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Nickel Removal from a Synthetic Nickel-Plating Wastewater Using Sulfide and Carbonate for Precipitation and Coprecipitation

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Abstract

The uses of soluble sulfide and carbonate were evaluated to determine their effectiveness in reducing nickel in a synthetic nickel plating wastewater. Nickel is a toxic substance and is detrimental to aquatic and human health as well as the operation of biological processes in wastewater treatment. Using a series of jar tests, an optimum pH range for nickel removal from a synthetic wastewater was found to be 10.0–11.0. The optimum removal occurred at pH 11 where a residual total nickel concentration of 0.1 mg/L was obtained with a sulfide:nickel weight ratio of 2.0 and a carbonate:nickel weight ratio of 20.0. A similar degree of removal was achieved at pH 10 where a residual total nickel concentration of 0.2 mg/L was obtained with a carbonate:nickel ratio of 10.0 and a sulfide:nickel ratio of 0.5. A mathematical model of the synthetic system was produced by multiple regression analysis. The model predicted the sample data trends quite effectively.

INTRODUCTION

A significant problem that plagues municipal wastewater treatment plants is the inefficient removal of toxic metal constituents. Certain metals can be concentrated to dangerous levels by microorganisms, fish, and plants in the

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human food chain. Ultimately, such metals can concentrate in human body tissue. The toxicity of a specific metal may depend on certain water characteristics such as pH, hardness, and whether synergistic effects with other metals are possible.

The primary source of toxic metals in municipal wastewater is industrial discharge. It has been estimated that there are between 11,000 and 14,000 metal electroplating-related firms in the United States (*1*). This does not include other types of plating operations or industrial users of toxic chemicals.

The EPA developed the Clean Water Act of 1977 (CWA) with several basic elements directed toward toxic metals pollution control. The CWA stipulates that by July 1, 1984, industry must apply "Best Available Technology" for toxic pollutant removal. The "New Source Performance Standards" and pretreatment standards are now aimed principally at control of toxic pollutants (*2*). The effluent guidelines for the Metal Finishing Category were developed from previous EPA studies and plant surveys and evaluations (*2*). These guidelines apply to plating processes which include copper, nickel, chromium, brass, bronze, zinc, tin, lead, cadmium, iron, and aluminum.

One of the metal-plating operations affected by the more stringent effluent standards established by EPA is nickel plating. This study, in part, was conducted to determine an efficient, economical approach to treat an industrial wastewater with a high nickel concentration. Additionally, this study was conducted to provide a more in-depth investigation on the effect of pH, total carbonate, and total sulfide content in the nickel precipitation-coprecipitation reactions. It was felt that results of such a study would be helpful in explaining the usefulness of sulfide treatment as a heavy metal precipitation alternative.

LITERATURE REVIEW

Several types of treatment processes have been employed to remove heavy metals from wastewater. Some of these techniques are: chemical precipitation, complexation, cementation, electrolysis, reverse osmosis, carbon adsorption, ion-exchange, evaporation, or some combination of these processes (*3–6*). The most common and successful method of reducing heavy metal (e.g., nickel) concentrations in solutions is chemical precipitation. Most metals are relatively insoluble as hydroxides, carbonates, or sulfides and can be precipitated in one of these forms (*7*). The most common form is hydroxide precipitation in which lime or caustic is added to the water to produce an alkaline pH. A precipitate then forms which will settle, thus producing a supernatant with a low metal concentration.

For hydroxide precipitation the theoretical optimum pH for minimum solubility of nickel is approximately 10.5. However, laboratory experimentation has indicated pH optima near 11. Patterson et al. (*6*) found the optimum pH to be 11. Their experimental results were based on a 4-h mixing period. The minimum achievable concentration was near 0.3 mg/L. Discrepancies between theoretical and actual solubilities are most often explained on the basis of incomplete reactions (time dependent), formation of soluble metal complexes other than those predicted by the equilibrium equations, or poor separation of the colloidal precipitates.

Two problems frequently encountered when hydroxide precipitation is used for metal removal are: (a) large sludge volumes and poor filterability which result because of the gelatinous nature of metal hydroxides, and (b) excessive chemical cost which results because of the necessity for wastewater neutralization following precipitation (*2, 6, 7*).

Metal carbonate precipitation is attractive as a treatment process because it occurs at a pH lower than hydroxide precipitation. It has been suggested that the precipitate formed separates readily from the solution and produces a dense sludge. However, Patterson et al. (*6*) determined that the carbonate system offered no advantages over the hydroxide system. They also indicated that the sludge characteristics were the same for the carbonate system as for the hydroxide system.

Often metals are added which act as coagulant aids to enhance the removal of the metal ions by forming a carbonate or hydroxide complex. A very common metal ion used as an aid to coagulation is iron added as either ferric chloride ($FeCl_3$) or ferrous sulfate ($FeSO_4$) (*8*). Sulfides, while used less than iron, can provide improved precipitation of heavy metals by forming relatively insoluble metal sulfides.

Some advantages to sulfide precipitation are:

(a) Good removal efficiency can be expected with metal sulfides because of their low solubility.
(b) Sulfide has the ability to remove chromates and dichromates without requiring the reduction of chromium to its trivalent state.
(c) Sulfide will precipitate metals complexed with most complexing agents (*2*).
(d) Sulfide precipitates exhibit less of an amphoteric nature than hydroxide precipitates and have less of a tendency to resolubilize.
(e) Bhattacharyya (*9*) indicates that studies show lower sludge volumes with sulfide than with hydroxide treatment.

