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Evaluation of Lime Precipitation for Treating Boiler Tube Cleaning Wastes

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by

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ABSTRACT

This research program was initiated with the overall objective of exploring the degree of metal removal achievable by lime precipitation treatment of boiler tubeside cleaning wastes (specifically those which use chelating or complexing cleaning reagents).

Samples of wastewaters from six boiler tubeside chemical cleanings using complexing and chelating agents were collected from actual cleanings at power plants. These samples represented the ammoniacal bromate/hydrochloric acid, thiourea-hydrochloric acid, hydroxyacetic-formic acid, ammoniated citric acid, and ammoniated EDTA types of cleaning systems. Samples of wastewaters from boiler fireside and air preheater washes were also collected. A bench-scale treatment methodology was investigated that involved dilution of the boiler tubeside wastewaters with a mixture of the fireside and air preheater wash wastewaters, precipitation with lime, and addition of polymers to enhance clarification. Total and dissolved iron, copper, nickel, zinc, and total suspended solids were analyzed in the supernatant after settling. The ammoniated EDTA cleaning system wastewater was selected as the "most-difficult-to-treat" wastewater from these data, and was used in subsequent investigations including the use of various pretreatments and further adjustments to pH and dilution ratio in an effort to minimize metal residuals and requirements for lime and diluent. After determining that a limitation of 1 mg/l for nickel could probably not be easily obtained for the ammoniated EDTA system, additional testing of the ammoniated citric acid and hydroxyacetic-formic acid wastewaters was also conducted to minimize pH and lime requirements. A statistical test was conducted to support proper interpretation of the testing data. Also, the lime sludge from treatment was investigated for settleability, filterability, and metal content.

The results indicate that, on a laboratory scale, lime treatment used in conjunction with dilution by fireside and air preheater wash wastewaters and addition of polymers is an effective means of attaining the current effluent guidelines limitations that call for 1 mg/l for iron and copper in treated wastewaters from boiler tubeside cleanings using complexing and chelating chemicals. In addition, results of tests for other metals listed as toxic showed that attainable zinc residuals ranged from less than 0.01 mg/l to 1 mg/l. Attainable nickel residuals were below 1 mg/l for all systems other than the ammoniated EDTA, for which the nickel residuals were not less than 5 mg/l.

I. INTRODUCTION

The EPA initiated this investigation to examine lime treatments as a practical means of removing metals from boiler tube cleaning wastes. Particular focus was placed on those wastewaters which contain chelating/complexing cleaning reagents. The treatment methodology employed in this investigation consisted of the following:

- Dilution of the boiler tubeside cleaning wastes with fireside and air preheater wash wastewaters in order to effect a shift in chemical equilibria, thereby aiding the precipitation of the subject metals by lime
- Lime treatment of the diluted wastewater
- The use of polymers to enhance settling and improve clarification.

The first phase of the investigation included the selection of the predominant boiler tubeside cleaning systems that use complexing and chelating agents. A description of these systems is presented in Section IV. Wastewaters from actual boiler cleanings using the selected systems were then sampled and composited for use in laboratory testing. Also, wastewater samples from two fireside/air preheater washings were collected and composited for use in the laboratory as diluent. Sampling efforts are described in greater detail in Section V.

The next phase of the investigation consisted of laboratory testing using matrices of varying dilution ratios and pH's, and various polymers with varying dosages. The main purpose of this phase was to single out a "most-difficult-to-treat" cleaning system wastewater, which would be used in further testing to attain effluent guidelines limitations that would be representative for all subject boiler tubeside cleaning wastewaters. This phase of the investigation is detailed in Sections VII-A, B, and C.

The following phase of the investigation consisted of optimizing the treatment process for the selected most-difficult-to-treat system wastewater with respect to residual metal concentrations and lime and diluent requirements. Further adjustments to pH's and dilution ratios were made and the effects of a number of pretreatment steps were investigated. Also, statistical testing to support data interpretation, and characterization of the resultant lime sludge were performed. This phase of the investigation is detailed in Sections VII-D, E, and F.

In the final phase of investigation, additional laboratory testing was conducted on the ammoniated citric acid and hydroxyacetic-formic acid tubeside cleaning wastewaters. Further adjustments to pH's and dilution ratios were made in an effort to minimize lime and diluent requirements for these two systems. Also, a fireside/air preheater wash wastewater from a coal-fired boiler was introduced into the testing, to determine diluent effects on dilution requirements, lime requirement, and supernatant metal residuals.

Results of experimentation are presented and discussed as the experimentation proceeds, in order to provide continuity and clarity. The overall results of experimentation as they apply to the feasibility of full-scale treatment are discussed separately in Section VIII. The experimental procedures followed in the laboratory to maintain a quality-controlled testing program are discussed in Section VI.

II. CONCLUSIONS

The results of laboratory testing program indicate that lime treatment used in conjunction with dilution by fireside and air preheater wash wastewaters and addition of polymers is an effective means of reducing iron and copper in treated wastewaters from boiler tubeside cleanings using complexing and chelating chemicals to below 1 mg/l level.

In addition, zinc residuals in treated wastewaters were found to be well below 1 mg/l. Nickel residuals no lower than 5 mg/l were found to be present in treated wastewater from the ammoniated EDTA type boiler cleaning; however, for the other systems tested, nickel residuals below 1 mg/l were attainable. Of the 96 Total Suspended Solids analysis performed 51 exceeded the 30 mg/l effluent guideline limitation for this class of wastewaters.

Although laboratory testing data indicate that 1 mg/l of iron and copper is achievable, it is still uncertain whether the 1 mg/l level for iron will be attainable in a full-scale treatment situation. Many of the industry contentions have been evaluated and have been found to be based on the position that continuous treatment will immediately follow the wastewater discharges from chemical cleaning. The treatment methodology under investigation requires that a large amount of diluent wastewater be stored, and such storage introduces the feasibility of batch treatment of a well-mixed raw wastewater with a high degree of flow control. However, the question remains as to what variability or loss of efficiency (from poor mixing), if any, will be introduced by scale-up to full-scale treatment equipment.

There is evidence that some power plants may encounter difficulties using the specific treatment methodology investigated under this program; specifically, they may not be able to generate the required amounts of fireside and air preheater wash wastewaters for treatment of boiler tubeside cleaning wastewaters. In these cases, substitute diluents such as cooling tower blowdown, pond water, or stream water may be required. It is also recognized that land for diluent storage may be required for this treatment methodology; this land may not be available at some power plants.

III. RECOMMENDATIONS

A full-scale demonstration of the proposed treatment methodology under investigation in this study is recommended, so that a proper assessment of any loss of efficiency or variability introduced by scale-up can be made. It is also recommended that the field demonstration be conducted on the ammoniated citric acid system which is the second "most-difficult-to-treat" wastewater. This recommendation stems from another recommendation, which is that because of the difficulty in removing nickel to levels below 5 mg/l, ammoniated EDTA cleaning wastewaters should not be treated by the dilution/lime precipitation system studied under this contract, unless low nickel levels can be guaranteed. It should be noted that other boiler cleaning system wastewaters can also be used for the field evaluation; however, the data obtained will be less representative of problems associated with this class of wastewaters.

There was some uncertainty whether supernatant total iron values of less than 1 mg/l could be reached when the fireside/air preheater from the coal-fired boiler was used as a diluent in the treatment of the ammoniated citric acid wastewater. Therefore, it is recommended that additional laboratory testing be conducted between the dilution ratios of 7:1 and 10:1, and the use of polymers again be investigated.

Because the treatment methodology involves the removal of metals but not the complexing or chelating agent, more research should be done on the environmental impact of the discharge of such contaminants. Some of the organics will have an effect on BOD and COD. Also, the amount of residual ammonia in some of the cleaning system treated wastewaters needs to be determined. Additionally, treatment chemicals such as inhibitors and passivation agents are known to be toxic and should be addressed prior to approval of this treatment methodology. A further investigative recommendation is a study of metal pick-up rates for each of the treated wastewaters, to determine any special needs for nonmetal equipment after clarification and prior to discharge. Finally, a more detailed investigation of metal and organic constituents in terms of disposal options and environmental considerations is recommended.

Lastly, many water conservation programs have recently been instituted by the power industry, which are not reflected by published data. Examples of such water conservation measures include the use of water recovery and recycle systems and waterless cleaning of air preheaters (shot cleaning). Before a final decision is made as to whether

the technology investigated under this contract be recommended as practical, a survey of present day diluent wastewater availability should be initiated, to uncover any changes induced by water conservation practices that could affect the feasibility of this treatment scheme.

IV. DESCRIPTION OF BOILER TUBESIDE CHEMICAL CLEANING SYSTEMS

A. Solutions with Metal Chelating and Complexing Properties Used for Boiler Cleaning

The generation of electricity using steam involves the boiling of water to produce the steam and directing that steam against blades of a turbine which rotates an electric generator. Heat, generated during the combustion of fossil fuels (or by nuclear reactions in nuclear power facilities), causes steam formation when it is transferred across the surfaces of boiler tubes, which surround the furnace area, and into the water which is contained within. Efficient boiler operation is dependent upon this heat transfer, therefore much attention is given to the condition of internal boiler tube surfaces. When deposits form due to the formation of scale and the accumulation of corrosion products, impairment of heat transfer results thus lowering efficiency of the boiler. In addition to the decrease in efficiency, tube failure may result due to localized overheating. Thus, chemical cleaning of tube surfaces is required for safety and economic reasons.

Chemical cleaning of boiler tubesides may be divided into single and multi-stage processes. These processes may utilize an acid or alkaline solution to affect dissolution and complexing of deposited metals. The following principal cleaning solutions have been found to exhibit metal chelating or complexing properties:

(1) Hydrochloric acid with copper complexors;

(2) Copper oxidizing and complexing solution used in conjunction with acid cleaning;

(3) Citric acid based solutions;

(4) Hydroxyacetic/formic acid;

(5) Ammoniated EDTA.

Selection of these five types of cleaning systems was based on technical data from the two predominant boiler cleaning service companies, Dow Industrial Service and Halliburton Services, Inc. (1,2). Although references to such cleaning agents as sulfuric, sulfonic, gluconic, and oxalic acids are encountered in the literature (3,4), none of the available reports of actual cleanings done by power companies or cleaning services (1,2) confirms use of these

chemicals. Although each solution is discussed separately, the following combinations may be employed, resulting in a multi-stage process:

(1) Any type of chemical cleaning may be preceded by an alkaline boil-out to remove oil-based compounds from tube surfaces, if oily substances constitute a relatively large proportion of the deposit to be removed. However, the relatively small amounts of oily substances usually found can be adequately handled by wetting agents that are often added during subsequent cleaning stages (5).

(2) Acid cleaning, especially with hydrochloric acid, may be followed by an alkaline boil-out and a subsequent passivation stage. Passivation is accomplished by circulating or soaking with a passivating solution such as hydrazine hydrate and ammonia hydroxide or sodium nitrite (5).

(3) Acid cleaning may be preceded or followed by copper oxidizing and complexing solutions. Most commonly employed are ammonium sodium bromate, ammonium bifluoride, potassium permanganate, and ammonium persulfate (6,7). Ammonium persulfate is used less commonly, because of its more hazardous nature (7). Its primary application is for the cleaning of the older once-through units with copper deposition, in which case it is used in combination with a non-halogenic solvent, such as hydroxyacetic-formic acid (5). Ammonium bifluoride has also been found to enhance the solubility of iron deposits and is used commonly.

(4) Cleaning with hydrochloric acid may be followed with citric acid rinse.

1. Solutions Using Hydrochloric Acid as the Principal Deposit Dissolver

a. General Description. Hydrochloric acid is a widely used boiler cleaning agent. It is very effective in handling a wide range of deposits. Usually, a 5 to 7.5 percent solution of inhibited hydrochloric acid is strong enough to dissolve most of the mineral and iron parts of deposits (5). However, the presence of copper warrants addition of copper complexing agents.

For copper complexing, Dowell Industrial Services uses straight thiourea while Halliburton has added a proprietary ingredient to their formulation (Cutain II) which

has been described as a cyclic derivative of thiourea (8). Characteristics of the two systems are very similar. The cleaning stage is often followed by a rinse with dilute citric acid and a passivation stage. Since citric acid is also a chelating chemical, treatment of wastewaters from a thiourea/citric acid cleaning may be more difficult.

The advantages of hydrochloric acid as a cleaning agent are well known (1,2). They include:

(1) Relatively low cost of chemicals involved

(2) Extensive experience accumulated by the industry

(3) Availability

(4) Compatibility with organic and inorganic additives. For example, fluoride salts (ammonium bifluoride) used to solubilize silicates are highly compatible with hydrochloric acid

(5) Availability and wide selection of suitable inhibitors.

However, several conditions exist which make the use of hydrochloric acid less desirable as compared with organic acids and EDTA. Hydrochloric acid is not recommended for use on once-through boilers since it presents a significant safety and corrosion hazard (9). Also, cleaning with hydrochloric acid will generate from five to six boiler volumes of wastewater, which may pose disposal problems for the utility.

b. Chemistry of Complexation. Two predominant copper complexing agents are used in conjunction with hydrochloric acid cleaning, namely thiourea and Cutain II®. The structure of thiourea is given below:

$$H_2N\overset{\overset{\displaystyle S}{\|}}{C}NH_2$$

Thiourea is a strong complexor of the cupric ion, with four molecules forming coordinate bonds with the copper, as described below (10):

$$Cu^{++} + 4H_2NCSNH_2 \qquad Cu.(H_2NCSNH_2)_4$$

The stability constant of the complex is cited as 2.5×10^{15} (9). Thiourea forms a much weaker complex with zinc, with

the stability constant ranging from 3.16 for the one ligand complex to 7.94 for the three ligand complex (11). No information was available on the stability of the iron-thiourea or nickel-thiourea complex.

Cutain II® is a proprietary formulation of Halliburton Services. It consists of a combination of thiourea and a cyclic derivative of thiourea. No information was available on the stability of metal complexes formed with Cutain II®, but one would assume that the stability constant is similar to that of thiourea. Cutain II® seems to include chloride as part of the complex, as evidenced by the following reaction equations (12).

Iron dioxide dissolution:

$$Fe_3O_4 + 8HCl + \text{Cutain II}^{®} \longrightarrow FeCl_2 + 2FeCl_3 + 4H_2O + \text{Cutain II}^{®}$$

Copper Complexing:

$$FeCL_3 + Cu^{o} + \text{Cutain II}^{®} \longrightarrow FeCl_2 + Cu{\cdot}Cl{\cdot}\text{Cutain II}$$

2. Copper Oxidizing and Complexing Solutions Used in a Separate Stage

a. General Description. These solutions preceed or follow the acid cleaning stage. Solutions used for copper removal generally contain free ammonia, ammonium salts, and an oxidizing agent such as potassium or sodium bromate, ammonium persulfate, nitrates or nitrites (13). Ammonium sodium bromate and ammonium persulfate have been used for the removal of large amounts of copper from boiler deposits (1,2). Dow Industrial Services uses ammonium sodium bromate almost exclusively (1) while Halliburton Services use both (2). However, it appears that the use of ammonium persulfate is not common because of its more hazardous nature (7).

b. Chemistry of Complexation. The active complexing agent in both ammonium sodium bromate and ammonium persulfate is the ammonia species. Molecular ammonia forms a strong complex with the cupric ion, with four ammonia molecules forming coordinate bonds with the central copper, as shown below (10):

$$Cu^{++} + 4NH_3 \longrightarrow Cu(NH_3)_4^{++}$$

This positively charged complex has a stability constant of $1x10^{13}$ at 25°C (14). It is recognized that this complex is

not the only metal-ligand species present, but is predominant. Ammonia also forms moderately strong complexes with nickel and zinc. The stability constant of the nickel-six ligand complex is 1.2×10^9 (25°C) while the predominant zinc-four ligand complex has a stability constant of 4.47×10^9 (14). No information was available on iron-ammonia complexes.

3. Citric Acid Based Solutions

a. General Description. Citric acid has strong chelating abilities toward the cupric and ferric ion. Combined with ammonia, it is used to clean moderately dirty boilers instead of hydrochloric acid with copper complexer. Because of its low corrosion rate and ease of disposal it may be preferred over stronger mineral acids.

A process developed by Halliburton Services uses ammoniated citric acid for cleaning deposits containing both iron and copper. This process, Citrosolv®, is a two stage, one solution procedure. Usually, a 3 percent solution of citric acid ammoniated to a pH of 3.5 is used as a first step at temperatures up to 200°F to dissolve iron oxides. When this reaction is complete the pH is raised to 9 or 10 by the addition of anhydrous ammonia to dissolve copper in the deposits. The second stage is accompanied by aeration (15).

The advantages of the Citrosolv® process are cited as (3,16):

(1) Low corrosion rate

(2) Relatively low toxicity, hence less hazardous

(3) Ease of disposal.

Limitations of the Citrosolv® process include:

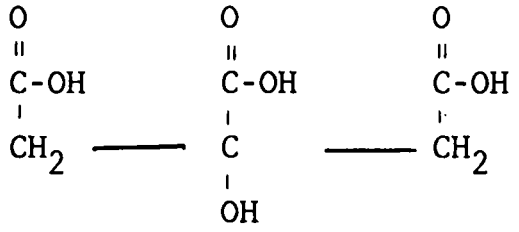
(1) Usually not used in boilers with heavy deposits (2)

(2) Cost of chemicals higher than that of other acids and cleaning agents (17)

(3) Fluoride salts normally used with other solvent systems to remove silicates, are not effective when used with Citrosolv®, hence there is a necessity to combine the Citrosolv® process with another treatment if silicates are present (16). Two stage treatment using

a solution of hydrochloric acid and ammonium bifluoride in conjunction with the citric acid stage is recommended for this problem (16).

b. Chemistry of Complexation. Ammoniated citric acid has strong complexing capacity towards the ferric and cupric ions. Citric acid serves to chelate both the cupric and ferric ions. Its structural formula suggests that it possesses very strong chelating ability.



The aeration stage, described above, is used to oxidize ferrous (2^+) iron to the ferric species (3^+), in order to form the strong ferric-citrate chelate. This is evidenced by a critical stability constant of 3.16×10^{11} (20°C) for the ferric chelate as compared to 2.51×10^{4} for the ferrous chelate at 20°C (11). There is evidence in the literature that citric acid may form hydrated complexes with copper with stabilities as high as 1.58×10^{33} (18). This is several orders of magnitude higher than any other metal-ligand stability constant mentioned in this study. Citric acid also forms strong hydrated complexes with ionic zinc and nickel, with stability constants being reported as high as 2.51×10^{9} and 1.66×10^{11}, respectively (18).

4. Hydroxyacetic/Formic Acid

a. General Description. Hydroxyacetic/formic acid is most widely used in cleaning of once-through boilers, where the use of inorganic acids is prohibitive. The hydroxyacetic/formic acid solution chelates iron effectively and in combination with a corrosion inhibitor and a copper oxidizing/complexing agent may produce good results in general boiler cleaning (19,20). Ammonium bifluoride or persulfate is commonly added in this respect, however, use of a halogen containing oxidizer precludes use on austenitic steels. A 2:1 mixture of hydroxyacetic/formic acid is usually applied for cleaning as 3 to 5 percent solution at 200°F (16,20).

The major advantages are cited as (20):

(1) Corrosion protection for bimetallic junctions

(2) Controlled chloride content for austenitic systems

(3) High iron pick-up

(4) Chelation properties assist in rinse operation

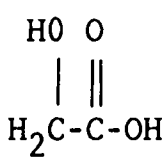
(5) Minimal corrosive damage from leaks

(6) More effective cleaning due to circulation

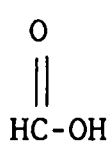
(7) Safest method for cleaning once-through boilers

(8) Generally less costly than citric acid.

b. Chemistry of Complexation. The chemistry of complexation of hydroxyacetic/formic acid mixtures is not well known. Roebuck (3) suggests that hydroxyacetic acid is the main chelating agent. Stability constants taken from Martell (11) suggest that formic acid may form strong hydrated complexes with ferric ions; however, this may only occur at alkaline pH values. Unhydrated complexes for all listed metal species were found to be relatively weak. An explanation for the strong chelation properties found in operation is a synergistic contribution of both formic and hydroxyacetic acids to form a much stronger chelation than the two alone. This hypothesis has neither appeared nor been verified in the available literature. The structure of the hydroxyacetic and formic acid molecules is given below:



Hydroxyacetic Acid



Formic Acids

Stability constants for complexes of hydroxyacetic acid and formic acids with various metal ions is given in Table 1.

TABLE 1. STABILITY CONSTANTS OF PREDOMINANT HYDROXYACETIC AND FORMIC ACID COMPLEXES (11)

Acid (L)	Metal ion (M)	Equilibrium	Log K
Formic	Ni^{2+}	$[ML]/[M][L]$	0.67 (30°C)
	CU^{2+}	$[ML_4]/[M][L]^4$	1.9-3.3 (25°C)
	Fe^{3+}	$[ML]/[M][L]$	3.1 (25°C)
		$[M_3L_6OH_2]/[M]^3[L]^6[OH]^2$	19.9-20.0 (20°C)
	Zn^{2+}	$[ML_3]/[M][L^3]$	1.20
Hydroxyacetic	Fe^{2+}	$[ML]/[M][L]$	1.33
	Ni^{2+}	$[ML_3]/[M][L]^3$	3.05
	CU^{2+}	$[ML_2]/[M][L]^2$	3.72-4.66
		$[ML_3]/[M][L]^3$	4.27
	Fe^{3+}	$[ML]/[M][L]$	2.90
	Zn^{2+}	$[ML_2]/[M][L]^2$	2.92 ± 0.02
		$[ML_3]/[M][L]^3$	3.2 ± 0.3

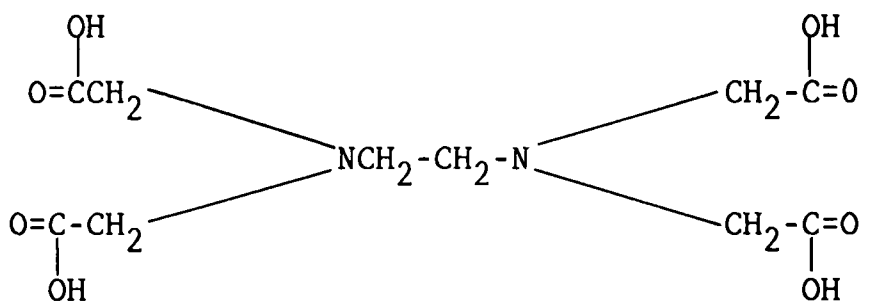
When ammonium compounds are added to enhance dissolution and complex formation, the chemistry is similar to that discussed earlier.

5. Ammoniated EDTA Based Cleaning Solutions

a. General Description. The Alkaline Copper Removal® Process is based on Vertan 675® chelate. Vertan 675® is a solution of the tetra-ammoniated salt of ethylenediamine-tetracetic acid (EDTA) containing organic nitrogen compounds to inhibit corrosion (21). The cleaning procedure is a one-solution two-stage process. The first stage consists of dissolving and chelating iron at pH of 9.0 to 9.5 at temperatures of up to 325°F. After all the iron has been chelated the temperature is dropped to 188°F and the solution is oxidized with air. This stage oxidizes the ferrous chelate to a ferric chelate and it, in turn, oxidizes the copper into solution and forms a stable cupric chelate. The cleaning is complete when the copper concentration levels off leaving a passivated surface. Among the advantages in using Vertan® its universality appears to be one of the most important. Dow claims that Vertan 675® can be used on all types and sizes of boilers, including austenitic alloys (3,22).

Low corrosion rate, low volume of wastes (usually 2 boiler volumes), low outage time (2 days) and safety are the features that may make Vertan 675® an attractive alternative to acid cleaning. However, the cost of chemicals involved may be higher than those for hydrochloric-based solutions. Vertan 675® is a proprietary formulation and is not marketed by Dow competitors which limits its share of the market.

b. Chemistry of Competition. EDTA is one of the most studied of all chelating agents. It is used in the form of a tetra-ammoniated salt to increase its solubility and enhance copper removal. The structure of EDTA is shown as follows (3).



EDTA exhibits very strong chelating properties for all metal species of concern. It possesses four active hydronium sites and two addition nitrogen ligands which suggest that one EDTA molecule may form up to six metal-ligand bonds with the chelated metal ion. This structural evidence is confirmed by the stability constants of EDTA with various metal ion species, as shown in Table 2.

TABLE 2. STABILITY CONSTANTS OF METAL-EDTA COMPLEXES (23)

Metal ion	log K (25°C)
Fe^{2+}	14.27-14.32
Fe^{3+}	25.00-25.10
Ni^{2+}	18.52-18.62
Cu^{2+}	18.70-18.80
Zn^{2+}	16.44-16.51

V. FIELD SAMPLING

A. Boiler Tubeside Chemical Cleaning Systems

Wastewater samples were collected from six tubeside chemical cleanings of power plant boilers. These specific cleanings were chosen to represent the five principal types of tubeside cleanings presently used in industry, which were discussed in the previous section. Collected samples were from the following principal cleaning types.

(1) Ammoniacal bromate/hydrochloric acid

(2) Hydroxyacetic-formic acid

(3) Thiourea-hydrochloric acid

(4) Ammoniated citric acid.

A cleaning using ammonium persulfate was also under consideration in response to a request by power industry representatives (5). However, sampling of this additional cleaning method was not included in the test plan on the grounds that (1) the copper/ammonia complex is adequately represented by the ammoniacal bromate system, as well as by ammonium bifluoride, bicarbonate, ammoniated EDTA, and ammoniated citric acid; and (2) ammonium persulfate is used rarely in comparison with ammoniacal bromate, ammonium bifluoride, and potassium permanganate (6,7).

It should be noted that the optimum sampling approach would involve collecting samples from several of each type of boiler cleaning and compositing them to form a representative sample. However, the financial and time constraints on the project limited sampling efforts to those described above. Sample collection of the specific tubeside cleanings is described in greater detail in the following sections.

1. Ammoniacal Bromate/Hydrochloric Acid

The sample of wastewaters from this type of boiler cleaning was collected during the cleaning of Unit #2 at the Tennessee Valley Authority's Gallatin Steam Plant, Gallatin, Tennessee, on September 12 to 14, 1978. Unit #2 is a Combustion Engineering twin coal-fired furnace, controlled circulation boiler with a holding capacity of 106,000 liters (24).

Cleaning was conducted using a 5 percent inhibited hydrochloric acid stage and two copper complexing stages,

each consisting of approximately 4 percent potassium bromate and 6 percent ammonium bicarbonate in solution. These chemical amounts correspond to the removal of 544 kg of deposited copper. Hydrazine, rodine, and trisodium phosphate were also added during the various cleaning stages.

A total of 10 stages were employed to complete the cleaning. They are listed below in chronological order:

(a) Hot water flush
(b) Ammoniated bromate stage
(c) First water rinse
(d) Hydrochloric acid stage
(e) Second water rinse
(f) Third water rinse
(g) Second ammoniated bromate stage
(h) Fourth water rinse
(i) Fifth water rinse
(j) Passivation stage.

