIPITATION OF SULFIDES

As shown in Figure 2-1, the solubilities of the sulfides of most of the common metals are orders of magnitude lower than the solubilities of the hydroxides. Therefore, the residual concentrations of one of these metals in a waste water after treatment by a soluble sulfide is expected to be lower than after precipitation by a hydroxide. This would make it appear that sulfide precipitation should be the method of choice. This is not necessarily the case. Attention must be given to the amenability of the precipitate to removal, economic factors, air pollution with hydrogen sulfide (H<sub>2</sub>S), byproduct disposal, and the actual environmental significance of the traces of metals that may remain.

Sulfide precipitation is usually accomplished by addition of Na<sub>2</sub>S or NaHS. Either compound, when dissolved in water, gives a solution in which the sulfur is largely in the form of HS<sup>-</sup>. The Na<sub>2</sub>S hydrolyses to give HS<sup>-</sup> and OH<sup>-</sup>, and thus produces a more alkaline solution, but there is very little S<sup>=</sup> unless the pH is above 12. The precipitation of a divalent metal is essentially as follows:



Sometimes, precipitation is accomplished by adding freshly prepared ferrous sulfide. An exchange reaction (metathesis) occurs, as follows:



From the relative solubilities of the hydroxides and the sulfides, it would appear that the residual metal concentration in a waste water would be much lower if sodium sulfide is used as the precipitant, but this is not necessarily so, because the amenability of the precipitate to separation by settling and filtration is an important factor. The sulfide precipitates have less tendency to flocculate and a greater inclination to produce colloidal precipitates than do the hydroxides.

There is a disinclination in industry to use the sulfide method because of the possibility of the mixing of the sulfide solution with an acid solution and the consequent release of H<sub>2</sub>S, a highly toxic gas that has claimed many lives in industrial

accidents. The hazard is greater when using NaHS or Na<sub>2</sub>S, but it can also happen with FeS.

Regardless of how the metals are precipitated, they will be removed as a sludge that must be disposed of in an environmentally acceptable manner.

## 2.4 OXIDATION

Chemical oxidation is another technique commonly used for the destruction of pollutants in a waste. The cheapest oxidant is air. Oxygen may be dissolved in the waste water by bubbling air through it, or by bringing the waste water and air into contact in some other way. Sometimes pure oxygen is used, and sometimes oxidation has been accomplished by the use of chlorine or hydrogen peroxide. Often, biological growths are instrumental in bringing about the reaction between oxygen and the substance (reducing agent) with which it reacts. The biological oxidation process is difficult to utilize on inorganic chemical industry wastes without addition of substantial quantities of dilution water and/or nutrient supplements. In addition, many of the pollutants found are toxic to biological growths. In the chemical subcategories studied herewith, only the sodium hydrosulfite industry currently employs biochemical oxidation of oxygen demand.

Oxidation by air was tested for treating waste waters from the sodium bisulfite and sodium hydrosulfite subcategories. The treatment was aimed at the reduction of the inorganic constituents which contribute to the high COD. The rationale of using air oxidation was that most of the COD present in the waste was believed to be due to sulfite and hydrosulfite, which will react with oxygen. It was found, however, that various other forms of sulfur are present and that elemental sulfur may be present or may be produced when the waste is acidified. Attempts to measure COD in such samples give highly erratic results.

## 2.5 CHROMATE REDUCTION

The reduction of chromium from the hexavalent form to the trivalent form is essential, since hexavalent chromium cannot be removed by alkaline precipitation (unlike the trivalent form).

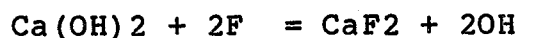
It should be noted that chromium sulfide does not exist in aqueous systems as it is readily oxidized to the hydroxide. Therefore, sulfide precipitation is not a viable technology for chromium removal.

Chromate is reduced in the chrome pigments industry by introduction of sulfur dioxide into the raw waste under acidic

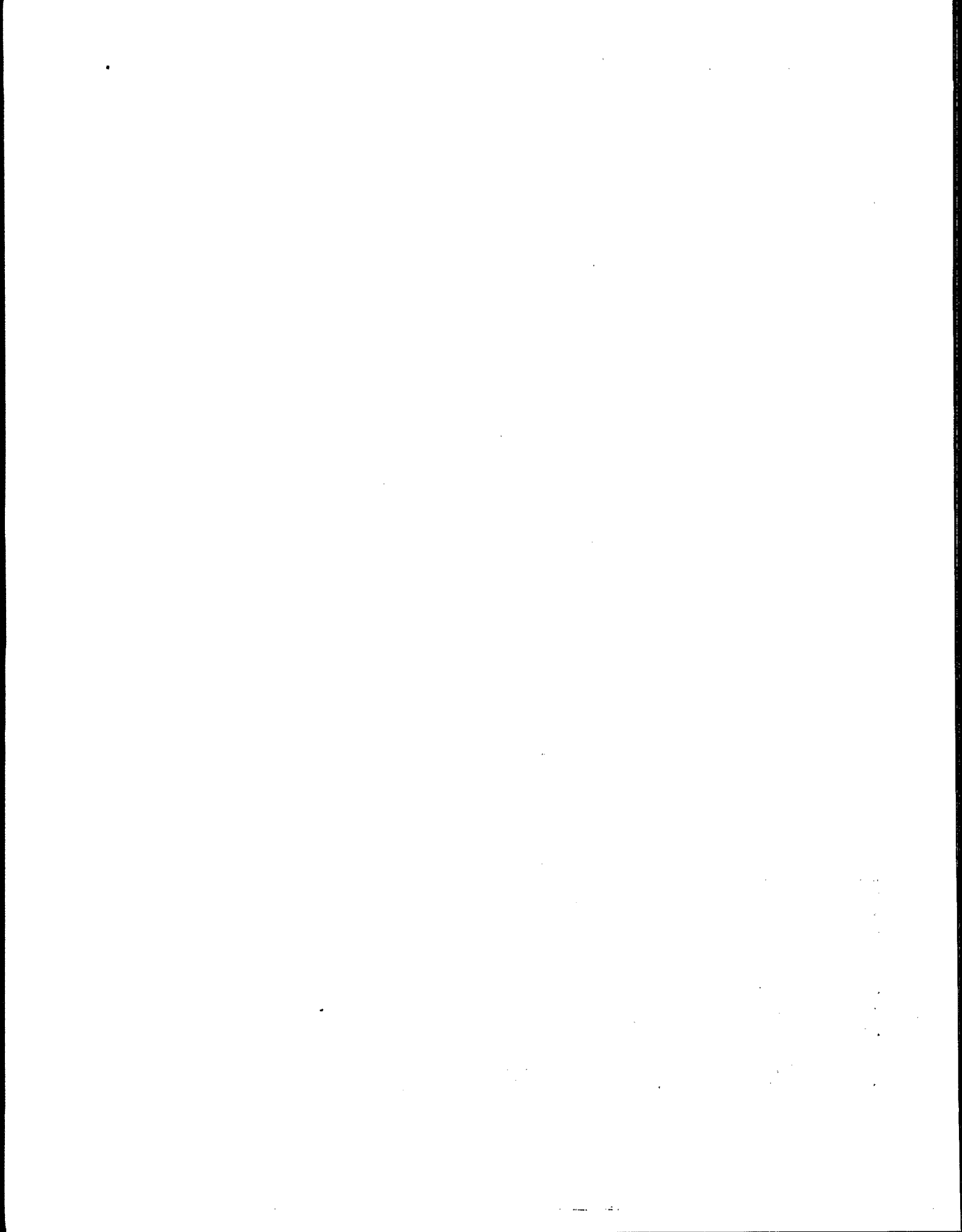
conditions. Chromate may also be reduced using ferrous chloride as is done in the sodium dichromate industry.

## 2.6 FLUORIDE PRECIPITATION

The conventional method of treating fluoride bearing wastes is to precipitate the fluoride as calcium fluoride by the addition of lime. The reaction is:



Using this process alone, it is difficult to remove free fluoride to concentrations less than 8 mg/l under ideal conditions due to the solubility of calcium fluoride.



## SECTION 3.0

### PROGRAM METHODOLOGY

#### 3.1 DESCRIPTION OF TEST APPARATUS DESIGN AND OPERATION

In order to study the variety of BAT treatment concepts under evaluation, pilot scale test equipment was designed to incorporate the following operations:

1. Chemical reactions, including:
  - a. pH adjustment
  - b. reduction
  - c. oxidation by air
  - d. precipitation
  - e. stirring
2. Sedimentation
3. Decantation
4. Filtration
5. Sludge removal

The various chemical treatment reactions were performed in a 30 gallon linear polyethylene tank with conical bottom and equipped with a stirrer. The conical bottom was designed to assist in sludge removal through a bottom valve. The amount of waste water treated was usually between 20 to 25 gallons.

In cases where treatment required addition of caustic soda or lime, the stirrer was started and the chemical was added until a selected pH was reached. Most other chemicals were added in predetermined amounts.

When aeration was required, air from a diaphragm compressor was fed to six porous media diffusers placed in the bottom of the

tank. The mixer was operated during aeration runs, to improve the dispersion of the air.

If the treatment included precipitation and clarification by settling, the supernatant was decanted by the use of a hose serving as a siphon, and the sludge was then withdrawn through the bottom of the tank. After the supernatant was returned to the tank, it was pumped to the filter.

The filter consisted of a 4-inch ID PVC column 40 inches high, with removable flange plates at each end. A stainless steel screen, 30 mesh with 0.01 inch diameter wire, was inserted into the column about six inches from the bottom, for support of the media. The bottom 9 inches of the media was silica sand with an effective size between 0.4 and 0.66 mm, supporting 18 inches of anthracite coal with an effective size between 0.7 and 1.7 mm and a uniformity coefficient of 1.7. The filter media was normally replaced before each test and it was washed with water for about 20 minutes before being used; therefore, no backwashing was practiced.

The flow to the filter was controlled by a needle valve and monitored by use of a rotameter. The rate in all cases was kept at 0.25 gpm, equivalent to a filtration rate of 3.1 gpm/ft<sup>2</sup>. By use of a throttling valve at the bottom, the liquid level over the filter media was usually kept between 1.0 and 1.5 inches. The flange closing the top of the filter permitted it to be operated under pressure.

Usually the filtrate was recirculated to the reaction tank for a period of generally 30 to 40 minutes to increase the efficiency of the filtration operation. Then the entire batch was filtered and the filtrate was sampled. Figures 3-1 and 3-2 illustrate the apparatus.

### 3.2 SAMPLING AND ANALYTICAL PROCEDURES

Samples were collected from the raw waste water, clarified supernatant, and the filtrate for each of the treatability tests. All the samples were split into three for analysis. One of the portions was unpreserved and utilized for the TSS determination. The second portion was filtered through a Whatman Filter Paper No. 40. All constituents of the filtered waste water were described as "dissolved". The filtrate was preserved by adding HNO<sub>3</sub> and was subsequently used for the determination of dissolved metals. The third portion was not filtered, but was also preserved with HNO<sub>3</sub>. This sample was subjected to "total" metals determinations. All samples were collected in one liter plastic containers. When the treatability tests were carried out in the field, the sample bottles were refrigerated with ice and sent by

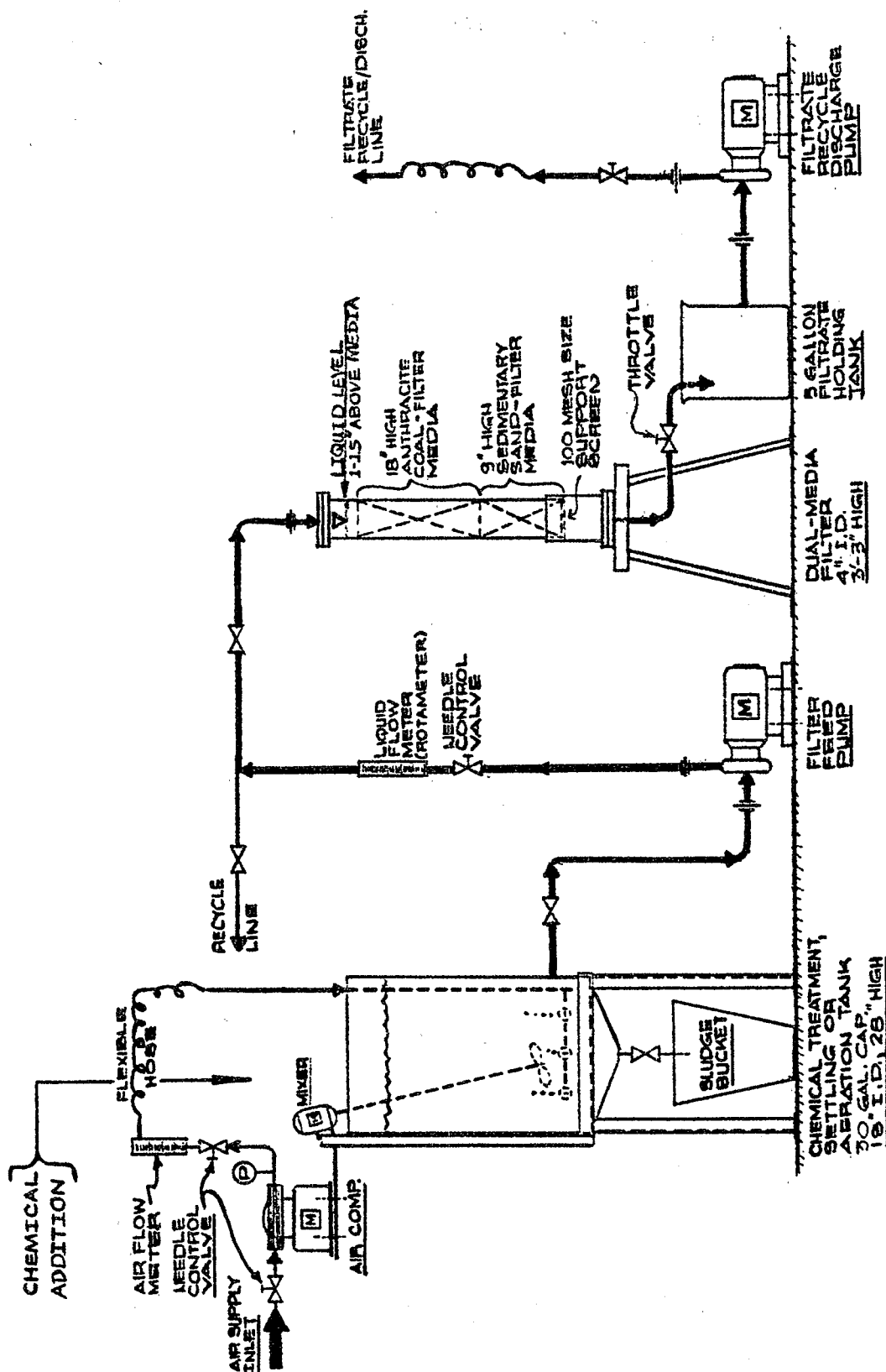


Figure 3-1. Inorganic waste water-treatment test system.

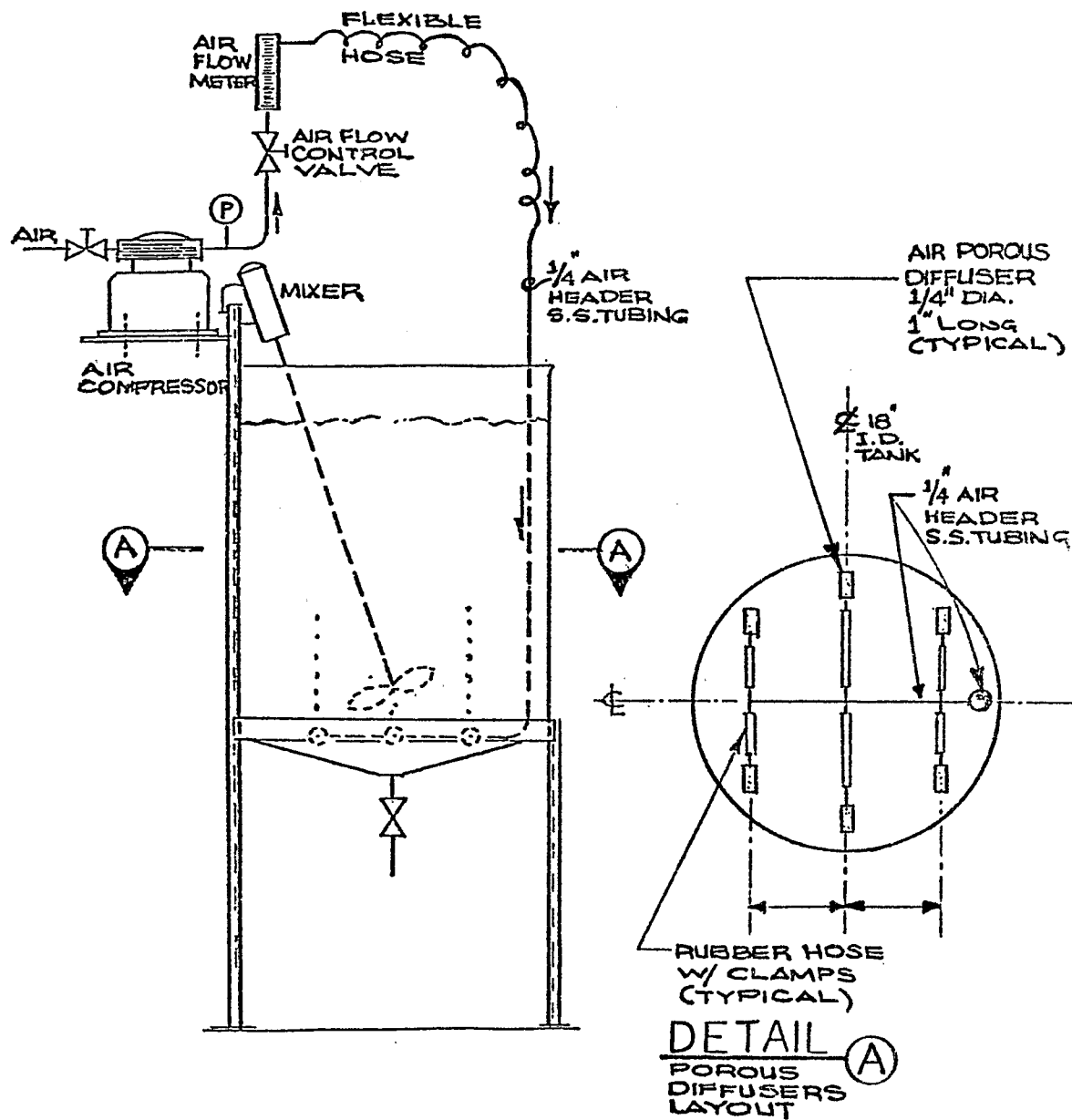


Figure 3-2. Aeration system.



overnight delivery to the analytical laboratories. The samples were always kept refrigerated following receipt until they were analyzed. Refrigeration of the samples prior to the analytical determinations was also practiced when the test runs were performed in the Pasadena and Springfield laboratories. The analytical determinations were done following methods approved by EPA as indicated in Table 3-1.

### 3.3 WASTE WATER CHARACTERIZATION

Waste water samples, usually 5 gallons, were collected for characterization from each subcategory prior to the test runs. Pollutant concentrations were determined, and in some cases, more complete analyses were made so as to provide a better understanding of the chemistry of the waste waters. The analytical methods used were EPA approved methods.

### 3.4 TREATMENT OPTIMIZATION

Characterization of the waste provided the basis for optimization of the treatability tests in each subcategory. In each series of treatability tests involving precipitation of heavy metals by alkaline treatment, the initial raw waste sample was used to determine the pH for optimum metal removal. This was accomplished by running a series of beaker tests at approximately pH intervals of 0.5 covering the theoretical optimum precipitation range for the pollutants under consideration. The concentration of the metals remaining in solution was determined at each pH value and on the basis of the test results, an optimum pH was selected.

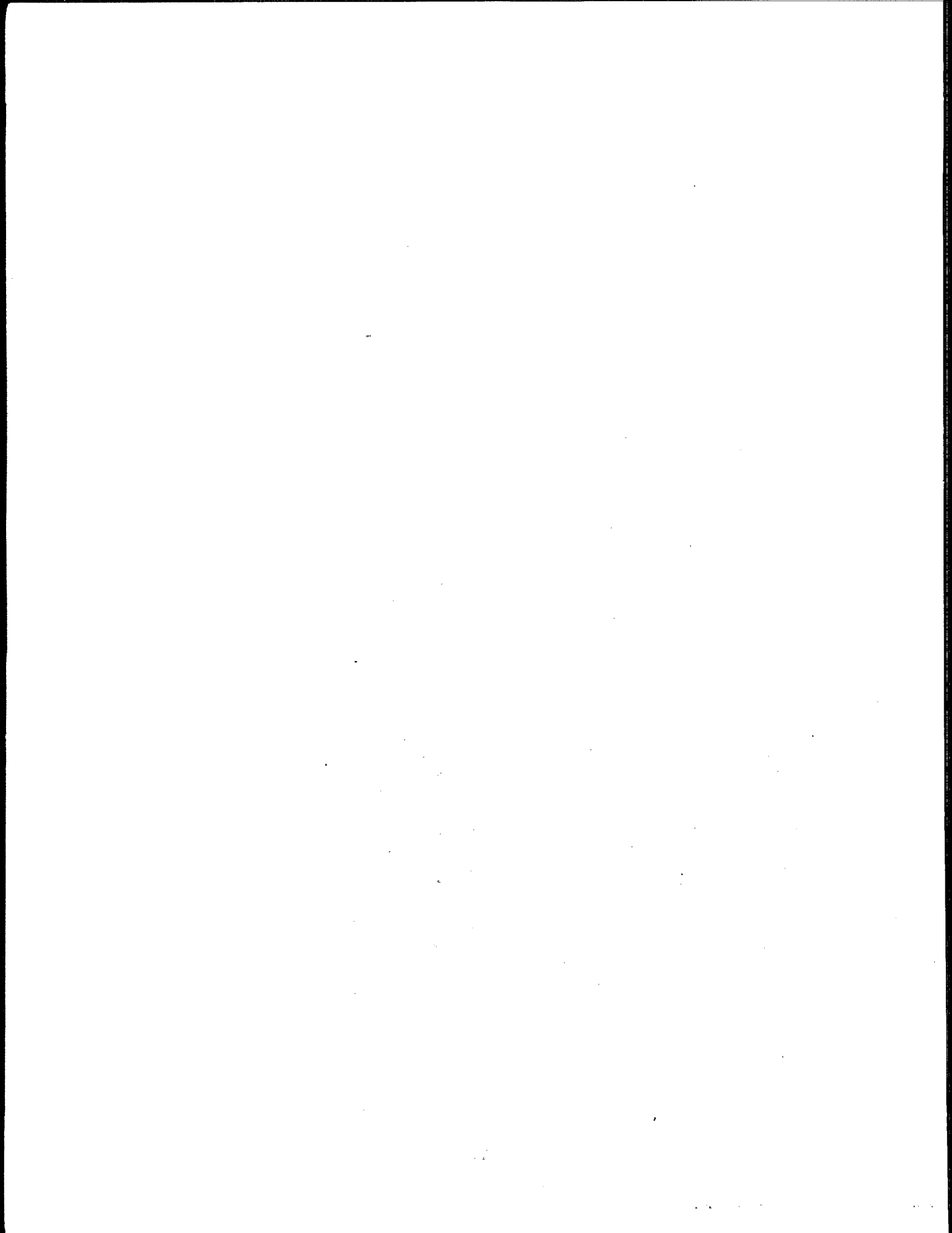
TABLE 3-1. LIST OF APPROVED ANALYTICAL TEST PROCEDURES USED

Parameter	Method
Acidity as CaCO <sub>3</sub>	Phenolphthalein end point
Alkalinity as CaCO <sub>3</sub>	Methyl orange end point
Methyl Orange Acidity as CaCO <sub>3</sub>	Methyl orange end point
Phenolphthalein Alkalinity as CaCO <sub>3</sub>	Phenolphthalein end point
Carbonate	Calculation based on alkalinity
Total Suspended Solids	Gravimetric GFC filtration, 104 degrees C
Total Dissolved Solids	Gravimetric GFC filtration, 180 degrees C
Total Residue	Gravimetric, 104 degrees C
Fixed Residue	Gravimetric, 550 degrees C
Total Nitrogen (Kjeldahl)	Digestion and distillation followed by titration or nesslerization
Sulfate	Gravimetric, BaSO <sub>4</sub> precipitation
Nitrate	Brucine method
Phosphate	Vanadomolybdophosphoric acid
Iodate demand	Iodide-iodate titration*
Chloride	Mercuric nitrate method
Fluoride (free)	Ion electrode

\*The iodide-iodate acid titration is not specific for any one compound, but it reacts with any sulfite, hydrosulfide, thiosulfate and possibly other substances. When one of these substances is dominant, the titration is treated as a measure of that substance.

TABLE 3-1 - continued

Parameter	Method
Fluoride (total)	Distillation followed by ion electrode
Total Hardness as CaCO <sub>3</sub>	EDTA titration
Calcium as Ca	Digestion followed by atomic absorption
Magnesium as Mg	Digestion followed by atomic absorption
Chemical Oxygen Demand	Dichromate reflux
pH	Ion electrode
Nickel	Digestion followed by atomic absorption
Zinc	Digestion followed by atomic absorption
Chromium (Total)	Digestion followed by atomic absorption
Lead	Digestion followed by atomic absorption
Cadmium	Digestion followed by atomic absorption
Selenium	Digestion followed by atomic absorption
Iron	Digestion followed by atomic absorption
Sodium	Digestion followed by atomic absorption
Potassium	Digestion followed by atomic absorption
Copper	Digestion followed by atomic absorption
Aluminum	Digestion followed by atomic absorption
Chromium (hexavalent)	Colorimetric, Diphenylcarbazide method



## SECTION 4.0

### PROGRAM DEVELOPMENT

#### 4.1 GENERAL CONSIDERATIONS

Preparations to conduct the treatability studies started in July 1979. Jacobs Engineering Group Inc. as part of Contract No. 68-01-5767 undertook the task of performing treatability tests on nine industrial subcategories in which the achievability of the proposed effluent limitations using BAT needed to be demonstrated. Jacobs developed a comprehensive work plan which included, for each subcategory, the following:

1. Selection of an industrial plant from each of the nine chemical subcategories under consideration. Whenever possible, this selection was based on considerations as to how representative the plant to be studied would be for the entire subcategory being considered.
2. Development of the treatability tests to be performed on each subcategory.
3. Review of the process flow diagrams for each of the plants selected in order to determine the most representative point for collection of the waste water to be used in the treatability tests.
4. Contacts with the appropriate plant personnel. This was essential and necessary in order to explain to them the purpose of the treatability studies and obtain their collaboration and permission to collect the required waste water samples.
5. Concurrently with the implementation of steps 1 through 4, work was started on the design, selection, and procurement of equipment, and assembly of treatability units.
6. Negotiations with Versar, Inc. for implementation of portions of the study.

#### 4.2 LOGISTICS CONSIDERATIONS

Most of the plants selected for study were located on the East Coast and in the South. Since Versar Inc. is centrally located with respect to plants in the East Coast and in the South, the treatability work was divided on a geographical basis to take full advantage of Versar's laboratory and mobile units. Jacobs concentrated on plants located on the West Coast.

## SECTION 5.0

### STATISTICAL ANALYSIS

#### 5.1 OBJECTIVES OF STATISTICAL ANALYSIS OF TREATABILITY DATA

As part of this treatability study, selected inorganic chemicals manufacturing plants employing various available treatment technologies, and thought to be representative of the inorganic chemicals industry, were chosen for study. Effluent samples were drawn from appropriate points in raw process waste water and treated waste water streams. The concentration levels (mg/l) of chemical pollutant parameters in these samples were determined by laboratory measurements and the resultant data presented for statistical analysis. The main objective of the analysis was the demonstration of achievable performance levels for BAT treatment technologies presently under consideration for effluent limitations guidelines in the Inorganic Chemicals Manufacturing Point Source Category.

A demonstration of this nature requires certain assumptions regarding the applicable statistical or probabilistic models used. These assumptions are outlined in the following sections.

#### 5.2 ASSUMPTIONS CONCERNING MEASUREMENT OF POLLUTANT CONCENTRATION LEVELS

In the formulation and calculation of statistical characteristics of treatability performance from laboratory measurements, individual sample measurements of pollutant concentration levels were assumed to follow the lognormal distribution, a well known and generally accepted statistical probability model used in pollution analysis, and which is appropriate for measurements of levels taken on a daily basis. This assumption is equivalent to the assertion that the logarithms of individual measurements follow a normal probability model. It was also assumed that sampling at a given plant was conducted responsibly, and in such a way that the resulting measurements can be considered statistically independent and,

therefore, amenable to standard statistical estimation procedures.

### 5.3 STATISTICAL METHODOLOGY OF PERFORMANCE ASSESSMENT

To measure treatability level for a given process employing a certain treatment technology, the "probability performance" was calculated for each parameter in the treated effluent stream. This quantity is the probability that a given stream will have a pollutant level (mg/l) that is within a stipulated effluent guideline limitation level. This amounts to the probability that a plant employing the proposed BAT effluent treatment will produce a 30-day average concentration less than the corresponding limitation level. Where a pollutant discharge level is measured by the average concentration in thirty individual daily measurements (the 30-day average), the probability performance represents the proportion or fraction of the 30-day averages that will be less than or equal to the given limitation level.

For this study, the maximum likelihood estimation procedure, based upon a sequence of "runs" of treatments, was used to estimate the probability performance. This method chooses as the estimated probability performance that value which is most likely to have produced the observed sample consistent with the model chosen. Standard maximum likelihood procedures are available and widely known, and are the methods on which the statistical estimation in this study are based.

The data included in the statistical analysis were successively screened for outliers through use of the t-statistic and on the basis of technical considerations. For each subcategory studied, the statistical results are presented in terms of both the screened and unscreened data. The t-statistic is defined by the equation:

$$t = \max \left( (x_{\max} - \bar{X})/S, (\bar{X} - x_{\min})/S \right)$$

Where:  $x_{\max}$  is the datum corresponding to the greatest parameter level in a particular run, and  $x_{\min}$  to the smallest.

$\bar{X}$  is the sample average over all repetitions of runs.

$s$  is the sample standard deviation of  $x$ .



For those cases where a treatability sample had a maximum value or minimum value sufficiently large or small so as to produce a t-statistic exceeding the 99 percent confidence limits from the t-distribution, that datum was rejected as an outlier and treatability statistics were recomputed on the screened sample.

#### 5.4 ASSUMPTIONS CONCERNING 30-DAY AVERAGE POLLUTANT LEVEL MEASUREMENTS

Even though individual pollution concentration measurements are assumed lognormally distributed, that assumption does not extend to the statistical behavior of averages, in this case where 30-day averages are to be used. However, if averages are taken over a "reasonably large" number of days, a statistical principle, the Central Limit theorem, assures that probabilities pertaining to such averages may be computed using the normal probability distribution. A 30-day average contains enough individual daily measurements to insure that the normal probability model is satisfactory for use in final calculation of probability performance.

#### 5.5 COMPUTATIONAL PROCEDURES

To compute the maximum likelihood estimates (MLE's) of probability performance, it is necessary to compute the MLE's of the long term average pollution level and the long term standard deviation of pollution level using logarithms of the individual measurements of data for each run. These estimates, the maximum likelihood estimates of the mean logarithm and standard deviation of logarithms are done using standard statistical formulae.

These estimates are computed and used to obtain the MLE's of the long term average,  $A$ , and long term standard deviation,  $S$ , of the pollutant concentration. Dividing the estimated long term standard deviation,  $S$ , by the square root of the number of days (30) in the average, gives  $S^*$ , the estimated standard error of the 30-day average, and which can be used in computing probability performance. For any limitation value,  $L$ , the estimated probability performance,  $p$ , is computed as:

$$\text{Probability(30-day average does not exceed } L) = \Pr(z)$$

$$\text{where } z = (L-A)/S^*$$

$$\text{and } \Pr(z) = \text{probability that a standardized normal value does not exceed } z.$$

Standard statistical measures of pollution level in treated effluent for each subcategory are tabulated and recorded in Appendix A. These include minimum (Min) arithmetic sample average (Avg), maximum (Max) standard deviation (Stdv), and coefficient of variation (C.Var).

Included with the technical analysis of each subcategory are the probability performance curves and estimates of long term average for each parameter. Note that the estimate of long term pollution average is obtained by maximum likelihood methods from the lognormal distribution and does not necessarily equal the sample arithmetic average given in Appendix A.

Where a parameter curve is quite "steep", i.e., for those parameters that show a sharp increase in probability (of a 30-day average not exceeding a given value) for a small increase in pollution concentration, this is primarily due to a relatively small standard deviation. In other words, the steepness of the curve relates to the degree of consistency in the sample results.

## SECTION 6.0

### NICKEL SULFATE SUBCATEGORY

#### 6.1 INTRODUCTION

##### 6.1.1 General Considerations

To test the BAT concept as proposed for this subcategory, a treatability model unit was set up at PJB Laboratories, a division of Jacobs, in Pasadena, California. The tests were carried out from September 4 to November 12, 1979, and a total of 24 runs were completed in this period.

Samples were collected from Plant #369 which operated on a non-daily, batch type basis, so waste water was not always available. In this case, the treatability team running the unit was advised in advance by plant personnel when to be ready for sample collection. It became evident, however, that it would not be possible to obtain enough samples from this plant alone to be statistically significant in the time span available to perform the tests. Therefore, Plant #120 was also selected for study. Arrangements were made to have a technician at that plant collect and send samples for three consecutive days. Enough waste water was collected during each sampling occurrence to run two tests, using lime and caustic soda solution, for pH adjustment. This was done in order to provide a basis for a direct comparison between the results obtained by each treatment method.

##### 6.1.2 Sample Point Location

Figures 6-1 and 6-2 are flow diagrams for the current waste water handling facilities of the two plants selected for study. Samples for use in performing treatability tests were collected from the locations indicated on the diagrams.

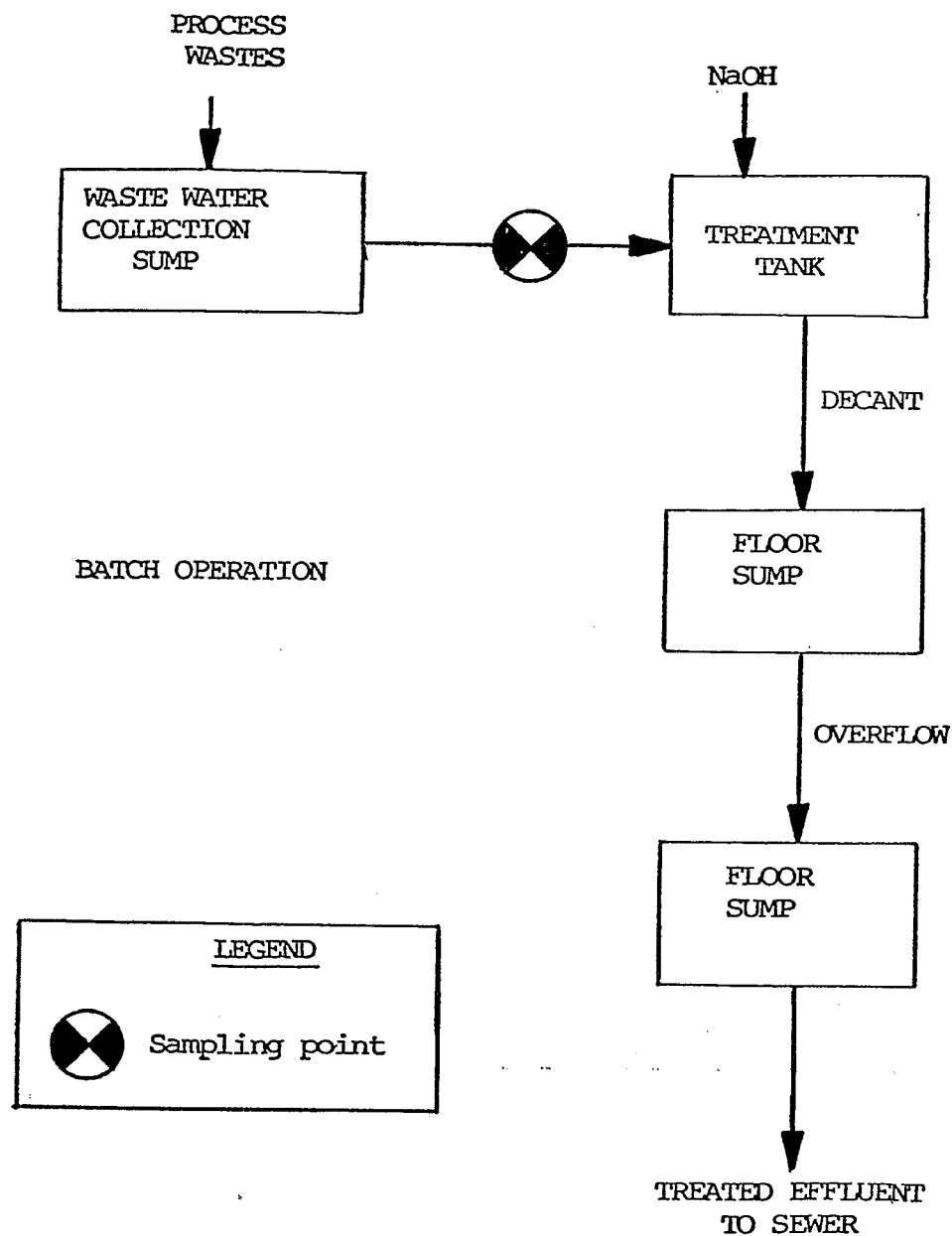


Figure 6-1. General waste water treatment process flow diagram showing the sampling point at plant #369. (Nickel sulfate manufacture.)

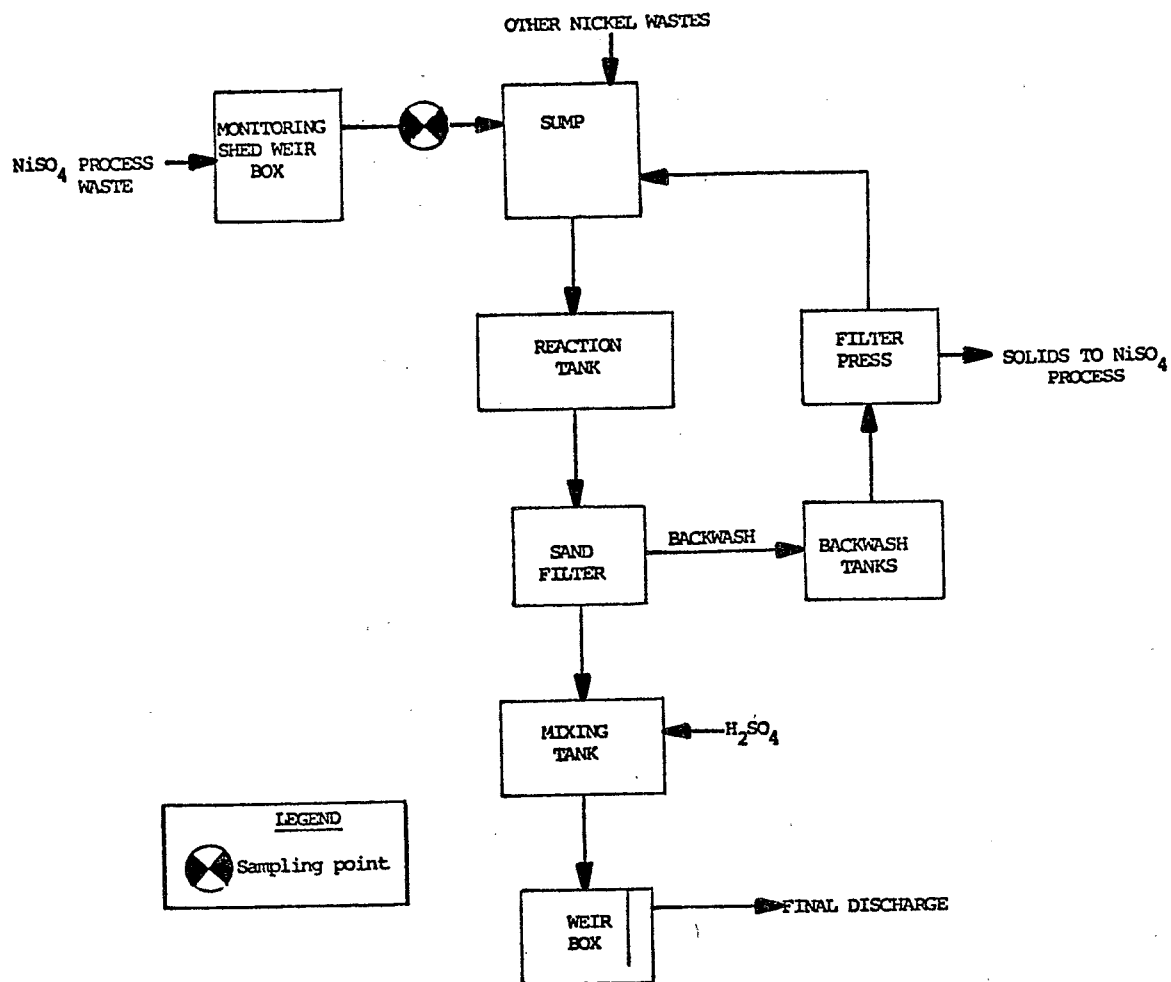


Figure 6-2. General waste water treatment process flow diagram at Plant #120 showing the sampling point. (Nickel sulfate manufacture.)

## 6.2 TREATABILITY TEST MODEL OPERATION

### 6.2.1 Treatment Technology Tested

Treatment consisted of three separate steps. These steps included removal of nickel as nickel hydroxide by chemical precipitation, followed by a settling period for solids separation and then dual media filtration of the clarified waste.

### 6.2.2 Waste Water Characterization

Table 6-1 shows the results of analysis of two waste water samples from Plant #369. A major difference between samples is that the first shows a large amount of phosphate, accompanied by high concentrations of sodium and potassium. The second shows no phosphate. The sample with phosphate is, of course, strongly buffered. Nickel was not precipitated until the pH was 12.5. Also, the nickel seemed to be complexed to a degree not accounted for by the phosphate. The sample contained ammonia and/or amines. However, the concentrations of these compounds were not large enough to account for the extensive complexation of nickel. Extraction of the solution showed the presence of a polyglycol which may contribute to the chelation.

The second sample also appeared to be buffered, in this case on the acid side. The buffering is provided by a bicarbonate system. No phosphate was detected, nor was there any polyglycol. Overall, this sample behaved in a manner predictable by solubility data with essentially complete precipitation of nickel at a pH of 10.

### 6.2.3 Details on Treatability Test Operation

Tables 6-2 and 6-3 show information related to treatment conditions for each of the treatability tests.

The treatability tests on waste water from Plant #369 were performed by first trying a pH of 10. If nickel precipitation and/or settling occurred after some observation period, the test was conducted following the normal procedure, namely, settling and dual media filtration of the clarified waste. When precipitation and/or settling did not occur, the pH was then readjusted to 12.5 and the test was conducted as before. This particular situation occurred during runs 1, 8, and 9 of Table 6-2 and runs 1, 4, 6, and 7 of Table 6-3.

The precipitations were carried out using a solution containing 333 g NaOH per liter, or a calcium hydroxide suspension made by adding 100 g of  $\text{Ca(OH)}_2$  to enough water to total one liter.

TABLE 6-1. WASTE WATER CHARACTERIZATION FOR THE NICKEL  
SULFATE SUBCATEGORY, PLANT #369(1)

Parameter	Results	
	Sample I	Sample II
pH	7.2	6.4
Temperature (degrees C)	24	25
Total Acidity (as CaCO <sub>3</sub> )	780	1,020
Total Alkalinity (as CaCO <sub>3</sub> )	3,500	140
Total Suspended Solids	1,090	725
Total Dissolved Solids	14,100	5,300
Total Residue	18,100	4,350
Fixed Residue	16,950	2,440
Nickel	470	890
Zinc	1.50	0.27
Sodium	1,250	435
Potassium	4,170	290
Calcium (as CaCO <sub>3</sub> )	12	68
Magnesium (as CaCO <sub>3</sub> )	29	36
Chloride	335	241
Sulfate	1,395	2,036
Nitrate	536	2.2
Phosphate	6,570	None detected
Kjedahl N	65.5	35.6

EFFECT OF pH ON NICKEL SOLUBILITY, PLANT #369

Sample I			Sample II		
NaOH	pH	Nickel	NaOH	pH	Nickel
518	7.98	480	50	7.01	970
1062	9.00	500	217	7.94	810
1214	9.86	510	819	8.49	130
1290	10.01	480	1139	8.97	34
1366	10.44	480	1215	9.48	11
1822	10.94	480	1291	9.71	9
2278	11.46	410	1291	10.02	2.5
3036	11.96	5.30	1291	10.30	3.1
4404	12.51	1.20	1367	10.57	3.7
7592	12.94	0.67	1746	11.60	7.5

(1) mg/l unless specified otherwise.

TABLE 6-2. TREATABILITY TEST CONDITIONS AND ANALYTICAL RESULTS

SUBCATEGORY: Nickel Sulfate

TREATMENT: Lime Plus Dual Media Filtration

Parameter	Plant #369											Plant #120			
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	10	11	12
Date	9/4	9/7	9/17	9/19	10/2	10/16	10/23	10/30	11/12	11/1	11/2	11/6	11/1	11/2	11/6
Volume of Waste Water Treated (gallons)	20	20	20	25	25	25	25	25	25	25	25	25	25	25	25
Raw Waste Water pH	7.32	NDA (1)	3.88	5.71	3.19	2.15	4.91	NDA (1)	NDA (1)	7.63	6.88	7.31	7.63	6.88	7.31
Volume of Precipitant Solution Used (mls)	3600	600	1600	780	3750	2830	850	650	2480	50	130	80	50	130	80
pH Achieved by Lime Addition	12.6	10.0	10.0	10.0	10.0	10.0	10.0	12.5	12.5	10.0	10.5	10.5	10.0	10.5	10.5
Mixing Time (mins)	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Settling Time (mins)	(2)	145	240	140	1010	240	180	255	255	145	120	120	145	120	120
Supernatant pH After Reaction	12.43	6.7	6.6	8.6	9.6	8.9	9.0	12.0	12.6	8.5	10.0	10.1	8.5	10.0	10.1
Filtrate pH	7.3	6.7	6.5	8.0	9.3	7.4	7.2	12.1	12.6	7.7	8.9	9.8	7.7	8.9	9.8
Filtration Time (mins)		45	35	60	40	30	60	50	40	65	60	45	65	60	45
ANALYTICAL RESULTS															
Nickel, mg/l	520	NDA	2340	1100	3360	550	1030	NDA	NDA	15	12	18	15	12	18
Raw Waste--	430	NDA	2280	990	3200	550	700	NDA	NDA	11	10	15	11	10	15
Total Ni															
Dissolved Ni															
Supernatant--															
Total Ni	0.35	1.00	2.60	1.70	1.60	0.65	4.0	1.10	0.47	2.4	1.20	1.20	2.4	1.20	1.20
Dissolved Ni	<0.05	1.00	2.40	0.45	1.10	0.92	3.5	0.29	0.01	0.8	0.05	0.12	0.8	0.05	0.12
Filter Effluent--															
Total Ni		0.09	3.20	0.70	0.21	1.20	3.9	0.29	0.05	0.1	0.03	<0.01	0.1	0.03	<0.01
Dissolved Ni		0.12	3.20	0.72	0.22	1.10	4.0	0.29	0.05	0.1	0.04	<0.01	0.1	0.04	<0.01
Total Suspended Solids, TSS, mg/l															
Raw Waste	1510	NDA	1240	910	730	155	3270	NDA	NDA	95	28	52	95	28	52
Supernatant	58	22	30	23	31	0	24	210	26	24	23	23	24	23	23
Filter Effluent		12	23	70	24	10	1	51	27	8	2	2	8	2	2

(1) - NDA = No data available.

(2) - Precipitate did not settle and therefore filtration was not carried out.



TABLE 6-3. TREATABILITY TEST CONDITIONS AND ANALYTICAL RESULTS

SUBCATEGORY: Nickel Sulfate

TREATMENT: Caustic Soda Plus Dual Media  
Filtration

Parameter	Plant #369										Plant #120		
	<u>TREATABILITY TEST CONDITIONS</u>												
Test Number	1	2	3	4	5	6	7	8	9		10	11	12
Date	9/5	9/6	9/14	9/21	9/28	10/17	10/22	10/30	11/9		11/2	11/5	11/6
Volume of Waste Water Treated (gallons)	20	20	20	25	25	25	25	25	25		25	25	25
Raw Waste Water pH	NDA <sup>(1)</sup>	6.51	5.40	6.33	3.26	2.00	4.95	6.43	6.70		7.65	7.66	7.92
Volume of Precipitant Solution Used (mls)	1250	300	500	1000	1280	1380	250	250	1430		40	30	30
pH Achieved by Lime Addition	12.6	10.0	10.0	12.6	10.0	12.6	10.0	10.0	12.6		10.5	10.7	10.7
Mixing Time (mins)	15	15	15	15	15	15	15	15	15		15	15	15
Settling Time (mins)	195	200	4150	135	3825	240	255	285	4185		120	105	120
Supernatant pH After Reaction	12.5	9.6	6.8	12.5	9.6	12.6	8.5	9.1	12.7		10.7	10.3	10.8
Filtrate pH	12.4	7.7	6.8	12.5	9.3	12.6	5.3	7.1	12.9		7.9	10.6	11.6
Filtration Time (mins)	90 <sup>(2)</sup>	35	30	45	40	40	45	105 <sup>(3)</sup>	35		65	65	50
	<u>ANALYTICAL RESULTS</u>												
<u>Nickel, mg/l</u>													
Raw Waste--													
Total Ni	NDA	1000	1900	520	4850	490	840	710	1170		12	11	19
Dissolved Ni	NDA	950	1650	300	4500	460	700	630	330		11	10	17
Supernatant--													
Total Ni	320	0.50	1.50	0.13	1.70	1.50	8.2	2.7	0.31		2.1	2.0	2.7
Dissolved Ni	0.49	0.14	1.50	0.06	1.40	0.20	8.2	7.6	0.21		0.2	0.05	0.07
Filter Effluent--													
Total Ni	0.5	0.06	1.50	<0.01	<0.01	0.55	7.2	5.2	0.11		0.05	0.14	0.20
Dissolved Ni	0.5	0.12	NDA	<0.01	<0.01	0.18	7.2	5.2	0.08		0.14	0.04	0.16
<u>Total Suspended Solids, TSS, mg/l</u>													
Raw Waste	NDA	920	1070	2620	800	132	1111	1090	7500		20	30	55
Supernatant	89	34	24	44	46	19	20	37	32		8	2	3
Filter Effluent	105	12	16	36	55	30	27	22	32		8	2	3

(1) - NDA = No data available.

(2) - Total recirculation of the filtrate back to the reaction tank practiced for 50 minutes.

(3) - Total recirculation of the filtrate back to the reaction tank practiced for 1 hour.

For treating waste water from Plant #120, tests were conducted at pH values of 10 and 10.5 (see run numbers 10, 11, and 12 of Tables 6-2 and 6-3). From conversations with plant personnel, it was learned that they run their nickel treatment system in that pH range. Hence, the same values were used in this study. Later bench scale experiments showed that a minimum pH value of 10 would be optimum for nickel removal from the waste from this particular plant.

Recirculation of the filtrate back to the settling tank was practiced for runs 1 and 8 of Table 6-3. In the other cases, recirculation was not practiced, but samples for analysis were taken only at the end of the filtration of the batch.

### 6.3 TEST RESULTS

#### 6.3.1 Discussion of Results

The analytical results for the treatability tests performed are presented in Tables 6-2 and 6-3.

These tables and Figure 6-3 show the dependence of pollutant removal on the final pH after the reaction has gone to completion. This pH value is, in turn, a function of the nickel concentration and buffering capacity of the waste being treated. Figure 6-3 also indicates that caustic soda and lime are essentially equivalent if compared at the same pH.

Poor nickel removal was observed in some of the tests. Unsatisfactory levels of nickel were obtained during runs 3, 6, and 7 when lime was the treating reagent added and during runs 3, 7, and 8 when caustic soda was the precipitant used. It appears that in some cases the precipitation reaction was slow, with the result that the pH continued to fall during the mixing period. When the available  $\text{OH}^-$  was exhausted, the pH was too low to carry the precipitation to completion. This is a condition that can be remedied in practice. BAT should be defined as treatment of the waste water with either lime or caustic soda to a final pH, after the precipitation reaction, of 9.5 or above. There were fourteen runs that came within this definition. These tests, therefore, can serve as a demonstration of the capability of this technology.

Finally, it should be pointed out that an amber, goldish coloration was observed in the filtrate from some of the tests when caustic soda was the precipitant used. This happened during runs 1, 4, 6, and 9 and indicates that the supernatant attacked the filter media, picking up some solids during its passage through the filter media. This may explain the poor TSS removal

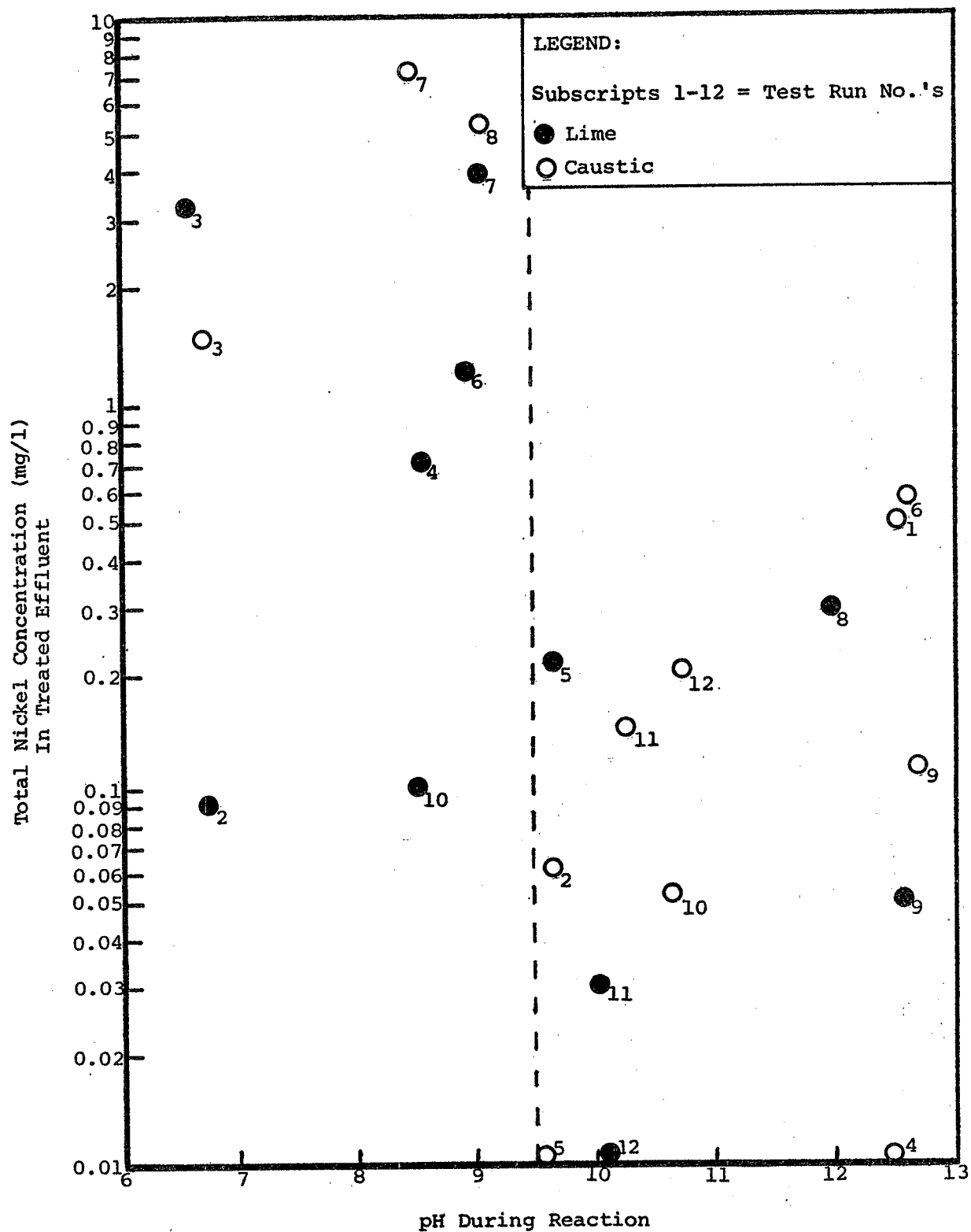


Figure 6-3. Effluent Nickel Concentration As a Function of pH.

observed for those 4 runs. An examination of Table 6-3 reveals that the filter media attack occurred at a pH value of 12.6.

### 6.3.2 Statistical Evaluation

A statistical analysis was performed for total suspended solids and nickel in Figures 6-4 and 6-5. The statistical parameters used to develop the analysis appear in Appendix A. A comparison between the proposed maximum 30-day average concentration and the estimated experimental 30-day average is presented in Table 6-4. The proposed BAT limitations are designed such that compliance can be achieved at least 95 percent (95th percentile) of the time. The curves presented in Figures 6-4 and 6-5 show the estimated probability performance for a range of maximum 30-day average values.

### 6.3.3 Conclusions

The treatability test results serve to indicate the general applicability of the proposed BAT regulations to the treatment technology applied. Results show that the pollutant concentration basis for the proposed BAT maximum 30-day average effluent limitations would not be achievable with the prescribed treatment technology under the conditions of the tests. The estimated long term average concentration for nickel is within the proposed BAT maximum 30-day average; however, the statistical analysis indicates that the proposed limitation can only be met 56 percent of the time. The test results indicate that the proposed BAT limitation be based on 0.27 mg/l for nickel which is consistent with levels reported in the literature.

Toxic metal removal by alkaline precipitation under the conditions of the test appears to be equally efficient when either caustic soda or lime are used. However, application of either treatment chemical may require evaluation on a case by case basis to guarantee that no interferences exist which would preclude the use of one chemical over the other.

Test results also indicate that dual media filtration appears to provide significant additional removal of nickel from the clarifier effluent and is needed to ensure consistent achievement of the desired effluent quality.

TABLE 6-4. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE  
FOR THE NICKEL SULFATE SUBCATEGORY (ALKALINE  
TREATMENT)

STREAM: FILTER EFFLUENT

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Nickel	0.20	0.32
Total Suspended Solids, TSS	47	57

SUBCATEGORY	POLLUTANT	PRECIPITANT
Nickel Sulfate	Nickel	Alkaline
Proposed Maximum 30-day Average	(mg/l):	0.20
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.32
Long Term Average	(mg/l):	0.19
Standard Deviation of 30-day Averages	(mg/l):	0.078
Probability of Achieving Proposed Maximum 30-day Average	(%):	56
Number of Observations:		14

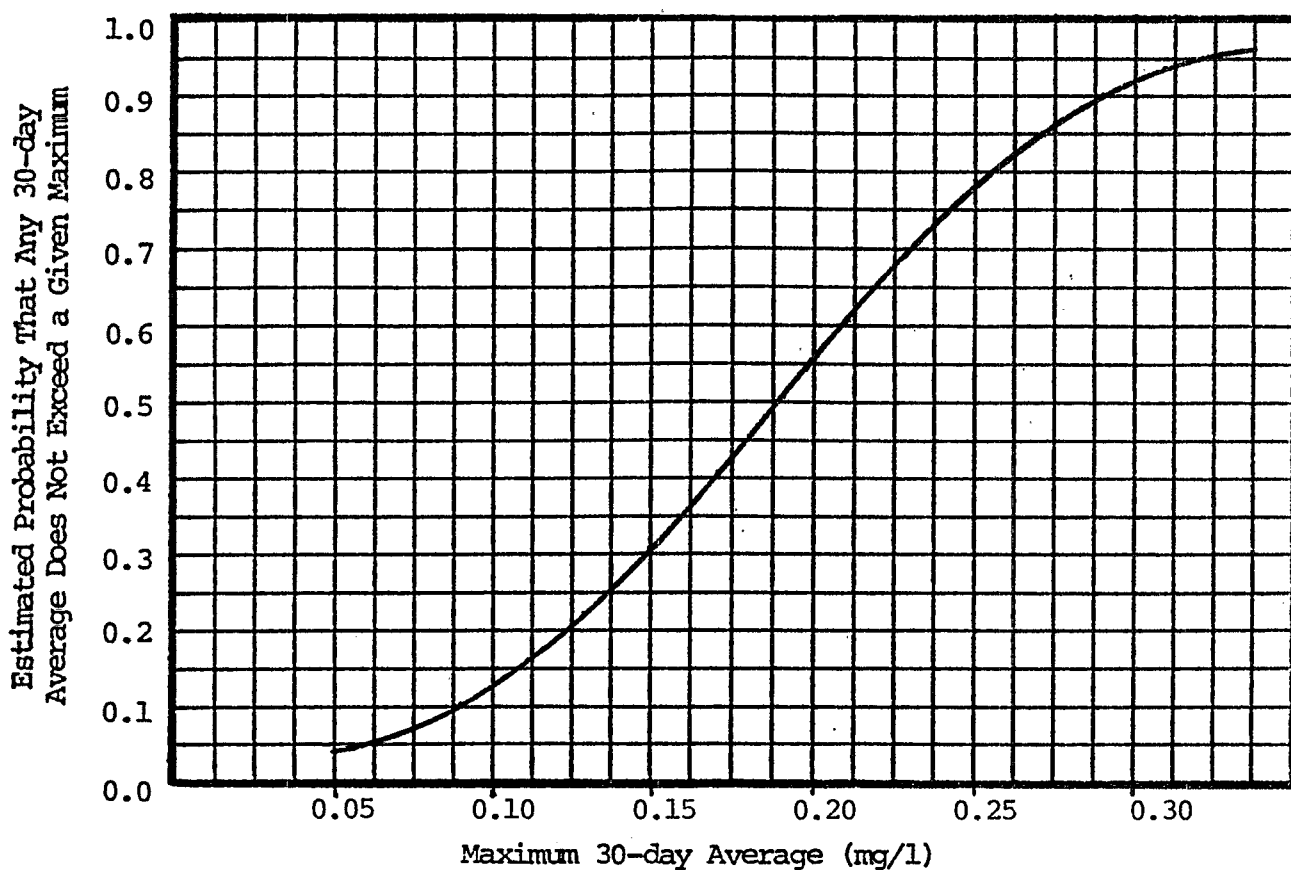


Figure 6-4. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Nickel Sulfate	Total Suspended Solids	Alkaline
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	47
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	57
Long Term Average	(mg/l):	34
Standard Deviation of 30-day Averages	(mg/l):	14
Probability of Achieving Proposed Maximum 30-day Average	(%):	82
Number of Observations:		14
<hr/>		

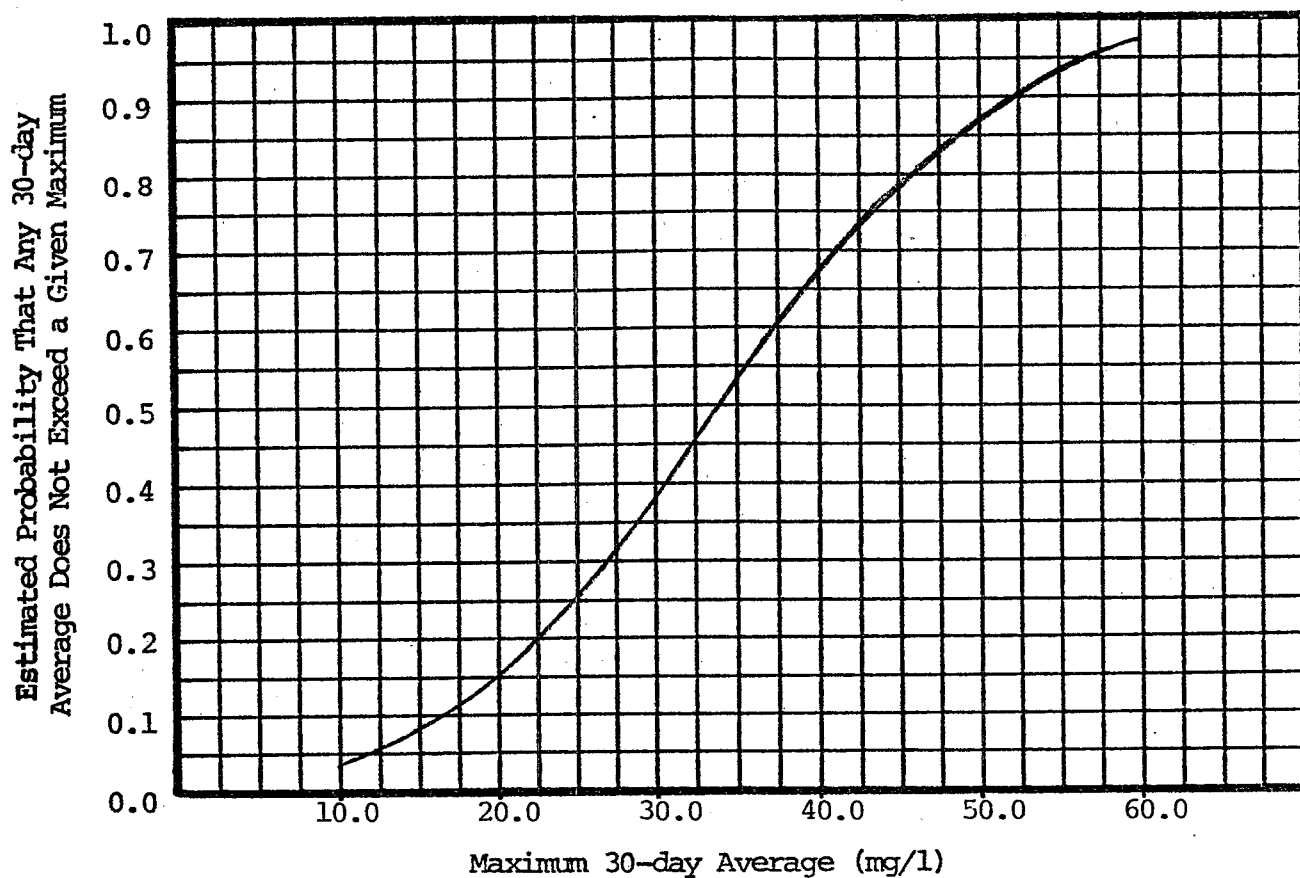
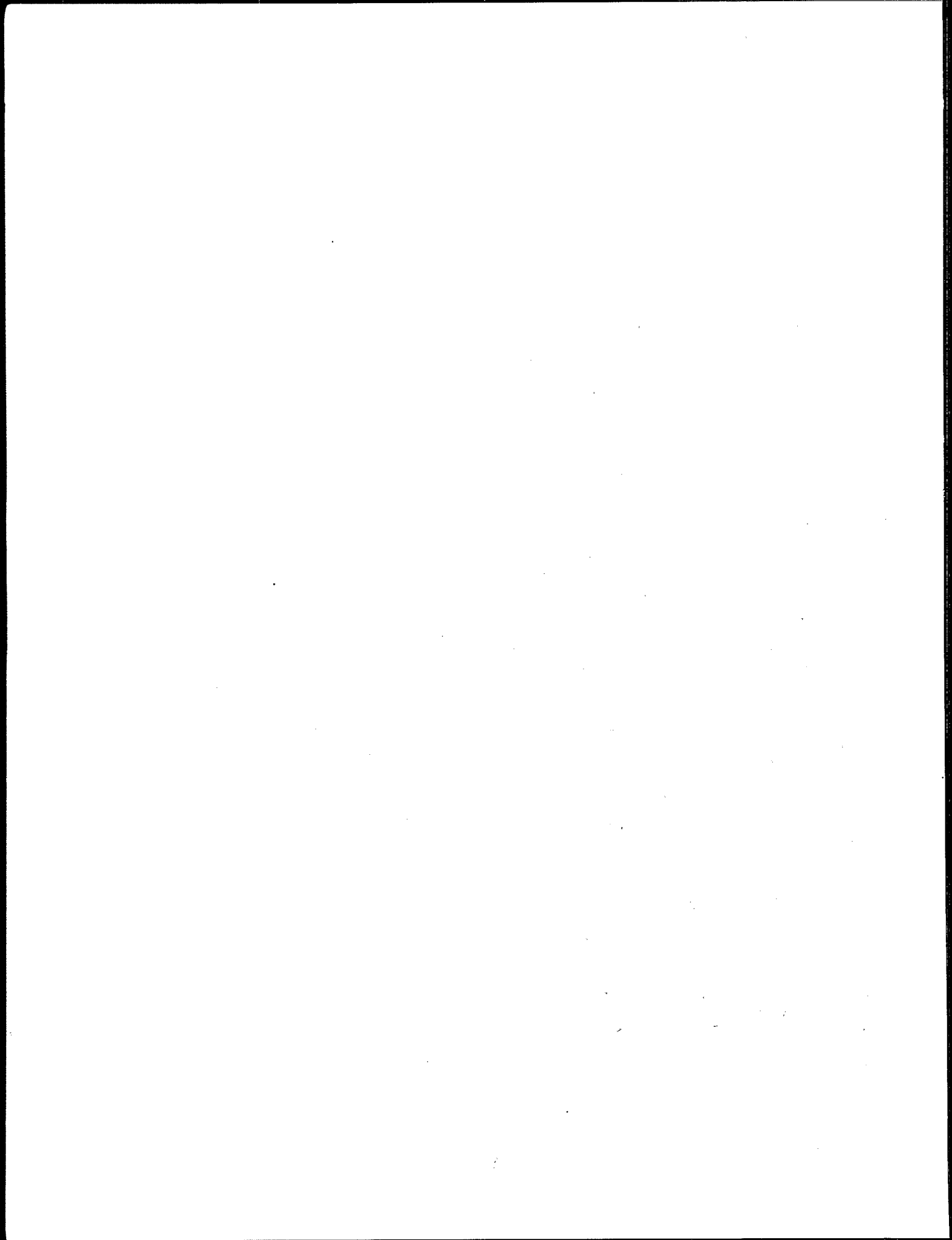


Figure 6-5. Estimated Performance of Proposed BAT Treatment





## SECTION 7.0

### HYDROFLUORIC ACID SUBCATEGORY

#### 7.1 INTRODUCTION

##### 7.1.1 General Considerations

Treatability studies were conducted in an experimental unit set up in the vicinity of the plant where the waste was generated. A fresh sample of the raw waste stream was collected each day. Between 4 September and 10 October 1979, seventeen treatability test runs were completed using the proposed BAT level treatment (lime treatment plus filtration).