Several problems with the use of sulfide as a precipitant have been discussed in the literature. The formation of H_2S at low pH's presents a gas and odor problem (*10*). Sulfides also exert an oxygen demand in the wastewater, and sulfides in excessive concentrations can be toxic. Lawrence et al. (*11*) discuss the toxic effect of sulfides in anaerobic treatment. These problems can be avoided, and sulfide treatment can be effective with the proper operation of different treatment schemes. One treatment scheme involves the addition of sulfides in a soluble form to the wastewater, possibly as sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS). The pH of the solution should be adjusted and maintained above 8 to prevent H_2S gas formation when the sulfide is added (*10*). Addition of small amounts of sulfide will prevent an excessive residual sulfide concentration in the effluent. Cherry (*2*) recommends dosages which will give residual concentrations of less than or equal to 0.3–0.5 mg/L as sulfide. Robinson (*10*) found optimum sulfide to heavy metal ratios in the range of approximately 1.0 to 2.5 times the stoichiometric sulfide reageant demand. Lawrence et al. estimated the ratio required to be in the range 0.5 to 1.0 for anaerobic digesters. These workers suggested that digesting sludge normally contains a relatively high sulfide concentration and that only small amounts of sulfide would need to be added to control excess heavy metals not already precipitated (*12*).

Another treatment scheme for sulfide precipitation is to add a sparingly soluble form of the sulfide. One common form is ferrous sulfide (FeS). A slurry can be added to the wastewater which provides sulfide ions to precipitate the heavy metal ions. Scott (*13*) has discussed a proprietary process called Sulfex (that utilizes an iron sulfide slurry) which he claims will provide a favorable economic comparison to hydroxide precipitation with better heavy metal removal efficiencies. Scott's report shows a 99% removal of nickel at pH 8.5 and influent concentration of 4 mg/L. Further, he indicates only 43% removal with the same influent nickel concentration at pH 7.5. The advantage to this sulfide treatment process is the absence of H_2S gas formation. The process reacts $FeSO_4$ with NaHS to form FeS. The FeS compound will dissociate slightly into Fe^{2+} and S^{2-} ions. When the metal ions combine with sulfide ions, additional FeS will dissociate to maintain the equilibrium concentration. Since most heavy metals form sulfides less soluble than FeS, they will precipitate. Sulfides added to a wastewater with metal hydroxide precipitates already present will cause the metal hydroxides to resolubilize. The sulfide ions will react with the additional metal ions to precipitate them as metal sulfides. Therefore, a significant reduction in sulfide demand can be accomplished by clarifying a wastewater to remove metal hydroxide particles prior to treating it with sulfide (*2*). However, Robinson et al. (*10*) indicate that a water which has been clarified to remove particles prior to sulfide addition will not provide adequate settleability for the sulfide precipitates. They conclude that particles are removed which provide nucleation surfaces for the metal sulfide precipitate and hence the smaller precipitates remain suspended longer. A disadvantage of the ferrous sulfide process is that the Fe^{2+} ions precipitate as $Fe(OH)_2$ which will increase the volume of sludge when compared with the hydroxide precipitation process (*13*).

Other treatment schemes include combinations of the previously discussed treatment schemes with the addition of staged treatment and filtration. Robinson et al. (*10*), in their studies for EPA, investigated several variations of soluble sulfide and hydroxide precipitation processes to treat metal-finishing wastewaters. The pilot plant test were conducted in continuous flow schemes. The treatment variations are summarized as follows:

(a) Lime only, clarified (LO-CL): This process uses lime to adjust the pH to precipitate metal hydroxides followed by clarification to separate the solids.
(b) Lime only, clarified, filtered (LO-CLF): This process is LO-CL with an additional filtration step downstream.
(c) Lime-with-sulfide, clarified (LWS-CL): This process uses the conventional lime treatment complimented with sulfide addition and followed by clarification.
(d) Lime-with-sulfide, clarified, filtered (LWS-CLF): This process is LWS-CL with an added filtration step.
(e) Lime, sulfide polished, filtered (LSPF): This process is lime addition and clarification for metal hydroxide removal followed by sulfide addition to the clarified wastewater and then filtration.

The group found that the LSPF and LWS-CLF processes were equally effective and better than the other processes in removing heavy metals (nickel removal efficiencies were 90.47 and 88.42%, respectively). The next most efficient processes were the LO-CLF and LWS-CL with nickel removal efficiencies of 87.9 and 84.12%, respectively. The least efficient process for removing nickel was the LO-CL at 84.02%.

Whang et al. (*14*), in their study of precipitation of heavy metals from electroplating facilities, found that hydroxide precipitation was not as efficient as sulfide precipitation. They concluded that soluble sulfide precipitation would be cost effective. Their conclusion was based on the following observations: (a) the low solubility of metal sulfides improved metal removal efficiencies over the conventional process; (b) even though metal sulfide precipitates are very fine, the problem can be overcome by adding an anionic flocculent to facilitate the solids–liquid separation; (c) metal sulfide sludge exhibits better thickening properties and dewaterability than hydroxide sludges; (d) metal sulfide sludge is three times less likely to leach (at pH 5.0 ± 0.2) over 24 h under oxidizing or nonoxidizing conditions (when compared to the hydroxide sludge). Kim et al. (*15*), however, found, as did Robinson et al. (*10*), that even though sulfide precipitation was effective in the removal of certain heavy metals, it was not more effective than hydroxide precipitation of nickel.

Several researchers have discussed the value of sulfide precipitation when competing species such as CN^- and chelating agents are present. This did not seem to be the case for Kim et al. Their procedure used the addition of sulfide in the form of a calcium sulfide (CaS) slurry. This method offers the advantages of lower chemical requirements than the insoluble FeS operation (the CaS requirement is near stoichiometric), and the calcium sulfide particles present act as nuclei for precipitation of metal sulfides, thus enhancing settleability (*15*). Whang (*14*) recommends the use of an anionic polymer to enhance settleability, while Kim (*15*) recommends cationic polymers to improve the settleability.

Kim states the H_2S is the cheapest source of the sulfide species. Sulfide can be produced by passing excess H_2S through $Ca(OH)_2$ to convert it to $Ca(HS)_2$. The reaction is rapid and complete at pH's greater than 12 which prevents loss of H_2S gas. Stoichiometric amounts of calcium and sulfur should be added to achieve the same properties as CaS. This process can be adapted to one- or two-stage operations. The single-stage process would involve the precipitation of metals as sulfides or sulfide-hydroxide mixtures. The two-stage process can be utilized to remove metals as hydroxide precipitates in the first stage and then achieve even greater removal in the second stage by adding CaS. In the two-stage process the sludge in the first stage is relatively nontoxic and easily disposed, while the sludge in the second stage is lower in volume but concentrated with heavy metals and sulfides.