Following each stage, the boiler was drained for a period of 1-1/4 hours. Samples of approximately 0.5 liter were taken of each drain every five minutes for a period of one hour. Composited samples from each drain were further composited in a 140-liter polyvinyl chloride (PVC) container in order to represent the total wastewater from the boiler cleaning.

2. Hydroxyacetic-Formic Acid

Wastewater samples from this type of cleaning were collected by Allegheny Power System personnel at the Hatfield Power Plant, Masontown, Pennsylvania, on October 10 to 12, 1978. The unit cleaned (Unit #1) is a Babcock & Wilcox supercritical, once-through, coal-fired boiler with a holding capacity of 261,200 liters (25). It was installed in 1969 and previously cleaned in April 1973.

Cleaning was conducted using a 4 percent solution of 2:1 mixture of hydroxyacetic and formic acids, respectively. Ammonium bifluoride was also added as a copper complexor. This stage was followed by two plant feedwater rinse stages and a final passivation using ammonia and hydrazine. Thus, a total of four stages were required for cleaning, as summarized below:

(a) Hydroxyacetic-formic acid stage

(b) First water rinse

(c) Second water rinse

(d) Passivation stage.

Two flow-proportional drain samples (114 liters each) were composited from samples taken every five minutes over an hour's time. One of the composite samples was taken during acid circulation and the other was taken during passivation. The composited samples do not contain the two rinse stage drainings and so the combined sample used in testing is approximately twice the concentration of the total actual wastewater from this cleaning.

3. Ammoniated EDTA

The wastewater sample from this type of cleaning was collected during the cleaning of Unit #1 at the Dickerson Power Generating Station, Dickerson, Maryland, on December 11 to 15, 1978. Unit #1 is a Combustion Engineering controlled circulation coal-fired boiler rated at 190 MW with a holding capacity of 106,000 liters (26).

The boiler cleaning was conducted using an 8.3 percent solution of ammoniated EDTA with a reported 91 to 136 kg of copper removed from the boiler (26). Two rinses with seal water were employed followed by a passivation stage using hydrazine. The stages used in the cleaning are listed below:

(a) Ammoniated EDTA stage

(b) First water rinse

(c) Second water rinse

(d) Passivation stage.

Grab samples of the four stages (38 liters each) were taken directly from the circulation pump after at least one hour of circulation, insuring representativeness. A deficient volume of sample (11 liters) was collected during the second rinse, and was therefore not used to make up the composite. However, passivation is not usually conducted after ammoniated EDTA cleanings, thus suggesting that a three-stage cleaning process is probably more common. The combined sample to be used in initial laboratory testing (with the second rinse omitted) is expected to have only slightly different metal concentrations than the total wastewater from a three-stage cleaning without passivation.

4. Thiourea-Hydrochloric Acid

Two samples of thiourea-hydrochloric acid cleaning wastewaters were collected for laboratory testing. The first wastewater sample was collected during the cleaning of Unit #4 boiler at Florida Power and Light Company's Fort Lauderdale Power Plant on December 13 to 15, 1978. Boiler #4 is a Babcock & Wilcox single-drum natural circulation reheat type oil-fired unit with a holding capacity of 113,562 liters (27). The cleaning solution was composed of approximately 1 percent thiourea (Cutain II)®, 5 percent hydrochloric acid, 0.2 percent ammonium bifluoride, and 0.2 percent inhibitor. The cleaning stage was followed by a water rinse and a second rinse consisting of 0.1 percent citric acid. Passivation was conducted using a soda ash boil-out. The stages used in cleaning are listed below:

(a) Thiourea-acid stage

(b) Water rinse

(c) Citric acid rinse

(d) Passivation stage.

Samples of the wastewaters from each of the four stages were collected continuously during the 1-1/2 hour drain period and composited in a 114-liter PVC container before shipment to the laboratory.

A second sample of a thiourea-hydrochloric acid boiler cleaning was collected at Baltimore Gas & Electric Co.'s Riverside Power Station, Turners Station, Maryland, on January 3, 1978. The cleaning was conducted on Boiler #4, which is a Babcock & Wilcox natural circulation drum-type oil-fired boiler with a holding capacity of 98,420 liters (28). The cleaning was conducted using an acid-thiourea (Cutain II)®stage consisting of about 5 percent hydrochloric acid, 0.4 percent Cutain II,®0.2 percent ammonium bifluoride and 0.2 percent inhibitor. The cleaning stage was followed by two water rinses and a soda ash boil-out for passivation. A total of four stages were required for cleaning, as listed below:

(a) Thiourea-acid stage

(b) First water rinse

(c) Second water rinse

(d) Passivation stage.

Composite samples of each of the four stages were taken every six minutes over a period of 1-1/4 hours. The composited samples of each stage were further composited in a 114-liter PVC container before shipment back to the laboratory. This second sample of the thiourea-type cleaning differs from the first in that no citric acid was used in the rinse.

5. Ammoniated Citric Acid

The samples of wastewaters from the ammoniated citric acid method were collected by Orange & Rockland Utilities personnel at the Lovett Power Plant, Tomkins Cove, New York, on February 16, 1979. The cleaning was conducted on Boiler #3, which is a Combustion Engineering natural circulation, tangentially fired, single-drum coal-fired boiler with a holding capacity of 51,100 liters (29).

A 5 percent solution of citric acid was used in the cleaning stage, which also contained approximately 0.4 percent ammonium bifluoride, and 0.8 percent sodium nitrite. The solution pH was raised to 9.5 by addition of 4,220 liters of aqua ammonia and 227 kg of ammonium bicarbonate, corresponding to concentrations of approximately 2.4 percent and 0.4 percent, respectively. The cleaning stage was followed by a first rinse with city water and a second with high-purity condensate water. Thus, a total of three stages were required for cleaning, as listed below:

(a) Citric acid rinse

(b) First water rinse

(c) Second water rinse.

A total of 38 liters of sample was taken during the draining of each stage, with a 3.8-liter volume being collected every 5 to 6 minutes over a period of one hour. Samples were contained in 3.8-liter glass jugs and picked up by Hittman personnel for transfer to the laboratory.

B. Boiler Fireside Air Preheater Wash Wastewater Composites

The washing of boiler firesides and air preheaters is conducted periodically to remove ash, slag, and soot deposits from heat exchange surfaces. These deposits accumulate as a

normal result of fuel combustion, and must be removed periodically to maintain efficient heat transfer in the boiler.

Samples of boiler fireside and air preheater wash wastewaters were collected for use in the laboratry testing scheme. These wastewaters were combined before use in the ratio of 2:1 air preheater wash volume to fireside wash volume. This ratio was based on relative generated volumes calculated from the frequency and batch volumes of the two types of cleanings (30) with the assumption that full scale treatment could well require collection and storage for a one-year period.

Two boiler fireside/air preheater wash wastewater composites were collected for this study.

The first of these composites was collected during the cleaning of Unit #4 at Baltimore Gas & Electric Company's Riverside Plant, on October 7 to 8, 1978. Unit #4 is a Babcock & Wilcox natural circulation drum-type boiler. This particular power plant uses predominantly #6 fuel oil which is believed to be extremely high in nickel, since analysis of the fly ash from this plant yielded a nickel concentration of 35,000 ppm (31). Thus, wastewaters from the fireside and air preheater washings of the boilers in this plant are expected to contain higher-than-normal concentrations of nickel.

The fireside cleaning was conducted with a high-pressure stream of water containing a surfactant to aid deposit breakup. BG&E personnel worked inside the boiler directing the high-pressure hose toward the fireside surface deposits. Wastewater from the cleaning trickled down to the sluice box, where samples were collected. The cleaning was done in shifts with approximately a 15-liter grab sample taken during each cleaning shift, corresponding to a total of 76-liters taken at the end of five cleaning shifts.

After cleaning of the fireside tube surfaces, automatic water jets inside the air preheaters were activated and ran continuously for approximately six hours. The wastewater from the cleaning drained into a sluiceway, where it was collected with a weir and small pump. Four 38-liter grab samples were collected at 1-1/2 hour intervals, resulting in a total of 150 liters of samples. Prior to testing, the two samples were composited in the abovementioned 2:1 ratio in the laboratory in a 230-liter polyethylene-lined drum.

The above composite sample was used during most of the laboratory testing.

A second boiler fireside/air preheater wash wastewater composite sample was collected during the latter stages of this study for the purposes of assessing dilution requirements when lower nickel concentrations were present. The second set of samples was collected during the cleaning of Unit #1 at Florida Power Corporation's Crystal River Plant November 8 to 11, 1979. Unit #1 is a Combustion Engineering tangentially fired boiler modified for coal burning (32). The fuel to this unit is a combination of high and low-sulfur coals from Illinois (Burnside Mine) and Eastern Kentucky (Coal Resources), respectively, and it was expected that nickel values would be relatively low as compared to levels in fuel oil.

Florida Power personnel conducted the fireside washing using a high-pressure water stream directed toward the surface deposits. Wastewater from the cleaning flowed into the sluice box with the overflow being collected in a cylindrical tank. Samples of the wastewater were collected from a tap at the bottom of the overflow tank. The cleaning was conducted intermittently over a number of shifts for a total washing time of approximately 12 hours. A 2-liter grab sample was taken every 15 minutes during a period of washing, corresponding to a total of 48 liters taken for the total fireside wash operation. Nineteen liters of this sample were shipped back to the laboratory.

After the fireside washing was completed, automatic water jets inside the air preheaters were activated and ran continuously for approximately 8 hours. The wastewater from preheater cleaning drained to a sluiceway thence to a wetwell, where samples were collected. A 2-liter grab sample was collected every 15 minutes for a total sample of 32 liters. Nineteen liters of this sample were shipped back to the laboratory.

A 2:1 preheater/fireside wash wastewater composite was prepared on an as-needed basis from these two samples for testing during the latter stages of this study.

VI. EXPERIMENTAL PROCEDURES

A. General Procedures

1. Storage of Samples

All boiler tubeside chemical cleaning wastewater samples were stored at ambient temperature in 19-liter polyethylene containers. The fireside/air preheater composite was stored in a 230-liter polyethylene-lined drum, also at ambient temperature. Because of the highly toxic nature of the wastewaters, biodegradation of samples is expected to be minimal during the period of investigation.

2. Sample Mixing

All samples were well mixed while compositing and taking aliquots and prior to transfer. Small volumes of samples were shaken vigorously by hand. Volumes of 7 to 20 liters were mixed with a propeller-type mixer. Larger volumes from 20 to 230 liters were mixed by circulation for 5 to 10 minutes using a 62 W (1/12 HP) centrifugal pump with an outlet pressure of 15 mPa and a measured flow rate of 18 liters per minute. The pump method was used extensively in the field and the laboratory to mix and transfer samples.

3. Supernatant Decanting

Supernatants were decanted by using a suction tube with a side outlet about 13 cm above the end of the tube. A Nalgene hand pump was used to provide necessary light suction. Decanted samples were aspirated into a sidearm flask. After every aspiration, the apparatus was rinsed several times with deionized water to prevent contamination from sample to sample. Aspirated samples were placed in acid-washed holding jars for storage until preparation for analysis.

4. Preparation of Polymer Solutions

Polymer solutions were prepared in accordance with manufacturer's directions. An automatic pipettor with disposable tips was used to make up stock and working solutions of polymers. Fresh stock and working solutions were made up daily, weekly, or monthly, depending on the shelf life of polymer solutions recommended by the manufacturer.

5. Acid-Washing of Laboratory Apparatus

All laboratory apparatus that had direct contact with the samples was acid-washed with 1:1 hydrochloric acid prior to use to prevent metal contamination. The Phipps and Bird stirrer paddles were washed with a dilute hydrochloric acid solution.

6. Quality Assurance

In the absence of an absolute reference for research materials, accuracy and precision must be estimated from data collected from the actual samples. This is most economically performed by using spiked samples (for accuracy) and by determining the values of some samples more than once (for precision). In the current study, aliquots of at least 10 percent of the samples were spiked with a known amount of the metal being analyzed or were determined in duplicate. In addition, 10 percent of the samples were determined in duplicate. These data showed that the accuracy and precision of the experimental technique should not prevent valid data interpretation.

B. Analytical Procedures

1. Total Suspended Solids-Preparation and Analysis

The procedure followed for preparation and analysis for total suspended solids is described as follows:

(a) Glass-fiber filters with 0.14 μm pore size were washed in distilled, deionized water. After successive cleanings, the filters were dried for one hour at 104°C and removed and placed in a desiccator to cool.

(b) The filters were then tared and placed in marked aluminum weighing tins.

(c) An all-glass Millipore Filtration Apparatus was used. The filtration apparatus was washed with 1:1 HCl to remove residue, then rinsed with distilled, deionized water.

(d) Each sample was vigorously shaken for one minute and then measured in a graduated cylinder to 50 ml or 100 ml, depending on available supernatant.

(e) A tared filter was placed in the filtration apparatus and the sample was poured in. The graduated cylinder was rinsed with distilled, deionized water and this rinse was poured into the apparatus. Walls of the apparatus were washed down to release all particles. The filtrate was collected in a 400-ml beaker and discarded.

(f) After filtering, the filter and filter cake were removed and placed in a marked aluminum weighing dish and dried in an oven for one hour at 104°C. The filtration apparatus was thoroughly rinsed with distilled, deionized water and set up for the next filtration.

(g) After all samples were filtered and dried in the dessicator, the filters were weighed, the tare weight was subtracted, and the appropriate factor was applied.

(h) Two blanks were analyzed. One hundred milliliters of distilled, deionized water was filtered through clean, weighed filters and dried in the oven as previously stated. Any weight found after drying and dessication was subtracted from the weights of the samples.

(i) Three or four duplicate samples were prepared as previously stated and used as a check on previous results.

2. Preparation of Samples for Total and Dissolved Metal Analysis

The procedures followed for preparation of samples for metals analysis are as follows:

Samples were shaken vigorously for one minute and 50 ml of sample was used for both filtered and digested analysis.

(a) Filtered Samples (dissolved metals). A 50-ml sample was filtered through Gelman glass-fiber filters and the filtrate was caught in a 150-ml beaker and transferred to an acid-washed boiling jar. The sample was acidified with 1:1 HNO_3 (250 µl). These samples were labeled with the assignment number and were ready for analysis.

(b) Digested Samples (total metals). 600-ml beakers were acid washed with 1:1 HCl and rinsed with

distilled, deionized water. Fifty milliliters of homogenous samples were placed into the beaker with 15 ml of high purity, concentrated HNO_3. The beaker was placed on a hot plate and allowed to fume but not boil.

(1) After complete drying, 5 to 10 ml of concentrated HNO_3 was added and a watch glass was placed over the beaker. The beaker was placed on a hot plate and allowed to fume but not boil. Sample was evaporated to dryness.

(2) Five to 10 ml of 1:1 HCl were added and the watch glass and beaker were replaced on the hot plate. Evolution of brown-orange gas occurred. After the sample had finished gassing, distilled, deionized water was added to the beaker and heated until the salt of the metals was dissolved. Care was taken not to add more than 50 ml of water.

(3) These samples were filtered through Gelman glass-fiber filters, stored in acid-washed bottles, labeled with the assignment number, and stored until analysis. Samples were diluted to 50 ml with distilled, deionized water.

(4) Duplicate blanks were prepared in the same manner.

3. Analysis of Metals

Analysis of total and dissolved iron, copper, nickel, and zinc in each sample was performed on a Perkin-Elmer 603 Atomic Absorption Spectrophotometer with Deuterium Arc Background Correction. Procedures followed are described below:

(a) Standards were prepared by serial dilutions of Fisher 1000 ppm Atomic Absorption standards. Lamps used were Perkin-Elmer Hollow Cathode Lamps or Electrodeless Lamps.

(b) 10-ml injections were used. An adjustable automatic pipet was used to deliver the sample.

(c) Background correction was used on all analysis.

(d) The blanks were analyzed first to establish the impurity level of the water.

(e) After all the samples were analyzed, duplicates and spiked samples were analyzed for quality control measures.

(f) Acquiring final values was accomplished by linear regression analysis. The standards and the corresponding absorbances are entered into the memory and a correlation coefficient is obtained. The absorbances acquired from the samples are automatically plotted on the standard line and the actual ppm or ppb reading is displayed. The blank value is then subtracted from the sample value.

VII. LABORATORY DETERMINATION OF BEST TREATMENT LEVELS FOR BOILER TUBESIDE CHEMICAL CLEANING WASTEWATERS

Laboratory testing to determine the best treatment levels for the boiler tubeside chemical cleaning wastewaters is detailed in the following sections. Under each distinct experiment, the procedure is presented, followed by the actual data, and a discussion of the results. In brief, testing began with an analysis of iron, nickel, copper, and zinc concentrations in the six chemical cleaning wastewaters and the fireside/air preheater wash wastewater composit from the oil-fired boiler. Then, matrix testing of the six boiler chemical cleaning wastewaters was conducted in which treatment involving various dilutions with a fireside/air preheater wash wastewater and lime addition to various pH's was investigated. Polymers were then introduced to enhance treatment and matrix testing using different polymers at different dosages was conducted on the best runs found from previous testing. From the results of treatment with polymers, a "most difficult to treat" boiler cleaning system wastewater was then selected. A number of pretreatment methods were then investigated in an effort to enhance metal removal efficiencies from the "most difficult to treat" wastewater. Also, an additional matrix test was performed in an effort to minimize the lime and diluent requirements for treatment. A statistical test was then conducted to support proper interpretation of results. The sludge from this treatment was characterized with respect to settleability, filterability, and metal content.

Latter stages of experimentation included testing of the two next "most difficult to treat" chemical cleaning wastewaters. Various dilutions were prepared with a newly collected fireside/air preheater wash composite from a coal-fired boiler. Lime was again added to the dilutions at various pH's for determination of metal removal.

A. Initial Analysis of Untreated Wastewater Samples

The composited chemical cleaning system wastewaters and the fireside/air preheater wash wastewater (oil-fired unit) were analyzed for concentrations of the four metals and for total suspended solids. Results of analysis are presented in Table 3.

It is noted that the hydroxyacetic-formic acid wastewater composite is about twice as concentrated as would be expected, since the two water rinse samples were omitted. Also, the ammoniated EDTA wastewater composite would be

TABLE 3. ANALYSIS OF UNTREATED WASTEWATER SAMPLES
(Values Reported in mg/l)

Type of Wastewater	Metals	Fe	Cu	Ni	Zn	TSS
Ammoniated Bromate-Hydrochloric Acid	Total	500	110	27	25	1400
Hydroxyacetic-Formic Acid	Total	5000	0.6	7	0.2	88
Ammoniated EDTA	Total	2200	330	74	11	147
	Dissolved	1900	330	43	10	
Thiourea-Hydrochloric Acid with Citric Rinse	Total	680	210	72	15	38
	Dissolved	660	86	83	15	
Thiourea-Hydrochloric Acid	Total	1500	31	7	15	16
	Dissolved	1400	31	7	14	
Ammoniated Citric Acid	Total	2000	95	30	5	98
	Dissolved	1600	95	26	4	
Fireside/Air Preheater Wash Composite (oil-fired)	Total*	4113	13	510	21	6319#
	Dissolved**	3009	12	195	20	

** Four-run average.*
***Two-run average.*
 # Four-run average.

slightly different in concentration from a standard three-stage cleaning of the same type, since the second water rinse sample was omitted and the optional passivation stage drain sample was substituted. These differences should not significantly impact the testing program.

Also, it was noted earlier that the fireside/air preheater wash composite was expected to be high in nickel, and this is confirmed in Table 3. Similar wastewaters from steam generating units burning oils from other sources or coal are expected to have much lower concentrations of nickel. Analysis of a fireside/air preheater wash wastewater from a coal-fired unit is presented in Section VII-G, in which nickel levels are substantially lower as expected.

B. Lime Precipitation Testing

Lime precipitation testing was conducted on six boiler tubeside chemical cleaning wastewater samples collected for this treatability study. The wastewaters correspond to the following types of cleanings:

(1) Ammoniated bromate/hydrochloric acid

(2) Hydroxyacetic-formic acid

(3) Ammoniated EDTA

(4) Thiourea-hydrochloric acid (2 samples collected)

(5) Ammoniated citric acid

The tubeside chemical cleaning wastewater samples were tested using various dilutions with fireside/air preheater wash wastewater. Testing for each sample consisted of adding lime to attain four pH's, i.e., 8.5, 9.5, 10.5, and 12.0. When some of the chemical cleaning wastewaters were initially alkaline, such as was the case with the ammoniated EDTA and citric acid systems, the pH was extended to 13.0 and/or the pH's lower than or equal to the initial pH of the wastewater were not used. The dilutions of fireside/air preheater wastewater to chemical cleaning wastewater were 0:1, 1:1, 3:1, and 10:1. Altogether, 16 runs of pH/dilution combinations (excluding quality control) were conducted for each of the six samples. After addition of lime to proper pH, the samples were allowed to settle for 24 hours and the supernatant was decanted as described under General Procedures.

After settling, supernatants were analyzed for total and dissolved iron, copper, nickel, and zinc, and total suspended solids. Also analyzed were the chemical cleaning samples before pH adjustment and dilution (total iron, copper, nickel, and zinc) and the fireside/air preheater wastewater composite (total and dissolved of above metals). To adjust pH, straight hydrated lime was slowly fed to the wastewater mixtures, while they were being stirred at 100 rpm by a Phipps and Bird Laboratory stirrer. The lime was added by teaspoon and after every addition, the lime was allowed to react for 5 to 10 minutes before a pH reading was taken with a pH meter. Smaller and smaller additions of lime were made until the desired pH was attained. The lime used in the study was a high calcium hydrated agricultural grade manufactured by J.W. Barrick & Sons, Woodsboro, Maryland, with an assay of 62 percent as CaO and 3 percent as MgO.

Results of the testing of the six chemical cleaning wastewaters at varying pH and dilutions with fireside/air preheater wash wastewaters are presented in Tables 4 through 10. Tables 4 through 9 present total and dissolved iron, copper, nickel, and zinc and total suspended solids for supernatants after 24 hours of settling. As can be seen from Figures 1 through 5 (ammoniated citric acid wastewater), the general trend is that supernatant metal residuals decrease as the pH and dilution ratio increase. Supernatant total suspended solids seemed to show a general downward trend with respect to pH and dilution increases. At the 0:1 dilution, however, this trend was not apparent. Slight differences in trends can be observed for each of the boiler cleaning wastewaters.

The ammoniated bromate/hydrochloric acid wastewater seemed to follow the general trend for copper, nickel, and zinc. It was observed that the supernatant total iron residual at pH 8.5 did increase at dilutions of 3:1 and 10:1. If it is statistically significant, this increase could be due to the contribution of iron from the diluent (fireside/air preheater wash wastewater). In general, the metal residuals were moderately low and dropped off quickly to levels of less than 1 mg/l starting at a dilution of 3:1 and a pH of 10.5. This system appears to be easiest to treat of all the wastewaters.

The hydroxyacetic-formic acid wastewater seemed to complex metals introduced by the diluent, as it was observed that copper and nickel residuals increased upon dilution to 1:1 and 3:1. This increase was noticeable at all pH's for copper and only at pH's 8.5 and 9.5 for nickel. Iron seemed to follow the general trend while zinc was almost a consistent 0.1-0.2 mg/l. Metal residuals below 1 mg/l were reached at a 10:1 dilution and a pH of 10.5 for all species.

The ammoniated EDTA wastewater did not follow the general trend. In all metals except copper, residuals first increased with a dilution to 1:1, then decreased upon further dilution. The general trend for pH at any specific dilution (except 0:1) was followed for all metals. It is obvious that this wastewater has strong chelating properties, and is chelating metals introduced by the diluent. Extremely high nickel residuals persisted even at the highest pH and dilution.