Determinations of pH, turbidity, and acidity were made at the site. Other analyses were made after overnight transportation of the sample to the laboratory in Pasadena.

Additional treatability studies were found necessary after completion of the initial 17 treatability runs. The purpose of these studies was to determine whether changes in the sample characteristics had occurred due to logistic lag time (the time between sample collection and laboratory analysis). These studies were conducted between 30 October and 8 November 1979 at the laboratory in Pasadena, California, and the time lag was reduced from overnight (16-18 hours) to three hours.

##### 7.1.2 Sample Point Location

Samples were collected directly at the point of the kiln discharge. At this point, the treated recycle water mixes with the expelled reacted ore (primarily gypsum solids) and is conveyed by open channel to the waste water treatment system. The process waste stream is currently neutralized with soda ash ( $\text{Na}_2\text{CO}_3$ ) prior to clarification in retention ponds.

## 7.2 TREATABILITY TEST MODEL OPERATION

### 7.2.1 Treatment Technology Tested

The proposed BAT level of treatment considered in the treatability investigation includes lime treatment of the raw waste water, clarification, and dual media filtration. BAT treatment proposes the removal of TSS, fluorides, and heavy metals in addition to acid waste neutralization.

### 7.2.2 Waste Water Characterization

The characteristics of a typical waste water sample from the HF plant selected for the tests is shown in Table 7-1. Portions of this waste water having an original pH of 3.1 were treated with NaOH to pH levels between 8 and 12. Additional tests were run at pH values of 3.1, 10, and 10.5 to determine the levels of complexed fluoride and aluminum. The upward adjustment of the pH was made with NaOH. The results are shown below.

	<u>pH = 3.10</u>	<u>pH = 10</u>	<u>pH = 10.51</u>
Fluoride, ion, mg/l	78	35	43
Fluoride, total, mg/l	193	109	101
Aluminum, mg/l	27	0.36	0.24

The non-free fluoride at the lowest pH may be due to un-ionized HF, and perhaps in part to  $\text{AlF}_6(-3)$ . In any case, the aluminum precipitates readily at the higher pH. There is the possibility that fluoride in the alkaline solutions is partly in the form of silicofluoride,  $\text{SiF}_6(-2)$ .

In order to assess possible interferences with the analytical procedures and determine if other pollutants were present, emission spectroscopic analysis of the raw sample total dissolved solid was performed. The results showed the major metal to be sodium; minor amounts of aluminum, calcium, magnesium, silicon, silver, and lead were indicated, as well as traces of boron, antimony, iron, and manganese. Quantitative tests for lead by atomic absorption were negative. The lead indicated on the emission spectrograph may have been a chance contaminant, or the amount was too small to be shown by atomic absorption under the conditions of the test.

When the results of the pH optimization tests are viewed, it would appear that in the pH range 10-11 the pollutant levels are minimized; hence, this is the preferred pH range for the treatment. At lower pH levels, nickel and zinc are still present in solution. At higher pH levels, it is anticipated that the

TABLE 7-1. WASTE WATER CHARACTERIZATION FOR THE  
HYDROFLUORIC ACID SUBCATEGORY(1)

Parameter	Result	Parameter	Result
pH	3.10	Potassium	91300
Temperature(deg.C)	23	Calcium (as CaCO <sub>3</sub> )	1650
Methyl Orange	514	Magnesium	260
Acidity (as CaCO <sub>3</sub> )		(as CaCO <sub>3</sub> )	
Phenolphthalein	969	Chloride	632
Acidity (as CaCO <sub>3</sub> )		Sulfate	45800
Total Suspended Solids	63000	Nitrate	22
Fixed Residue	24900	Aluminum	27
Free Fluoride	78	Nickel	0.57
Total Fluoride	193	Zinc	0.84
Sodium	24100	Total Chromium	0.29
		Hex. Chromium	None detected

EFFECT OF pH ON SOLUBILITY OF POLLUTANTS

NaOH Added	pH	Free Fluoride	Zinc	Nickel	Total Chromium
0	3.1	78	0.84	0.57	0.09
690	8.07	41.4	0.13	0.39	0.08
800	9.04	32.7	0.01	0.24	0.08
850	9.74	32.7	0.01	0.17	0.08
880	9.98	35.3	0.01	0.01	0.08
930	10.22	38.5	0.01	0.01	0.08
935	10.51	42.6	0.01	0.01	0.08
940	10.98	50.7	0.01	0.01	0.08
1290	12.00	111.2	0.04	0.01	0.08

(1) All values expressed in mg/l unless otherwise specified.

solubility of zinc and aluminum would increase since they are amphoteric.

### 7.2.3 Details on Treatability Test Operation

The conditions of the treatability tests are presented in Table 7-2 for the initial seventeen test runs.

In general, operation parameters including pH adjustment, mixing time, settling time, and filtration time were varied within the anticipated ideal range to optimize treatment process efficiency in the test model. The need to vary these operation parameters became apparent during the course of study, since the removal of fluorides, TSS, and nickel did not achieve anticipated levels. Additional test runs and laboratory experimentation discussed in Section 7.3.3 were performed to verify these anomalies.

Alterations in the test model reaction tank were found to be necessary in runs 6 through 17 since the settled sludge blanket level interfered with the tank outlet. An "L" tube was placed inside the tank to position the outlet level approximately three inches above the settled sludge blanket for mitigation of the interference. The solids captured by the "L" tube after settling were wasted before the beginning of each filter run.

Turbidity and pH in the filtered effluent was carefully monitored during runs 6 through 17 to ensure that the dual media filter performance was properly established before effluent sample collection. Methyl orange and phenolphthalein acidity was monitored for the raw waste to determine the variability of this waste characteristic, and also to check on measurements of lime slurry dosage requirements.

## 7.3 TEST RESULTS

### 7.3.1 Investigation of Anomalous Results

The laboratory results for the 17 treatability test runs are tabulated in Table 7-3. Note that the total fluoride concentration was monitored only in the supernatant and filter effluent waste streams.

Review of the experimental results during the treatability test runs revealed the following observations:

- 1) The free fluoride concentration in the treated waste water effluent varied widely between 27 and 65 mg/l, and was not appreciably improved through the dual media filtration process.

TABLE 7-2. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Hydrofluoric Acid		Treatment: Lime Plus Dual Media Filtration																
Test Number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Date		9/4	9/5	9/6	9/7	9/18	9/19	9/20	9/21	9/25	9/26	9/27	9/28	10/1	10/2	10/3	10/8	10/9
Volume of Waste Water Treated (gallons)		20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Methyl Orange Acidity (2)	(1)	NDA	NDA	NDA	NDA	1379	2044	2222	5418	1006	7800	1054	487	2141	0	0	1865	2060
Phenolphthalein Acidity (2)		NDA	NDA	NDA	NDA	2595	3114	3066	5839	1444	8353	1590	1054	2611	324	270	2303	2547
Raw Waste Water pH		2.8	2.4	2.6	2.8	2.8	2.6	2.6	2.2	2.8	1.9	2.8	3.2	2.6	6.0	4.4	2.5	2.5
Volume of Lime Slurry Used (mls)		NDA	NDA	NDA	NDA	1300	1690	1410	2780	960	3720	900	590	1200	200	200	1120	1140
pH Achieved by Lime Addition		10.9	10.6	10.5	10.6	10.3	10.3	10.5	10.5	10.3	10.3	10.3	10.2	10	10	10.3	10.3	10.3
Mixing Time (mins)		30	45	15	30	45	60	60	60	60	20	15	15	15	15	20	15	15
Settling Time (mins)		80	60	70	60	120	165	135	120	90	60	120	120	120	120	120	120	120
Supernatant pH After Reaction		10.9	10.6	10.4	10.5	10.1	10.2	10.2	10.3	10.1	10.1	10.2	10.1	10.1	10.0	10.3	10.2	10.2
Filtrate pH		10.6	10.4	10.3	10.4	9.7	9.8	9.9	9.9	9.8	9.9	10.0	9.8	10.0	9.9	10.2	10.0	10.0
Time of Filter Effluent After Start of Filtration (mins)		60	55	57	60	30	40	35	30	25	32	30	30	30	30	30	30	30
Filtrate Turbidity (NTU)		NDA	NDA	NDA	NDA	1.3	0.7	1.0	1.0	1.1	2.1	0.7	1.0	1.0	1.3	1.3	1.0	2.0

(1) NDA - No Data Available

(2) mg/l as CaCO<sub>3</sub>

TABLE 7-3. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR STUDY  
IN THE HYDROFLUORIC ACID SUBCATEGORY

Treatment: Idina Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
All reported values in mg/l																	
<u>Total Chromium, Cr (T)</u>																	
Raw Waste --																	
Total Cr (T)	0.17	0.15	0.24	0.23	0.37	0.47	0.44	0.48	0.40	0.40	0.34	0.29	0.27	0.21	<0.01	0.33	0.36
Dissolved Cr (T)	0.11	0.15	0.22	0.22	0.36	0.42	0.41	0.43	0.38	0.36	0.29	0.23	0.20	0.08	0.07	0.23	0.31
Supernatant --																	
Total Cr (T)	0.07	0.05	0.04	0.09	0.07	0.06	0.01	0.09	0.11	0.10	0.06	0.06	0.06	0.07	<0.01	0.15	0.14
Dissolved Cr (T)	0.07	0.05	0.04	0.09	0.07	0.06	0.001	0.09	0.11	0.10	0.06	0.06	0.05	0.06	<0.01	0.15	0.11
Filter Effluent --																	
Total Cr (T)	0.08	0.05	0.04	0.08	0.06	0.05	0.01	0.11	0.11	0.10	0.07	0.06	0.04	0.07	<0.01	0.15	0.12
Dissolved Cr (T)	0.09	0.05	0.04	0.08	0.06	0.05	0.02	0.11	0.11	0.10	0.07	0.06	0.04	0.09	<0.01	0.15	0.13
<u>Zinc, Zn</u>																	
Raw Waste --																	
Total Zn	0.93	0.75	0.86	1.20	1.40	1.60	1.80	1.50	1.20	1.20	1.20	1.30	1.10	1.00	0.54	0.57	0.77
Dissolved Zn	0.88	0.78	0.88	1.20	1.40	1.60	1.80	1.40	1.20	1.10	1.20	1.20	1.10	0.90	0.51	0.59	0.77
Supernatant --																	
Total Zn	0.22	0.14	0.17	0.43	0.05	0.14	0.01	0.02	0.03	<0.01	0.01	0.08	0.01	0.13	0.02	<0.01	0.05
Dissolved Zn	0.17	0.11	0.14	0.48	0.06	0.04	0.01	0.02	<0.01	<0.01	0.01	0.05	0.02	0.11	0.06	0.04	0.04
Filter Effluent --																	
Total Zn	0.26	0.12	0.12	0.32	0.06	0.04	0.1	<0.01	<0.01	<0.01	0.01	0.02	<0.01	0.10	0.01	0.02	0.02
Dissolved Zn	0.19	0.13	0.12	0.26	UND(1)	0.04	0.1	<0.01	<0.01	<0.01	0.02	0.03	0.02	0.15	0.04	0.02	0.03
<u>Nickel, Ni</u>																	
Raw Waste --																	
Total Ni	1.15	0.86	0.85	1.40	0.69	1.10	1.00	1.00	1.10	0.99	1.50	1.90	1.50	1.60	1.30	1.20	1.30
Dissolved Ni	1.39	0.46	0.58	1.40	0.64	1.00	1.00	1.00	1.10	0.95	1.50	1.90	1.50	1.60	1.30	1.20	1.20
Supernatant --																	
Total Ni	0.56	0.29	0.82	0.75	0.06	0.15	0.07	0.14	0.13	0.12	0.60	1.00	0.88	0.95	0.48	0.69	0.74
Dissolved Ni	0.58	0.23	0.38	0.78	0.06	0.10	0.09	0.11	0.10	0.12	0.60	1.10	0.84	1.10	0.48	0.67	0.71
Filter Effluent --																	
Total Ni	0.52	0.34	1.10	0.78	0.03	0.10	0.16	0.10	0.09	0.11	0.60	0.98	0.78	0.98	0.44	0.64	0.58
Dissolved Ni	0.53	0.19	0.25	0.78	0.02	0.10	0.05	0.10	0.10	0.10	0.50	0.86	0.75	0.93	0.44	0.58	0.87
<u>Free Fluoride ion</u>																	
Raw Waste	77.7	122.2	251.0	338.0	415.0	465.0	132.0	890.0	96.0	114.0	340.0	249.0	93.6	51.4	62.4	65.9	109.2
Supernatant	84.6	44.8	31.7	48.6	27.9	31.0	34.1	35.4	43.0	41.9	36.0	36.7	44.3	48.5	70.4	30.6	53.3
Filter Effluent	63.5	43.3	31.1	48.6	27.4	29.0	37.0	37.4	45.3	38.2	33.3	35.8	43.0	63.5	65.4	30.0	48.0
<u>Total Fluoride</u>																	
Supernatant	UND	UND	UND	UND	131	120	105	138	130	139	112	104	76	125	76	78	94
Filter Effluent	UND	UND	UND	UND	102	95	94	109	81	95	109	97	67	80	81	79	77
<u>Total Suspended Solids, TSS</u>																	
Raw Waste	11000	730	1380	220	5590	16400	240	360	330	360	2060	540	640	2450	2740	1680	1000
Supernatant	297	245	117	99	371	136	359	230	233	223	747	157	100	857	399	260	400
Filter Effluent	240	310	40	120	100	40	150	260	170	190	270	130	50	100	360	10	30

(1) - UND - Unable to Determine

- 2) The total suspended solids concentration varied between 11 and 363 mg/l, with an overall average of 153 mg/l in the treated waste water effluent. The dual media filtration process showed very poor removal of suspended solids in spite of both visual and instrumental improvement of turbidity.
- 3) The removal efficiency for nickel was very poor, with an average concentration of 0.49 mg/l in the treated waste water effluent.

In view of these anomalies, it was determined that additional control experiments would be necessary to assess whether the poor removal of suspended solids and other parameters was a result of logistical lag times between sample collection and analysis, or the existence of colloidal solids not amenable to removal by the filtration processes. In the event that the poor removal of suspended solids was a result of a colloidal suspension, it was also a goal to determine what steps may be taken to improve the removal of solids.

Raw hydrofluoric acid waste samples were transported from the waste source to the treatability test model within a three hour period to minimize logistic lag time for the experiments.

Control experiments to determine the effect of logistic lag times indicated that the removal of free fluoride, nickel, and TSS was consistent with observations made in the previous seventeen runs. TSS levels remained high and unchanged through the dual media filter, even with extended recycle, indicating the existence of a fine colloidal suspension.

Since these results were not conclusive in eliminating the existence of possible logistical problems, an additional experiment on the relationship between time and suspended solids was performed on the clarified supernatant and filtered effluent samples for a period of one week. During this time, free fluoride and TSS concentrations were monitored. The results of the laboratory analyses revealed that the suspended solids concentration almost doubled within a six day period for the clarified supernatant. The result was particularly surprising in view of the fact that the same trend was not observed for the treated waste after passing through the dual media filter. The increase in TSS indicates formation of a crystalline precipitate. The concentration of free fluoride increased by approximately 5 mg/l within six days, possibly because of a slow release of fluoride from its complexes.

In summary, it can be concluded that both time lag and existence of fine suspended solids contribute to observations of poor and inconsistent removal of TSS in the treatability test

runs and that the free fluoride concentration is also subject to variations due to logistic lag time.

### 7.3.2 Discussion of Treatment Results

Results of the treatability investigations indicate that the proposed BAT effluent limitations were not consistently achieved for fluoride and nickel at the selected plant. All other toxic pollutant parameters appear in good agreement with anticipated removal performance. The observations of unachievable performance were given careful consideration throughout the course of study, and a number of conclusions were found to partly explain these results.

#### Free and Total Fluoride Removal

The solubility of  $\text{CaF}_2$  in pure water would yield about 8 mg/l of  $\text{F}^-$  at ordinary temperatures. It was anticipated that this level could be approached in practice. However, the treatability test results indicated fluoride concentrations achieved in practice may be due, at least in part, to the slowness of the attainment of equilibrium conditions between solid and solution. In other words, super-saturation may play a role. Support for this hypothesis is seen in the fact that there was no precipitation until the fluoride ion concentration reached 65 mg/l, and then, up to a point, the residual fluoride decreased as the initial concentration increased. Figure 7-1 shows that residual fluoride decreased to about 35 mg/l when the initial fluoride was at concentrations above 300 mg/l.

The high ionic strength in the waste is another factor that tends to increase the solubility of the free fluoride over and above the effect of super-saturation. It is believed that observations of free fluoride removal is plant specific in nature. Lower fluoride values should be attainable where treatment with soda ash ( $\text{Na}_2\text{CO}_3$ ) and plant recycle are not practiced. It is likely that the fluoride residual could be decreased by raising the level of calcium ion, but it cannot be raised significantly until most of the sulfate and carbonate have been precipitated. This might be accomplished if the initial neutralization of the waste water were accomplished with lime instead of  $\text{Na}_2\text{CO}_3$ . In treatment systems where soda ash is employed to facilitate effluent reuse, fluoride concentrations would tend to increase as a result of a deficiency of available calcium in the presence of excess sulfate and carbonate/bicarbonate ions. In the tests conducted, even the use of lime for neutralization and alkaline precipitation did not provide sufficient available calcium for efficient fluoride removal because of the calcium demand exerted by the high levels of sulfate and carbonate species already present in the reused treatment system effluent.



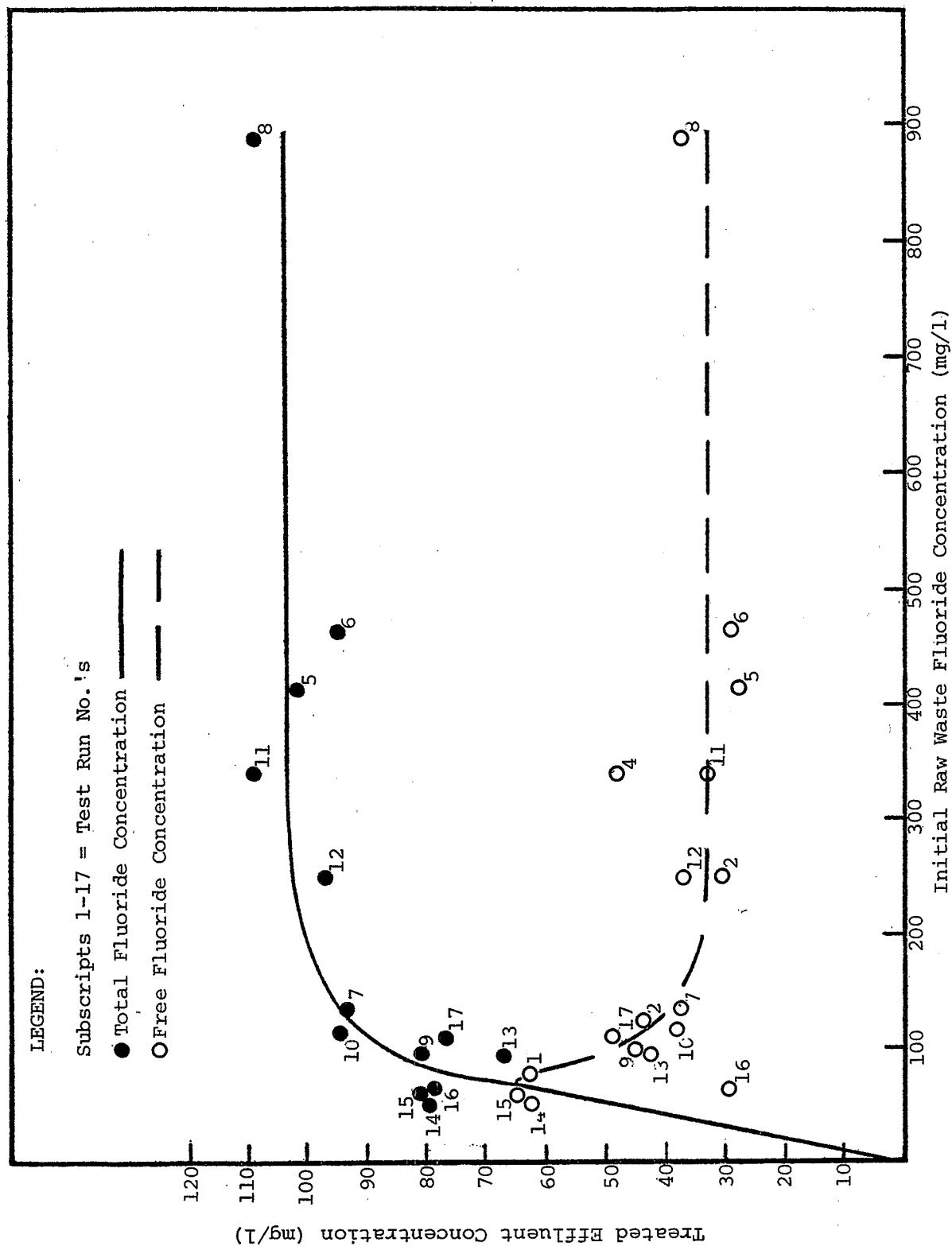


Figure 7-1. Relationship of Free and Total Fluoride Concentration In the Raw and Treated Waste.

### Total Suspended Solids Removal

The treatability results indicate that the dual media filter will not effectively remove TSS concentrations below approximately 150 to 200 mg/l. The high TSS concentration can be attributed to colloidal or fine suspended solids not amenable to physical separation in the filter. The composition of the suspended solids is believed to be fine  $\text{CaF}_2$  and trace quantities of  $\text{CaSO}_4$ . Examination of the suspended solids results indicates evidence that the suspended  $\text{CaSO}_4$  is effectively removed by dual media filtration, whereas the  $\text{CaF}_2$  resists separation.

### Total Nickel Removal

Removal of nickel in the form of a hydroxide precipitate is dependent on a specific equilibrium solubility which may be strongly influenced by high ionic strength and the presence of fluoride. Thus, nickel removal would tend to be less efficient and possibly erratic at plants where soda ash is used for neutralization and effluent reuse.

### 7.3.3 Statistical Evaluation

A comparison between the proposed BAT limitations and the estimated treatability performance for each of the pollutants of concern is presented in Table 7-4. A statistical analysis of the treatability test runs is presented in Figures 7-2 through 7-6. Appendix A summarizes key statistical parameters used in the analysis.

### 7.3.4 Conclusions

The treatability test results do not provide an adequate basis for assessing the general applicability of the proposed BAT regulations for the Hydrofluoric Acid Subcategory. The particular plant selected for study was an extreme case in the sense that the kiln raw waste slurry incorporated a totally reused treatment system effluent as the carrier. Thus, the kiln solid residues were undoubtedly typical of the industry, but the slurry transport medium was not because of the plant's practice of 100 percent effluent reuse following soda ash treatment. The high effluent concentrations of fluoride observed in the lime treatment tests were not unreasonable under these circumstances, although the problem was not anticipated at the time the plant was selected as the source of raw waste water for this study.

The results on nickel removal with lime treatment may also be viewed as atypical of this technology possibly due to the effects of ion pair or complex formation (resulting in a low

TABLE 7-4. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR  
THE HYDROFLUORIC ACID SUBCATEGORY

STREAM: Filter Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Fluoride (T)	33	94
Nickel	0.15	0.81
Zinc	0.52	0.11
Chromium	0.04	0.096
Total Suspended Solids, TSS	68	230

SUBCATEGORY	POLLUTANT	PRECIPITANT
Hydrofluoric Acid	Fluoride	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	33
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	94
Long Term Average	(mg/l):	90
Standard Deviation of 30-day Averages	(mg/l):	2.3
Probability of Achieving Proposed Maximum 30-day Average	(%):	<0.01
Number of Observations:		13

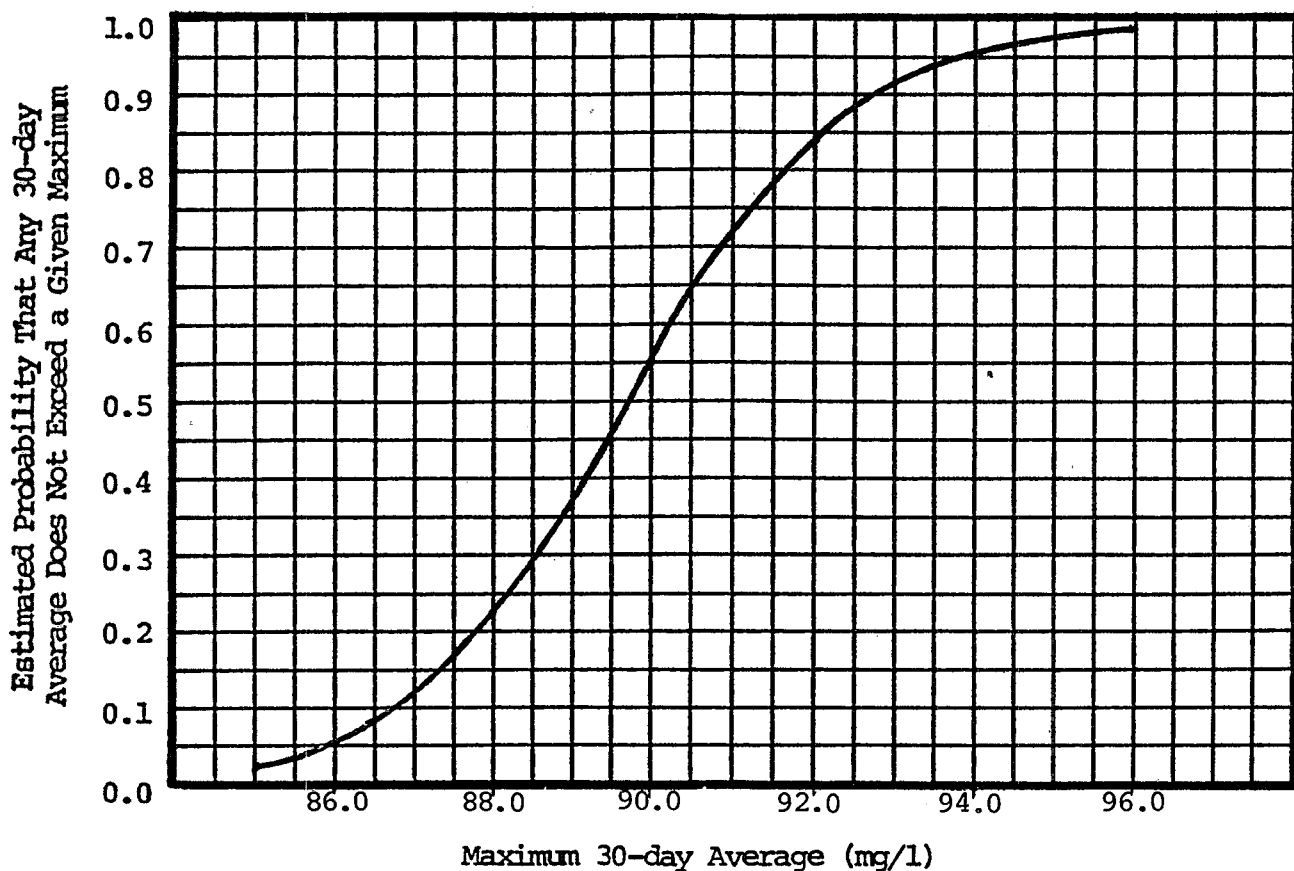


Figure 7-2. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Hydrofluoric Acid	Nickel	
Proposed Maximum 30-day Average	(mg/l):	0.15
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.81
Long Term Average	(mg/l):	0.57
Standard Deviation of 30-day Averages	(mg/l):	0.15
Probability of Achieving Proposed Maximum 30-day Average	(%):	0.24
Number of Observations:		17

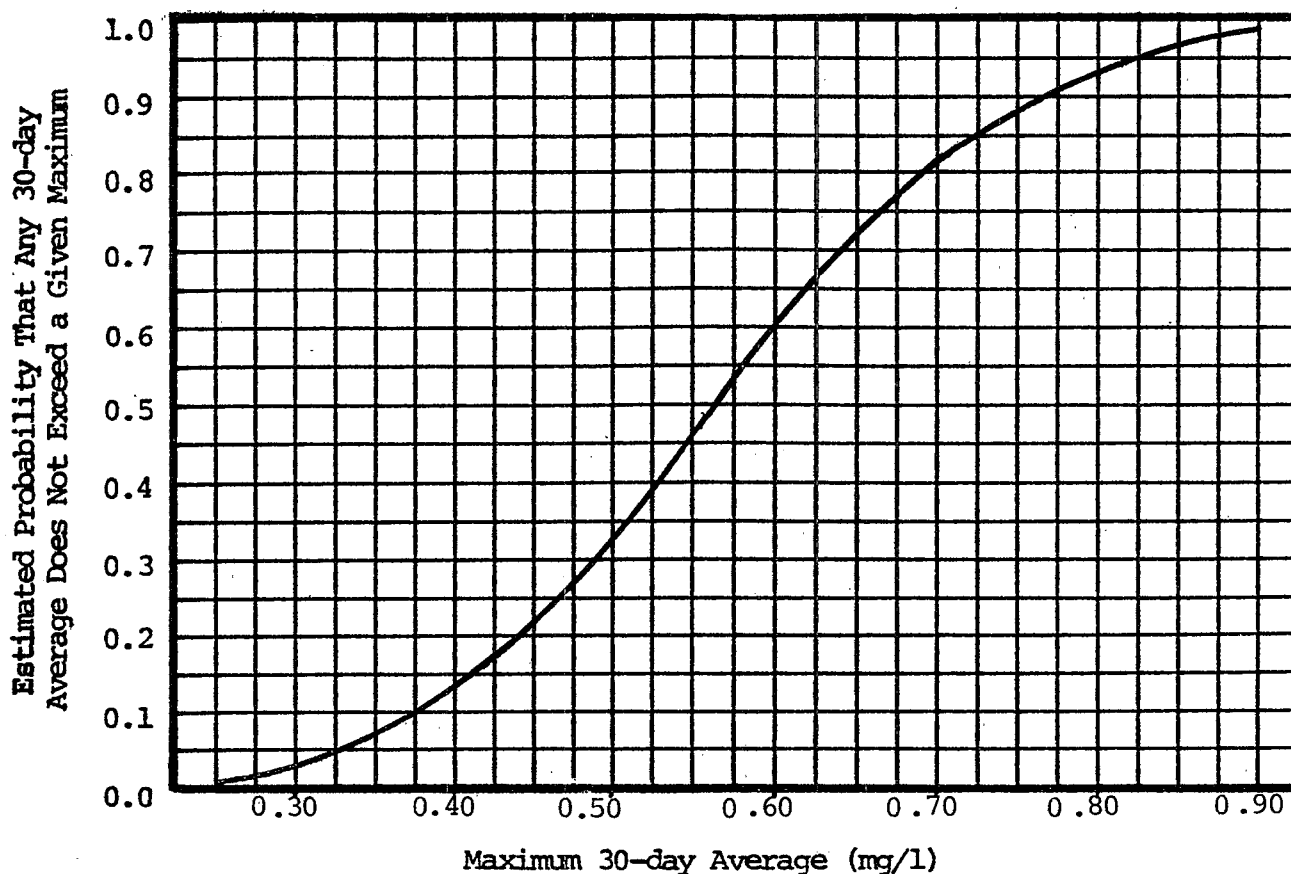


Figure 7-3. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Hydrofluoric Acid	Zinc	
Proposed Maximum 30-day Average	(mg/l):	0.52
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.11
Long Term Average	(mg/l):	0.074
Standard Deviation of 30-day Averages	(mg/l):	0.024
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		17

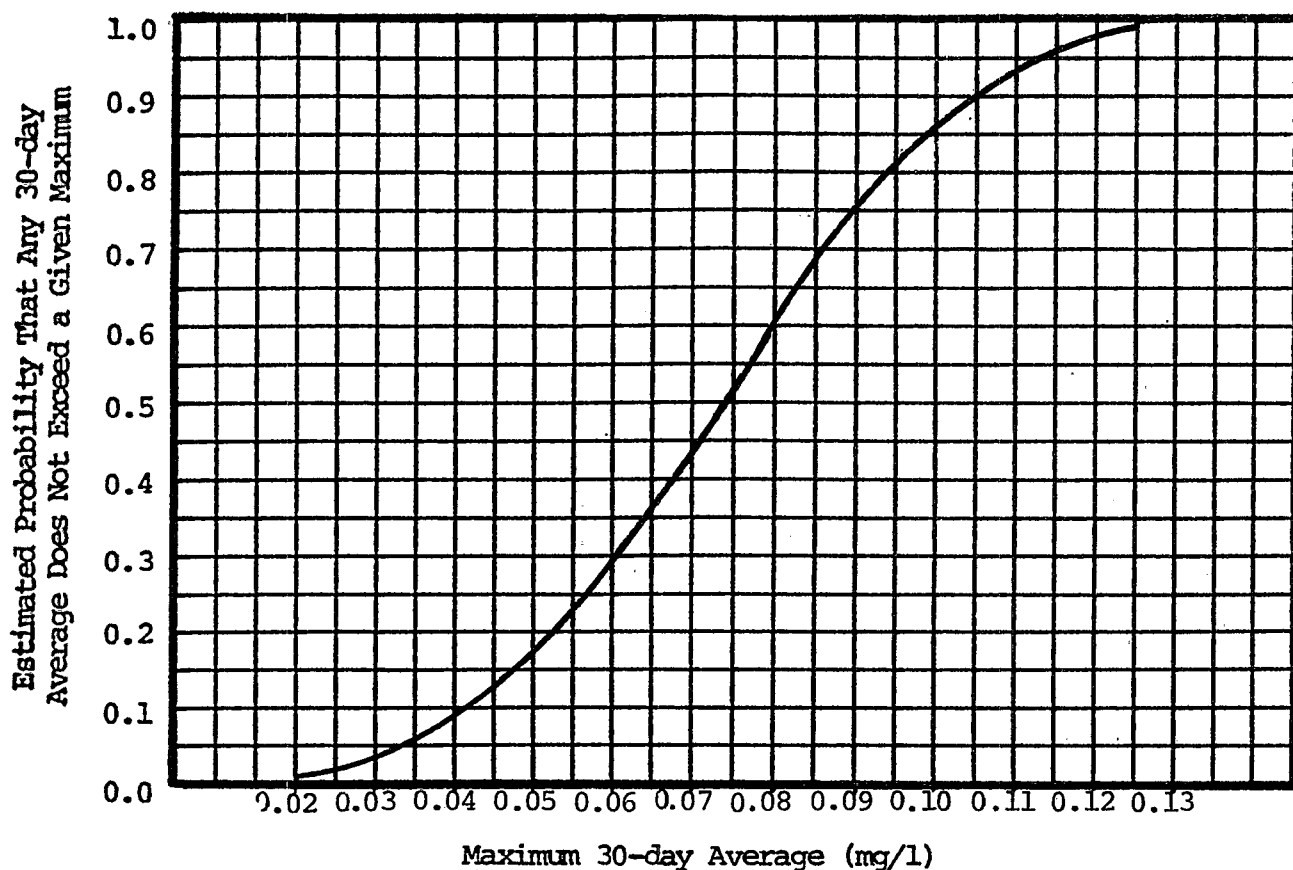


Figure 7-4. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Hydrofluoric Acid	Chromium	

Proposed Maximum 30-day Average (mg/l): 0.040

95th Percentile ( $Z = 1.64$ ) (mg/l): 0.096

Long Term Average (mg/l): 0.076

Standard Deviation of 30-day Averages (mg/l): 0.012

Probability of Achieving Proposed  
Maximum 30-day Average (%): 0.13

Number of Observations: 17

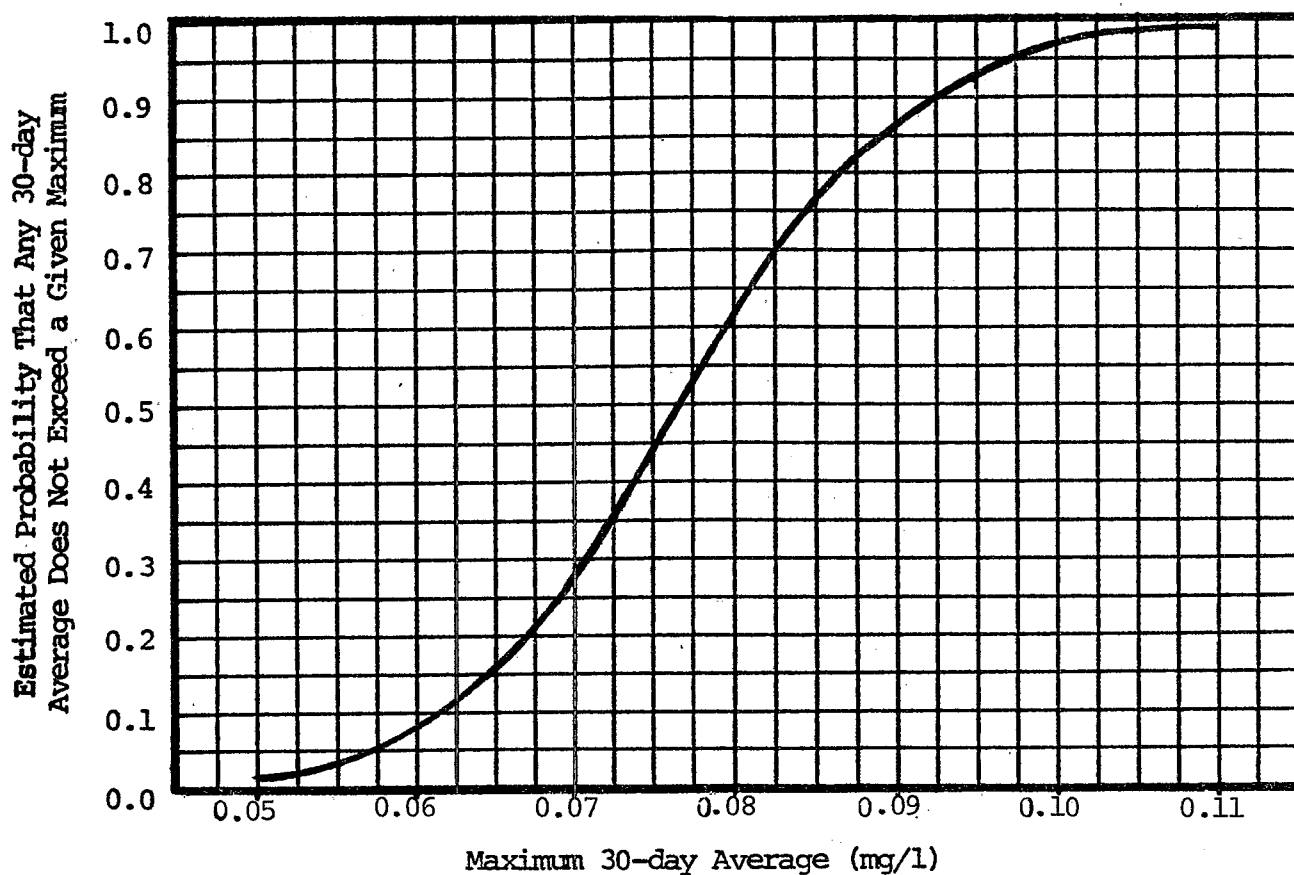


Figure 7-5. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Hydrofluoric Acid	Total Suspended Solids	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	68
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	230
Long Term Average	(mg/l):	170
Standard Deviation of 30-day Averages	(mg/l):	36
Probability of Achieving Proposed Maximum 30-day Average	(%):	0.36
Number of Observations:		17
<hr/>		

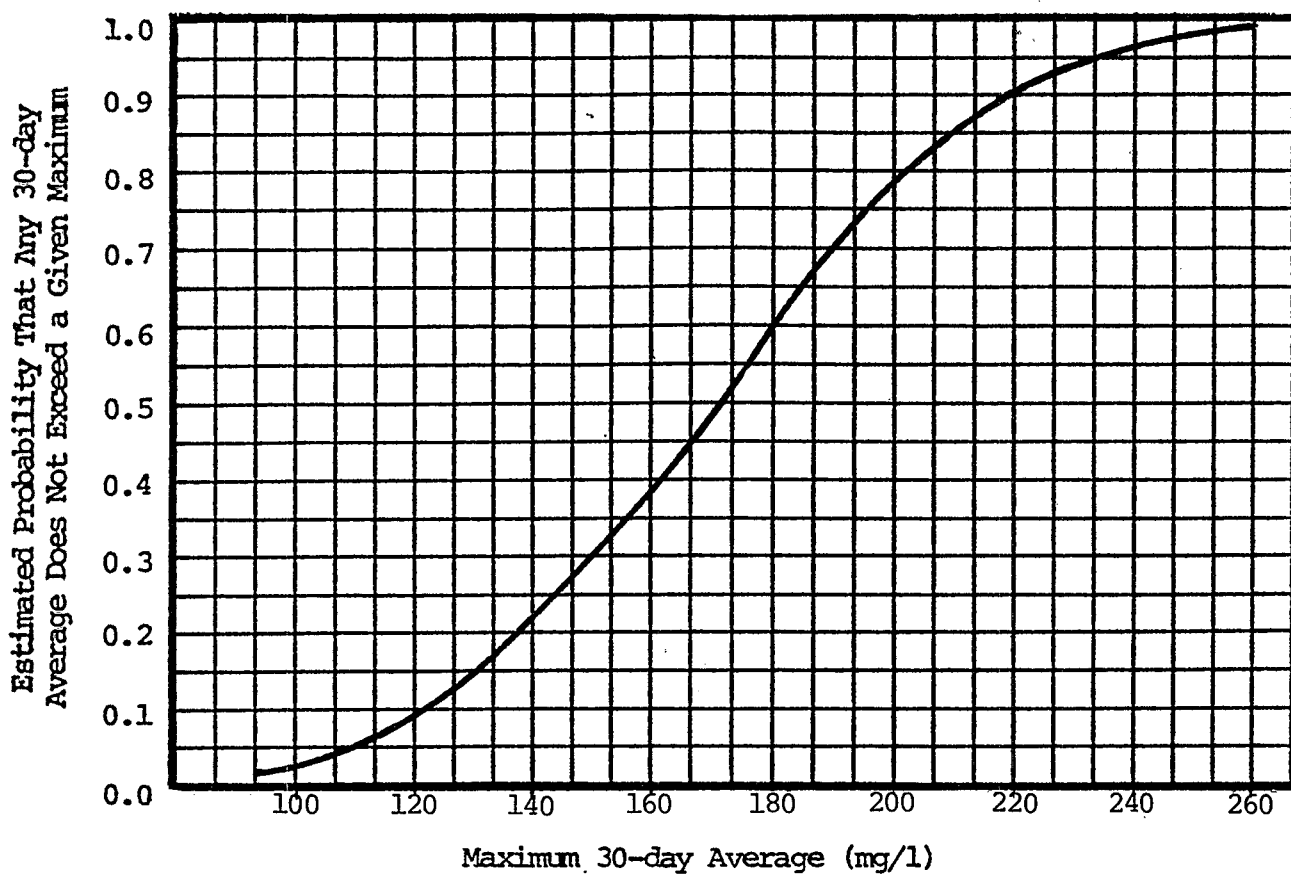
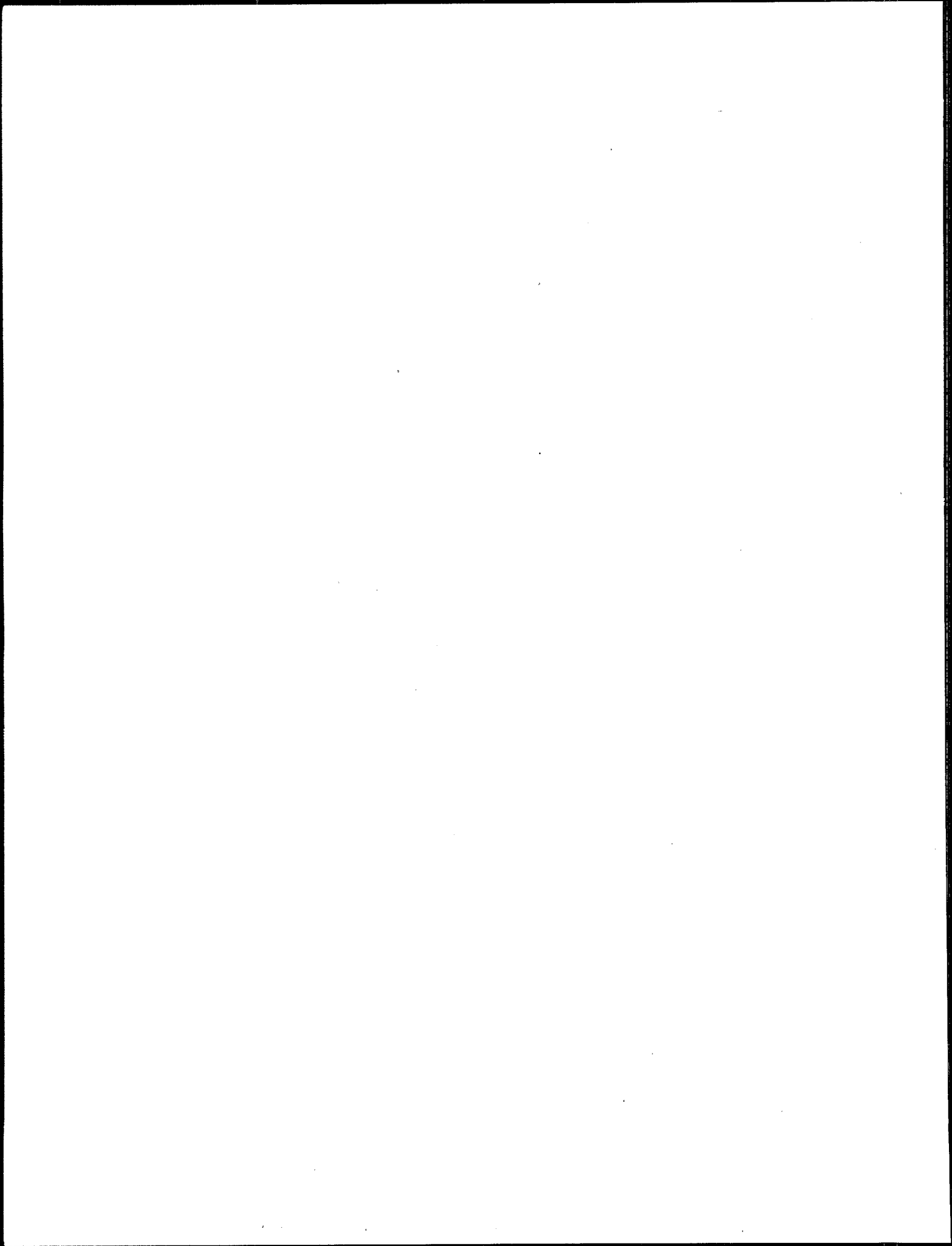


Figure 7-6. Estimated Performance of Proposed  
BAT Treatment



activity coefficient for nickel) at the high ionic strengths encountered.

A major conclusion that can be drawn from this study is that the addition of dual media filtration after alkaline precipitation and settling is not particularly effective for the reduction of final TSS and total fluoride concentrations. Further, dual media filtration does not appear to be justified on the basis of additional toxic metal removal judging by the results presented in Table 7-3.



## SECTION 8.0

### COPPER SULFATE SUBCATEGORY

#### 8.1 INTRODUCTION

##### 8.1.1 General Considerations

The treatability tests for the copper sulfate subcategory were conducted at the in-house laboratory facilities of Versar, Inc. located in Springfield, Virginia. Eight samples were collected at Plant #034 and expeditiously transported to the laboratory facility where the test runs were conducted. A total of 24 test runs were completed between October 19 and November 14, 1979, and all test runs were made within one week after raw waste sample collection.

##### 8.1.2 Sample Point Location

Figure 8-1 shows a general process schematic flow diagram for Plant #034 showing the raw waste sample point location selected for study. The stream sampled includes wastes from leaks, spills, and washdown which collects at a sump in the basement of the facility. About one quarter of this waste water by volume is comprised of contaminated ground water from the immediate area.

#### 8.2 TREATABILITY TEST MODEL OPERATION

##### 8.2.1 Treatment Technology Tested

The proposed BAT treatment includes alkaline precipitation of toxic metal pollutants with either lime or caustic, followed by clarification of suspended solids and final polish through a dual media filter.

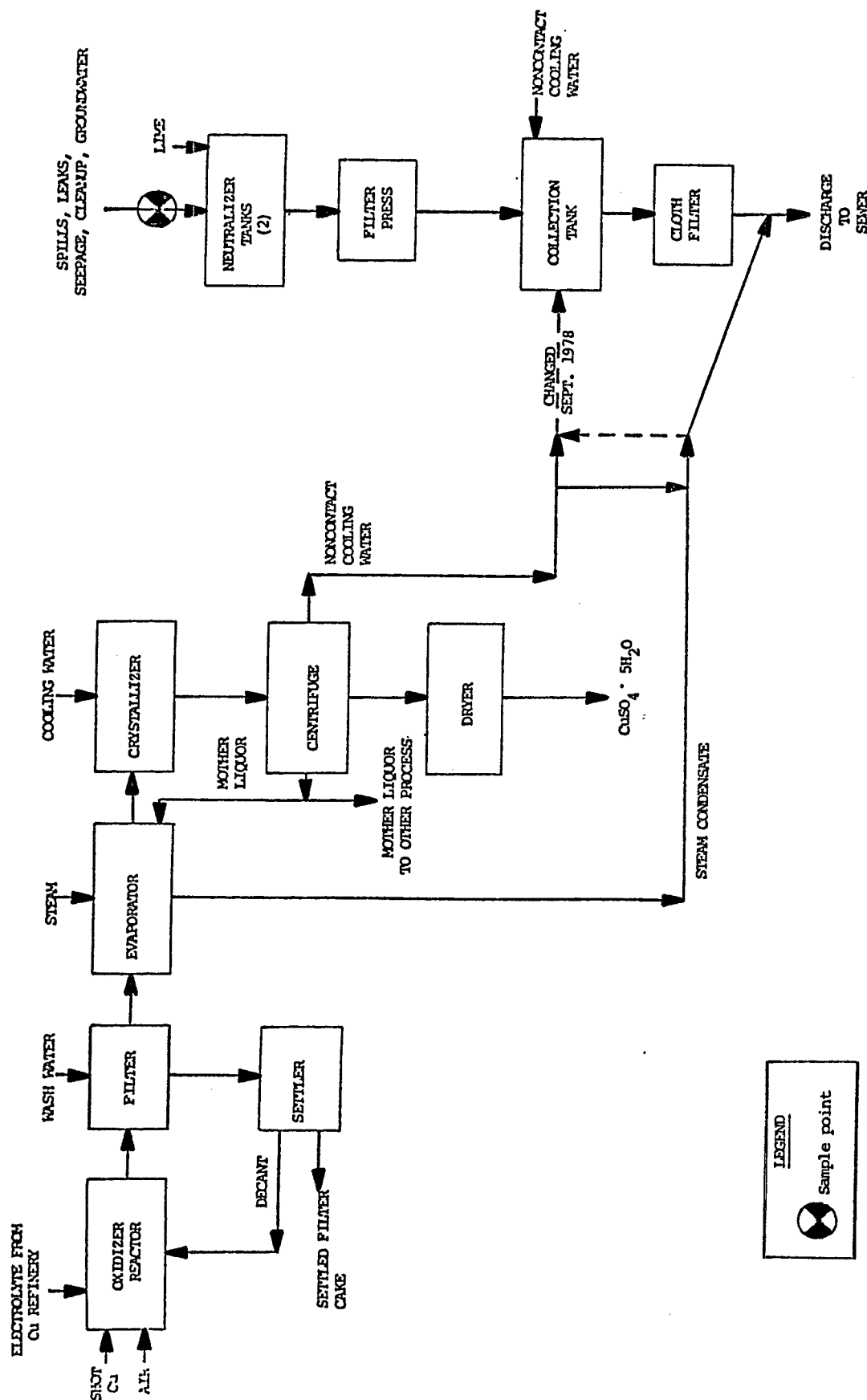


Figure 8-1. General process flow diagram at plant #034 showing the sampling point. (Copper sulfate manufacture.)

### 8.2.2 Waste Water Characterization

The major toxic pollutants studied for this subcategory include copper, nickel, and selenium. Since optimum removal of nickel and copper by alkaline precipitation occurs at slightly different pH values, it was necessary to determine the pH for optimum removal of pollutants. Therefore, a five gallon sample of waste water was collected for study prior to the treatability test runs. Results of the characterization are presented in Tables 8-1 and 8-2. The copper concentration increases slightly at higher pH values indicated in Table 8-2 as anticipated (Figure 2-1). Since the minimum solubility for all the pollutants occurred at a pH of 10, it was decided to conduct the treatability test runs at this pH value.

### 8.2.3 Treatability Test Operation

The BAT concept was tested comparing both lime and caustic soda for alkaline precipitation of metals. Total recirculation of the filter effluent back to the reaction/settling tank was practiced for runs 1 through 4; however, the filter was operated on a once-through basis for runs 5 through 12 because recirculation was found to have no appreciable effect on the efficiency of solids removal.

Chemical dosages for metal precipitation are shown in Tables 8-3 and 8-5 for each of the treatability test runs. Data pertaining to the pH of raw and treated waste water, settling time, time of filter effluent sampling after start of filtration, and mixing time are also included in these tables.

## 8.3 TEST RESULTS

### 8.3.1 Discussion of Results

The analytical results tabulated in Tables 8-4 and 8-6 show that both lime and caustic soda are effective in lowering the concentrations of copper, nickel, and total suspended solids. However, no significant removal of selenium was shown. Selenium was present only in very low concentrations, probably as selenite and selenate, both of which are relatively unaffected by pH.

Recirculation of the filter effluent back to the reaction/settling tank did not seem to improve the filter removal efficiencies for any of the pollutants under consideration. It is clear from an examination of Tables 8-4 and 8-6 that a 50 minute once-through filtration time was adequate in the test model to provide a good solids separation.

TABLE 8-1. WASTE WATER CHARACTERIZATION FOR THE PLANT  
SELECTED FOR STUDY IN THE COPPER SULFATE SUBCATEGORY

	Specific Waste Constituent (mg/l)		
	Copper	Nickel	Selenium
Total	221	22	0.20
Dissolved	213	22	0.17

TABLE 8-2. EFFECT OF pH ON SOLUBILITY OF POLLUTANTS

Final pH	Precipitant			
	Sodium Hydroxide		Lime	
	Copper	Nickel	Copper	Nickel
7.0	7.6	7.4	2.6	16.2
8.0	9.7	6.7	2.5	10.0
9.0	9.6	2.2	3.5	2.2
10.0	13.4	1.6	4.7	0.7

TABLE 8-3. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Copper Sulfate		TREATMENT: Lime Plus Dual Media Filtration											
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	
Date	9/14	9/18	9/21	9/28	10/1	10/3	10/5	10/10	10/12	10/16	10/17	10/18	
Volume of Waste Water Treated (Gallons)	20	20	20	20	20	20	20	20	20	20	20	20	
Raw Waste Water pH	3.3	3.2	3.3	3.1	3.1	3.1	3.0	3.0	3.1	3.0	3.0	3.1	
Precipitant Dosage Required ( $\frac{\text{gm CaO}}{\text{gal of waste}}$ )	1.9	1.6	1.7	1.6	2.1	1.9	2.1	2.2	2.2	2.5	2.2	2.9	
pH Achieved by Lime Addition	9.8	10.0	10.4	10.1	9.7	9.9	9.9	10.1	9.8	10.0	9.8	10.0	
Mixing Time (mins)	20	20	30	20	15	20	15	15	15	15	15	15	
Setting Time (mins)	180	150	180	150	90	120	120	180	120	120	120	150	
Supernatant pH After Reaction	9.3	9.5	9.5	9.8	9.4	9.5	9.5	9.7	9.7	10.0	9.6	10.0	
Filtrate pH	7.3	9.2	7.8	7.5	7.5	9.2	9.1	8.9	7.7	9.5	8.1	8.5	
Filtration Time (mins.)	140	140	140	140	50	50	50	50	50	50	50	50	

TABLE 8-4. ANALYTICAL RESULTS FOR THE COPPER SULFATE SUBCATEGORY

TREATMENT: Lime Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
	All reported values in mg/l											
<u>Copper, Cu</u>												
Raw Waste												
Total Cu		296	249	155	159	270	230	210	205	210	290	300
Dissolved Cu	316	296	238	155	78	245	230	205	200	210	300	200
Supernatant												
Total Cu	0.52	1.70	1.50	2.10	0.65	1.31	1.22	0.49	1.09	1.36	0.72	0.58
Dissolved Cu	0.17	0.29	2.40	2.60	0.21	0.36	0.20	0.16	0.18	0.25	0.24	0.40
Filter Effluent												
Total Cu	0.08	0.56	0.25	0.28	0.09	0.18	0.14	0.15	0.12	0.10	0.13	0.06
Dissolved Cu	0.09	0.31	0.29	0.16	0.12	0.14	0.10	0.09	0.10	0.09	0.12	0.08
<u>Nickel, Ni</u>												
Raw Waste												
Total Ni	28.4	29.9	39.3	NDA <sup>(1)</sup>	33.4	34.0	35.0	39.0	39.0	38.0	27.0	37.0
Dissolved Ni	28.0	30.1	38.9	30.7	33.1	33.0	35.0	37.0	38.0	37.0	37.0	36.0
Supernatant												
Total Ni	0.09	0.26	0.29	0.36	0.24	0.20	0.19	0.05	0.19	0.23	0.15	0.11
Dissolved Ni	0.07	0.08	0.19	0.47	0.13	0.05	<0.05	<0.05	<0.05	<0.05	0.09	0.09
Filter Effluent												
Total Ni	0.05	0.21	0.41	0.13	0.12	0.07	<0.05	<0.05	<0.05	<0.05	0.06	0.08
Dissolved Ni	0.05	0.21	0.11	0.12	0.12	0.08	<0.05	<0.05	<0.05	<0.05	0.07	0.07

(1) NDA = No Data Available

(1) NDA = No Data Available



TABLE 8-4 - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
All reported values in mg/l												
<u>Selenium, Se</u>												
Raw Waste												
Total Se	0.18	0.13	0.14	0.12	0.11	0.12	0.14	0.12	0.13	0.12	0.13	0.09
Dissolved Se	0.18	0.13	0.11	0.11	0.12	0.12	0.13	0.12	0.13	0.13	0.12	0.12
Supernatant												
Total Se	0.13	0.11	0.14	0.10	0.12	0.18	0.13	0.12	0.11	0.12	0.14	0.15
Dissolved Se	0.13	0.13	0.12	0.11	0.12	0.11	0.12	0.13	0.14	0.14	0.12	0.14
Filter Effluent												
Total Se	0.15	0.12	0.11	0.11	0.10	0.11	0.16	0.11	0.11	0.13	0.12	0.14
Dissolved Se	0.14	0.11	0.15	0.10	0.10	0.11	0.12	0.12	0.12	0.13	0.12	0.13
<u>Total Suspended Solids, TSS</u>												
Raw Waste	105	162	90	148	108	157	43	94	98	167	113	147
Supernatant	1.8	9.0	10.2	20.6	9.2	18.0	14.4	5.2	14.9	16.8	4.9	3.3
Filter Effluent	0.9	1.6	3.5	3.5	14.0	9.0	5.6	4.2	6.0	0.9	2.2	3.2

TABLE 8-5. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Copper Sulfate

TREATMENT: Caustic Soda Plus Dual Media  
Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
Date	9/17	9/19	9/24	10/1	10/2	10/4	10/9	10/11	10/15	10/16	10/17	10/19
Volume of Waste Water Treated (Gallons)	20	20	20	20	20	20	20	20	20	20	20	20
Raw Waste Water pH	3.4	3.2	3.1	3.0	3.1	3.1	3.0	3.0	3.0	3.0	3.1	3.1
Precipitant Dosage Required $\left(\frac{\text{gm CaO}}{\text{gal of waste}}\right)$	2.4	2.4	2.2	2.8	2.5	2.5	2.5	2.4	2.5	2.0	2.7	2.4
Precipitant Solution Strength	6N <sup>(1)</sup>	6N	6N	6N	10N	10N	10N	10N	10N	10N	10N	10N
pH Achieved by Lime Addition	9.8	10.4	10.2	10.5	10.5	9.9	9.7	10.0	9.8	9.6	9.6	9.6
Mixing Time (mins)	20	20	20	15	15	15	15	15	15	15	15	15
Settling Time (mins)	120	120	150	90	90	96	120	120	120	120	120	150
Supernatant pH After Reaction	8.0	9.7	9.7	9.5	10.0	9.1	9.5	9.6	9.5	9.4	9.4	9.3
Filtrate pH	7.5	7.7	7.5	9.0	9.5	8.5	9.4	9.2	7.6	7.4	7.8	8.0
Filtration Time (mins)	140	140	140	50	50	50	50	50	50	50	50	50

(1) N = Normality

TABLE 8-6. ANALYTICAL RESULTS FOR THE COPPER SULFATE SUBCATEGORY

TREATMENT: Caustic Soda Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
	All reported values in mg/l											
<u>Copper, Cu</u>												
Raw Waste												
Total Cu	324	278	151	NDA <sup>(1)</sup>	260	230	240	210	200	255	300	300
Dissolved Cu	313	258	152	NDA	262	230	233	205	210	255	290	300
Supernatant												
Total Cu	1.80	1.53	4.49	0.43	0.88	0.57	1.27	1.04	0.78	1.98	0.74	0.05
Dissolved Cu	0.15	1.11	0.31	0.09	0.12	0.14	0.20	0.17	0.14	0.11	0.25	0.07
Filter Effluent												
Total Cu	0.40	0.32	0.66	9.79	0.11	0.08	0.27	0.15	0.22	0.17	0.07	0.14
Dissolved Cu	UTD <sup>(2)</sup>	0.19	0.29	0.10	0.09	0.13	0.45	0.12	0.21	0.32	0.07	0.10
<u>Nickel, Ni</u>												
Raw Waste												
Total Ni	28.4	37.1	30.0	32.8	34.0	35.0	37.0	39.0	38.0	39.0	36.0	37.0
Dissolved Ni	28.2	34.9	30.0	33.7	33.0	35.0	36.0	38.0	37.0	39.0	36.0	38.0
Supernatant												
Total Ni	0.53	0.27	0.61	0.11	0.11	0.13	0.30	0.14	0.15	0.38	0.16	0.15
Dissolved Ni	0.09	0.07	0.08	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	0.08
Filter Effluent												
Total Ni	0.14	0.10	0.20	0.71	<0.05	<0.05	0.08	<0.05	0.06	0.12	0.06	0.08
Dissolved Ni	UTD <sup>(2)</sup>	0.11	0.20	0.05	<0.05	<0.05	0.08	<0.05	0.06	0.16	0.06	0.05

(1) NDA = No Data Available

(2) UTD = Unable to Determine

TABLE 8-6 - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
All reported values in mg/l												
<u>Selenium, Se</u>												
Raw Waste												
Total Se	0.15	0.14	0.12	0.11	0.14	0.12	0.14	0.11	0.12	0.12	0.15	0.11
Dissolved Se	0.14	0.13	0.13	0.10	0.14	0.12	0.12	0.14	0.14	0.14	0.11	0.12
Supernatant												
Total Se	0.13	0.12	0.11	0.12	0.14	NDA <sup>(1)</sup>	0.12	0.14	0.15	0.16	0.12	0.18
Dissolved Se	0.13	0.13	0.13	0.12	0.11	NDA	0.11	0.13	0.15	0.16	0.11	0.13
Filter Effluent												
Total Se	0.13	0.13	0.13	0.11	0.15	0.13	0.13	0.12	0.16	0.16	0.11	0.13
Dissolved Se	0.13	0.12	0.12	0.13	0.14	0.13	0.14	0.13	0.16	0.14	0.11	0.12
<u>Total Suspended Solids, TSS</u>												
Raw Waste	122	104	173	19	101	79	95	169	172	110	126	199
Supernatant	3.3	17.3	15.4	76.0	8.2	8.0	12.6	3.4	18.9	8.2	10.9	4.3
Filter Effluent	2.6	1.1	8.5	4.5	8.2	7.4	12.6	3.4	2.3	8.2	2.0	3.5

(1) NDA = No Data Available

### 8.3.2 Statistical Evaluation

Tables 8-7 and 8-8 compare the proposed BAT maximum 30-day average concentration with the estimated treatability 30-day average for lime and caustic treatment, respectively. The results are based on the statistical analysis presented in Figures 8-2 through 8-9 and information in Appendix A.