Mukai et al. (*16*) investigated removal of heavy metals by precipitation, coprecipitation, and flotation. In their study the effect of time on precipitation of various metals was observed. The metals compared were zinc, cadmium, copper, and mercury. The report indicates that copper and zinc could be coprecipitated with ferric hydroxide very easily when compared to mercury and cadmium. The copper and zinc solutions were maintained at a pH approximately equal to 9.3, and contained 1 mg/L of either copper or zinc and 10 mg/L of Fe^{3+}. Copper was 97% coprecipitated at 10 min and 100% coprecipitated at 30 min. Zinc was nearly 100% coprecipitated within 10 min. Cadmium required 20 h to reach a 100% coprecipitation, and mercury only approached a 97% coprecipitation after 14 h.

Huang (*17*) investigated a technology which would be capable of precipitating and removing toxic metals from municipal wastewater without simultaneously removing the organic suspended and settleable solids. The process utilized an upflow-expanded sand bed with a lime feed to promote coprecipitation of metals, calcium carbonate, and calcium hydroxyapatite on the sand grains. This process would remove the heavy metals ahead of the conventional municipal treatment, thereby producing primary and secondary sludges with lower metal content (*17*). The metals investigated were cadmium, chromium, copper, nickel, lead, and zinc. The evaluations were made over a pH range of 9.0 to 10.5. He observed a 33% removal of total nickel at pH 10.5, 36% at pH 10.0, 13.8% at pH 9.5, and 13.5% at pH 9.

EXPERIMENTAL METHODS AND PROCEDURES

Precipitation and coagulation experiments were conducted to determine the treatability of a synthetic nickel-plating wastewater. The research was divided into four phases to determine the optimum pH range, total carbonate concentration (C_T), and total sulfide concentration (S_T) for removal of soluble and insoluble nickel by precipitation from the wastewater.

Synthetic Wastewater

Synthetic nickel solutions, containing 10 mg/L of nickel, were prepared by mixing a 1000-ppm atomic absorption (AA) nickel standard with a solution of sodium chloride (NaCl) and distilled water. The addition of NaCl produced a solution with a 0.01-*M* ionic strength. The pH of the solutions was adjusted to approximately 3 with concentrated sulfuric acid to prevent premature precipitation.

Phase I: Optimum pH for Precipitation of Nickel

In this phase of the research, experiments were based on jar tests performed with 1 L samples of synthetic wastewater. The pH was adjusted by dropwise addition of 10 *N* or 1 *N* sodium hydroxide (NaOH) and an equivalent amount of 10 *N* or 1 *N* calcium chloride ($CaCl_2$) to simulate lime ($Ca(OH)_2$) addition. Lime addition was simulated in this manner because of its tendency to dissolve slowly. During the mixing period the pH was maintained with 1 *N* NaOH and $CaCl_2$ or 1 *N* HCl. The pH range was 6–11. After chemical addition the samples were rapid mixed at approximately 100 rpm for 1 min before slow mixing at about 20 rpm for 1 h. Slow mixing was followed by a 1-h settling period. Periodically, aliquots were drawn from 1 to 2 in. below the surface of the water sample, filtered through 0.45 μm membrane filters, and the filtrate acidified. Atomic absorption analysis for soluble nickel concentrations were conducted during the 1-h slow mix period, while both total and soluble concentrations were determined during the 1-h settling period.

Phase II: Optimum pH-Total Carbonate Combination for Precipitation of Nickel

The effect of the carbonate concentration was studied during this phase. The preparation of the nickel solutions differed from Phase I by including carbonate species in the form of sodium bicarbonate ($NaHCO_3$). Total carbonate:nickel ratios (by weight) of 5:1, 10:1, and 20:1 were investigated. The same range of pH's were covered in this phase as were covered in Phase I. The same sampling and analysis procedures were followed in this phase as were followed in Phase I.

Phase III: Optimum pH-Sulfide Combination for Precipitation of Nickel

The effect of sulfide was studied during this phase. The preparation of the nickel solutions differed from Phase I by the addition of varying amounts of 1 *M* sodium sulfide ($Na_2S \cdot 9H_2O$). The pH was adjusted prior to sulfide addition to prevent excessive hydrogen sulfide (H_2S) gas evolution. This would be the expected procedure at the industrial plant. Sulfide:nickel ratios (by weight) of 0.5:1, 1.0:1, and 2.0:1 were investigated. The same range of pH's were covered in this phase as were covered in Phase I.

Phase IV: Optimum pH-Carbonate-Sulfide Combination for Precipitation of Nickel

In this phase the previous three phases were combined to investigate the effect of carbonate and sulfide in nickel precipitation. For each pH in the range of interest and each carbonate:Ni ratio, the sulfide:Ni ratio was varied as in Phase III.

DISCUSSION

Phase I: pH Adjustment of the Synthetic Wastewater

Initially, results of these experiments were analyzed graphically by constructing plots of the residual soluble and total nickel concentrations in mg/L versus time for the pH range covered. These plots are presented in Figs. 1 and 2. The system responses shown in these figures indicate that:

(a) Nickel precipitation and sedimentation are strongly pH dependent.
(b) Maximum precipitation occurs at pH 11, although pH 10 gives practically equivalent results.