TABLE 4. LIME PRECIPITATION/DILUTION OF AMMONIATED BROMATE/HYDROCHLORIC ACID BOILER CLEANING WASTEWATERS
(Values reported in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	8.5	Total	0.6	29.7	17	2.0	0
		Dissolved	<0.1	29.0	17	0.5	
0:1	9.5	Total	0.3	37.4	19	2.4	0
		Dissolved	0.1	33.4	20	2.7	
0:1	10.5	Total	0.3	15.7	8.0	1.2	24
		Dissolved	0.1	15.4	8.0	0.9	
0:1	12.0	Total	0.3	2.8	0.3	0.5	115
		Dissolved	0.1	1.5	0.2	0.4	
1:1	8.5	Total	0.3	1.1	4.2	0.3	90
		Dissolved	0.1	1.3	4.5	0.1	
1:1	9.5	Total	0.4	1.6	2.5	0.3	95
		Dissolved	0.1	1.5	2.6	0.1	
1:1	10.5	Total	0.3	0.5	0.3	0.4	37
		Dissolved	0.1	0.5	0.3	0.1	
1:1	12.0	Total	0.3	0.3	0.2	0.2	45
		Dissolved	0.1	0.2	0.2	0.1	
3:1	8.5	Total	1.3	0.6	2.7	0.1	27
		Dissolved	0.2	0.4	3.0	0.1	
3:1	9.5	Total	0.6	0.6	1.6	0.1	36
		Dissolved	0.2	0.6	1.6	0.1	
3:1	10.5	Total	0.2	0.5	0.3	0.2	4
		Dissolved	0.1	0.5	0.2	0.1	
3:1	12.0	Total	0.2	0.2	0.2	0.2	0
		Dissolved	0.1	0.2	0.1	0.1	
10:1	8.5	Total	1.9	0.2	1.8	0.1	49
		Dissolved	0.3	0.2	1.7	0.1	
10:1	9.5	Total	0.6	0.3	0.5	0.1	*
		Dissolved	0.2	0.2	0.4	0.1	
10:1	10.5	Total	0.3	0.1	0.3	0.1	15
		Dissolved	0.1	0.1	0.2	0.1	
10:1	12.0	Total	0.3	0.1	0.3	0.1	26
		Dissolved	0.1	0.1	0.2	0.1	

**Insufficient amount of supernatant available for TSS.*

TABLE 5. LIME PRECIPITATION/DILUTION OF HYDROXYACETIC-FORMIC ACID BOILER CLEANING SYSTEM WASTEWATERS
(Values reported in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	8.5	Total	460.0	0.4	2.9	0.1	20
		Dissolved	480.0	0.4	2.8	0.1	
0:1	9.5	Total	3.8	0.3	1.3	0.1	12
		Dissolved	3.4	0.3	1.4	0.1	
0:1	10.5	Total	1.7	0.3	0.3	0.1	4
		Dissolved	1.1	0.2	0.4	0.1	
0:1	12.0	Total	2.8	0.3	0.3	0.2	27
		Dissolved	2.0	0.2	0.3	0.1	
1:1	8.5	Total	16.1	2.4	10.6	0.2	10
		Dissolved	11.5	2.5	10.5	0.1	
1:1	9.5	Total	3.0	2.4	2.6	0.1	16
		Dissolved	2.6	2.5	2.8	0.1	
1:1	10.5	Total	0.5	2.4	0.4	0.1	14
		Dissolved	0.2	2.7	0.4	0.1	
1:1	12.0	Total	0.8	2.3	0.2	0.2	14
		Dissolved	0.3	2.2	0.2	0.1	
3:1	8.5	Total	14.2	1.0	9.7	0.1	92
		Dissolved	9.8	0.8	9.8	0.1	
3:1	9.5	Total	1.2	1.2	1.1	0.1	28
		Dissolved	0.3	0.9	1.1	0.1	
3:1	10.5	Total	0.7	1.0	0.2	0.1	20
		Dissolved	0.1	0.7	0.1	0.1	
3:1	12.0	Total	1.2	1.0	0.2	0.1	18
		Dissolved	0.1	0.9	0.1	0.1	
10:1	8.5	Total	1.3	0.4	0.8	0.2	22
		Dissolved	0.1	0.2	0.8	0.1	
10:1	9.5	Total	0.8	0.4	0.3	0.1	31
		Dissolved	0.1	0.3	0.3	0.1	
10:1	10.5	Total	0.5	0.5	0.1	0.3	23
		Dissolved	<0.1	0.3	0.1	0.1	
10:1	12.0	Total	1.0	0.5	0.1	0.2	16
		Dissolved	<0.1	0.2	0.2	0.1	

TABLE 6. LIME PRECIPITATION/DILUTION OF AMMONIATED EDTA BOILER CLEANING SYSTEM WASTEWATERS
(Values reported in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	10.5	Total	3.0	333.0	47.0	2.3	42
		Dissolved	0.2	329.0	48.0	2.2	
0:1	12.0	Total	12.0	283.0	45.0	0.8	212
		Dissolved	5.0	227.0	45.0	0.7	
0:1	13.0	Total	7.3	177.0	47.0	0.9	56
		Dissolved	2.6	125.0	47.0	0.8	
1:1	8.5	Total	629.0	116.0	189.0	12.0	330
		Dissolved	584.0	114.0	155.0	12.0	
1:1	9.5	Total	308.0	80.0	165.0	8.0	798
		Dissolved	127.0	83.0	156.0	8.0	
1:1	10.5	Total	28.0	3.0	141.0	0.2	100
		Dissolved	0.2	3.3	119.0	0.2	
1:1	12.0	Total	1.1	0.4	100.0	0.1	17
		Dissolved	0.1	0.4	97.0	0.1	
3:1	8.5	Total	492.0	5.8	87.0	8.6	230
		Dissolved	357.0	5.5	81.0	7.9	
3:1	9.5	Total	446.0	0.6	68.0	7.5	633
		Dissolved	243.0	0.6	59.0	6.4	
3:1	10.5	Total	87.0	0.2	51.0	0.1	445
		Dissolved	17.0	0.2	48.0	0.1	
3:1	12.0	Total	1.6	0.2	36.0	0.1	24
		Dissolved	0.1	0.2	39.0	0.1	
10:1	8.5	Total	119.0	0.2	26.0	5.2	82
		Dissolved	95.0	0.2	26.0	5.0	
10:1	9.5	Total	46.0	0.2	15.0	3.2	114
		Dissolved	33.0	0.1	13.0	2.7	
10:1	10.5	Total	77.0	0.1	10.0	0.2	310
		Dissolved	3.5	0.1	9.5	0.1	
10:1	12.0	Total	0.5	0.1	6.8	0.2	22
		Dissolved	0.1	0.1	5.5	<0.1	

TABLE 7. LIME PRECIPITATION/DILUTION OF THIOUREA-HCL (CITRIC ACID RINSE) BOILER CLEANING SYSTEM WASTEWATERS
(Values reorted in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	8.5	Total	1.4	25.3	1.7	0.2	27
		Dissolved	0.2	24.6	1.4	0.1	
0:1	9.5	Total	3.3	4.7	0.9	0.1	42
		Dissolved	0.3	4.0	0.5	0.1	
0:1	10.5	Total	1.6	6.8	0.6	0.2	10
		Dissolved	0.4	6.3	0.4	0.1	
0:1	12.0	Total	2.4	0.7	0.6	0.2	15
		Dissolved	0.2	0.8	0.3	0.1	
1:1	8.5	Total	1.7	0.9	1.7	0.2	362
		Dissolved	0.7	0.9	1.5	0.1	
1:1	9.5	Total	0.5	0.7	0.6	0.2	29
		Dissolved	0.1	0.6	0.5	0.2	
1:1	10.5	Total	0.3	0.6	0.4	0.1	53
		Dissolved	0.1	0.4	0.3	0.1	
1:1	12.0	Total	0.4	0.5	0.4	0.1	20
		Dissolved	0.1	0.5	0.3	<0.1	
3:1	8.5	Total	1.4	0.5	1.2	0.1	17
		Dissolved	0.1	0.4	0.9	<0.1	
3:1	9.5	Total	0.5	0.4	0.4	0.1	44
		Dissolved	0.1	0.4	0.3	<0.1	
3:1	10.5	Total	0.3	0.3	0.3	0.1	48
		Dissolved	0.1	0.2	0.3	0.1	
3:1	12.0	Total	0.4	0.2	0.3	0.1	34
		Dissolved	0.1	0.1	0.2	<0.1	
10:1	8.5	Total	1.1	0.4	0.9	0.1	17
		Dissolved	0.3	0.2	0.8	0.1	
10:1	9.5	Total	0.8	0.3	0.5	0.1	27
		Dissolved	0.1	0.2	0.4	0.1	
10:1	10.5	Total	0.6	0.4	0.3	0.1	29
		Dissolved	0.1	0.2	0.2	0.1	
10:1	12.0	Total	1.4	1.5	0.9	0.3	12
		Dissolved	0.1	0.2	0.2	<0.1	

TABLE 8. LIME PRECIPITATION/DILUTION OF THIOUREA-HCL BOILER CLEANING SYSTEM WASTEWATERS
(Values reported in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	8.5	Total	0.3	0.5	0.4	0.1	42
		Dissolved	0.2	0.5	0.3	--*	
0:1	9.5	Total	0.3	0.5	0.4	0.1	62
		Dissolved	0.1	0.5	0.3	0.1	
0:1	10.5	Total	0.4	0.6	0.4	0.1	14
		Dissolved	0.2	0.7	0.3	0.1	
0:1	12.0	Total	0.3	0.3	0.4	0.1	61
		Dissolved	0.2	0.3	0.3	0.1	
1:1	8.5	Total	0.2	0.3	0.6	0.1	16
		Dissolved	<0.1	0.3	0.6	<0.1	
1:1	9.5	Total	1.3	0.5	0.5	0.1	40
		Dissolved	<0.1	0.6	0.3	0.1	
1:1	10.5	Total	0.2	0.2	0.2	0.1	21
		Dissolved	<0.1	0.2	0.2	<0.1	
1:1	12.0	Total	0.1	0.2	0.2	0.1	28
		Dissolved	<0.1	0.2	0.2	<0.1	
3:1	8.5	Total	0.2	0.2	0.7	0.1	34
		Dissolved	<0.1	0.2	0.7	0.1	
3:1	9.5	Total	0.2	0.2	0.3	0.1	295
		Dissolved	<0.1	0.2	0.3	0.1	
3:1	10.5	Total	0.1	0.2	0.2	0.1	56
		Dissolved	<0.1	0.2	0.2	0.1	
3:1	12.0	Total	0.1	0.2	0.1	0.1	16
		Dissolved	<0.1	0.2	0.1	0.1	
10:1	8.5	Total	0.2	0.2	0.4	0.2	44
		Dissolved	<0.1	0.2	0.4	<0.1	
10:1	9.5	Total	0.2	0.2	0.3	0.1	75
		Dissolved	<0.1	0.2	0.3	0.1	
10:1	10.5	Total	0.1	0.2	0.2	0.1	49
		Dissolved	<0.1	0.2	0.2	0.1	
10:1	12.0	Total	0.1	0.2	0.2	0.1	27
		Dissolved	<0.1	0.1	0.1	0.1	

**Sample lost*

TABLE 9. LIME PRECIPITATION/DILUTION OF AMMONIATED CITRIC ACID BOILER CLEANING SYSTEM WASTEWATERS
(Values reported in mg/l)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
0:1	9.5	Total	2800	87	65	4.2	29
		Dissolved	2700	95	59	3.9	
0:1	10.5	Total	270	44	32	1.1	258
		Dissolved	270	42	28	0.7	
0:1	12.0	Total	1.2	5.0	2.2	0.5	45
		Dissolved	0.3	4.8	2.2	0.4	
1:1	8.5	Total	1200	37	269	3.9	1041
		Dissolved	990	36	262	3.5	
1:1	9.5	Total	120	17	124	0.9	577
		Dissolved	38.4	15	102	0.3	
1:1	10.5	Total	31	9.0	64	0.1	35
		Dissolved	14	8.4	31	<0.1	
1:1	12.0	Total	4.2	0.3	3.6	0.1	39
		Dissolved	1.6	0.2	2.7	0.1	
3:1	8.5	Total	150	0.3	152	0.4	505
		Dissolved	64	0.1	152	0.4	
3:1	9.5	Total	9.6	0.3	49	0.2	35
		Dissolved	2.8	0.2	49	0.1	
3:1	10.5	Total	1.2	0.3	4.3	0.1	37
		Dissolved	0.3	0.3	4.1	<0.1	
3:1	12.0	Total	1.7	--*	2.1	0.1	44
		Dissolved	0.5	0.1	0.7	0.1	
10:1	8.5	Total	15.3	0.2	24.6	0.1	78
		Dissolved	1.3	0.1	19.3	0.1	
10:1	9.5	Total	1.1	0.2	2.9	0.1	33
		Dissolved	0.4	0.1	2.6	0.1	
10:1	10.5	Total	0.7	0.2	0.7	0.1	33
		Dissolved	0.3	0.2	0.7	<0.1	
10:1	12.0	Total	0.6	0.1	0.4	0.1	27
		Dissolved	0.3	0.1	0.3	0.1	

*Sample lost

TABLE 10. SUMMARY OF BEST RUNS FOR LIME PRECIPITATION/ DILUTION OF SIX BOILER CLEANING WASTEWATERS (Values reported in mg/l)

System Description	pH	Dilution Ratio	Supernatant Residuals (Total) Fe	Cu	Ni	Zn	TSS
Ammoniated Bromate/HCl	10.5	1:1	0.3	0.5	0.3	0.4	37
	12.0	1:1	0.3	0.3	0.2	0.2	45
	10.5	3:1	0.2	0.5	0.3	0.2	4
	10.5	10:1	0.3	0.1	0.3	0.1	15
Ammoniated Citric Acid (Citrosolv)	10.5	10:1	0.7	0.2	0.7	0.1	33
	12.0	10:1	0.6	0.1	0.4	0.1	27
Ammoniated EDTA (Vertan)	12.0	10:1	0.5	0.1	6.8	0.1	22
Thiourea-HCl System	8.5	0:1	0.3	0.5	0.4	0.1	42
	10.5	0:1	0.4	0.6	0.4	0.1	14
	10.5	1:1	0.2	0.2	0.2	0.1	21
	10.5	3:1	0.1	0.2	0.2	0.1	56
Hydroxyacetic-Formic Acid System	9.5	10:1	0.8	0.4	0.3	0.1	31
	10.5	10:1	0.5	0.5	0.1	0.3	23
Thiourea-HCl/ Citric System	9.5	1:1	0.5	0.7	0.6	0.2	29
	10.5	1:1	0.3	0.6	0.4	0.1	53
	9.5	3:1	0.5	0.4	0.4	0.1	44
	10.5	3:1	0.3	0.3	0.3	0.1	48

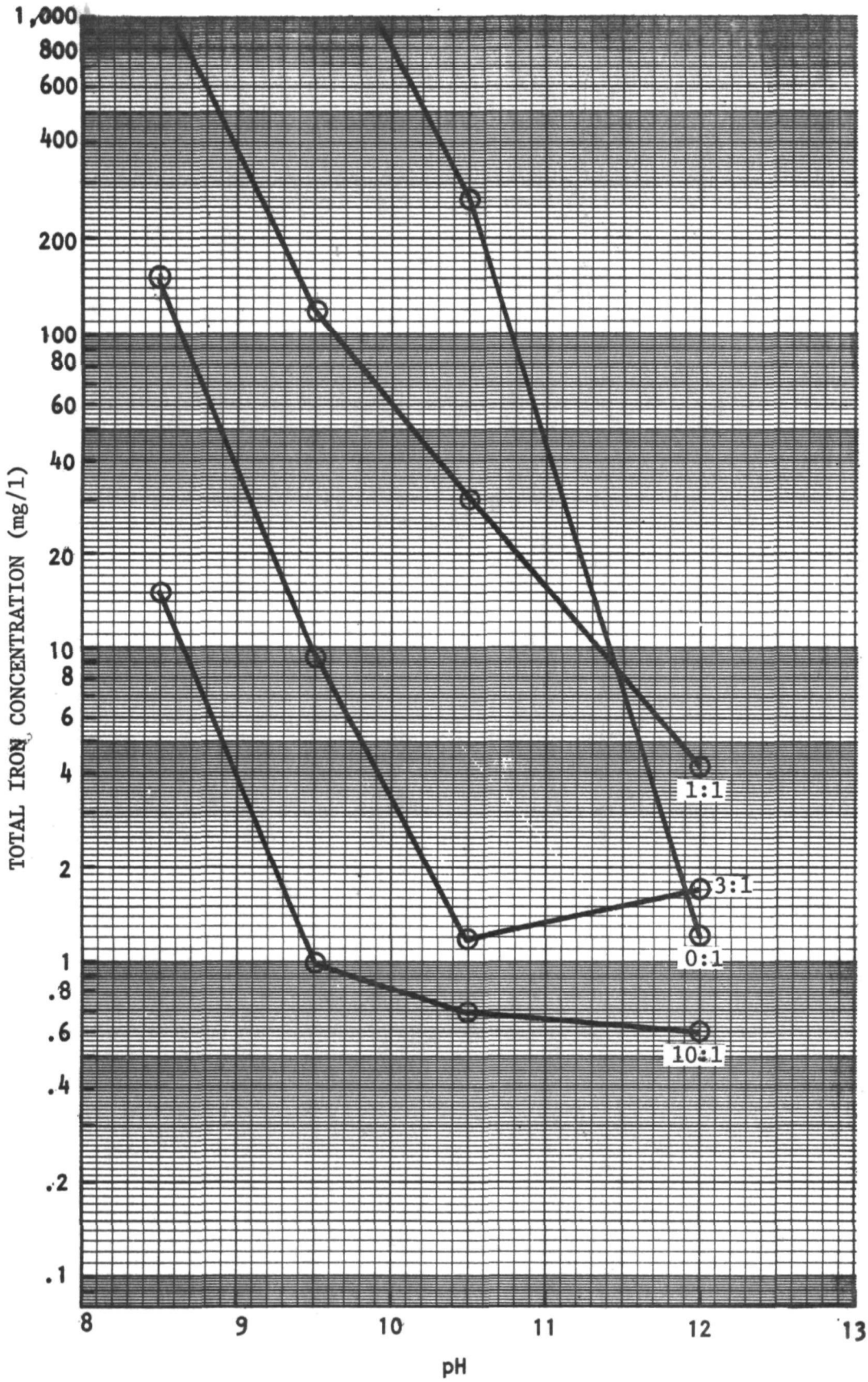


Figure 1. Ammoniated Citric Acid System
Iron Residual vs. pH at Four Dilutions
with Fireside Washwater

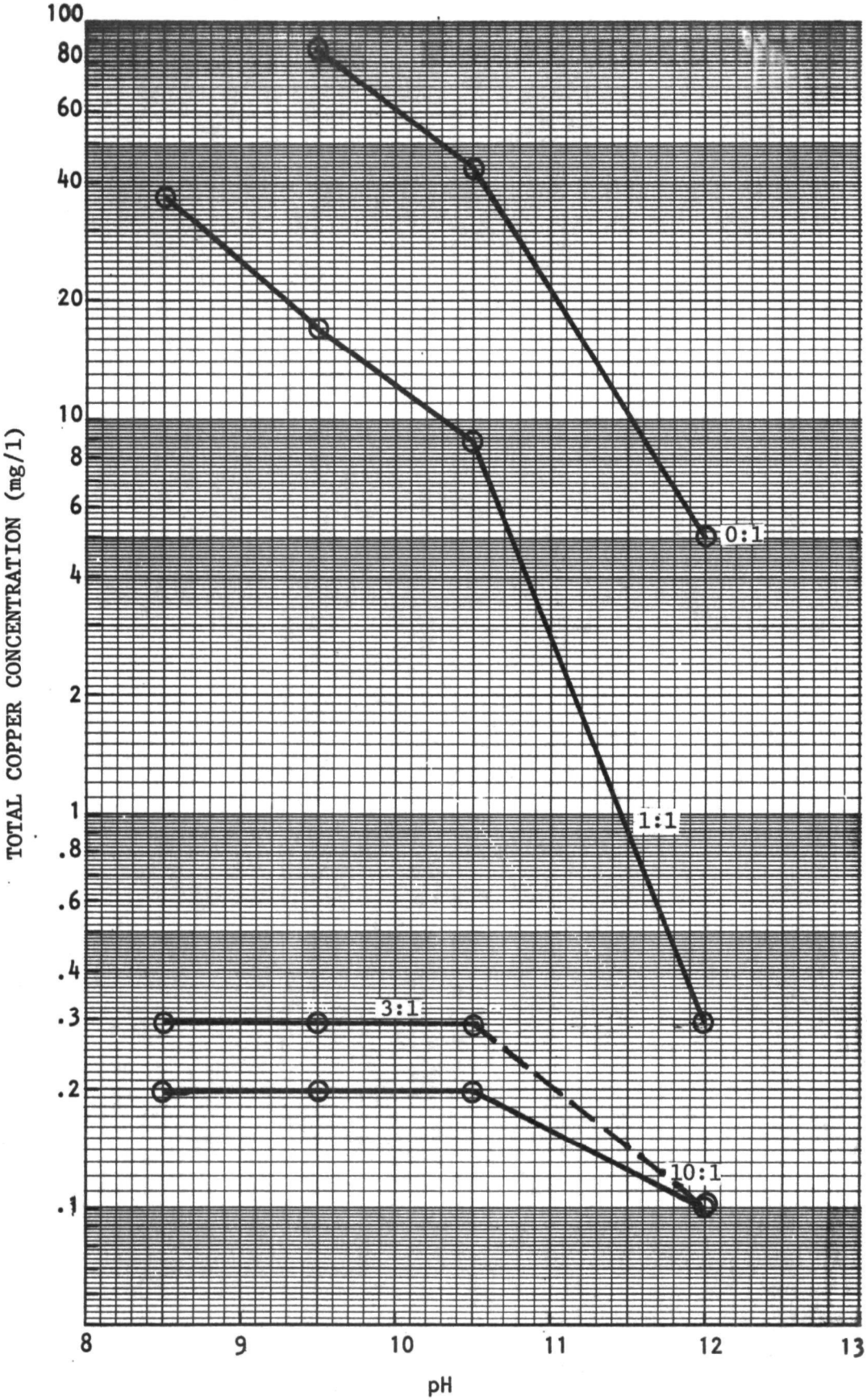


Figure 2. Ammoniated Citric Acid System Copper Residuals vs. pH at Four Dilutions with Fireside Washwater

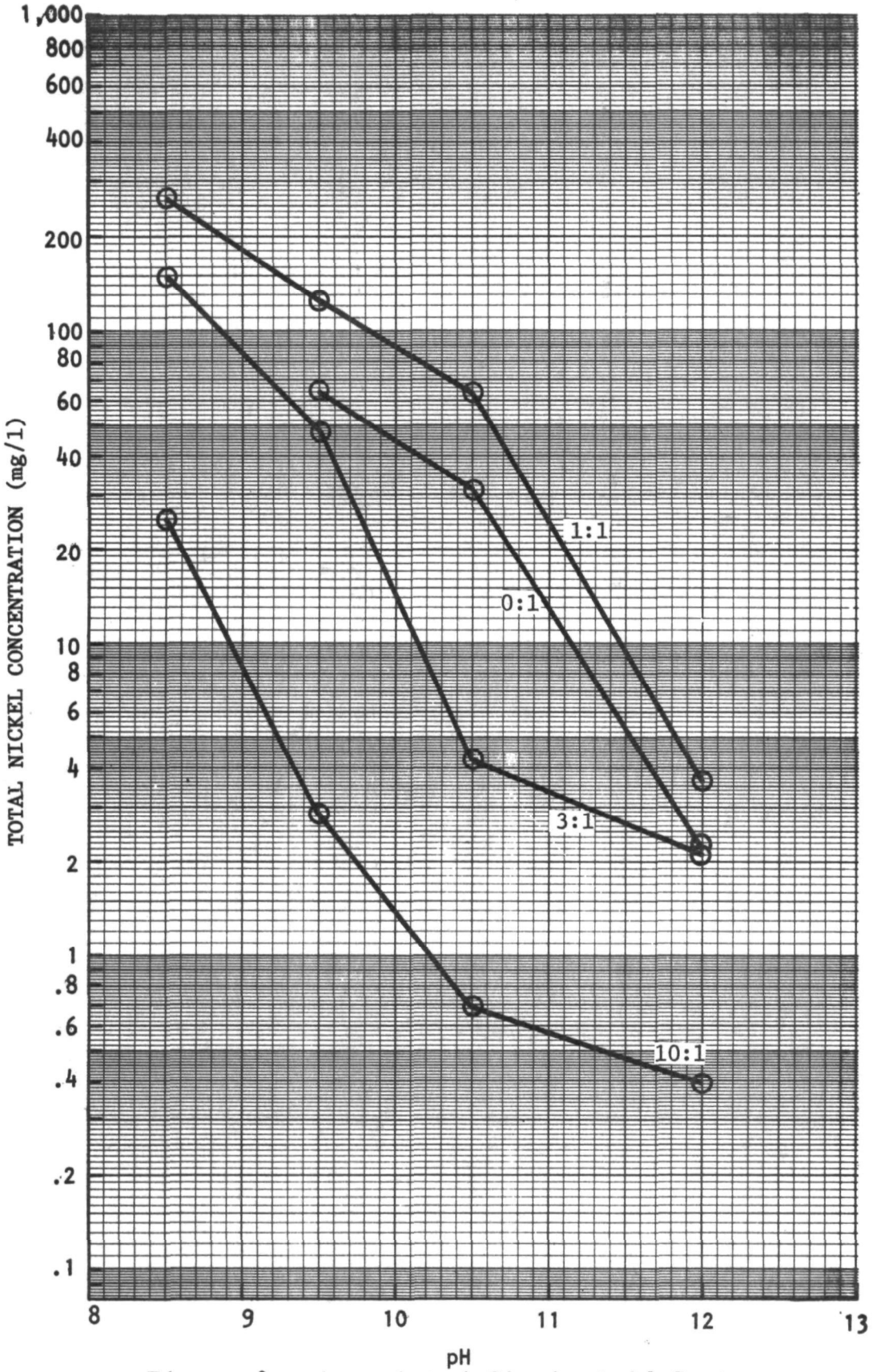


Figure 3. Ammoniated Citric Acid System Nickel Residual vs. pH at Four Dilution Ratios with Fireside Washwater

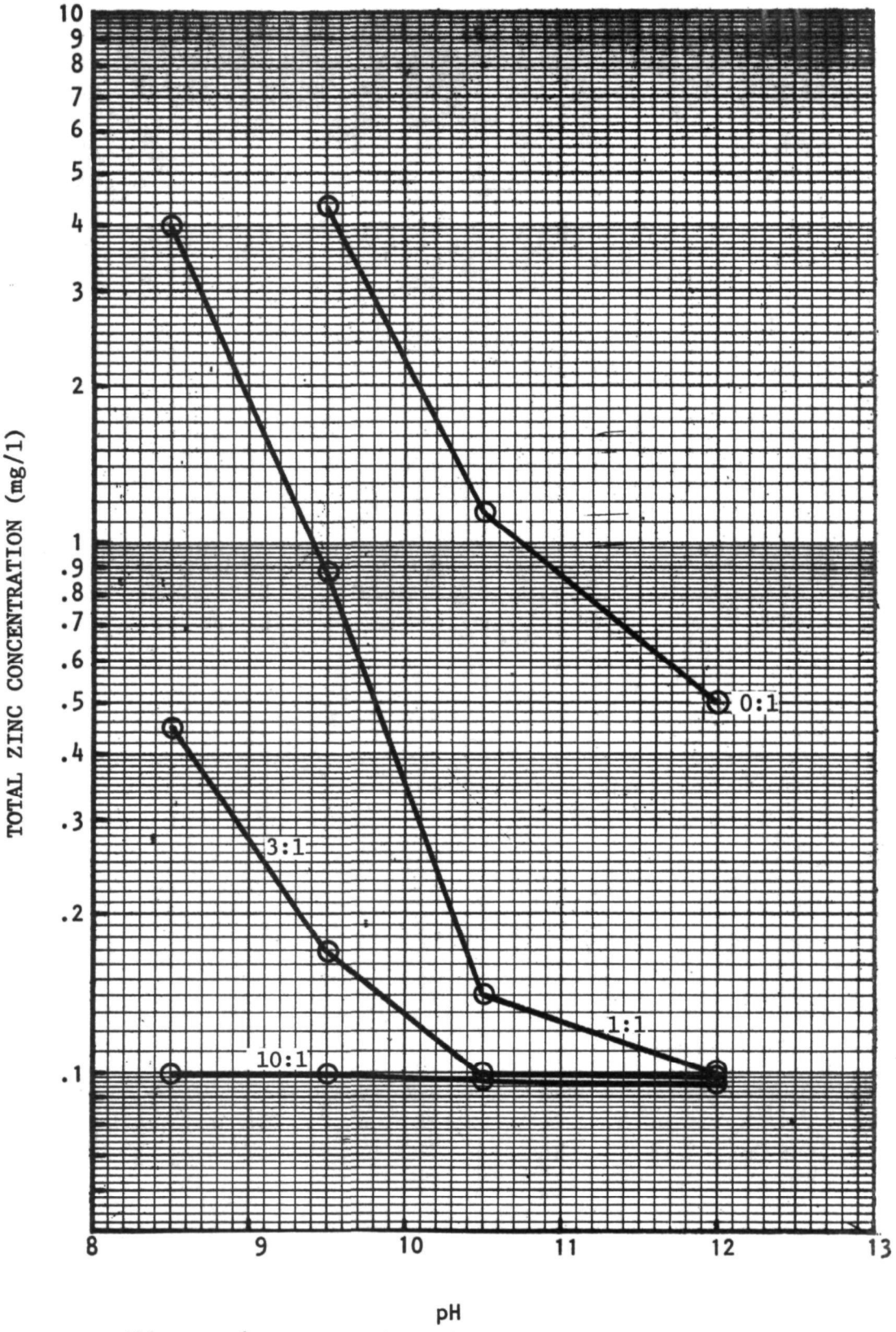


Figure 4. Ammoniated Citric Acid System Zinc Residual vs. pH at Four Dilutions with Fireside Washwater