It should be pointed out that the proposed BAT limitations must be met at least 95 percent of the time by any industry having to comply with the limitations.

### 8.3.3 Conclusions

The proposed BAT treatment is effective for the removal of pollutants whether lime or caustic is used as the treatment chemical. Removal of selenium by alkaline precipitation is ineffective at the low raw waste concentrations observed. The initial selenium concentrations were near the lower limit of treatability which is the basis of the proposed maximum 30-day average limitation. Therefore, conclusions may not be made regarding use of proposed BAT treatment in situations where selenium may conceivably exist at higher concentration levels.

TABLE 8-7. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR THE  
COPPER SULFATE SUBCATEGORY (LIME TREATMENT)

STREAM: FILTER EFFLUENT

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Copper	0.40	0.21
Nickel	0.10	0.13
Selenium	0.10	0.13
Total Suspended Solids, TSS	25	6.0

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Copper	Lime
Proposed Maximum 30-day Average	(mg/l):	0.40
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.21
Long Term Average	(mg/l):	0.17
Standard Deviation of 30-day Averages	(mg/l):	0.020
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		12

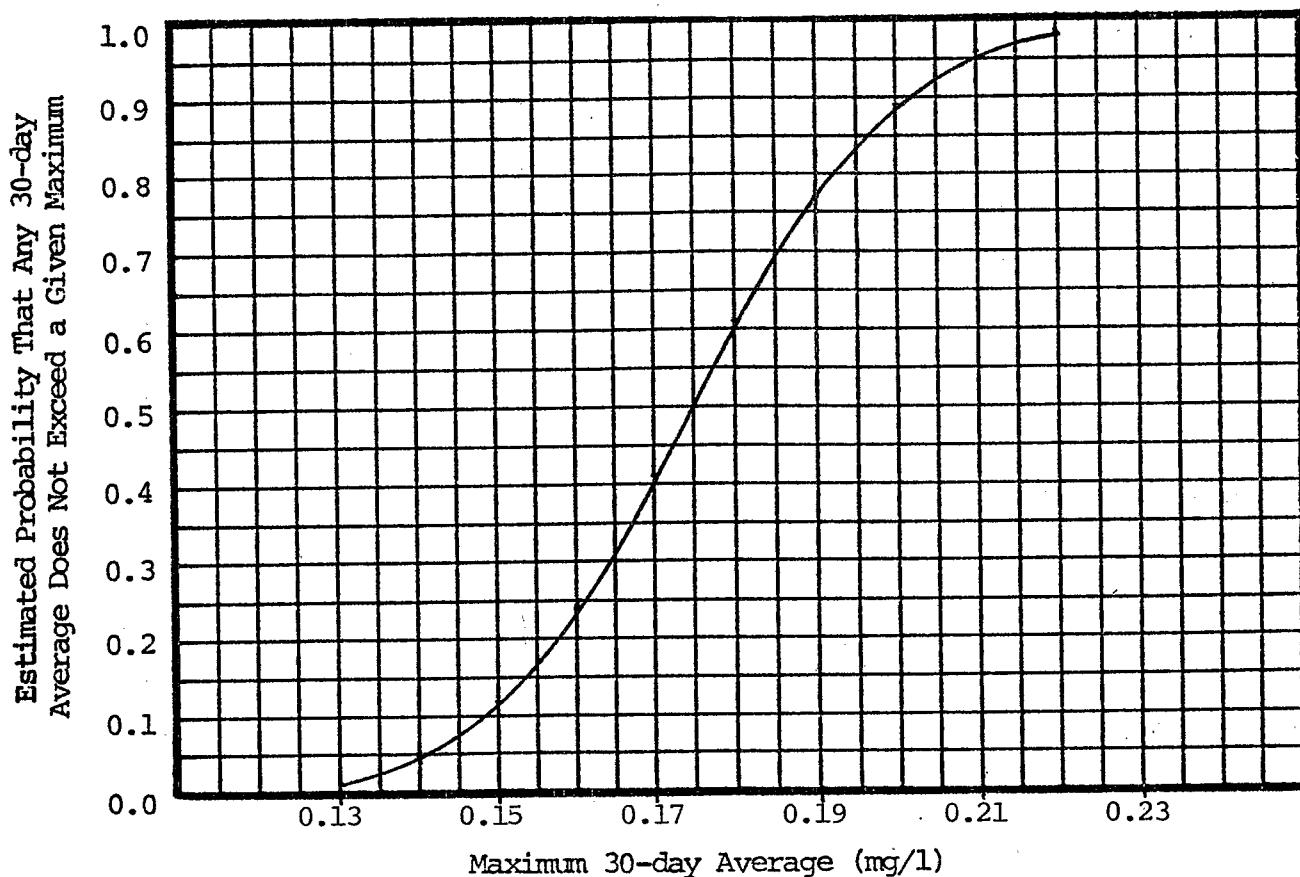


Figure 8-2. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Nickel	Lime
Proposed Maximum 30-day Average	(mg/l) :	0.10
95th Percentile ( $Z = 1.64$ )	(mg/l) :	0.13
Long Term Average	(mg/l) :	0.11
Standard Deviation of 30-day Averages	(mg/l) :	0.014
Probability of Achieving Proposed Maximum 30-day Average	(%) :	36
Number of Observations:		12

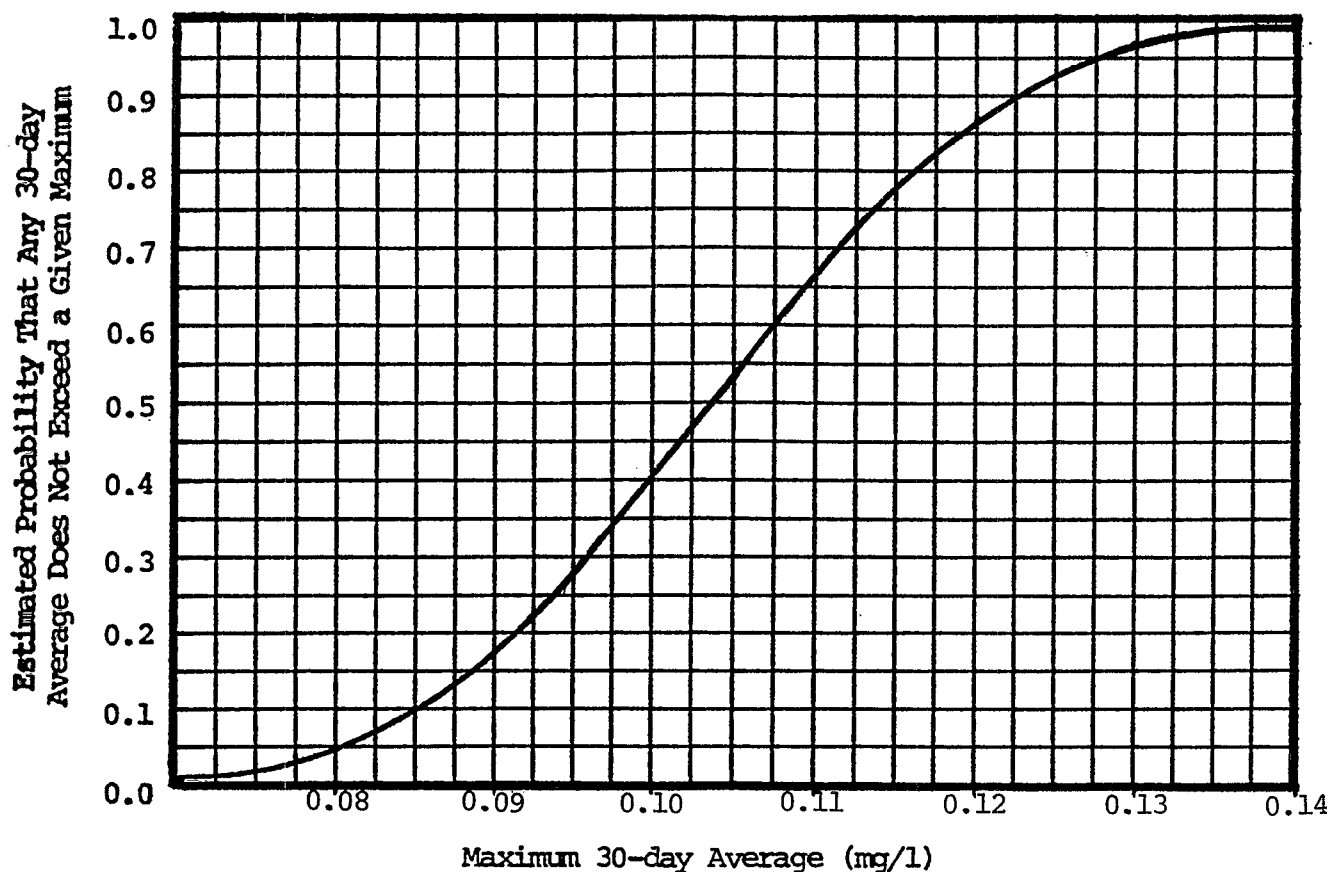


Figure 8-3. Estimated Performance of Proposed BAT Treatment



SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Selenium	Lime
Proposed Maximum 30-day Average	(mg/l):	0.10
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.13
Long Term Average	(mg/l):	0.12
Standard Deviation of 30-day Averages	(mg/l):	0.0031
Probability of Achieving Proposed Maximum 30-day Average	(%):	<0.01
Number of Observations:		12

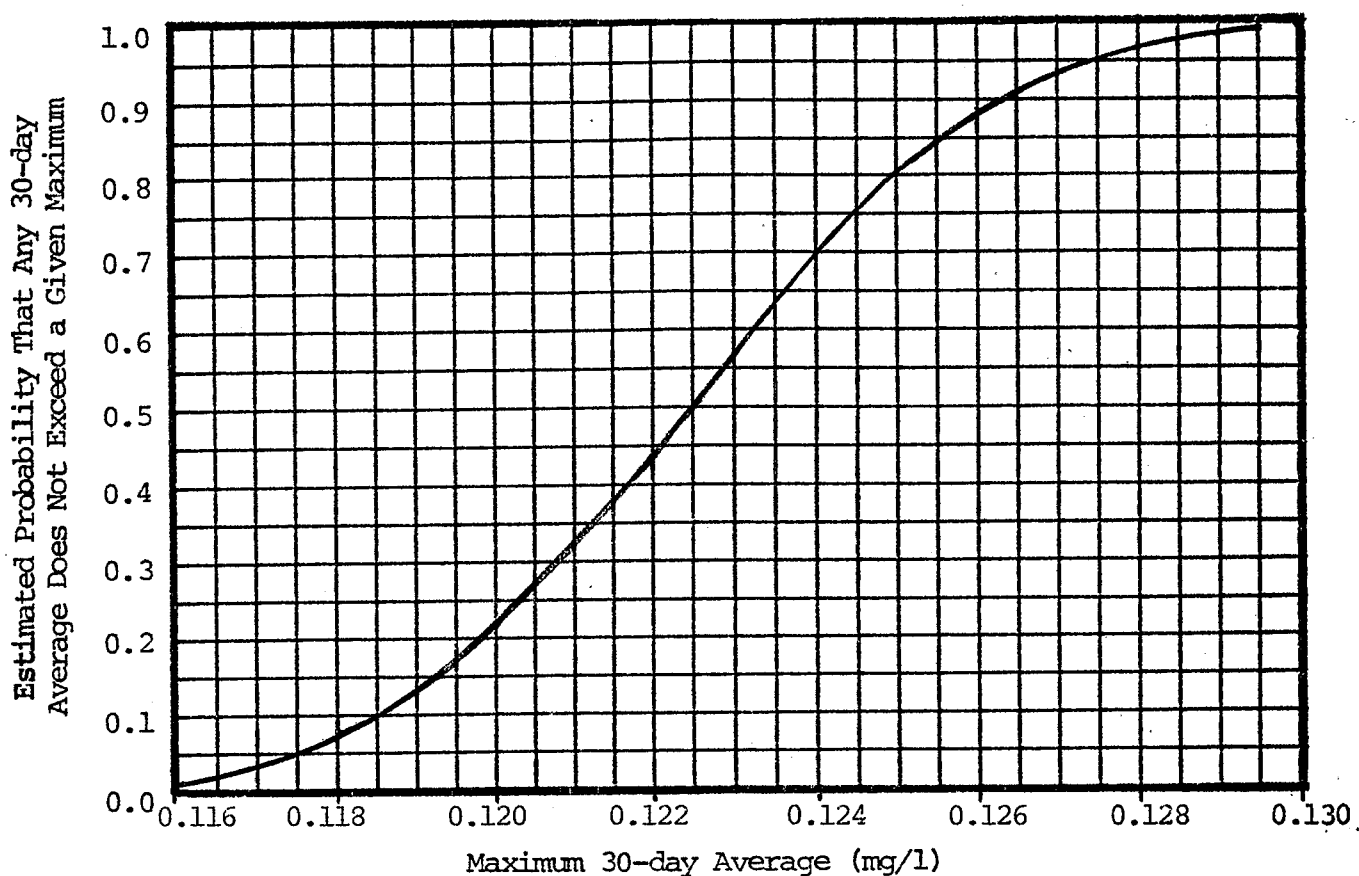


Figure 8-4. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Total Suspended Solids	Lime
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	25
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	6.0
Long Term Average	(mg/l):	4.7
Standard Deviation of 30-day Averages	(mg/l):	0.82
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		12
<hr/>		

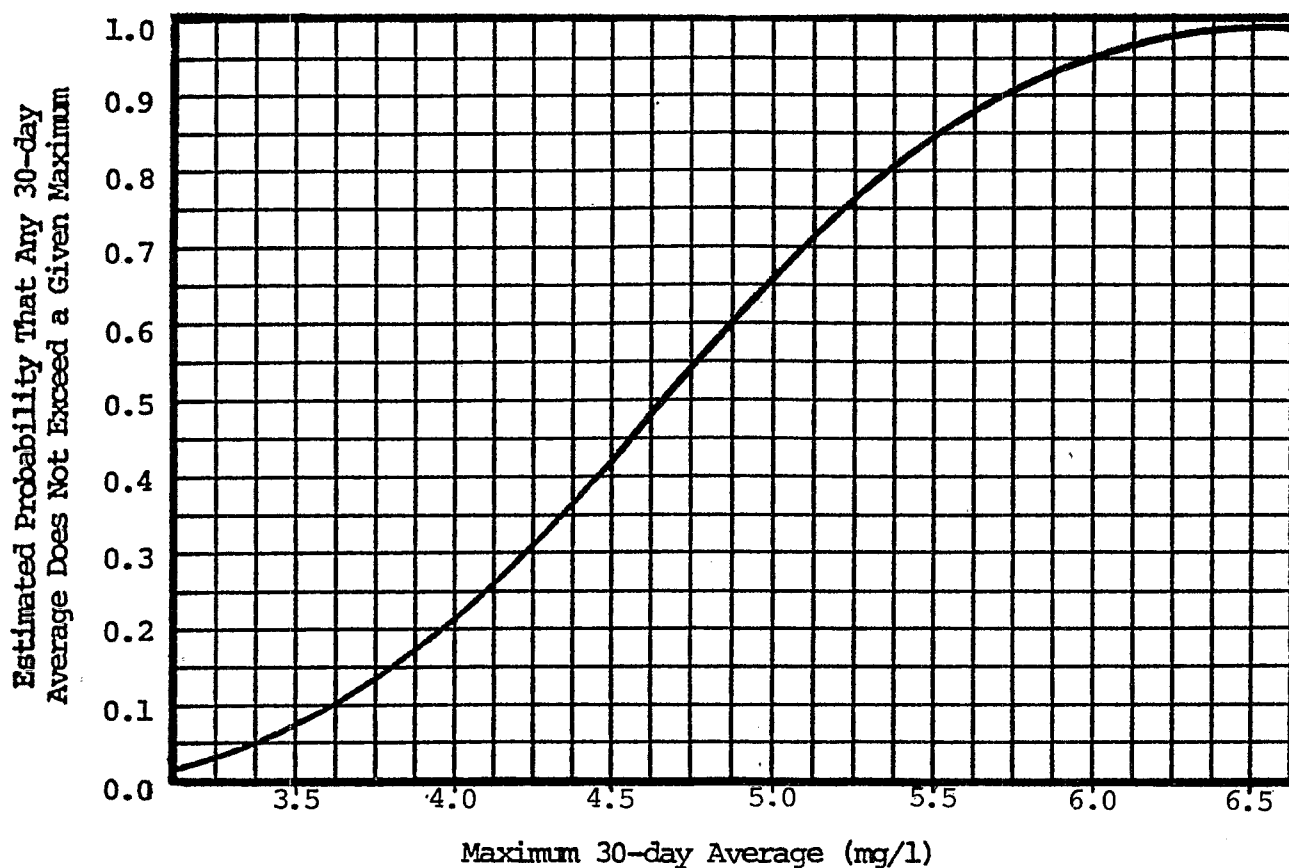


Figure 8-5. Estimated Performance of Proposed BAT Treatment

TABLE 8-8. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR THE  
COPPER SULFATE SUBCATEGORY (CAUSTIC TREATMENT)

STREAM: FILTER EFFLUENT

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Copper	0.40	0.30
Nickel	0.10	0.10
Selenium	0.10	0.14
Total Suspended Solids, TSS	25	7.0

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Copper	Caustic Soda
Proposed Maximum 30-day Average	(mg/l):	0.40
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.30
Long Term Average	(mg/l):	0.25
Standard Deviation of 30-day Averages	(mg/l):	0.034
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		11

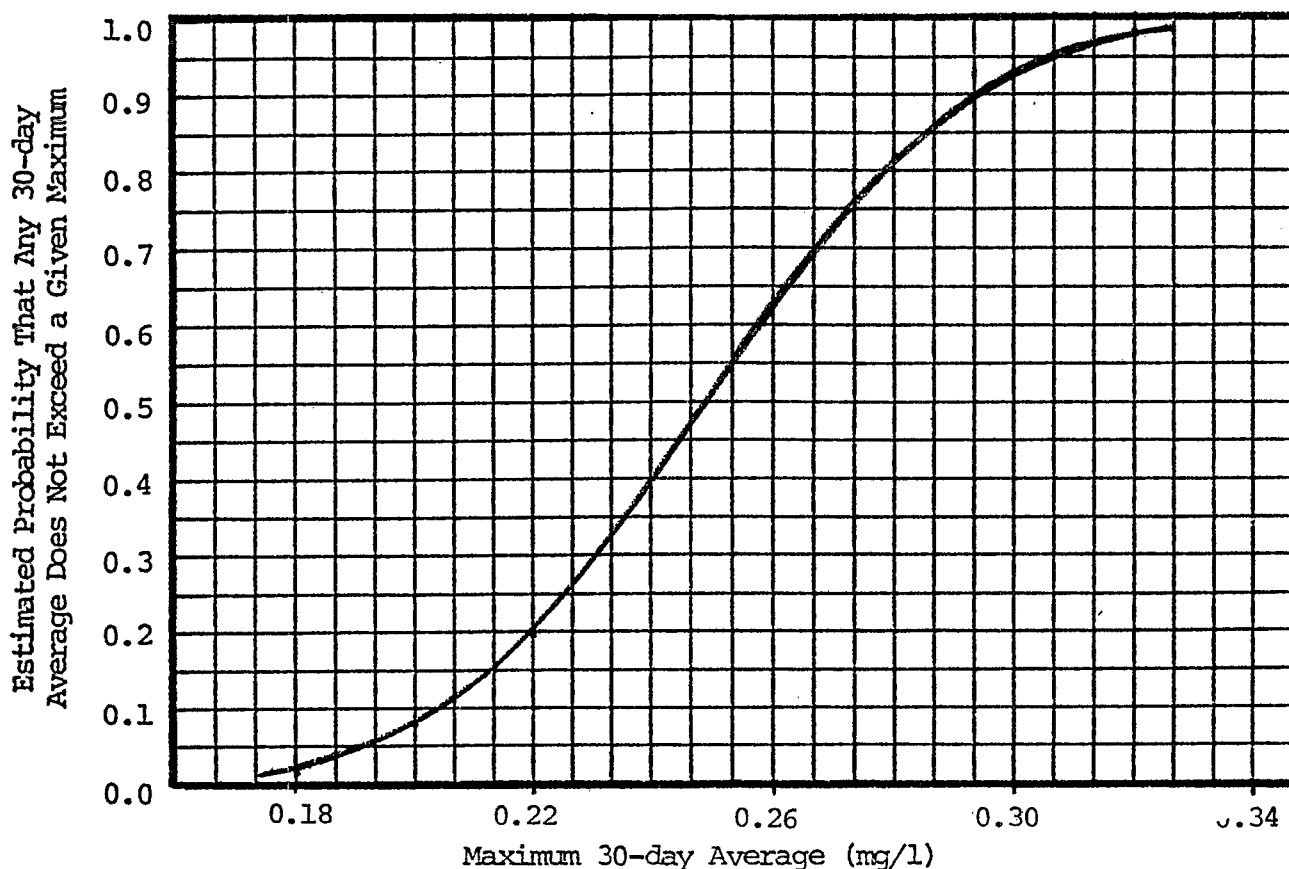


Figure 8-6. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Nickel	Caustic Soda
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	0.10
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.10
Long Term Average	(mg/l):	0.089
Standard Deviation of 30-day Averages	(mg/l):	0.0076
Probability of Achieving Proposed Maximum 30-day Average	(%):	92
Number of Observations:		11
<hr/>		

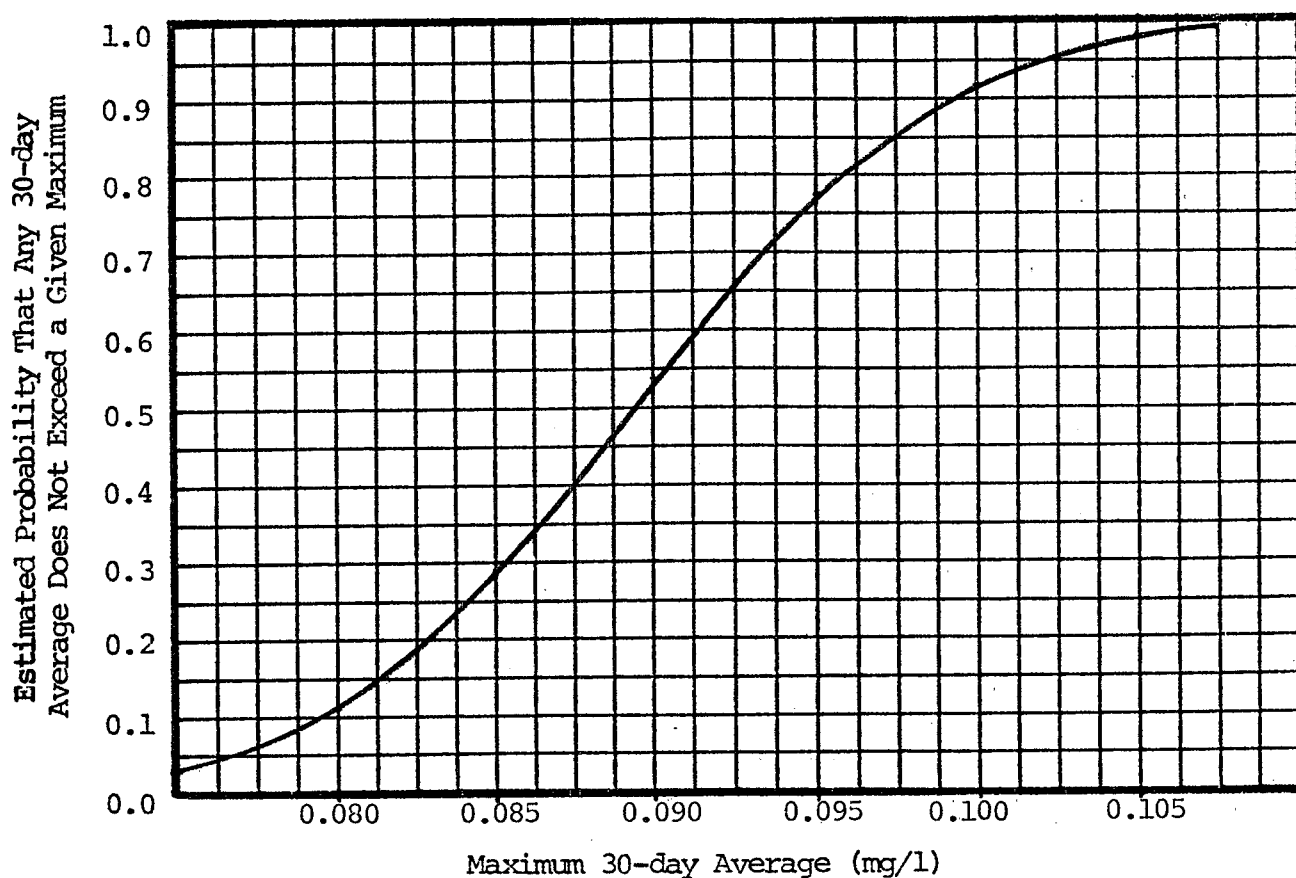


Figure 8-7. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Selenium	Caustic Soda
Proposed Maximum 30-day Average	(mg/l):	0.10
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.14
Long Term Average	(mg/l):	0.13
Standard Deviation of 30-day Averages	(mg/l):	0.0026
Probability of Achieving Proposed Maximum 30-day Average	(%):	<0.01
Number of Observations:		11

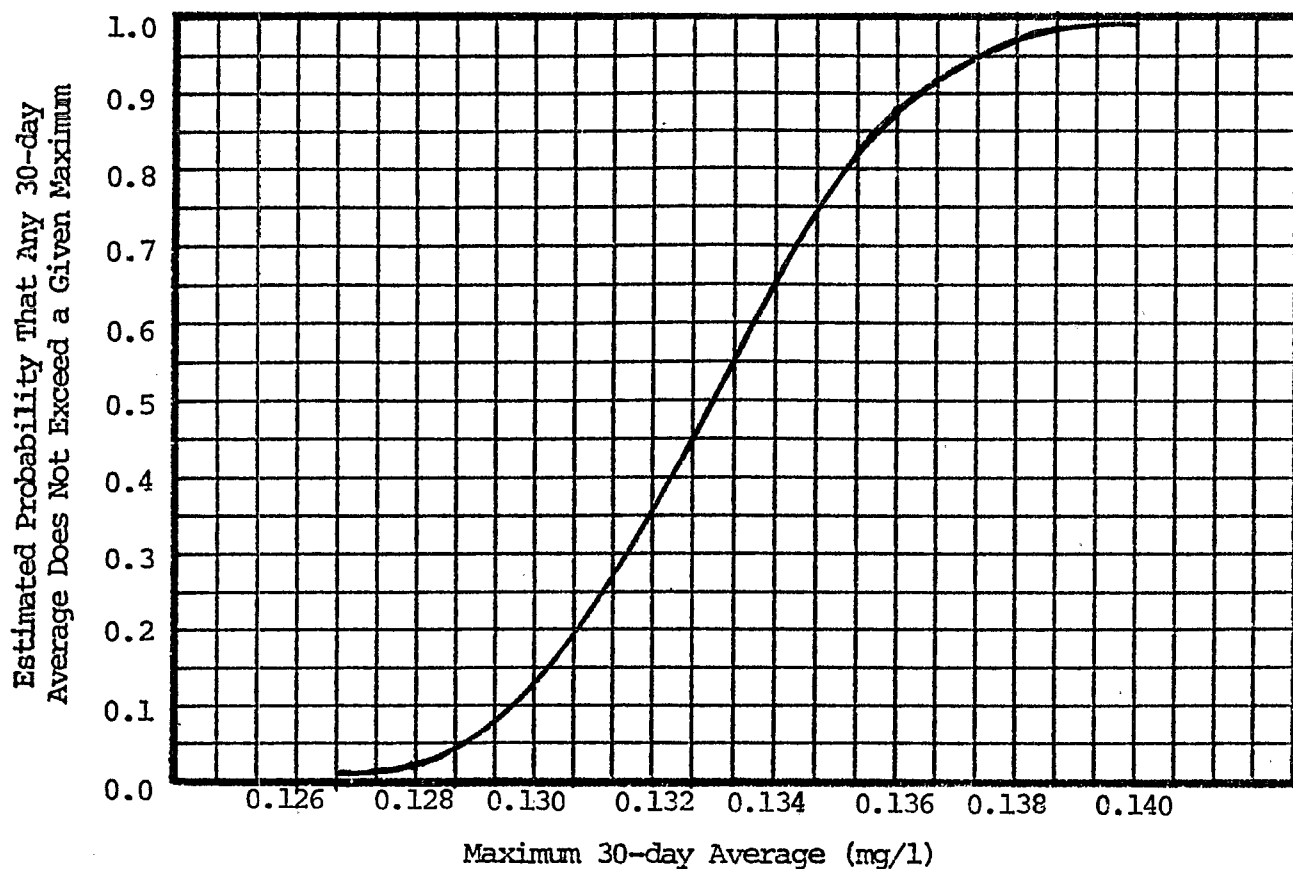


Figure 8-8. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Copper Sulfate	Total Suspended Solids	Caustic Soda
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	25
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	7.0
Long Term Average	(mg/l):	5.6
Standard Deviation of 30-day Averages	(mg/l):	0.86
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		11
<hr/>		

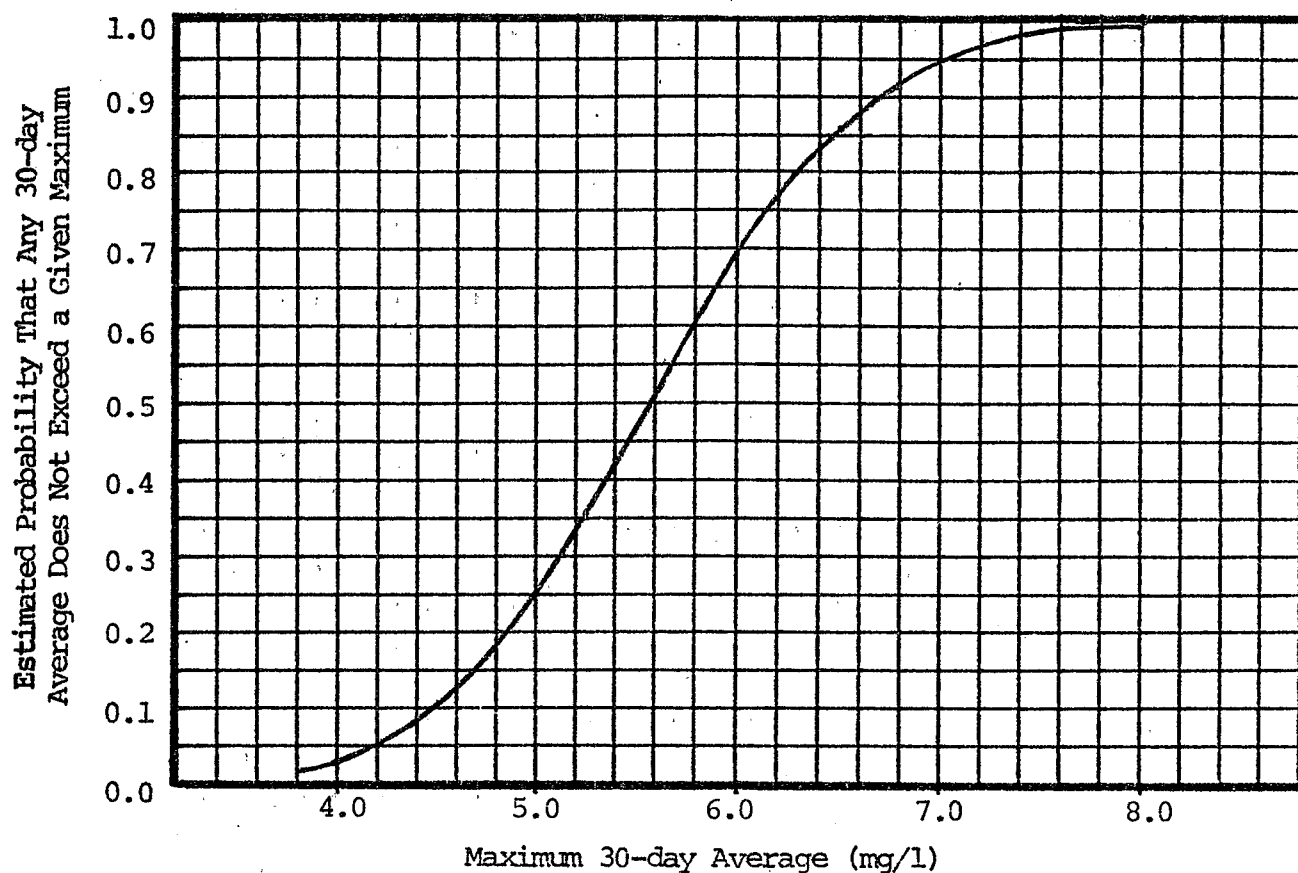
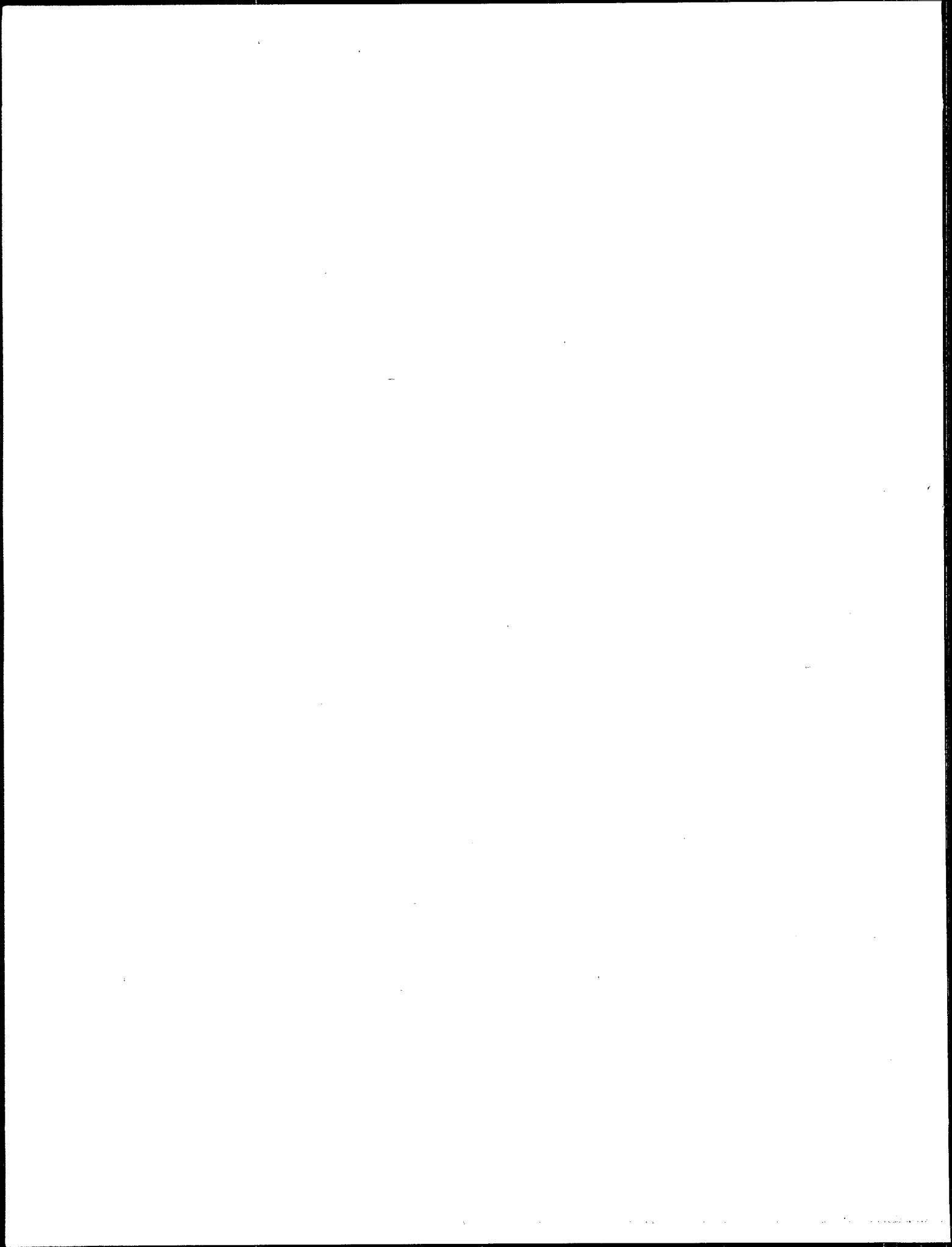


Figure 8-9. Estimated Performance of Proposed BAT Treatment





## SECTION 9.0

### CHLOR-ALKALI SUBCATEGORY (DIAPHRAGM CELL/GRAPHITE ANODE)

#### 9.1 INTRODUCTION

##### 9.1.1 General Considerations

The on-site treatability studies were conducted at Plant #967 which was selected for study. A total of 15 runs were performed using raw waste water collected on a daily basis in the period between October 2 and October 23, 1979. Raw waste water samples were split with plant personnel at their request during the time the waste collection took place.

##### 9.1.2 Sample Point Location

Figure 9-1 is a process flow schematic indicating the waste water sampling point location for the treatability study. The sampling point largely contains cell room wastes which are normally laden with lead and asbestos.

#### 9.2 TREATABILITY TEST MODEL OPERATION

##### 9.2.1 Treatment Technology Tested

The treatability experiments for the waste water in this subcategory involved an assessment of lead, chromium, nickel, and total suspended solids (TSS) removal.

BAT treatment consists of pH adjustment to accomplish alkaline precipitation of the heavy metals from the waste water, followed by removal of the settled hydroxide metal sludge by gravity separation. This is followed by treatment of the clarified waste with a ferrous sulfide suspension for additional metal precipitation. Dual media filtration of the clarified, sulfide-treated waste completes the overall treatment for this type of waste.



### 9.2.2 Waste Water Characterization

Table 9-1 presents the results of the initial characterization tests on the raw waste water. Beaker scale treatability tests were performed to determine the pH for optimum removal of pollutants. The results of those tests are presented in Table 9-1. It can be seen from an inspection of the data that treatment of the waste water to a pH of around 10 produces the lowest concentrations of heavy metals in solution. Therefore, this pH value was utilized to carry out the alkaline precipitation process in the treatability test runs.

Beaker tests were not used to determine sulfide dosage for optimum removal of the metals under consideration from the supernatant after removal of the hydroxide sludge. The dosage and concentration of the ferrous sulfide suspension used in the treatability tests is given in Table 9-3.

### 9.2.3 Treatability Test Operation

As pointed out above, a pH of 10 was found to be optimum for removal of lead and nickel. However, measurement of the raw waste pH always showed a value above 11 when the treatability tests were performed. Therefore, it was always necessary to adjust the pH of the raw waste below 10 by addition of acid if the effectiveness of lime in removing those metals was to be demonstrated.

Adjustment of the pH to 10 was accomplished by adding sulfuric acid and then making the final adjustment by adding lime.

Table 9-2 summarizes the operation parameters for the 15 treatability test runs.

## 9.3 TEST RESULTS

### 9.3.1 Discussion of Results

Analytical results are tabulated in Table 9-3 for the toxic pollutant parameters of concern; namely, lead, nickel, and chromium.

Review of the results indicates a relatively poor and inconsistent removal of metals. Total lead concentrations vary from 3.3 to <0.05 mg/l in the filter effluent, nickel from 1.21 to <0.05 mg/l and chromium from 0.138 to 0.04 mg/l.

TABLE 9-1. WASTE WATER CHARACTERIZATION FOR THE PLANT  
SELECTED FOR STUDY IN THE CHLOR-ALKALI SUBCATEGORY,  
DIAPHRAGM CELL (GRAPHITE ANODE) (1)

Parameter	Result	Parameter	Result
Methyl Orange Alkalinity (as CaCO <sub>3</sub> )	23,000	Calcium (as CaCO <sub>3</sub> )	14
Hydroxide Alkalinity (as CaCO <sub>3</sub> )	17,800	Magnesium (as CaCO <sub>3</sub> )	1.3
Total Suspended Solids	166	Chloride	92,471
Total Dissolved Solids	180,000	Sulfate	260
Total Residue	179,000	Nitrate	0.40
Fixed Residue	171,000	Sodium	65,900
		Potassium	30
		Chromium	0.14
		Lead	1,160
		Nickel	0.80

(1) All values in mg/l unless specified.

EFFECT OF pH ON SOLUBILITY OF POLLUTANTS (1)

pH	Chromium	Lead	Nickel
8.0	0.18	10.9	4.13
8.5	0.19	5.5	3.74
9.0	0.06	4.5	3.26
9.5	0.21	4.3	2.48
10.0	0.06	2.4	2.58
11.0	0.17	26.5	4.13

(1) All values in mg/l unless specified.

TABLE 9-2. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Chlor-Alkali, Diaphragm Cell (Graphite Anode) TREATMENT: Alkaline Precipitation of Metals by pH Adjustment Followed by Sulfide Treatment and Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Date	10/2	10/3	10/4	10/8	10/9	10/10	10/11	10/12	10/15	10/16	10/17	10/18	10/22	10/22	10/23
Volume of Waste Water Treated (gallons)	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Raw Waste Water pH	11.7	11.6	11.6	11.6	11.5	11.7	11.6	11.5	11.5	11.4	11.5	11.5	11.4	11.5	11.6
pH Achieved by Acid Addition	6.6	1.0	5.9	7.0	6.5	6.5	6.3	6.8	5.9	6.4	6.5	6.4	5.8	1.5	5.1
Lime Addition (gms)	15	287	20	15	42.5	17	20	20	22.3	20	18	25	27	155	31
pH Achieved by Lime Addition	8.4	9.1	8.6	8.6	9.9	9.9	9.9	9.9	9.9	9.9	9.9	10.0	10.0	9.9	9.9
Mixing Time (mins)	45	30	45	12	15	15	30	15	15	15	15	15	15	30	15
Settling Time (mins)	150	90	915	30	15	15	20	20	15	20	15	15	20	15	15
Volume of Liquor Decanted and Treated After Sludge Removal (liters)	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
Ferrous Sulfide (2) Addition (mg/l)	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13
Mixing Time (mins)	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Settling Time (mins)	45	1200	75	100	90	105	75	75	90	120	60	72	150	780	132
Filtrate pH	7.5	7.4	7.9	8.1	9.1	8.3	8.0	9.2	8.4	7.9	7.8	8.6	6.5	5.7	NDA (1)
Filtration Time (mins)	20	30	20	12	20	15	15	15	30	15	15	15	15	15	15

(1) NDA = No Data Available

(2) The ferrous sulfide suspension added consisted of 0.9 gms of  $\text{Na}_2\text{S}$  and 3.0 gms of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in approximately 280 mls of deionized water.

TABLE 9-3. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR STUDY  
IN THE CHLOR-ALKALI SUBCATEGORY

TREATMENT: Alkaline Precipitation of Metals by pH Adjustment Followed by Sulfide Treatment  
Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	All reported values in mg/l														
<b>Lead, Pb</b>															
Raw Waste --															
Total Pb	790	590	300	630	660	530	280	460	284	409	530	600	460	24	13
Dissolved Pb	66	510	180	560	490	460	300	245	271	268	470	510	370	4	300
Supernatant -- (After Lime Addition)															
Total Pb	18	9.1	2.4	19	24	29	34	51.3	57.8	54.6	27	31	11	16	31
Dissolved Pb	9.6	2.7	2.8	9.1	7.0	4.5	3.0	5.24	3.92	7.53	6.2	6.7	2.1	8.0	160
Supernatant -- (After Sulfide Addition)															
Total Pb	18	0.33	4.7	11	6.5	11	34	10.5	10.7	5.83	11	9.4	3.3	0.94	6.2
Dissolved Pb	8.8	0.31	3.1	7.6	3.1	6.5	8.9	7.4	5.0	3.6	5.2	4.3	2.1	0.66	1.8
Filter Effluent --															
Total Pb	2.0	0.29	0.05	3.3	<0.05	0.05	<0.05	0.53	0.53	0.60	0.06	<0.05	<0.05	0.08	<0.05
Dissolved Pb	2.2	0.35	0.11	3.6	0.05	0.05	0.10	0.61	0.59	0.75	0.12	0.10	0.14	0.20	0.16
Sulfide Sludge --	710	340	53	200	1600	650	650	747	590	870	520	660	290	110	360
<b>Nickel, Ni</b>															
Raw Waste --															
Total Ni	0.26	0.16	0.06	0.06	0.11	0.10	<0.05	0.69	0.74	0.57	0.96	1.31	0.56	0.11	0.49
Dissolved Ni	0.15	0.07	<0.05	<0.05	<0.05	0.08	<0.05	0.62	0.71	0.58	0.83	1.50	0.51	0.09	0.56
Supernatant -- (After Lime Addition)															
Total Ni	0.10	0.16	<0.05	0.06	0.06	<0.05	<0.05	0.75	0.72	0.55	1.04	1.29	0.53	0.17	0.54
Dissolved Ni	0.11	0.11	<0.05	<0.05	<0.05	<0.05	<0.05	0.76	0.65	0.54	0.85	1.35	0.50	0.17	0.61
Supernatant -- (After Sulfide Treatment)															
Total Ni	0.10	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0.71	0.71	0.52	0.91	1.16	0.48	0.18	0.54
Dissolved Ni	0.09	0.10	<0.05	<0.05	<0.05	<0.05	<0.05	0.73	0.71	0.51	0.81	0.134	0.48	0.17	0.47
Filter Effluent --															
Total Ni	0.11	0.11	<0.05	<0.05	0.05	<0.05	<0.05	0.70	0.72	0.52	0.86	1.21	0.50	0.19	0.56
Dissolved Ni	0.15	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0.70	0.70	0.52	0.97	1.39	0.47	0.17	0.55
Sulfide Sludge --	0.66	0.39	0.20	0.11	0.40	0.39	0.56	1.01	0.84	0.82	1.00	1.52	0.94	0.38	0.74

TABLE 9-3 - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
All reported values in mg/l															
<u>Total Chromium, Cr (T)</u>															
Raw Waste --															
Total Cr (T)	0.17	0.09	0.06	0.07	0.08	0.05	0.06	0.29	0.10	0.07	0.06	0.08	0.09	0.02	0.05
Dissolved Cr (T)	0.11	0.11	0.05	0.08	0.09	0.05	0.04	0.10	0.08	0.06	0.07	0.07	0.06	0.02	0.04
Supernatant --															
(After Lime															
Addition)															
Total Cr (T)	0.11	0.13	0.05	0.07	0.10	0.08	0.04	0.08	0.05	0.07	0.05	0.08	0.07	0.04	0.04
Dissolved Cr (T)	0.12	0.16	0.07	0.11	0.08	0.06	0.07	0.08	0.07	0.07	0.06	0.06	0.07	0.05	0.05
Supernatant --															
(After Sulfide															
Treatment)															
Total Cr (T)	0.12	0.15	0.07	0.09	0.08	0.04	0.04	0.08	0.08	0.08	0.04	0.71	0.06	0.05	0.05
Dissolved Cr (T)	0.09	0.17	0.06	0.07	0.09	0.08	0.04	0.04	0.08	0.07	0.06	0.08	0.05	0.04	0.04
Filter Effluent --															
Total Cr (T)	0.11	0.14	0.06	0.08	0.07	0.07	0.04	0.13	0.10	0.06	0.06	0.08	0.09	0.04	0.04
Dissolved Cr (T)	0.14	0.14	0.06	0.08	0.09	0.04	0.05	0.11	0.09	0.07	0.06	0.08	0.05	0.03	0.05
Sulfide Sludge --	0.22	0.39	0.09	0.09	0.31	0.16	0.14	0.26	0.12	0.32	0.16	0.27	0.20	0.26	0.10
<u>Total Suspended Solids, TSS</u>															
Raw Waste	470	134	39	297	208	63	96	106	166	160	33	74	161	7	140
Supernatant	208	100	30	42	113	44	53	103	167	156	90	61	37	97	189
(After Lime															
Addition)															
Supernatant	220	70	73	1370	44	764	77	106	551	119	83	53	35	6	94
(After Sulfide															
Treatment)															
Filter Effluent	92.0	64.6	10.9	9.8	15.1	15.1	13.5	38.2	82.6	54.8	14.8	7.7	10.8	<1.0	25.7

Review of Table 9-3 also indicates that pH adjustment achieves a relatively high removal of the initial dissolved lead concentration. However, the lead hydroxide precipitate formed by the lime treatment process did not settle well in some cases. Treatability tests 6, 7, 8, 9, 10, 12, and 15 indicated relatively high concentrations of suspended lead hydroxide after lime treatment. In view of these high concentrations of lead hydroxide before sulfide treatment, it has been determined that the experimental dose of ferrous sulfide proved insufficient to meet the sulfide demand of suspended lead hydroxide for runs 8, 9, and 10 and of nickel hydroxide for those tests in which the total nickel concentration in the supernatant after lime addition is greater than 0.53 mg/l. Since lead is preferentially precipitated as lead sulfide, there was not an adequate concentration of free sulfide in most cases to appreciably remove the nickel. Therefore, better metal removal efficiencies can be obtained by either improving the metal hydroxide removal prior to sulfide treatment or by increasing the sulfide dosage to satisfy the suspended metal hydroxide demand. In addition to this observation, evidence appears in Table 9-3 to support the conclusion that insufficient contact time was provided in the sulfide reaction prior to discharge. Review of the dissolved lead concentrations before and after filtration indicates a consistent improvement in the lead removal. Since this improvement cannot be associated with a physical separation process, it may be concluded that reaction of dissolved lead with unreacted ferrous sulfide continued during the filtration step.

Dual media filtration was observed to achieve a high removal of the lead sulfide indicating the poor settling characteristics of the metal sulfides and the need for filtration to achieve a physical removal.

Review of the suspended solids results indicates that the 15 to 20 minute settling time after lime treatment failed to provide a good removal of TSS. Percent removal efficiencies after lime treatment and settling periods up to 15 hours were attempted without improvement in the clarified supernatant characteristics. Filtration substantially improved TSS concentrations but failed to provide low levels on a consistent basis.

### 9.3.2 Statistical Evaluation

Table 9-4 shows a comparison between the proposed BAT maximum 30-day average and the estimated treatability 30-day average. Figures 9-2 through 9-5 and Appendix A present the statistical analysis.



TABLE 9-4. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND ESTIMATED TREATABILITY PERFORMANCE FOR THE CHLOR-ALKALI SUBCATEGORY

STREAM: Filter Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum	Est. Treat. Performance 30-Day Average
	Maximum 30-Day Average	
Lead	0.22	0.085
Chromium	0.05	0.087
Nickel	0.10	0.66
Total Suspended Solids, TSS	12	51

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chlor-Alkali	Lead	
<hr/>		
Proposed Maximum 30-day Average	(mg/l) :	0.22
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l) :	0.085
Long Term Average	(mg/l) :	0.073
Standard Deviation of 30-day Averages	(mg/l) :	0.0075
Probability of Achieving Proposed Maximum 30-day Average	(%) :	> 99
Number of Observations:		10
<hr/>		

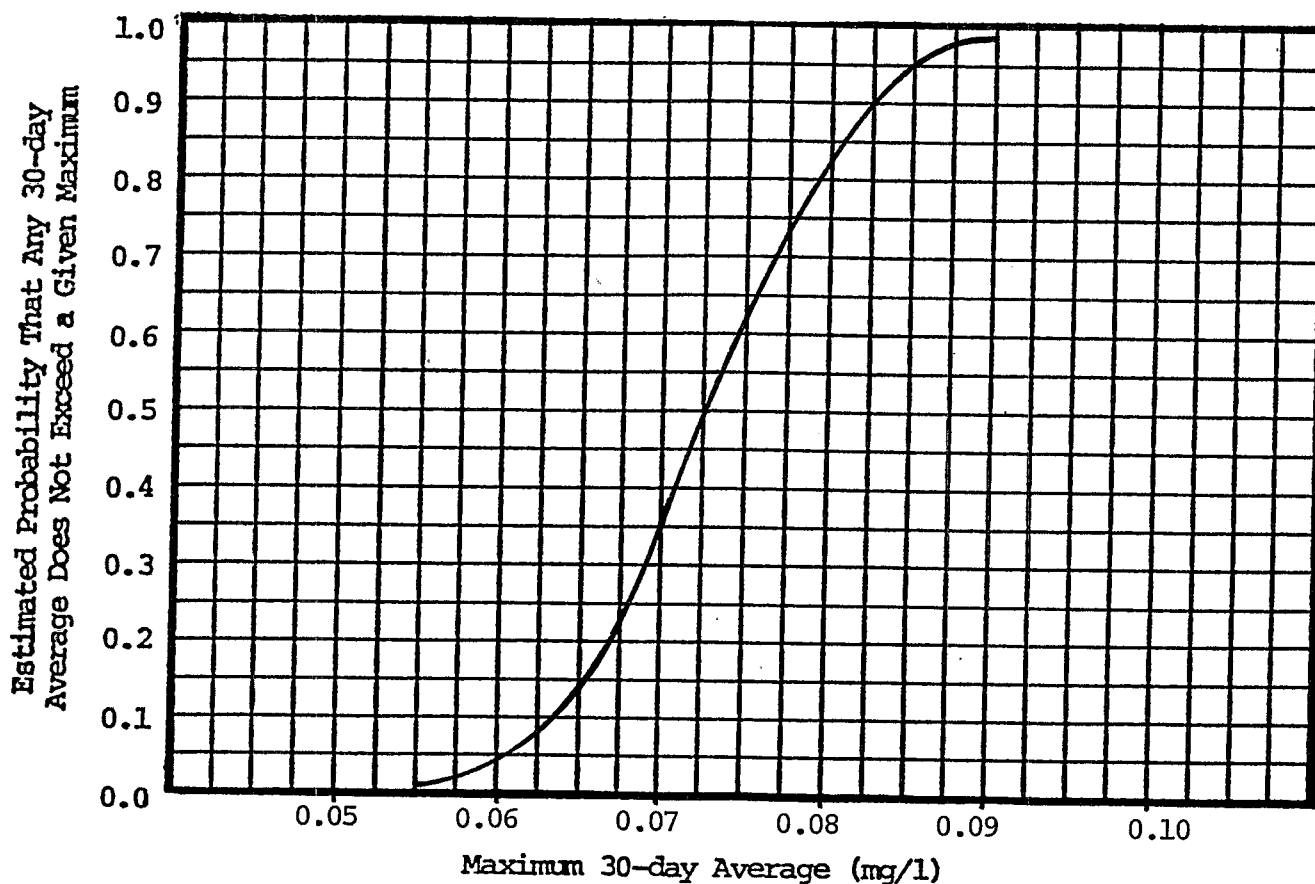


Figure 9-2. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chlor-Alkali	Chromium	
Proposed Maximum 30-day Average	(mg/l):	0.05
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.087
Long Term Average	(mg/l):	0.077
Standard Deviation of 30-day Averages	(mg/l):	0.0059
Probability of Achieving Proposed Maximum 30-day Average	(%):	<0.01
Number of Observations:		15

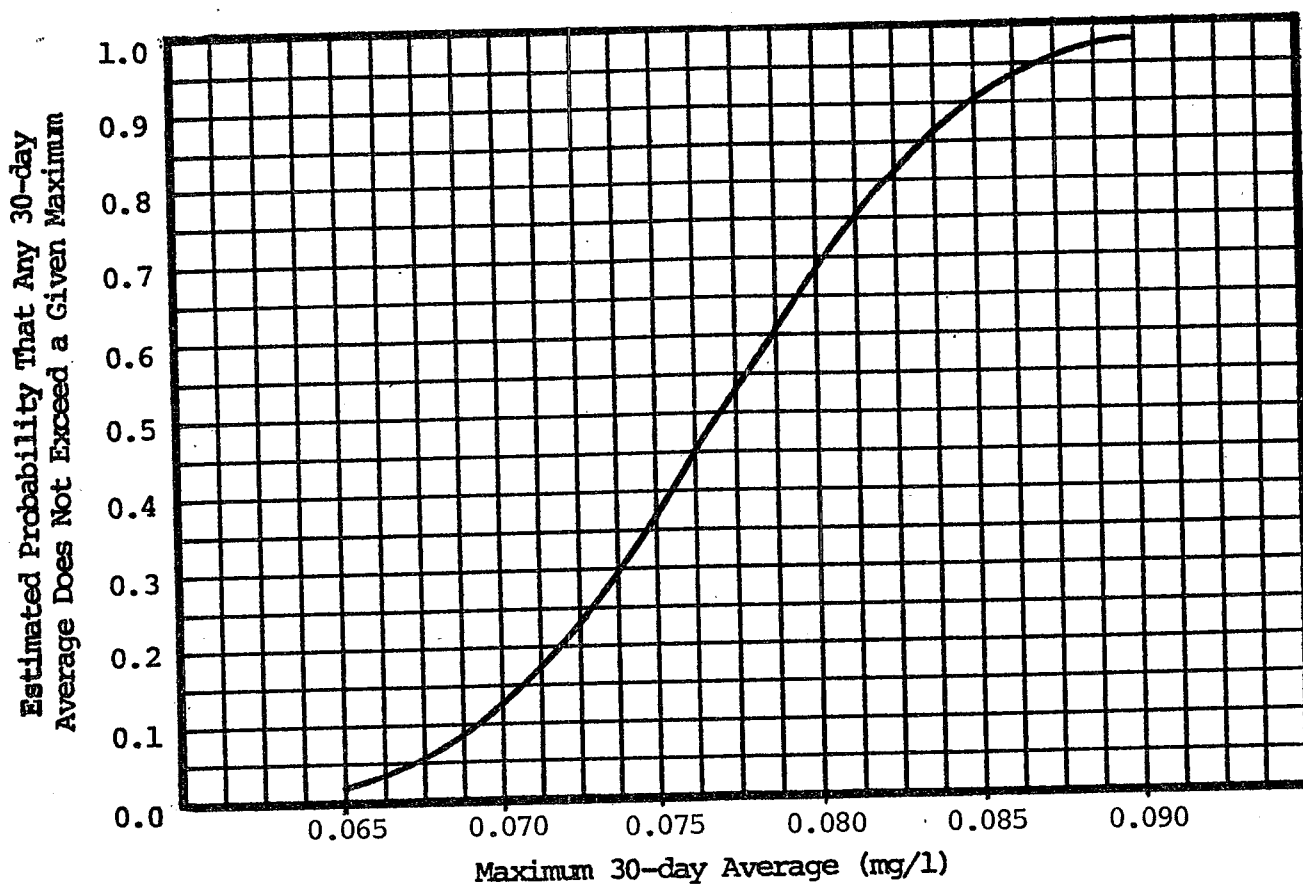


Figure 9-3. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chlor-Alkali	Nickel	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	0.10
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.66
Long Term Average	(mg/l):	0.43
Standard Deviation of 30-day Averages	(mg/l):	0.14
Probability of Achieving Proposed Maximum 30-day Average	(%):	0.99
Number of Observations:		15
<hr/>		

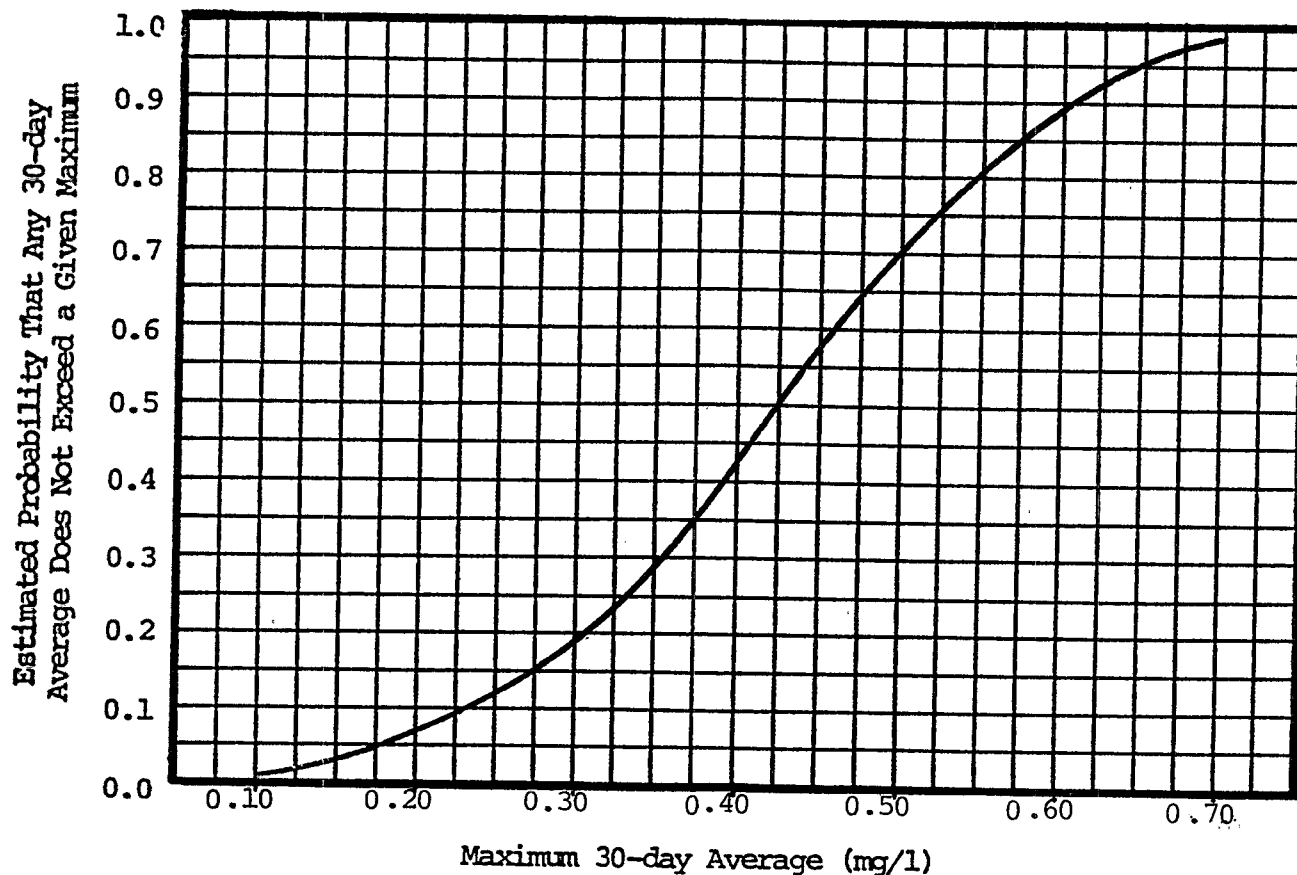


Figure 9-4. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chlor-Alkali	Total Suspended Solids	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	12
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	51
Long Term Average	(mg/l):	35
Standard Deviation of 30-day Averages	(mg/l):	9.9
Probability of Achieving Proposed Maximum 30-day Average	(%):	1.1
Number of Observations:		15
<hr/>		

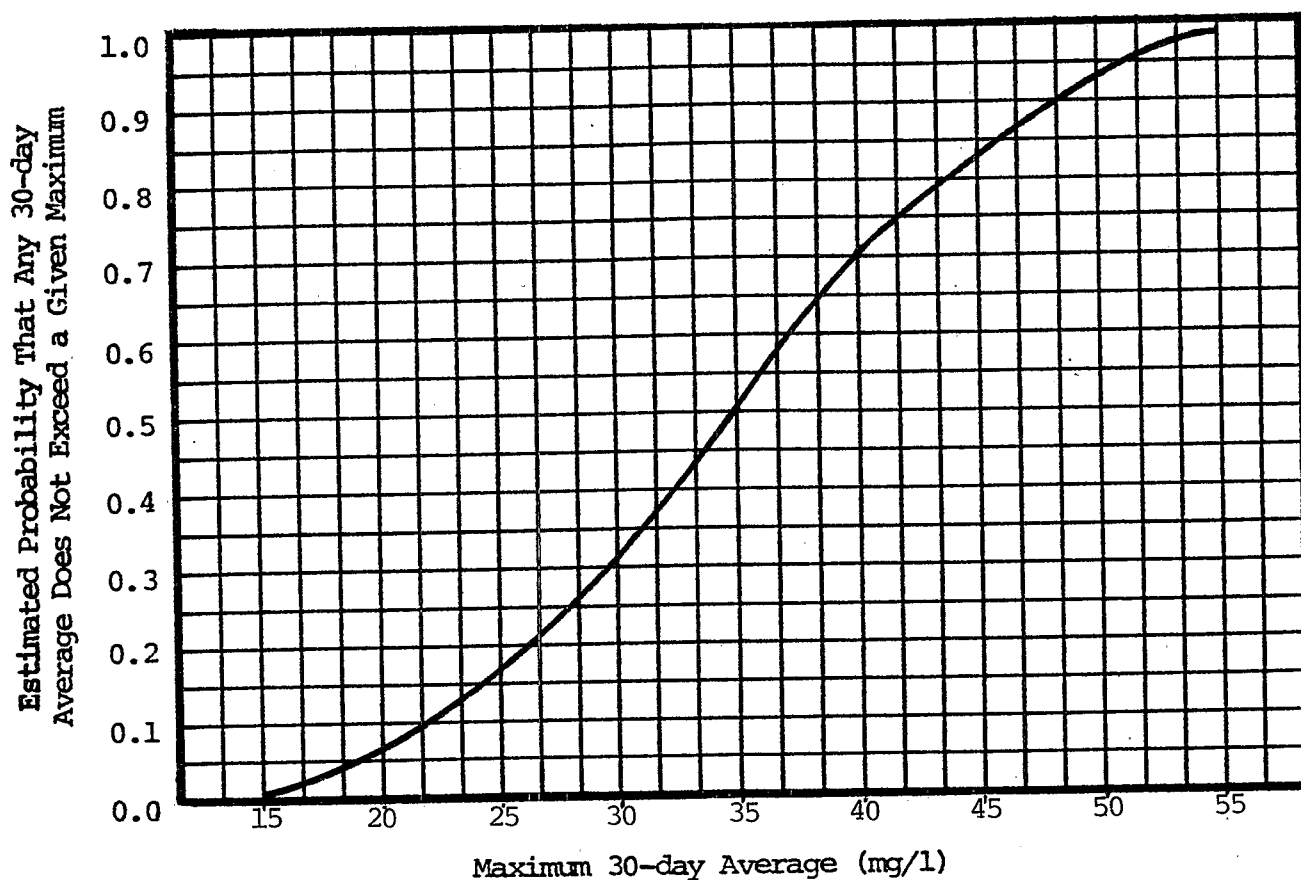


Figure 9-5. Estimated Performance of Proposed BAT Treatment

Table 9-4 and Figure 9-2 show the results that are obtained after screening of the analytical data for lead data outliers. Test numbers 8, 9, and 10 have been rejected on a technical basis and runs 1 and 4 on statistical grounds.

### 9.3.3 Conclusions

The treatability study conducted for the diaphragm cell segment of the Chlor-Alkali Subcategory did not provide an adequate basis for evaluating the performance of the proposed BAT treatment. The extremely poor settling characteristics of the metal hydroxide sludge formed during lime treatment precluded any meaningful testing of the subsequent treatment steps involving sulfide precipitation and filtration. The hydroxide settling problem was not identified in time to attempt corrective measures that would bring the results more in line with the known practical capabilities of the treatment technology. The use of coagulating agents in conjunction with adequate mixing and longer settling periods may provide considerably improved separation. The technique of recycling a portion of the sludge to "seed" each batch may also prove to be helpful. Although lime was selected as the source of alkalinity, largely because of its low cost, a serious disadvantage in its use may have been incurred in this case due to the presence of sulfate that was introduced when the pH of the raw waste was lowered with sulfuric acid. A mixed precipitate of negatively charged particles of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and metal hydroxides may well have interfered with the coagulation/settling process. Substituting soda ash or caustic soda for lime would circumvent this potential source of interference with the sludge settling process.