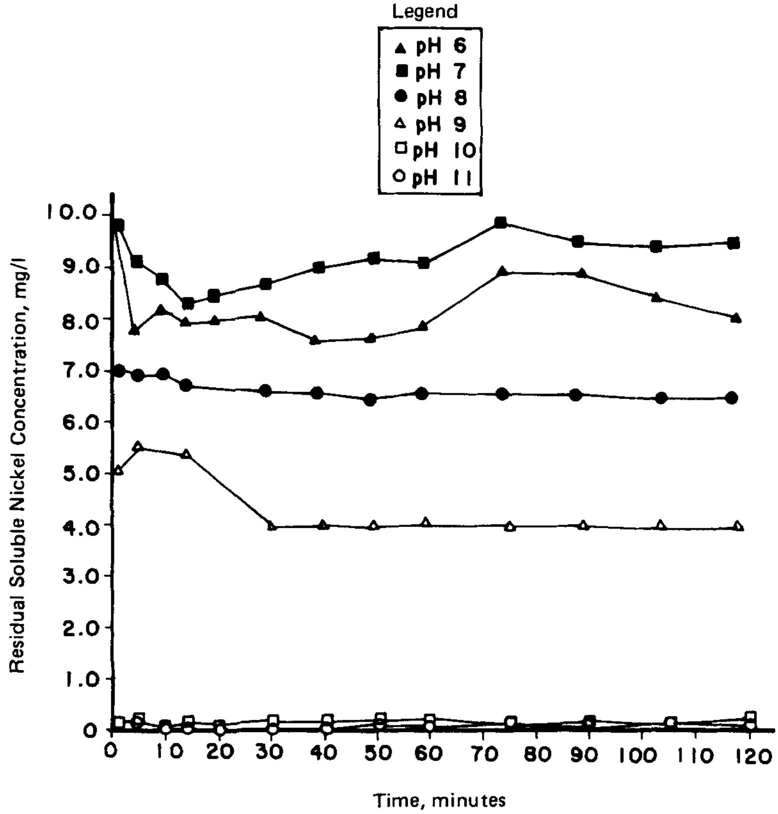


FIG. 1. Comparison of the soluble nickel concentration for the synthetic wastewater at pH's 6–11 at various time intervals.

(c) As the pH of the solutions decreases, the removal efficiency decreases. However, the data presented in Fig. 1 indicate that pH 6 is slightly more efficient than pH 7 in this case. Still, in other phases of the work the general trend is for decreasing removal with decreasing pH.

(d) pH 9 seemed to be a transition point between good precipitation at pH's 10 and 11, and poor precipitation at pH's 6–8.

(e) Precipitation and coagulation were virtually complete within the first few minutes of the mixing period.

(f) The relationship between pH and total residual nickel followed the same pattern as that between pH and soluble residual nickel (see Fig. 2).

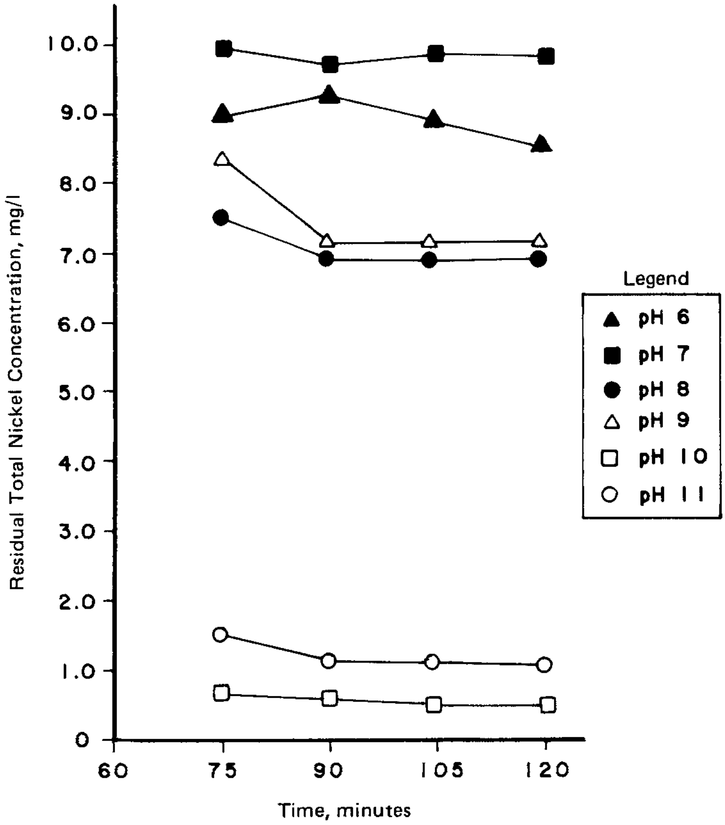


FIG. 2. Comparison of the residual total nickel concentration for the synthetic wastewater at pH's 6–11 at various time intervals.

Figure 1 shows residual soluble nickel concentrations after 2 h, for pH's 11, 10, 9, 8, 7, and 6 of 0.1, 0.2, 4.0, 6.7, 9.5, and 8.2 mg/L, respectively, while Fig. 2 shows residual total nickel concentrations for the same pH's and time for 1.2, 0.5, 7.6, 7.5, 10.0, and 8.7 mg/L, respectively. Figure 2 shows the deviation from the norm at pH 11 for the residual total nickel concentration with a total carbonate (C_T) of zero and with zero sulfide addition. Observations during the jar test indicated that the flocs were finer and more buoyant than at pH 10. The residual soluble nickel concentrations at pH 11 were nearly the same as those at pH 10. This observation would suggest that the treatment efficiency may deteriorate from pH 10 to pH 11 due to the settling characteristics of the floc.

Jenkins et al. (*18*) report soluble nickel concentrations less than 0.05 mg/L at pH 10. Results in this experiment are consistently higher. However, it should be realized that Jenkins et al. performed their test over a 1-week period as compared to 2 h for this experiment. The solubility product constants for a fresh precipitate (this experiment) will generally be larger than for an aged precipitate (Jenkins' experiment). This phenomenon occurs because of the disordered crystal lattice of the fresh precipitate, but as the precipitate ages, larger, more ordered, crystals develop. These crystals are less soluble than the disordered structures (*7*).