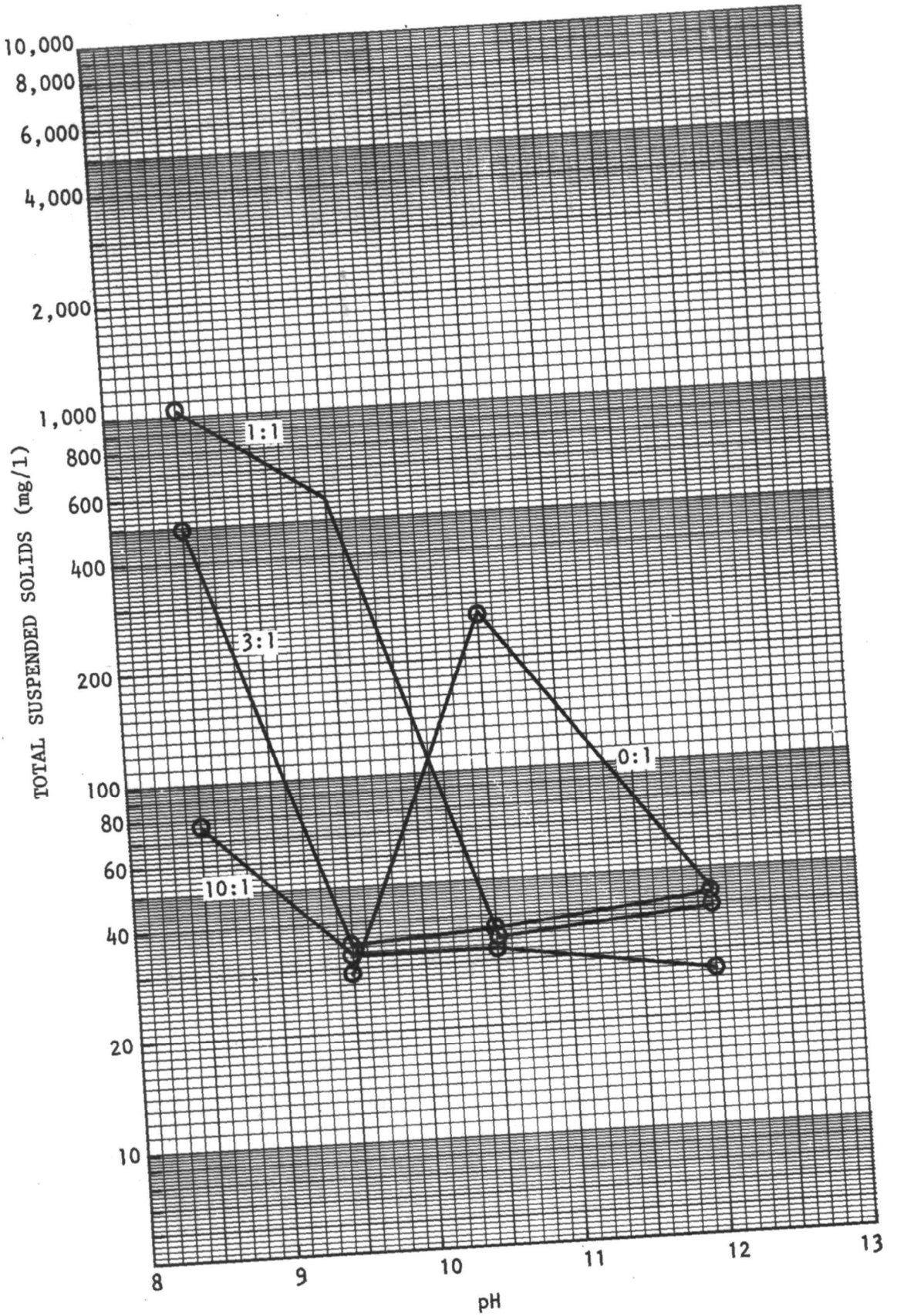


Figure 5. Ammoniated Citric Acid System
Total Suspended Solids vs. pH at Four Dilutions
with Fireside Washwater

The thiourea-hydrochloric acid (citric acid rinse) wastewater seemed to follow the general trends for all metals. Its residuals were low compared to those of other wastewaters, and did not present a treatment problem. Metals residuals for the straight thiourea/hydrochloric acid wastewater were the lowest found, being under 1 mg/l for all metals at a 0:1 dilution and a pH of 8.5.

The ammoniated citric acid wastewater also seemed to complex metals introduced by the diluent, as nickel residuals were observed to increase upon dilution to 1:1, with a subsequent decrease upon further dilution. Iron was extremely high at the lower pH and dilution range, but dropped off quickly with an increase in both parameters, following the general trends. Copper and zinc also followed the general trend. Acceptable metal residuals were found only at a dilution of 10:1 and a pH of 12.0.

Observation of the data in Tables 4 through 9 indicated that in some cases values for total metals were lower than the corresponding dissolved metal values. This was particularly apparent in nickel analysis when levels were higher than 1 mg/l. However, statistical analysis (student's t-test for related measures) indicated that no significant difference existed and the data were within the limits of statistical variability.

The "best runs" for each cleaning system wastewater are presented for comparison in Table 10. Best runs are based on pH and dilutions yielding metal residuals substantially lower than 1 mg/l. For many of the chemical cleaning wastewaters, a number of different conditions give comparable results. Where a decision has to be made with respect to ease or difficulty of treatment, the economic aspect of pH and dilution becomes important and the lower pH's and dilution ratios are given priority.

The ammoniated bromate-hydrochloric acid and the two thiourea-hydrochloric acid systems appear to be easiest to treat, with all total metals reaching 0.5 mg/l or less at a pH of 10.5 and dilution of 3:1. Hydroxyacetic-formic acid ranks next in ease of treatment, with all total metals less than or equal to 0.5 mg/l at a pH of 10.5 and a dilution of 10:1. The ammoniated citric acid and ammoniated EDTA systems appear as the two systems most difficult to treat. Total metal residuals for the two systems at a pH of 12.0 and a 10:1 dilution appear comparable, except that total and dissolved nickel values for the ammoniated EDTA composite were 6.8 and 5.5 mg/l, respectively. These values are well above the goal of 1 mg/l, and for this reason, the ammoniated EDTA system can be considered the most troublesome wastewater with respect to lime treatment technology.

C. Lime Precipitation/Polymers Testing

The effect of using polymers in conjunction with lime precipitation and dilution to treat the six boiler tubeside chemical cleaning wastes was investigated as the next phase in the testing program. Four polymers were to be used at four different dosages. The selection of polymers and starting dosages was based on vendor recommendations and previous experience with use of polymers by the industry.

Four polymers were selected for initial testing, which include Betz 1115L (liquid, anionic), Nalco 7766 (liquid anionic), Dow XD-7817.01 (solid, nonionic), and Hercofloc 815 (solid, cationic). The Betz, Nalco, and Hercofloc polymers were recommended by manufacturers for the treatment of metal-laden wastewaters. A similar Dow nonionic polymer was used successfully in the treatment of an ammoniated EDTA cleaning wastewater sample (33). Early in the testing program, Magnifloc 834A (solid, anionic) was substituted for the Hercofloc 815 polymer, which yielded poor results. Magnifloc 834A was selected as a substitute because it was used in a previous treatability study of wastewaters from an ammoniated EDTA cleaning (34).

1. Preliminary Testing

A preliminary run using the initial four polymers was conducted. The ammoniated EDTA system, which was the most troublesome system from the lime precipitation experiment, was used to determine dosage ranges for each polymer and the better of two mixing cycles. Replicates of the ammoniated EDTA system wastewater diluted 10:1 with the fireside/air preheater composite and limed to a pH of 12.0 were employed in the testing of the initial four polymers. Two polymer dosages, presumably representing high and low values with respect to the recommended dosage range, were used in this run. The dosages are listed below:

(a) Betz 1115L - 0.5 ppm, 2 ppm

(b) Nalcolyte 7766 - 1 ppm, 3 ppm

(c) Dow XD-7817.01 - 0.0025 ppm, 0.05 ppm

(d) Hercofloc 815 - 5 ppm, 10 ppm.

The two mixing cycles chosen differed only in the duration of slow mixing (30 rpm), one being 10 minutes and the other 20 minutes. Polymers were added to the limed replicates during rapid mix (RM) at 100 rpm. Approximately fifteen

seconds after polymer addition, the slow mix cycle (SM) was initiated.

After the slow mix period, the samples were settled for 24 hours. Supernatant samples were drawn off after one hour and four hours settling and analyzed for total suspended solids. After 24 hours settling, the remaining supernantant was also analyzed for total suspended solids.

Results are presented in Table 11. It is apparent that Betz 1115L performed better at the longer mixing cycle and the higher concentration. The Nalcolyte polymer performed better at 1 ppm with the shorter mixing cycle. Dow XD7817 performed better at 0.0025 ppm using the longer mixing cycle. Hercofloc 815, the only cationic polymer used, performed poorly in all but two cases. It was decided that for future testing, the Hercofloc polymer should be replaced with another polymer, preferably not cationic. Magnifloc 834A (solid, anionic) was substituted, since it had previously been used in a similar lime treatability study. The dosages selected were based on manufacturer's recommended ranges, and the longer mixing mode was selected, since it performed better with three out of the four polymers previously tested.

TABLE 11. PRELIMINARY TESTING OF POLYMERS WITH AMMONIATED EDTA WASTEWATER COMPOSITE

(All values in mg/l)

		10 Minute Slow Mix Total Suspended Solids After Settling			20 Minute Slow Mix Total Suspended Solids After Settling		
Polymer	Dosage	1 hr	4 hr	24 hr	1 hr	4 hr	24 hr
Betz 1115L	0.5	26	25	24	83	35	44
	2.0	23	21	13	23	0	0
Nalcolyte 7766	1.0	45	12	10	29	16	16
	3.0	26	29	24	12	31	36
Dow XD7817.01	0.0025	27	18	17	14	10	15
	0.05	115	72	28	26	27	20
Hercofloc 815	5.0	57	50	33	32	31	31
	10.0	36	26	45	42	37	25

The polymer dosage ranges selected for the next phase of testing were based on levels that showed optimum performance.

2. Determination of Best Treatment Levels Using Dilution-Lime Precipitation - Polymer Addition Technology

This phase of testing was employed in order to determine the best treatment levels attainable for each cleaning system wastewater using dilution, lime precipitation, and polymer addition. Based on "best run" values, a "most-difficult-to-treat" wastewater will then be selected.

Five boiler chemical cleaning wastewater samples were used in this phase of the testing. The thiourea/hydrochloric acid (with no citric rinse) was excluded from further testing, since metals levels attained in its previous testing were all less than or equal to 0.2 mg/l.

For each chemical cleaning wastewater sample, the pH and dilution ratio showing maximum metal removals from the previous experiment was designated for testing with selected dosages and mixing cycles. For sets of parameters showing comparable metal removal efficiencies, economics became the deciding factor and the lower pH's and dilution ratios were chosen. The chemical cleaning systems at selected parameters are listed below:

System	pH	Dilution
Ammoniated Bromate/HCl	12.0	1:1
Hydroxyacetic-Formic Acid	9.5	10:1
Ammoniated EDTA	12.0	10:1
Thiourea-HCl/Citric Acid	10.5	3:1
Thiourea-HCl	10.5	1:1
Ammoniated Citric Acid	12.0	10:1

Four polymers were to be employed at four dosages using the better of the two mixing cycles as determined in the preliminary testing. The dosages to be used were also determined from the previous step. As mentioned earlier, Magnifloc 834A was substituted for the Hercofloc polymer. Dosages and the mixing cycle for the Magnifloc polymer were selected based on manufacturer's recommendations, and results of previous testing with other polymers. A listing of the dosages and mixing cycles employed for each polymer is given below:

Flocculant	Dosages (ppm)	Mixing Mode
Betz 1115L	0.5, 1.0, 1.5, 2.0	RM-15 sec., SM-20 min.
Nalcolyte 7766	0.5, 1.0, 1.5, 2.0	RM-15 sec., SM-10 min.
Dow XD 7817.01	0.0025, 0.01, 0.025, 0.05	RM-15 sec., SM-20 min.
Magnifloc 834A	0.5, 1.0, 1.5, 2.0	RM-15 sec., SM-20 min.

Dilution, pH, adjustment, and polymer addition were conducted as described in previous procedures. After mixing, the samples were allowed to settle for a total of 24 hours. Again, two supernatant samples were drawn off, one after 4 hours of settling and the other after 24 hours. Both supernatant samples were analyzed for TSS total and dissolved iron, copper, nickel, and zinc.

The results of this experiment are presented in Tables 12 through 16. In most cases, polymers caused a net reduction in total and sometimes dissolved metals, as data were compared to previous runs without polymer addition.

The effect of settling time on metal residuals was variable and seemed to be dependent on the specific wastewater. Total suspended solids were also generally lower with the use of the polymers.

The ammoniated bromate/hydrochloric acid wastewater seemed to follow the above general observations. With respect to settling time, total iron was observed to increase slightly at the end of 24 hours, while the other metals were basically unaffected. Total suspended solids were considerably lower than those obtained without the use of polymers. All four polymers seemed to give comparable results.

The thiourea-hydrochloric acid/citric acid wastewater seemed to show a decrease in metal residuals caused by the use of polymers. There was no significant difference between metal residuals at different settling times. Total suspended solids were generally lower with the use of polymers. All four polymers gave comparable results.

The hydroxyacetic-formic acid wastewater showed a decrease in total iron and copper residuals after 24 hours settling; however, there seemed to be no significant change in nickel and zinc residuals. Also, total suspended solids were generally higher than those experienced without the use of polymers. Total and dissolved iron decreased significantly from 4 to 24 hours settling.

Polymers had varying effects on the ammoniated EDTA wastewater. No significant effects were observed with respect to differences in iron, copper, zinc, and total suspended solids. Nickel residuals varied widely, depending on the polymer tested. Dow XD 7817.01 yielded extremely high nickel residuals (15 to 20 mg/l) when compared with the other polymers. The other polymers yielded nickel values in the range of 3 to 9 mg/l. No significant effect of settling times was observed.

TABLE 12. DILUTION/LIME PRECIPITATION/POLYMER ADDITION TREATMENT OF AMMONIATED BROMATE/HCL BOILER CLEANING SYSTEM WASTEWATERS

		Layer Thickness(2)		Four Hour Supernatant Residuals(3)									24 Hour Supernatant Residuals(3)								
				Fe		Cu		Ni		Zn			Fe		Cu		Ni		Zn		
Flocculant	Dosage(1)	Sludge	Sprnt.	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS
Betz 1115L	0.5 ppm	8.4	2.8	0.4	0.3	0.2	0.3	0.3	0.6	< 0.1	< 0.1	23	0.3	< 0.1	0.2	0.2	0.3	0.3	< 0.1	< 0.1	39
	1.0	6.3	2.8	0.4	0.2	< 0.1	0.1	0.3	0.3	< 0.1	< 0.1	24	1.3	1.3	0.1	0.1	0.3	0.4	< 0.1	< 0.1	38
	1.5	6.5	1.5	0.8	0.5	0.3	0.3	0.4	0.5	< 0.1	< 0.1	35	0.5	0.1	0.3	0.2	0.3	0.2	< 0.1	< 0.1	32
	2.0	6.3	2.1	1.2	0.8	0.3	0.2	0.7	0.6	< 0.1	< 0.1	27	0.4	0.1	0.1	0.1	0.3	0.3	< 0.1	< 0.1	43
Nalco 7766	0.5	6.4	2.3	0.9	0.2	0.1	0.1	0.3	0.4	< 0.1	< 0.1	29	0.4	< 0.1	0.1	0.2	0.3	0.3	< 0.1	< 0.1	1
	1.0	6.4	2.4	1.0	0.2	0.1	< 0.1	0.5	0.4	< 0.1	< 0.1	14	3.9	3.8	0.1	< 0.1	0.8	0.8	< 0.1	< 0.1	10
	1.5	6.6	2.1	0.4	0.2	< 0.1	< 0.1	0.3	0.4	< 0.1	< 0.1	8	0.4	< 0.1	< 0.1	0.1	0.3	0.3	< 0.1	< 0.1	9
	2.0	6.0	1.6	0.4	0.1	< 0.1	0.1	0.3	0.3	< 0.1	< 0.1	4	0.4	< 0.1	0.1	0.1	0.3	0.3	< 0.1	< 0.1	1
Dow XD...	0.0025	6.4	2.1	0.8	0.5	2.4	2.6	0.3	0.3	0.1	< 0.1	17	0.3	< 0.1	1.9	2.0	0.2	0.2	< 0.1	< 0.1	11
	0.01	5.9	2.2	0.4	0.2	2.1	2.3	0.3	0.3	< 0.1	< 0.1	7	0.4	< 0.1	1.6	1.7	0.2	0.1	< 0.1	< 0.1	15
	0.025	6.3	2.4	0.4	< 0.1	0.1	0.3	0.4	0.2	< 0.1	< 0.1	25	0.3	< 0.1	0.1	< 0.1	0.2	0.2	< 0.1	< 0.1	6
	0.05	6.1	2.1	0.4	< 0.1	0.2	0.3	0.2	0.2	< 0.1	< 0.1	26	0.3	< 0.1	0.2	0.2	0.2	0.2	< 0.1	< 0.1	6
Cyanamid 834A	0.5	5.9	1.5	0.5	0.3	0.3	0.3	0.4	0.4	< 0.1	< 0.1	35	0.7	0.5	0.1	0.2	0.3	0.4	< 0.1	< 0.1	28
	1.0	6.5	1.5	1.0	0.6	0.2	0.2	0.6	0.6	< 0.1	< 0.1	32	0.4	0.2	0.2	0.3	0.3	0.2	< 0.1	< 0.1	15
	1.5	6.5	1.7	0.4	0.1	0.4	0.4	0.3	0.3	0.1	< 0.1	42	0.4	< 0.1	0.2	0.3	0.2	0.1	< 0.1	< 0.1	13
	2.0	5.9	1.5	0.7	0.3	0.3	0.3	0.5	0.5	< 0.1	< 0.1	34	0.5	0.2	0.2	0.1	0.3	0.3	< 0.1	< 0.1	0

(1) Polymer dosage reported in ppm.
(2) Layer thickness reported in cm.
(3) All metals and total suspended solids reported in mg/l.

TABLE 13. DILUTION/LIME PRECIPITATION/POLYMER ADDITION TREATMENT OF THIOUREA/HCL/CITRIC ACID BOILER CLEANING SYSTEM WASTEWATERS

		Layer Thickness(2)		Four Hour Supernatant Residuals(3)									24 Hour Supernatant Residuals(3)								
				Fe		Cu		Ni		Zn			Fe		Cu		Ni		Zn		
Flocculant	Dosage(1)	Sludge	Sprnt.	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS
Betz 1115L	0.5	9.6	3.4	0.1	< 0.1	0.2	0.2	0.1	0.1	< 0.1	< 0.1	23	2.9	0.3	0.2	< 0.1	0.5	0.1	< 0.1	< 0.1	30
	1.0	6.6	6.0	< 0.1	< 0.1	0.2	0.1	0.2	0.1	< 0.1	< 0.1	22	0.6	0.3	0.2	0.1	0.2	0.1	< 0.1	< 0.1	25
	1.5	7.7	4.8	0.1	< 0.1	0.2	0.1	0.3	0.1	< 0.1	< 0.1	23	0.6	< 0.1	0.2	0.1	0.3	0.1	< 0.1	< 0.1	9
	2.0	6.9	5.8	0.3	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	27	0.3	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	6
Nalco 7766	0.5	8.8	3.4	0.3	< 0.1	0.4	0.4	0.1	0.1	< 0.1	< 0.1	9	0.6	0.3	0.3	0.3	0.2	0.1	< 0.1	< 0.1	19
	1.0	9.3	3.4	1.5	< 0.1	0.4	0.4	0.1	0.1	< 0.1	< 0.1	10	0.3	< 0.1	0.3	0.3	0.1	0.1	< 0.1	< 0.1	26
	1.5	7.1	5.9	0.1	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	26	0.6	0.3	0.2	0.1	0.1	0.1	< 0.1	< 0.1	16
	2.0	7.6	9.0	0.1	< 0.1	0.2	0.1	0.1	< 0.1	< 0.1	< 0.1	23	0.2	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	1
Dow XD...	0.0025	6.4	6.6	0.2	< 0.1	0.4	0.4	0.1	0.1	< 0.1	< 0.1	30	0.4	0.2	0.3	0.1	0.1	0.1	< 0.1	< 0.1	70
	0.01	4.2	8.3	0.3	< 0.1	0.3	0.2	0.1	0.1	< 0.1	< 0.1	31	0.2	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	42
	0.025	5.2	7.5	0.4	< 0.1	0.2	0.2	0.1	0.1	< 0.1	< 0.1	11	0.1	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1	22
	0.05	6.2	6.8	0.2	< 0.1	0.2	0.2	0.1	0.1	< 0.1	< 0.1	2	0.3	< 0.1	0.2	0.1	< 0.1	0.1	< 0.1	< 0.1	25
Cyanamid 834A	0.5	4.0	4.8	0.1	< 0.1	0.1	0.1	0.2	0.1	< 0.1	< 0.1	13	1.3	0.2	0.2	0.1	0.1	0.1	< 0.1	< 0.1	4
	1.0	3.9	8.9	0.1	< 0.1	0.2	0.1	0.3	0.1	< 0.1	< 0.1	20	1.3	0.2	0.3	< 0.1	0.1	0.1	< 0.1	< 0.1	7
	1.5	9.2	3.6	0.2	< 0.1	0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	15	0.4	0.2	0.2	< 0.1	0.2	0.1	< 0.1	< 0.1	4
	2.0	9.4	3.4	0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	< 0.1	< 0.1	17	0.6	0.1	0.1	< 0.1	0.1	0.1	< 0.1	< 0.1	0

(1) Polymer dosage reported in ppm.
(2) Layer thickness reported in cm.
(3) All metals and suspended solids reported in mg/l.

TABLE 14. DILUTION/LIME PRECIPITATION/POLYMER ADDITION TREATMENT OF HYDROXYACETIC/FORMIC ACID BOILER CLEANING SYSTEM WASTEWATERS

		Layer Thickness(2)		Four Hour Supernatant Residuals(3)									24 Hour Supernatant Residuals(3)								
				Fe		Cu		Ni		Zn			Fe		Cu		Ni		Zn		
Flocculant	Dosage(1)	Sludge	Sprnt.	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS
Betz 1115L	0.5 ppm	7.3	1.4	1.1	0.8	0.3	0.2	0.7	0.8	0.12	< 0.1	54	0.3	0.2	0.2	0.2	0.5	0.5	< 0.10	< 0.1	40
	1.0	6.9	1.6	0.9	0.5	0.3	0.2	0.6	0.5	0.13	< 0.1	57	0.8	0.4	0.2	0.1	0.5	0.4	< 0.10	< 0.1	38
	1.5	6.9	1.5	0.7	0.4	0.3	0.3	0.6	0.7	< 0.10	< 0.1	56	0.6	0.3	0.2	0.2	0.6	0.5	0.12	< 0.1	43
	2.0	5.8	2.2	0.7	0.3	0.3	0.2	0.6	0.6	< 0.10	< 0.1	61	0.6	0.3	0.2	0.1	0.5	0.4	0.10	< 0.1	26
Nalco 7766	0.5	10.5	2.5	1.2	0.8	0.3	0.2	0.8	0.7	0.10	< 0.1	49	0.8	0.1	0.2	0.2	0.7	0.5	< 0.10	< 0.1	59
	1.0	9.7	3.0	1.0	0.4	0.3	0.2	0.6	0.6	< 0.10	< 0.1	50	0.2	0.1	0.2	0.2	0.5	0.4	< 0.10	< 0.1	39
	1.5	9.6	3.1	0.9	0.4	0.3	0.2	0.6	0.5	0.25	< 0.1	28	0.3	<0.1	0.2	0.1	0.5	0.4	< 0.10	< 0.1	59
	2.0	9.6	3.1	0.9	0.3	0.3	0.3	0.6	0.5	< 0.10	< 0.1	42	0.2	<0.1	0.2	0.2	0.5	0.4	< 0.10	< 0.1	62
Dow XD...	0.0025	9.5	3.0	0.7	0.3	0.3	0.3	0.6	0.5	< 0.10	< 0.1	53	0.2	<0.1	0.2	0.2	0.5	0.4	< 0.1	< 0.1	58
	0.01	10.5	2.5	0.6	0.2	0.3	0.3	0.6	0.5	< 0.10	< 0.1	45	0.3	<0.1	0.3	0.2	0.5	0.4	0.13	< 0.1	52
	0.025	9.3	3.4	0.7	0.2	0.3	0.3	0.6	0.5	0.10	< 0.1	103	0.3	0.1	0.2	0.2	0.5	0.4	< 0.10	< 0.1	59
	0.05	9.6	3.1	0.9	0.2	0.3	0.3	0.6	0.5	0.21	< 0.1	43	0.3	0.1	0.2	0.2	0.5	0.4	< 0.10	< 0.1	41
Cyanamid 834A	0.5	9.2	2.8	0.9	0.3	0.3	0.2	0.6	0.6	0.10	< 0.1	65	0.5	0.1	0.2	0.2	0.6	0.4	0.25	< 0.1	74
	1.0	9.7	2.8	0.7	0.2	0.3	0.3	0.6	0.5	< 0.10	< 0.1	60	0.3	<0.1	0.2	0.2	0.5	0.4	< 0.1	< 0.1	74
	1.5	9.8	2.7	0.9	0.1	0.3	0.3	0.6	0.5	0.11	< 0.1	55	0.5	<0.1	0.2	0.2	0.5	0.4	0.10	< 0.1	68
	2.0	9.2	2.5	0.9	0.2	0.3	0.2	0.7	0.7	0.11	< 0.1	51	2.4	0.1	0.2	0.2	0.9	0.4	< 0.1	< 0.1	76

(1) Polymer dosage reported in ppm.
(2) Layer thickness reported in cm.
(3) All metals and suspended solids reported in mg/l.