Thus, the experimental results presented for this subcategory represent the outcome of the particular set of experiments that were conducted during the relatively short time frame available. They do not represent the actual performance capabilities of the proposed BAT treatment. This work should be taken as a starting point for the design of a more comprehensive series of tests on this technology.

## SECTION 10.0

### TITANIUM DIOXIDE SUBCATEGORY (CHLORIDE PROCESS)

#### 10.1 INTRODUCTION

##### 10.1.1 General Considerations

The treatability tests were performed on-site at the selected plant from October 16 to October 27, 1979. A total of 16 test runs were completed in this period.

Due to time limitations, waste water was always collected in large enough composite samples to run two tests at the same time. All samples generated by both treatability units were split with the plant personnel in addition to the sample collected for initial waste characterization.

##### 10.1.2 Sampling Point Locations

The manufacture of titanium dioxide from rutile ore by the chloride process produces several waste streams. At the selected facility, the four main waste water streams go to sumps where they commingle and are pumped to the treatment facility. These waste sources and flows are tabulated below:

TREATABILITY WASTE SAMPLE COMPOSITION			
Waste Source	Flow (gal/min)	Percent of Total Flow	Estimated Treatability Sample Composition By Sources (Percent)
1) Chemical sump, oxidation step and area runoff	200	18	20
2) Filter sump, filtration and acid wash plus spills	375	33	35

3) Boiler and cooling tower sump	275	24	25
4) First reactor, chlorination step and scrubber blowdown	280	25	20
<hr/>			
TOTAL	1130	100	100
<hr/>			

The "first reactor" is, in effect, a sump where the chlorination water mixes with the chlorine recovery scrubber (caustic) blowdown. This reactor is located next to the liming mixer or reactor which is the reactor where the aqueous wastes are collected for treatment.

Since there is no one place to sample the combined waste, a composite sample was put together from the four principal waste water sumps as shown in Figure 10-1. The amount of water from each source composited for the test sample on the first day was in nearly exact proportion to the flows from the different sources, as shown in the table above. However, difficulties arose in keeping solids uniformly suspended (especially the very dense solids from the first reactor) while transferring less than a full sample container. Consequently, volumes of waste water were thereafter apportioned so that full containers were used for each of the treatability units. This resulted in the proportions shown in the last column of the above table. As noted, the mixture was a good approximation of the composite raw waste from all sources.

## 10.2 TREATABILITY TEST MODEL OPERATION

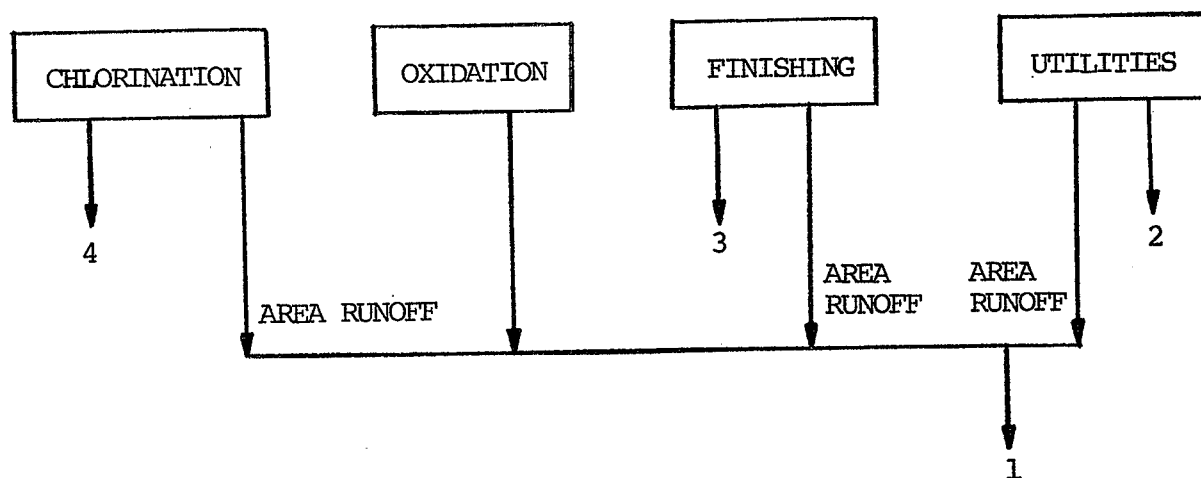
### 10.2.1 Treatment Technology Tested

The BAT treatment used for the titanium dioxide waste water consisted of alkaline precipitation of the metallic ions present in the waste, followed by settling and removal of sludge. A dual media filter was then used to polish the clarified waste.

### 10.2.2 Waste Water Characterization

Results of the waste water characterization are shown in Table 10-1. An initial series of laboratory tests were carried out to determine the effect of increasing pH on the solubility of the metals present in the raw waste. The results of these tests





1. CHEMICAL SUMP
2. BOILER AND COOLING TOWER BLOWDOWN
3. FILTRATES
4. FIRST REACTOR

Figure 10-1. Sources of waste samples for the titanium dioxide subcategory (chloride-process)

TABLE 10-1. WASTE WATER CHARACTERIZATION FOR THE PLANT  
SELECTED FOR STUDY IN THE TITANIUM DIOXIDE  
SUBCATEGORY (CHLORIDE PROCESS)

Constituent	Concentration (mg/l)
pH*	4.0-6.5
Calcium (as CaCO <sub>3</sub> ):	4,250
Chromium (Hexavalent):	0.025
Chromium:	50.0
Copper:	0.11
Iron:	136
Potassium:	11.6
Magnesium (as CaCO <sub>3</sub> ):	34.8
Sodium:	292
Nickel:	1.29
Zinc:	0.69
Total Suspended Solids:	381
Total Residual:	10,930
Fixed Residue:	7,620
Total Dissolved Solids:	7,134
Methyl Orange Acidity (as CaCO <sub>3</sub> ):	600
Total Hardness (as CaCO <sub>3</sub> ):	4,300
Chloride:	390
Nitrate:	0.41

\*As indicated in Table 10-3, sixteen samples of the raw waste water showed pH values ranging between 4.0 and 6.5.

are presented in Table 10-2. Note that the metallic species in the waste show the lowest overall solubility at pH values of 9.8 and above, and so 9.8 was chosen for the treatability test.

### 10.2.3 Details on Treatability Test Operation

The precipitant used in all the tests was agricultural grade hydrated lime. This material was always fed to the reaction tank as a powder.

After the initial addition of lime, the pH of the waste water dropped to 8.5 and 9.5 for runs 1 and 2 respectively. In order to bring the pH back up to more favorable levels for metal removal, additional amounts of lime were added. These amounts were 1.25 and 2.55 grams, respectively. The final pH values obtained were 9.05 and 10 as indicated in Table 10-3. Recirculation of the filtrate back to the reaction tank was practiced for 15 minutes for all of the runs. Values reported for the filtration time do not include this 15 minute recirculation period.

Table 10-3 is a tabulation of operation parameters and observations for the sixteen treatability test runs performed for the Titanium Dioxide Subcategory.

## 10.3 TEST RESULTS

### 10.3.1 Discussion of Results

The pollutants studied in this subcategory included iron, chromium (T), zinc, nickel and total suspended solids (TSS). The analytical results for these parameters are presented in Table 10-4.

A review of the analytical results presented in this table indicates that it is possible to meet the proposed limitations for the pollutants under consideration by application of the BAT level of treatment proposed for the Titanium Dioxide Subcategory.

As noted in Table 10-4, the concentrations of zinc in the filtrate stream increased as the supernatant passed through the filter. Contamination of the samples seems to be the most likely explanation because the increase in concentration occurred for both the dissolved and undissolved portions of that metal. In other words, the increase in the dissolved zinc did not occur at the expense of the total zinc. Sample contamination from the filter media may have been favored at the low pH values reported for the final effluent as indicated in Table 10-3.

TABLE 10-2. EFFECT OF pH ON TOXIC METAL SULUBILITY  
(All values in mg/l except pH)

pH	Chromium	Copper	Iron	Nickel	Zinc	Hexavalent Chromium
7.0	0.02	0.04	0.08	0.85	0.028	<0.004
7.5	0.01	0.04	0.09	0.65	0.011	<0.004
8.0	0.03	0.04	0.08	0.47	0.021	0.004
8.5	0.02	0.09	0.07	0.25	0.011	0.004
9.0	0.03	0.03	0.07	0.19	0.038	0.004
9.5	0.02	0.04	0.09	0.13	0.030	0.004
9.8	0.02	0.03	0.08	0.14	0.021	<0.004
10.0	0.02	0.04	0.07	0.12	0.014	0.008
11.0	0.05	0.03	0.07	0.12	0.014	0.004
12.0	0.03	0.03	0.07	0.10	0.011	<0.004

TABLE 10-3. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Titanium Dioxide (Chloride Process)		TREATMENT: Lime Plus Dual Media Filtration														
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Date	10/16	10/16	10/18	10/18	10/22	10/22	10/23	10/23	10/24	10/24	10/25	10/25	10/26	10/26	10/27	10/27
Volume of Waste Water Treated (gallons)	28	28	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5
Raw Waste Water pH	6.5	6.1	4.0	4.1	6.4	6.5	5.7	5.7	4.5	4.2	5.7	5.7	5.7	5.9	4.4	4.4
Amount of Lime Used (gms)	33.7	37.4	61.6	65.1	79.5	69.4	81.3	85.9	85.9	94.6	85.1	88.9	75.1	72.7	87.9	96.0
pH Achieved by Lime Addition	9.0	10.0	9.8	9.8	10.0	9.8	9.8	9.8	9.8	9.8	9.8	9.9	9.6	9.9	9.8	9.8
Mixing Time (mins)	50	25	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Settling Time (mins)	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
Supernatant -- (pH After Reaction)	8.5	8.5	9.1	9.1	9.0	9.1	9.1	9.0	8.9	8.9	8.9	9.1	9.1	9.2	8.6	8.7
Filtrate pH	3.7	3.5	5.7	5.8	NDA (1)	NDA	5.5	5.7	5.3	4.7	4.5	NDA	NDA	4.6	4.7	4.8
Filtration Time (mins)	90	90	90	90	90	90	60	60	35	35	60	50	75	75	30	30

(1) NDA = No Data Available

TABLE 10-4. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR STUDY  
IN THE TITANIUM DIOXIDE (CHLORIDE PROCESS) SUBCATEGORY  
TREATMENT: Lime Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
All reported values in mg/l																
<u>Chromium</u>																
Raw Waste																
Total Cr (T)	32.0	28.0	74.0	86.0	63.0	49.0	61.0	51.0	37.0	44.0	65.0	59.0	51.0	51.0	47.0	54.0
Dissolved Cr (T)	0.53	0.351	3.9	3.5	0.092	0.083	0.26	0.057	0.90	1.9	0.37	0.066	0.038	0.056	0.88	1.1
Supernatant																
Total Cr (T)	0.077	0.084	5.9	4.7	0.145	0.23	0.36	0.27	0.17	0.17	0.19	0.25	0.12	0.14	0.015	0.14
Dissolved Cr (T)	0.052	0.040	5.5	4.5	0.032	0.031	0.037	0.028	0.047	0.041	0.039	0.039	0.052	0.045	0.050	0.025
Filter Effluent																
Total Cr (T)	0.030	0.027	4.9	4.1	0.037	0.051	0.042	0.042	0.042	0.033	0.051	0.047	0.032	0.12	0.060	0.040
Dissolved Cr (T)	0.032	0.032	4.9	4.2	0.064	0.060	0.042	0.042	0.033	0.035	0.046	0.028	0.037	0.045	0.045	0.044
<u>Zinc</u>																
Raw Waste																
Total Zn	0.289	0.297	0.985	1.08	0.402	0.360	0.668	0.582	0.538	0.439	0.868	0.830	0.771	0.794	0.857	0.851
Dissolved Zn	0.028	0.02	0.931	0.994	0.009	0.010	0.009	0.005	0.384	0.332	0.264	0.255	0.260	0.246	0.892	1.32
Supernatant																
Total Zn	0.010	0.007	0.017	0.019	0.011	0.006	0.013	0.009	0.022	0.012	0.013	0.015	0.020	0.027	0.024	0.135
Dissolved Zn	0.008	0.011	0.020	0.012	0.016	0.006	0.004	0.012	0.010	0.016	0.017	0.011	0.018	0.028	0.040	0.024
Filter Effluent																
Total Zn	0.021	0.033	0.019	0.024	0.030	0.036	0.027	0.030	0.031	0.026	0.055	0.059	0.080	0.077	0.059	0.056
Dissolved Zn	0.062	0.035	0.031	0.032	0.043	0.060	0.021	0.030	0.031	0.024	0.041	0.043	0.054	0.063	0.084	0.171
<u>Nickel</u>																
Raw Waste																
Total Ni	0.60	0.63	1.57	1.52	0.99	0.93	1.45	1.35	0.81	0.80	1.53	1.50	1.04	1.06	1.20	1.15
Dissolved Ni	0.38	0.39	1.50	1.46	0.60	0.59	0.08	0.09	0.68	0.75	1.29	1.34	0.88	0.93	1.18	1.18
Supernatant																
Total Ni	0.05	0.06	0.11	0.09	0.07	0.09	0.09	0.07	0.09	0.07	0.05	0.04	0.08	0.08	0.08	0.08
Dissolved Ni	0.07	0.07	0.09	0.09	0.06	0.07	0.09	0.12	0.07	0.06	0.05	0.09	0.06	0.06	0.07	0.06
Filter Effluent																
Total Ni	0.06	0.07	0.08	0.10	0.09	0.10	0.08	0.09	0.08	0.09	0.10	0.13	0.10	0.09	0.08	0.07
Dissolved Ni	0.04	0.06	0.09	0.09	0.07	0.08	0.08	0.09	<0.05	0.07	0.06	0.08	0.07	0.09	0.08	0.10

TABLE 10-4 - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
All reported values in mg/l																
<u>Iron</u>																
Raw Waste																
Total Fe	93.0	109	166	171	204	178	0.16	179	129	131	225	232	195	200	177	177
Dissolved Fe	11.5	14.6	0.27	0.22	109	98	0.84	0.12	116	123	175	175	123	126	156	160
Supernatant																
Total Fe	0.20	0.21	0.51	0.67	0.33	0.56	0.89	0.56	0.87	0.47	0.66	0.80	0.21	0.32	0.390	0.277
Dissolved Fe	0.12	0.06	0.11	0.12	0.15	0.10	0.07	0.08	0.30	0.09	0.21	0.09	0.05	0.05	0.059	0.053
Filter Effluent																
Total Fe	0.11	0.03	0.11	0.12	0.15	0.08	0.11	0.15	0.11	0.12	0.20	0.20	0.12	0.69	0.350	0.185
Dissolved Fe	0.08	0.05	0.10	0.10	0.10	0.12	0.12	0.10	0.11	0.24	0.12	0.11	0.08	0.38	0.119	0.086
<u>Total Suspended Solids, TSS</u>																
Raw Waste	3380	3020	1370	1110	413	2600	6150	16200	2940	3370	6010	5200	3370	2980	2130	1270
Supernatant	10.3	11.4	12.3	12.6	18.4	21.2	40.8	22.3	26.8	25.2	149	19.6	11.9	21.4	14	12.9
Filter Effluent	3.8	2.0	8.5	6.5	7.2	5.8	6.9	5.6	7.4	6.8	20	18.8	13.6	19.5	14	11.5

Excellent removal of total chromium was observed for most of the tests. Since Cr+6 does not precipitate by pH adjustment, the removal observed can be explained only if the chromium was present in a reduced form, that is, as Cr+3.

The analytical results for total chromium show poor removal for runs 3 and 4 as indicated in Table 10-4. The high values reported may be the result of operational problems in the titanium dioxide plant which led to the production of an atypical waste. The chlorine recovery refrigeration compressor broke down and the excess chlorine was pumped into the waste system. Also, oil from the broken compressor was drained off into the chemical waste sump during sampling. It will be noted that the concentrations of chromium was exceptionally high in the raw waste on that day. Furthermore, at pH levels at which trivalent chromium would be quite insoluble, the analyses of supernatant and filtrate show both total and dissolved chromium at similar high concentrations. It is concluded that the chromium was in the hexavalent form. The treatment applied was not designed to remove chromate, and the capability of the method to yield low-chromium concentrations should not be judged on the basis of the abnormal waste water containing chromate. The chromate probably came from the cooling tower, since as far as is known, it does not arise in the processes of titanium dioxide production. Therefore, chromium results for test runs 3 and 4 were rejected from the statistical analysis.

Even though the dual media filter was effective in reducing TSS from the clarified waste, its benefits are only marginal as can be noted in Table 10-4.

#### 10.3.2 Statistical Evaluation

Table 10-5 and Figures 10-2 through 10-6 show the results obtained from a statistical analysis of the treatment data. It should be pointed out that Figure 10-3 presents the probability performance for total chromium after screening the data and rejecting runs 3 and 4 for the reasons stated above.

#### 10.3.3 Conclusions

The treatability test results provide a good basis for assessing the general applicability of the proposed BAT regulations for the chloride process segment of the Titanium Dioxide Subcategory. Results show that the pollutant concentration basis for the proposed BAT maximum 30-day average effluent limitations are achievable with the prescribed treatment technology under the conditions of these tests.



TABLE 10-5. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR THE TITANIUM  
DIOXIDE (CHLORIDE PROCESS) SUBCATEGORY

STREAM: Filter Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Iron	2.5	0.21
Chromium	0.14	0.051
Nickel	0.20	0.093
Zinc	0.50	0.047
Total Suspended Solids, TSS	64	12.0

SUBCATEGORY	POLLUTANT	PRECIPITANT
Titanium Dioxide	Iron	
Proposed Maximum 30-day Average	(mg/l):	2.5
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.21
Long Term Average	(mg/l):	0.17
Standard Deviation of 30-day Averages	(mg/l):	0.023
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		16

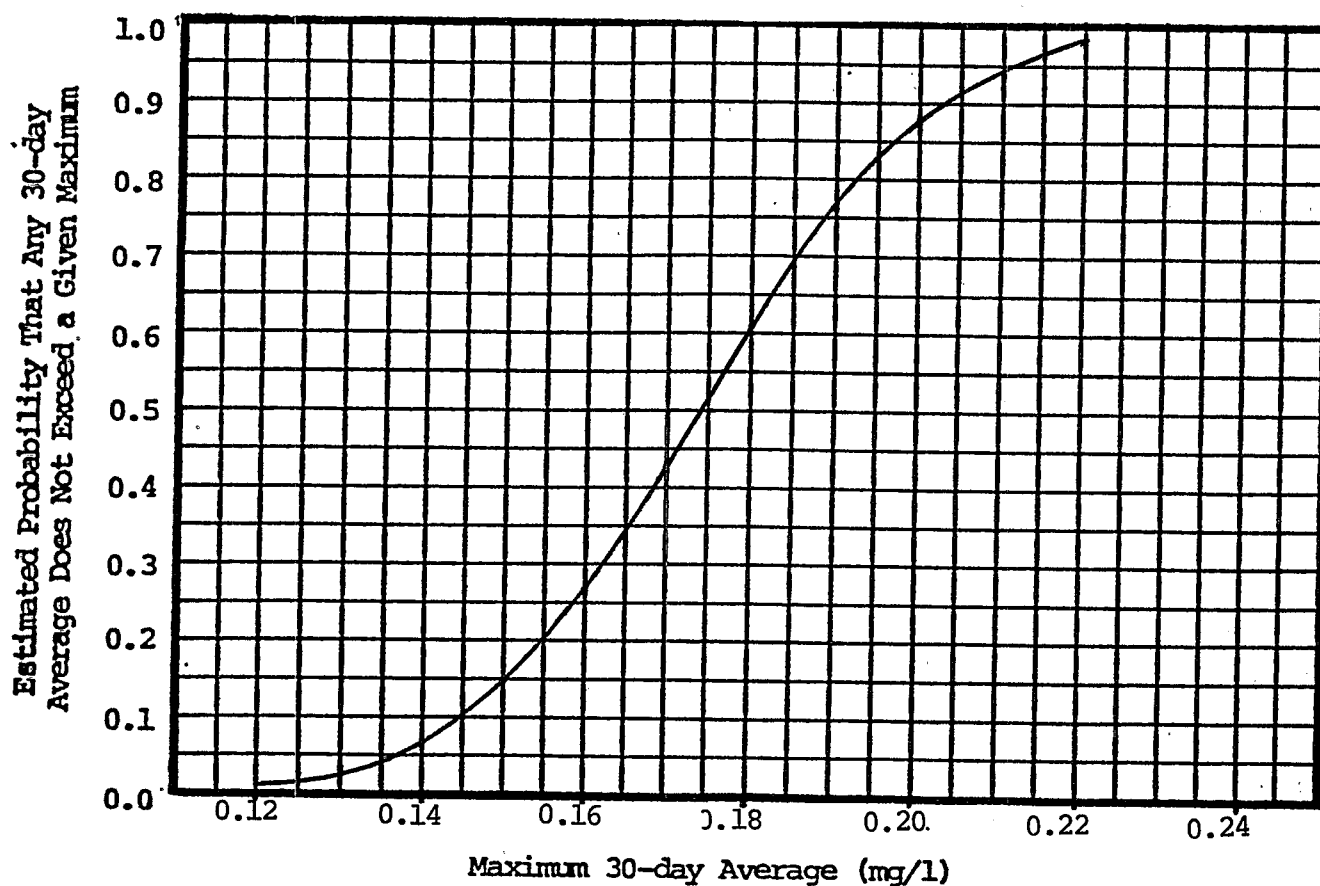


Figure 10-2. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Titanium Dioxide	Chromium	
Proposed Maximum 30-day Average	(mg/l):	0.14
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.051
Long Term Average	(mg/l):	0.046
Standard Deviation of 30-day Averages	(mg/l):	0.0030
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		14

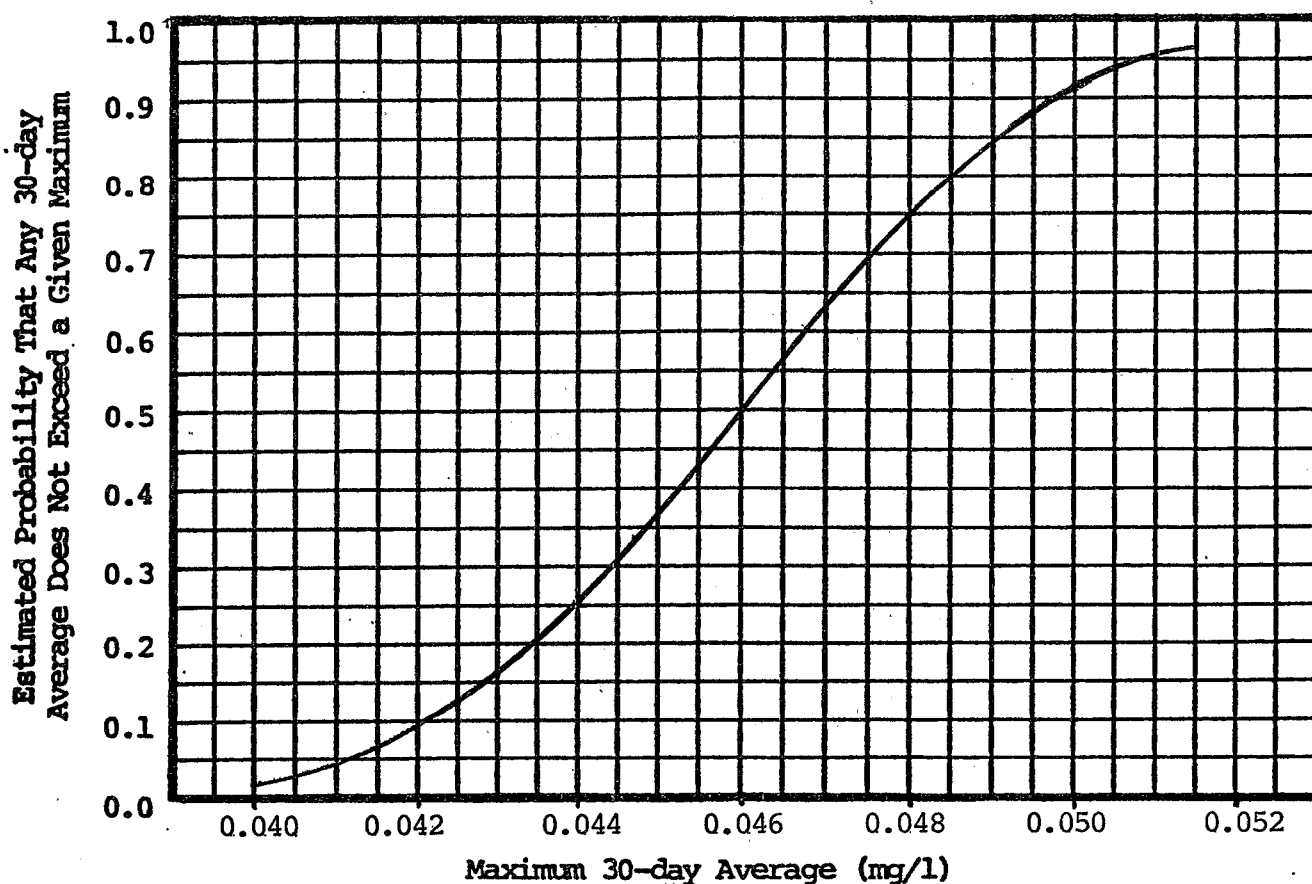


Figure 10-3. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Titanium Dioxide	Nickel	
Proposed Maximum 30-day Average	(mg/l) :	0.20
95th Percentile ( $Z = 1.64$ )	(mg/l) :	0.093
Long Term Average	(mg/l) :	0.088
Standard Deviation of 30-day Averages	(mg/l) :	0.0028
Probability of Achieving Proposed Maximum 30-day Average	(%) :	>99
Number of Observations:		16

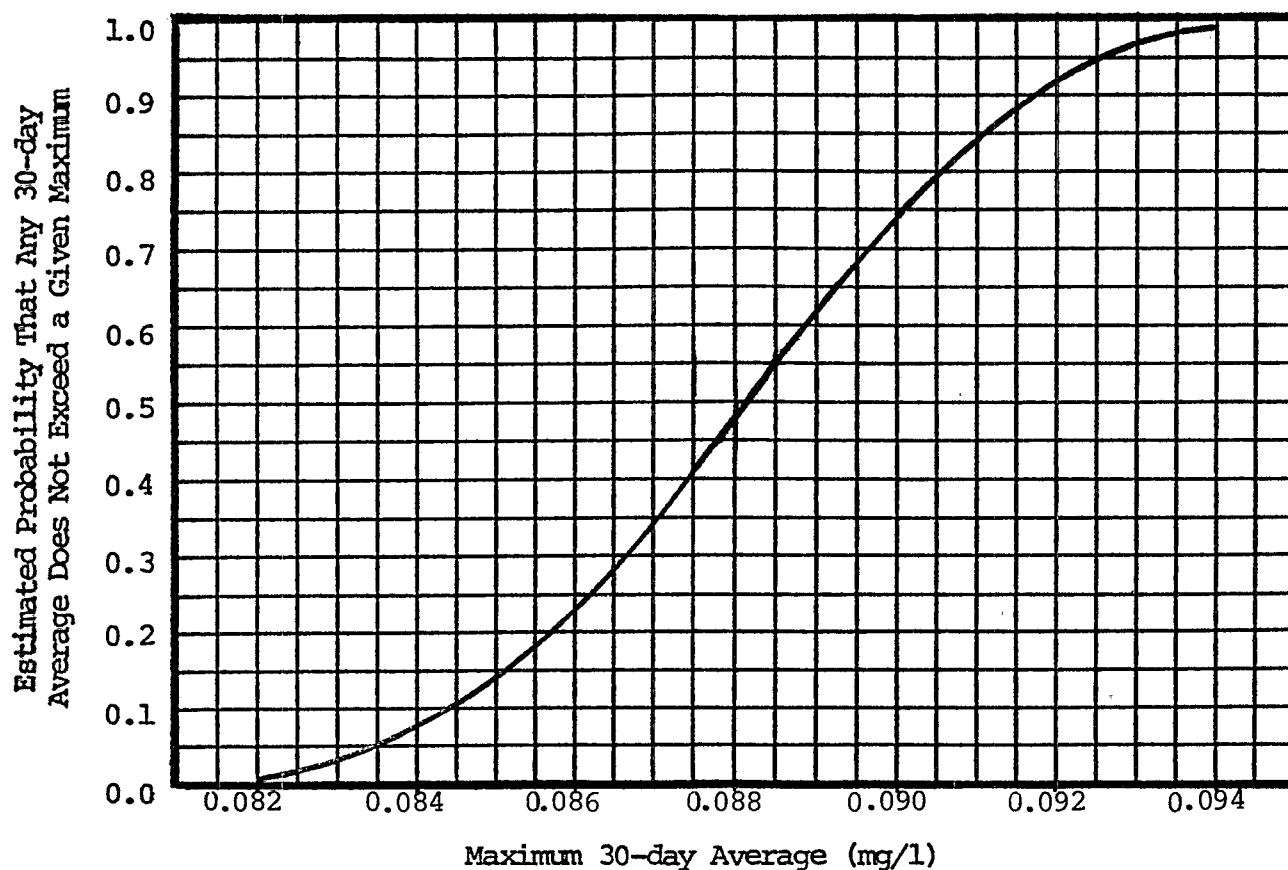


Figure 10-4. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Titanium Dioxide	Zinc	
Proposed Maximum 30-day Average	(mg/l) :	0.50
95th Percentile ( $Z = 1.64$ )	(mg/l) :	0.047
Long Term Average	(mg/l) :	0.041
Standard Deviation of 30-day Averages	(mg/l) :	0.0035
Probability of Achieving Proposed Maximum 30-day Average	(%) :	≥99
Number of Observations:		16

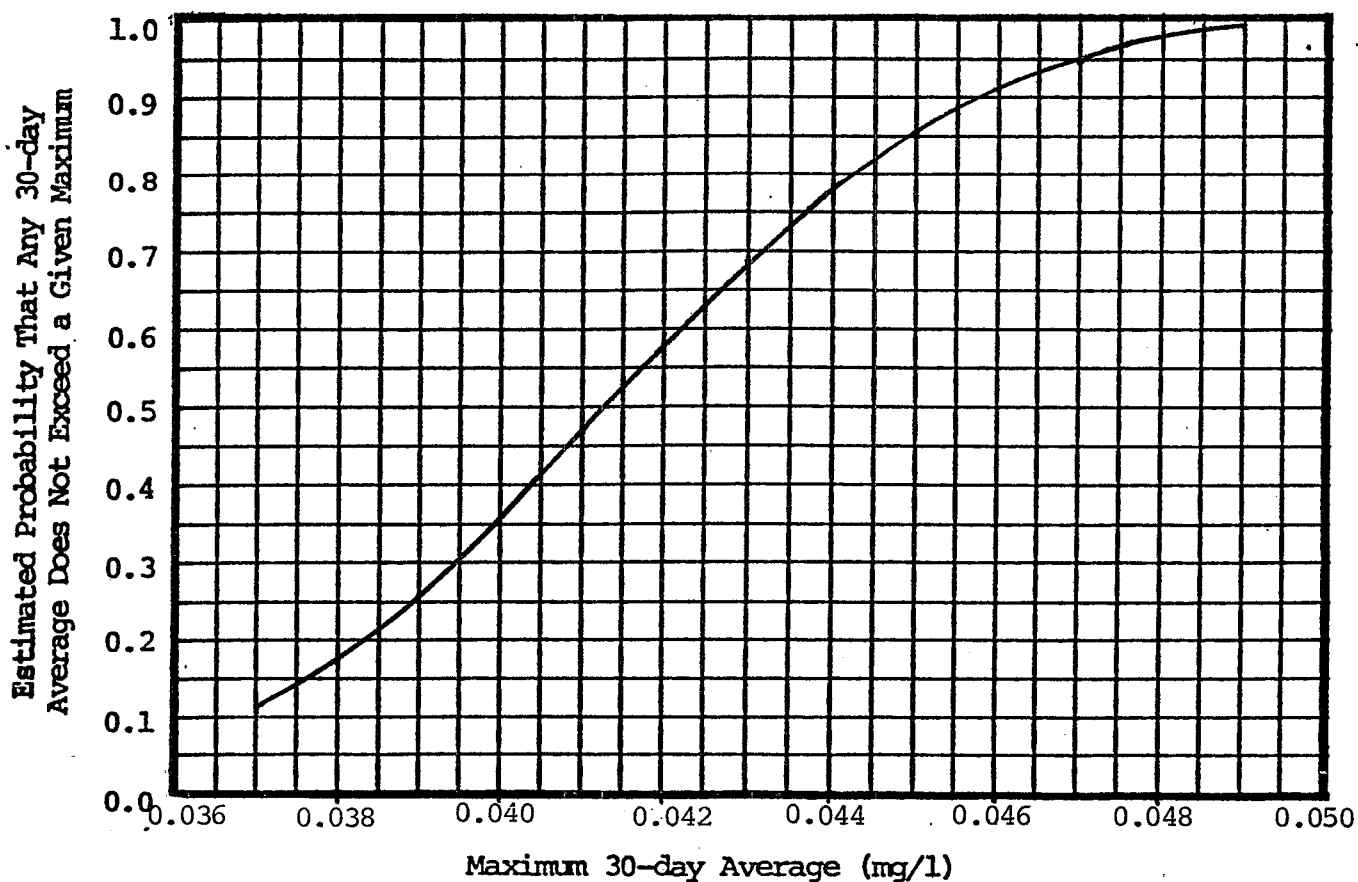


Figure 10-5. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Titanium Dioxide	Total Suspended Solids	
Proposed Maximum 30-day Average	(mg/l) :	64
95th Percentile ( $Z = 1.64$ )	(mg/l) :	12
Long Term Average	(mg/l) :	10
Standard Deviation of 30-day Averages	(mg/l) :	1.2
Probability of Achieving Proposed Maximum 30-day Average	(%) :	>99
Number of Observations:		16

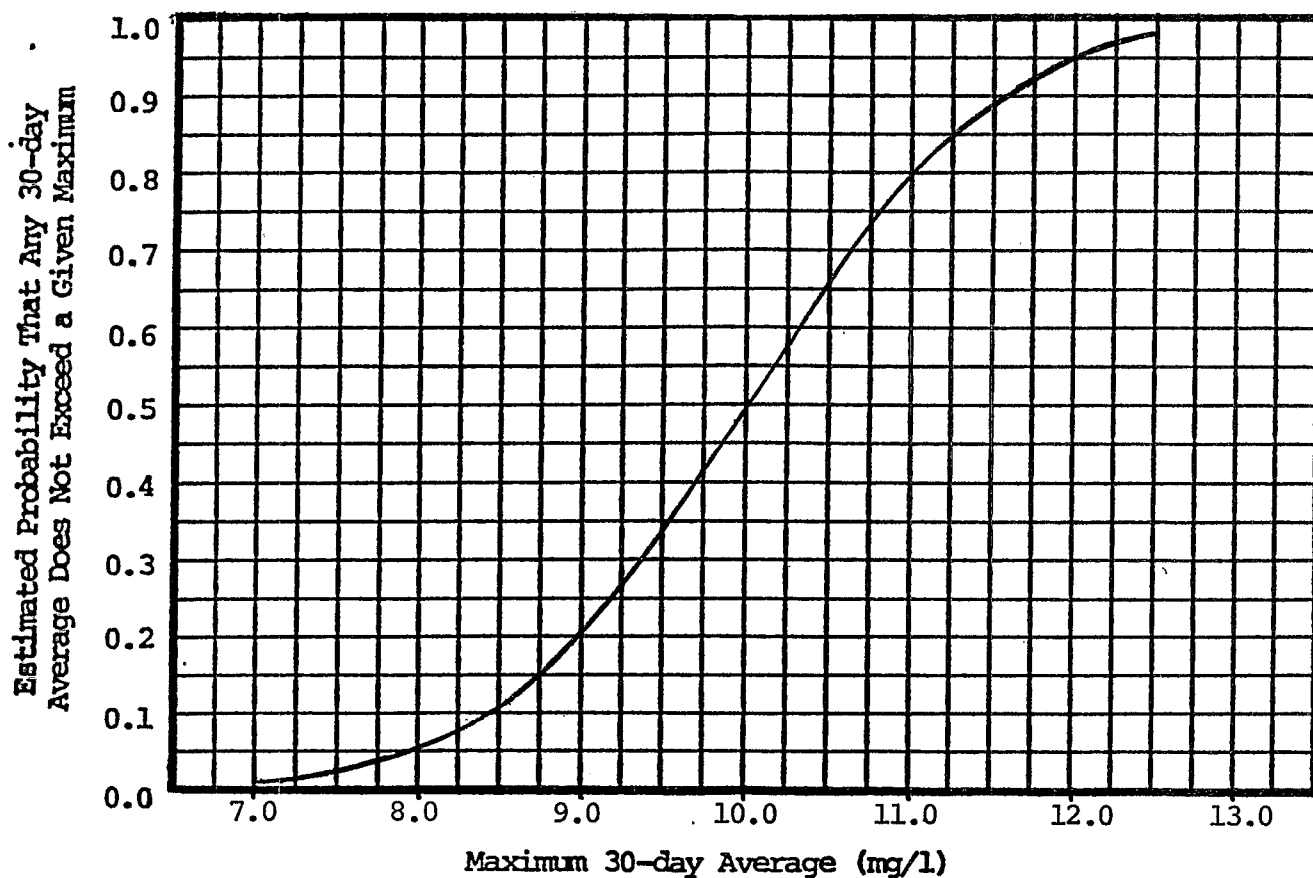
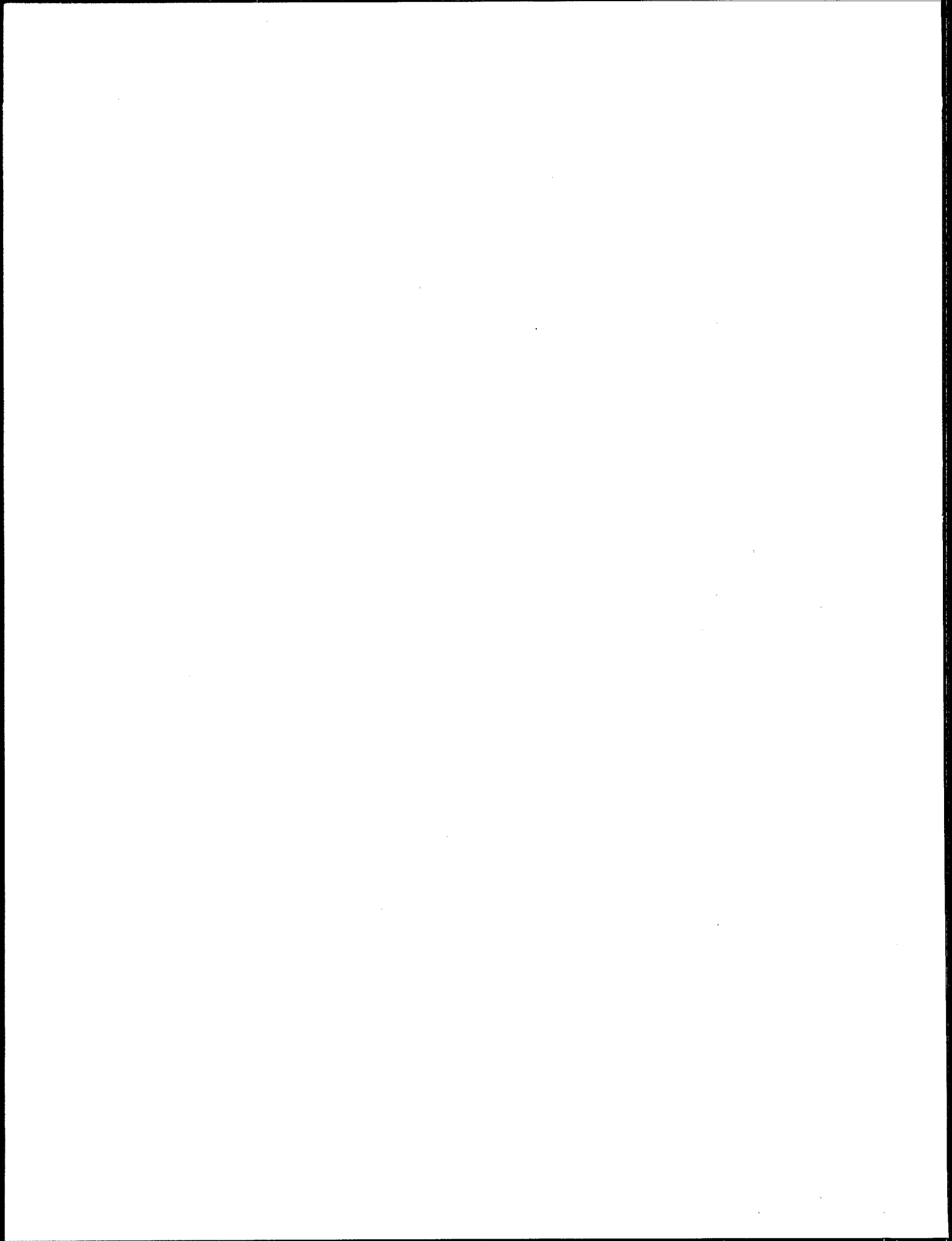


Figure 10-6. Estimated Performance of Proposed  
BAT Treatment

The results further indicate that depending on specific plant raw waste characteristics, compliance with the proposed BAT regulations may be achievable without the filtration process. However, elimination of the filtration process would require that the alkaline precipitation of metals is carefully controlled at the optimum pH and that sufficient settling time is given. In addition, the proper operating conditions would have to be established on a plant by plant basis giving careful consideration to variability in raw waste characteristics.





## SECTION 11.0

### CHROME PIGMENTS SUBCATEGORY

#### 11.1 INTRODUCTION

##### 11.1.1 General Considerations

The treatability tests were carried out on-site at Plant #894. A total of fourteen runs were completed from September 5 to September 24, 1979. Waste water samples were collected daily and used for each run. Both raw and treated waste samples were split with the plant personnel.

##### 11.1.2 Sample Point Location

The selected plant is currently practicing BPT treatment as shown in Figure 11-1. Waste samples used in the treatability study for the proposed BAT level treatment were collected at the point of clarified effluent discharge. The sample point location is indicated in Figure 11-1 for the selected plant.

#### 11.2 TREATABILITY TEST MODEL OPERATION

##### 11.2.1 Treatment Technology Tested

The treatment technology evaluated in the treatability tests on chrome pigments consisted of additional metal precipitation as metal sulfides. After settling and removal of the sulfide sludge, the clarified waste was polished by means of a dual media filter.

##### 11.2.2 Waste Water Characterization

Results of the initial raw waste characterization are shown in Table 11-1. Following the waste characterization, treatability experiments were performed by adding 1.0 to 3.0

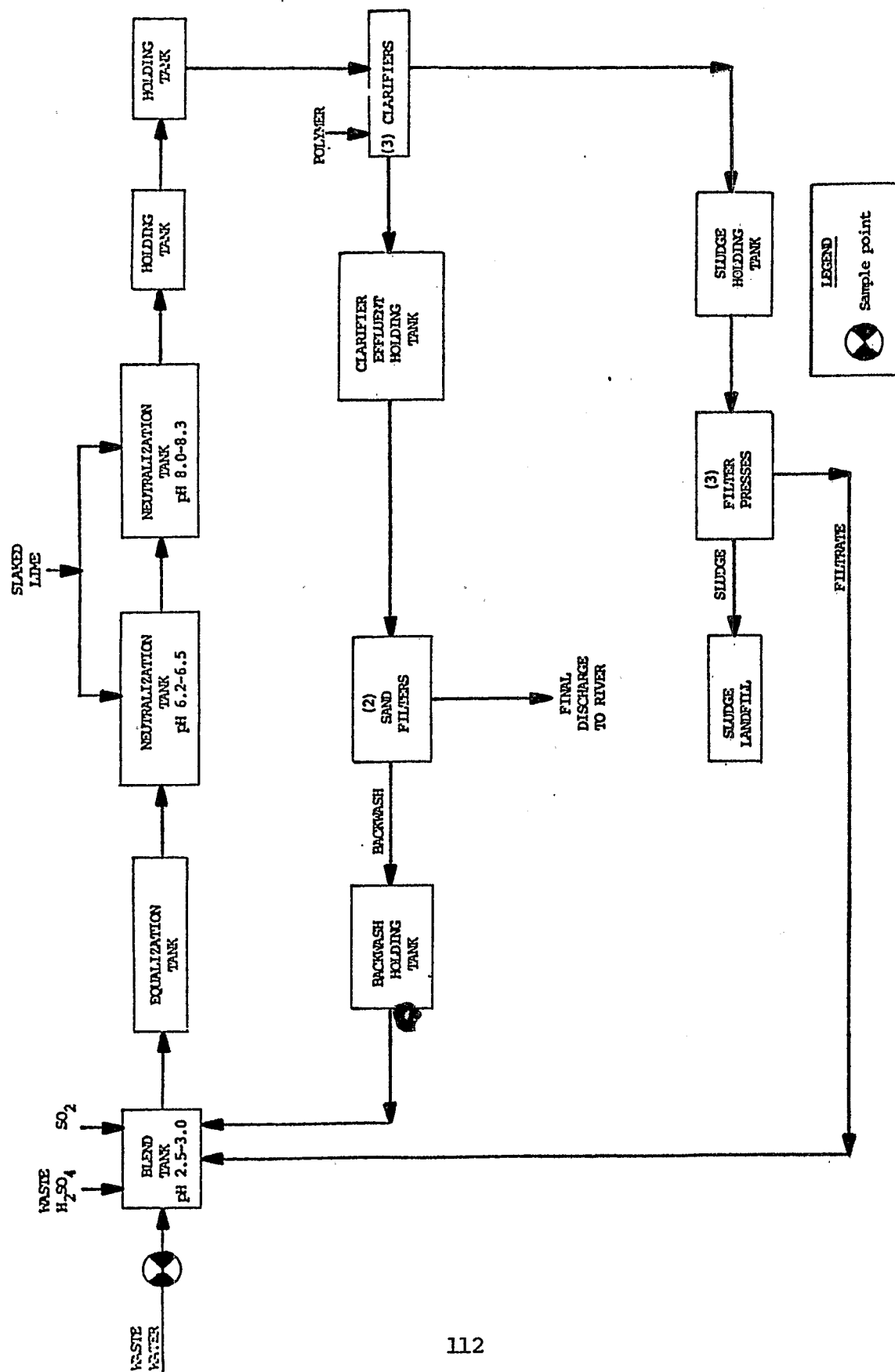


Figure 11-1. General waste water treatment process flow diagram at plant #894 showing the sampling point. (Chrome pigment manufacture.)

TABLE 11-1. CHARACTERIZATION OF RAW WASTE WATER FROM THE  
CHROME PIGMENT SUBCATEGORY

	Specific Waste Constituent (mg/l)				
	Cadmium	Chromium	Iron	Lead	Zinc
Total	0.04	0.23	0.32	0.27	0.006
Dissolved	0.04	0.10	0.18	0.27	0.006

TABLE 11-2. EFFECTS OF ADDITION OF FERROUS SULFIDE TO THE  
CHROME PIGMENTS WASTE WATER

Amount Sulfide Added (Percent Stoichio- metric Requirement)*	Remaining Metal Concentration in Solution (mg/l)			
	Cadmium	Chromium	Lead	Zinc
0	0.04	0.10	0.27	0.006
50	0.05	0.07	0.20	0.110
75	0.04	0.07	0.20	0.040
100	0.04	0.08	0.20	0.030
125	0.04	0.08	0.20	0.030
150	0.04	0.08	0.20	0.020
200	0.04	0.08	0.20	0.050
400	0.04	0.07	0.20	0.020

\* Fourteen treatability tests performed later showed that the pH of the raw waste varied from 7.93 to 8.60.

times the stoichiometric amounts of ferrous sulfide required for precipitation of the metals present in the waste. This was necessary to determine the ferrous sulfide dosage for optimum removal of the metals that would have to be used during the test runs. However, all of the added material was found to dissolve and no precipitate formation could be observed. Chemical analyses of the resulting treated waste water solutions showed negligible reductions in the cadmium, chromium, and lead levels as seen in Table 11-2. To overcome this problem, the procedure was then modified so that the amount of ferrous sulfide added in each treatability test was twice that required to form a saturated solution (2) of this material. This resulted in a solid phase still being present after initial dissolution of some of the added ferrous sulfide. This condition was assumed to be optimum for metal removal and was utilized throughout the experiments.

### 11.2.3 Details on Treatability Test Operation

As shown in Figure 11-1, the waste water used in the tests was not collected from any of the raw waste streams being generated by the plant. Instead, the waste utilized came from the clarified effluent. It was reasoned that the plant selected for study was already practicing BPT and that there was no point in repeating observations on this level of treatment.

A constant amount of ferrous sulfide reagent (260 ml) was added to the waste during each of the test runs. The reagent contained 2,800 mg/l of ferrous sulfide.

Total recirculation of the filtrate back to the reaction/settling tank was practiced for all the runs with the exception of run 14. Recycle time varied from 45 to 90 minutes. This provided seasoning of the filter bed prior to collection of the waste sample for analysis and ensured efficient removal of TSS from the supernatant.

Table 11-3 is a tabulation of the operational parameters and observations made during the fourteen treatability test runs. Review of the table reveals a relatively consistent operation of the treatability test apparatus providing a very uniform effluent quality.

- (2) Solubility for FeS from the Handbook of Chemistry and Physics, 51st Edition, Robert C. Weast, Ed. The Chemical Rubber Company, 1970-1971, pg. B99

TABLE 11-3. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Chrome Pigments

TREATMENT: Sulfide Plus Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Date	9/5	9/6	9/7	9/10	9/11	9/12	9/13	9/14	9/17	9/18	9/19	9/20	9/21	9/24
Volume of Waste Water Treated (gallons)	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Raw Waste Water pH	8.1	8.0	7.9	8.2	8.0	8.2	8.2	8.1	8.1	8.1	8.4	8.6	8.3	8.1
Ferrous Sulfide* Addition (mg/l)	13	13	13	13	13	13	13	13	13	13	13	13	13	13
Mixing Time (mins)	15	20	15	15	15	15	15	15	15	15	15	15	15	15
Settling Time (mins)	45	60	90	195	72	45	45	60	45	45	60	60	45	60
Filtrate pH	7.2	7.1	NDA <sup>(1)</sup>	5.4	8.0	NDA	6.1	7.3	NDA	NDA	NDA	NDA	NDA	NDA
Filtration Time (mins)	60	60	75	90	90	90	90	75	60	45	60	60	45	20

(1) NDA = No Data Available

### 11.3 TEST RESULTS

#### 11.3.1 Discussion of Results

Analytical results for the treatability test runs are tabulated in Table 11-4 for the major pollutant parameters. This table summarizes results for cadmium, chromium, lead, zinc, and TSS. Review of Table 11-4 indicates very low initial concentrations of the pollutants in the waste water samples. The results indicate the importance of dual media filtration to achieve further reduction of metal concentrations when initial concentrations are too low for effective settling. Observation of the experiments showed that formation of a sulfide sludge blanket did not occur. This may be correlated with observations of poor metal removal efficiencies in the clarification step.

The initial metal concentrations were consistent throughout the period of the treatability investigations. Toxic metal levels in the treated effluent also appear at consistent levels.

#### 11.3.2 Statistical Evaluation

A comparison between the proposed BAT limitations, which were developed on the basis of a 95 percent likelihood compliance by any industry, and the estimated treatability performance is presented in Table 11-5. The statistical analysis for each of the pollutants is presented in Figures 11-2 through 11-6 and Appendix A.

#### 11.3.3 Conclusions

The treatability tests conducted to evaluate the proposed BAT treatment for the Chrome Pigments Subcategory are inconclusive as to the practical viability of sulfide precipitation for the removal of additional toxic metals following the BPT alkaline precipitation step. Due to a highly efficient BPT system at the plant studied, the initial toxic metal concentrations (BPT clarified effluent) were already near the lower limit of removal obtainable with sulfide precipitation. The results indicate that the major application of sulfide precipitation and/or dual media filtration would be in specific plant situations where less efficient BPT systems require additional treatment to meet the BAT regulations.

TABLE 11-4. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR STUDY  
IN THE CHROME PIGMENTS SUBCATEGORY

TREATMENT: Sulfide Precipitation of Metals  
Followed by Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
All reported values in mg/l														
<u>Total Chromium, Cr(T)</u>														
Raw Waste --														
Total Cr (T)	0.327	0.366	0.366	0.40	1.28	0.46	0.53	0.55	0.15	0.27	0.30	0.25	0.48	0.36
Dissolved Cr (T)	0.121	0.182	0.287	0.30	1.07	0.32	0.33	0.24	0.04	0.14	0.21	0.06	0.11	0.12
Supernatant														
Total Cr (T)	0.157	0.386	0.287	0.38	1.26	0.51	0.50	0.44	0.15	0.28	0.30	0.18	0.36	0.37
Dissolved Cr (T)	0.089	0.085	0.011	0.20	0.47	0.20	0.13	0.19	0.05	0.10	0.10	0.13	0.15	0.11
Filter Effluent														
Total Cr (T)	0.014	0.030	0.020	0.01	0.18	0.05	0.03	0.04	0.02	0.04	0.02	0.03	0.04	0.02
Dissolved Cr (T)	0.016	0.012	0.021	0.09	0.22	0.05	0.05	0.04	0.02	0.03	0.04	0.02	0.03	0.02
<u>Lead, Pb</u>														
Raw Waste														
Total Pb	0.190	0.229	0.241	0.190	0.34	0.17	0.18	0.18	0.25	0.24	0.45	0.29	0.58	0.15
Dissolved Pb	0.124	0.126	0.190	0.09	0.30	0.17	0.15	0.18	0.05	0.14	0.31	0.13	0.23	0.03
Supernatant														
Total Pb	0.198	0.237	0.249	0.110	0.30	0.19	0.30	0.22	0.26	0.30	0.50	0.29	0.47	0.17
Dissolved Pb	0.118	0.134	0.086	0.05	0.24	0.16	0.12	0.24	0.05	0.12	0.24	0.20	0.26	0.04
Filter Effluent														
Total Pb	0.086	0.110	0.078	0.05	0.24	0.10	0.16	0.05	0.03	0.07	0.16	0.10	0.17	0.03
Dissolved Pb	0.070	0.078	0.110	0.07	0.19	0.10	0.10	0.09	0.03	0.06	0.15	0.09	0.17	0.03
<u>Cadmium, Cd</u>														
Raw Waste														
Total Cd	0.049	0.104	0.109	0.04	0.16	0.06	0.05	0.05	0.02	0.06	0.07	0.05	0.05	0.01
Dissolved Cd	0.039	0.106	0.104	0.03	0.15	0.05	0.04	0.04	0.02	0.06	0.06	0.04	0.04	0.01
Supernatant														
Total Cd	0.039	0.099	0.104	0.03	0.15	0.06	0.05	0.05	0.02	0.05	0.07	0.04	0.04	0.01
Dissolved Cd	0.034	0.064	0.021	0.03	0.12	0.04	0.04	0.04	0.01	0.04	0.06	0.04	0.04	0.01
Filter Effluent														
Total Cd	0.016	0.049	0.046	0.02	0.10	0.03	0.03	0.03	0.01	0.03	NDA	0.04	0.03	0.01
Dissolved Cd	0.021	0.044	0.046	0.02	0.09	0.03	0.03	0.04	0.01	0.03	0.05	0.03	0.04	0.01

TABLE 11-4 - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
All reported values in mg/l														
<u>Zinc, Zn</u>														
Raw Waste														
Total Zn	0.035	0.023	0.029	0.03	0.02	0.02	0.07	0.05	0.023	0.018	0.017	0.015	0.030	0.006
Dissolved Zn	0.023	0.023	0.019	0.01	0.02	0.02	0.05	0.03	0.014	0.015	0.014	0.014	0.016	<0.005
Supernatant														
Total Zn	0.061	0.035	0.059	0.01	0.05	0.02	0.04	0.03	0.552	0.067	0.086	0.047	0.067	0.012
Dissolved Zn	0.037	0.035	0.076	0.02	0.02	0.02	0.03	0.03	0.011	0.053	0.069	0.042	0.063	0.008
Filter Effluent														
Total Zn	0.029	0.030	0.053	0.03	0.03	0.03	0.05	0.05	0.017	0.058	0.072	0.054	0.074	0.047
Dissolved Zn	0.033	0.049	0.057	0.03	0.03	0.03	0.07	0.05	0.012	0.069	0.069	0.060	0.079	0.045
Total Suspended Solids, TSS														
Raw Waste	56.4	10.5	42.0	45.0	14.7	2.0	4.8	4.7	5.9	11.0	14.6	30.7	10.0	12.8
Supernatant	10.6	36.7	70.0	74.0	43.0	59.0	63.3	11.9	48.4	9.1	10.3	4.8	17.2	18.4
Filter Effluent	3.4	4.3	9.6	4.3	5.2	9.1	5.5	4.7	2.9	1.7	1.0	3.8	5.0	1.6



TABLE 11-5. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE  
FOR THE CHROME PIGMENTS SUBCATEGORY

STREAM: Filter Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Chromium	1.1	0.044
Lead	1.4	0.13
Zinc	1.1	0.050
Cadmium	0.19	0.041
Total Suspended Solids, TSS	37	5.5

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chrome Pigments	Chromium	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	1.1
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	.044
Long Term Average	(mg/l):	.036
Standard Deviation of 30-day Averages	(mg/l):	.0050
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		14
<hr/>		

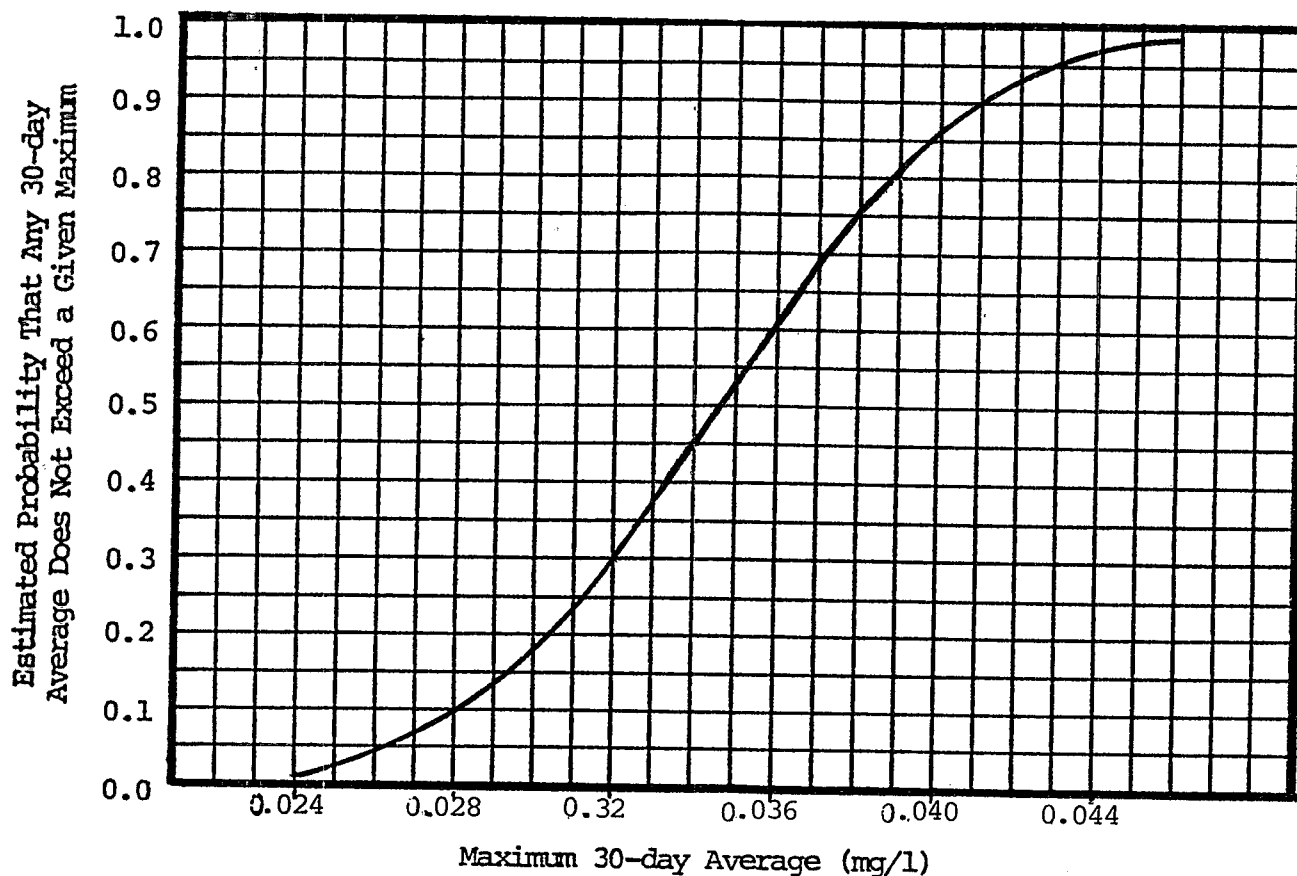


Figure 11-2. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chrome Pigments	Lead	
Proposed Maximum 30-day Average	(mg/l):	1.4
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.13
Long Term Average	(mg/l):	0.10
Standard Deviation of 30-day Averages	(mg/l):	0.013
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		14

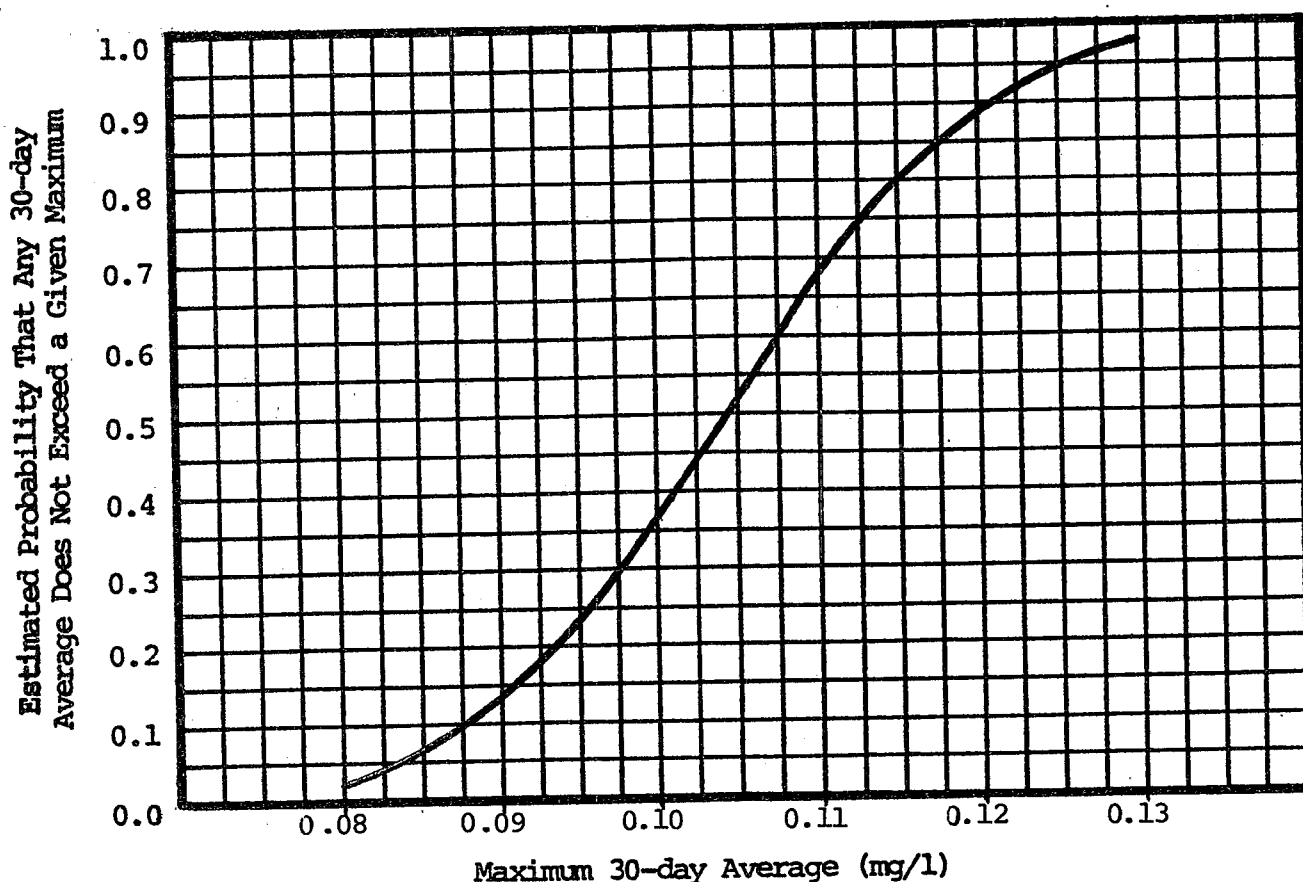


Figure 11-3. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chrome Pigments	Zinc	
Proposed Maximum 30-day Average	(mg/l):	1.1
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.050
Long Term Average	(mg/l):	0.045
Standard Deviation of 30-day Averages	(mg/l):	0.003
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		14

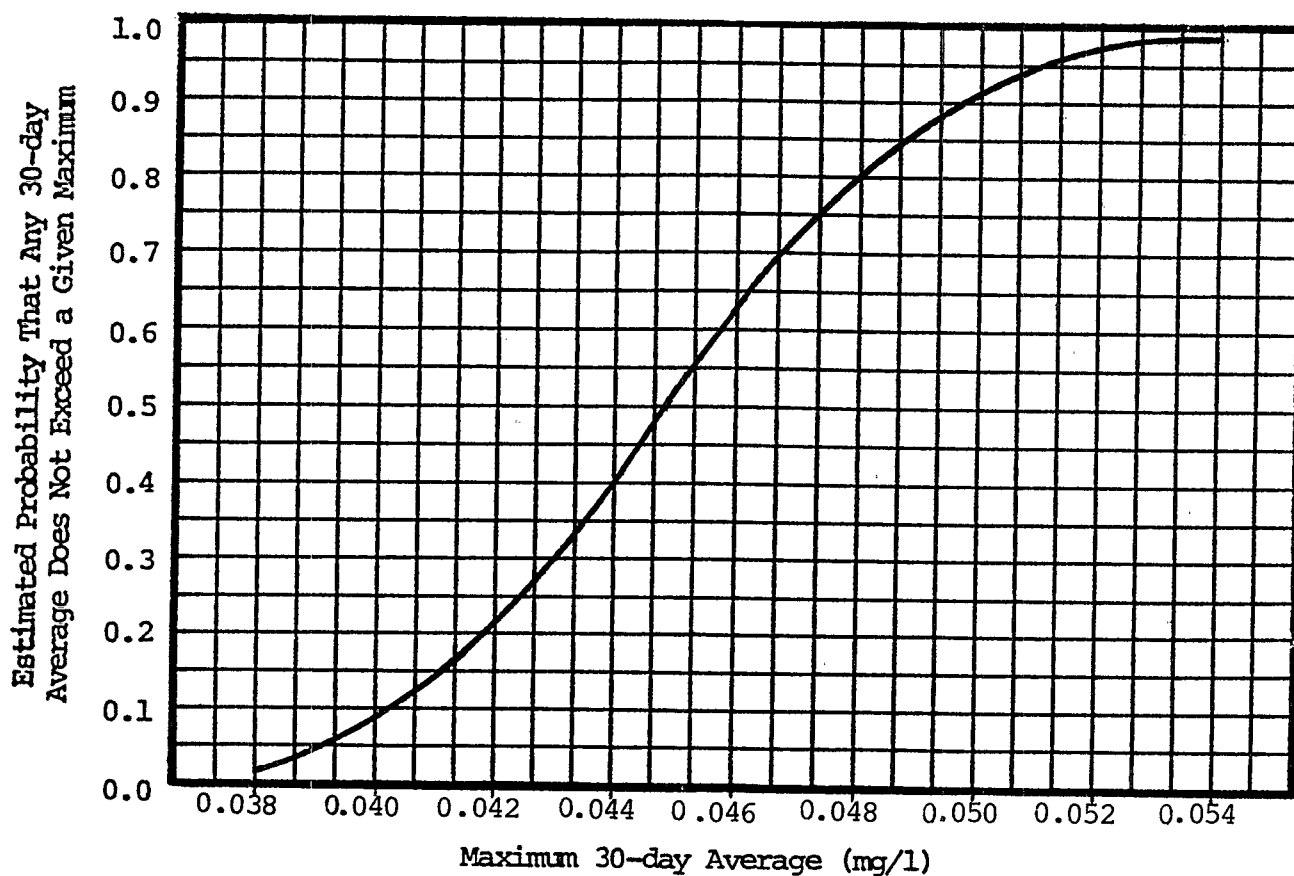


Figure 11-4. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chrome Pigments	Cadmium	
Proposed Maximum 30-day Average	(mg/l):	0.19
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.041
Long Term Average	(mg/l):	0.034
Standard Deviation of 30-day Averages	(mg/l):	0.0040
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		13

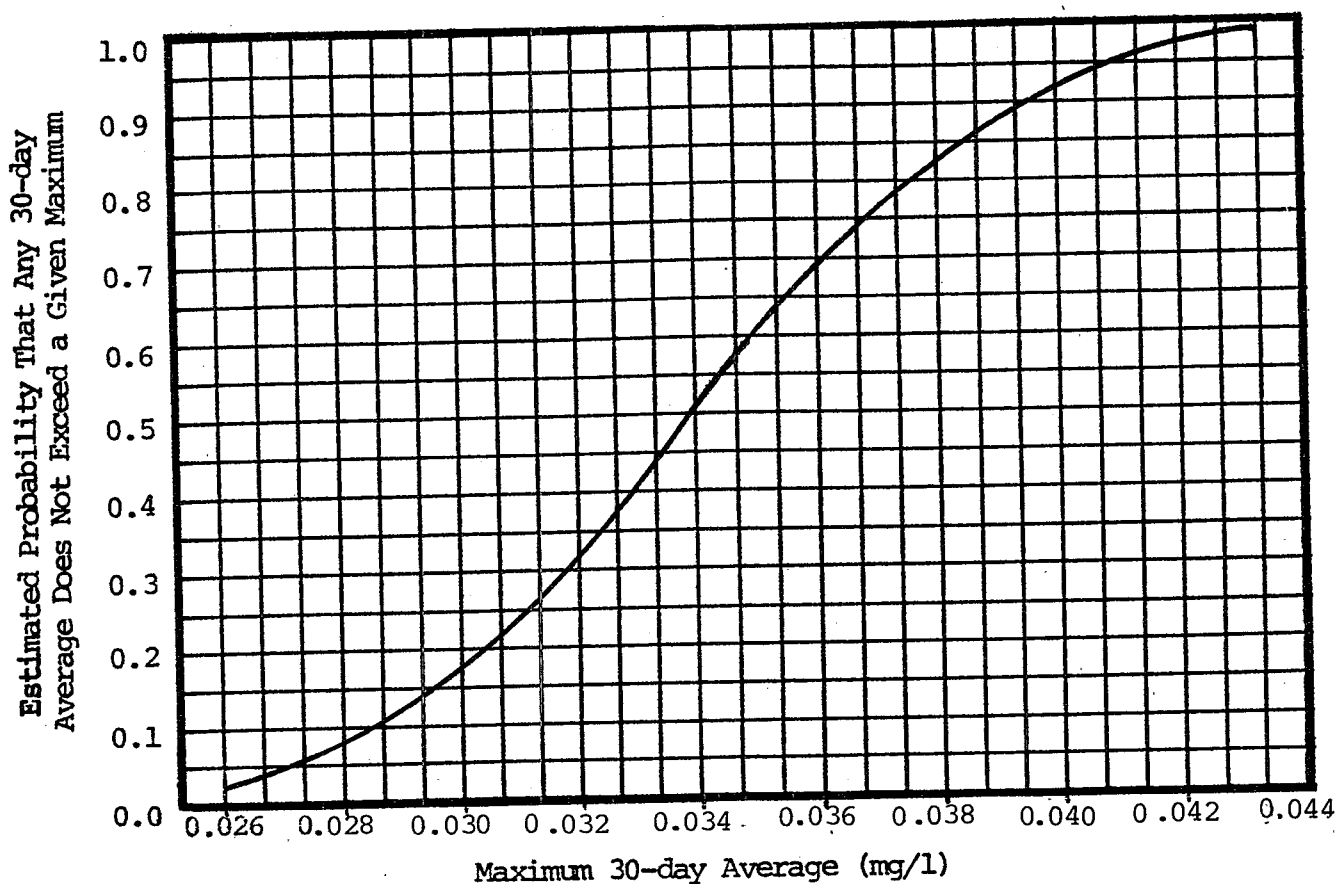


Figure 11-5. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Chrome Pigments	Total Suspended Solids	
Proposed Maximum 30-day Average	(mg/l):	37
95th Percentile ( $Z = 1.64$ )	(mg/l):	5.5
Long Term Average	(mg/l):	4.5
Standard Deviation of 30-day Averages	(mg/l):	0.56
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		14

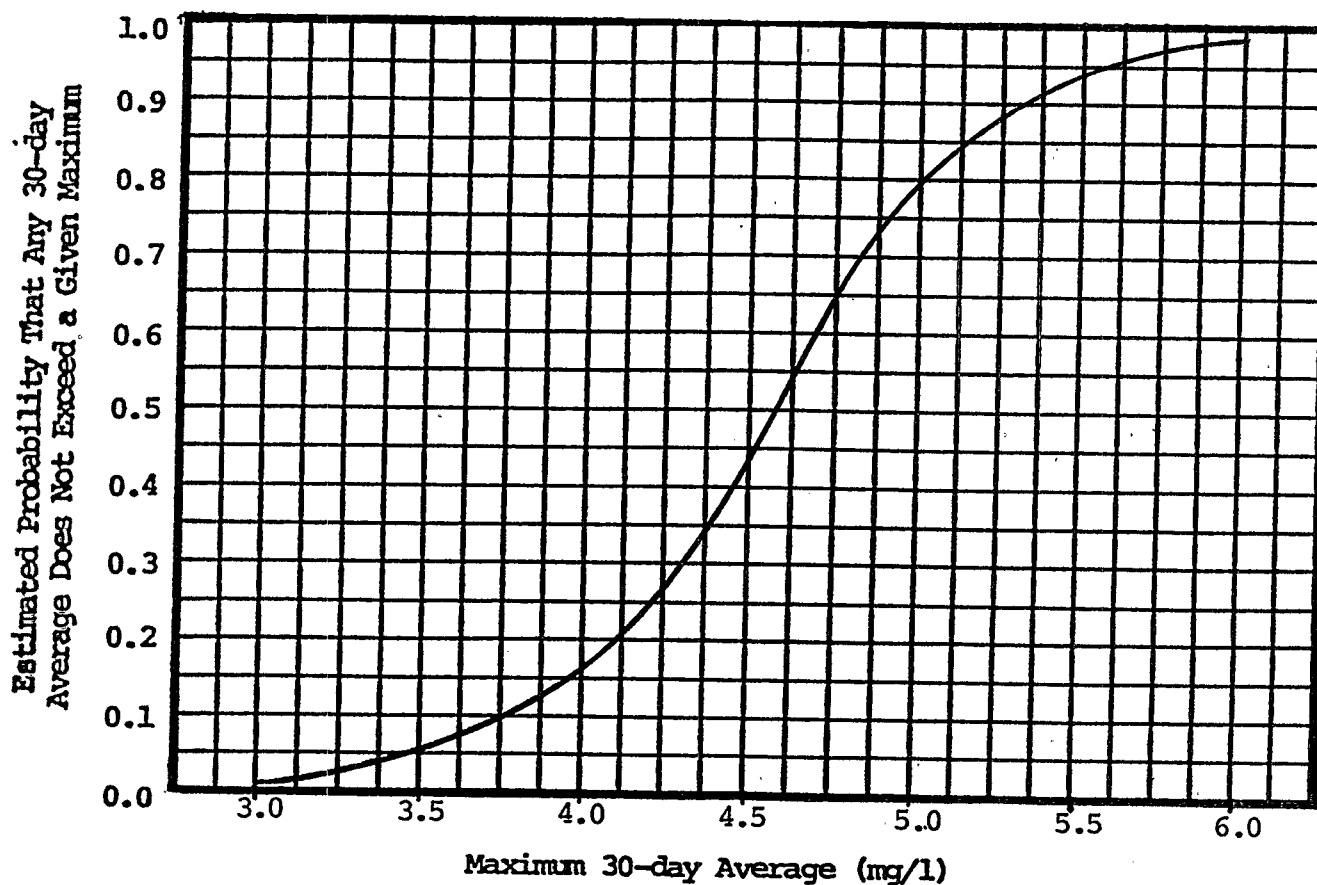


Figure 11-6. Estimated Performance of Proposed BAT Treatment

## SECTION 12.0

### SODIUM DICHROMATE SUBCATEGORY

#### 12.1 INTRODUCTION

##### 12.1.1 General Considerations

The treatability test runs for this subcategory were performed at the in-house laboratory facilities of Versar, Inc. located in Springfield, Virginia, between November 8 and December 5, 1979 for Plant #493. During this period, a total of 18 test runs were completed utilizing the proposed BAT treatment concept.