Results from this study suggest that the $Ni(OH)_2^0$ species may not be important when considering soluble nickel concentrations. Figure 3 represents a comparison of the theoretical equilibrium prediction (based on the reactions presented in Table 1) for the synthetic wastewater and the experimental residual soluble nickel concentration. A comparison is made with and without the equilibrium equation for the ion pair $Ni(OH)_2^0$. The theoretical curve, when not considering the ion pair, explains the results more accurately in the pH region 8–11. Additionally, concentrations at pH 11 tend to be lower than what is theoretically predicted. Discrepancies between theoretical and actual solubilities are most often explained by incomplete reactions, formation of insoluble metal complexes other than those indicated by the equilibrium equations, and poor separation of colloidal precipitates.

Perhaps an extended precipitation period would give results approximating the theoretical conditions when considering the $Ni(OH)_2^0$ species. Baes et al. (*19*) present equilibrium equations describing such a system for "aged" precipitates. These equilibrium equations have been compared (as in Fig. 3) to the residual soluble concentrations for the synthetic wastewater in Fig. 4. In this case the $Ni(OH)_2^0$ species is much less significant and the minimum solubility is much lower than the experimental residual soluble concentrations. Therefore, this system of equations does not appropriately describe the reactions. Practical operation of the industrial treatment process probably would not be conducive to an aged precipitate condition. An apparent model

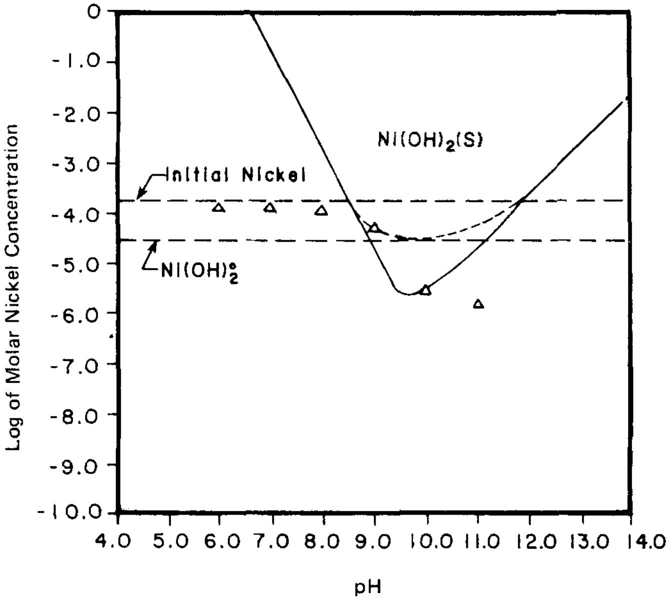


FIG. 3. Comparison of the residual soluble nickel concentration for the synthetic wastewater at pH's 6–11 and the theoretical equilibrium equations (hydroxide system).

which considers the equilibrium reactions for a fresh precipitate without the $Ni(OH)_2^0$ species (Fig. 3) can explain the experimental results more accurately.

Phase II: Optimum pH-Total Carbonate Combination for Precipitation of Nickel

The results of these experiments are presented graphically in Figs. 5 and 6. Observations from Phase I indicated that the residual concentrations could be plotted for a single time period at 2 h (this includes 1 h mixing and 1 h settling) and still give an acceptable comparison. The total carbonate concentration of the synthetic wastewater was varied by adding sodium bicarbonate to give concentrations of 0, 50, 100 and 200 mg/L as $CaCO_3$. The residual soluble nickel concentrations were less than 0.25 mg/L in all cases at pH 11 and less than 0.5 mg/L at pH 10. The residual total nickel concentrations were less than 0.5 mg/L (except for 0 mg/L C_T) at pH 11 and approximately 0.5 mg/L at pH 10. The discussion presented for Phase I pertains to this phase. Attention should be drawn to the fact that the

TABLE 1
Equilibrium Equations for the Nickel–Water System

Equilibrium reaction	Log of equilibrium constant
$Ni(OH)_2(S) \rightleftharpoons Ni^{2+} + 2OH^-$	−14.7
$Ni(OH)_2(S) \rightleftharpoons Ni(OH)^+ + OH^-$	−11.3
$Ni(OH)_2(S) \rightleftharpoons Ni(OH)_2^0$	−4.5
$Ni(OH)_2(S) + OH^- \rightleftharpoons Ni(OH)_3^-$	−1.7

unusually high value for the total nickel concentration (1.2 mg/L) at pH 11 for the 0 mg/L C_T (Fig. 6) is due to the use of the precipitation data from Phase I (the hydroxide system). Therefore, possible reasons for this anomaly were previously discussed. Figure 7 incorporates Fig. 3 (equilibrium predictions for the hydroxide system) along with the equilibrium predictions for the carbonate system. These results further support the suggestion that the $Ni(OH)_2^0$ species is not significant in describing this system. Since the residual concentrations illustrate a pattern very similar to the system

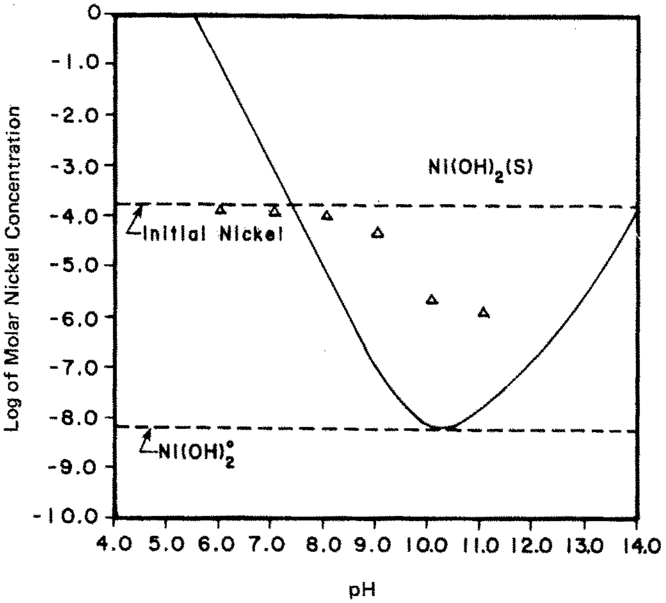


FIG. 4. Comparison of residual soluble nickel concentration for the synthetic wastewater at pH's 6–11 and the theoretical equilibrium equations for an "aged" precipitate (*19*).