TABLE 15. DILUTION/LIME PRECIPITATION/POLYMER ADDITION TREATMENT OF AMMONIATED EDTA BOILER CLEANING SYSTEM WASTEWATERS

		Layer Thickness(2)		Four Hour Supernatant Residuals(3)									24 Hour Supernatant Residuals(3)								
				Fe		Cu		Ni		Zn			Fe		Cu		Ni		Zn		
Flocculant	Dosage(1)	Sludge	Sprnt.	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS
Betz 1115L	0.5 ppm	6.9	5.6	0.4	< 0.1	0.1	0.2	4.6	4.5	< 0.1	< 0.1	39	0.2	< 0.1	< 0.1	< 0.1	5.2	5.3	< 0.1	< 0.1	60
	1.0	7.7	5.8	0.2	< 0.1	0.1	< 0.1	4.8	4.9	< 0.1	< 0.1	34	< 0.1	< 0.1	< 0.1	< 0.1	5.4	5.4	< 0.1	< 0.1	23
	1.5	7.0	5.4	0.2	< 0.1	0.1	< 0.1	4.8	4.8	< 0.1	< 0.1	20	0.1	< 0.1	< 0.1	< 0.1	4.7	5.3	< 0.1	< 0.1	38
	2.0	3.7	8.7	0.4	< 0.1	0.1	< 0.1	3.2	3.5	< 0.1	< 0.1	24	0.2	0.1	< 0.1	< 0.1	3.1	4.1	< 0.1	< 0.1	10
Nalco 7766	0.5	4.0	4.8	0.4	0.1	0.1	< 0.1	5.0	5.1	< 0.1	< 0.1	23	2.8	0.8	< 0.1	< 0.1	5.3	5.7	< 0.1	< 0.1	22
	1.0	8.8	4.2	0.3	0.2	0.1	< 0.1	5.1	5.0	< 0.1	< 0.1	29	0.3	< 0.1	< 0.1	< 0.1	5.4	5.5	< 0.1	< 0.1	24
	1.5	7.3	5.3	0.3	< 0.1	0.1	< 0.1	9.5	9.1	< 0.1	< 0.1	34	0.2	< 0.1	0.1	< 0.1	8.8	8.8	< 0.1	< 0.1	35
	2.0	6.2	5.8	0.4	< 0.1	0.2	< 0.1	7.9	7.9	< 0.1	< 0.1	2	0.2	< 0.1	0.1	< 0.1	7.4	7.6	< 0.1	< 0.1	21
Dow XD...	0.0025	7.2	5.8	0.3	0.1	0.1	< 0.1	20.8	19.9	< 0.1	< 0.1	42	0.2	< 0.1	< 0.1	< 0.1	17.7	19.9	< 0.1	< 0.1	60
	0.01	6.2	6.3	0.2	< 0.1	0.1	< 0.1	19.8	20.5	< 0.1	< 0.1	34	0.2	< 0.1	< 0.1	< 0.1	17.9	19.2	< 0.1	< 0.1	35
	0.025	6.0	6.0	0.4	< 0.1	0.1	< 0.1	18.7	18.7	< 0.1	< 0.1	68	0.4	< 0.1	< 0.1	< 0.1	16.8	17.7	< 0.1	< 0.1	34
	0.05	6.6	6.4	0.3	< 0.1	0.1	< 0.1	18.5	17.5	< 0.1	< 0.1	35	0.2	< 0.1	< 0.1	< 0.1	14.9	16.1	< 0.1	< 0.1	38
Cyanamid 834A	0.5	8.2	4.3	0.3	< 0.1	0.2	< 0.1	6.9	7.2	< 0.1	< 0.1	25	0.2	< 0.1	< 0.1	< 0.1	7.2	7.1	< 0.1	< 0.1	26
	1.0	8.1	4.6	0.5	< 0.1	0.2	< 0.1	7.4	7.2	< 0.1	< 0.1	16	0.2	0.1	0.1	< 0.1	6.6	7.0	< 0.1	< 0.1	1
	1.5	7.5	5.0	0.4	< 0.1	0.1	< 0.1	7.5	7.4	< 0.1	< 0.1	33	0.2	< 0.1	< 0.1	< 0.1	7.7	7.4	< 0.1	< 0.1	41
	2.0	7.4	5.6	0.3	< 0.1	< 0.1	< 0.1	7.8	7.4	< 0.1	< 0.1	24	0.2	< 0.1	< 0.1	< 0.1	7.1	7.4	< 0.1	< 0.1	21

(1) Polymer dosage reported in ppm.
(2) Layer thickness reported in cm.
(3) All metals and total suspended solids reported in mg/l.

TABLE 16. DILUTION/LIME PRECIPITATION/POLYMER ADDITION TREATMENT OF AMMONIATED CITRIC ACID BOILER CLEANING SYSTEM WASTEWATERS

		Layer Thickness[2]		Four Hour Supernatant Residuals[3]									24 Hour Supernatant Residuals[3]								
				Fe		Cu		Ni		Zn			Fe		Cu		Ni		Zn		
Flocculant	Dosage[1]	Sludge	Sprnt.	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.	TSS
Betz 1115L	0.5 ppm	8.3	4.2	0.8	0.1	<0.1	<0.1	0.4	0.3	0.16	<0.1	26	0.2	<0.1	0.1	<0.1	0.3	0.3	<0.10	<0.1	47
	1.0	8.2	4.3	0.2	0.1	<0.1	<0.1	0.3	0.2	<0.10	<0.1	22	0.4	0.1	<0.1	<0.1	0.3	0.3	<0.10	<0.1	38
	1.5	8.2	3.8	0.4	0.2	<0.1	<0.1	0.3	0.3	<0.10	<0.1	15	0.3	<0.1	<0.1	<0.1	0.4	0.3	0.12	<0.1	25
	2.0	8.7	4.0	0.7	0.1	<0.1	<0.1	0.3	0.3	<0.10	<0.1	31	0.2	<0.1	<0.1	<0.1	0.3	0.2	<0.10	<0.1	14
Nalco 7766	0.5	8.9	4.2	0.3	0.2	<0.1	<0.1	0.3	0.2	<0.10	<0.1	22	1.6	<0.1	<0.1	<0.1	0.5	0.2	<0.11	<0.1	25
	1.0	8.6	4.1	0.4	<0.1	<0.1	<0.1	0.3	0.3	<0.10	<0.1	29	0.2	<0.1	<0.1	<0.1	0.3	0.2	0.10	<0.1	26
	1.5	5.3	2.8	0.7	0.3	0.2	0.2	0.4	0.3	<0.10	<0.1	33	2.1	1.7	0.2	0.1	0.6	0.4	<0.10	<0.1	60
	2.0	7.4	1.2	0.7	0.5	0.2	0.2	0.4	0.3	<0.10	<0.1	38	3.5	2.6	0.2	0.1	0.6	0.5	<0.10	<0.1	74
Dow XD...	0.0025	9.1	2.9	0.3	<0.1	0.1	<0.1	0.3	0.3	0.17	<0.1	41	0.5	<0.1	<0.1	<0.1	0.4	0.4	<0.10	<0.1	26
	0.01	10.0	3.0	0.4	0.1	0.1	<0.1	0.3	0.3	<0.10	<0.1	28	0.1	<0.1	<0.1	<0.1	0.3	0.2	<0.10	<0.1	11
	0.025	9.0	3.7	0.4	<0.1	0.1	<0.1	0.3	0.2	0.13	<0.1	33	4.5	<0.1	0.1	<0.1	0.8	0.2	<0.10	<0.1	77
	0.05	8.5	4.2	(4)	<0.1	0.1	<0.1	1.1	0.3	0.14	<0.1	14	0.5	<0.1	0.3	<0.1	0.3	0.2	<0.10	<0.1	7
Cyanamid 834A	0.5	9.1	3.9	0.4	<0.1	<0.1	<0.1	0.3	0.3	0.10	<0.1	34	0.2	<0.1	0.1	<0.1	0.3	0.2	<0.10	<0.1	135
	1.0	8.4	4.6	0.4	0.2	0.1	<0.1	0.3	0.3	0.13	<0.1	29	0.3	<0.1	0.1	<0.1	0.3	0.2	<0.10	<0.1	25
	1.5	8.2	4.5	0.6	0.2	0.1	<0.1	0.4	0.3	<0.10	<0.1	19	0.5	0.3	<0.1	<0.1	0.3	0.3	<0.10	<0.1	30
	2.0	7.9	4.9	(4)	<0.1	<0.1	<0.1	1.6	0.3	<0.10	<0.1	3	0.4	<0.1	<0.1	<0.1	0.3	0.3	0.15	<0.1	13

(1) Polymer dosage reported in ppm.
(2) Layer thickness reported in cm.
(3) Metals and total suspended solids reported in mg/l.
(4) Supernatant samples contaminated with sludge layer.

The ammoniated citric acid wastewater data showed no significant differences in metal residuals with respect to the use of polymers. Some very low supernatant suspended solids values were obtained, suggesting enhanced clarification by the use of polymers for this particular system. Little if any effect could be attributed to differences in settling time.

It is important that total iron at the end of 24 hours' settling seems to be somewhat variable. This is believed to be caused by entrainment of solids during the second decanting, since the sludge interface is much closer to the decanting apparatus during this operation.

A summary of "best runs" is presented in Table 17. Best runs were selected by observing which runs gave best overall performance based on metal and suspended solid residuals and sludge volume. Where two dosages of the same polymer gave comparable results, the lesser of the two dosages was selected as the best run, for economic reasons.

The data show that for most systems, the 1 mg/l limitation is attainable on a laboratory scale. Also, suspended solids residuals were below 30 mg/l for most systems. Table VII-14 clearly indicates two exceptions:

(a) Values for supernatant total suspended solids for hydroxyacetic-formic acid appear high. Out of all runs on Table VII-12, only two showed suspended solids below 30 mg/l (one is shown as a best run).

(b) Supernatant nickel residuals are extremely high for the ammoniated EDTA wastewater, being at least 3.1 mg/l for total nickel. Since it is understood that EPA is planning to limit nickel and zinc emissions as well as iron and copper, this becomes an important consideration.

With respect to the hydroxyacetic-formic acid system, it is important to note that suspended solids levels obtained in previous testing (no polymers) at the higher pH levels were as low as 2 mg/l in some cases and were generally lower than those experienced with the use of polymers. Supernatant from such treatment may have to be filtered prior to discharge if polymers are used.

A problem does seem apparent when observing treatment data for ammoniated EDTA. This problem involves the high nickel residuals in the supernatant. Evidence suggests that nickel forms a strong bond with the tetra-ammonium EDTA salt used in the cleaning formulation. It was observed that the dissolved nickel level in the fireside/air preheater waste-

TABLE 17. SUMMARY OF BEST RUNS FOR DILUTION/LIME PRECIPITATION/POLYMER ADDITION TESTING OF FIVE BOILER CLEANING WASTEWATERS

(All metals and suspended solids reported in mg/l)

System Description	Polymer	Dosage (ppm)	Settling Time (hr)	Supernatant Residuals				
				Total Fe	Total Cu	Total Ni	Total Zn	TSS
Ammoniated Bromate/ HCl (Dilution to 1:1; pH→ 12)	Dow XD...	0.05	4	0.2	0.2	0.1	< 0.1	2
	Cyanamid 834A	1.5	4	0.2	0.1	0.1	< 0.1	15
	Nalco 7766	2.0	24	0.2	0.2	0.1	< 0.1	1
Thiourea/HCl (Dilution to 3:1; pH→ 10.5)	Dow XD...	0.025	24	0.3	0.1	0.2	< 0.1	6
Hydroxyactetic/Formic Acid (Dilution to 10:1; pH→ 9.5)	Naclo 7766	1.0	24	0.2	0.2	0.5	< 0.1	39
	Betz 1115L	2.0	24	0.6	0.2	0.5	0.1	26
Ammoniated EDTA (Dilution to 10:1; pH→ 12)	Betz 1115L	2.0	24	0.2	< 0.1	3.1	< 0.1	10
	Nalco 7766	2.0	24	0.2	0.1	7.4	< 0.1	21
Ammoniated Citric Acid (Dilution to 10:1; pH →12)	Betz 1115L	2.0	24	0.2	< 0.1	0.3	< 0.1	14
	Dow XD..	0.01	24	0.1	< 0.1	0.3	< 0.1	11

water was 195 mg/l, which may further contribute to an unfavorable equilibrium condition for attaining levels below 1 mg/l by lime precipitation.

As discussed earlier, in some cases total nickel values were lower than their dissolved counterparts; however, these values were within statistical limits. For data interpretation purposes, the higher of the two values should be considered indicative of the total concentration.

D. Optimization Testing of the Ammoniated EDTA System Wastewater

After review of the data generated from the previous investigations, the ammoniated EDTA cleaning wastewater was selected for representing the "most-difficult-to-treat" of the five basic kinds of cleaning system wastewaters. The main criterion for its selection was the fact that supernatant nickel residuals could not be reduced below 3 to 4 mg/l and that nickel is presently considered as much as 5 times as toxic as copper (35). The major direction in optimization testing for the ammoniated EDTA wastewater was (a) to introduce a pretreatment step in an effort to reduce nickel levels in the supernatant, and (b) to minimize the diluent and lime requirements for effective treatment of the waste. Three preliminary tests were required to determine what pretreatment practices, if any, would facilitate the removal of nickel from the ammoniated EDTA wastewater. These tests and the subsequent investigations that followed are described below.

1. Investigation of Pretreatment Effectiveness

The effects of aeration, oxidation via hydrogen peroxide, and pretreatment of diluent were investigated to determine if nickel residuals could be reduced below 2 mg/l. As mentioned above, three sets of preliminary experiments were conducted in order to gather the required data.

The first experiment consisted of five different treatments. Three 100-ml aliquots of the ammoniated EDTA wastewater (not diluted) were limed to a pH of 11.0 and aerated to reduce ammonia concentration. The three aliquots were then dosed with 0.5 percent, 1.0 percent, and 2.0 percent hydrogen peroxide, respectively and allowed to react until bubbling (if any) had subsided. A fourth aliquot of the ammoniated EDTA wastewater was aerated but did not undergo pH adjustment, and was dosed with 2 percent hydrogen peroxide. The fifth aliquot did not undergo any of the above

pretreatments for it was the control. All five beakers were then diluted with a 10:1 ratio of fireside/air preheater wash wastewater and limed to a pH of 12.0. The samples were dosed with 2 ppm Betz 1115L polymer, rapid mixed for 15 seconds, slow mixed for 20 minutes, and allowed to settle for 24 hours. The supernatant was analyzed for total and dissolved nickel, iron, and copper.

After this first experiment, further investigation into the chemistry of hydrogen peroxide oxidation indicated that the optimum pH for oxidation was in the range of 4.0 to 5.5 (36). A second experiment was run in order to determine the effect of hydrogen peroxide addition within this pH range. Again five different treatments were investigated. First, five 100-ml aliquots of the ammoniated EDTA wastewater (not diluted) were aerated as is (pH of 9.4). Three of these aliquots were adjusted to a pH of 4.5 with 1 + 1 H_2SO_4 and dosed with 0.1 percent, 0.5 percent, and 1 percent hydrogen peroxide, respectively, and allowed to react overnight. The fourth aliquot was first diluted to a 10:1 ratio with fireside/air preheater wash wastewater, then adjusted to a pH of 4.5 and dosed with 0.5 percent hydrogen peroxide. The fifth aliquot did not undergo any treatment (excepting aeration) for this was the control. After their respective treatments, the aliquots were diluted (if not already done so) to a 10:1 ratio with fireside/air preheater wash wastewater and limed to a pH of 12.0. All treatments were dosed with 2 ppm Betz 1115L polymer, rapid mixed for 15 seconds, slow mixed for 20 minutes, and allowed to settle for four hours. The supernatant after settling was analyzed for total and dissolved nickel, iron, and copper.

The third experiment was conducted to investigate the combined effects of peroxide oxidation, and the use of pretreated fireside/air preheater wash wastewater, ferrous sulfate, and lime/caustic soda pH adjustment. Six different treatments were incorporated in the experiment. All runs except #6 concluded with liming to a pH of 12.0 with addition of 2 ppm Betz 1115L polymer, 15-second rapid mix, 20-minute slow mix and four hours settling. Total and dissolved nickel and iron in the supernatant were analyzed. The treatments differentiating each of the six runs are listed below:

Run #3a - A 10:1 mixture of ammoniated EDTA wastewater and pretreated fireside/air preheater wash wastewaters was adjusted to pH 5.5 with H_2SO_4, dosed with 200 ppm ferrous sulfate and 0.5 percent H_2O_2 and allowed to react overnight.

Run #3b - An aliquot of ammoniated EDTA wastewater was adjusted to pH 5.5 with H_2SO_4, dosed with 200 ppm ferrous sulfate and 1 percent H_2O_2, allowed to react overnight, and diluted to a 10:1 ratio with pretreated fireside/air preheater wash wastewater.

Run #3c - 500 ppm of ferrous sulfate was added to the 10:1 mixture of ammoniated EDTA and the untreated fireside/air preheater wash wastewater at pH of 12.0.

Run #3d - Pretreated fireside/air preheater wash wastewater was used for the 10:1 mixture with the ammoniated EDTA waste.

Run #3e - Pretreated fireside/air preheater wash wastewater was used for the 10:1 mixture with the ammoniated EDTA waste, and 500 ppm of ferrous sulfate was added after the mixture had been adjusted (with lime) to pH 12.0.

Run #3f - A 10:1 mixture of ammoniated EDTA wastewater and untreated fireside/air preheater wash wastewater was adjusted to a pH of 9.5 with lime, and further adjusted to a pH of 12.0 with caustic soda.

The pretreated fireside/air preheater wash wastewater was prepared by addition of lime to a pH of 10.5, settling overnight, and filtering through a Whatman #31 filter paper. The pretreated fireside/air preheater had nickel and iron concentrations of 0.1 mg/l and 0.2 mg/l, respectively. The use of ferrous sulfate for two different functions was investigated. Ferrous sulfate was added to samples prior to peroxide addition to enhance formation of free radical hydroxides (Fenton's reagent) and in turn oxidation of organics (36). The addition of ferrous sulfate during coagulation was also conducted for the purpose of effecting a reduction of any higher oxidation states of nickel back to the bivalent form (this was done in an attempt to reduce soluble nickel). The effect of using a combination of lime and caustic soda was also studied for the purpose of evaluating what is believed to be a more economical alternative (at higher pH's) than treatment with lime alone (37).

The results for the three runs are presented in Table 18 so that differences in treatments can be compared against supernatant residual data.

Much information can be derived from Table 18. It appears that aeration and oxidation do not enhance the re-

TABLE 18. SUMMARY OF PRETREATMENT EFFECTIVENESS FOR AMMONIATED EDTA SYSTEM WASTEWATER

Designation	Treatment Conditions - Runs #1 and #2						Supernatant Residuals (mg/l)						Observations
							Fe		Cu		Ni		
	Aeration[1]	Aeration pH[2]	Dilution[3]	H_2O_2 Dosage	Oxidation pH[3]	Settling Time	Total	Diss.	Total	Diss.	Total	Diss.	
1a	Yes	11.0	No	0.5%	11.0	24 hours	0.4	<0.1	<0.1	<0.1	17	17	No reaction
1b	Yes	11.0	No	1.0%	11.0	24 hours	0.3	<0.1	<0.1	<0.1	16	16	No reaction
1c	Yes	11.0	No	2.0%	11.0	24 hours	0.3	<0.1	<0.1	<0.1	19	20	Slight bubbling
1d	Yes	9.4	No	2.0%	9.4	24 hours	0.6	<0.1	0.1	0.1	26	25	Vigorous bubbling
1e	No	-	No	-	-	24 hours	0.5	<0.1	0.1	<0.1	12	12	-
2a	Yes	9.4	No	0.1%	4.0-4.5	4 hours	2.1	<0.1	<0.1	<0.1	44	44	No visible reaction
2b	Yes	9.4	No	0.5%	4.0-4.5	4 hours	0.3	<0.1	<0.1	<0.1	80	76	Delayed reaction, slight color change
2c	Yes	9.4	No	1.0%	4.0-4.5	4 hours	0.8	<0.1	<0.1	<0.1	68	66	Delayed vigorous reaction; pronounced color change
2d	Yes	9.4	No	-	-	4 hours	1.2	<0.1	<0.1	<0.1	16	16	-
2e	Yes	9.4	Yes	0.5%	4.0-4.5	4 hours	0.4	<0.1	<0.1	<0.1	28	25	Immediate vigorous reaction

Designation	Treatment Conditions - Run #3						Settling Time	Supernatant Residuals (mg/l)				Observations
								Fe		Ni		
	Aeration	Dilution[3]	Pretreated FAPWW[4]	H_2O_2 Dosage	Oxidation pH[3]	Other Chemicals		Total	Diss.	Total	Diss.	
3a	No	Yes	Yes	0.5%	5.5	200 ppm ferrous sulfate	24 hours	0.3	0.6	4.2	4.4	Delayed reaction, color change
3b	No	No	Yes	1%	5.5	-	24 hours	0.5	0.4	5.0	4.9	Delayed reaction, color change
3c	No	-	No	-	-	500 ppm ferrous sulfate	24 hours	0.6	0.2	13.7	13.2	-
3d	No	-	Yes	-	-	-	24 hours	0.4	0.1	5.0	4.8	White sludge
3e	No	-	Yes	-	-	500 ppm ferrous sulfate	24 hours	0.4	0.1	4.9	4.6	Turned green upon addition of ferrous sulfate
3f	No	-	No	-	-	Limed to pH=8.5; adjusted to pH=12.0 with NaOH	24 hours	1.4	0.1	17.0	17.0	Supernatant cloudy

[1] Samples are aerated for 15 minutes.

[2] pH is adjusted with lime or H_2SO_4.

[3] Sample is diluted to 10:1 mixture before oxidation.

[4] Fireside/air preheater wash wastewater treatment at pH=10.5 to removal metals.

moval of nickel. A comparison of runs 1e and 2d can illustrate the effects of aeration. The only essential differences between the two runs are the settling times at which the supernatants were decanted and the addition of an aeration step to 2d. However, data from Table 15 suggest that the difference between settling times of 4 and 24 hours is, at most, about 4 mg/l nickel. Together, these data suggest that aeration (15 minutes) has no significant effect on removal of nickel. With respect to iron, it is apparent that any differences in total concentration are within the range of the statistical variation, as shown later in Table 21. It is interesting to note that total iron is higher than 1 mg/l for one of the runs (2d) at the end of 4 hours' settling. Whether aeration would serve to lower lime and diluent requirements has not been determined, and one can only conclude that aeration had no effect at that specific pH and dilution ratio.

The effects of hydrogen peroxide oxidation seem to be statistically significant. It is believed that very little oxidation took place during Run #1. Although some bubbling was observed, this was probably caused mainly by the decomposition of hydrogen peroxide to water and oxygen. However, it is interesting to note that nickel residuals were observed to be slightly higher in the Run #1 samples where the bubbling was noticed (1c and 1d). It was later learned that the optimum pH range for hydrogen peroxide oxidation was between 4.0 and 5.5 (36) and the second set of runs was oxidized in a pH range of 4.0 to 4.5. Noticeable reactions did take place in Runs 2b, 2c, and 2e; that is, although bubbling with a noticeable color change, the reactions were not immediate in all cases. Another difference in the second run is that the samples were allowed to stand overnight. Upon analysis of the supernatant after lime precipitation and 4 hours' settling, nickel residuals in oxidized samples were as much as five times higher than the unoxidized control (2d). Nickel was almost three times higher in the run where no visible reaction was observed (2a). Nickel was slightly higher in the run which was oxidized at the 10:1 dilution with fireside/air preheater wash. There seemed to be no significant reduction or increase in iron or copper residuals caused by peroxide oxidation.

It was hypothesized that the high concentration of nickel in the fireside/air preheater wash wastewater probably is contributing to this problem. Also, there is some evidence that nickel can be oxidized to a higher oxidation state (Ni^{3+} or Ni^{4+}), which has been found to form soluble complexes with hydroxide (38). However, the exact nature of this phenomenon is not known, and attempts to define it would be beyond the scope of this research.

In a further effort to reduce supernatant nickel residuals, two additional treatments were introduced. One involved the use as a diluent of a pretreated fireside/air preheater wash wastewater, which had nickel levels of 0.1 mg/l. Also, ferrous sulfate was introduced during liming to possibly reduce any high-valence nickel. These treatments were the basis for Run #3. Also investigated were the use of ferrous sulfate as a coagulant and the use of sodium hydroxide and lime in combination for pH adjustment.

The results from Run #3 showed a decrease in supernatant nickel residuals when pretreated diluent was used. This is evident when data from 3a and 3b are compared with 1e. However, comparison of 3a and 3b with 3d suggests that hydrogen peroxide oxidation does little if any good as far as nickel is concerned. No significant difference in supernatant iron residuals is apparent when pretreated diluent is used. All in all, hydrogen peroxide oxidation is not recommended for treatment of ammoniated EDTA wastewaters containing significant amounts of nickel. Its use should not be discounted with other boiler chemical cleaning system wastewaters or where nickel is virtually absent. However, further testing is required to determine its usefulness in the above situation. Ferrous sulfate was used for two purposes in Run #3. The first purpose was to introduce ferrous ion as a catalyst to the formation of free radical hydroxide groups (the essence of the peroxide oxidation reaction). No comparison was made with respect to its effect. The second purpose for introducing ferrous sulfate was to possibly reduce any higher oxidation states of nickel back to the bivalent form, so that they could be precipitated. Comparison of Runs 1e and 3e suggests that no significant difference in nickel or iron concentration was caused by addition of ferrous sulfate. (It is not unusual to have differences of more than 1 mg/l in replicates analyzed on different days, as will be discussed later in this report.)

An alternative pH adjustment procedure was also investigated, involving liming to a pH of 8.5 with adjustment to a pH of 12.0 with caustic soda. Results from this treatment (3f) indicate that supernatant nickel residuals are significantly higher than in the run using straight lime (1e). Also, total iron values after 24 hours' settling were high (1.4 mg/l), suggesting that the settling characteristics of the floc created by caustic soda are not as good as those of the floc created by lime alone. Both of these observations have been confirmed in the literature. Lime increases dissolved metal removal in the ammoniated EDTA wastewater, because the calcium cation has a high affinity for the EDTA molecule, and readily exchanges with other metals (39). The sodium cation does not possess this characteristic to any great extent. Also, it has been found

that sodium hydroxide flocs do not settle as well as lime flocs, possibly because the impurities in the lime enhance settleability (37).

The last observation to be made from this set of data is that the control (1e) for this experiment was significantly higher in supernatant nickel residuals than identical treatments done in previous testing (see Tables 6 and 15). This corresponded to the fact that a new container of sample was started for the pretreatment investigation, and so provisions for the testing of homogeneity from sample to sample had to be incorporated in the future testing.

In summary, the only treatment that was found to be effective in reducing supernatant nickel residuals was the pretreatment of fireside/air preheater wash wastewater prior to mixing with the ammoniated EDTA wastewater. It was recognized that such a treatment scheme was probably economically infeasible because of the need for two lime treatments, and the selection of a diluent which was low in nickel would probably be the most practical approach. However, it should be noted that even this would probably not reduce nickel levels to below 1 mg/l, unless the ammoniated EDTA wastewater being treated was originally at or only slightly above this level. Use of pretreated fireside/air preheater wash wastewater has been omitted from further testing, based on the above considerations. None of the other pretreatments will be investigated further.

2. Optimization of Lime and Diluent Requirements

An effort was made to reduce the requirements for lime and diluent, since the lime dosage needed to raise the pH to 12.0 averaged about 60 to 75 grams per liter of the 10:1 wastewater mixture, and any reduction in diluent volume would be a direct reduction in lime requirement. Also, it was recognized that a pH of 12.0 might be over and above the pH required, and that a slightly lower pH would reduce lime requirements and may even result in lower nickel residuals in the supernatants. No pretreatment steps were involved in the procedure, for it was decided that pretreatment would not be further investigated, based on the limited success in minimizing nickel residuals and the economic infeasibility of pretreatment.