Two treatability test units were operated at the same time to expedite the study and ensure completion of the tests within the required time period. Since the selected plant was at a considerable distance from the laboratory test unit location, the waste water samples were collected in two large batches of 120 gallons each and transported by truck from the plant site. All test runs were completed within three weeks from receipt of the raw waste to prevent the possibility of sample deterioration to the maximum extent practical.

##### 12.1.2 Sample Point Location

Figure 12-1 shows the general waste water treatment process flow diagram for Plant #493 and indicates the appropriate sample point location used in the study. The sampling location includes waste water from three primary sources including boiler and cooling tower blowdown, scrubber water from a by-product sodium sulfate operation, and spent ore residue.

#### 12.2 TREATABILITY TEST MODEL OPERATION

##### 12.2.1 Treatment Technology Tested

The proposed BAT treatment concept includes dual media filtration added to BPT treatment to achieve a higher level of

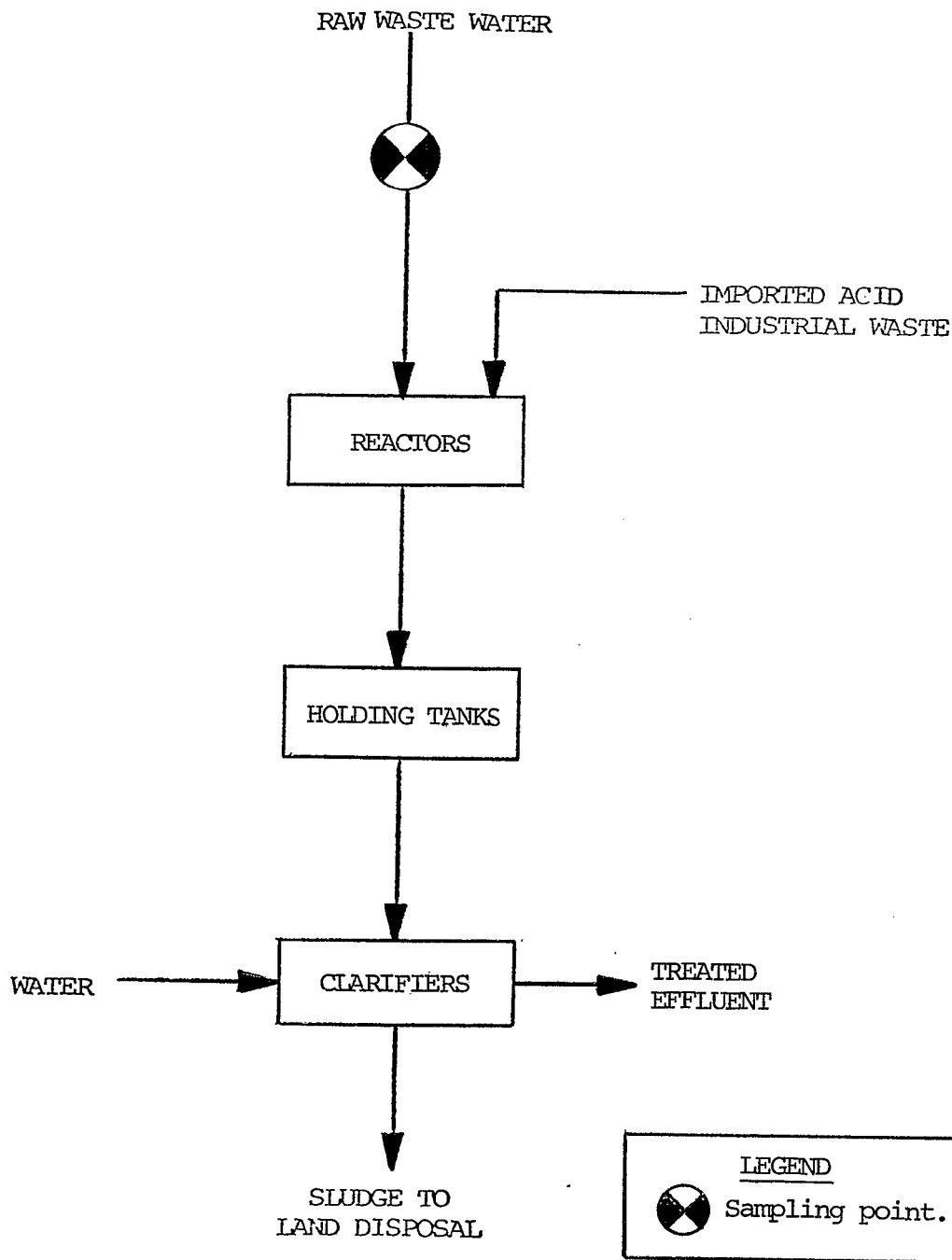
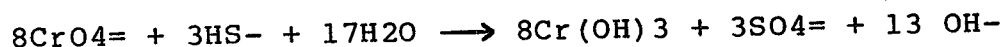


Figure 12-1. General waste water treatment process flow diagram at plant #493 showing the sampling point. (Sodium dichromate manufacture.)



suspended solids removal including metal hydroxides and sulfides. Originally, it was proposed to apply BAT treatment utilizing sodium bisulfide to reduce chromate to trivalent chromium and precipitate other heavy metals followed by alkaline treatment and clarification. However, this BPT treatment approach had to be abandoned because of a number of operational difficulties which could not be conveniently and/or expeditiously mitigated. These difficulties are outlined below:

1. It was discovered, during the initial waste characterization, that addition of sodium sulfide at recommended pH levels above 8 to avoid H<sub>2</sub>S evolution required excessive reaction times to reduce chromate to the trivalent form. During the characterization, a series of tests were performed to determine the sodium sulfide dosage for effective chromate reduction. These tests were performed at 1.3, 1.5, 2.0, 5.0, and 10.0 times the calculated stoichiometric sulfide demand which was based on the analysis of heavy metals. Results of these tests indicated that the reaction required one day or more to reduce most of the chromate present. Specific results of these tests are summarized in Table 12-1 which presents residual chromate concentration after 10-day reaction times at the various sodium sulfide doses. Review of the table indicates that chromate concentrations remained at significant levels between 0.9 and 2.4 mg/l after excessive reaction times. Evidence of the slow reaction could be observed visually as the waste solutions slowly turned from a bright orange to green followed by the formation of a precipitate. During the slow reaction, the pH was observed to shift further to the basic side making circumstances ideal for alkaline precipitation. The pH shift is well known to occur and can be described by the following reaction:



When Na<sub>2</sub>S dissolves in water, HS<sup>-</sup> becomes the prevalent species which reacts with the sodium dichromate. Since hydroxyl ions are one of the reaction products, the final pH correspondingly increases. Formation of the hydroxyl ions would not, however, preclude the use of lime for final pH adjustment in providing a control measure to consistently achieve the optimum pH for alkaline precipitation.

2. In view of difficulties encountered with slow reaction times, other tests were performed at pH values below 8. Results of these tests indicated a more rapid reaction rate after addition of the sodium sulfide, but was complicated by evolution of H<sub>2</sub>S gas. Since H<sub>2</sub>S gas emissions are a potential safety hazard to personnel conducting the tests, the method was abandoned. It is believed that this treatment approach may have a potential application to best available technology if conducted in a closed treatment system. However, time constraints

prevented a complete evaluation and redesign of a test model treatment system that could be used to fully investigate the technique without the safety hazard.

In view of the difficulties encountered with the use of sodium sulfide for chromate reduction, this BPT treatment alternative was abandoned and substituted by a second viable alternative using ferrous chloride and hydrochloric acid (pickle liquor). The treatment concept studied includes chromate reduction with pickle liquor followed by alkaline precipitation with lime, clarification, and dual media filtration for final polish of the clarifier effluent.

#### 12.2.2 Waste Water Characterization

Tables 12-1 through 12-4 present the results of the sodium dichromate raw waste characterization. An initial sample was collected to perform the tests. Results of the analyses are shown in Tables 12-1 and 12-2. Table 12-3 presents additional analyses performed on the two 120 gallon batches used for the test runs. Review of the data revealed a wide range of variability in raw waste metal and suspended solids concentrations. The wide variability was most likely due to the heterogeneous nature of the waste. Suspended solids were observed to settle readily and required a considerable amount of agitation when taking samples for the test runs.

Table 12-4 presents the analyses performed on the pickle liquor. It should be noted that the pickle liquor used for the test runs was from a different source than that used by the selected plant. Review of the data shows that the hydrochloric acid (HCl) concentration was approximately eight percent; whereas, the pickle liquor currently used by the plant has an HCl content of 15 percent.

#### 12.2.3 Details on Treatability Test Operation

A complete presentation of the operational parameters for the test runs is shown in Table 12-5. In general, operational parameters were selected to the degree possible on the basis of plant experience. The primary differences between plant practices and the test treatment conditions were, a) concentrated HCl was required as a supplement to the pickle liquor used for the test runs and, b) the raw waste temperature was 25 degrees C instead of 50 to 70 degrees C encountered at the plant. In actual practice, the plant uses pickle liquor with a higher HCl content precluding the need of additional acid for pH adjustment.

TABLE 12-1. ANALYSES OF TREATED CHROMATE WASTE WATER  
SOLUTIONS AFTER 10 DAYS REACTION TIME WITH SODIUM  
SULFIDE AT pH OF GREATER THAN 8.0

Ratio of Sulfide Used to Stoichiometric Sulfide Requirement	Residual Chromate Concentration (mg/l)
1.3	0.9
1.5	1.0
2.0	0.9
5.0	2.4
10.0	1.2

TABLE 12-2. CHARACTERIZATION OF SODIUM DICHROMATE WASTE WATER

Parameter	Amount Present (mg/l)
Total Suspended Solids	75,800
Total Residue Solids	76,900
Fixed Residue	70,800
Total Dissolved Solids	7,000
pH	9.5
Total Hardness (as CaCO <sub>3</sub> )	4,000
Chlorides	275
Sulfate	3,100
Nitrate	0.80
Carbonate (as CaCO <sub>3</sub> )	3,000
Bicarbonate (as CaCO <sub>3</sub> )	40,000

TABLE 12-3. CHARACTERIZATION OF SODIUM DICHROMATE BATCHES  
USED FOR THE TEST RUNS

Parameter	Concentration (mg/l)	
	Batch A	Batch B
Chromium (Total)	1,500	800
Chromium (Hexavalent)	1,490	560
Nickel	7.82	0.60
Total Suspended Solids	5,500	7,100
Total Dissolved Solids	15,710	8,800

TABLE 12-4. CHARACTERIZATION OF PICKLE LIQUOR

Parameter	Concentration (mg/l)
Ferrous Chloride (as Fe)	150,000
Chromium (Trivalent)	78 to 85
Nickel	250
Hydrochloric Acid	80,000

TABLE 12-5. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Sodium Dichromate		TREATMENT: Chloride Based Pickle Liquor Treatment Followed by Alkaline Precipitation and Dual Media Filtration																
		Reactant Solution: Pickle Liquor																
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Run Date	11/8	11/14	11/16	11/16	11/20	11/20	11/27	11/27	11/29	11/30	11/30	12/3	12/3	12/4	12/4	12/4	12/5	12/5
Amount of Waste Water Treated (Gal)	20	20	6.5	6.5	6.5	6.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Raw Waste Water pH	10.2	10.1	10.1	10.1	10.1	10.1	10.3	10.2	10.2	10.0	10.7	10.7	10.5	10.6	10.5	10.8	10.4	10.5
Raw Waste Water Temp (°C)	NDA	(1) 22	NDA	NDA	NDA	NDA	NDA	NDA	22	20	19	14	18	18	18	17	19	19
Amount of FeCl <sub>2</sub> Solution (Qt)	8 (lb) +	4.3	1.0	1.0	1.0	1.0	1.3	0.7	0.7	0.7	4.4	4.4	4.8	4.8	0.8	0.8	4.0	4.0
pH After FeCl <sub>2</sub> Solution Addition	NDA	NDA	4.6	5.4	NDA	5.4	4.9	4.9	6.8	5.0	3.6	3.4	3.5	3.6	6.4	6.4	3.4	3.6
Amount of HCl Solution (ml)	250	2250	950	NDA	1200	NDA	NDA	NDA	1400	900	150	NDA	400	500	1500	1550	800	650
pH After Adjustment	2.7	2.8	2.9	3.0	2.6	3.0	3.4	3.0	3.2	2.8	3.2	2.8	3.0	2.8	2.8	2.8	3.0	2.9
Mixing Time (hrs)	3.0	2.0	2.2	2.0	3.8	2.0	2.0	2.0	3.0	3.0	3.0	3.0	3.0	3.0	4.0	4.0	4.8	4.0
Settling Time (hrs)	17.25	26	68.5	1.25	1.25	1.7	15	0	0	0	0	0	0	0	0	0	0	0
Tapwater Dilution	0	3:1	3:1	3:1	3:1	3:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
pH After Dilution and Settling	NDA	NDA	3.2	NDA	2.4	3.6	3.4	NDA	3.6	2.9	4.3	3.1	3.7	3.0	3.6	3.3	3.7	3.3
Precipitant Added	NaOH	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	*	CaO	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub>	CaO	Slurry	CaO	CaO
Amount Precipitant Solution (g)	NDA	NDA	NDA	135	NDA	150	NDA	290	360	255	*	500	1200	1600	2400	2200	600	4000
Precipitant Solution Strength	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG	RG
pH After Precipitant Addition	8.4	9.9	9.5	8.5	9.0	8.4	8.4	8.4	8.9	8.4	8.6	8.1	8.6	8.5	8.3	8.4	8.5	8.3
Mixing Time (hr)	1.5	1.0	1.0	NDA	0.8	1.0	0.7	NDA	1.5	1.3	2.3	5.0	1.8	2.0	0.3	0.5	0.5	0.5
Settling Time (hr)	66.3	15.7	3.0	0.5	16.3	2.0	1.5	14.0	1.0	2.7	14.2	13.0	14.3	1.3	1.8	1.5	14.3	14.3
Clarified Water pH	NDA	9.5	9.5	NDA	9.5	NDA	7.2	NDA	7.3	7.3	7.5	5.9	8.1	8.3	7.9	7.9	7.5	6.0
Filter Run Length (min)**	30	15	15	15	15	60	15	15	15	15	15	15	30	15	15	15	20	15
Filtrate pH	NDA	7.9	8.0	5.0	7.1	NDA	5.8	4.5	5.7	3.3	4.0	3.4	3.4	NDA	5.6	3.8	NDA	NDA
(1) NDA - No Data Available																		
+ - FeSO <sub>4</sub> Utilized																		
	RG - ACS Reagent Grade																	
	* - CaO (RG) 450 g																	
	Ca(OH) <sub>2</sub> (AG) 112 g																	
	** - Minutes after start of filtration																	

The basic treatment concept used involved addition of pickle liquor in an amount equivalent to more than two times the stoichiometric amount required for chromate reduction. The mixture was then adjusted between pH 2 and 3 with concentrated hydrochloric acid and stirred for approximately three hours. Dilution of the waste with additional water was necessary, as was also practiced at the plant, due to the high solids content. After stirring, the waste was adjusted to a pH of 9 with lime for optimum heavy metal removal by alkaline precipitation.

Aeration of the waste water during alkaline pH adjustment was practiced for all the test runs. Aeration was applied to oxidize the remaining ferrous iron to its ferric form since ferric iron has a lower solubility in alkaline conditions and the possibility of coprecipitation with other metals may improve settling characteristics of the sludge.

## 12.3 TEST RESULTS

### 12.3.1 Discussion of Results

The analytical results for the 18 treatability test runs are tabulated in Table 12-6. Treatment results for the chromate ion are also included in the table to ascertain the proportion of total chromium contributed by the presence of chromate in the final treated effluent.

The results presented in Table 12-6 show high total chromium concentrations in the filter effluent for test runs 1, 5, 9, 15, and 16. Test run number 1 is questionable since the chromium concentration in the filtered effluent exceeds the concentration in the treated supernatant by an amount greater than the expected experimental error.

The poor results for runs 5, 9, 15, and 16 may all be related to insufficient pickle liquor dosage to completely reduce all the available chromate to trivalent chromium. This result is not unlikely since the raw waste was very heterogeneous and therefore highly variable in chromate content. In addition, oxidation of some of the ferrous iron in the pickle liquor may have occurred during storage, thereby decreasing its effectiveness. It should be noted that the high effluent chromium concentrations occurred more frequently in the later runs which would tend to support this conclusion.

There is an apparent correlation between the pH of the treated waste after the addition of pickle liquor and the poor removal of total chromium for runs 9, 15, and 16. As shown in Table 12-5, the pH's for these runs were 6.80, 6.40, and 6.40 which are much higher than any of the pH values reported for the

TABLE 12-6. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR STUDY  
IN THE SODIUM DICHROMATE SUBCATEGORY

Treatment: Chloride Based Pickle Liquor Treatment Followed by  
Alkaline Precipitation and Dual Media Filtration

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
All reported values in mg/l																		
<u>Total Chromium, Cr (T)</u>																		
Raw Waste --																		
Total Cr (T)	820	730	960	1300	790	730	630	630	680	720	1100	1060	1420	1210	1230	1500	1520	1320
Dissolved Cr (T)	520	560	670	630	580	630	570	570	590	570	1600	1600	1580	1760	1490	1550	1480	1470
Supernatant --																		
Total Cr (T)	0.15	0.15	0.29	0.07	10	0.08	NDA	(1) 0.22	60	0.85	0.12	0.50	0.19	0.49	71	70	0.17	0.18
Dissolved Cr (T)	0.09	0.11	0.15	0.09	8.7	0.08	NDA	0.21	61	0.26	0.11	0.19	0.12	0.20	66	67	0.13	0.13
Filter Effluent --																		
Total Cr (T)	3.9	0.79	0.09	0.23	8.8	0.17	0.27	0.24	56	0.23	0.18	0.21	0.10	0.50	64	66	0.10	0.16
Dissolved Cr (T)	1.8	0.79	0.09	0.16	8.6	0.16	0.29	0.21	55	0.25	0.18	0.15	0.11	0.24	63	70	0.12	0.13
<u>Chromate</u>																		
Raw Waste --																		
Total Chromate	590	530	530	510	480	590	560	560	590	550	1415	1453	NDA	1440	1418	1475	1390	1390
Dissolved Chromate	560	550	550	570	570	580	600	600	620	630	1505	1525	1440	1540	1488	1540	1440	1455
Supernatant --																		
Total Chromate	0.014	0.017	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA
Dissolved Chromate	0.012	0.010	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA	NDA
Filter Effluent --																		
Total Chromate	0.90	0.50	0.005	<0.004	7.55	<0.004	<0.04	<0.04	50	<0.04	0.007	0.011	0.007	<0.04	59	53.5	<0.04	<0.04
Dissolved Chromate	1.1	0.40	0.006	<0.004	2.65	0.004	<0.04	<0.04	54	<0.04	0.010	0.011	0.005	<0.04	60	52	<0.04	<0.04
<u>Nickel, Ni</u>																		
Raw Waste --																		
Total Ni	0.47	0.37	0.34	0.37	0.63	0.32	0.44	0.44	0.35	0.47	7.8	0.35	7.4	7.5	7.5	7.6	4.3	7.8
Dissolved Ni	0.10	<0.05	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Supernatant --																		
Total Ni	0.47	<0.05	<0.05	0.07	<0.05	0.10	NDA	<0.05	<0.05	<0.05	<0.05	12.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Dissolved Ni	0.45	<0.05	<0.05	0.10	<0.05	0.06	NDA	<0.05	<0.05	<0.05	<0.05	12.3	<0.05	<0.05	0.06	<0.05	<0.05	<0.05
Filter Effluent --																		
Total Ni	0.50	<0.05	<0.05	0.11	<0.05	0.06	<0.05	<0.05	0.06	0.06	<0.05	12.6	<0.05	0.11	0.07	0.07	0.05	0.08
Dissolved Ni	0.49	0.05	0.05	0.08	<0.05	0.09	<0.05	0.05	0.07	<0.05	0.07	12.4	<0.05	<0.05	0.05	<0.05	<0.05	0.08
<u>Total Suspended Solids, TSS</u>																		
Raw Waste	2010	76950	13250	240	16790	3960	456600	456600	19640	15220	21930	29400	127850	171300	107590	92190	43410	63620
Supernatant	39.6	13.1	69.3	5.8	85	3.6	NDA	14.3	13.8	25.8	26.7	24.8	21.9	12	1420	1068	31.9	190
Filter Effluent	70.0	21.6	49.0	3.0	25.5	4.1	11.2	76.4	7.2	13.2	97.3	14.7	23.8	131	587	785	401	832

(1) NDA - No Data Available

other test runs. Even though this fact may have some bearing upon the reduction of chromate, it should not be a limiting factor in the reduction process because the pH of the pickle liquor treated waste was always adjusted to around 2.8 by addition of HCl which would accelerate the reduction of chromate. Test runs 1, 5, 9, 15, and 16 were rejected from consideration in the statistical analysis for chromium due to the aforementioned difficulties.

Good total suspended solids (TSS) removal efficiencies were obtained during lime precipitation where low TSS values may be correlated with good sludge blanket settling characteristics. However, the filtration step is very unpredictable and inconsistent in its overall performance.

### 12.3.2 Statistical Evaluation

Table 12-7 presents a comparison of the proposed BAT maximum 30-day average concentration and the estimated treatability performance developed in the statistical analysis. The statistical analysis is presented in Figures 12-2 through 12-5 in addition to Appendix A for the pollutants studied. Test run numbers 1, 5, 9, 15, and 16 for total chromium have been rejected on technical grounds as explained in the previous section. Application of the t-statistic resulted in elimination of test run 12 for nickel.

### 12.3.3 Conclusions

The treatability test results can be viewed as strongly indicative, but not entirely conclusive, of what the proposed BAT treatment concept for the Sodium Dichromate Subcategory is able to achieve. Although the proposed maximum 30-day average concentration for chromium and nickel was achieved after screening out the questionable results, more comprehensive results could be obtained by evaluating the kinetic aspects of the treatment process variables and utilizing appropriate equipment to improve the mixing of reactants and the measurement of chemical dosages.

A major conclusion to be drawn from this study is that dual media filtration does not appear to improve significantly the clarifier effluent quality on a consistent basis. Sludge blanket settling characteristics appear very effective for the reduction of suspended solids including metal hydroxide precipitates from the liquid phase. It is anticipated that careful design and operation of a clarifier unit should preclude the need for dual media filtration to reduce toxic metal pollutants as indicated by the results presented in Table 12-6.



TABLE 12-7. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR THE  
SODIUM DICHROMATE SUBCATEGORY

STREAM: Filter Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Chromium	0.32	0.29
Hexavalent Chromium	0.050	0.20
Nickel	0.17	0.095
Total Suspended Solids, TSS	26	460

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Dichromate	Chromium	
Proposed Maximum 30-day Average	(mg/l):	0.32
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.29
Long Term Average	(mg/l):	0.25
Standard Deviation of 30-day Averages	(mg/l):	0.029
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		13

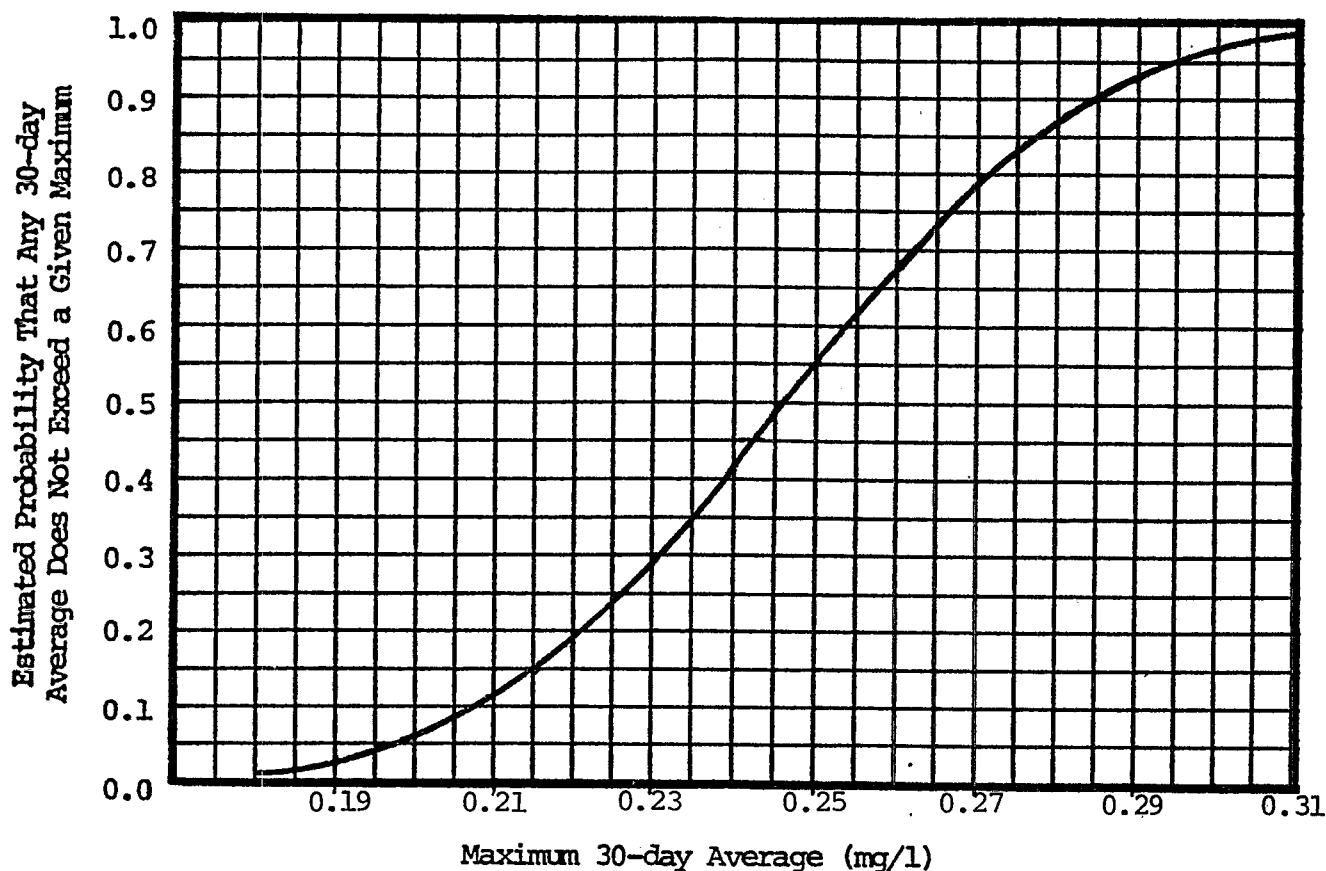


Figure 12-2. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Dichromate	Hexavalent Chromium	
Proposed Maximum 30-day Average	(mg/l):	0.050
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.20
Long Term Average	(mg/l):	0.096
Standard Deviation of 30-day Averages	(mg/l):	0.062
Probability of Achieving Proposed Maximum 30-day Average	(%):	23
Number of Observations:		14

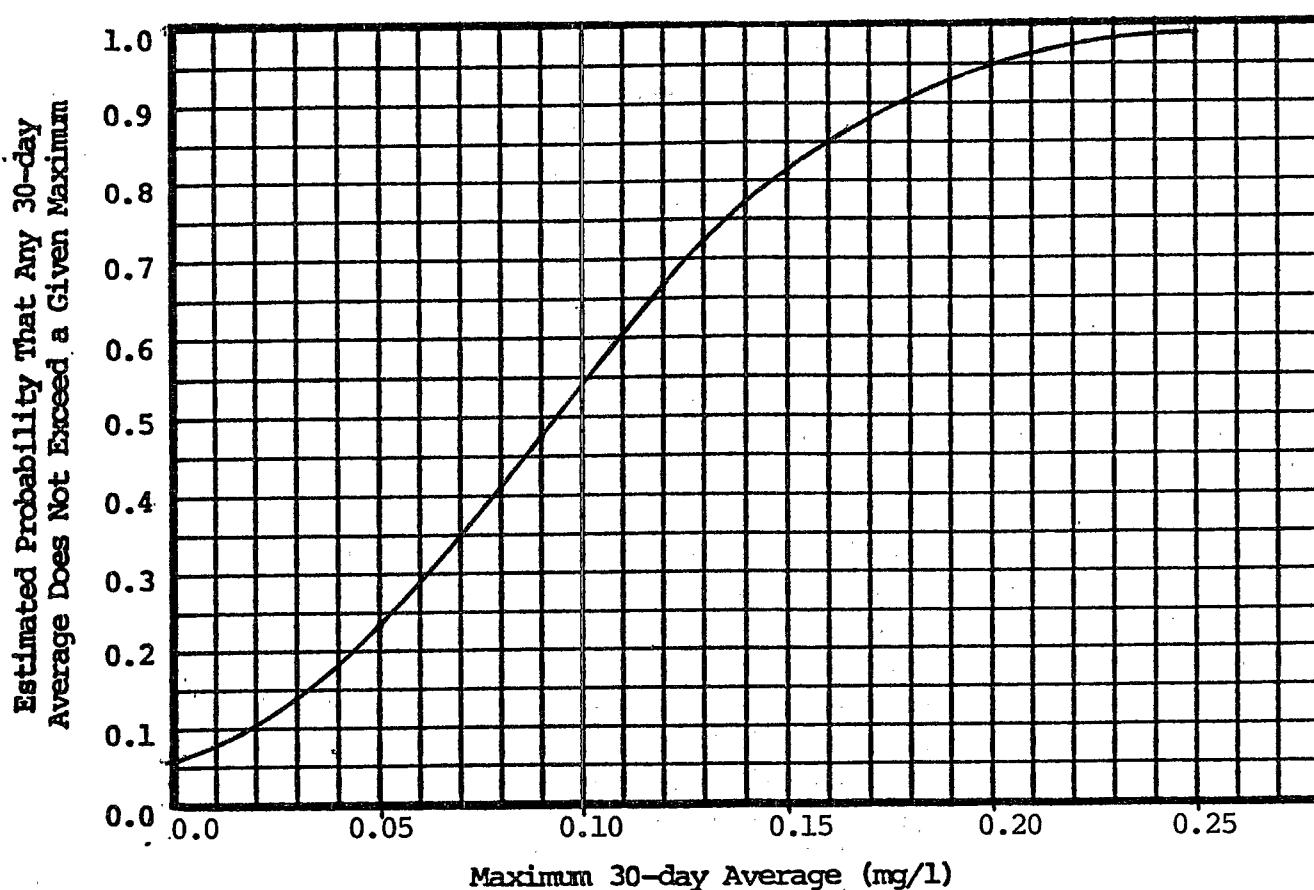


Figure 12-3. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Dichromate	Nickel	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	0.17
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	0.095
Long Term Average	(mg/l):	0.081
Standard Deviation of 30-day Averages	(mg/l):	0.0088
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		17

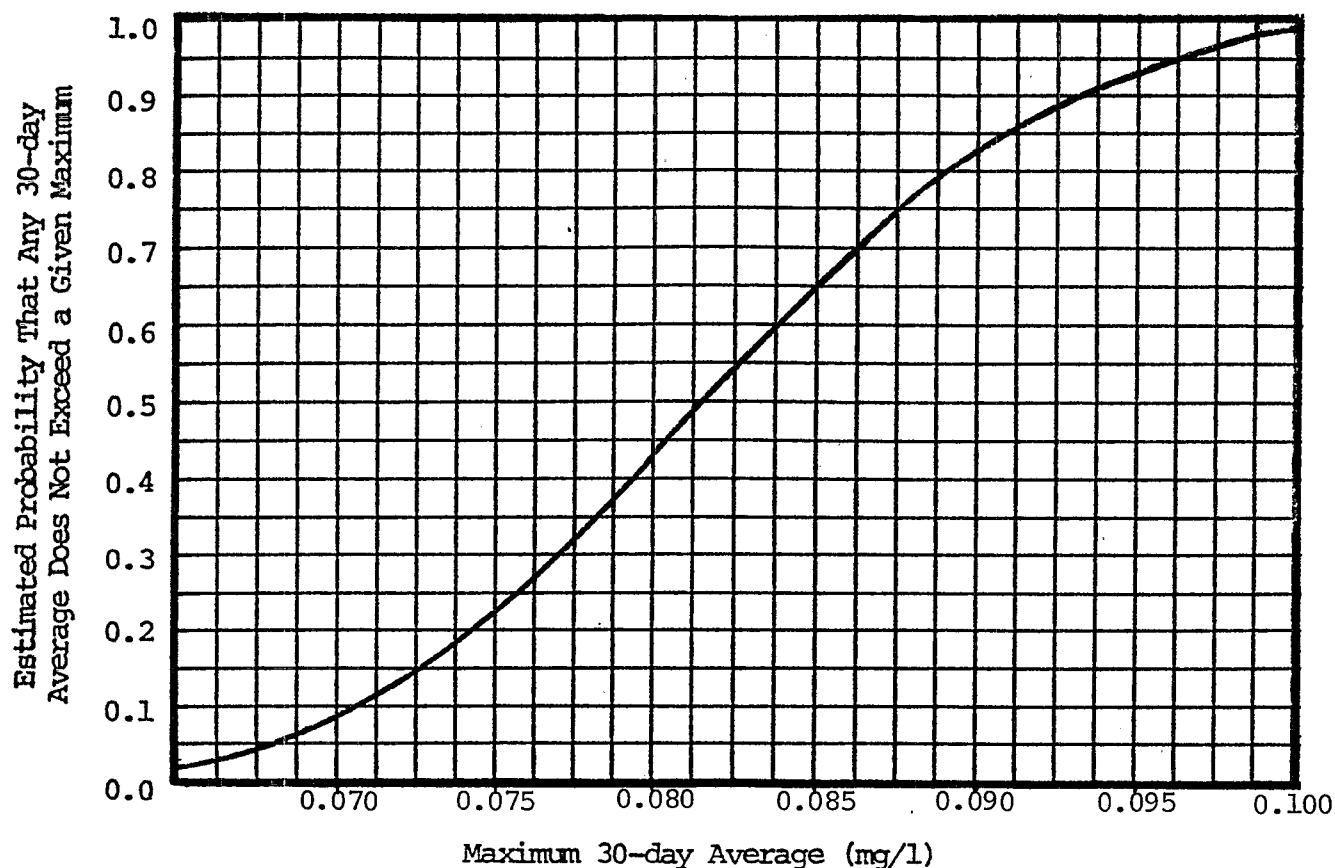


Figure 12-4. Estimated Performance of Proposed  
BAT Treatment After Screening of Data

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Dichromate	Total Suspended Solids	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	26
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	460
Long Term Average	(mg/l):	200
Standard Deviation of 30-day Averages	(mg/l):	160
Probability of Achieving Proposed Maximum 30-day Average	(%):	13
Number of Observations:		18

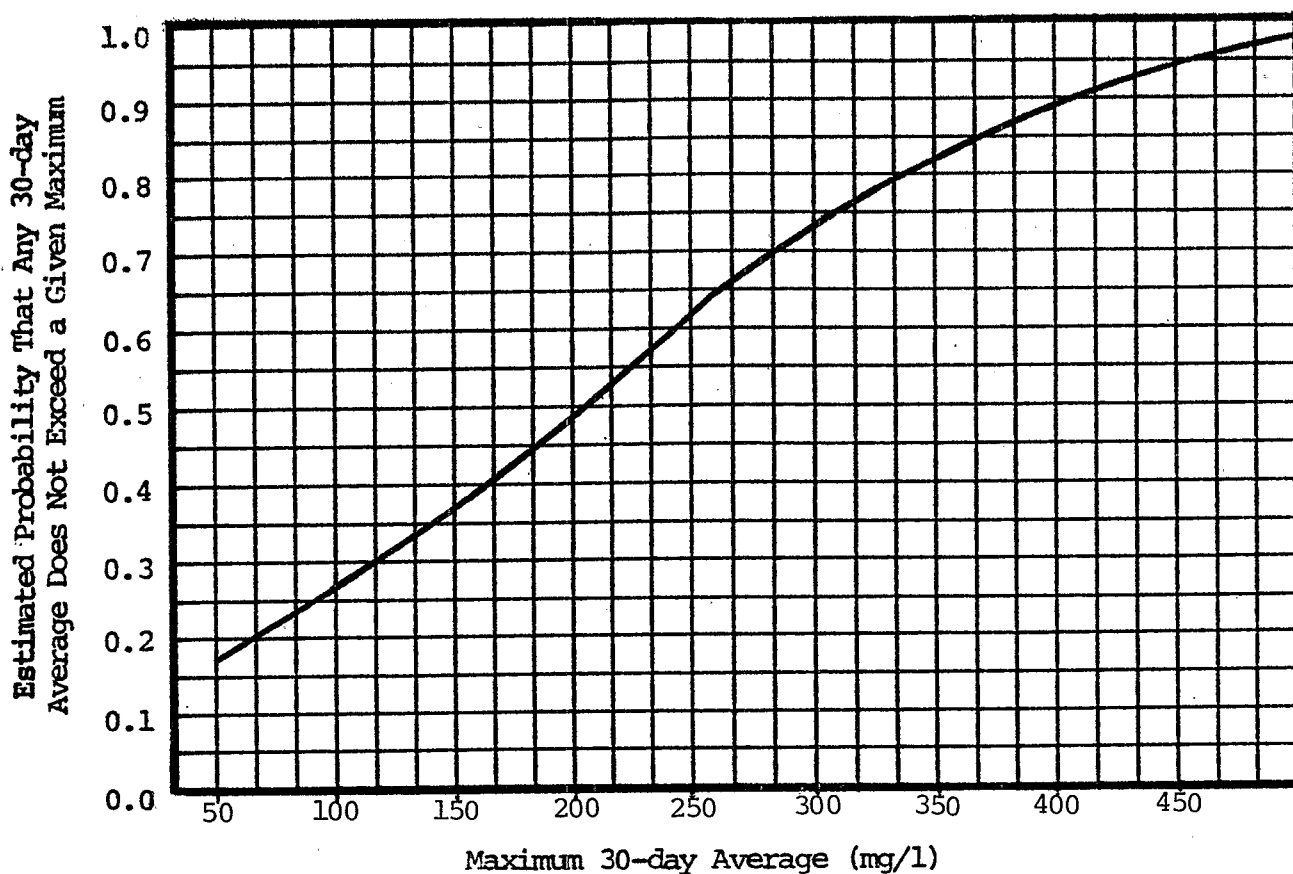
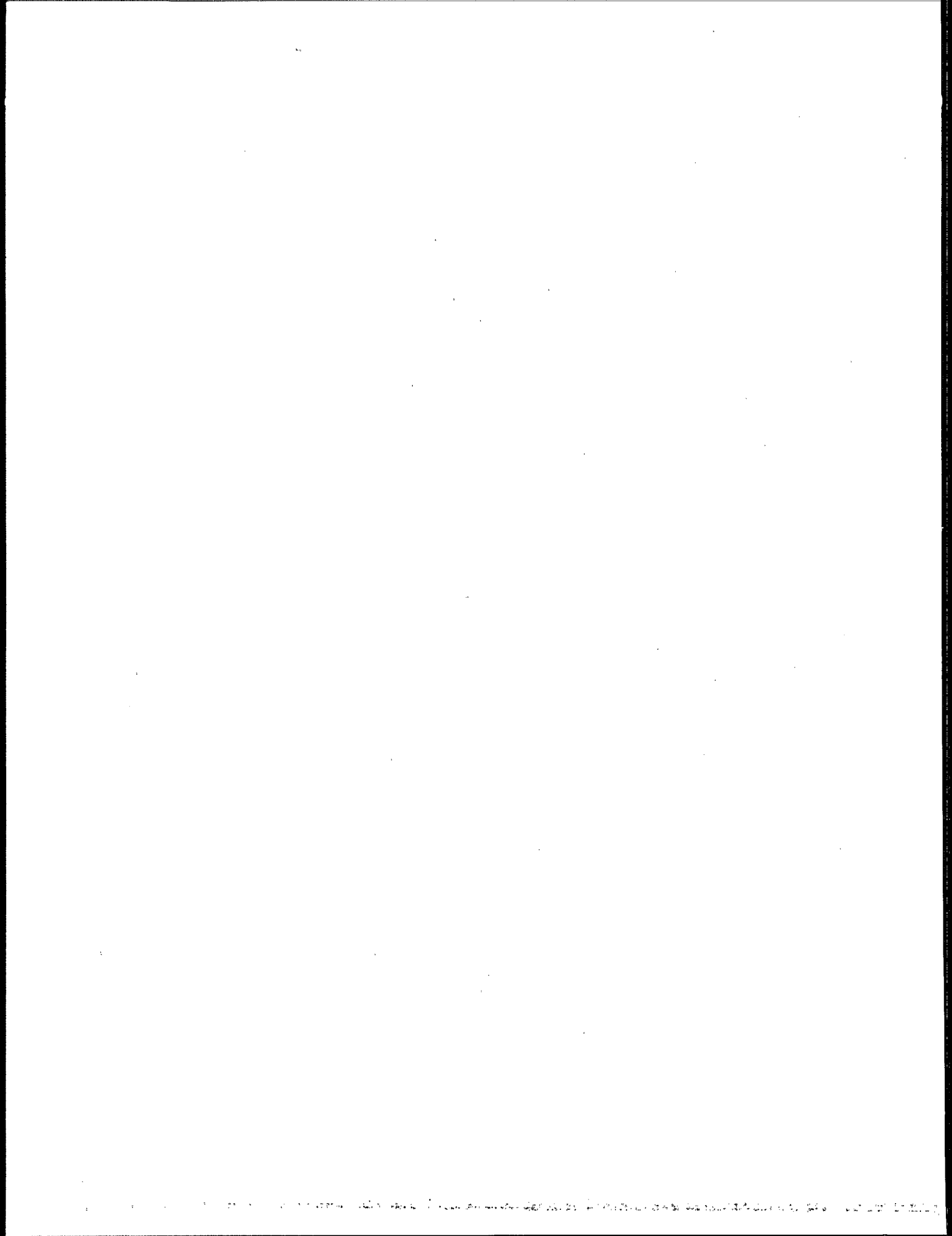


Figure 12-5. Estimated Performance of Proposed  
BAT Treatment



## SECTION 13

### SODIUM BISULFITE SUBCATEGORY

#### 13.1 INTRODUCTION

##### 13.1.1 General Considerations

The treatability studies were carried out at PJB Laboratories, a division of Jacobs, in Pasadena, California. A total of 17 test runs were made between September 24 and November 5, 1979, using seven batches of waste water obtained from Sodium Bisulfite Plant #282.

##### 13.1.2 Sample Point Location

Figure 13-1 is a schematic representation of Plant #282 which was selected for study. The treatability tests were made using waste water collected from the waste stream to the effluent holding tanks as indicated in the figure.

The plant operated on a non-continuous program. Therefore, an agreement was made to provide the sampling containers and the plant personnel would collect the waste water and immediately inform Jacobs' personnel that the samples were ready for pick up. Enough waste water was always collected in air tight containers to run two or more tests from each sample batch. All test runs were performed expeditiously after receipt of the samples.

#### 13.2 TREATABILITY TEST MODEL OPERATION

##### 13.2.1 Treatment Technology Tested

The waste water from this industry has a high capability to react with elemental oxygen. Therefore, the main objective of the treatment is to reduce this oxygen-consuming capacity. A simple aeration process was used. Determinations of TSS and zinc were made, but this test was not designed to provide optimum

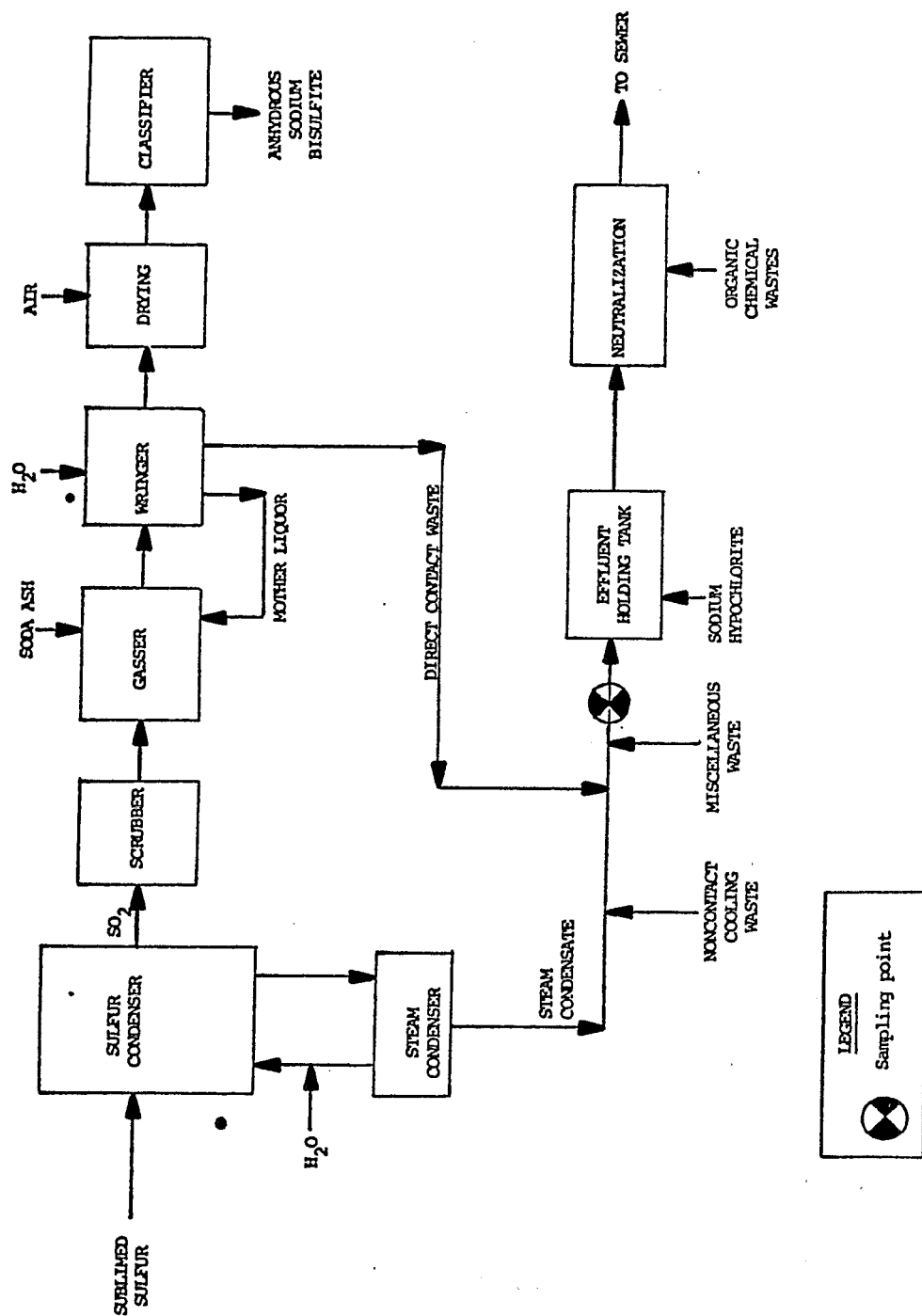


Figure 13-1. General process flow diagram at plant #282 showing the sampling points. (sodium bisulfite manufacture.)



conditions for the precipitation of zinc and other metals or for physical separation of the solids.

### 13.2.2 Waste Water Characterization

An analysis of a sample of the waste water yielded the results shown in Table 13-1. The possible presence of sulfur compounds other than sulfite and sulfate was not excluded. It is highly probable that substances such as thiosulfate are also present, but a complete determination of the many possible forms of sulfur in the water was not undertaken.

### 13.2.3 Details on Treatability Test Operation

Table 13-2 shows the operational conditions for the treatability tests made in the sodium bisulfite subcategory.

Five different air flow rates were used during the course of study. These were: 11.5, 23, 35, 46, and 57 SCFH (standard cubic feet per hour).

Following a procedure similar to that used by a plant practicing this technology, the initial pH of the waste water was always adjusted to around 9.5. After pH adjustment, the air flow rate was then adjusted to the desired value. The progress of the reaction was followed by continuous monitoring of iodate demand by titrations in acid solution in the presence of iodide. This is the EPA approved method for determining sulfite) see 41 FR 52780, 12/1/76). The iodate demand was then expressed in terms of the equivalent oxygen demand exerted by the sulfite/bisulfite in solution. COD determinations were also made, but as explained later, the nature of the samples makes it impossible to obtain reproducible results in that test.

## 13.3 TEST RESULTS

### 13.3.1 Discussion of Results

The analytical results are presented in Tables 13-3 to 13-10.

It was anticipated that the principal impurity in the waste water from this subcategory would be bisulfite, either as HS03- or S205= which could be eliminated by oxidizing it to sulfate with aeration. The waste is, in fact, more complex.

The simplest way to determine the presence of bisulfite if no other reducing agents are present, is by titration with iodate in the presence of iodide and acid. The amount of sulfite

TABLE 13-1. SODIUM BISULFITE WASTE WATER CHARACTERIZATION

Parameter	Value
pH	4.8
Temperature, Degrees C	25
	<u>mg/l</u>
Total Acidity (as CaCO <sub>3</sub> )	780
Total Suspended Solids	310
Total Dissolved Solids	4,700
Total Residue Solids	5,400
Fixed Residue Solids	4,800
Chemical Oxygen Demand	1,400
Zinc	1.3
Iodate Demand, as SO <sub>3</sub> =	1,500
Sodium	1,540
Potassium	9.5
Calcium (as CaCO <sub>3</sub> )	150
Magnesium (as CaCO <sub>3</sub> )	66
Chloride	270
Sulfate	2,170
Nitrate	<0.1
Ammonia	260
Thiourea	22*

\* Calculated

TABLE 13-2. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Sodium Bisulfite																	TREATMENT: Extended Aeration						
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17						
Batch Number	1	1	2	2	2	3	3	4	4	4	5	5	5	6	6	7	7						
Date	9/12	9/14	9/16	9/17	9/18	10/1	10/3	10/12	10/15	10/16	10/22	10/23	10/24	10/29	10/31	11/2	11/5						
Volume of Waste Water Aerated (Gallons)	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20						
Raw Waste Water pH	6.0	5.8	6.5	6.5	6.5	5.3	5.0	7.0	7.0	7.0	6.6	6.5	6.5	NDA (1)	6.4	8.1	8.1						
Amount of Caustic for pH Adjust. (mls) (2)	250	325	75	75	80	775	750	300	300	300	225	275	250	380	525	85	75						
pH Reached by Caustic Addition	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5	9.5						
Aeration Rate (SCFH) (3)	11.5	46.0	35.0	11.5	23.0	35.0	46.0	57.0	11.5	35.0	23.0	46.0	57.0	11.5	46.0	23.0	57.0						
Aeration Time (Hrs)	27.0	24.0	24.0	24.0	23.3	29.0	22.3	22.3	22.8	23.0	6.3	23.8	23.8	22.8	22.5	25.3	22.5						

(1) NDA - No Data Available

(2) The caustic soda solution used had a concentration of 333.3 gm/liter

(3) SCFH: Standard cubic feet per hour

TABLE 13-3. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR  
STUDY IN THE SODIUM BISULFITE SUBCATEGORY

Test Number	TREATMENT: Extended Aeration																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	All reported values in mg/l																
<u>Chemical Oxygen Demand, COD</u>																	
Raw Waste --																	
Total COD	1850	1050	800	560	640	320	800	1120	800	880	400	400	240	1520	1280	2400	2160
Aerated Waste --																	
Total COD	NDA <sup>(1)</sup>	NDA	400	560	400	960	560	560	320	80	160	80	240	720	880	480	400
<u>Iodate Demand as Oxygen</u>																	
Raw Waste	360	360	140	174	184	942	1046	808	856	800	388	382	398	1160	1064	2328	2272
Aerated Waste	37	32	16	22	20	26	20	6	7	8	7	3	2	50	16	84	62
<u>Zinc, Zn</u>																	
Raw Waste --																	
Total Zn	1.30	0.88	0.58	1.40	0.30	0.67	1.00	0.49	0.38	0.32	1.00	1.40	1.10	4.60	3.30	0.30	0.35
Dissolved Zn	0.74	0.06	0.42	0.66	0.63	0.50	1.00	0.30	0.19	0.17	0.80	1.30	0.69	1.10	0.57	0.15	0.17
Aerated Waste --																	
Total Zn	0.12	NDA	0.39	0.12	0.30	0.63	0.93	0.58	0.38	0.034	1.10	0.85	0.32	4.00	4.00	0.34	0.30
Dissolved Zn	0.06	NDA	0.11	0.12	0.04	0.06	0.10	0.01	0.04	0.06	0.07	0.19	1.00	0.08	0.08	NDA	0.04
<u>Total Suspended Solids, TSS</u>																	
Raw Waste	310	250	155	330	150	130	150	230	180	190	130	NDA	130	610	730	210	210
Aerated Waste	240	NDA	155	330	150	200	230	210	160	150	120	140	120	620	690	200	170

(1) NDA - No Data Available

TABLE 13-4. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 1

RUN 1	9/12/79	AIR FLOW RATE:	11.5 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	9.6	360	1850
0.5	9.5	236	1690
1.0	9.5	230	1100
1.5	9.5	218	1020
3.75	9.7	140	1090
4.75	9.7	108	790
6.25	9.9	96	880
7.75	9.8	85	930
9.75	9.9	75	930
11.75	9.9	68	1030
13.75	9.9	60	860
22.0	9.4	44	930
24.0	9.2	41	960
25.25	9.4	40	1020
25.75	9.3	40	
26.0	9.3	37	
27.0	9.2	37	

RUN 2	9/12/79	AIR FLOW RATE:	46 SCFH
0.0	9.5	360	1050
1.0	9.6	256	1050
1.5	9.65	236	980
2.0	9.6	236	920
4.0	10.0	152	880
6.0	9.9	106	850
8.0	9.9	84	860
10.0	9.9	64	880
12.0	10.0	52	820
14.0	10.0	50	860
24.0	9.5	32	

TABLE 13-5. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 2

RUN 1	9/26/79	AIR FLOW RATE:	35 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	9.5	140	800
1.0	9.4	122	560
1.5	9.4	110	640
2.0	9.4	102	640
4.25	9.2	60	880
5.25	9.0	54	720
6.25	8.9	46	880
23.0	8.5	16	480
24.0	8.4	16	400
RUN 2	9/27/79	AIR FLOW RATE:	23 SCFH
0.01	9.8	174	560
0.5	9.8	160	320
1.0	9.8	148	640
1.5	9.8	126	640
3.25	9.8	100	640
4.25	9.7	88	560
23.0	9.6	22	800
24.0	8.4	22	560
RUN 3	9/28/79	AIR FLOW RATE:	23 SCFH
0.0	6.5	184	640
1.0	9.5	160	400
1.5	9.5	146	2400
2.75	9.4	100	480
4.75	9.4	82	560
6.25	9.3	68	400
9.25	9.0	50	480
22.25	8.6	20	480
23.25	8.6	20	400

TABLE 13-6. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 3

RUN 1	10/1/79	AIR FLOW RATE:	35 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	10.2	942	320
1.0	10.4	810	960
1.5	10.6	608	800
3.0	10.5	348	640
4.5	10.4	246	640
6.0	10.2	210	720
9.5	10.0	98	560
22.5	9.1	40	400
23.5	9.0	36	560
24.5	9.0	34	480
29.0	8.8	26	960

RUN 2	10/3/79	AIR FLOW RATE:	46 SCFH
0.0	5.0	1046	880
0.5	9.4	1004	800
1.0	9.9	740	880
1.5	10.8	568	560
3.0	10.9	198	560
4.5	10.7	152	640
6.0	10.5	116	640
9.75	10.1	68	560
22.25	9.2	20	560

TABLE 13-7. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 4

RUN 1	10/12/79	AIR FLOW RATE:	57 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	7.0	808	1120
0.5	9.5	568	560
1.0	9.6	348	480
1.5	9.6	172	480
2.0	9.7	120	480
3.5	9.7	58	560
4.5	9.7	45	640
5.0	9.7	39	640
6.0	9.6	31	640
22.25	9.3	6	560
RUN 2	10/15/79	AIR FLOW RATE:	11.5 SCFH
0.0	7.0	856	800
0.5	9.6	684	480
1.0	9.5	568	400
1.5	9.5	398	260
2.0	9.6	316	400
4.0	9.7	84	400
5.0	9.7	58	
6.5	9.8	38	
9.75	9.7	22	
22.75	9.6	7	
RUN 3	10/16/79	AIR FLOW RATE:	35 SCFH
0.0	9.6	800	880
0.5	9.5	476	480
1.0	9.5	460	400
1.5	9.6	268	320
2.0	9.6	166	320
4.0	9.6	68	320
5.5	9.6	46	320
7.0	8.6	34	240
10.0	9.7	20	320
23.0	9.6	8	80



TABLE 13-8. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 5

RUN 1	10/22/79	AIR FLOW RATE:	23 SCFH
Aeration Time, hrs.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	6.6	388	400
0.25	9.5	276	400
0.75	9.9	172	400
1.25	10.0	90	240
1.75	10.2	50	240
2.25	10.2	40	160
4.25	10.2	14	240
5.25	10.1	12	160
6.25	10.1	7	160
RUN 2	10/23/79	AIR FLOW RATE:	46 SCFH
0.0	9.5	382	400
0.5	10.6	242	240
1.0	10.9	160	240
1.5	10.95	102	160
2.0	11.0	80	160
4.0	10.85	30	160
6.0	10.5	14	160
8.0	10.5	8	160
23.75	9.8	3	80
RUN 3	10/24/79	AIR FLOW RATE:	57 SCFH
0.0	9.5	398	240
0.5	10.35	250	160
1.0	10.2	118	160
1.5	10.4	60	160
2.0	10.4	38	160
2.5	10.5	28	320
4.5	10.4	12	320
6.5	10.4	6	320
23.75	9.2	2	240

TABLE 13-9. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 6

RUN 1	10/29/79	AIR FLOW RATE:	11.5 SCFH
Aeration Time, hr	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	9.7	1160	1520
0.5	10.2	874	1120
1.0	10.4	774	1120
1.5	10.4	648	1040
2.0	10.4	530	1520
3.5	10.6	208	640
5.0	10.6	178	720
6.5	10.6	140	720
10.0	10.5	112	640
22.75	9.9	50	720

RUN 2	10/31/79	AIR FLOW RATE:	46 SCFH
0.0	9.4	1064	1280
0.5	9.6	890	1120
1.0	9.7	716	960
1.5	9.8	508	960
3.0	10.0	148	800
4.5	10.0	92	880
6.0	10.0	70	960
9.5	9.8	42	880
22.5	9.3	16	880

TABLE 13-10. SODIUM BISULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 7.