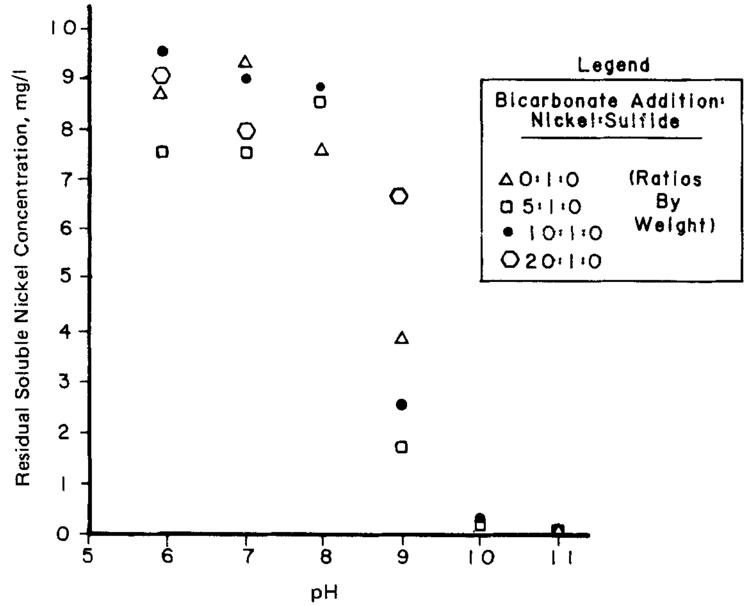


FIG. 5. Residual soluble nickel concentration as a function of pH, various ratios (by weight) of bicarbonate: nickel and a constant S_T:Ni ratio of 0.0 for the synthetic wastewater.

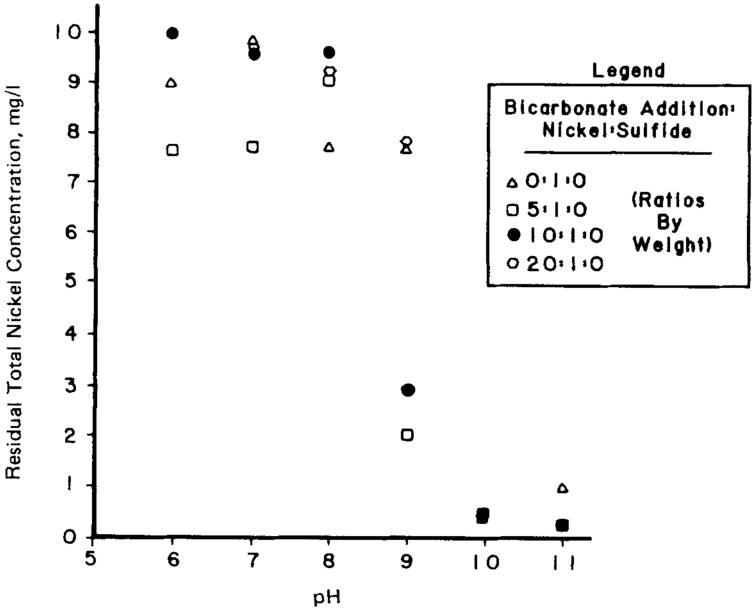


FIG. 6. Residual total nickel concentration as a function of pH, various ratios (by weight) of bicarbonate: nickel and a constant S_T:Ni ratio of 0.0 for the synthetic wastewater.

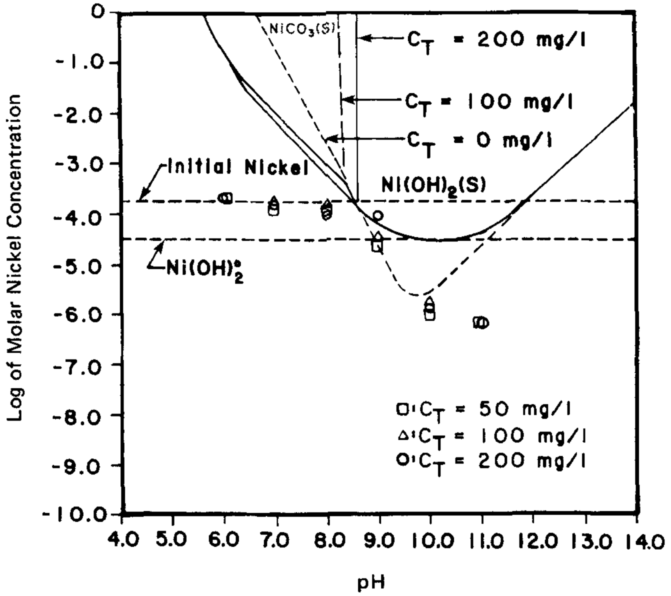


FIG. 7. Comparison of residual soluble nickel concentration for the synthetic wastewater at pH's 6–11 and the theoretical equilibrium predictions for $C_T = 0$, 100, 200 mg/L as $CaCO_3$.

containing no carbonate (or limited carbonate because none was added), it is possible that the hydroxide system is the kinetically dominant response during the time frame considered.