A 24-run matrix test was conducted in which six dilutions and four pH's were used. The dilutions included 10:1, 8:1, 7:1, 6:1, 5:1, and 4:1 with fireside/air preheater wash wastewater. The pH's 10.5, 11.0, 11.5, and 12.0 were incorporated into the matrix. Treatment consisted of lime addition, a 15-second rapid mix for polymer addition (2 ppm

Betz 1115L), a 20-minute slow mix, and settling for four hours. Total and dissolved iron and nickel in the supernatant after four hours' settling were reported, along with supernatant and sludge layer measurements. From previously generated data (Table 6), copper data and zinc were expected to be below 1 mg/l in all of these runs. Therefore, they were not analyzed.

The data from the above experiment are presented in Table 19. The data from this table must be given a close look to determine accurately the effects of changes in pH and dilution ratio. The statistical data later presented in Tables 21, 22, and 23 were used as a basis for analysis. Since all analyses were done on the same calibration curve, differences over 1.3 mg/l and 0.7 mg/l or more are statistically significant for total and dissolved nickel, respectively. Differences of over 0.7 mg/l and 0.1 mg/l are considered significant with respect to total and dissolved iron, respectively.

The general trend observed is that supernatant nickel values increase slowly as the pH and the dilution ratio are lowered. Nickel concentrations range from 10 mg/l (dissolved) at a 10:1 dilution and a pH of 12.0 to 54 mg/l (dissolved) at a 4:1 dilution and a pH of 10.5. Iron seems to stay below 1 mg/l until the pH is lowered to 10.5. This trend applies in all cases except at 8:1 dilution at pH 11.0. Iron concentrations then jump to from below 1 mg/l to 7 to 62 mg/l.

More detailed examination reveals that increases are not steady, but seem to be a function of the pH and dilution ratio. As an example, at a 10:1 dilution, nickel values show a steady increase as a function of a decrease in pH, while at the 7:1 dilution, differences are not apparent until a pH of 10.5 is reached. A look at iron at a pH of 10.5 versus various dilutions shows an increase in iron residual, then a marked decrease at the 6:1 dilution, with a resuming increase for the rest of the dilution range.

For the particular ammoniated EDTA wastewater sample being tested, optimization still corresponds to a pH of 12.0 and a dilution of 10:1. However, it is important to note that the reduction of the lime and diluent requirements may be possible for other ammoniated EDTA wastewaters. This sample represents a "worst case" wastewater in that nickel values before treatment are substantially higher than the norm. Some of the nickel data at lower dilutions (8:1, 7:1, 6:1), suggest no significant increase in supernatant residuals in the pH range of 11.0 to 12.0, and so it may be possible to treat some ammoniated EDTA wastewaters at a pH of

TABLE 19. OPTIMIZATION OF LIME AND DILUENT REQUIREMENTS

(Values reported in mg/l)

		Fe		Ni		Sprnt.	Sludge	
				Layer		Layer		
Dilution	pH	Total	Diss.	Total	Diss.		(cm)	(cm)
10:1	10.5	14	14	19	18		5.6	4.8
10:1	11.0	0.4	0.1	14	14		5.1	5.3
10:1	11.5	0.3	0.1	12	12		4.8	5.6
10:1	12.0	0.3	0.1	11	10		5.3	5.6
8:1	10.5	20	20	24	24		5.6	4.6
8:1	11.0	24*	24*	20	20		5.1	5.3
8:1	11.5	0.4	0.1	15	15		6.1	5.1
8:1	12.0	0.4	0.1	15	16		5.8	5.1
7:1	10.5	34	32	23	22		5.6	5.1
7:1	11.0	0.4	0.1	16	16		5.3	5.3
7:1	11.5	0.3	0.1	15	16		5.3	5.3
7:1	12.0	0.3	0.1	15	15		5.3	5.3
6:1	10.5	7	7	29	29		5.1	5.1
6:1	11.0	0.3	0.1	21	22		5.1	5.3
6:1	11.5	0.3	0.1	21	21		5.1	5.3
6:1	12.0	0.3	0.1	20	20		4.8	5.6
5:1	10.5	17	17	38	38		5.3	5.1
5:1	11.0	0.3	0.1	37	38		5.1	5.3
5:1	11.5	0.3	0.1	27	29		4.8	4.6
5:1	12.0	0.6	0.1	29	31		4.6	6.1
4:1	10.5	62	62	53	54		5.3	5.1
4:1	11.0	0.6	0.2	42	43		4.8	5.6
4:1	11.5	0.3	0.1	37	37		4.6	6.1
4:1	12.0	0.3	0.2	32	35		4.3	7.1

**This value is suspect.*

11.0. The same conclusions apply to the dilution ratio as well, and it may be possible to treat some wastewaters at a dilution of as little as 4:1. In summary, the minimum lime and dilutent requirements for successful treatment will be different for each batch of wastewater, depending greatly on initial metal concentrations in both the ammoniated EDTA wastewater and the diluent wastewater. For our particular wastewater sample, no reduction of the lime or diluent requirement was possible, and further testing was continued at a pH of 12.0 and a dilution of 10:1.

E. Statistical Testing

Two experiments were conducted for the purpose of gathering statistical information to support proper interpretation of data. The first test was conducted in response to observed significant differences in supernatant nickel residuals from replicate treatments of the ammoniated EDTA wastewater, i.e. the control in Table 18 as compared to its replicate in Table 15. It was found that different sample containers were used in the two tests. It was suspected that the aliquots from different containers, originally believed to be identical in concentration, were actually somewhat heterogeneous even though the total sample was well mixed while proportioning to separate sample containers. Identical lime treatments were conducted on aliquots from five different containers of ammoniated EDTA wastewater as described below:

(a) The sample that was being used in lime precipitation and best treatment levels testing

(b) The sample that had just been used in optimization testing

(c) Two previously unopened containers

(d) A one-gallon aliquot that was refrigerated at 4°C.

Once again, the treatment consisted of diluting the ammoniated EDTA aliquot to a ratio of 10:1 with fireside/air preheater wash wastewater, liming to pH 12.0, adding 2 ppm Betz 1115L polymer, rapid mixing for 15 seconds, and slow mixing for twenty minutes. After four hours' settling, a sample of the supernatant was decanted and analyzed for dissolved nickel. Results are presented in Table 20.

TABLE 20. HOMOGENEITY OF AMMONIATED EDTA ALIQUOTS

Source	Supernatant Dissolved Nickel (mg/l)
Sample used in lime precipitation testing	4.9
Sample used in pretreatment testing	9.7
Unused container #1	9.9
Unused container #2	13.3
Refrigerated sample	12.6

The results indicate that the ammoniated EDTA samples were probably not entirely homogeneous, even though they were well mixed before transferring. In subsequent testing, the sample from unused container #1 was used which was closest to the average of the five runs (10.1 mg/l). The other metals may also have variations in their residual concentrations due to sample heterogeneity. However, since values of iron, copper, and zinc were usually below 1 mg/l, this effect is not considered consequential at this time.

The second statistical experiment was run to determine statistical variations in metals analysis, total suspended solids, lime requirements, and supernatant/sludge layer thicknesses. Two sets of six treatments each were run and the total analyses for each set were done separately on consecutive days. This approach provided data needed for a statistical analysis, based on the experimental and analytical procedure. Day-to-day variation in testing caused by factors such as humidity, room temperature, and line voltage fluctuations, were also taken into account by this methodology.

Replicates were prepared using the ammoniated EDTA wastewater sample that yielded nickel values closest to the averaged nickel residuals from the five samples tested.

The replicates were all treated at conditions yielding the lowest nickel residuals, namely a 10:1 mixture with fireside/air preheater wash wastewater, a pH of 12.0, the use of 2 ppm Betz 1115L polymer, rapid mixing for 15 seconds, and slow mixing for 20 minutes. Two decanters were taken off the supernatant after settling times of two and four hours. All analyses conducted in previous testing were included in this experiment, namely total and dissolved iron, copper, nickel, and zinc, total suspended solids, and sludge and supernatant layer thicknesses.

Values obtained for the statistical runs are presented in Table 21. Sample numbers 1 to 6 and 7 to 12 were analyzed on consecutive days using different calibration curves.

Student's t-test was used to determine day-to-day variation in total iron, total nickel, total suspended solids, layer thickness, and lime requirement. Since copper and zinc values were not variable, statistical analysis on these metals was not conducted. The data are presented in Tables 22 and 23. In Table 22, alpha (α) is called the level of significance and indicates the probability that the two samples come from the same population. Traditionally, an alpha value of less than 0.05 has been the criterion for "significant difference." An alpha of 0.05 indicates that there is one chance in 20 that the two sample sets in question come from the same population. This level of significance is also termed the 95 percent level.

The data in Table 22 indicate that day-to-day variation may be significant in isolated cases. For example, total iron with four-hour settling time and lime requirement shows significant day-to-day variation. However, the relation, at least in the case of iron, appears spurious since the two-hour iron does not show a similar trend. This apparently spurious correlation indicates that statistical tests must not be applied blindly.

Table 23 is a statistical treatment of the data in Table 21. In this table, s is the unbiased standard deviation and t refers to the t-statistic when (as defined above) is 0.05. The interval $\bar{X} \pm ts$ is the region in which 95 percent of the data points should lie, assuming a normal distribution. There are 19 chances in 20 that the population mean of the (normally distributed) sampled population lies within $\bar{X} \pm ts/\sqrt{n}$, where n = the number of samples.

TABLE 21. STATISTICAL TESTING OF REPLICATE TREATMENTS

Sample No.	Settling Time (hr.)	Supernatant Residuals (mg/l) Fe Total	Fe Diss.	Cu Total	Cu Diss.	Ni Total	Ni Diss.	Zn Total	Zn Diss.	TSS	Layer Thickness (cm) Supernatant	Sludge	Lime Requirement (g)
1	2	0.5	0.1	<0.1	<0.1	7.7	7.4	<0.1	<0.1	13	6.0	7.5	61.5
2	2	1.1	0.2	<0.1	<0.1	7.0	7.4	<0.1	<0.1	45	5.8	8.0	63.8
3	2	0.6	0.2	<0.1	<0.1	7.4	8.3	<0.1	<0.1	38	5.9	8.6	57.8
4	2	0.4	<0.1	<0.1	<0.1	7.9	8.3	<0.1	<0.1	33	5.9	8.6	57.5
5	2	0.4	0.1	<0.1	<0.1	7.4	8.3	<0.1	<0.1	26	6.0	8.5	58.3
6	2	0.4	0.1	<0.1	<0.1	7.2	7.4	<0.1	<0.1	29	6.0	9.0	59.7
7	2	1.2	0.2	<0.1	<0.1	7.8	8.1	<0.1	<0.1	48	6.0	7.5	52.3
8	2	0.5	<0.1	<0.1	<0.1	7.4	7.4	<0.1	<0.1	8	6.3	8.2	52.3
9	2	0.6	<0.1	<0.1	<0.1	6.9	7.2	<0.1	<0.1	31	5.7	9.3	50.5
10	2	0.6	0.1	<0.1	<0.1	7.4	7.8	<0.1	<0.1	34	6.5	8.0	57.8
11*	2	0.6	-	<0.1	-	6.5	-	0.1	-	-	1.0	13.5	53.4
12	2	0.6	0.1	<0.1	<0.1	7.0	7.2	<0.1	<0.1	41	6.0	8.7	56.0
1	4	0.3	0.1	<0.1	<0.1	7.4	7.7	<0.1	<0.1	69	6.0	7.5	61.5
2	4	0.4	0.1	<0.1	<0.1	7.0	7.2	<0.1	<0.1	24	5.8	8.0	63.8
3	4	0.4	0.1	<0.1	<0.1	7.2	7.3	<0.1	<0.1	27	5.9	8.6	57.8
4	4	0.7	<0.1	<0.1	<0.1	7.2	7.4	<0.1	<0.1	8	5.9	8.6	57.5
5	4	0.3	<0.1	<0.1	<0.1	7.0	7.0	<0.1	<0.1	16	6.0	8.5	58.3
6	4	0.6	<0.1	<0.1	<0.1	7.5	7.4	<0.1	<0.1	19	6.0	9.0	59.7
7	4	1.1	0.1	<0.1	<0.1	7.4	8.0	<0.1	<0.1	11	6.0	7.5	52.3
8	4	-	0.1	<0.1	<0.1	8.1	7.4	<0.1	<0.1	0	6.3	8.2	52.3
9	4	0.7	0.1	<0.1	<0.1	6.8	7.4	<0.1	<0.1	2	5.7	9.3	50.5
10	4	1.4	0.2	<0.1	<0.1	6.8	7.8	<0.1	<0.1	25	6.5	8.0	57.8
11*	4	-	-	-	-	-	-	-	-	-	1.0	13.5	53.4
12	4	-	0.1	<0.1	<0.1	7.4	7.4	<0.1	<0.1	18	6.0	8.7	56.0

*Sample No. exhibited only minimal settling.

TABLE 22. RESULTS OF STUDENT'S T-TEST ON DAY-TO-DAY VARIATION*

	Fe		Ni		TSS		Layer Thickness		Lime Req.	
	t	α	t	α	t	α	t	α	t	α
Student's t-test										
2-hour Settling Time, Day 1 vs. Day 2	-0.763 (df=10)	α<0.1	1.160 (df=10)	α>0.1	-0.220 (df=9)	α>0.5	-0.9040 (df=10)	α>0.1	4.055 (df=10)	α<0.01
4-hour Settling Time, Day 1 vs. Day 2	-3.735 (df=7)	α<0.01	-0.353 (df=9)	α>0.5	1.504 (df=10)	α>0.1	-0.9040 (df=10)	α<0.1	4.055 (df=10)	α<0.01

In this table, α reflects the probability that the two samples are identical, and df refers to the degrees of freedom.

TABLE 23. MEAN, STANDARD DEVIATION, AND CONFIDENCE INTERVAL FOR DAY-TO-DAY VARIATION

	Total Fe				Total Ni			
	X	s	X ± ts*	X ± t s/√n	X	s	X ± ts	X ± ts/√n
Day 1								
2-hour Settling (Samples 1-6)	0.6	0.3	0.0-1.4	0.3-0.9	7.4	0.3	6.6-8.2	7.1-7.7
Day 2								
2-hour Settling (Samples 7-12)	0.7	0.3	0.0-1.5	0.4-1.0	7.2	0.5	5.9-8.5	6.7-7.7
Day 1								
4-hour Settling (Samples 1-6)	0.4	0.2	0.0-0.9	0.2-0.6	7.2	0.2	6.7-7.7	7.0-7.4
Day 2								
4-hour Settling (Samples 7-12)	1.1	0.4	0.0-2.8	0.1-2.1	7.3	0.5	5.9-8.7	6.7-7.9

Negative values taken to be zero. Value of t obtained from Fischer & Yates, Statistical Tables for Biological, Agricultural, and Medical Research, Oliver & Boyd Ltd., Edinburgh, 1951 (rather than from previous calculation). The t calculated and given in Table 21 refers to the variation between two groups of data while the t used in this table refers to the variation within each group.

TABLE 23. (Continued)

	Total Fe				Total Ni			
	X	s	X ± ts*	X ± t s/$\sqrt{n}$	X	s	X ± ts	X ± ts/$\sqrt{n}$
Day 1								
2-hour Settling (Samples 1-6)	31	11	2.7-59	19-43	8.4	0.5	7.1-9.7	7.9-8.9
Day 2								
2-hour Settling (Samples 7-12)	32	15	0-74	13-51	9.2	2.2	3.5-14.9	6.9-11.5
Day 1								
4-hour Settling (Samples 1-6)	27	22	0-84	4-50	8.4	0.5	7.1-9.7	7.9-8.9
Day 2								
4-hour Settling (Samples 7-12)	11	11	0-42	0-25	9.2	2.2	3.5-14.9	6.9-11.5

TABLE 23. (Continued)

	Lime Requirement			
	$\bar{X}$	s	$\bar{X} \pm ts$	$\bar{X} \pm ts/\sqrt{n}$
Day 1				
Samples 1-6	59.8	2.5	53.4-66.2	57.2-62.4
Day 2				
Samples 7-12	53.7	2.7	46.8-60.6	50.9-56.5

The $\bar{X} \pm ts/\sqrt{n}$ values for total iron suggest that the average value for supernatant total iron will rarely exceed 1 mg/l. One value for $\bar{X} \pm ts/\sqrt{n}$ for total iron suggested a higher range (0.1-2.1 mg/l) for the mean, however, this value was based on a significantly lower degree of freedom (7 as opposed to 9) than the other values. The $\bar{X} \pm ts/\sqrt{n}$ for nickel suggest that the average value should not exceed 8.0 mg/l, however previous treatment of the ammoniated EDTA wastewaters from different containers resulted in total nickel residuals of over 13 mg/l and this fact should be considered when determining the statistical validity of the investigation. The $\bar{X} \pm ts/\sqrt{n}$ values for total suspended solids suggests that the average value has a moderate probability of exceeding the 30 mg/l effluent limitation guideline.

Layer thicknesses were somewhat variable, according to Table 23; however, this was expected since some of the sludge layer is lost when the sample is transferred to a settling jar. There were no observed differences in sludge layer thickness between two and four hours' settling. It should be noted that one of the samples (#11) underwent minimal settling (see Table 21). This fact suggests the possibility of operational difficulties in full scale lime treatment and clarification. The reason the sample did not settle is not known.

The lime requirement to achieve a pH of 12.0 was also observed to vary significantly. The definite cause for the variation is not known; however, possible explanations include day-to-day temperature variation, variation in the composition of different aliquots of lime, and/or error introduced by the precision of the weighing method (triple-beam balance).

F. Sludge Characterization

1. Zone Settling Tests

Sludge settling tests were performed on the five runs used in the previous section for testing sample homogeneity, for the purpose of evaluating required settling time with respect to full-scale feasibility. These settling tests were conducted during the four-hour settling time used for the homogeneity experiment. This was accomplished by transferring the unsettled samples (after slow moving) to 1,000-ml graduated cylinders and recording the height of the supernatant/sludge interface with time. Interface heights were recorded every two minutes for 30 minutes, then every five minutes for an hour, and then each hour up to 4 hours settling.

Interface heights vs. time for the five runs is presented in Table 24.

Figures 6 through 10 show settling curves for the five runs. A residue analysis of the sludge before settling was performed on one sample, with the result being 101,189 mg/l or 10.1 percent solids. Tangents to the elbows of the settling curves have been constructed to determine detention times required to concentrate to a specified solids content. For example, if 20 percent solids concentration is specified for the sludge after thickening, the following equation is used to determine corresponding interface height (40).

$$H_1 = \frac{C_o H_o}{C_1}$$

where: H_1 = interface height

C_1 = 20 percent solids

H_o = initial interface height

C_o = initial solids concentration.

A horizontal line is extended from H_1 to intersect tangent line and a vertical line is extended from this point to read required settling time. If 10.1 percent solids is the initial concentration before settling, then the detention times required, as calculated from the five settling curves, would be as follows:

(a) Run #1 - 1.58 hours

(b) Run #2 - 1.46 hours

(c) Run #3 - 1.46 hours

(d) Run #4 - 1.20 hours

(e) Run #5 - 1.60 hours

(f) Average - 1.46 hours.

The above detention times correspond to a conventional thickener and are not applicable to a pond system.

TABLE 24. SLUDGE SETTLING DATA

	Interface Height (cm)				
Minutes	Run #1	Run #2	Run #3	Run #4	Run #5
0	27.6	28.5	26.6	27.0	26.0
2	27.5	28.3	26.4	26.8	25.7
4	27.0	27.7	26.1	26.3	25.4
6	26.3	27.1	25.5	25.6	24.9
8	25.5	26.5	24.9	24.9	24.1
10	24.9	26.0	24.4	24.2	23.6
12	24.1	25.3	23.6	23.6	22.8
14	23.6	24.7	23.2	22.9	22.2
16	23.0	24.1	22.6	22.3	21.5
18	22.4	23.4	21.9	21.6	20.6
20	21.6	22.5	21.1	20.7	19.7
22	20.9	21.7	20.4	19.9	18.6
24	20.0	20.9	19.5	19.0	17.8
26	19.0	19.8	18.5	17.9	17.4
28	18.1	18.8	17.4	17.1	17.1
30	17.7	18.4	16.9	16.7	16.9
35	17.1	17.6	16.3	16.0	16.3
40	16.6	17.1	15.8	15.5	15.9
45	16.3	16.6	15.5	15.1	15.6
50	16.0	16.3	15.2	14.8	15.3
55	15.6	16.1	14.9	14.5	15.0
60	15.4	15.9	14.6	14.2	14.7
65	15.2	15.8	14.4	14.0	14.5
70	15.0	15.7	14.2	13.9	14.3
75	14.8	15.6	13.9	13.6	14.1
80	14.6	15.6	13.8	13.5	13.9
85	14.5	15.6	13.6	13.4	13.9
90	14.4	15.6	13.4	13.4	13.7
95	14.2	15.6	13.3	13.3	13.6
155	13.8	15.6	12.7	13.0	13.1
215	13.7	15.6	12.7	13.0	13.1
240	13.7	15.6	12.7	13.0	13.1