RUN 1	11/2/79	AIR FLOW RATE:	23 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0.0	9.5	2328	2400
0.5	9.5	2164	2160
1.0	9.6	2052	2000
1.5	9.6	1830	1360
2.0	9.7	1450	1360
4.0	10.2	876	880
6.0	11.0	338	880
22.75	10.1	84	480
25.25	10.0	84	480

RUN 2	11/5/79	AIR FLOW RATE:	57 SCFH
0.0	9.5	2272	2160
0.5	9.6	2158	2160
1.0	9.6	1948	1840
1.5	9.7	1734	1680
2.0	9.8	1538	1600
4.5	10.7	450	800
6.5	11.0	232	640
9.75	10.6	152	480
22.50	9.8	62	400

present cannot be greater than indicated by this titration. However, other compounds including sulfide, thiosulfate, polysulfide, etc., will also react with iodate, so there may be less sulfite than indicated by the titration. Despite this lack of specificity, the test was a useful one as an indicator of the course of oxidation when the sample was aerated.

In cases where the only reducing agent is tetravalent sulfur (sulfur dioxide, sulfite, bisulfite, or metabisulfite), the COD should be the same as the oxygen demand from the iodate. The actual COD determinations nearly always gave results that were much higher than could be accounted for by the iodate titration (Table 13-4 through 13-10). This is no doubt due to compounds that are oxidized to sulfate in the COD test, but that are not oxidized by iodate or that are oxidized only to sulfur or tetrathionate or possibly other intermediate products.

Of greatest concern is the fact that sulfur, thiosulfate, and any other compounds that yield sulfur as an intermediate are not likely to be fully oxidized in the COD test because elemental sulfur is difficult to oxidize by wet reagents. The amount that will be oxidized will vary, depending upon seemingly trivial variations in the conditions of the test. Since the samples were relatively high in COD, small aliquot sizes were used in the analysis which may also cause variation due to the difficulty involved in making small liquid measurements. The reduction of COD in the aeration treatments generally appeared to be less than 50 percent of the original COD.

Whatever the explanation, the conventional COD tests were notably erratic, with variations much greater than are expected when oxidizing organic matter.

The proposed treatment would be expected to oxidize slowly the sulfide and sulfite, but other forms of sulfur would be oxidized only partially or not at all. The iodate titration results showed good consistency, and quite satisfactorily indicated the progress of aeration. The total reduction of iodate demand was generally 90 to 99 percent of the initial values.

The rate of reduction of iodate demand does not bear any consistent relationship to the rate of air application over the range of 11.5 to 57 SCFM. Evidently, the rate was determined by the kinetics of the reaction rather than the supply of oxygen. The rate always declines as the reaction proceeds, yet there is not a consistent relationship between the iodate demand and its rate of decline when comparing different runs. In the first two batches, iodate demand (expressed as oxygen) seemed to level off at about 3 to 5 mg/l after 24 hours, but in the others it was lower, down to a few tenths of a mg/l in some cases. It is possible that this residual demand is due to thiosulfate.

### 13.3.2 Statistical Evaluation

A statistical analysis was performed for chemical oxygen demand (COD), iodate demand, total suspended solids, and zinc in Figures 13-2 through 13-5 and Appendix A. Results of the analysis are summarized in Table 13-11 where the proposed BAT maximum 30-day average is compared to the estimated performance 30-day average values. The proposed BAT limitations are designed such that compliance can be achieved at least 95 percent of the time.

The statistical analysis for COD is based on values obtained at the termination of the aeration test run. This approach for data selection was used since it incorporates variability due to sample collection with variability in the laboratory analysis which should relate well to actual practice. Data point selection for iodate demand was similar although not as critical since the analytical results were very uniform throughout the test runs. Appendix B presents the iodate demand curves based on data in Tables 13-3 through 13-10.

### 13.3.3 Conclusions

The treatability test results serve as a good indication of the general applicability of the treatment technology considered to the proposed BAT regulations. Results show that the pollutant concentration basis for the proposed BAT maximum 30-day average effluent limitations is achievable for COD with the prescribed treatment technology. However, in view of the wide variability observed for the conventional COD test, it is recommended that the iodate/iodide test be considered for possible use as the basis for an effluent limitation on sulfite/bisulfite or the equivalent oxygen demand.

The zinc concentration was determined during the course of study before and after pH adjustment with caustic soda. Results indicate that there is a significant reduction in the dissolved zinc concentration due to alkaline precipitation. In actual practice, clarification and possibly the use of chemical coagulating or flocculating agents may be required to assist in separating the metal hydroxide precipitates.

TABLE 13-11. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE  
FOR THE SODIUM BISULFITE SUBCATEGORY

STREAM: Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Chemical Oxygen Demand COD	680	600
Total Suspended Solids, TSS	22	274
Iodate Demand (as Oxygen)	—(1)	37

(1) Recommended in place of conventional COD for the proposed limitations.

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Bisulfite	Chemical Oxygen Demand	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	680
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	600
Long Term Average	(mg/l):	480
Standard Deviation of 30-day Averages	(mg/l):	75
Probability of Achieving Proposed Maximum 30-day Average	(%):	>99
Number of Observations:		15

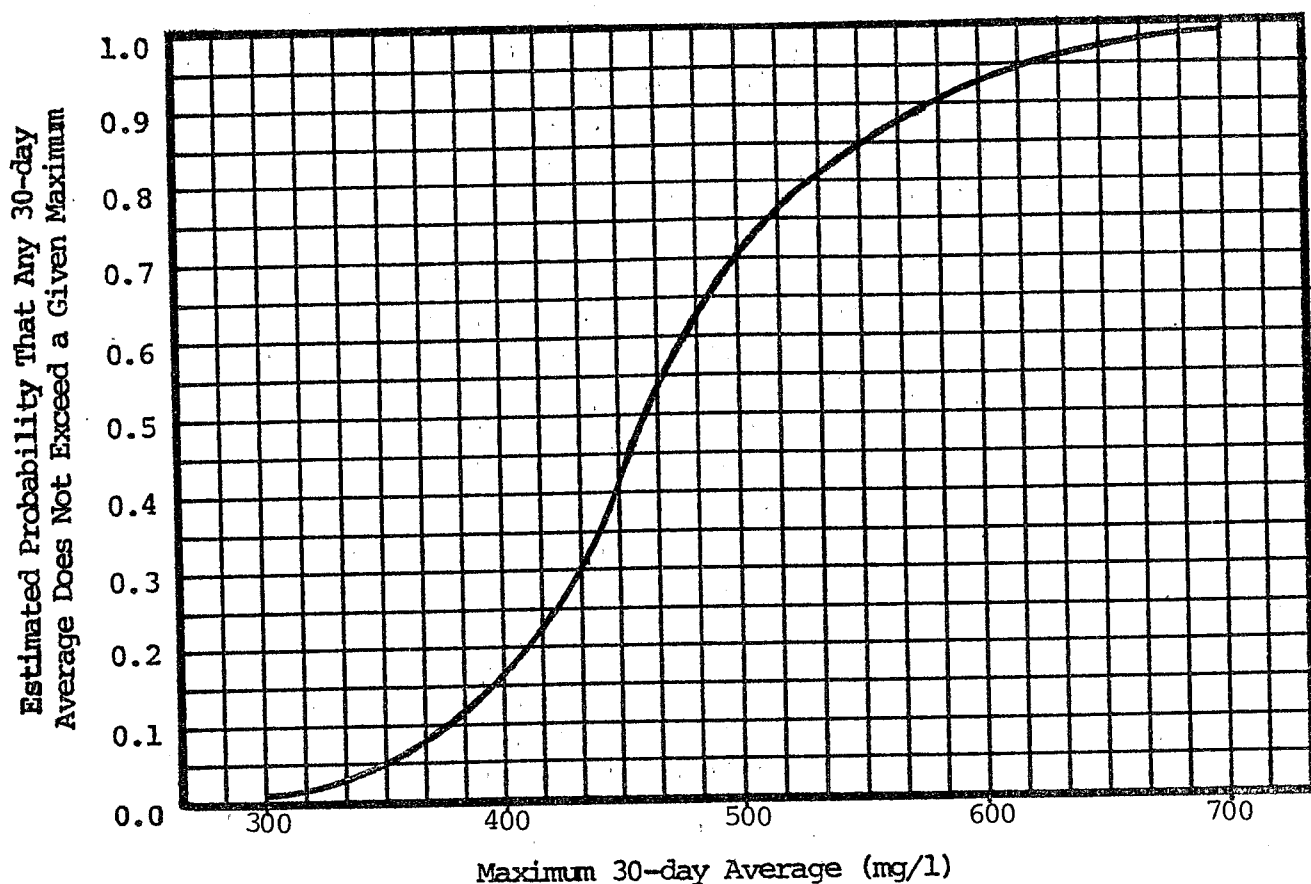


Figure 13-2. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Bisulfite	Total Suspended Solids	
<hr/>		
Proposed Maximum 30-day Average	(mg/l):	22
<hr/>		
95th Percentile ( $Z = 1.64$ )	(mg/l):	270
Long Term Average	(mg/l):	240
Standard Deviation of 30-day Averages	(mg/l):	23
Probability of Achieving Proposed Maximum 30-day Average	(%):	<0.01
Number of Observations:		16
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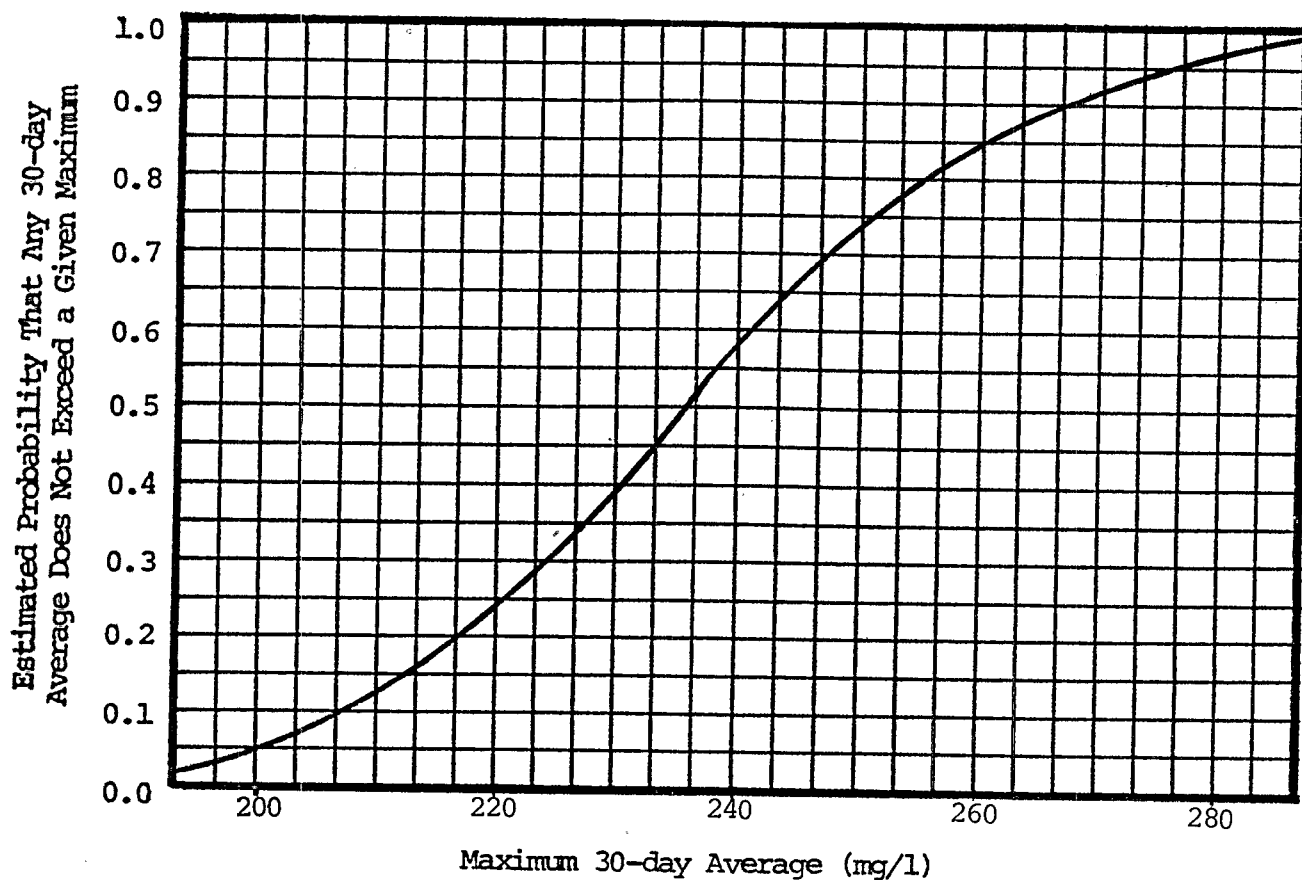


Figure 13-3. Estimated Performance of Proposed  
BAT Treatment



SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Bisulfite	Iodate Demand	
Proposed Maximum 30-day Average	(mg/l):	None
95th Percentile ( $Z = 1.64$ )	(mg/l):	37
Long Term Average	(mg/l):	27
Standard Deviation of 30-day Averages	(mg/l):	6.5
Probability of Achieving Proposed Maximum 30-day Average	(%):	Not Applicable
Number of Observations:		14

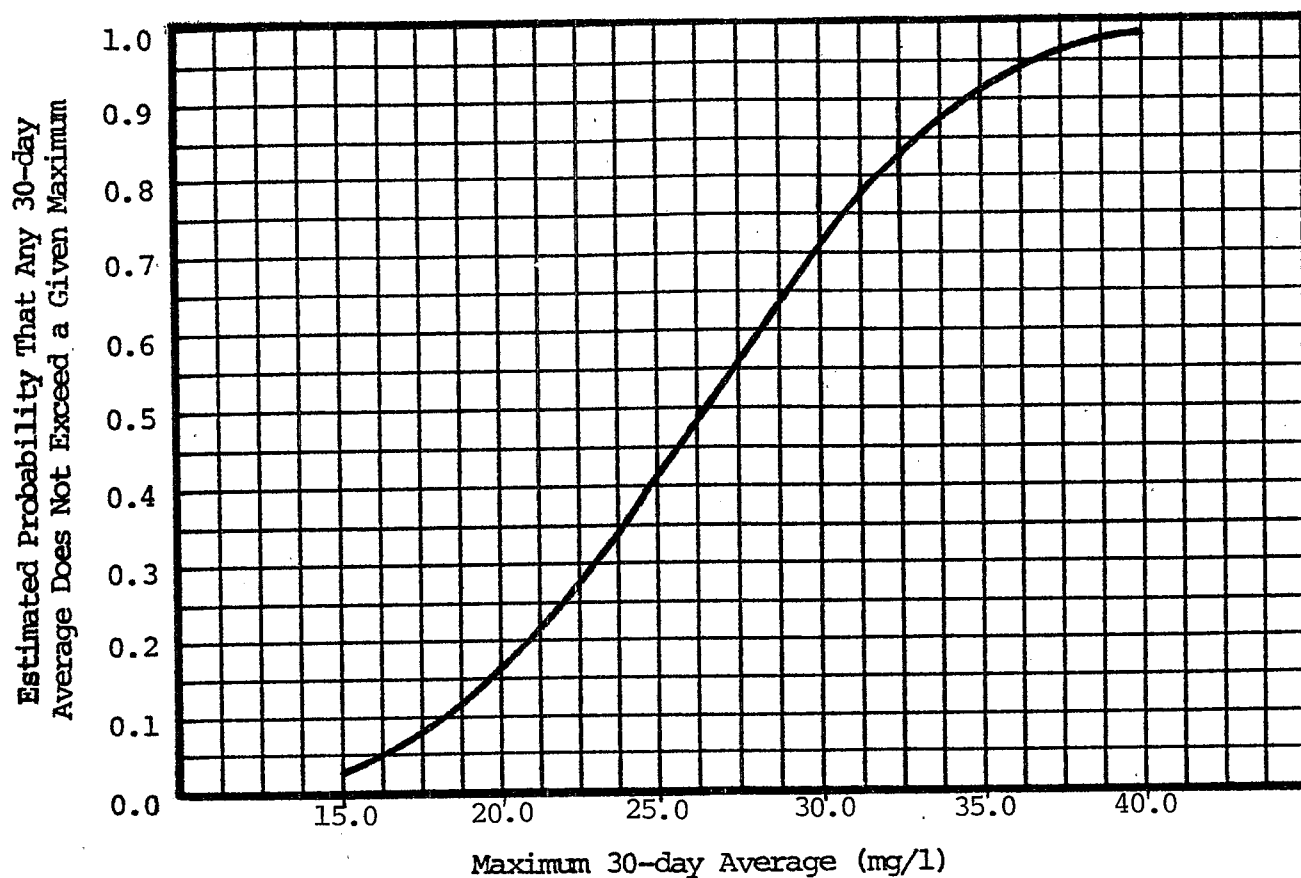


Figure 13-4. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Bisulfite	Zinc	
Proposed Maximum 30-day Average	(mg/l):	0.50
95th Percentile ( $Z = 1.64$ )	(mg/l):	1.2
Long Term Average	(mg/l):	0.85
Standard Deviation of 30-day Averages	(mg/l):	0.20
Probability of Achieving Proposed Maximum 30-day Average	(%):	Not Applicable
Number of Observations:		16

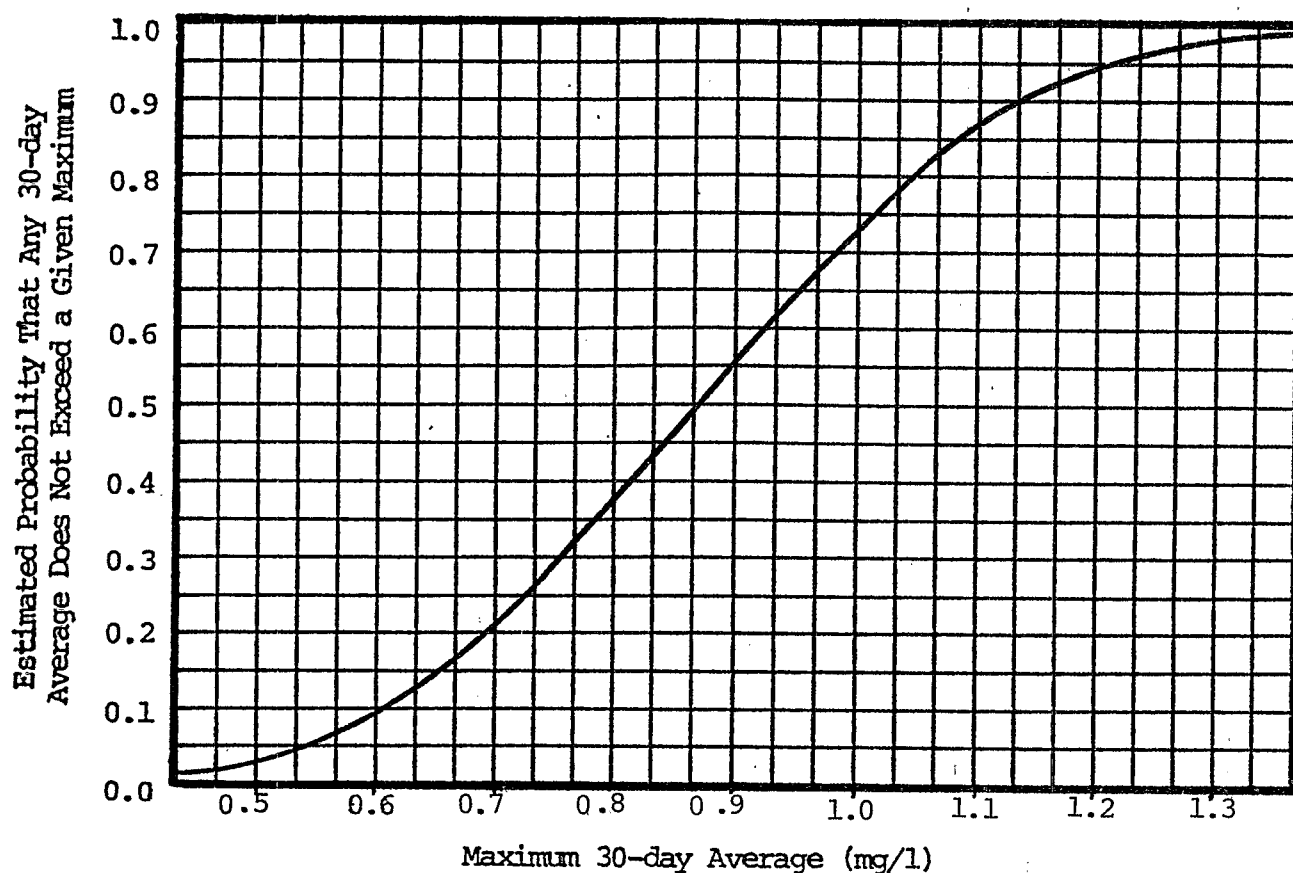


Figure 13-5. Estimated Performance of Proposed  
BAT Treatment

## SECTION 14.0

### SODIUM HYDROSULFITE SUBCATEGORY (FORMATE PROCESS)

#### 14.1 INTRODUCTION

##### 14.1.1 General Considerations

The treatability tests were carried out at Plant #672 from September 10 to October 11, 1979. During this period, a total of 18 test runs were completed. Enough waste water was collected most of the time to run two tests simultaneously.

##### 14.1.2 Sample Point Location

Samples were collected from the sodium hydrosulfite waste stream as indicated in the process waste flow schematic in Figure 14-1 for the selected plant. Sample collection was made at the end of the storage pond pipe inlet.

#### 14.2 TREATABILITY TEST MODEL OPERATION

##### 14.2.1 Treatment Technology Tested

The waste treatment processes tested for this subcategory consisted of physical (mechanical) aeration to treat readily oxidized chemical oxygen demand (COD) such as sulfite, and to also test the use of dual media filtration. In view of the difficulty involved in establishing a properly seeded and representative biochemical oxidation system on a small test scale, only chemical oxidation (i.e., physical aeration) was studied. However, it should be understood that this technology may be coupled with a well established biochemical oxidation process to further oxidize biodegradable forms of COD and fully represent the performance of the best available technology.

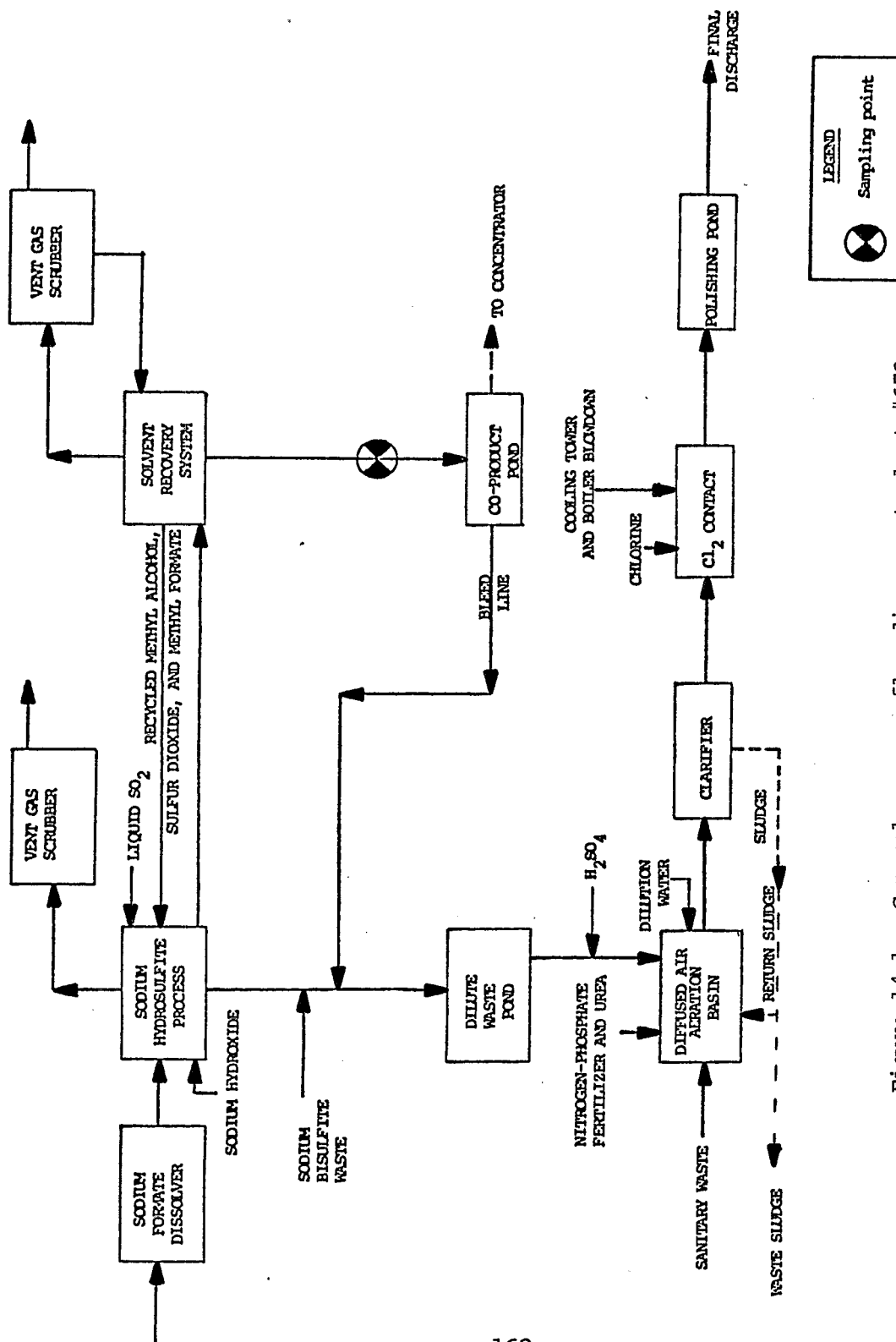


Figure 14-1. General process flow diagram at plant #672 showing the sampling points. (Sodium hydrosulfite manufacture.)

#### 14.2.2 Waste Water Characterization

The results of the waste water characterization for the sodium hydrosulfite subcategory are presented in Table 14-1. Review of the results indicates a high concentration of organics and heat unstable inorganics at levels of approximately 1200 mg/l. Organics and heat unstable inorganics such as elemental sulfur are determined as the difference between the total residue solids and fixed residue solids.

#### 14.2.3 Details on Treatability Test Operation

Table 14-2 presents the operational parameters for the treatability tests made in the sodium hydrosulfite subcategory.

The removal of COD in the waste water was accomplished by diffusing air through the waste. Five different air flow rates were used in the study including 11.5, 23, 35, 46, and 57 SCFH (standard cubic feet per hour). The pH of the raw waste water was always adjusted to around 7.2 by the use of lime or H<sub>2</sub>SO<sub>4</sub> as required. Following this, and after adjustment of the air flow rate to the desired value, the progress of the COD reduction was followed by repeated iodate titrations.

### 14.3 TEST RESULTS

#### 14.3.1 Discussion of Results

The analytical results and removal efficiencies for COD, iodate demand, zinc, chromium, and TSS are shown in Table 14-3. The variations in COD and oxygen demand from iodate (in acid iodide solution) during aeration are shown in Tables 14-4 through 14-14 for each of the test runs made. Chemical oxygen demand values obtained during test runs 1 through 6 in Tables 14-4 through 14-6 are from Table 14-3 which presents results obtained at the Springfield, Virginia laboratory. All other COD values were determined at the test site in a mobile laboratory. Even though results are presented for chromium and zinc, the main objective of this study was the removal of COD and TSS. Any removal of chromium and zinc can only be considered as incidental to the aeration tested.

Organic matter as well as sulfur compounds are present in this waste water. The COD values in the raw waste show a wide range, from about 2,000 mg/l to more than 20,000 mg/l. This demand declines during aeration, but the results are erratic. The COD test does not appear to be a very good parameter for monitoring degree of treatment when physical aeration is applied. This is perhaps due to the difficulty of oxidizing the sulfur

TABLE 14-1. WASTE WATER CHARACTERIZATION FOR THE SODIUM  
HYDROSULFITE SUBCATEGORY

Parameter	Amount Present (mg/l)
Calcium	6.9
Chromium (total)	0.035
Chromium (hexavalent)	0.004
Potassium	15
Magnesium	8
Sodium	9,000
Zinc	0.29
Total Suspended Solids	264
Total Residual Solids	26,856
Fixed Residue Solids	25,780
Total Dissolved Solids	26,000
Methyl Orange Alkalinity (as CaCO <sub>3</sub> )	10,220
Chloride	155
Sulfate	4,500
Nitrate	0.33
Carbonate (as CaCO <sub>3</sub> )	2,160
Bicarbonate (as CaCO <sub>3</sub> )	8,060

TABLE 14-2. TREATABILITY TEST CONDITIONS

SUBCATEGORY: Sodium Hydrosulfite		TREATMENT: Extended Aeration Plus Dual Media Filtration																
Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Batch Number	1	1	2	2	3	3	4	5	5	6	6	7	7	8	9	9	10	11
Date	9/10	9/10	9/11	9/11	9/17	9/17	9/17	9/19	9/24	9/24	9/26	9/26	10/1	10/1	10/4	10/8	10/8	10/11
Volume of Waste Water Aerated (gallons)	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26
Raw Waste Water pH	7.3	7.3	7.2	7.2	7.3	7.0	7.0	6.5	9.1	8.5	6.8	7.1	11.8	8.4	11.5	10.1	9.4	11.5
pH Reached by Caustic or Acid Addition	7.3	7.3	7.2	7.2	7.3	7.0	7.0	7.2	7.3	7.3	7.5	7.1	7.5	8.4	5.6	7.4	5.5	NDA
Aeration Rate (SCFH)*	57	57	57	57	46	46	46	46	46	46	35	35	35	35	23	23	23	11.5
Aeration Time (Hrs.)	16	16	34	34	52	60	60	29	24	44	56	36	50	63	20	49	31	16
Setting Time (Hrs.)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Time Filter Effluent Sampling After Start of Filtration (Mins.)	100	82	60	60	60	60	60	60	80	90	60	90	90	90	60	50	90	60

\*SCFH - Standard cubic feet per hour.

TABLE 14-3. ANALYTICAL RESULTS FOR THE PLANT SELECTED FOR  
STUDY IN THE SODIUM HYDROSULFITE SUBCATEGORY

Test Number	TREATMENT: Extended Aeration Plus Dual Media Filtration																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
All reported values in mg/l																		
Chemical Oxygen Demand, COD (1)																		
Raw Waste																		
Total COD	3190	3270	1940	1940	4080	1480	11520	1460	1460	3410	3410	7340	7340	6700	2410	4900	4340	2410
Dissolved COD	2630	2710	2330	2330	3570	3570	9860	1230	1230	3650	3650	7620	7620	4960	2450	3870	7380	2450
Supernatant (2)																		
Total COD	2710	2460	1750	1860	1190	2060	14690	728	958	2870	3350	4140	3260	4570	1850	3320	NDA	901
Dissolved COD	2550	2300	1550	1630	950	1700	14410	460	996	2790	3210	4140	2350	4260	2130	3100	NDA	901
Filter Effluent																		
Total COD	2460	2140	1320	1470	1130	1740	14450	383	536	2720	3030	3880	4060	4330	2210	2950	NDA	901
Dissolved COD	2300	2200	1360	1550	1030	1660	13900	NDA	690	2640	3260	7620	3260	4100	2210	1790	NDA	917
Iodate Demand as Oxygen																		
Raw Waste	2.5	25.7	26.5	26.5	236.7	236.7	929.1	39.1	41.8	439.0	232.0	949.0	800.0	273.0	88.6	47.2	223.4	484.8
Aerated Waste	16.6	13.6	0.2	0.4	1.0	6.5	0.3	0.4	0.3	2.2	0.4	5.4	10.0	0.3	0.4	0.9	164.4	0.6
Total Chromium, Cr (T)																		
Raw Waste	1.01	1.78	0.26	0.03	1.11	1.11	0.38	0.07	0.07	0.10	0.10	0.45	0.05	0.03	0.15	0.15	0.32	0.39
Total Cr (T)	0.02	0.047	0.02	0.02	0.13	0.13	2.10	0.01	0.01	0.05	0.03	0.03	0.74	0.09	0.09	0.06	0.06	0.04
Dissolved Cr (T)																		
Supernatant (2)																		
Total Cr (T)	0.14	0.11	0.10	0.01	0.32	0.52	9.09	0.08	0.13	0.05	10	0.13	0.15	1.50	0.40	0.03	1.81	NDA
Dissolved Cr (T)	0.03	0.02	0.05	0.01	0.10	0.06	8.70	0.01	0.02	0.02	9.8	0.10	0.11	1.45	0.33	0.01	1.70	NDA
Filter Effluent																		
Total Cr (T)	0.007	0.011	0.05	0.02	0.10	0.11	9.09	0.01	0.05	0.01	8.5	0.09	0.03	1.53	0.27	0.01	1.42	NDA
Dissolved Cr (T)	0.005	0.010	0.01	0.01	0.07	0.08	9.38	0.01	0.03	0.01	9.3	0.09	0.04	1.56	0.27	0.02	1.74	NDA

(1) All COD values reported are from laboratory analyses performed in Springfield, Virginia on samples shipped from the test site.

(2) After aeration.



TABLE 14-3. - continued

Test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
All reported values in mg/l																		
<u>Zinc, Zn</u>																		
Raw Waste	5.32	24.80	0.94	0.94	5.85	5.85	4.21	0.93	0.93	0.67	0.67	2.70	2.70	0.27	1.04	1.04	1.59	2.54
Total Zn	0.06	0.15	0.13	0.13	0.50	0.50	1.44	0.06	0.06	0.34	0.34	0.43	0.43	6.24	0.59	0.59	0.11	0.32
Dissolved Zn																		
Supernatant	0.37	0.33	0.53	0.64	1.80	2.51	8.18	0.32	0.07	0.52	2.81	9.97	6.24	7.45	1.75	0.28	3.41	NDA
Total Zn	0.12	0.11	0.35	0.43	0.53	0.36	7.82	0.13	0.04	0.48	2.85	9.97	3.89	7.45	1.67	0.17	3.49	NDA
Dissolved Zn																		
Filter Suspended																		
Total Zn	0.09	0.09	0.04	0.49	0.52	0.52	7.87	0.06	0.03	0.42	2.45	9.93	0.65	7.41	1.75	0.22	3.41	
Dissolved Zn	0.08	0.06	0.36	0.45	0.40	0.36	8.03	0.06	0.04	0.42	2.90	9.86	0.63	7.52	1.51	0.20	3.25	
Total Suspended																		
Solids, TSS																		
Raw Waste	830	900	300	300	290	290	550	108	108	219	219	111	111	810	93			
Supernatant	92	94.5	16	184	216	220	132	86	283	41	38	125	294	62	26			
Filter Effluent	4.8	5.6	38	58	14	51	126	12	7.8	8	13	63	55	13	0.3	28.6		0.3

TABLE 14-4. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 1

RUN 1	9/10/79	AIR FLOW RATE:	57 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD (1) mg/l
0	7.3	25.3	3190
2	7.8	27.6	-
4	7.9	27.4	-
6	8.0	27.6	-
8	8.24	22.8	-
10	8.27	21.4	-
12	8.24	19	-
16	8.25	16.6	2710

RUN 2	9/10/79	AIR FLOW RATE:	57 SCFH
0	7.3	25.7	3270
2	7.8	25.0	-
4	8.14	24.7	-
6	8.25	21.8	-
8	8.3	18.6	-
10	8.3	18.0	-
12	8.35	15.2	-
16	8.3	13.6	2460

(1) From Table 14-3

TABLE 14-5. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 2

RUN 3	9/13/79	AIR FLOW RATE:	57 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD (1) mg/l
0	7.3	26.5	1940
2	7.5	26.3	-
4	7.93	23.0	-
6	8.11	20.9	-
8	8.15	18.6	-
10	8.16	16.7	-
14	8.2	14.0	-
18	8.16	12.4	-
22	7.0	8.7	-
26	7.2	2.9	-
30	6.24	0.2	-
34	6.71	0.2	1750

RUN 4	9/13/79	AIR FLOW RATE:	57 SCFH
0	7.2	26.5	1940
2	7.27	27.7	-
4	7.26	25.1	-
6	7.4	22.9	-
8	7.3	21.8	-
10	7.28	21.2	-
14	7.25	16.0	-
18	6.74	9.8	-
22	6.05	4.2	-
26	6.14	1.4	-
30	6.17	0.4	-
34	6.02	0.4	1860

(1) From Table 14-3

TABLE 14-6. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 3

RUN 5	9/19/79	AIR FLOW RATE:	46 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD (1) mg/l
0	7.01	236.7	4080
2	7.51	234	-
6	7.79	223.9	-
12	8.15	111.8	-
18	8.60	27.3	-
20	8.62	21	-
24	8.53	11.8	-
28	8.38	10	-
32	8.14	8.8	-
36	8.05	7.4	-
44	8.09	5.2	-
48	8.14	4.4	-
52	8.09	2.9	-
56	8.12	1.0	-
60	8.16	1.03	1190

RUN 6	9/19/79	AIR FLOW RATE:	46 SCFH
0	7.01	236.7	4080
2	7.16	283.5	-
6	7.22	272.2	-
12	7.04	155.4	-
18	7.65	10.1	-
20	7.64	9.6	-
24	7.75	9.2	-
28	7.86	8.6	-
32	7.93	9.0	-
36.5	7.85	8.6	-
44	8.02	7.6	-
48	8.14	6.8	-
52	8.28	6.5	2060

(1) From Table 14-3

TABLE 14-7. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 4

RUN 7	9/20/79	AIR FLOW RATE:	46 SCFH
Aeration Time hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	6.5	929.1	11520
1			22800
2			22420
3			21840
4	6.75	425.3	21460
8	6.46	340.8	20120
13	2.6	5.2	20310
17	2.6	0.5	18010
23	2.6	0.24	17240
29	2.6	0.3	14690 <sup>(1)</sup>

(1) From Table 14-3

TABLE 14-8. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 5

RUN 8	9/24/79	AIR FLOW RATE:	46 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	9.2	39.1	1460
1	7.75	34.2	843
2	7.86	37.9	728
3	8.07	32.2	613
4	8.17	33.4	1130
8	8.16	29.6	-
12	8.08	25.3	1090
20	7.8	0.5	854
24	8.2	0.4	892

RUN 9	9/24/79	AIR FLOW RATE:	57 SCFH
0	8.80	41.8	1460
1	7.78	36.2	1050
2	7.98	38.4	1160
3	8.04	32.6	1160
4	8.16	38.3	1160
8	8.15	34.0	1090
12	8.16	30.3	1010
20	8.20	23.5	1010
24	8.17	19.9	854
28	8.12	13.3	854
32	8.10	7.0	776
36	8.25	1.2	854
40	8.05	0.4	698
44	8.01	0.3	776

TABLE 14-9. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 6

RUN 10	9/26/79	AIR FLOW RATE:	35 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	6.89	439.0	3410
1	-	-	5620
2	-	-	5300
3	-	-	5300
4	7.54	285.3	5220
8	7.57	279.0	5220
12	7.54	227.7	4740
16	7.61	188.6	4620
20	7.58	162.1	4340
24	7.48	111.5	4400
28	7.40	72.1	4300
32	7.40	43.0	4220
36	7.46	23.8	4100
40	7.48	15.8	3980
46	7.22	12.5	3670
50	7.00	5.5	3390
56	6.90	2.2	3310

RUN 11	9/26/79	AIR FLOW RATE:	35 SCFH
0	7.1	232	3410
1	-	-	5380
2	-	-	5540
3	-	-	5500
4	3.2	0.66	5260
8	2.75	3.0	4790
12	2.81	3.1	4640
16	2.82	2.8	4170
20	2.82	2.0	4100
24	2.82	2.0	3710
28	2.90	0.4	3720
32	2.93	0.3	3720
36	2.97	0.4	3400

TABLE 14-10. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 7

RUN 12	10/1/79	AIR FLOW RATE:	35 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	11.8	947	7340
2	-	-	8750
3	7.46	947	7950
5	-	-	8030
6	7.4	869.2	-
10	-	-	17600
14	5.81	83	18560
18	5.31	110.2	9200
22	5.19	5.4	5760
26	5.1	5.6	6320
30	5.0	5.0	5600
38	4.9	4.1	4560
42	4.9	4.3	4650
46	4.88	5.4	4400
50	4.9	5.4	4240
RUN 13	10/1/79	AIR FLOW RATE:	35 SCFH
0	8.4	800	7340
2	-	-	-
3	8.36	800	6610
5	-	-	6570
6	8.44	614.8	-
10	-	-	5290
14	8.93	181	5850
18	8.99	111.4	5170
22	8.97	62.2	4970
26	8.9	42.6	4770
30	8.8	27.3	4730
38	8.6	17.8	4090
42	8.7	17.3	4330
46	8.5	14.7	4330
50	8.5	12.9	4180
54	8.6	11.1	3700
63	8.67	10.0	3630



TABLE 14-11. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 8

RUN 14		10/4/79	AIR FLOW RATE:	35 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l	
0	11.46	273	6700	
1	-	-	5320	
2	-	-	5130	
3	-	-	4730	
4	3.5	0.4	4580	
8	3.07	0.4	4650	
20	3.12	0.3	4500	

TABLE 14-12. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 9

RUN 15	10/8/79	AIR FLOW RATE:	23 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	9.35	88.6	2410
1	5.97	81.1	2740
2	5.88	78.6	3020
3	5.78	83.1	2940
4	5.68	75.7	2780
9	4.13	8.2	2460
17	4.18	2.6	2600
21	4.18	2.2	2600
25	4.18	2.1	2520
29	4.17	0.7	2520
31	4.18	0.6	2450
33	4.17	0.4	2370

RUN 16	10/8/79	AIR FLOW RATE:	23 SCFH
0	10.4	47.2	2410
1	1.48	98.6	1320
2	7.55	100.8	1350
3	7.62	106.7	1320
4	7.65	90.7	1400
9	7.75	79.9	1290
17	7.80	58.7	1260
21	8.13	42.8	1220
25	8.13	37.8	1180
29	7.79	26.8	1180
33	7.66	19.6	1140
41	7.58	10.0	1080
45	7.58	4.6	1010
49	7.30	0.9	1010

TABLE 14-13. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 10

RUN 17	10/10/79	AIR FLOW RATE:	23 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	7.27	223.4	4340
1	7.29	200.2	3600
4	7.44	173	3720
13	7.52	212.2	3720
18	7.57	188.2	3440
24	7.60	176.6	3320
28	7.66	177	3080
37	7.62	164.4	3000

TABLE 14-14. SODIUM HYDROSULFITE SUBCATEGORY  
TREATMENT BY AERATION. Batch 11

RUN 18	10/11/79	AIR FLOW RATE:	23 SCFH
Aeration Time, hr.	pH	Iodate Demand as Oxygen, mg/l	COD mg/l
0	11.5	484.8	4900
1	4.85	347.2	4430
2	3.89	337.6	4030
6	2.34	0.8	3640
16	4.10	0.6	3400

from some of its intermediate oxidation states, such as elemental sulfur. Sulfide was sometimes present, as noted by the odor, and it is quite likely that elemental sulfur would be produced to some extent in the oxidation processes. The amount of this sulfur that would be oxidized by chromic acid in the COD test would be variable and not reproducible in the standard procedure. The extent of oxidation of COD by aeration was generally in the range of 20% to 60%.

The iodate demand, as determined by titration in the presence of acid and iodate, was monitored during the aeration test runs. The results are shown in terms of the equivalent oxygen demand. The iodine produced from the iodate reacts with sulfide, polyfides, sulfite, thiosulfate, and possibly with some other sulfur species. The iodate demand (as oxygen) was always much less than the COD. The ratio was highly erratic, but was usually between 1% and 10%.

During the aeration runs, the iodate demand declined. The results are somewhat erratic, possibly indicating poor reproducibility with this particular waste. However, the iodate demand does approach zero after a sufficient period, usually within 24 hours. The air supply rate, ranging from 11.5 SCFH to 57 SCFH, did not appear to affect the rate of decline of the demand. The rate evidently is controlled by the kinetics of the reaction rather than the air supply over the range of conditions of the runs.

The pH generally declined during aeration, and sometimes it declined sharply to levels between 2.5 and 5.0. In these cases, the disappearance of iodate demand was very rapid.

The decline of iodate demand shows that sulfide, sulfite, and hydrosulfide were approaching zero. These are substances that react with oxygen fairly readily although the rate limiting steps in the reaction mechanisms are not known. The iodate demand test is probably an adequate indication of the tendency of the waste water to deplete oxygen from receiving waters by chemical reactions. There remains the possibility that biochemical processes can cause oxygen depletion, and use of a properly established biochemical oxidation treatment system should further reduce the COD, as is currently practiced.

#### 14.3.2 Statistical Evaluation

Table 14-15 and Figures 14-2 through 14-6 show the results obtained from a statistical analysis of the treatment data. A statistical analysis is included for zinc, chromium, and iodate demand although the treatment technology tested was specifically designed to evaluate chemical oxygen demand and total suspended solids removal only.

TABLE 14-15. COMPARISON BETWEEN PROPOSED BAT LIMITATIONS AND  
ESTIMATED TREATABILITY PERFORMANCE FOR  
THE SODIUM HYDROSULFITE SUBCATEGORY (FORMATE PROCESS)

STREAM: Effluent

Pollutant	Concentration Basis (mg/l)	
	Proposed BAT Maximum 30-Day Average	Est. Treat. Performance 30-Day Average
Chemical Oxygen Demand, COD	2600	3000
Total Suspended Solids, TSS	25	110

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Hydrosulfite	Chemical Oxygen Demand	
Proposed Maximum 30-day Average	(mg/l) :	2600
95th Percentile ( $Z = 1.64$ )	(mg/l) :	3000
Long Term Average	(mg/l) :	2600
Standard Deviation of 30-day Averages	(mg/l) :	270
Probability of Achieving Proposed Maximum 30-day Average	(%) :	58
Number of Observations:		17

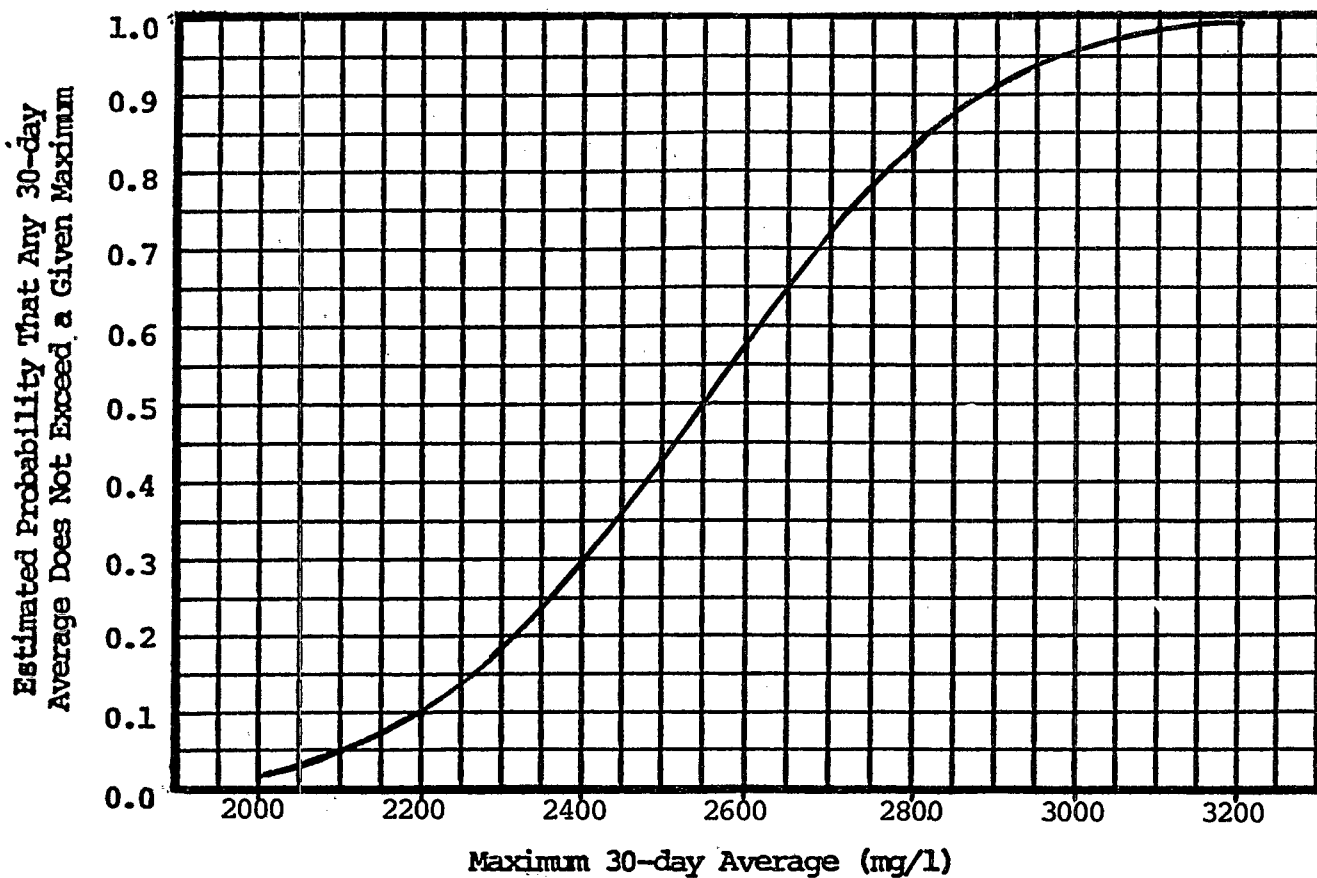


Figure 14-2. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Hydrosulfite	Total Suspended Solids	
Proposed Maximum 30-day Average	(mg/l):	25
95th Percentile ( $Z = 1.64$ )	(mg/l):	110
Long Term Average	(mg/l):	50
Standard Deviation of 30-day Averages	(mg/l):	34
Probability of Achieving Proposed Maximum 30-day Average	(%):	24
Number of Observations:		17

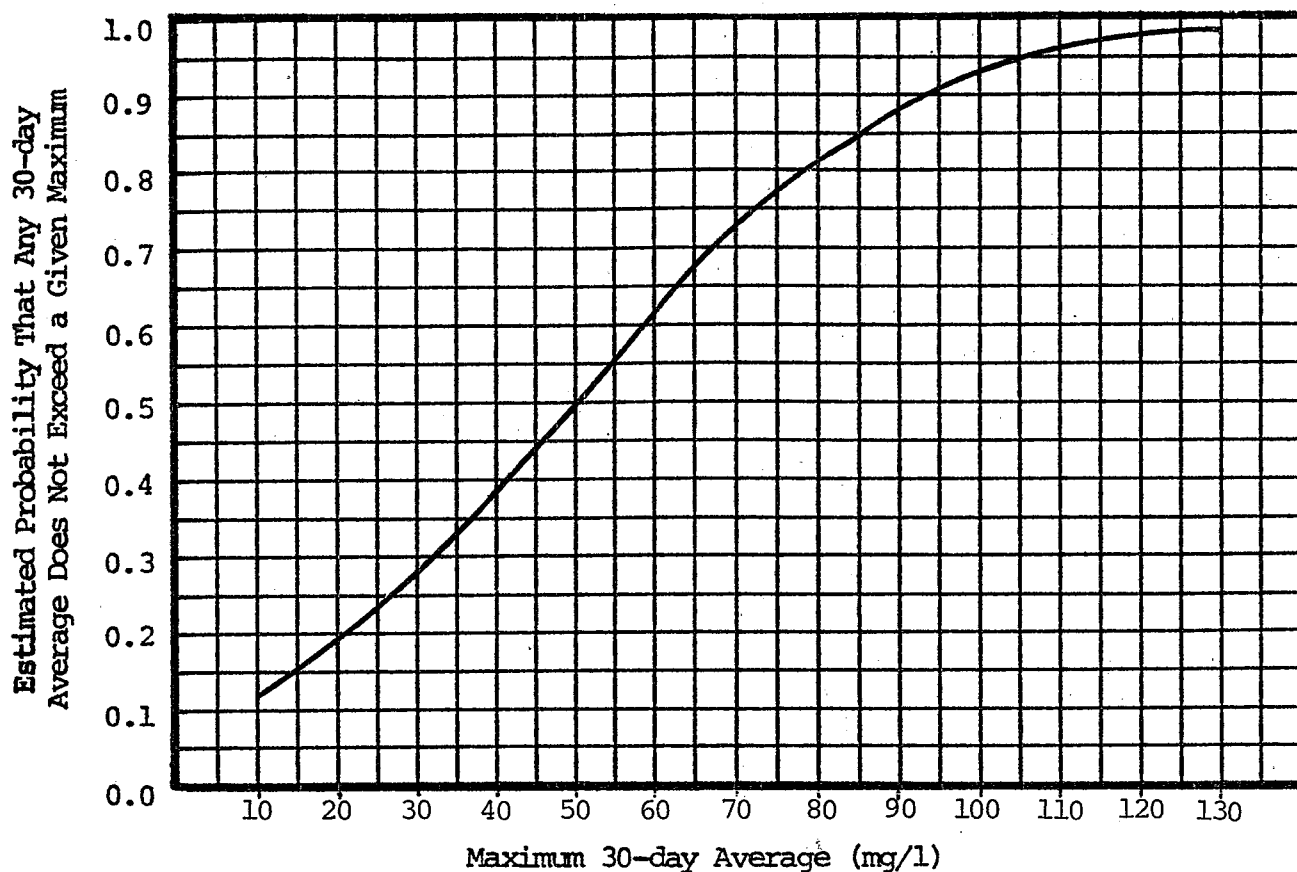


Figure 14-3. Estimated Performance of Proposed  
BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Hydrosulfide	Zinc	
Proposed Maximum 30-day Average	(mg/l):	0.50
95th Percentile ( $Z = 1.64$ )	(mg/l):	7.5
Long Term Average	(mg/l):	2.9
Standard Deviation of 30-day Averages	(mg/l):	2.8
Probability of Achieving Proposed Maximum 30-day Average	(%):	Not Applicable
Number of Observations:		17

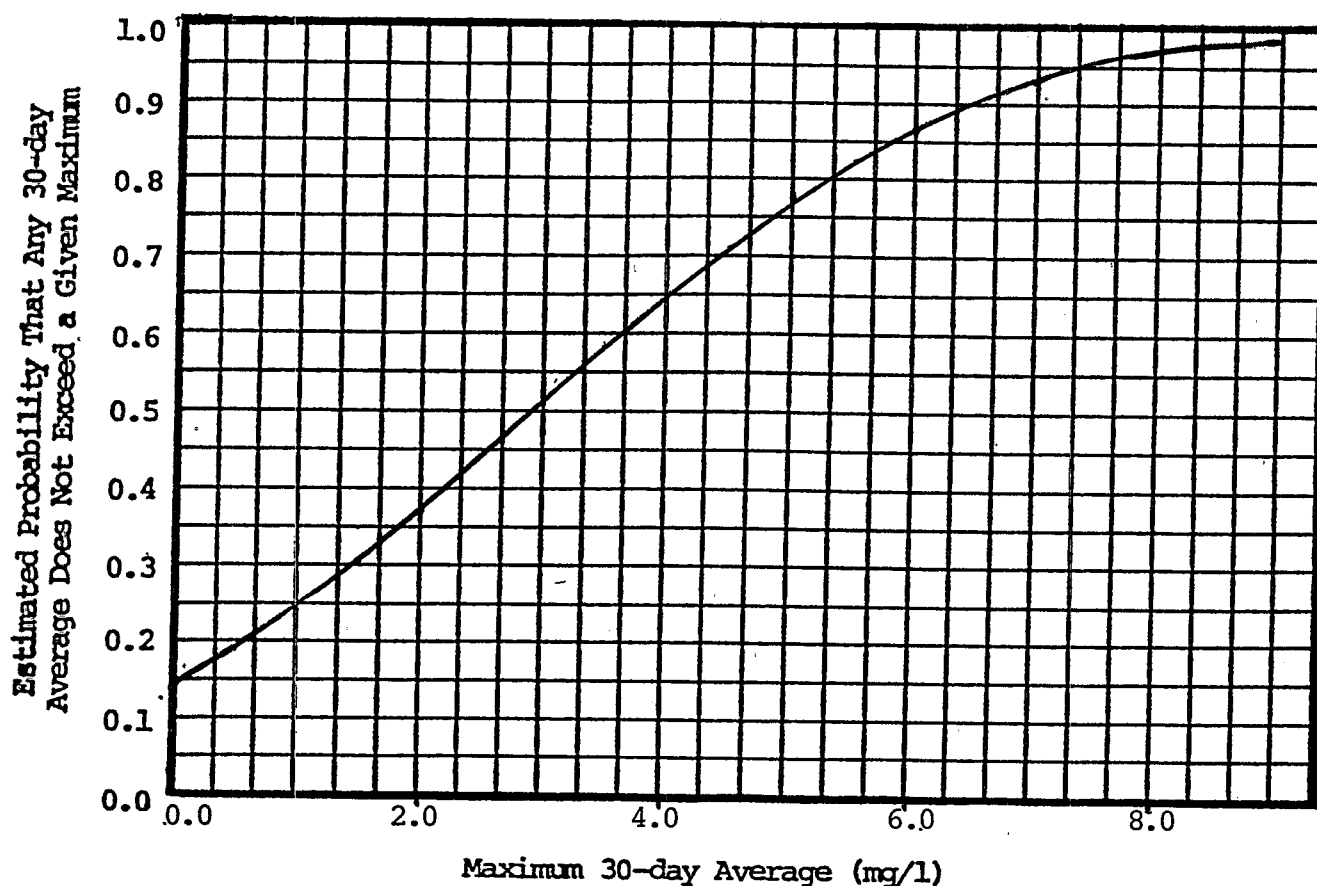


Figure 14-4. Estimated Performance of Proposed BAT Treatment



SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Hydrosulfite	Chromium	
Proposed Maximum 30-day Average	(mg/l):	0.10
95th Percentile ( $Z = 1.64$ )	(mg/l):	6.5
Long Term Average	(mg/l):	1.3
Standard Deviation of 30-day Averages	(mg/l):	3.2
Probability of Achieving Proposed Maximum 30-day Average	(%):	Not Applicable
Number of Observations:		17

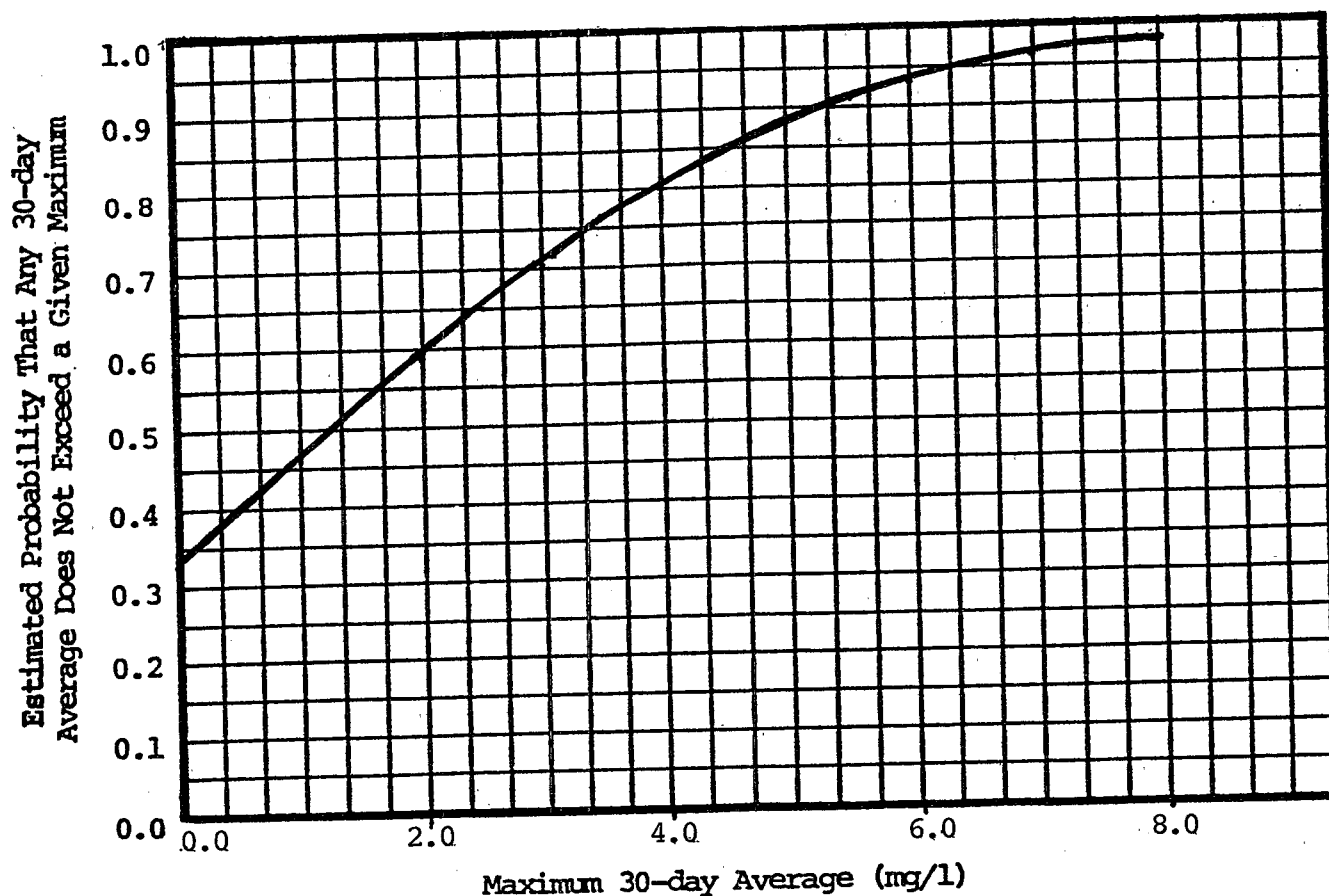


Figure 14-5. Estimated Performance of Proposed BAT Treatment

SUBCATEGORY	POLLUTANT	PRECIPITANT
Sodium Hydrosulfite	Iodate Demand	
Proposed Maximum 30-day Average	(mg/l) :	None
95th Percentile ( $Z = 1.64$ )	(mg/l) :	6.4
Long Term Average	(mg/l) :	3.5
Standard Deviation of 30-day Averages	(mg/l) :	1.8
Probability of Achieving Proposed Maximum 30-day Average	(%) :	Not Applicable
Number of Observations:		17

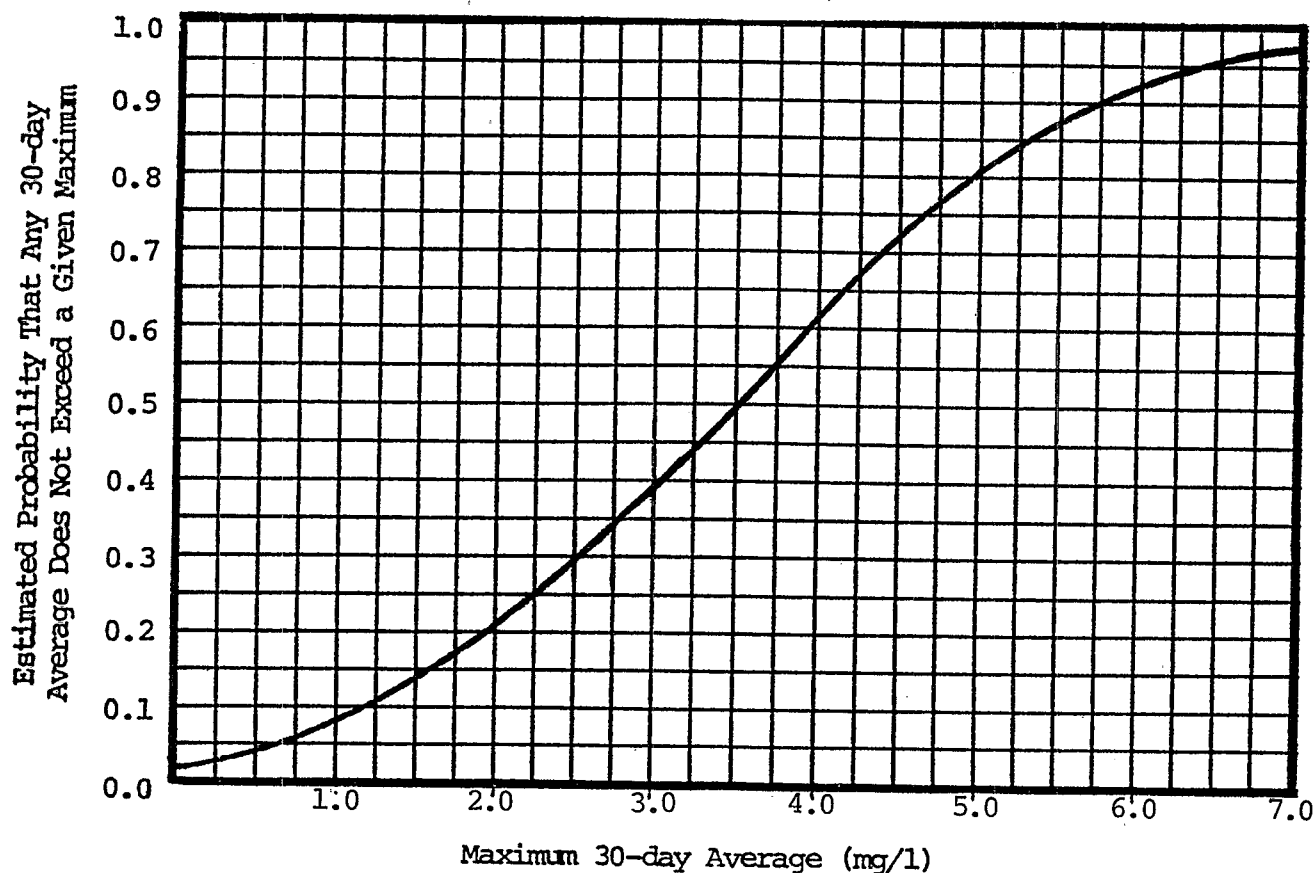


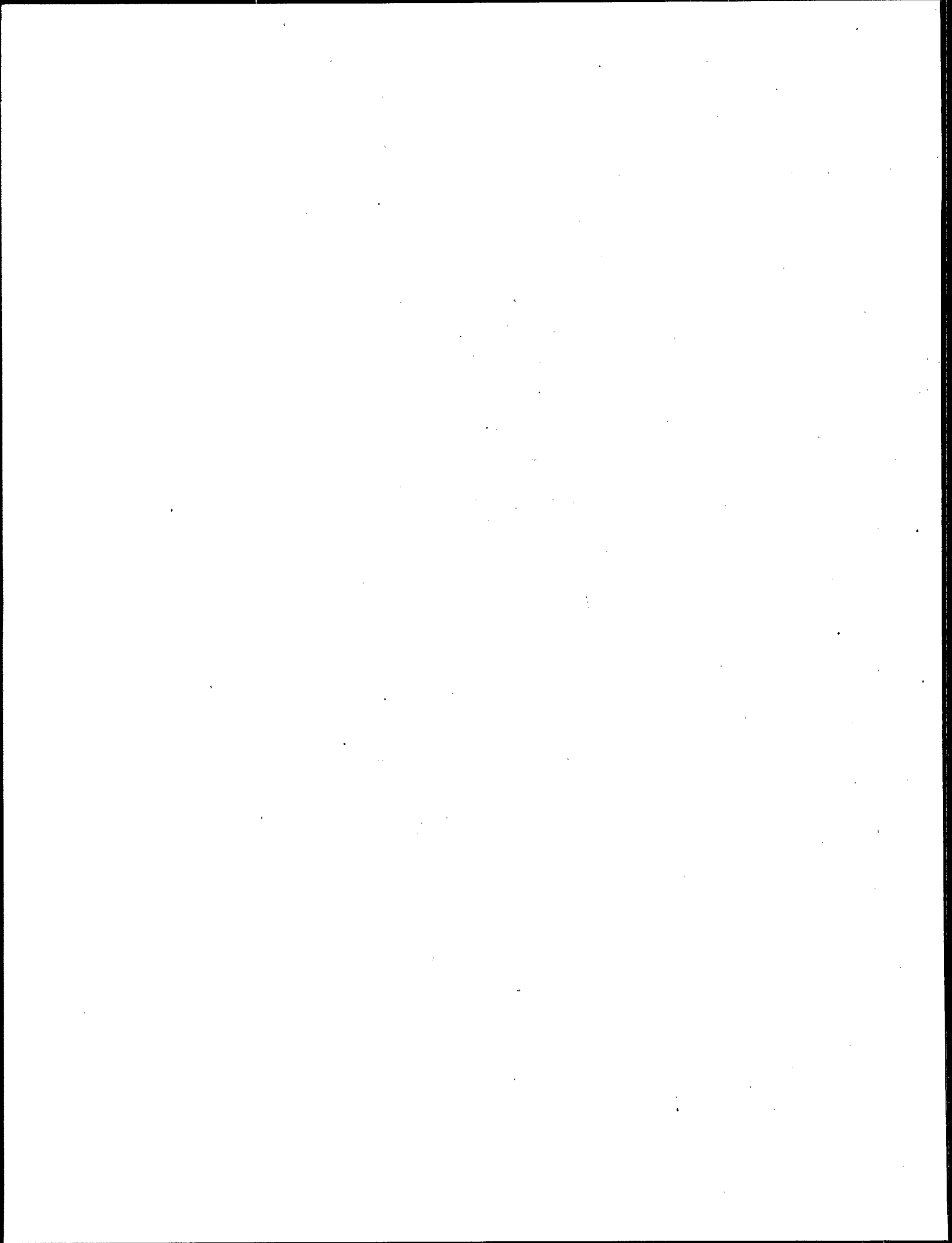
Figure 14-6. Estimated Performance of Proposed BAT Treatment

### 14.3.3 Conclusions

The treatability test results indicate that physical aeration does not significantly reduce the overall chemical oxygen demand in the sodium hydrosulfite waste water. Table 14-14 shows the estimated performance 30-day average which exceeds the proposed BAT maximum 30-day average concentration (achieved with biochemical oxidation) by 400 mg/l. It can be concluded from these tests that biochemical oxidation is an essential waste treatment process for the reduction of COD for this subcategory.