Phase III: Optimum pH-Sulfide Combination for the Precipitation of Nickel

The results of these experiments are presented graphically in Figs. 8 and 9. These figures present the data at the end of the 2-h treatment period for pH's 6–11. No carbonate was added to the system while the sulfide concentration was varied from 0, 5, 10 to 20 mg/L. The residual soluble nickel concentrations at pH 11 were generally less than 0.1 mg/L and less than 0.2 mg/L at pH 10. The residual total nickel concentrations were less than 0.6 mg/L (except at 0 mg/L S_T) at pH 11 and less than 0.6 mg/L at pH 10. This system also demonstrated a response similar to that observed in the previous two phases. Figure 10 represents a comparison of the theoretical equilibrium predictions for an S_T of 5, 10, and 20 mg/L, and the actual residual soluble nickel observed in the experiments. The curves representing the sulfide-hydroxide system were plotted using the following equation (7):

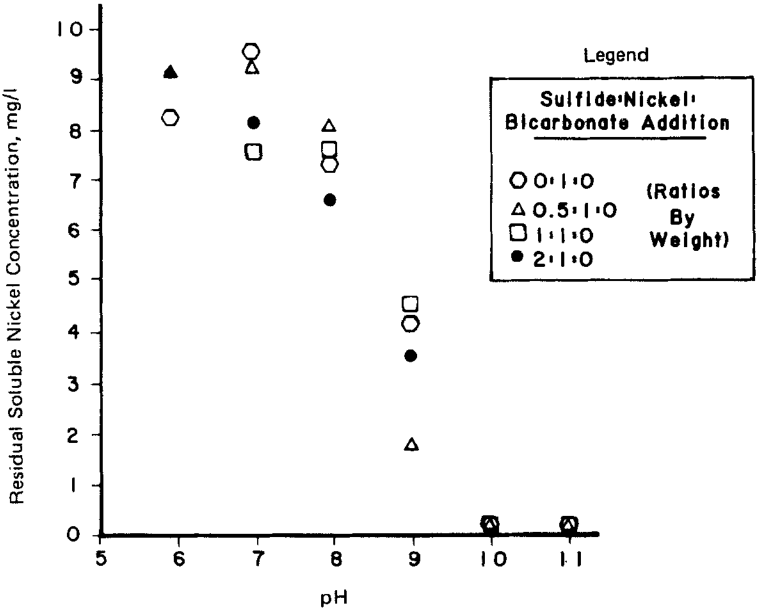


FIG. 8. Residual soluble nickel concentration as a function of pH, various S_T:Ni ratios (by weight) and zero initial bicarbonate addition for the synthetic wastewater.

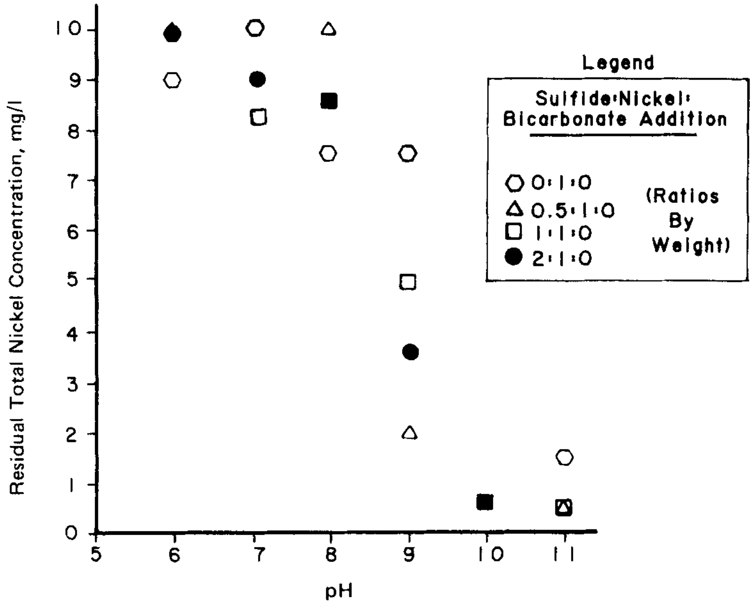


FIG. 9. Residual total nickel concentration as a function of pH, various S_T:Ni ratios (by weight) and zero initial bicarbonate addition for the synthetic wastewater.

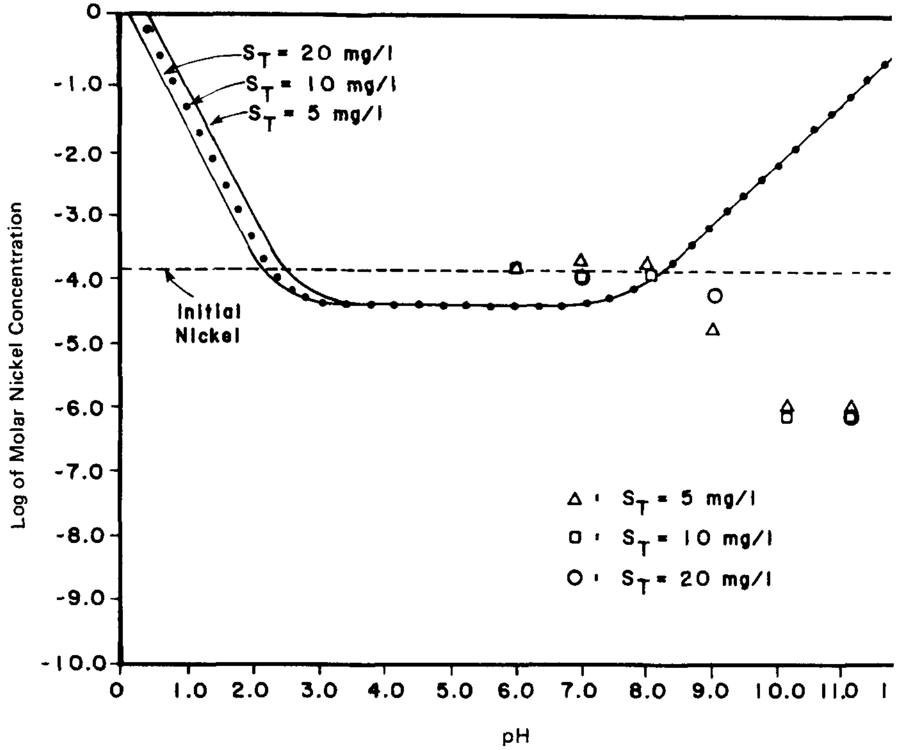


FIG. 10. Comparison of residual soluble nickel concentration for the synthetic wastewater at pH's 6–11 and the theoretical equilibrium predictions (representing an $S_T = 5$, 10, and 20 mg/L).