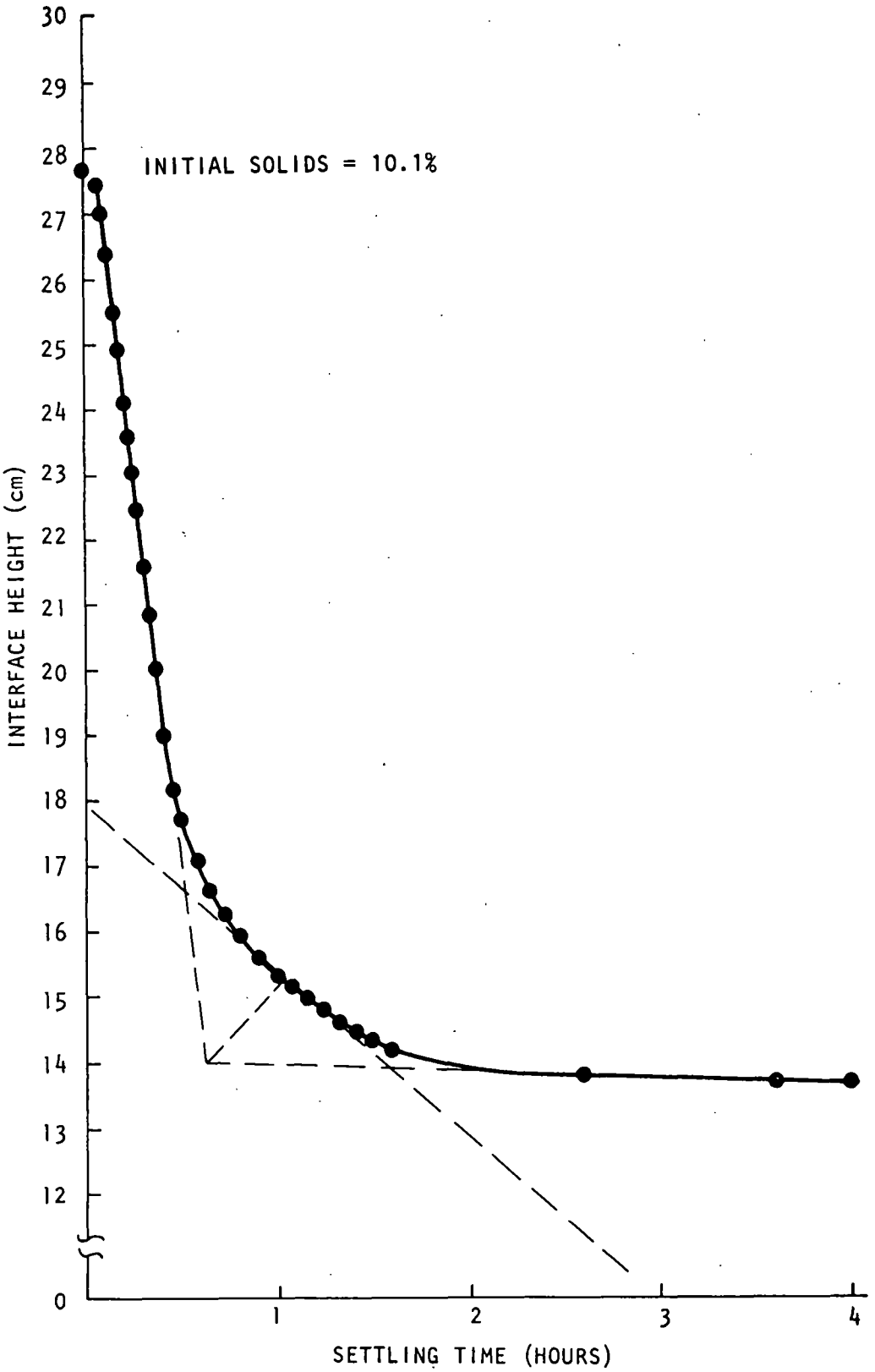


Figure 6. Settling Curve - Run #1

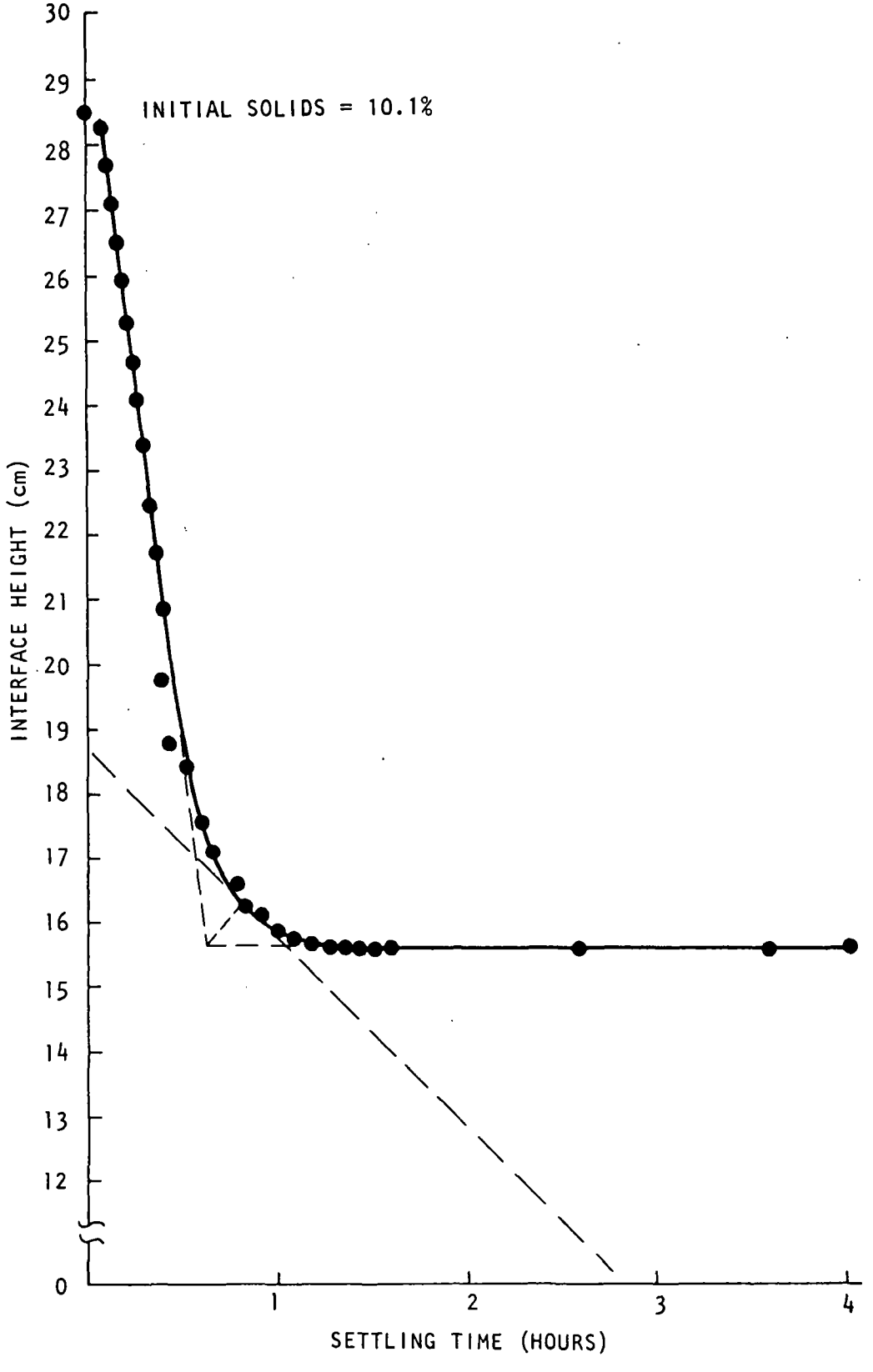


Figure 7. Settling Curve - Run #2

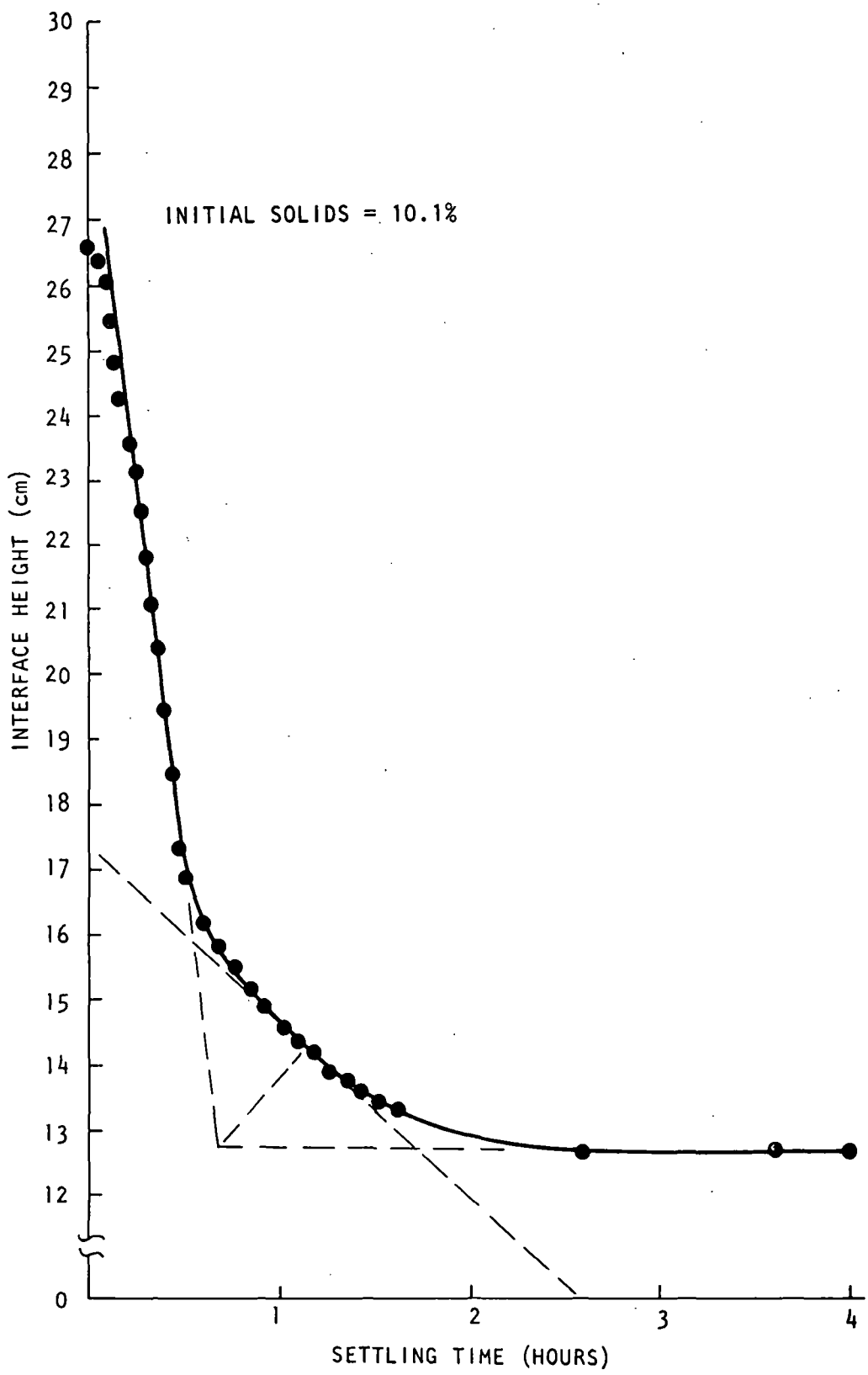


Figure 8. Settling Curve - Run #3

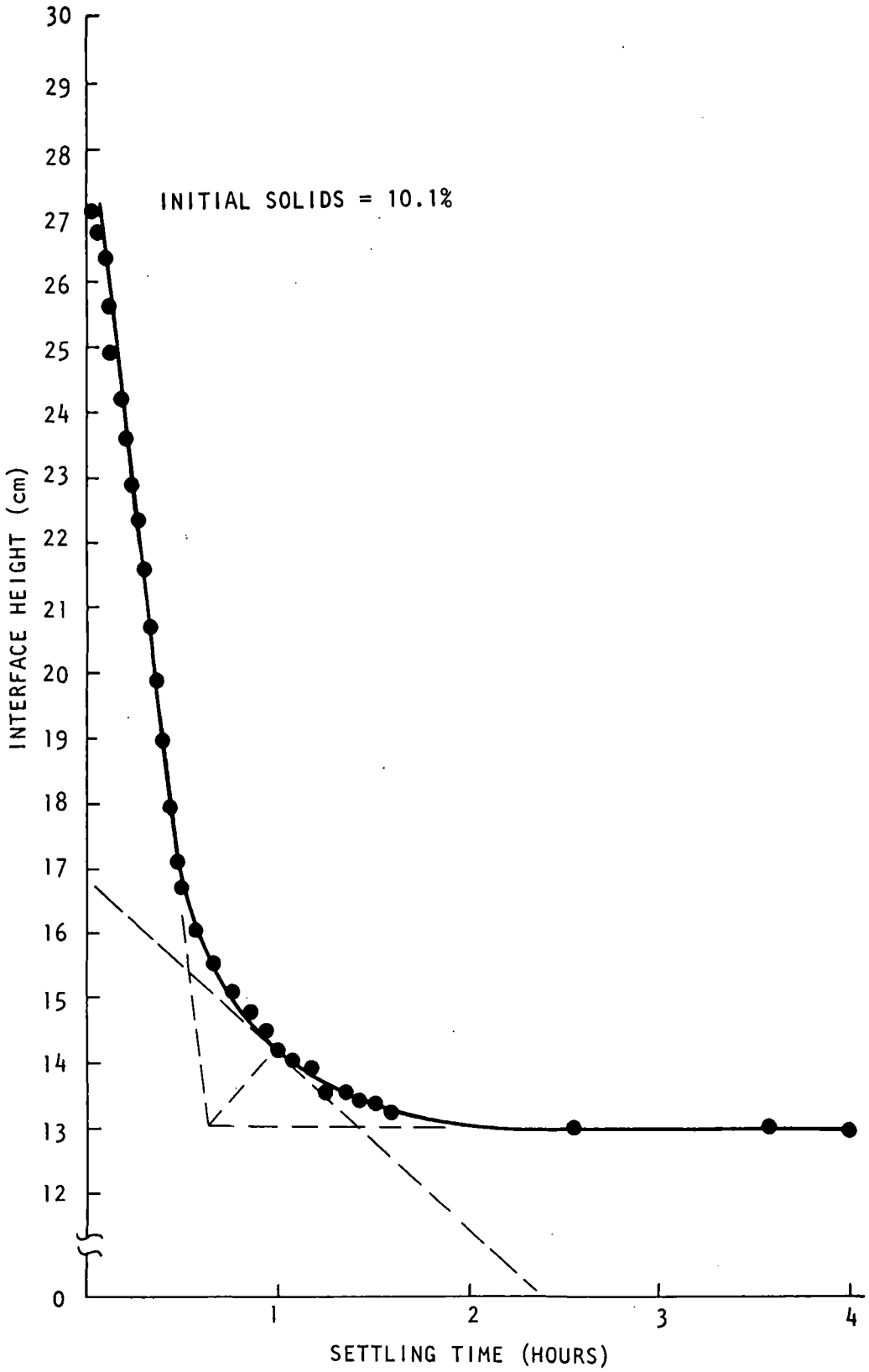


Figure 9. Settling Curve - Run #4

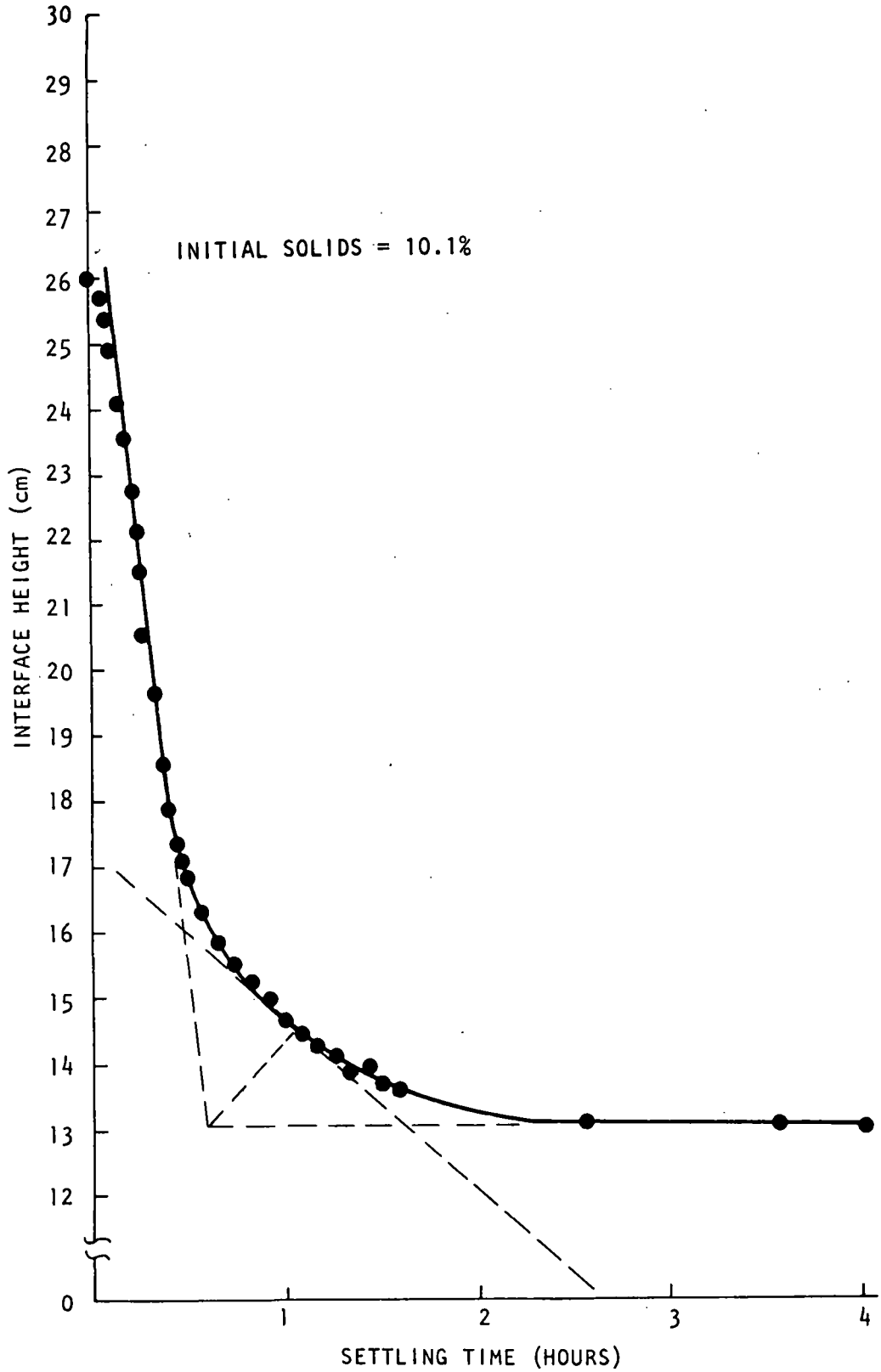


Figure 10. Settling Curve - Run #5

Conversely, if a definite detention time is required for supernatant clarification, the corresponding sludge concentration can then be calculated. A detention time of two hours would then yield an average sludge concentration of 22.9 percent solids.

It must be noted that a picket stirrer was not used during these experiments. The slope of the tangent would probably be slightly less had a picket stirrer been used, hence lesser detention times and greater sludge compaction.

However, the data adequately show that a reasonable amount of time is required for sludge settling, and the treatment is suitable for full scale-up to a conventional thickening unit. It is recognized that the thickened sludge has a high solids content and special transport equipment would be required.

2. Filterability Testing

For the purposes of assessing the feasibility of dewatering the lime sludge by filtering, the Buchner Funnel Test was conducted on the sludges of 5 replicates of the 12-replicate statistical run. The procedure for the test is as follows:

(a) Prepare the Buchner funnel by placing a wire mesh or screen under the filter paper to ensure drainage (see Figure 11).

(b) Moisten the filter paper with water and adjust the vacuum to obtain a seal.

(c) Condition the sludge if necessary; mix it and permit it to stand 30 seconds to 1 minute; use 200 ml samples.

(d) Transfer it to the Buchner funnel, allow sufficient time for a cake to form (5 to 10 seconds), and apply the vacuum.

(e) Record the ml of filtrate after selected time intervals (usually 5 to 10 seconds).

(f) Continue filtration until the vacuum break

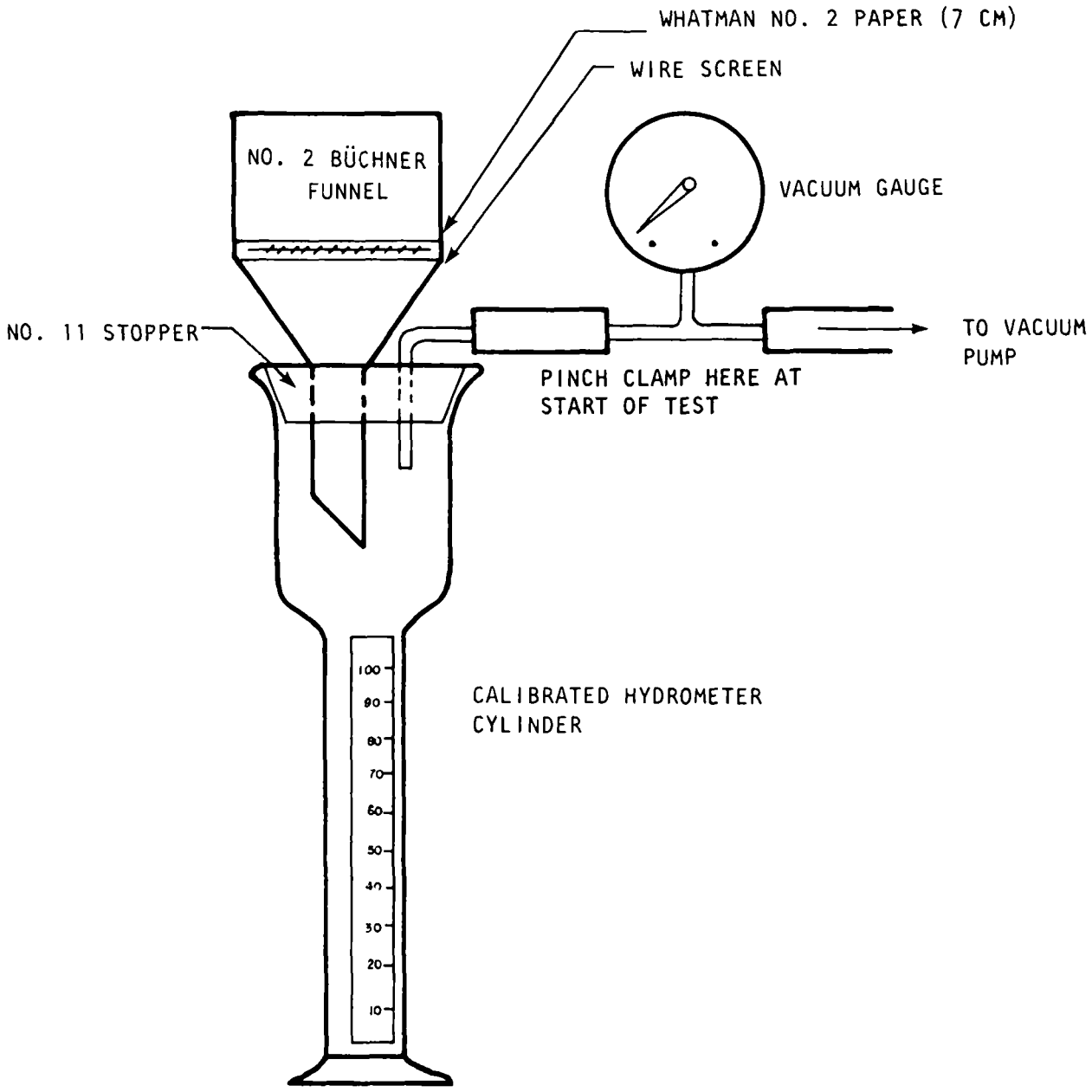


Figure 11. Apparatus for Büchner Funnel Test

(g) Determine the initial and final solids in the feed sludge and cake

(h) Record the data obtained and calculate the specific resistance in accordance with the following equation (41):

$$r = \frac{2bPA2}{\mu C}$$

where: r = specific resistance of cake

P = vacuum (g/cm^3)

A = filtration area (cm^2)

μ = filtrate viscosity (g/sec-cm)

C = weight of solids per unit volume of filtrate (%)

b = slope of plot of t/v vs. V

V = volume of filtrate (cm^3 or ml)

t = filtration time (seconds)

(i) The weight of solids per unit volume of filtrate can be calculated from the following equation (derived from 41):

$$C = \frac{C_i C_f}{100\ (C_f - C_i)}$$

where: C_i = Initial solids content (%)

C_f = Final solids content of filter cake (%)

In the test, the volume of filtrate was measured every five minutes until a vacuum break occurred. Also recorded were the initial and final solids in the sludge and the vacuum applied. Filterability data are presented in Table 25.

The following conditions apply to the Buchner Funnel Test and will be used in subsequent calculations:

(a) Initial total sludge solids = 21.85 percent

(b) Filter diameter = 7 cm

TABLE 25. SLUDGE FILTERABILITY TESTING

	Run #1		Run #2		Run #3		Run #4		Run #5	
Filter Cake (% Solids)	32.7		33.1		34.6		34.9		32.9	
Time (sec)	V(ml)	t/V	V(ml)	t/V	V(ml)	t/V	V(ml)	t/V	V(ml)	t/V
0	10	0	10	0	5	0	8	0	10	0
5	15	.33	19	.26	8	.63	10	.50	20	.25
10	20	.35	27	.37	22	.45	26	.38	25	.40
15	20	.75	31	.48	26	.58	33	.45	30	.50
20	26	.77	38	.53	35	.57	40	.50	38	.53
25	30	1.00	41	.61	40	.63	46	.54	40	.63
30	35	1.00	50	.60	46	.65	50	.60	43	.70
35	39	1.02	52	.67	48	.73	53	.66	50	.70
40	42	1.07	55	.73	50	.80	60	.66	52	.77
45	43	1.16	57	.79	52	.86	62	.73	55	.82
50	43	1.3	60	.83	56	.89	68	.74	58	.86
55	48	1.25	62	.89	60	.92	70	.79	60	.92
60	50	1.3	67	.90	62	.97	75	.80	62	.97
65	51	1.37	70	.93	63	1.03	78	.83	65	1.00
70	55	1.36	73	.96	68	1.03	80	.88	68	1.03
75	60	1.33	76	.99	70	1.07	84	.89	70	1.07
80	63	1.35	78	1.03	75	1.07	88	.91	72	1.11
85	67	1.34	80	1.06	78	1.09			74	1.15
90	68	1.40	82	1.1	80	1.13			76	1.18
95	70	1.43	85	1.2	82	1.16			78	1.22
100	71	1.48	88	1.44	83	1.20			80	1.75
105	73	1.51	90	1.17	84	1.25			83	1.27
110	75	1.53	91	1.21	85	1.29			85	1.29
115	76	1.58	92	1.25	88	1.31			88	1.31
120	78	1.60	95	1.26						
125	80	1.63	97	1.29						
130	82	1.65								
135	84	1.67								
140	86	1.69								
145	88	1.70								
Slope (b) by linear regression (sec/cm^6)	0.017		0.014		0.012		0.009		0.016	

(c) Filtration area = $\frac{d^2}{4}$ = 38.5 cm^2

(d) Vacuum = avg. 19.5 in. Hg = 686.4 g/cm^2

(e) Viscosity of filtrate (water) = 0.01 g/sec-cm.

Calculations for specific cake resistance have been made for each run using the data shown. Specific resistance is presented below:

Run No.	1	2	3	4	5	Mean
Specific Resistance (sec^2/g)	1.4×10^5	1.2×10^5	1.1×10^5	8.1×10^4	1.3×10^5	1.2×10^5

These values are much lower than values reported for the specific resistance of lime sludges from water and municipal wastewater treatment plants. Typical values for specific resistance of wastewater lime sludges were reported to range from 1.0×10^9 to 24.0×10^9 sec^2/g (42). The concentrations of solids in the sludge before and after filtration were typical of lime treatment with respect to thickening and dewatering (42).

The explanation for the apparent decrease in specific cake resistance lies with the use of polymer for clarification. It is well known that polymers have been used successfully to improve the filterability of lime sludges.

In summary, dewatering of the lime sludge seems to present very little problem and will result in a sludge with a very high solids content of about 34 percent. The main will involve sludge transportation since initial sludge solids content is over 20 percent which is considered too high for conventional pumping. It is believed that sludge characteristics will be similar in the treatment of wastewaters from the other chemical cleaning systems.

3. Sludge and Filtrate Metal Concentrations

Metal concentrations of three settled but unfiltered lime sludges from the statistical experiment were analyzed for total residue (percent solids), and total iron, copper, nickel, and zinc. These values and the calculated concentrations of metals in a filtered sludge with an average of 33.6 percent solids (average solids after filtration) are given in Table 26. Table 26 also gives metal concentrations

TABLE 26. SLUDGE AND FILTRATE METAL CONCENTRATIONS

Sample	Metal Concentration (mg/l)							
	Fe		Cu		Ni		Zn	
	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.
Sludge before	7,540	-	79	-	1,040	-	38.5	-
Filtration[1]	7,860	-	83	-	1,080	-	40.7	-
(21.85% Solids)	7,920	-	83	-	1,070	-	40.7	-
Sludge after	11,600	-	121	-	1,600	-	59.0	-
Filtration[2]	12,100	-	128	-	1,660	-	63.0	-
(33.6% Solids)	12,200	-	128	-	1,650	-	63.0	-
Filtrate[3]	-	<0.1	-	0.1	-	8.0	-	<0.1
	-	<0.1	-	0.2	-	7.3	-	<0.1
	-	<0.1	-	0.2	-	7.3	-	<0.1
	-	<0.1	-	<0.1	-	7.1	-	<0.1
	-	<0.1	-	0.1	-	6.6	-	<0.1

[1]Three sludge samples were analyzed.

[2]Metal values are calculated.

[3]Five filtrates are analyzed.

in the sludge filtrates to determine acceptability for discharge.

The data show that the resultant dewatered sludge is very high in toxic metals, particularly nickel. The filtrate dissolved metals were comparable to supernatant values, and effluent limitations established for the supernatant should be applicable to these wastewaters as well.

G. Additional Testing of Ammoniated Citric Acid and Hydroxyacetic-Formic Acid Wastewaters

Additional testing was conducted on the ammoniated citric acid and hydroxyacetic-formic acid wastewaters, for the purposes of optimizing lime and diluent requirements and evaluating the effects of a low nickel diluent. This final phase of laboratory work incorporated in the use of (1) the high nickel fireside/air heater wash wastewater sample from the oil-fired boiler collected at the start of laboratory testing; and (2) the newly collected fireside/air heater wash wastewater from a coal-fired unit, presumably low in nickel. The two chemical cleaning wastewaters and two fireside/air preheater wash wastewaters were analyzed for concentrations of iron, copper, nickel, zinc and total suspended solids. Results of analysis are presented in Table 27. Metal concentrations of the three previously analyzed samples are comparable to original values, shown in Table 3.

TABLE 27. ANALYSIS OF AMMONIATED CITRIC ACID, HYDROXYACETIC-FORMIC ACID, AND FIRESIDE/AIR PREHEATER WASH WASTEWATERS

Type of Wastewater	Metals	Fe	Cu	Ni	Zn	TSS
Hydroxyacetic-Formic Acid	Total	7110	0.2	9.0	2.3	86
	Dissolved	7600	0.1	8.0	2.2	
Ammoniated Citric Acid	Total	3600	91	51	4.7	745
	Dissolved	3150	86	47	4.2	
Fireside/Air Preheater Wash Composite (Oil-Fired)	Total	4200	14	600	19	15,000
	Dissolved	1100	12	660	21	
Fireside/Air Preheater Wash Composite (Coal-Fired)	Total	2000	3.2	7.7	3.0	6600
	Dissolved	1300	2.6	7.5	2.6	

Laboratory testing consisted of dilutions of the chemical cleaning wastewaters with one of the fireside/air preheater wash wastewaters, addition of lime to specified pH, settling

for 24 hours, and analysis of supernatant for total and dissolved iron, copper, nickel, and zinc and total suspended solids. A summary of the various pH's and dilutions used for the two chemical cleaning wastes is given below:

Diluent	pH	Dilution Ratio
Citrosolv System Waste:		
(1) Fireside/Air Preheater Wash from Oil-Fired Boiler (High Ni)	10.5	5,7,10
	11.0	5,7,10
(2) New Fireside/Air Preheater Wash from Coal-Fired Boiler (Low Ni)	10.0	1,3,5,7
	10.5	1,3,5,7
	11.0	1,3,5,7
HAF System Waste		
(3) Existing Fireside/Air Preheater Wash from Oil-Fired Boiler (High Ni)	10.5	3,5,7
	11.0	3,5,7
(4) New Fireside/Air Preheater Wash from Coal-Fired Boiler (Low Ni)	10.0	1,3,5,7
	10.5	1,3,5,7
	11.0	1,3,5,7

The specific dilution ratios and pH's used in testing with the "oil-based" fireside/air preheater wash wastewater were developed in order to complete total range of dilutions, which is incomplete between the 3:1 and 10:1 dilutions, as shown in Tables 5 and 9. Also, the two pH's were chosen in an effort to investigate lower lime dosages, as it is generally agreed that a lime treatment system operating at pH 12.0 would be troublesome.