Review of the results also indicates that dual media filtration removes substantial quantities of suspended solids although a greater removal appears achievable when preceded by biochemical treatment.

The experimental results presented herewith represent the outcome of the particular set of experiments conducted during the available time frame. Hence, the results do not represent the actual performance capabilities of the proposed BAT treatment.



APPENDIX A  
STATISTICAL SUMMARIES OF  
TREATMENT DATA

Table No: A-01

Statistical Summary of Treatment Data for  
Chlor-Alkali (Diaphragm Cell)

Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	15	1.00	30.44	92.00	29.20	0.96
Nickel	15	0.05	0.38	1.21	0.37	0.97
Total Chromium	15	0.04	0.08	0.14	0.03	0.41
Lead	10	0.05	0.08	0.29	0.08	0.96
-----						

Table No: A-02

Statistical Summary of Treatment Data for  
Hydrofluoric Acid

## Treatment Effluent

Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
Total Suspended Solids	17	11.00	149.74	363.00	106.98	0.71
Nickel	17	0.03	0.49	1.10	0.36	0.72
Zinc	17	0.01	0.07	0.32	0.09	1.26
Total Chromium	17	0.01	0.07	0.15	0.04	0.53
Fluoride	13	67.00	89.69	109.00	13.10	0.15

Table No: A-04

Statistical Summary of Treatment Data for  
Titanium Dioxide (Chloride Process)

## Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	16	2.00	9.85	20.00	5.69	0.58
Nickel	16	0.06	0.09	0.13	0.02	0.19
Zinc	16	0.02	0.04	0.08	0.02	0.48
Total Chromium	14	0.03	0.05	0.12	0.02	0.49
Copper	16	0.03	0.04	0.05	0.01	0.21
Iron	16	0.03	0.18	0.69	0.15	0.87
-----						



Table No: A-06

Statistical Summary of Treatment Data for  
Chrome Pigments

## Treatment Effluent

Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
Total Suspended Solids	14	1.00	4.44	9.60	2.51	0.57
Zinc	14	0.02	0.04	0.07	0.02	0.39
Total Chromium	14	0.01	0.04	0.18	0.04	1.09
Lead	14	0.03	0.10	0.24	0.06	0.59
Cadmium	13	0.01	0.03	0.10	0.02	0.69

Table No: A-08

Statistical Summary of Treatment Data for  
Sodium Dichromate

## Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	18	3.00	175.29	832.40	277.13	1.58
Nickel	17	0.05	0.09	0.50	0.11	1.20
Total Chromium	13	0.09	0.25	0.79	0.19	0.77
Hexavalent Chromium	14	0.00	0.12	0.90	0.26	2.16
-----						

Table No: A-11C

Statistical Summary of Treatment Data for  
Copper Sulfate

Caustic Treatment

Treatment Effluent

Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
Total Suspended Solids	11	1.10	5.44	12.60	3.69	0.68
Nickel	11	0.05	0.09	0.20	0.05	0.53
Copper	10	0.07	0.25	0.66	0.18	0.72
Selenium	10	0.11	0.13	0.16	0.01	0.11

Table No: A-11L

Statistical Summary of Treatment Data for  
Copper Sulfate

Lime Treatment

Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	12	0.90	4.55	14.00	3.78	0.83
Nickel	12	0.05	0.11	0.41	0.11	0.96
Copper	12	0.06	0.18	0.56	0.14	0.77
Selenium	12	0.10	0.12	0.16	0.02	0.15
-----						

Table No: A-12A

Statistical Summary of Treatment Data for  
Nickel Sulfate

Alkaline Treatment

Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	14	2.00	27.79	105.00	28.55	1.03
Nickel	14	0.01	0.16	0.55	0.18	1.12
-----						

Table No: A-14

Statistical Summary of Treatment Data for  
Sodium Bisulfite

Unfiltered Supernatant

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	16	120.00	242.81	690.00	169.82	0.70
Zinc	16	0.12	0.92	4.00	1.23	1.34
-----						

Table No: A-14

Statistical Summary of Treatment Data for  
Sodium Bisulfite

Unfiltered Supernatant

Maximum Aeration Time

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Chemical Oxygen Demand	15	80.00	453.33	960.00	264.76	0.58
Sulfite(Iodate)	17	2.00	24.59	84.00	22.64	0.92
-----						

Table No: A-15

Statistical Summary of Treatment Data for  
Sodium Hydrosulfite

Treatment Effluent

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Total Suspended Solids	17	0.30	29.32	126.00	32.89	1.12
Zinc	17	0.03	2.11	9.93	3.18	1.50
Total Chromium	17	0.01	1.25	9.09	2.88	2.30
-----						



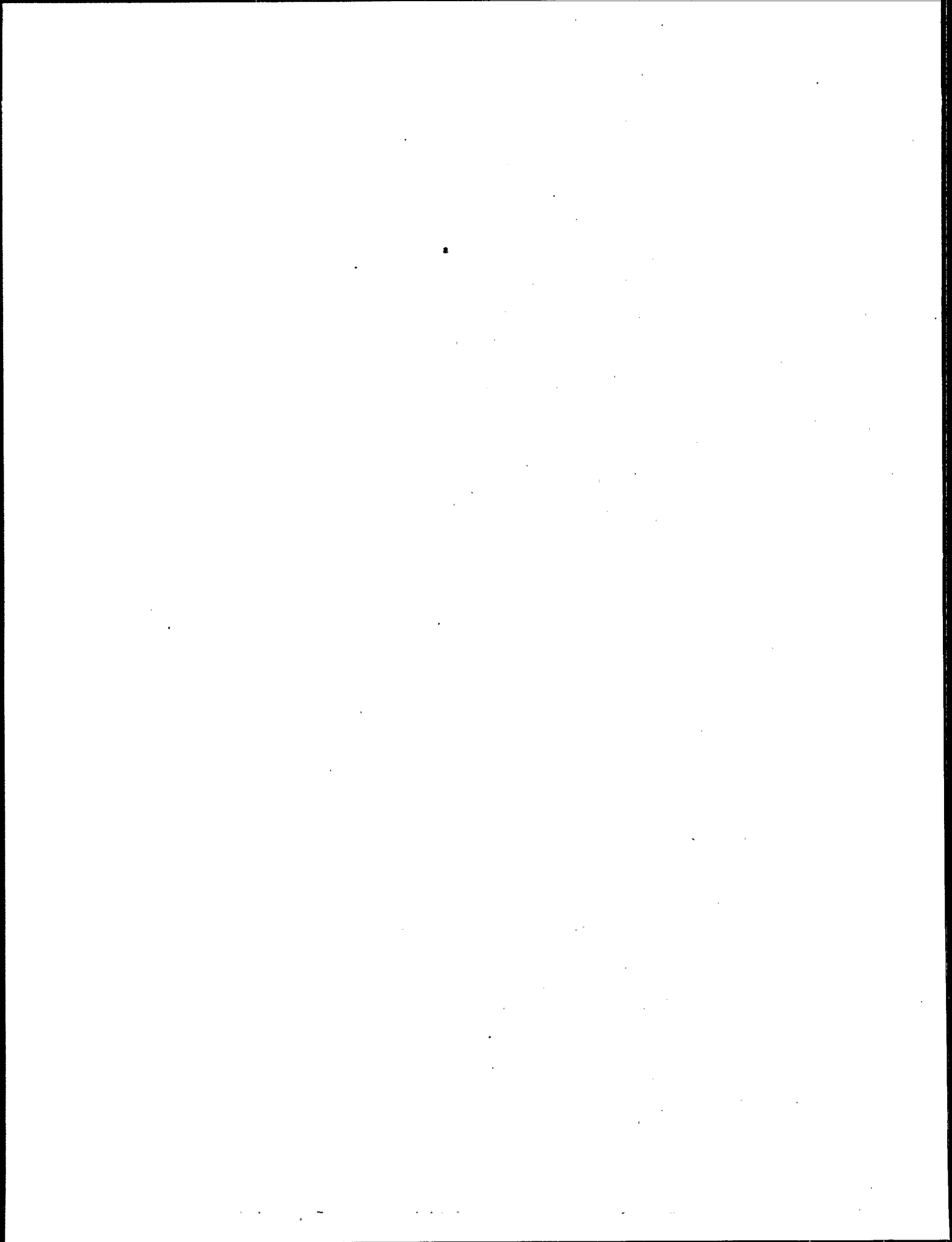
Table No: A-15

Statistical Summary of Treatment Data for  
Sodium Hydrosulfite

Unfiltered Supernatant

Maximum Aeration Time

=====						
Parameter (mg/l)	No	Min	Avg	Max	Stdv	C.Var
-----						
Chemical Oxygen Demand	17	776.0	2503.4	4500.0	1160.6	0.46
Sulfite(Iodate)	17	0.20	3.50	16.60	5.19	1.48
-----						



APPENDIX B

IODATE DEMAND CURVES FOR  
SODIUM BISULFITE

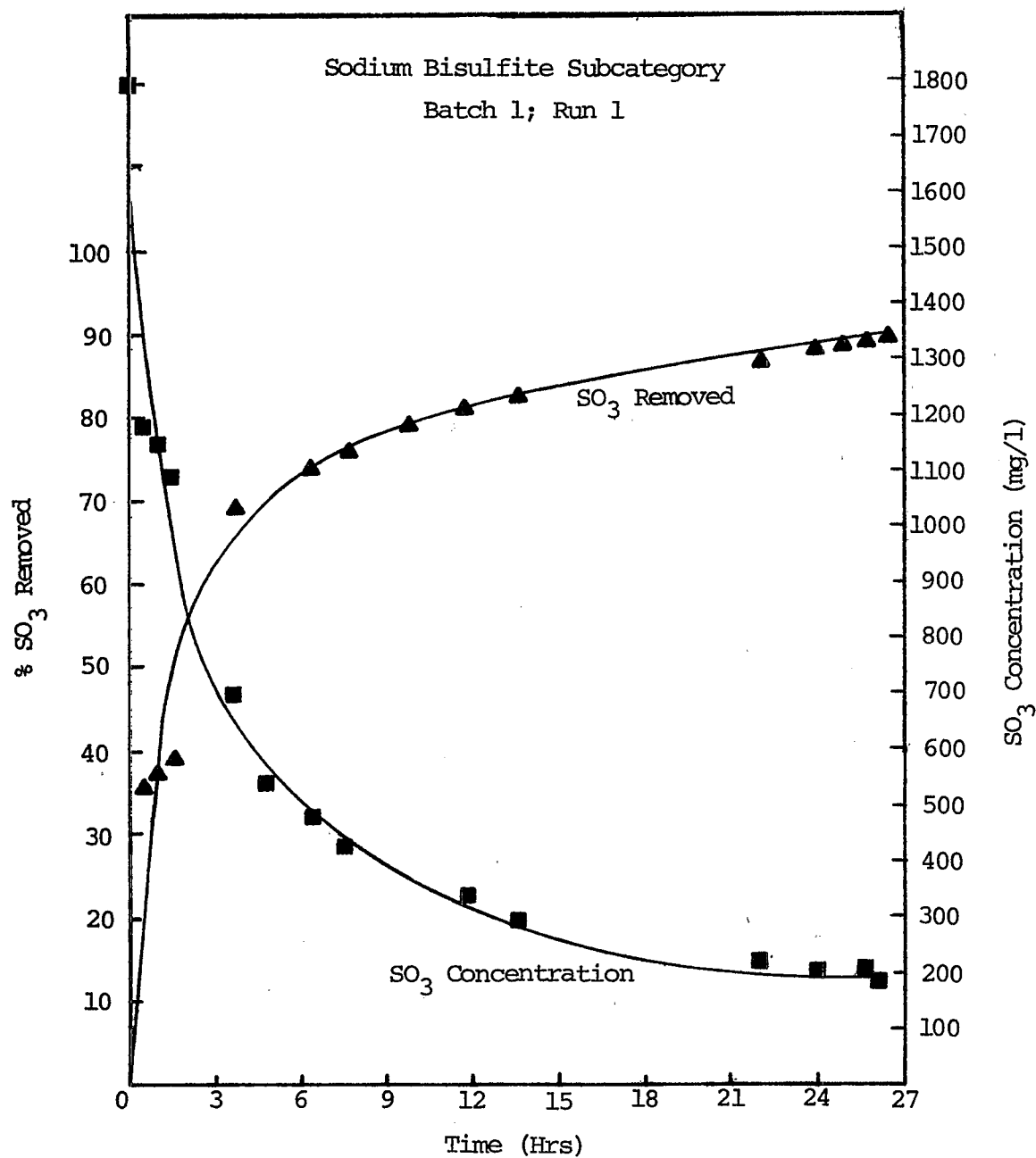


Figure B-1 . Effect of aeration on sulfite concentration.  
(airflow rate: 11.5 SCFH)

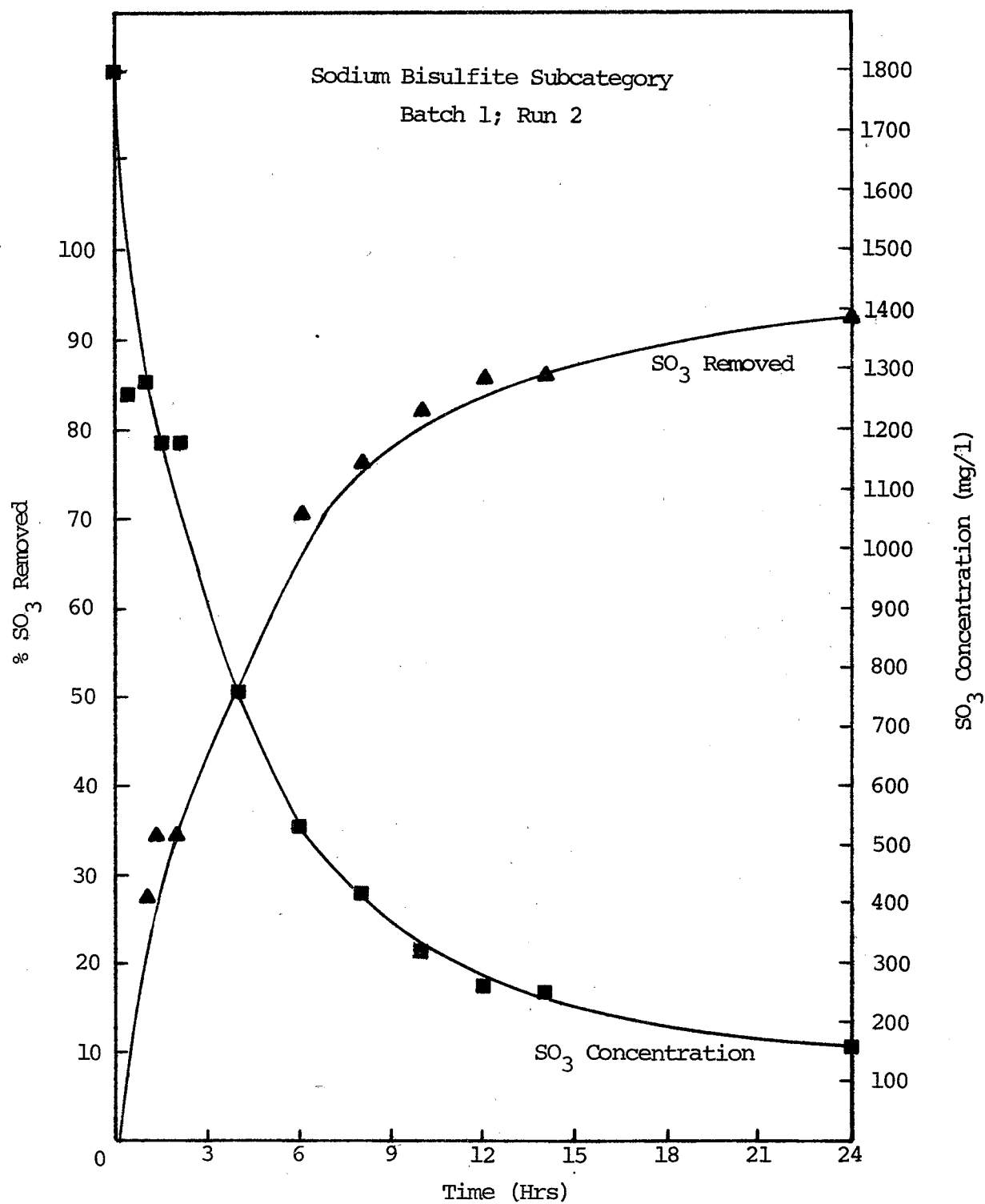


Figure B-2 . Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

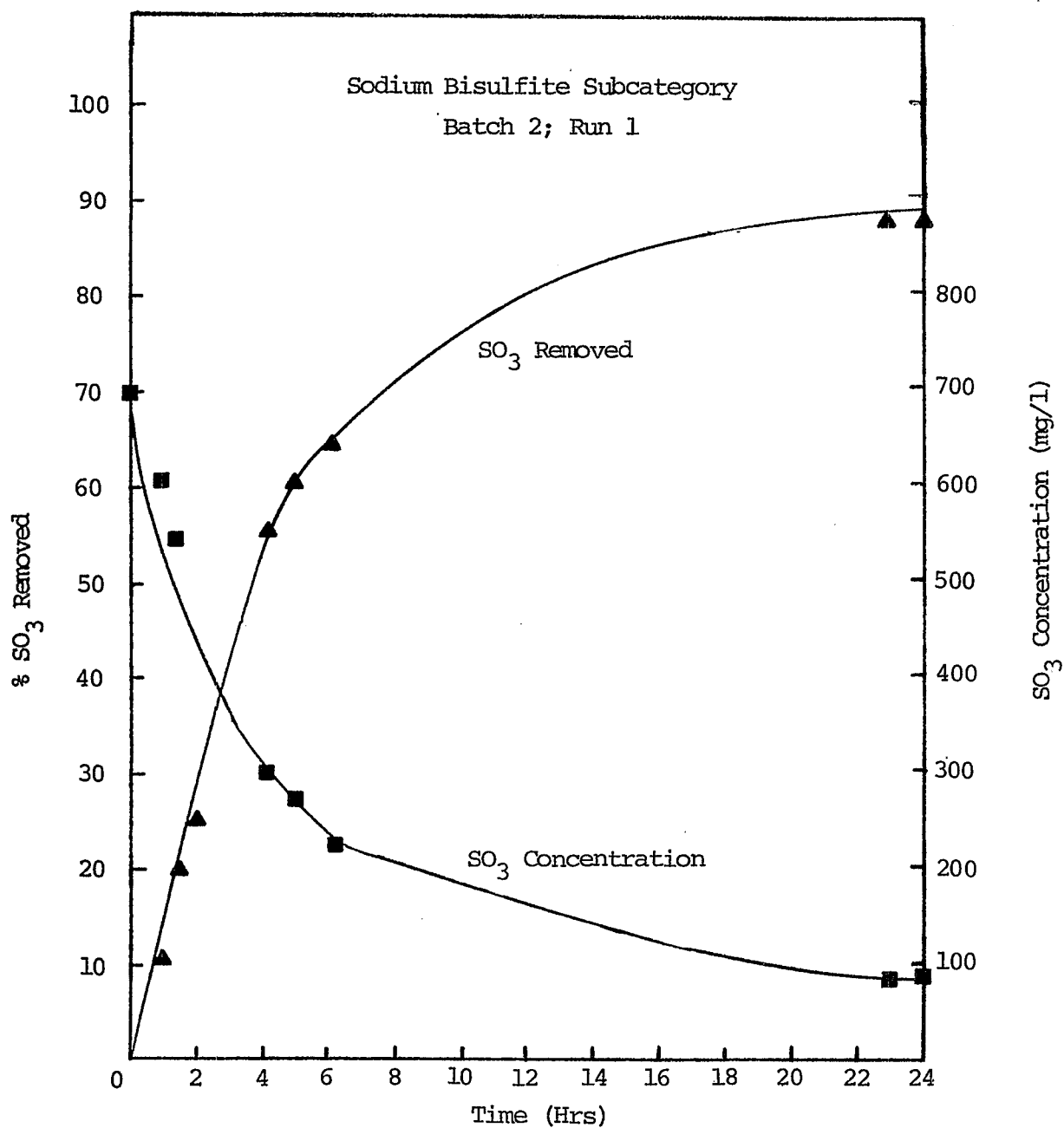


Figure B-3 . Effect of aeration on sulfite concentration  
(airflow rate: 35.0 SCFH)

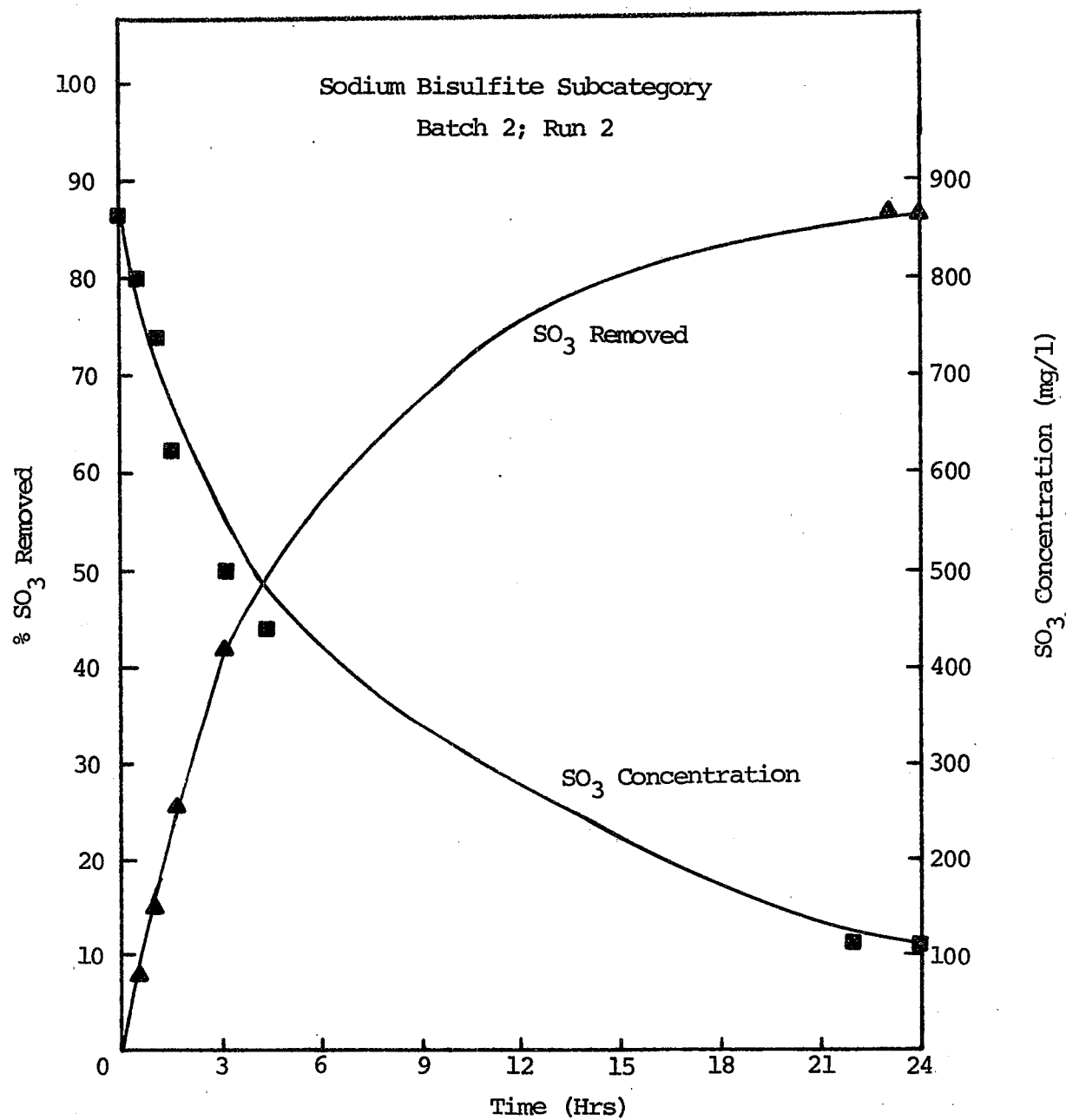


Figure B-4 . Effect of aeration on sulfite concentration  
(airflow rate: 11.5 SCFH)

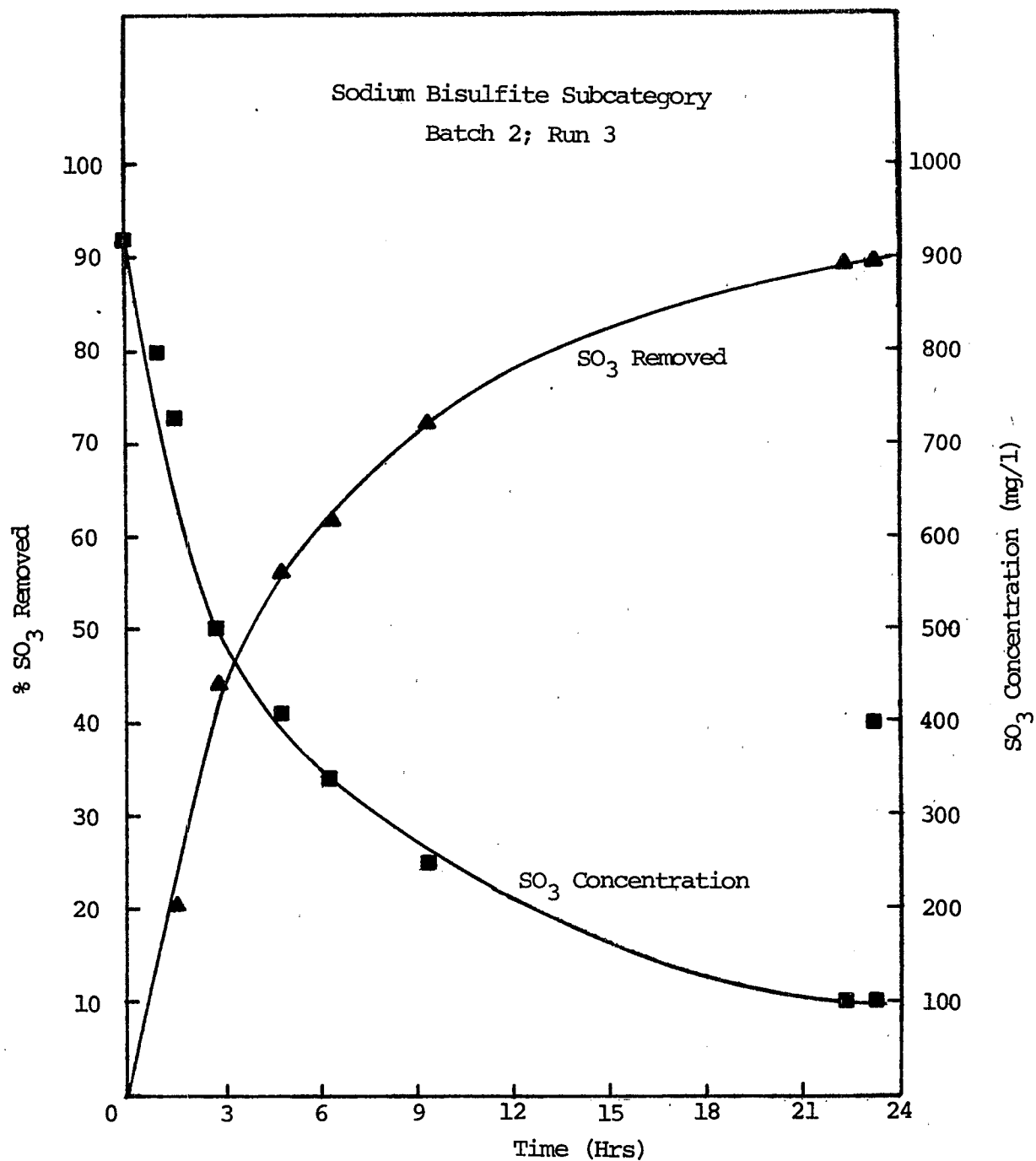


Figure B-5 . Effect of aeration on sulfite concentration  
(airflow rate: 23.0 SCFH)



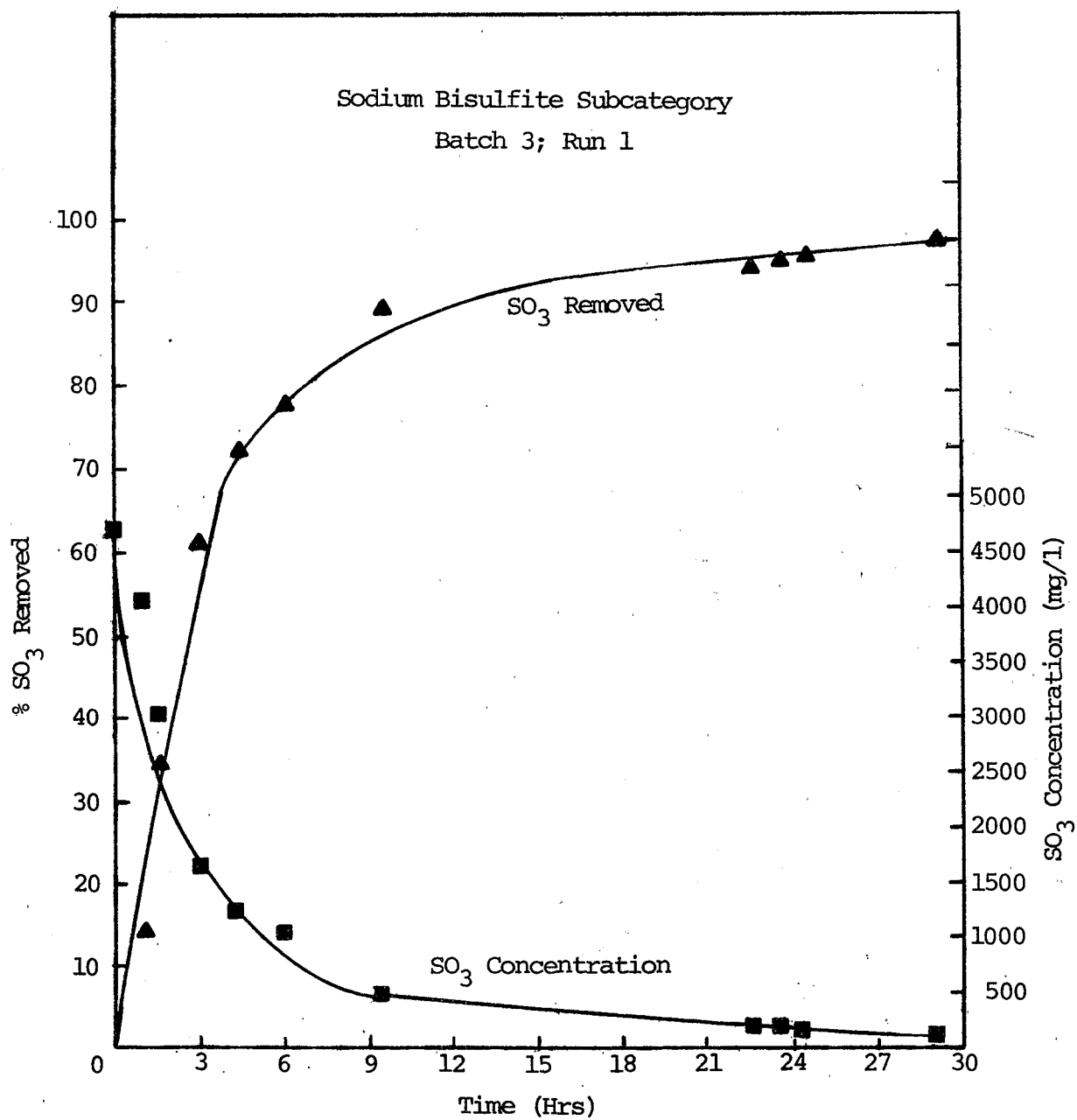


Figure B-6 . Effect of aeration on sulfite concentration.  
(airflow rate: 35.0 SCFH)

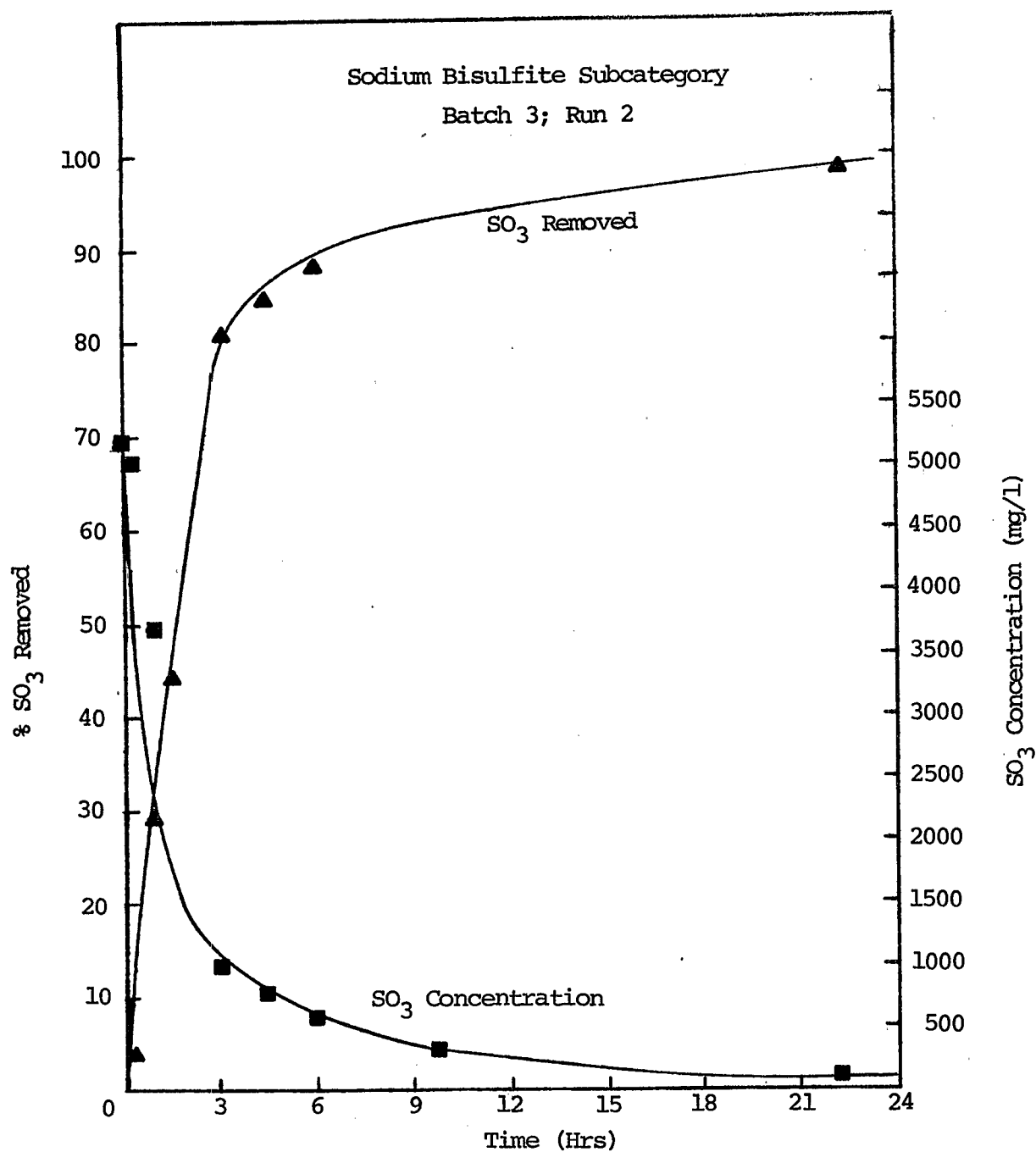


Figure B-7 . Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

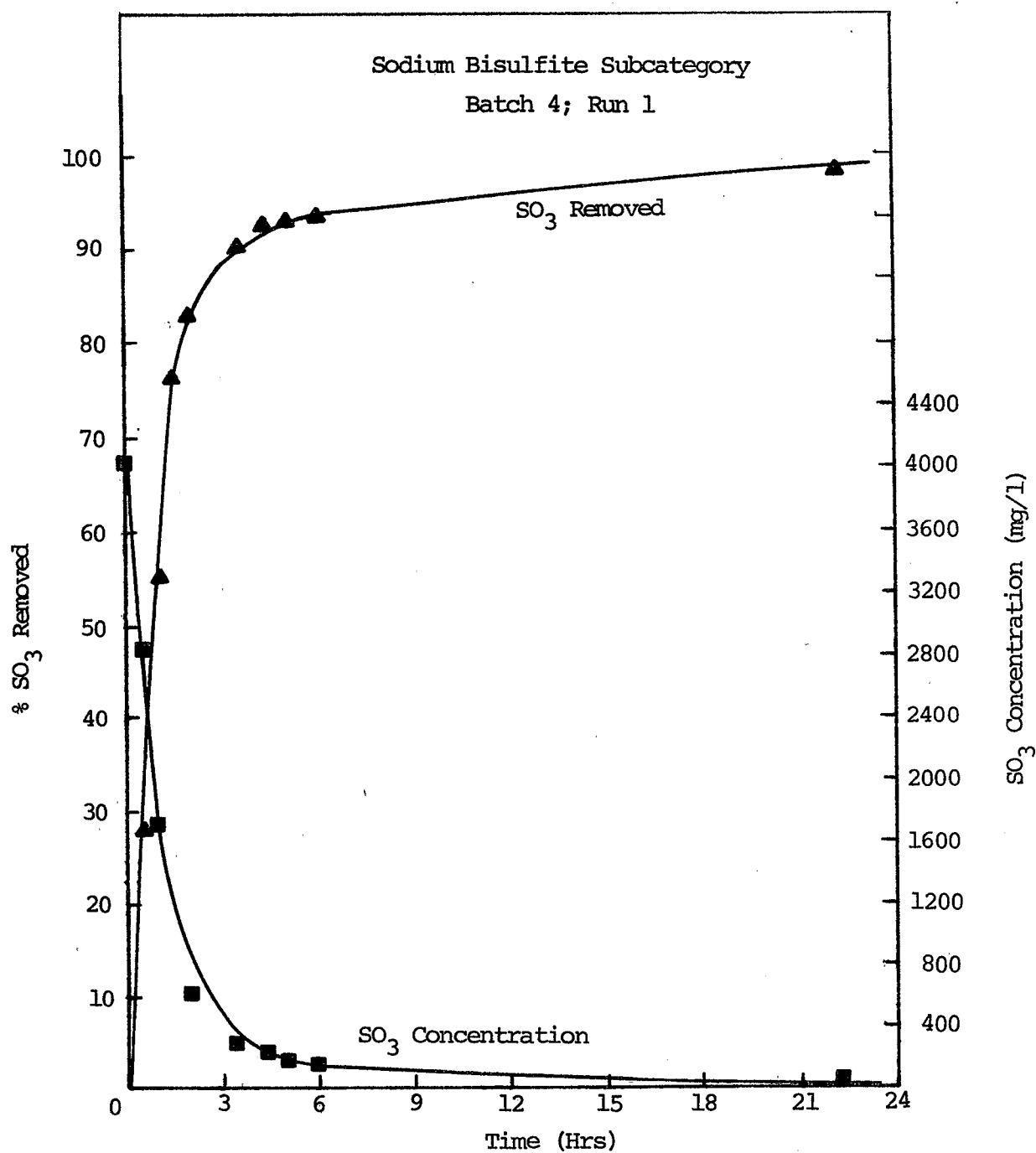


Figure B-8 . Effect of aeration on sulfite concentration  
(airflow rate: 57.0 SCFH)

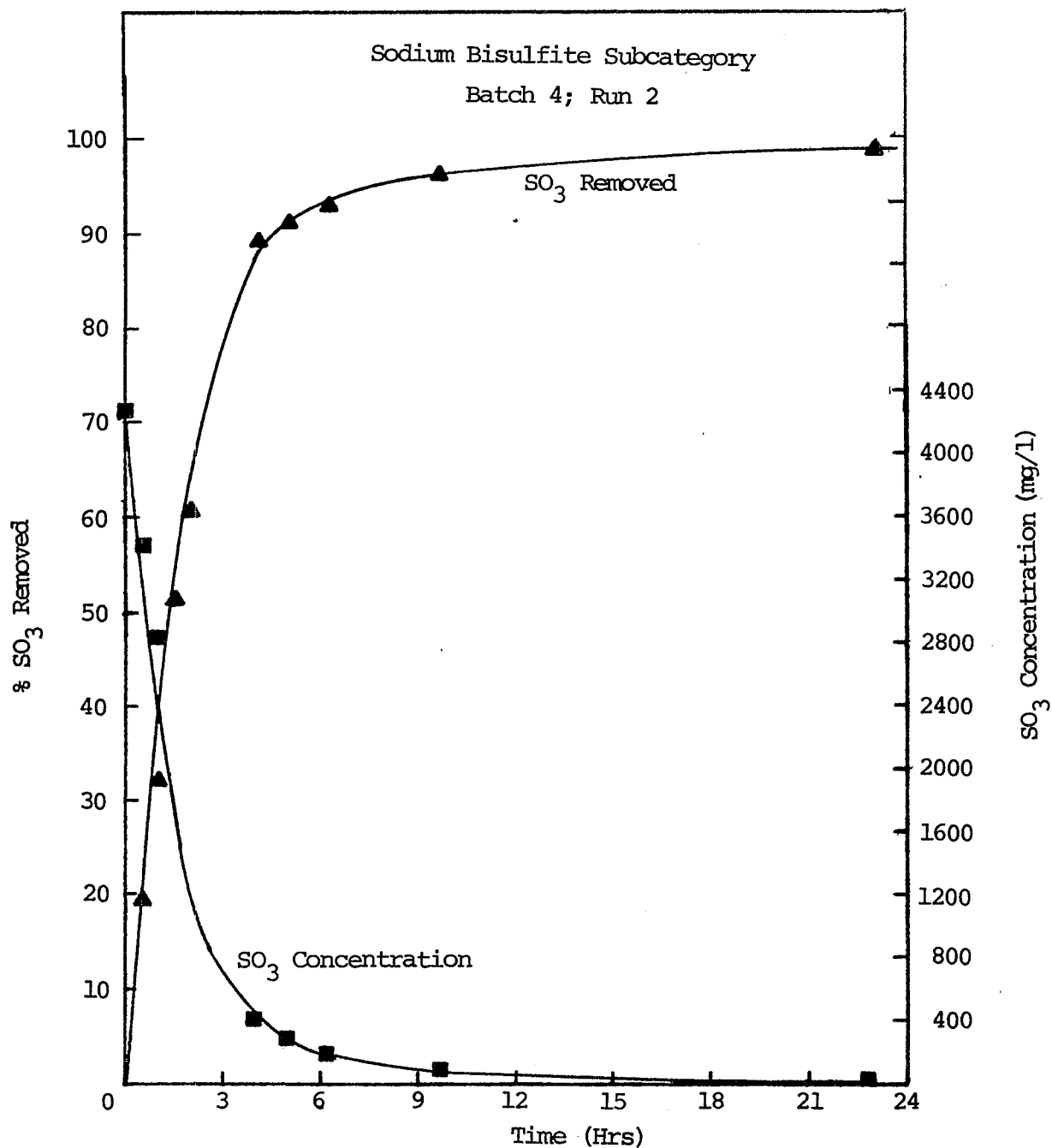


Figure B-9 . Effect of aeration on sulfite concentration  
(airflow rate: 11.5 SCFH).

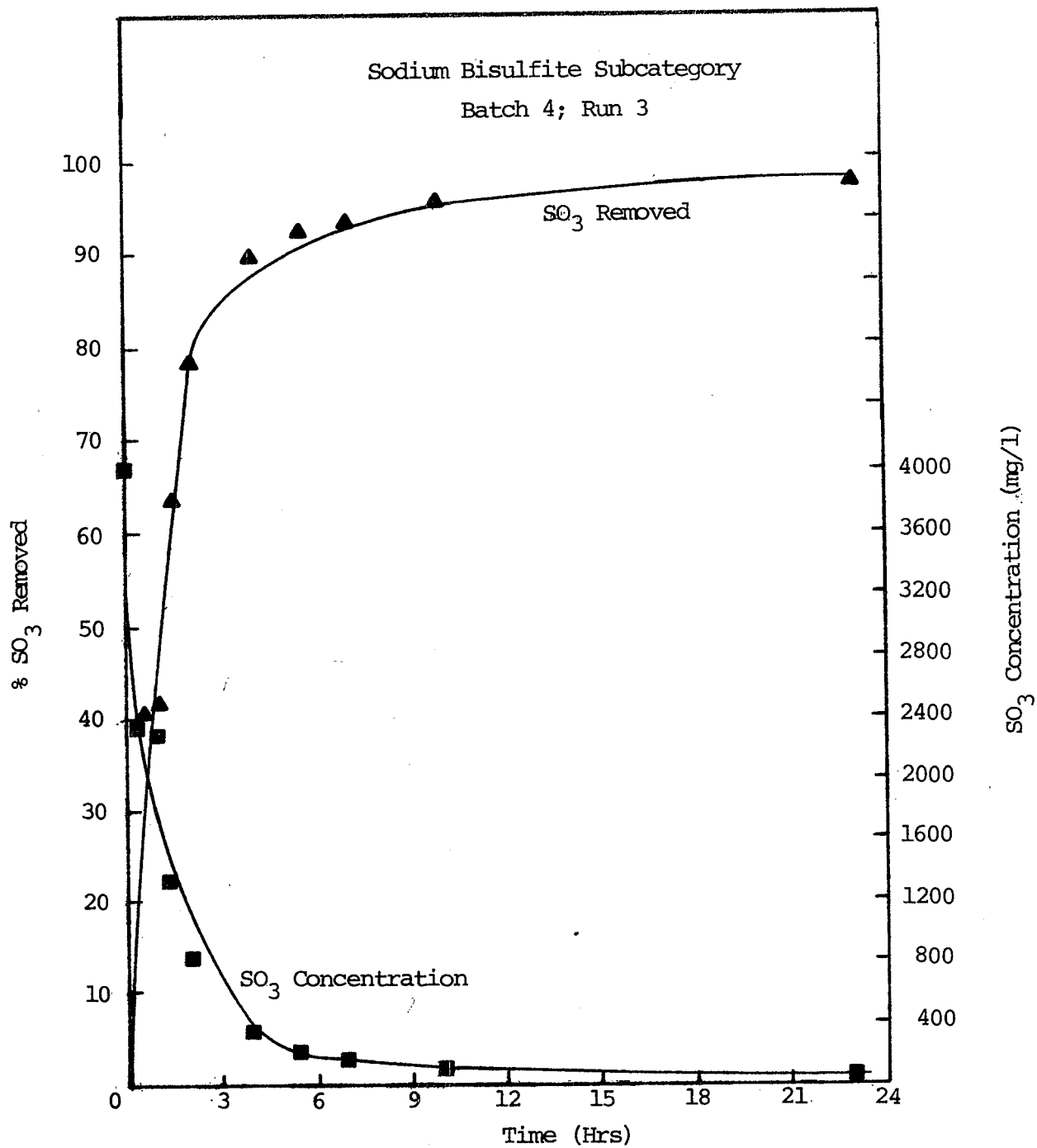


Figure B-10. Effect of aeration on sulfite concentration.  
(airflow rate: 35.0 SCFH)

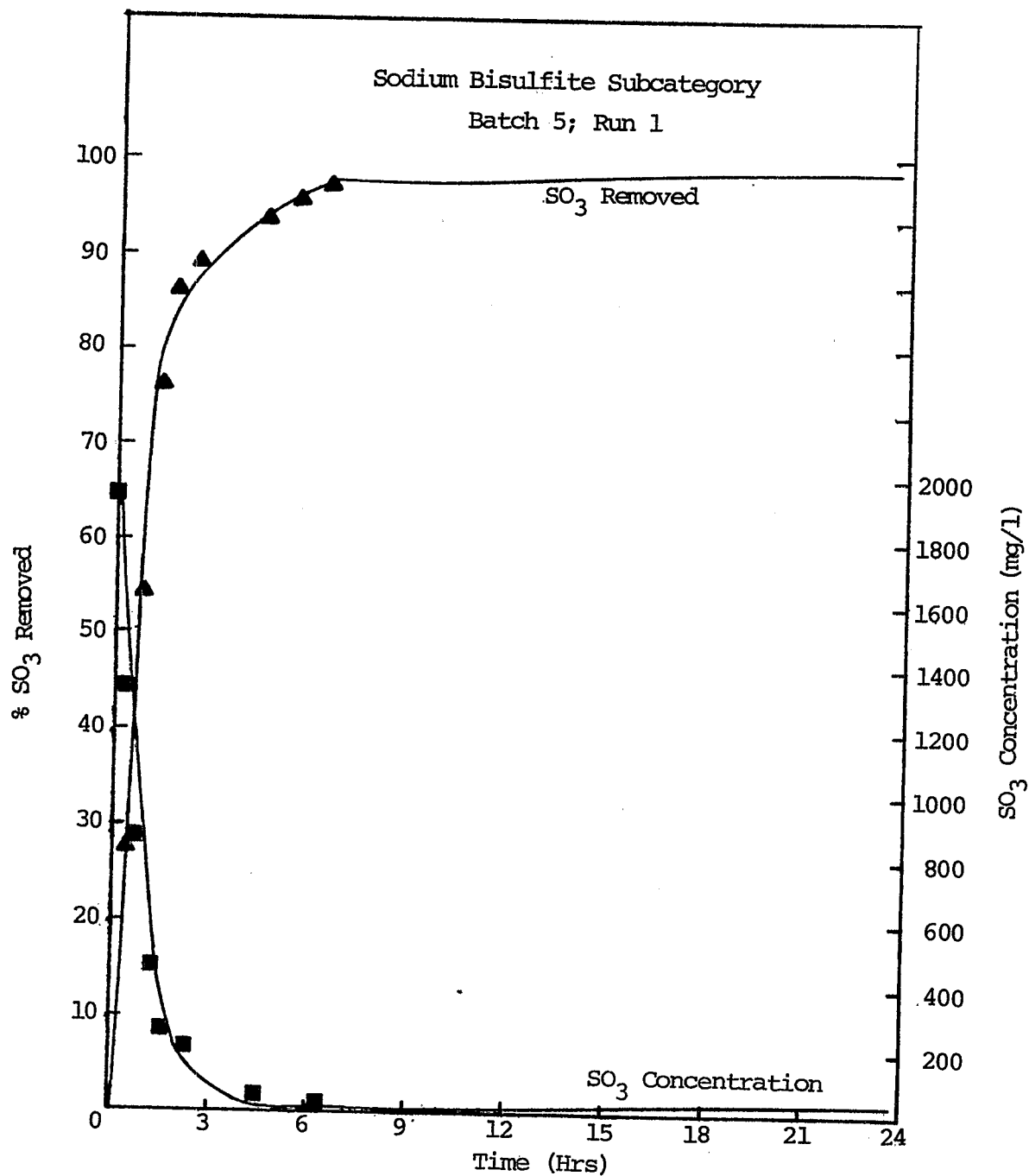


Figure B-11. Effect of aeration on sulfite concentration  
(airflow rate: 23 SCFH)

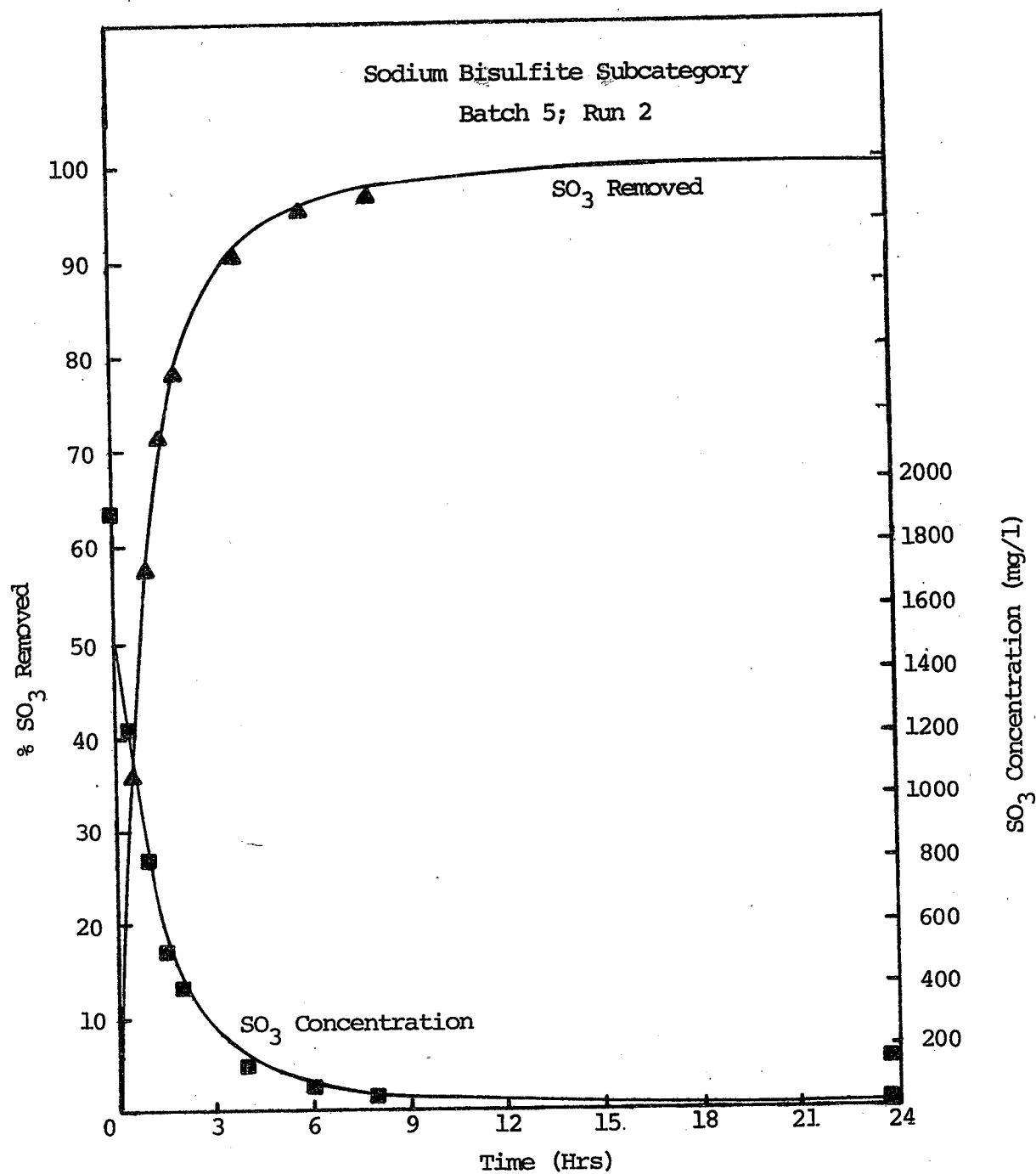


Figure B-12. Effect of aeration on sulfite concentration  
(airflow rate: 46 SCFH)

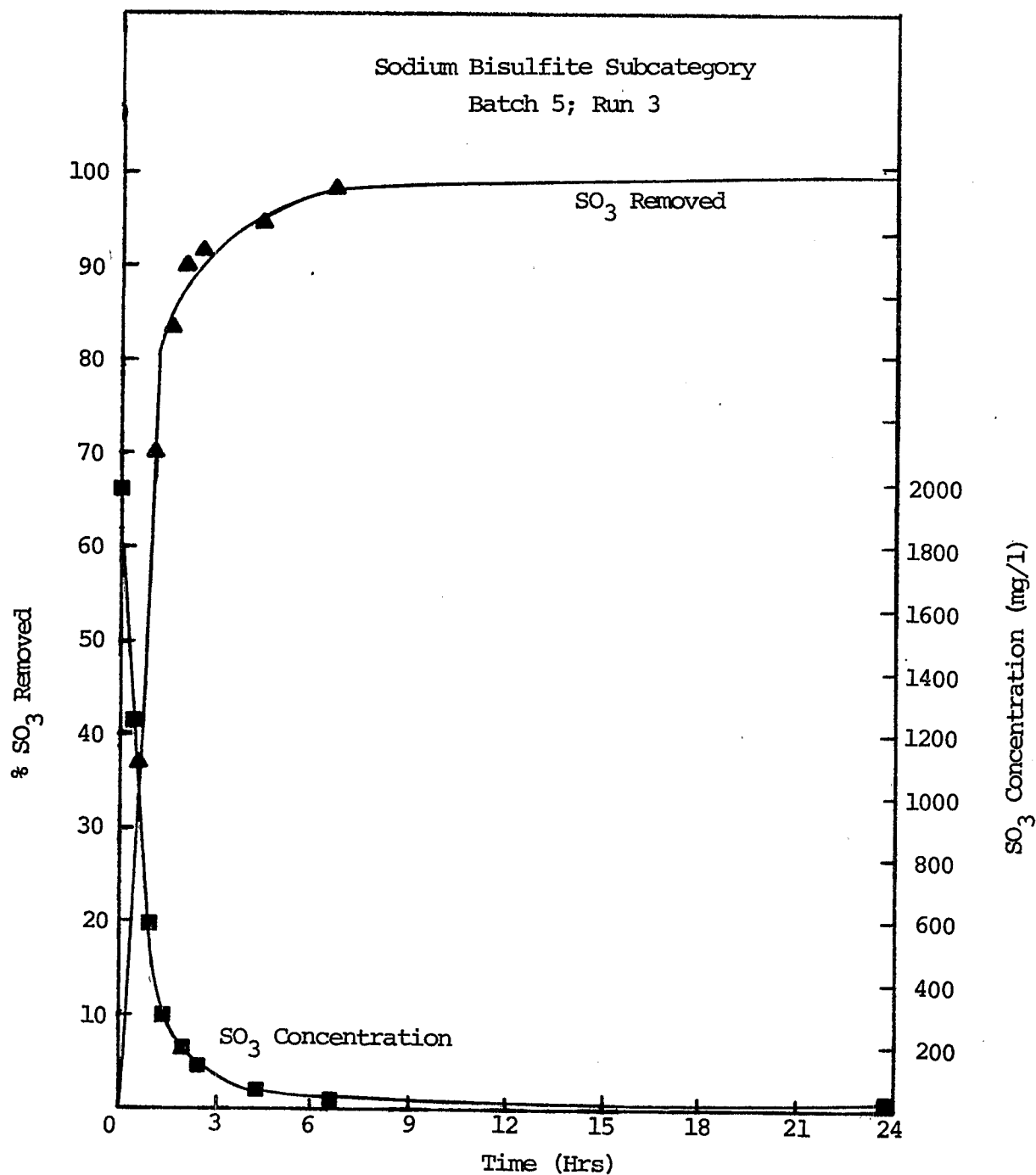


Figure B-13. Effect of aeration on sulfite concentration  
(airflow rate: 57 SCFH)



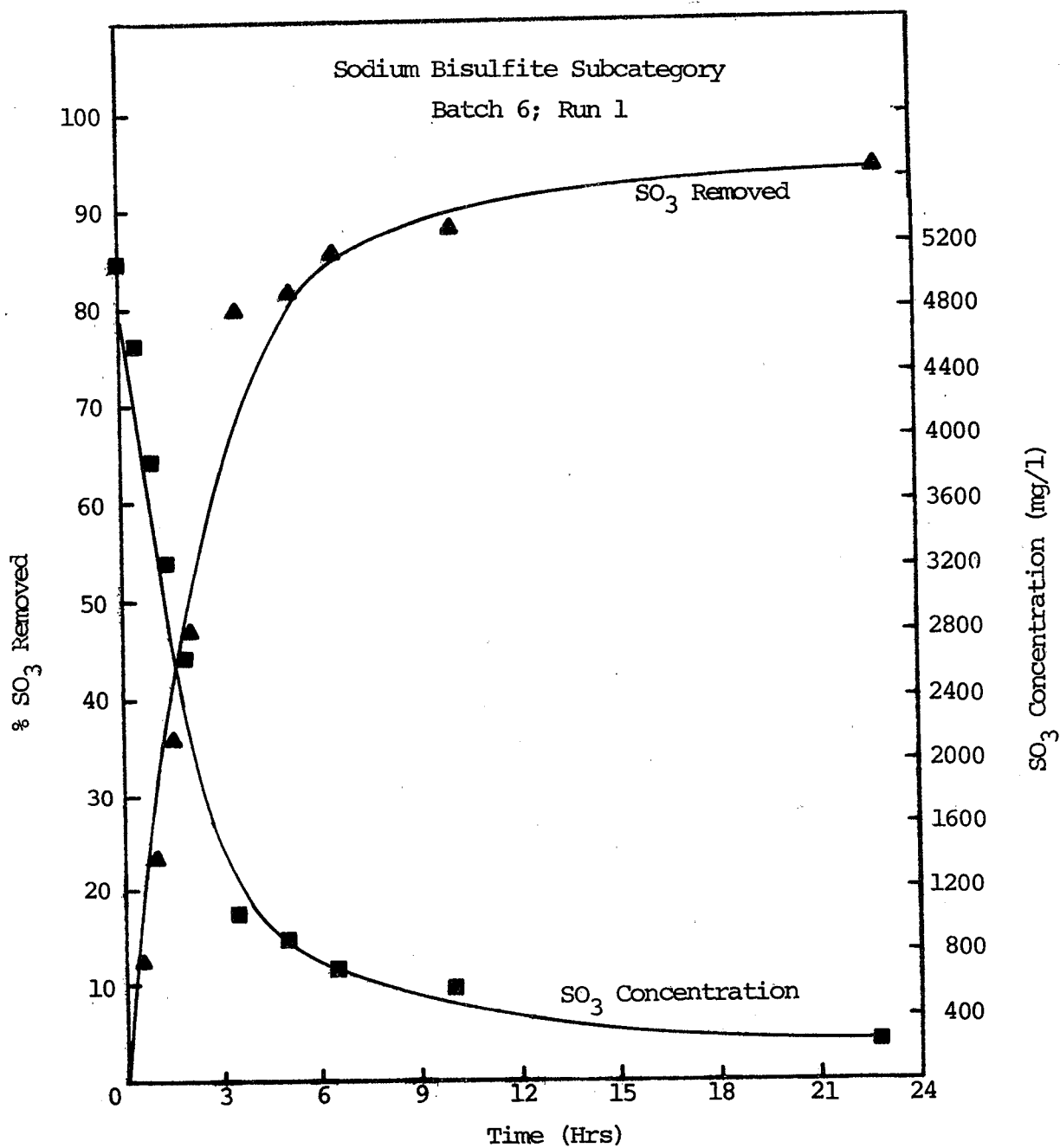


Figure B-14. Effect of aeration on sulfite concentration.  
(airflow rate: 11.5 SCFH)