The specific dilution ratios and pH's used in testing with the "coal-based" fireside/air preheater wash wastewater were developed from data in Tables 5 and 9, taking into account that lower pH's and dilution ratios would be needed because of the anticipated lower diluent nickel concentrations. The expectation proved true, as can be seen from Table 27. In fact, all metals tested were significantly lower in the fireside/air preheater wash wastewater from the coal-fired unit than that of the oil-based.

The results of lime precipitation/dilution studies for the ammoniated citric acid wastewater are given in Table 28. Results of Run #1 along with results given in Table 9 suggests that supernatant metal residuals substantially below 1 mg/l

TABLE 28. ADDITIONAL LIME PRECIPITATION/DILUTION TESTING OF AMMONIATED CITRIC ACID SYSTEM BOILER CLEANING WASTEWATERS

(Values reported in mg/l)

Run #1 - FAPWW[1] From Oil-Fired Boiler (High Ni)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
5:1	10.5	Total	0.5	0.4	2.6	<0.1	82
		Dissolved	0.2	0.3	2.4	<0.1	
5:1	11.0	Total	0.3	0.1	1.1	<0.1	62
		Dissolved	0.1	0.1	0.9	<0.1	
7:1	10.5	Total	0.3	0.2	1.2	<0.1	97
		Dissolved	0.1	0.2	1.1	<0.1	
7:1	11.0	Total	0.2	0.1	0.7	<0.1	56
		Dissolved	0.1	0.1	0.5	<0.1	
10:1	10.5	Total	0.2	0.1	0.7	<0.1	92
		Dissolved	0.2	0.1	0.5	<0.1	
10:1	11.0	Total	0.3	0.1	0.4	<0.1	70
		Dissolved	0.1	<0.1	0.3	<0.1	

Run #2 - FAPWW[1] From Coal-Fired Boiler (Low Ni)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
1:1	10.0	Total	430	23	18	0.5	120
		Dissolved	570	24	21	0.4	
1:1	10.5	Total	280	23	13	0.2	87
		Dissolved	290	24	13	0.2	
1:1	11.0	Total	120	0.5	3.5	0.1	38
		Dissolved	110	0.5	3.5	<0.1	
3:1	10.0	Total	180	0.1	2.6	0.1	64
		Dissolved	190	0.1	2.4	<0.1	
3:1	10.5	Total	100	0.1	0.8	<0.1	84
		Dissolved	80	<0.1	0.8	<0.1	
3:1	11.0	Total	26	0.1	0.5	<0.1	40
		Dissolved	17	<0.1	0.5	<0.1	
5:1	10.0	Total	57	0.1	0.8	<0.1	100
		Dissolved	37	<0.1	0.8	0.1	
5:1	10.5	Total	8.6	0.1	0.5	0.1	72
		Dissolved	2.3	<0.1	0.4	0.1	
5:1	11.0	Total	2.3	0.1	0.4	<0.1	27
		Dissolved	1.7	<0.1	0.4	<0.1	
7:1	10.0	Total	1.4	0.1	0.4	<0.1	32
		Dissolved	0.4	<0.1	0.4	<0.1	
7:1	10.5	Total	1.2	0.1	0.4	0.1	43
		Dissolved	0.5	<0.1	0.3	<0.1	
7:1	11.0	Total	1.4	0.1	0.4	<0.1	39
		Dissolved	0.7	<0.1	0.4	<0.1	

[1] *FAPWW - Fireside/Air Preheater Wash Wastewater*

fireside/air preheater wash wastewater from the oil-fired boiler, and a pH of 11.0

Suspended solids were generally higher in Run #1 than in those shown in Table 9. This corresponded to the fact that supernantants during this run were observed to be cloudier than those of similar runs. Upon further examination, it was found that higher lime dosages were required to attain desired pH's during this additional testing compared with dosages during the original testing approximately nine months before. It is believed that the higher lime dosages contributed to a greater amount of unsettleable particles being present in the supernatant, hence a generally higher suspended solids values. Loss of reactivity due to carbonation during storage is accountable for the higher lime dosages observed in the latter phase of testing.

These facts suggest that hydrated lime should not be stored for long periods of time, since process as well as cost efficiency could suffer. Proper storage of lime includes the use of air-tight containers for periods of not more than 1 year.

Results of Run #2 in Table 28 reflect the effect of using a diluent low in nickel. As can be seen, nickel values of 0.5 mg/l were attainable at a dilution of 3:1 and a pH of 11.0. A pH of 11.0 was also sufficient to attain supernatant nickel residuals below 0.5 mg/l at a 10:1 dilution with the high nickel fireside/air preheater wash wastewater used as diluent. The above criteria suggest that: (1) a pH of 11.0 or even lower may be sufficient to attain the desired results; and (2) less dilution is required with a low nickel diluent.

Table 28 also shows that iron residuals were higher in Run #2 than in Run #1, if one compares the data from treatments using 5:1 and 7:1 dilutions. At a pH of 10.5 and a 5:1 dilution, both total and dissolved iron residuals were more than an order of magnitude higher than the results of the similar treatments in Run #1. These results are not as pronounced in the runs involving higher pH's and dilution. However, it can be seen that values of supernatant residual iron substantially below 1 mg/l were not attained when the coal-based fireside/air preheater was used as diluent. A comparison of the two fireside/air preheater wash wastewaters in Table 27 indicates that initial iron concentrations were actually higher in the fireside/air preheater wash from the oil-fired unit, which seems to conflict with the results after precipitation.

No scientifically supported hypothesis was formulated to explain the higher iron residuals in Run #2, however the

results demonstrate that iron residuals may not always attain the 1 mg/l limit stipulated by EPA when treating ammoniated citric acid wastewaters. It would have been helpful if dilutions of 10:1 with the coal-based diluent had been run, to see if iron levels then dropped below 1 mg/l. However, the scope of this study did not allow for additional analytical efforts which could potentially provide supplementary data adequate to resolve the above uncertainties. Based on previous experience with the effects of dilution ratio on metal residuals, it is believed that dilution beyond 7:1 would have yielded total iron levels below 1 mg/l. However, further testing with the ammoniated citric acid wastewater and other fireside/air preheater wash wastewaters including that used in Run #2 is recommended.

Results of testing with the hydroxyacetic-formic acid, boiler cleaning wastewater (Table 29) indicated that metal residuals well below 1 mg/l could be attained for all metals at dilutions of 5:1 and a pH of 10.5 for the oil-based fireside wash. Lime requirements for successful treatment using the coal-based fireside/air preheater wash wastewater were less, with a pH of 10.0 yielding metal levels well below 1 mg/l at the 5:1 dilution. Total suspended solids as compared to those presented in Table 5, were higher, probably for reasons similar to those developed above for the ammoniated citric acid system. High iron residuals did not occur in Run #2 of Table 4, as was the case with the ammoniated citric acid wastewater.

TABLE 29. ADDITIONAL LIME PRECIPITATION/DILUTION TESTING OF HYDROXYACETIC-FORMIC ACID SYSTEM BOILER CLEANING WASTEWATERS

(Values reported in mg/l)

Run #1 - FAPWW[1] From Oil-Fired Boiler (High Ni)

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
5:1	10.5	Total	0.2	0.2	0.2	<0.1	209
		Dissolved	<0.1	0.1	0.1	<0.1	
5:1	11.0	Total	0.2	0.3	0.2	<0.1	71
		Dissolved	<0.1	0.2	0.1	<0.1	
7:1	10.5	Total	0.2	0.1	0.2	<0.1	308
		Dissolved	0.1	0.1	0.1	<0.1	
7:1	11.0	Total	2.0	0.1	0.3	<0.1	92
		Dissolved	0.1	<0.1	0.1	<0.1	
10:1	10.5	Total	0.1	0.1	0.2	<0.1	870
		Dissolved	<0.1	<0.1	0.1	0.1	
10:1	11.0	Total	0.6	0.2	0.2	<0.1	90
		Dissolved	0.1	0.1	0.1	<0.1	

Run #2 - FAPWW[1] from Coal-Fired Boiler

Dilution	pH	Metals	Fe	Cu	Ni	Zn	TSS
1:1	10.0	Total	0.5	0.9	0.3	<0.1	70
		Dissolved	0.4	0.8	0.2	<0.1	
1:1	10.5	Total	1.1	0.7	0.3	<0.1	52
		Dissolved	0.7	0.6	0.2	<0.1	
1:1	11.0	Total	1.5	0.8	0.3	<0.1	50
		Dissolved	1.1	0.7	0.3	<0.1	
3:1	10.0	Total	0.7	0.3	0.2	<0.1	46
		Dissolved	0.2	0.2	0.2	<0.1	
3:1	10.5	Total	0.5	0.5	0.2	<0.1	52
		Dissolved	0.2	0.4	0.2	<0.1	
3:1	11.0	Total	0.4	0.4	0.3	<0.1	46
		Dissolved	0.2	0.4	0.2	<0.1	
5:1	10.0	Total	0.2	0.1	0.1	<0.1	54
		Dissolved	0.2	0.1	0.1	<0.1	
5:1	10.5	Total	0.2	0.3	0.1	<0.1	29
		Dissolved	0.1	0.2	0.1	<0.1	
5:1	11.0	Total	0.4	0.2	0.2	<0.1	32
		Dissolved	0.2	0.2	0.1	<0.1	
7:1	10.0	Total	0.2	0.1	0.1	<0.1	29
		Dissolved	0.1	0.1	0.1	<0.1	
7:1	10.5	Total	0.3	0.2	0.1	<0.1	40
		Dissolved	0.1	0.1	0.1	<0.1	
7:1	11.0	Total	0.2	0.1	0.2	<0.1	38
		Dissolved	0.1	0.1	0.2	<0.1	

[1] *FAPWW - Fireside/Air Preheater Wash Wastewater*

VIII. APPLICABILITY OF LABORATORY TESTS TO FULL-SCALE TREATMENT

Assessing the applicability of laboratory treatability data to a full-scale treatment process involves consideration of many factors, including the following:

- Conditions in the field that are not encountered in bench-scale testing. This includes availability of diluents, use of substitute diluents, storage facilities for both chemical cleaning and diluent wastewaters, and mixing of wastewaters.
- Process conditions in full-scale treatment, such as changes in flow and temperature, concentration gradients, and pH controllability.
- Availability of the specific process plant equipment needed for successful treatment of the wastewater and sludges.

A. Field Conditions

Conditions in the field will be quite different from the controlled conditions in the laboratory. One important difference may be the availability and type of diluent wastewater, and the provisions needed for storage. Dilution ratios yielding successful treatment ranged from 3:1 to 10:1 for tubeside cleaning wastewaters and ranged from 1:1 for the ammoniated bromate/HCl wastewater to 10:1 for successful treatment of ammoniated EDTA wastewater. Lime treatment for the ammoniated EDTA wastewater is presently not recommended, based on the fact that supernatant nickel residuals are such a problem. Therefore, a representative dilution ratio covering the general treatment of tubeside wastewaters has been selected based on the ammoniated citric acid wastewater, the next most difficult to treat. Data in Table 28 suggest that a dilution ratio of 7:1 will be generally adequate to attain successful treatment of tubeside cleaning wastewaters, as long as filtration is used (this requirement is based on data of Run #2, Table 28, in which total iron did not drop below 1 mg/l at the 7:1 dilution).

In a full-scale situation, assuming a typical total volume of chemical cleaning wastewater of 760 m^3, the corresponding volume of diluent wastewater to give a 7:1 dilution would be 6,080 m^3. Such a volume would require about 2,533 m^2 of land for a storage pond (2.4 m pond depth).

Most power plants could probably provide for this additional storage area. However, it is less certain whether a power plant would generate the required volume of fireside and/or air preheater wastewater for dilution of a specific volume of tubeside cleaning wastewater. The tubeside cleaning wastewater might have to be stored until enough fireside/air preheater wastewater was generated, or a substitute diluent such as coal pile runoff could be used as a supplement to attain the desired dilution. Table 30 shows the ratio of air preheater wash wastewater volume to tubeside cleaning volume collected over the interval between tubeside cleanings for four boilers of power plants surveyed during the preparation of the development document (30). It is obvious that amounts of available air preheater wash wastewater vary widely from plant to plant. More detailed data are available on the flow rates of fireside and air preheater wash wastewaters that may prove useful in further defining the percentage of power plants having an adequate volume of these diluents (43,44). However, a substantial amount of data compilation is required, as existing data is presented as a function of power plant type and capacity, rather than on the basis of boiler unit. Recommendations to more clearly define the relative availability of fireside and air preheater wash wastewaters include compiling fireside and air preheater data on a boiler unit basis, or perhaps developing data on flowrates of tubeside cleanings on a plant or megawatt basis. It seems imperative that such an analysis be conducted if recommended treatment is to cover the whole steam electric power generating point source category.

Coal pile runoff would be a suitable alternative or supplemental diluent wastewater, based on reported loadings of 64,000 to 32,000 m^3 per year with average figures of 75,000 to 100,000 m^3 per year (30). It is evident that an adequate amount of diluent should be available for all coal-fired power plants. However, for power plants running entirely on oil or gas, other sources of substitute diluents may have to be found if there is an inadequate volume of fireside and air preheater wash wastewater.

The effect of using substitute diluent has not been investigated in the laboratory. However, comparison of coal pile runoff wastewaters to fireside/air preheater wash wastewater used in laboratory testing shows that metals of concern are present in much lower quantities in the coal pile runoff. Chemical characteristics of coal pile runoff from two plants are shown in Table 31. The data suggest coal pile runoff would be very suitable for use as diluent in treatment of chemical cleaning wastes.

TABLE 30. RATIO OF AVAILABLE AIR PREHEATER WASTEWATER VOLUME TO TUBESIDE CLEANING WASTEWATER VOLUME (30)

Plant Code[2]	Boiler Volume (m^3)	Cleaning Frequency (yr^{-1})		Batch Volume[1] (m^3)		Ratio of Collected Volumes[3]
		Air Preheater	Boiler Tubeside	Air Preheater	Boiler Tubeside	
3409	174	12	0.5	409	696	3.5
3410	106	12	1	852	424	24
3412	215	12	0.5	2272	860	63
3414	303	6	1	163	1212	0.8

[1] Four cleaning stages were assumed for calculation of batch volume for boiler tubeside cleanings.

[2] Refers to number designation of power plant in the EPA development document cited above.

[3] Refers to ratio of air preheater wash wastewater volumes to tubeside cleaning volume collected over the interval between tubeside cleanings.

TABLE 31. CHARACTERISTICS OF COAL PILE DRAINAGE (45)

Constituents	Concentration mg/l (unless otherwise indicated) Plant J	Plant L
Acidity (total), as $CaCO_3$	1,700	270
Calcium	240	350
Chemical Oxygen Demand	9	--
Chloride	0	--
Conductance, umho/cm	2,400	2,100
Dissolved Solids (total)	3,200	1,500
Hardness, as $CaCO_3$	600	980
Magnesium	1.2	0.023
pH, unit	2.9	2.9
Potassium	--	--
Silicon (dissolved)	91	--
Sodium	--	4.1
Sulfate	2,600	--
Suspended Solids (total)	550	810
Turbidity, JTU	300	--
Aluminum	190	--
Arsenic	0.01	0.009
Barium	--	0.1
Beryllium	--	0.01
Cadmium	0.001	0.006
Chromium	0.005	0.005
Copper	0.56	0.18
Iron	510	830
Lead	0.01	0.023
Manganese	27	110
Mercury	0.0002	0.027
Nickel	1.7	0.32
Selenium	0.03	0.003
Titanium	1	--
Zinc	3.7	1.0

Proportioning and mixing of the chemical cleaning and diluent wastewaters, although not a problem in the laboratory, may present some challenges in the field. Two basic methodologies for mixing wastewaters in the field are apparent. The first methodology involves mixing the wastewaters in the diluent wastewater holding pond. If this method is chosen, the volume of diluent wastewater in the pond must be known, so that provisions can be made to attain the proper ratio for dilution of the chemical cleaning wastewater. Preliminary testing should be done on a sample of the composite chemical cleaning wastewater to determine the minimum dilution requirement along with other parameters. The chemical cleaning wastewater should be held in temporary storage if the volume of diluent water in the holding pond is excessive, so that the excess can be pumped out and minimum costs are incurred during treatment. The chemical cleaning waste can be added directly to the diluent holding pond if the diluent volume is known to be less than the anticipated requirement. However, the best approach may be temporary storage of the chemical cleaning wastewaters until treatment parameters have been established in the laboratory. Mixing the wastewaters to insure homogeneity can be accomplished in the diluent holding pond by recirculation or aeration. Mixing for a few days prior to treatment should insure adequate homogeneity.

The second methodology for proportioning and mixing wastewaters would require separate storage facilities for chemical cleaning waste and diluent wastewater. Proportioning the wastewaters would be accomplished by controlling flow rates as the two wastewaters were pumped into an equalization pond. Mixing in the equalization pond could be accomplished by aeration, recirculation, and/or proper baffling. This second methodology introduces the additional advantage of treating the chemical cleaning waste a little at a time as the diluent wastewater becomes available, thus reducing storage requirements.

In summary, it is believed that, although field conditions may present challenges in some cases, diluting chemical cleaning wastewater with fireside and air preheater washings, coal pile runoff, or another suitable diluent is applicable to full-scale treatment at most power plants.

B. Process Conditions

Process conditions that may be present in full-scale treatment must be considered when a laboratory treatability study is assessed with respect to probable success in the field. Such conditions include flow, temperature, concentration, and pH variability.

Flow variability would have an effect on general removal efficiencies in a full-scale treatment process, because of resulting variations in pH; detention times for rapid mixing, slow mixing, and settling; and polymer dosage. Since the process will involve batch treatment that can be well regulated by pumping rates, the effects of flow variability on treatment are expected to be minimal.

Temperature variations are expected to have significant effects on the efficiency and economics of the full-scale treatment process. However, temperatures are expected to vary on a seasonal basis, and should not fluctuate during the time interval for batch treatment. However, there is a possibility that a temperature gradient could exist in the holding pond(s). Since the pond depth is expected to be relatively shallow (3 m), the temperature gradient in such a pond is not expected to be greater than 3°C (46). Two methods are available to minimize any temperature gradient within the holding pond(s). The first is some form of mixing, either aeration or recirculation. The second involves treating the waste in mid- to late summer, when the temperature profile will be almost vertical, with no effective change in temperature with depth (46).

As mentioned above, the seasonal temperature is most important, and treatment should be conducted during mid- and late summer, when water temperature is also highest. Investigations show that an increase in wastewater temperature of 10°C has marked beneficial effects on almost all wastewater treatment unit operations. Specific references have been made to increases in temperature resulting in more rapid floc formations, shorter settling times, and decreased coagulant (in this case, lime) requirements (47). Table 32 presents a summary of temperature effects on the size requirement and efficiencies of various wastewater treatment processes.

Variability of concentrations of metals in the untreated wastewaters can be introduced by incomplete mixing, either in the holding ponds or during equalization. The data in Table 19 give much insight into probable effects, since changes in dilution ratios can be thought of as changes in initial metal concentrations. The data suggest that supernatant residual iron concentrations (both total and dissolved) will be relatively unaffected by concentration changes of 100 percent providing the pH is 11.0 or above. Supernatant nickel residuals (Table 9) at dilution ratios of 7:1 to 10:1 will be relatively unaffected by changes in concentration provided the pH is maintained above 10.5. Data from Tables 4 through 9 suggest that, for most systems, copper and zinc will be unaffected by changes in concentration, provided a pH above 10.5 is maintained. This assump-

TABLE 32. SUMMARY OF UNIT SIZE AND EFFICIENCY CHANGES DUE TO 10°C TEMPERATURE INCREASE (20°C to 30°C) (47)

Unit Operation	Change Due to Temperature Increase	
	% Change in Unit Size	% Change in Unit Efficiency
Grit Chamber	16.5	13
Primary Clarifier	20	13
Aeration Basin	10	12
Trickling Filter	68	30
Stabilization Pond	48	15
Aerated Basin	52	8
Final Clarifier	20	*
Chlorine Contact Tank	28	*
Thickener	20.5	*
Anaerobic Digestor	38.5	8.2
Vacuum Filter	14	9
Centrifuge	20	25
Filtration (Strat.)	19	20
Rapid Sand	*	60
Backwash Rate	*	-16
Activated Carbon	-8	29
Foam Separation	*	-5
Nitrification	27	65
Dentrification (.S.)	92	47
Ammonia Stripping	50	14
Anaerobic Column	*	*
(Nitrogen Removal)		28
Pure O_2 Activitated Sludge	*	114
Coagulation	*	50

*Not calculated

Note: Minus sign indicates an increase in unit size or a decrease in efficiency. No sign indicates a decrease in unit size or an increase in efficiency.

tion is based on comparison of supernatant residuals at dilutions of 3:1 and 10:1. The above criteria suggest that as long as pH is maintained at 11.0 or above, there will be little change in supernatant metal residuals with respect to normally encountered variations in untreated wastewater metal concentrations.

As mentioned above, changes in pH should have little effect on supernatant metal residuals provided that the pH is maintained at 11.0 or above. A pH above 11.0 should be maintained if good clarification is expected, because of the enhancing effect of magnesium hydroxide precipitation (42). Therefore, operating at a pH of between 11.0 and 11.5 should accommodate any fluctuations inherent in pH control with a straight lime system.

C. Requirements for Process Equipment and Materials

Treatment of boiler chemical cleaning wastewaters as practiced in the laboratory is applicable to full-scale treatment. However some special considerations must be made with respect to the equipment and materials needed for specific unit operations. Proportioning and mixing of wastewaters has been treated in a previous section and will not be discussed here.

A major consideration with respect to required process equipment and materials involves high lime requirement for treatment. Generally, a slurry of lime will be used rather than the solid form and a softened water is recommended as a solvent. The slurry could either be mixed from hydrated lime or purchased as a 20 percent mixture (chemline slurry). All necessary provisions for a high lime system will be required, including the use of plugged pipe fittings to allow cleanout, compatible pumps, and proper pacing and control systems. Daily maintenance of pH instrumentation will be essential for adequate control.

The large amount of lime sludge that is expected to be generated will require a clarifier with a large sludge-handling capacity. Detention times for suspended solids removal and zone settling are not abnormally high, and should present no major problems. It should be remembered that batch treatment should be conducted during mid- to late summer, in order to minimize the requirement for lime. The resulting lime sludge before dewatering was found to contain an average of over 20 percent solids; therefore, heavy-duty pumps applicable to lime sludges will be required. Not enough data were available to assess special requirements for dewatering equipment.

Also, because of the high solids content, a specially designed flocculator may be necessary, with an aeration system assisting the rotating paddles to provide adequate mixing.

Some type of neutralization system will be required, to adjust effluent pH to between 6.0 and 9.0. Because of the high pH's required for successful treatment, a recarbonation system would be more suitable than acid neutralization, since neutralization by acid would result in a treated wastewater with very high total solids.

The materials of construction are an important consideration after the lime precipitation and clarification operations have occurred. It must be recognized that strong chelating agents will still be present in the supernatant after treatment. Chelants such as ammoniated EDTA and citric acid could pick up metals from any source that is contacted prior to discharge. Sources include piping materials, neutralization or recarbonation equipment, and filtration equipment and media (if used). Therefore, equipment and piping materials following clarification may have to be fabricated from such non-metal leaching materials as polyvinyl chloride. It should be noted that this effect is possible but not definite. Further experimentation with the wastewaters under investigation is required before an accurate assessment of this problem can be made.

Filtration may, in some cases, be required for successful suspended solids treatment. In all but one of the wastewaters (hydroxyacetic-formic acid cleaning system), suspended solids below 30 mg/l could be achieved with polymers after four hours' settling. An average of 20 mg/l was achieved on the statistical run for the ammoniated EDTA system after four hours of settling. This is considered representative of the other wastewaters, excepting the hydroxyacetic-formic acid system. Results from additional testing of ammoniated citric acid and hydroxyacetic-formic acid wastewaters (Tables 28 and 29) indicate that the use of excessive amount of lime (when caused by reactivity loss upon storage or low reactivity to begin with) could result in higher suspended solids concentrations in the supernatant. Hence, in a field condition where large amounts of lime may be stored for long periods of time, and where clarification may not be as efficient as in the laboratory, filtration should probably be included in the treatment scheme. Neutralization of the wastewater is necessary prior to filtration to insure against leaching of iron under alkaline conditions. To insure against any possible leaching, a high-purity media containing as little iron and other metals as possible should be used. Again, the metal pickup properties of the supernatants have not been adequately treated and additional research is needed.

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16. ABSTRACT The report gives results of an evaluation of lime precipitation for treating boiler tube cleaning wastes. In this project, wastewater samples were collected from six boiler tubeside chemical cleanings, using complexing and chelating agents. The samples represented: (1) ammoniacal bromate/hydrochloric acid, (2) thiourea-hydrochloric acid, (3) hydroxyacetic-formic acid, (4) ammoniated citric acid, and (5) ammoniated EDTA cleaning systems. Wastewater samples were also collected from boiler fireside and air preheater washes. A treatment methodology was investigated that involved: dilution of the boiler tubeside cleaning wastewater with a mixture of the fireside and air preheater wash wastewaters, precipitation with lime, and addition of polymers for clarification. After settling of the solids, the supernatant was analyzed for total and dissolved iron, copper, nickel, zinc, and total suspended solids. Major variations in testing included adjustments in pH and dilution ratio. Results indicate that, on a bench scale, the treatment methodology effectively reduced the concentration of iron, copper, and zinc in the tubeside cleaning wastewater to < 1 mg/l. Attainable nickel residuals were also < 1 mg/l for wastes from all except the ammoniated EDTA system, for which nickel residuals were not < 5 mg/l.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Precipitation	Pollution Control	13B	07D
Boiler Tubes	Evaluation	Stationary Sources	13A	14B
Chemical Cleaning	Complex Compounds		13H, 07A	07C
Waste Water	Chelation			
Waste Treatment	Polymers			
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