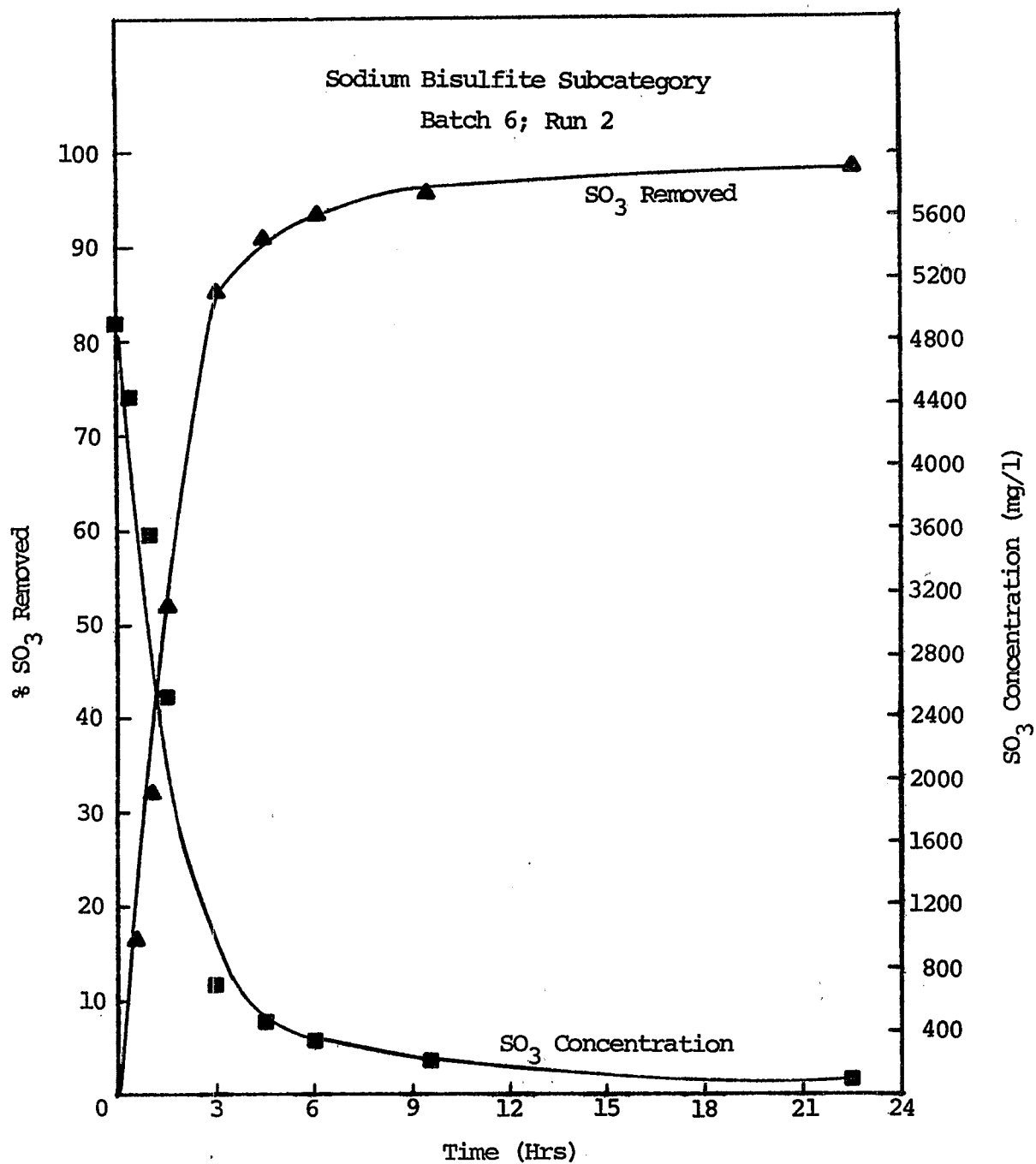


Figure B-15. Effect of aeration on sulfite concentration  
(airflow rate: 46 SCFH)

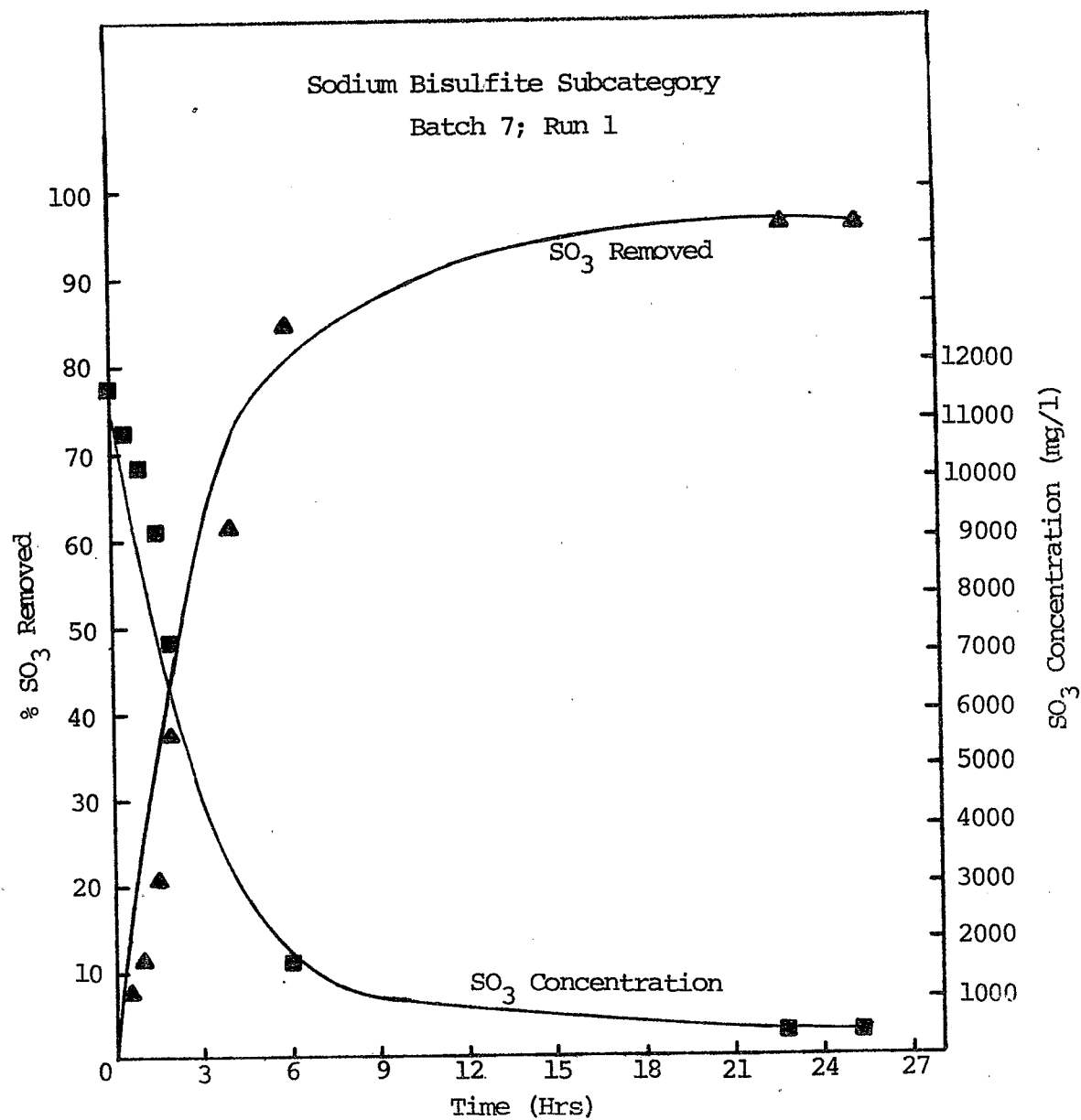


Figure B-16. Effect of aeration on sulfite concentration  
(airflow rate: 23 SCFH)

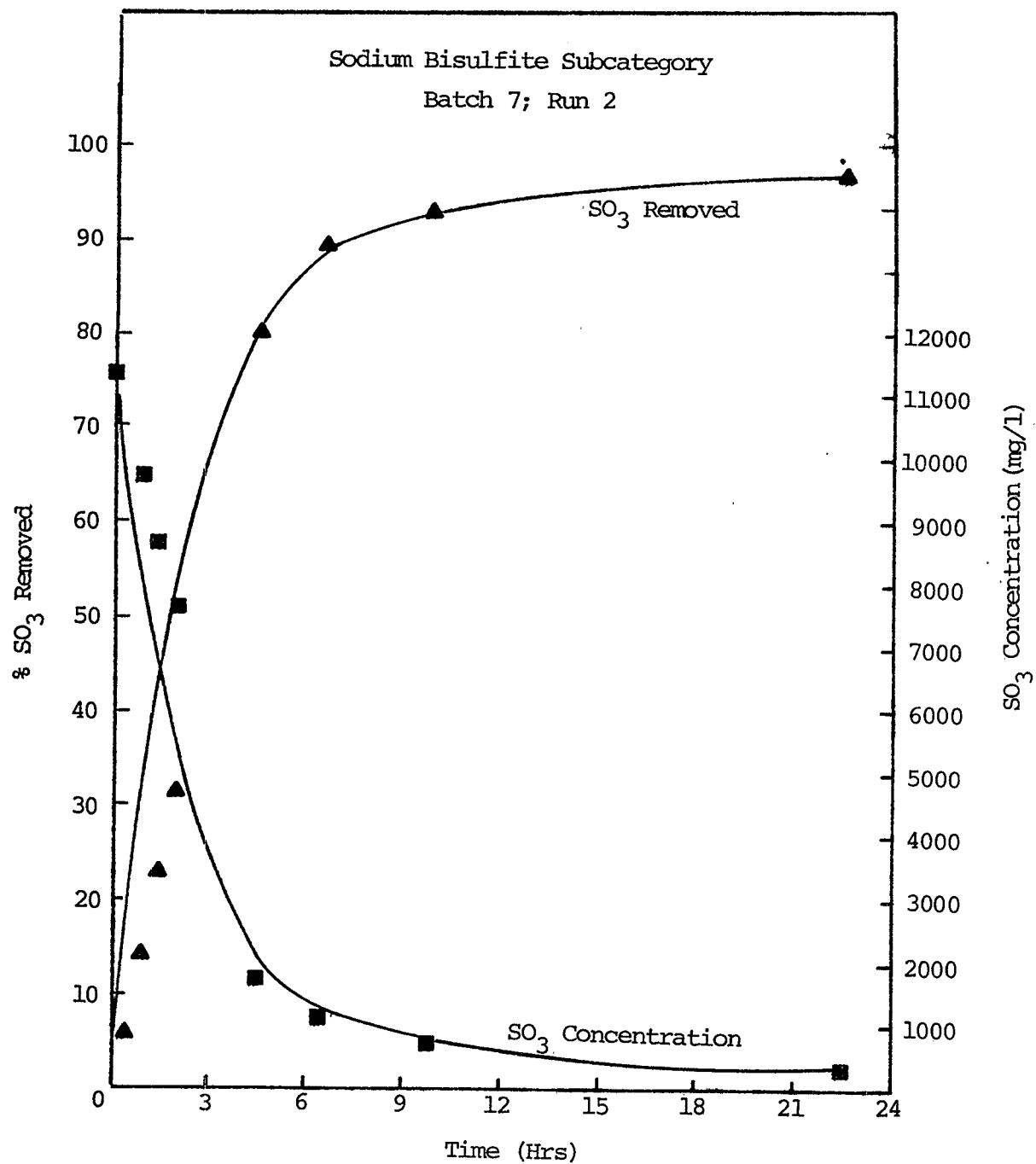


Figure B-17. Effect of aeration on sulfite concentration  
(airflow rate: 57.0 SCFH)

APPENDIX C

IODATE DEMAND CURVES FOR  
SODIUM HYDROSULFITE

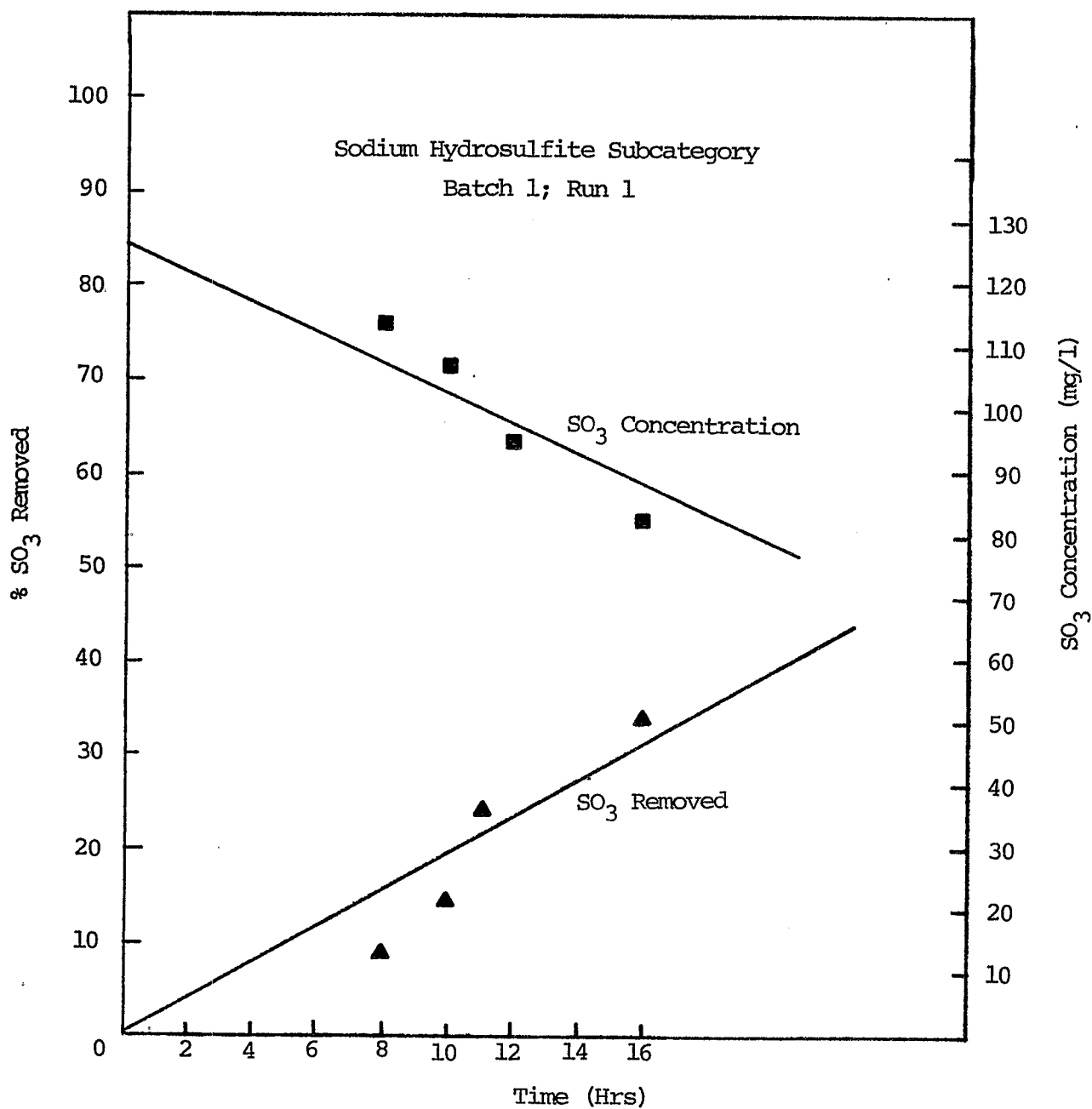


Figure C-1 . Effect of aeration on sulfite concentration  
(airflow rate: 57.0 SCFH)

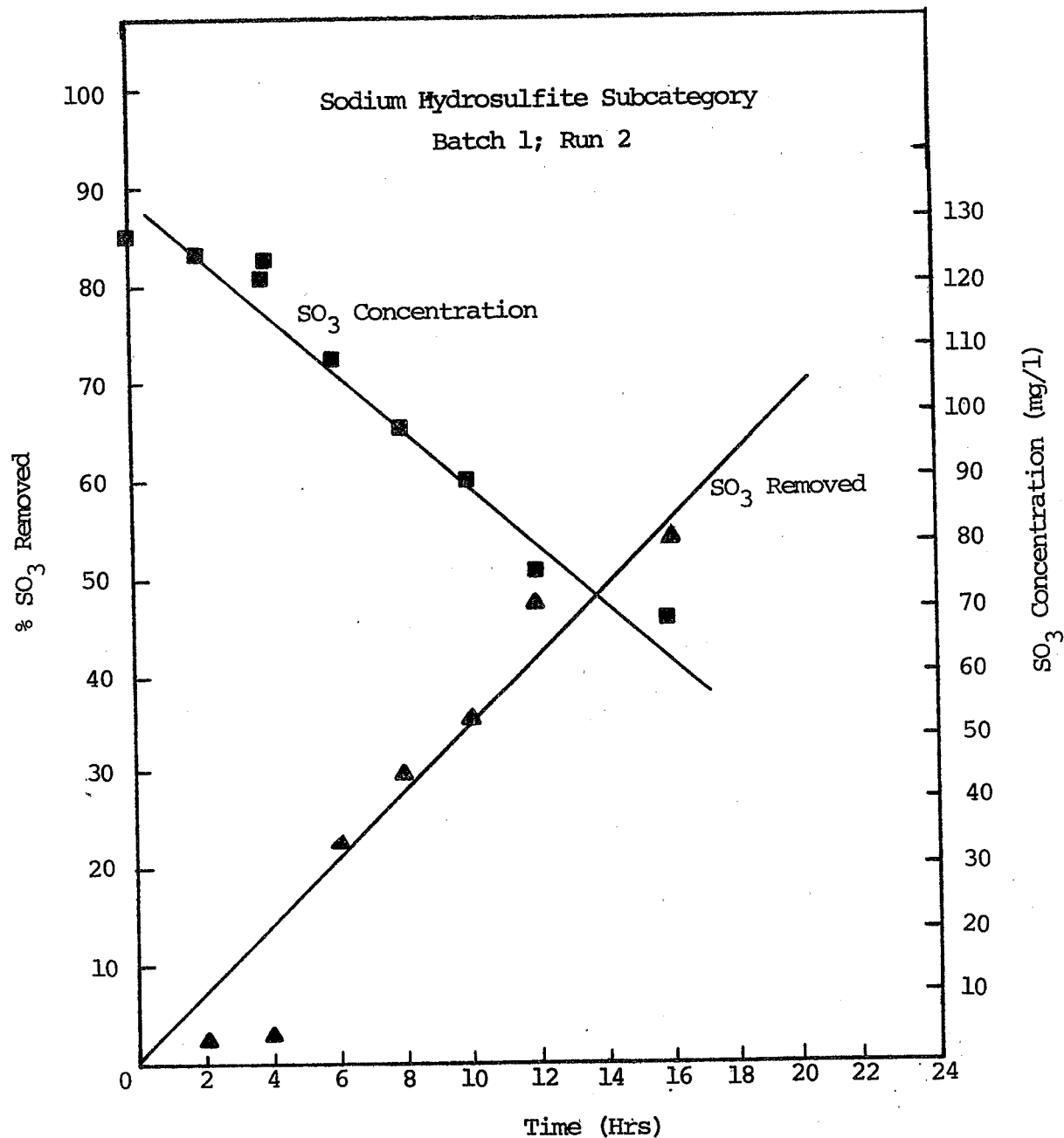


Figure C-2. Effect of aeration on sulfite concentration.  
(airflow rate: 57.0 SCFH)

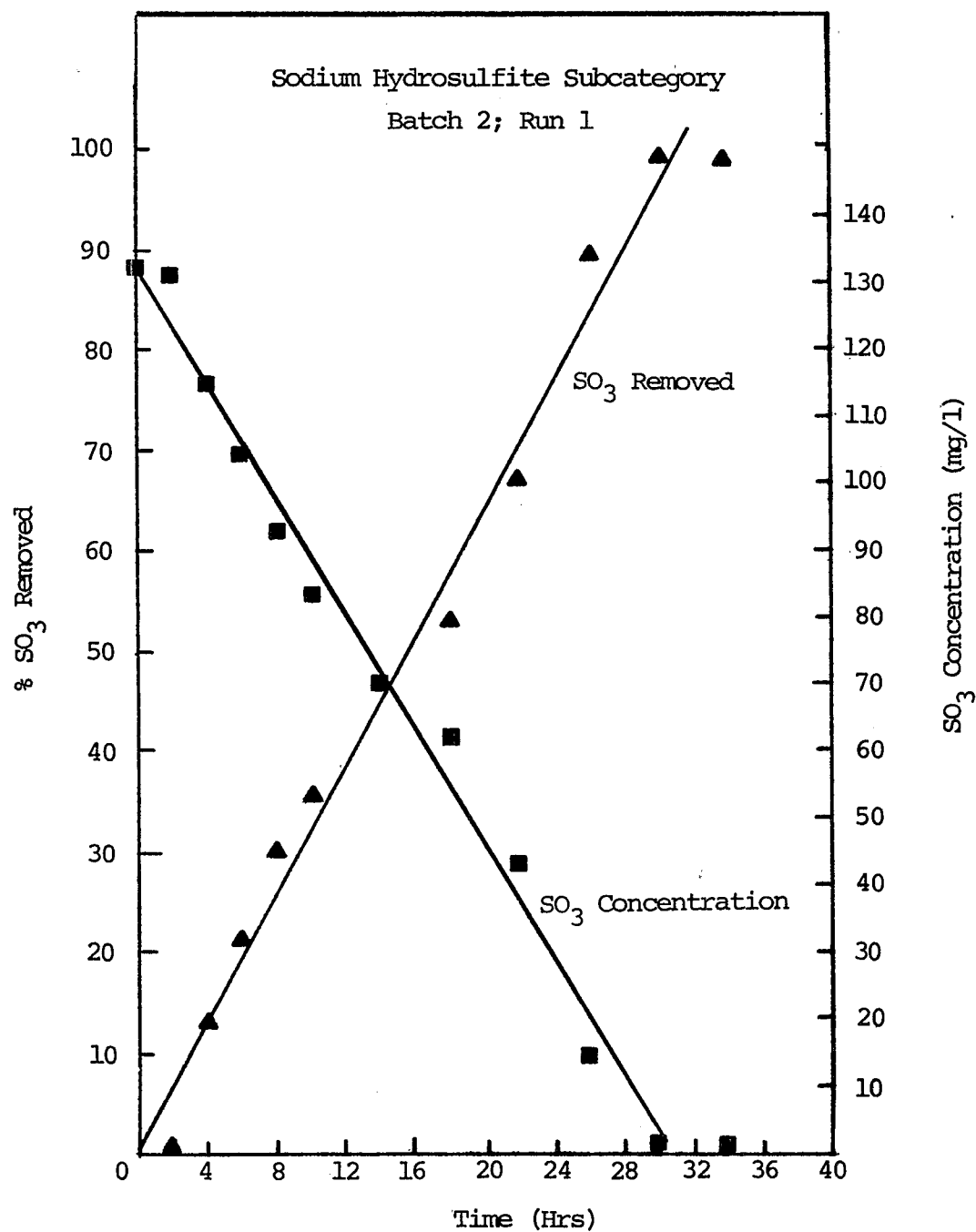


Figure C-3. Effect of aeration on sulfite concentration  
(airflow rate: 57.0 SCFH)



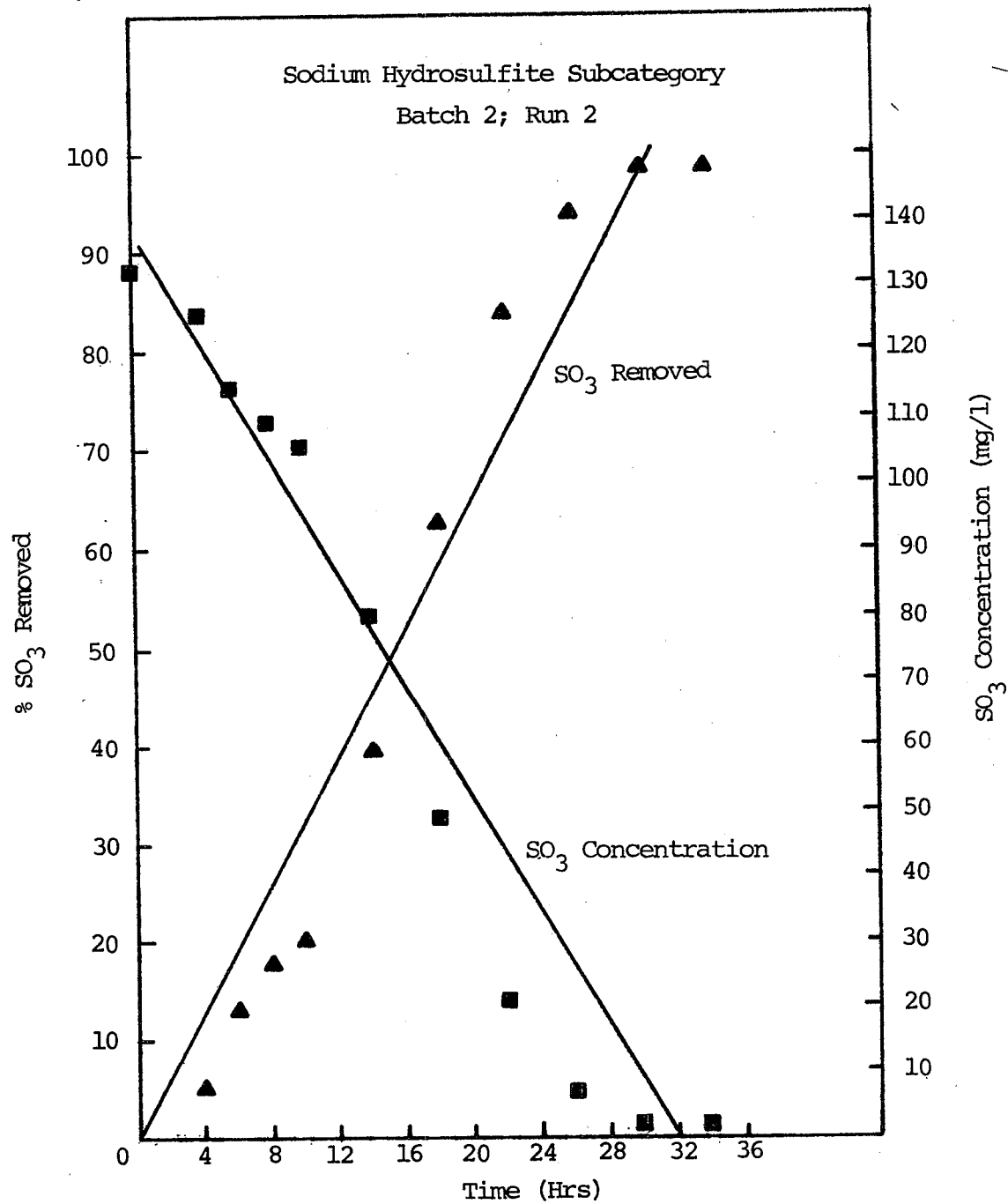


Figure C-4 . Effect of aeration on sulfite concentration .  
(airflow rate: 57.0 SCFH)

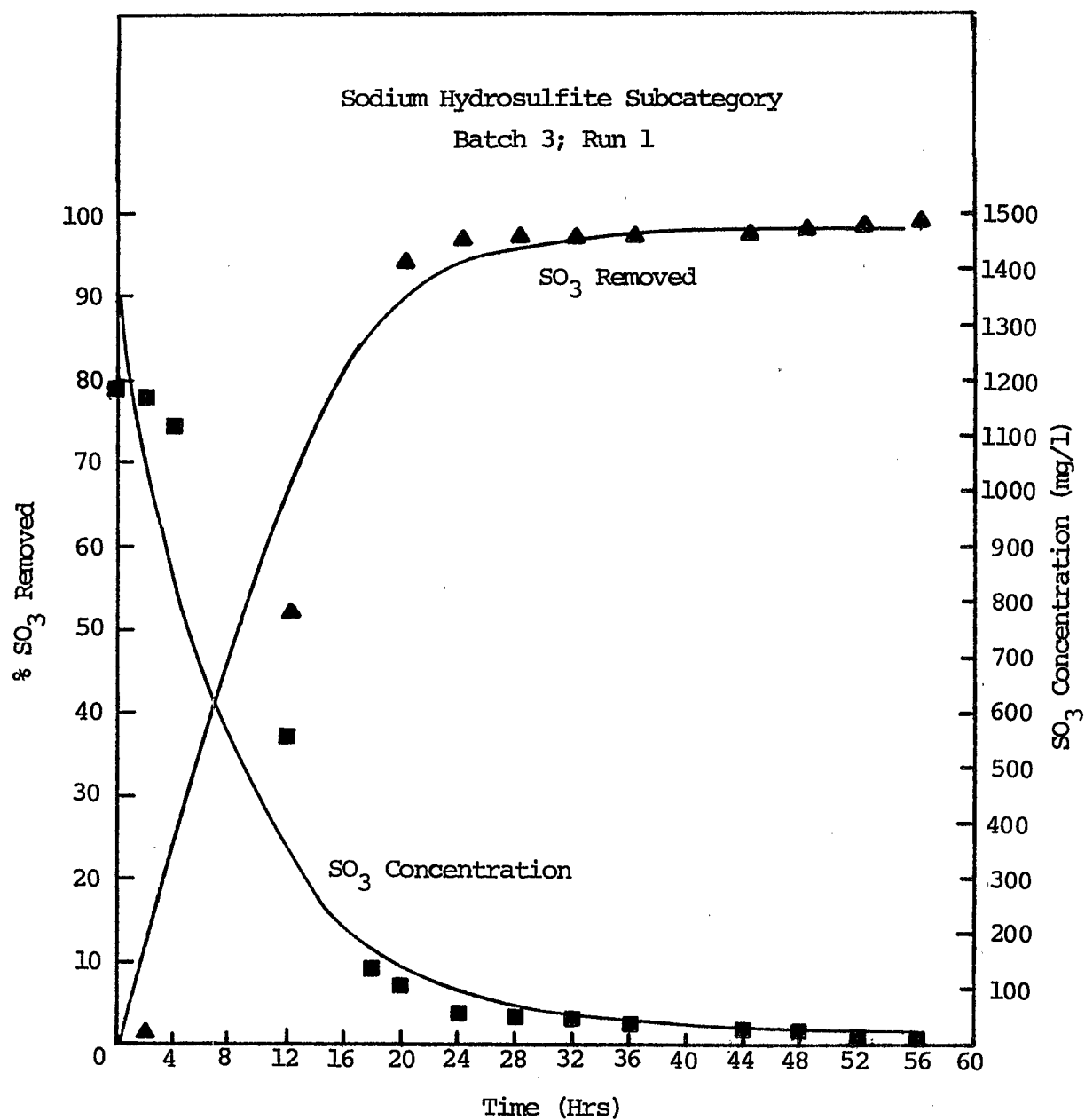


Figure C-5. Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

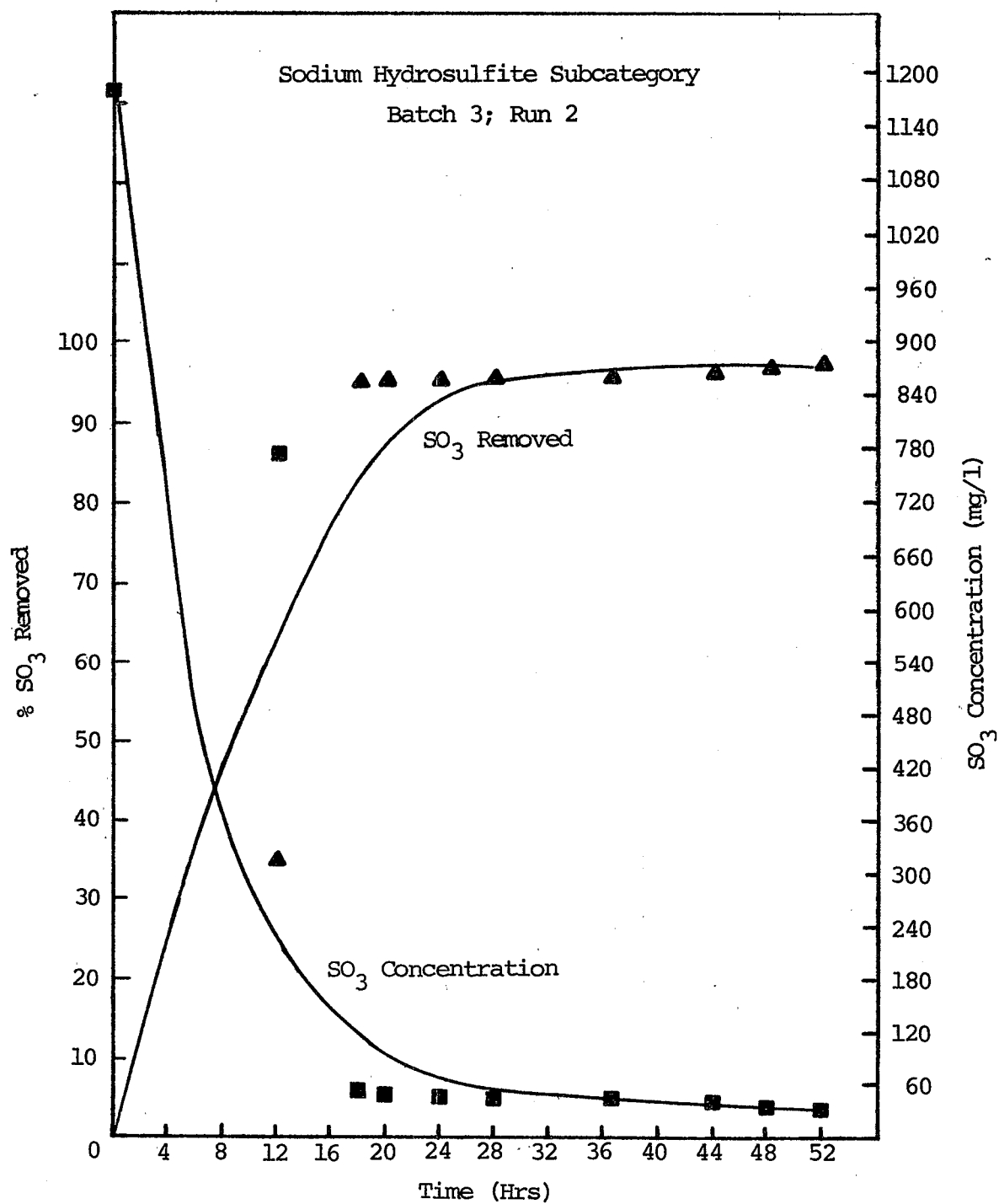


Figure C-6. Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

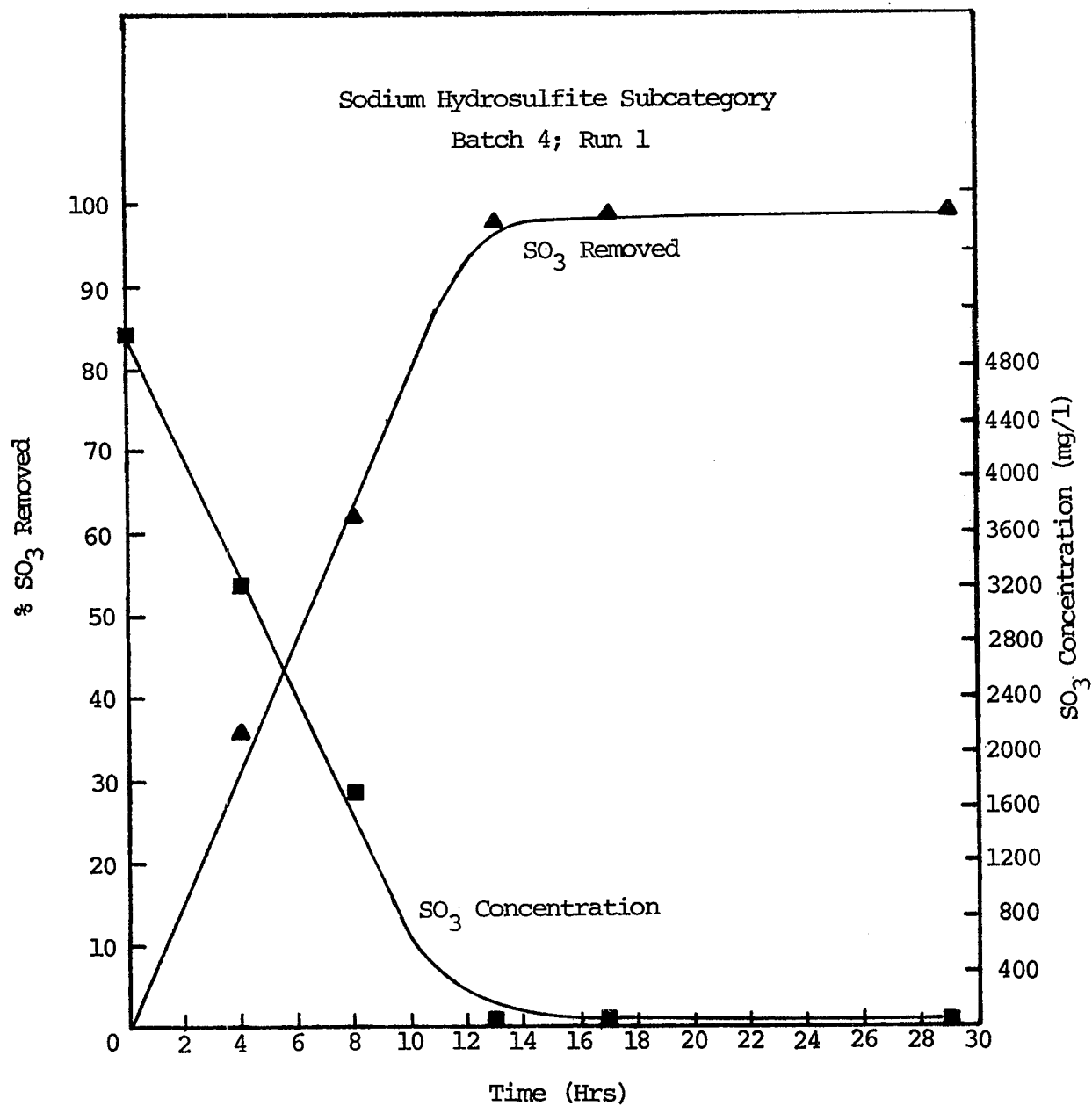


Figure C-7 . Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

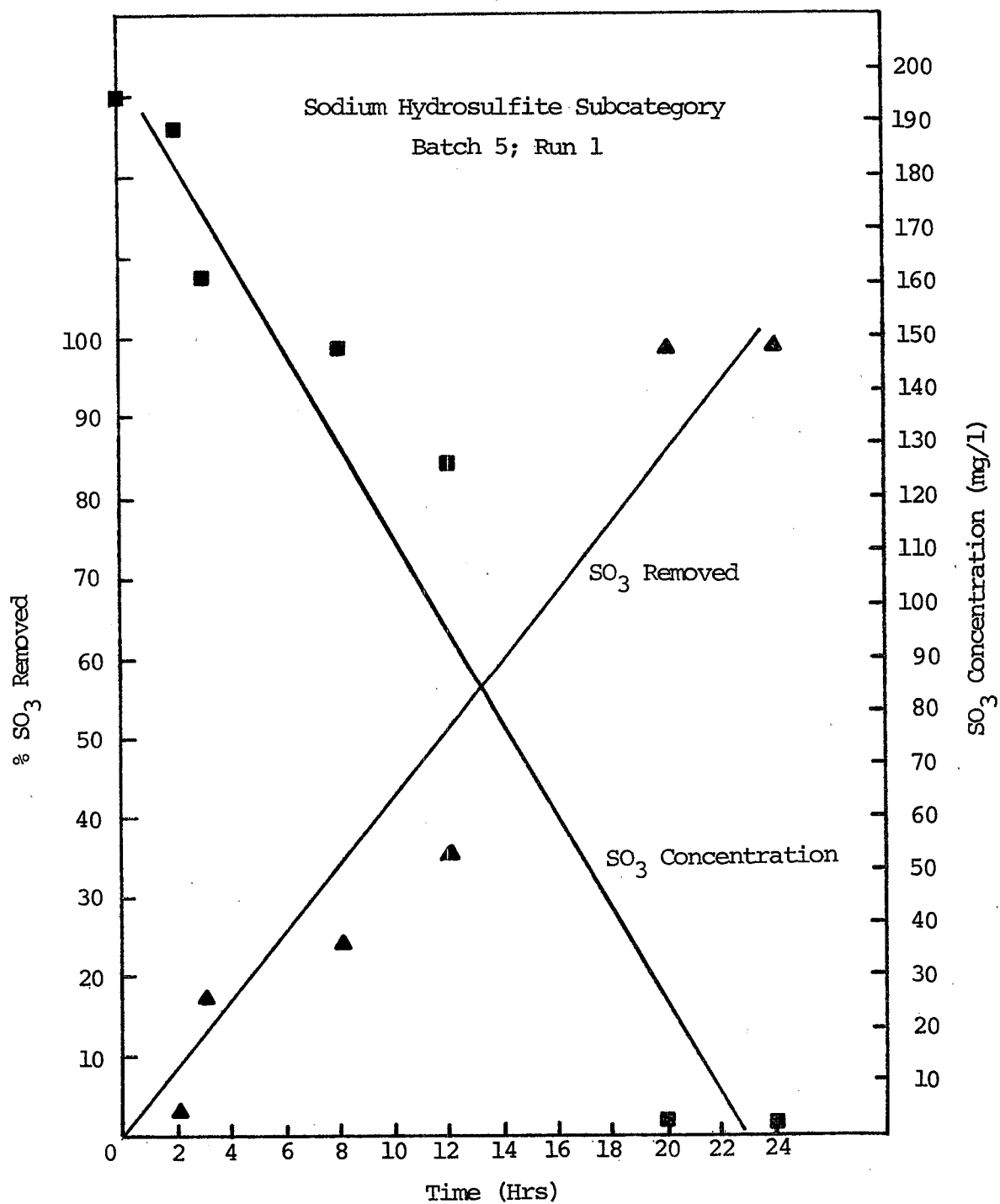


Figure C-8. Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

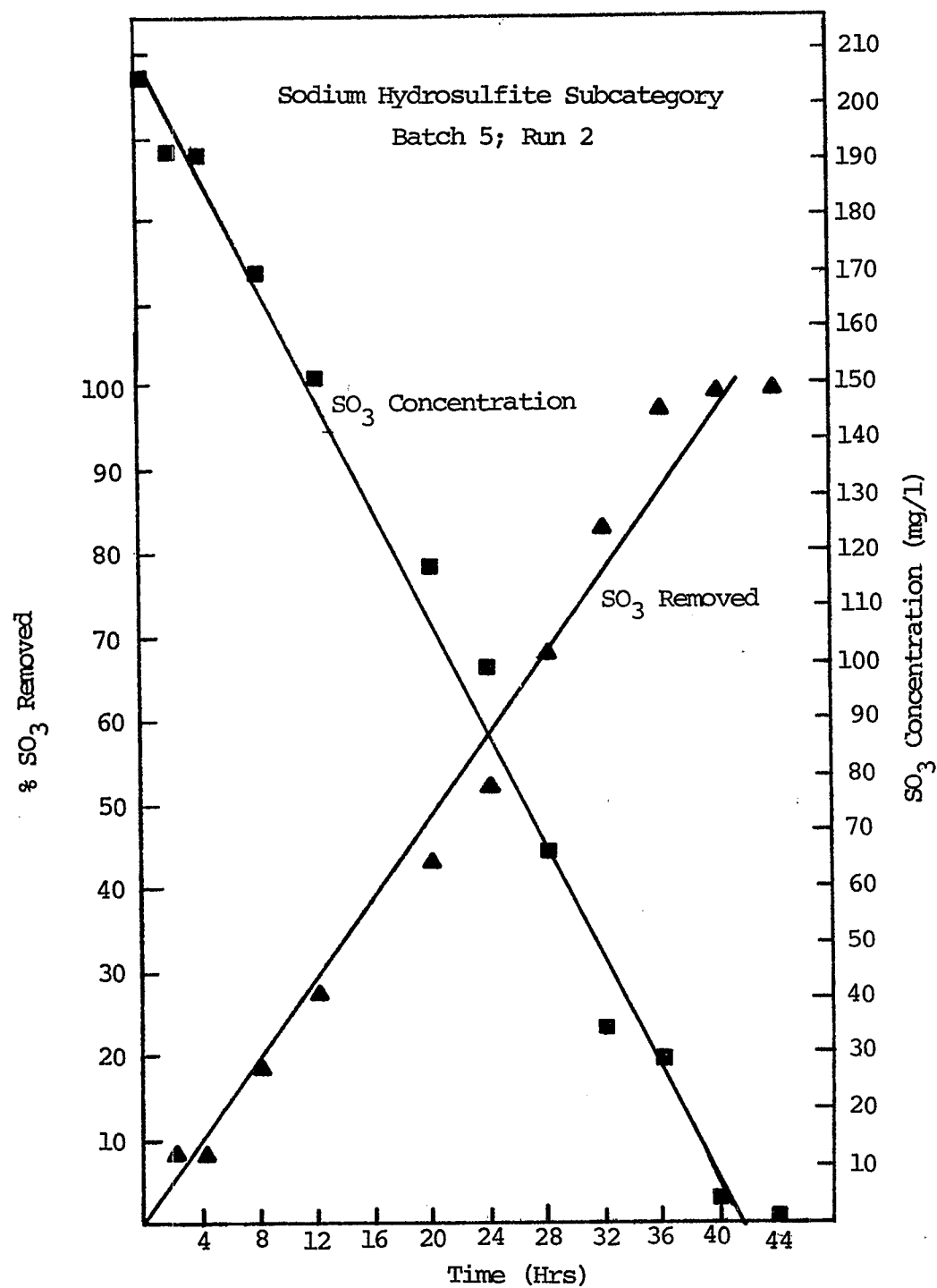


Figure C-9 . Effect of aeration on sulfite concentration  
(airflow rate: 46.0 SCFH)

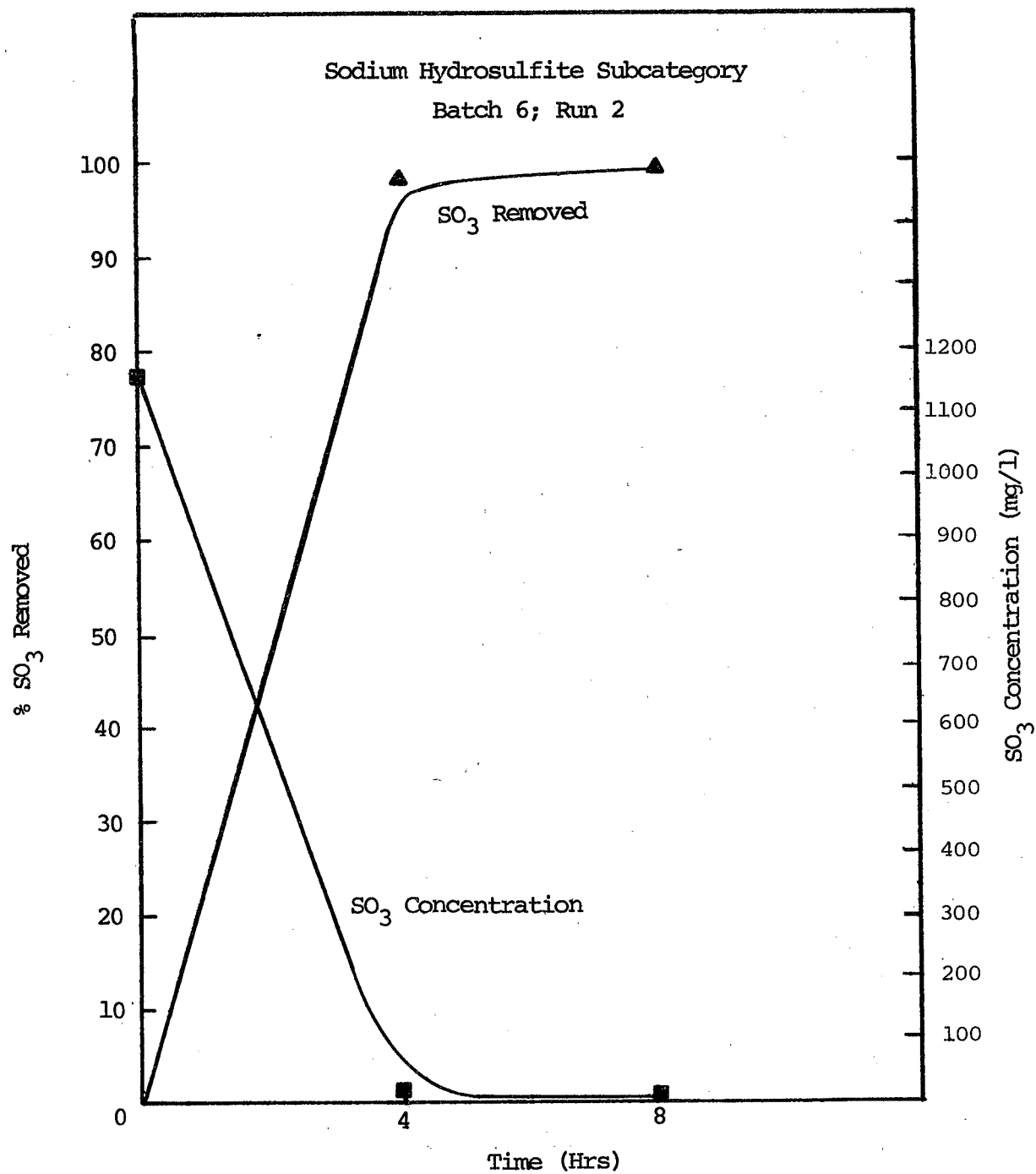


Figure C-11. Effect of aeration on sulfite concentration  
(airflow rate: 35.0 SCFH)

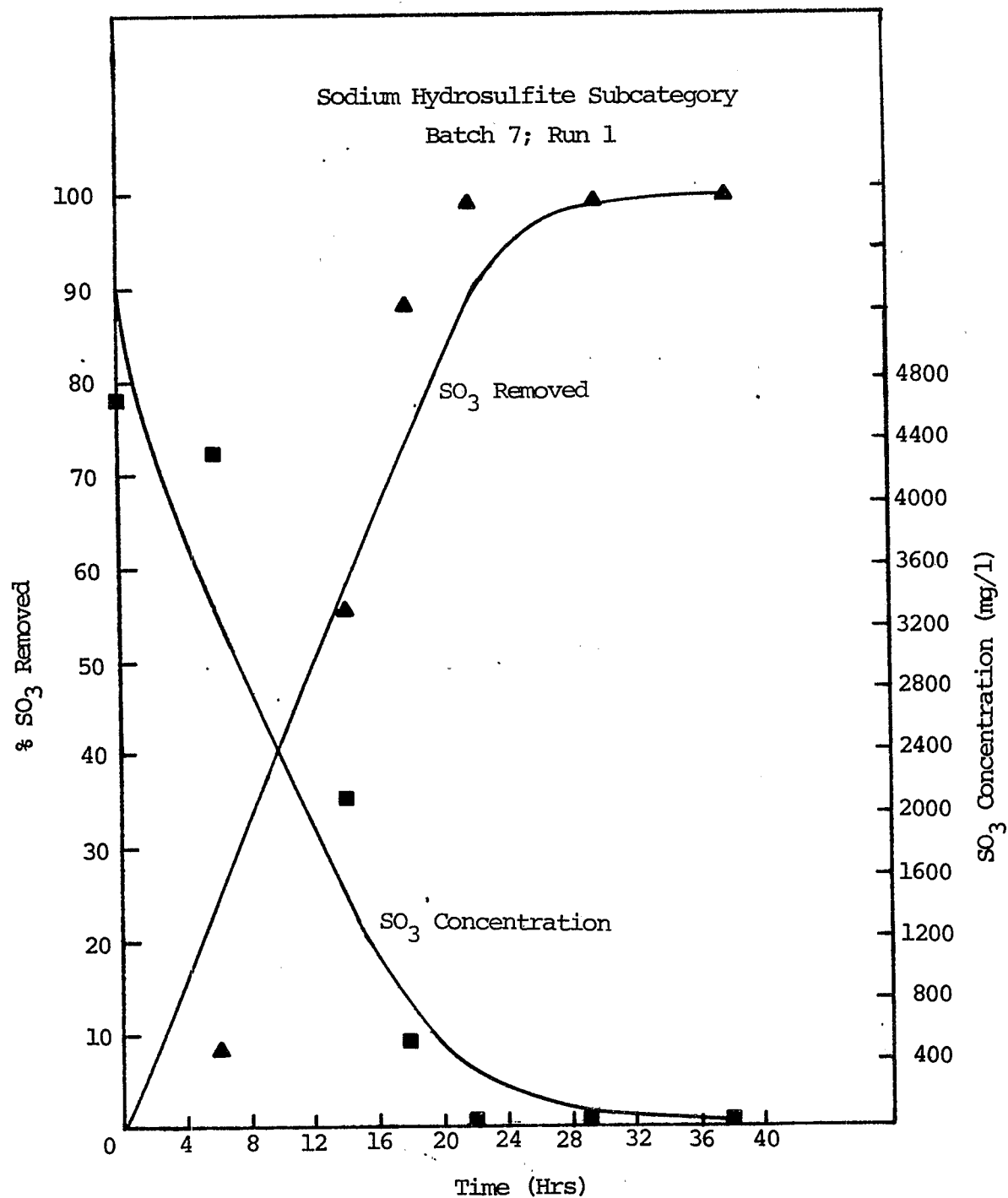


Figure C-12. Effect of aeration on sulfite concentration  
(airflow rate: 35.0 SCFH)



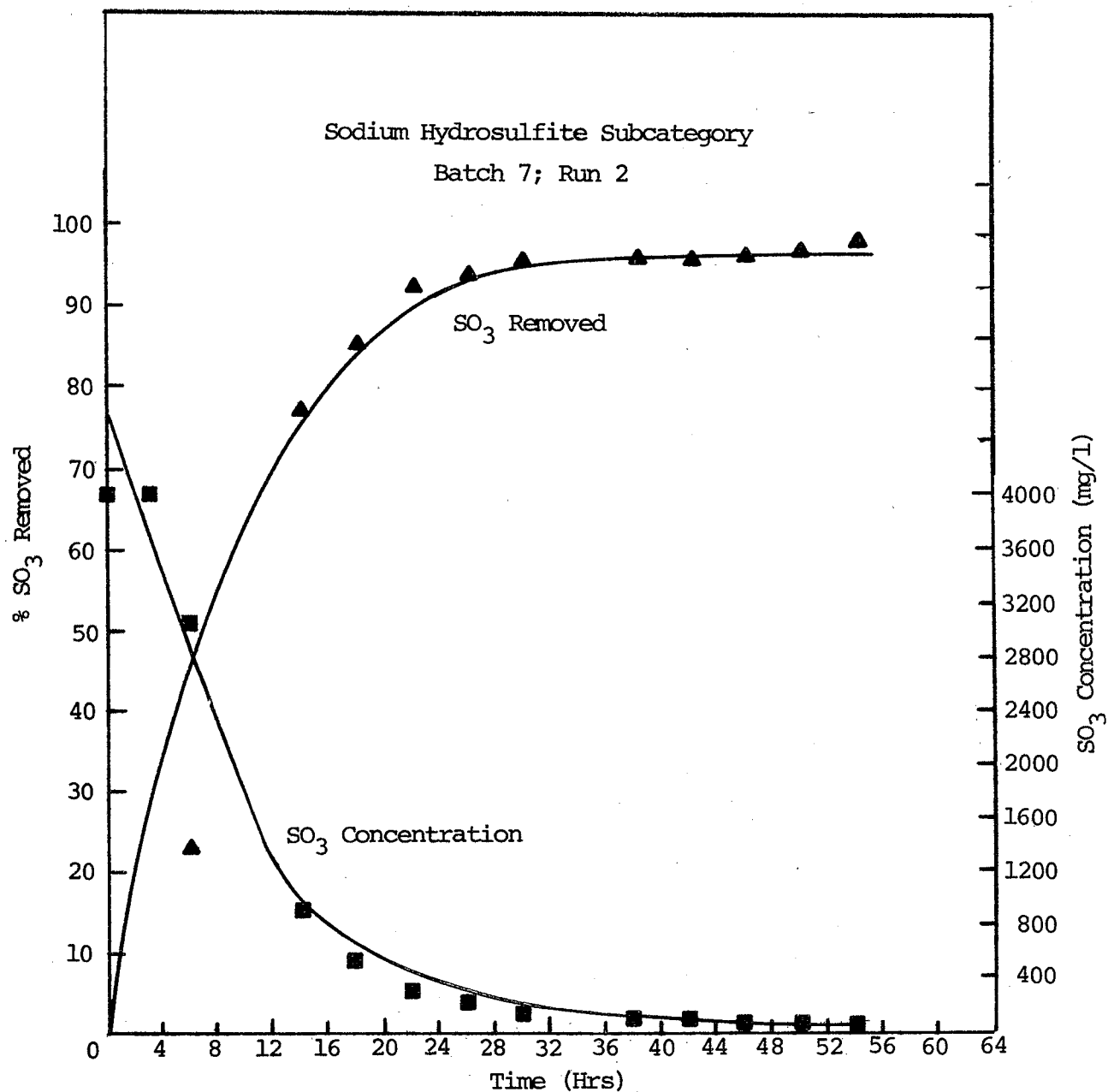


Figure C-13. Effect of aeration on sulfite concentration  
(airflow rate: 35.0 SCFH)

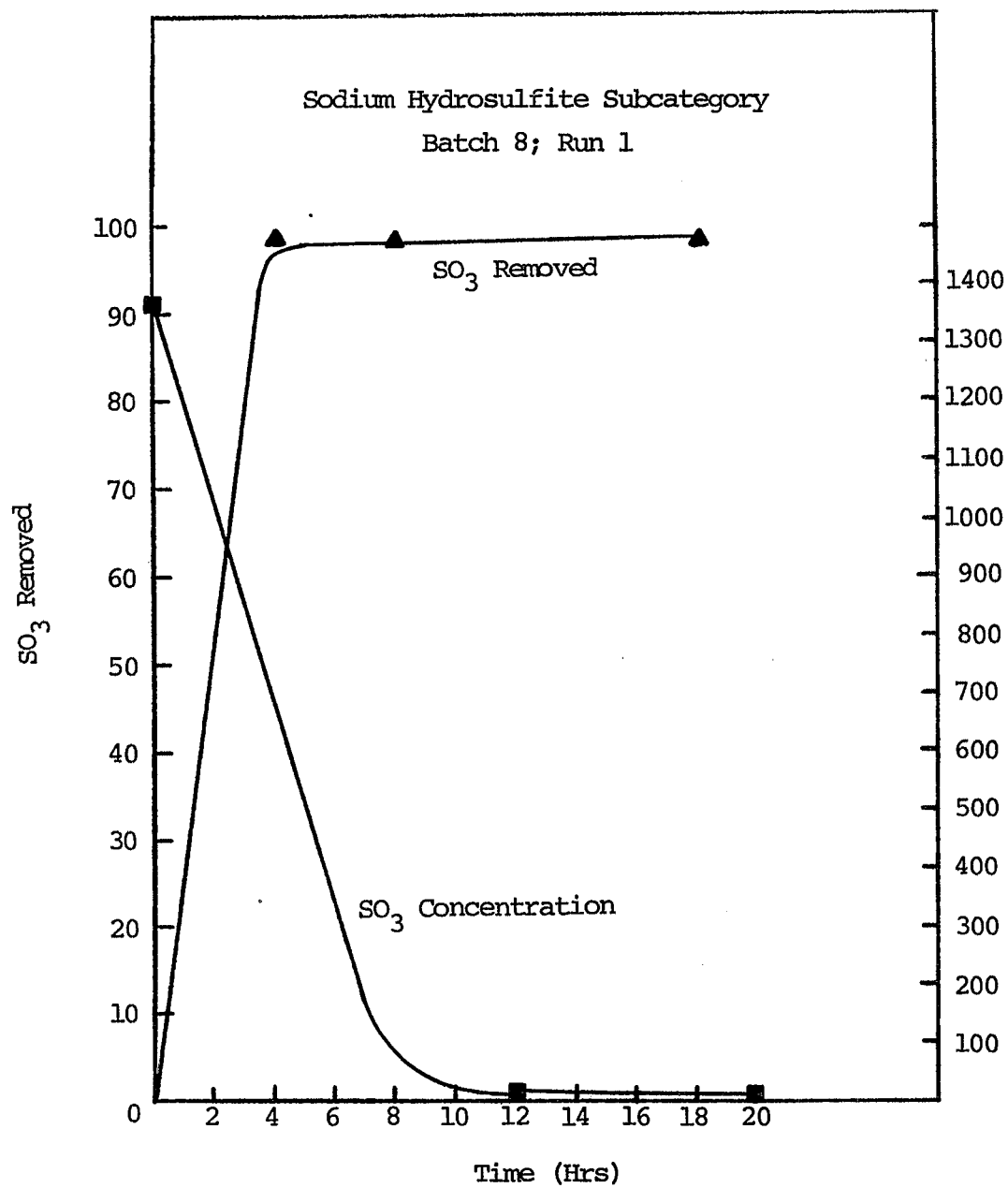


Figure C-14. Effect of aeration on sulfite concentration  
(airflow rate: 35.0 SCFH)

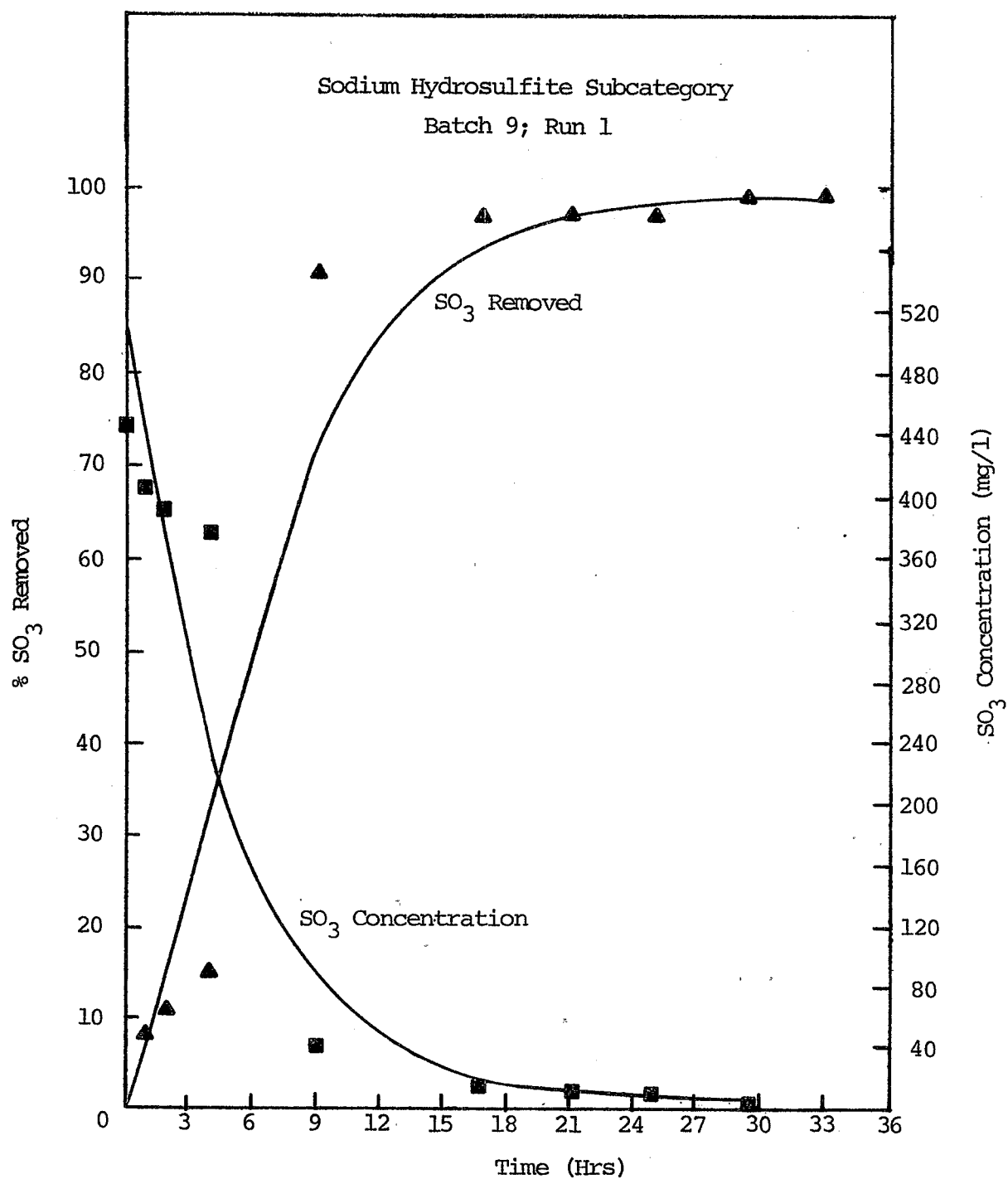


Figure C-15. Effect of aeration on sulfite concentration  
(airflow rate: 23.0 SCFH)

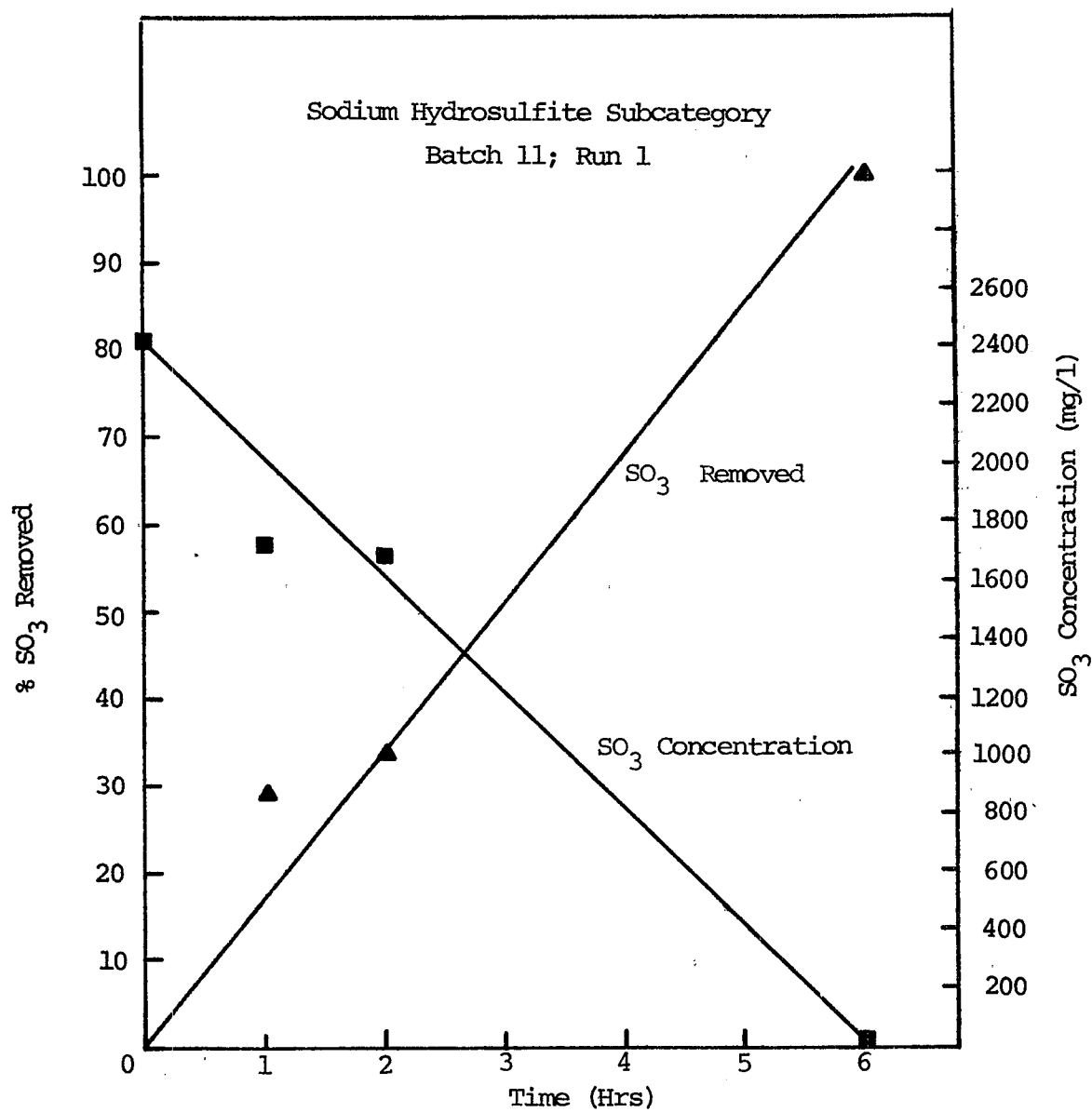


Figure C-18. Effect of aeration on sulfite concentration  
(airflow rate: 11.5 SCFH)