$$[\mathrm{Ni}]_T = 10^{-24}/\alpha_2 S_T + 10^{-11.3}[\mathrm{H}^+] + 10^{-4.5} + 10^{-12.3}/[\mathrm{H}^+] \qquad (1)$$

where $[\mathrm{Ni}]_T$ = total soluble nickel species, mol/L
S_T = total sulfide concentration, mol/L
$\alpha_2 = 1/([\mathrm{H}^+]^2/K_1K_2 + [\mathrm{H}^+]/K_2 + 1) = [S^{2-}]/S_T \qquad (2)$
$[\mathrm{H}^+]$ = hydrogen ion concentration, mol/L
K_1, K_2 = ionization constants for H_2S
$[S^{2-}]$ = sulfide ion concentration, mol/L

Equation (1) predicts that an increase in sulfide concentration from 5 to 20 mg/L will provide no improved nickel precipitation for pH's greater than 3.5. The data also indicate that the sulfide was insignificant in providing improved removal. The general response of the data is best illustrated by the theoretical hydroxide system curve excluding the $Ni(OH)_2^0$ species (Fig. 3).

Phase IV: Optimum pH-Total Carbonate-Sulfide Combination for Nickel Precipitation

The results of these experiments are presented in tabular form in Table 2. In this series of experiments the sulfide concentrations were varied from 0, 5, 10 to 20 mg/L for each variation of C_T from 0, 50, 100 to 200 mg/L as $CaCO_3$. Table 2 lists the residual soluble and total nickel concentrations at the end of the 2-h treatment period. The residual soluble nickel concentrations were less than or equal to 0.1 mg/L at pH 11, and less than or equal to 0.9 mg/L (most were less than 0.5 mg/L) at pH 10. The residual total nickel concentrations were less than or equal to 0.3 mg/L at pH 11, and less than or equal to 3.5 mg/L (most were less than 0.7 mg/L) at pH 10.

Statistical Analysis

Predictive models for residual concentration of soluble and total nickel for combinations of pH, C_T, and S_T over the range of 6–11, 0–200, and 0–20, respectively, were obtained by fitting response surfaces to the data on residual nickel concentration from Phase IV. A forward, stepwise multiple regression procedure was used that elected the best model of a given size by maximizing the coefficient of determination, R. For both soluble and total residual nickel concentrations, the optimum models were chosen by examining models of increasing complexity (measured as the number of terms in the model) until the ratio of the C_P statistic (*20*) and the degrees of freedom in the model approached unity.

The response surface equation fit to the data were polynomials of the general form:

$$N = b_0 + b_1(\text{pH}) + b_2(S) + b_3(\text{pH})(S) + b_n \text{ [any combination of pH, } S, C \text{ up to 3rd order]} \tag{3}$$

where b = regression coefficients
$C = C_T$:Ni ratio (by weight)
N = residual nickel concentration (total or soluble) in mg/L
pH = pH of water
$S = S_T$:Ni ratio (by weight)

The stepwise regression analysis for the synthetic wastewater produced the following mathematical equation for the residual total nickel concentration:

$$\begin{aligned}N = {} & -183.278 + 72.922(\mathrm{pH}) - 8.877(\mathrm{pH})^2 + 2.416(C) + 0.052(C)^2 \\ & + 0.344(\mathrm{pH})^3 + 5.56(S)^2 - 0.002(C)^3 + 0.082(\mathrm{pH})^2(S) \\ & - 0.011(\mathrm{pH})^3(S) - 1.695(\mathrm{pH})(S)^2 + 0.123(\mathrm{pH})^2(S)^2 \\ & - 1.103(\mathrm{pH})(C) + 0.143(\mathrm{pH})^2(C) - 0.006(\mathrm{pH})^3(C) \\ & + 0.0001(\mathrm{pH})(C)^2 + 0.078(\mathrm{pH})(S)(C) - 0.002(\mathrm{pH})^2(S)^2(C) \\ & - 0.140(S)^2(C) - 0.031(S)(C)^2 + 0.013(S)^2(C)^2 \qquad (4)\end{aligned}$$

The results of the analysis are shown in Table 3. As expected, pH had the greatest effect on total nickel removal. The regression analysis indicated that the $(\mathrm{pH})^2$ term alone produced an R^2 of 0.836, which accounts for more than 90% of the total data variability accounted for in the 20-term model. The best two-term model added C^2 to pH but only increased the R^2 by 0.4%. The best three-term model added S^3 to pH and C^2 yet only increased the R^2 by another 0.4%. The model corroborates the general observations concerning the practicality of sulfide or carbonate treatment. Figures 11(a)–(d) present response surface plots for the residual total nickel concentrations versus pH and sulfide variation. These figures represent the response of the residual nickel concentration for the sequence of carbonate:nickel ratios of 0, 0.5, 1.0, and 2.0 based on Eq. (4). The greatest effect is observed at pH 11 which does indicate an improvement in removal efficiency with increasing sulfide dosage and increasing carbonate concentration. Figures 11(a)–(d) show optimum improvement near the 1.0 S_T:Ni weight ratio. This concentration of sulfide would be about twice the stoichiometric requirement which is in the higher region of the 1.0 to 2.5 range recommended by Cherry (*2*), Kim (*15*), or Whang (*14*). Figures 11(a)–(d) also show an improvement in nickel removal at the high pH's with increasing carbonate concentrations. An R^2 of 0.922 indicates that the model provides an excellent description of residual total nickel concentration.

The regression analysis for residual soluble nickel in the wastewater gives a response surface very similar to the total nickel, but with lower nickel residuals. The equation for residual soluble nickel concentration has the form:

TABLE 2

Residual Soluble and Total Nickel Concentrations at the End of a 2-h Treatment Period for Various Combinations of pH-Sulfide-Carbonate Concentrations in the Synthetic Wastewater

Sulfide concentration (S_T), mg/L, as S^{2-}	pH	Total carbonate (C_T), mg/L, as $CaCO_3$, residual soluble nickel	$C_T = 0$, residual total nickel	$C_T = 50$		$C_T = 100$		$C_T = 200$	
				Residual soluble nickel	Residual total nickel	Residual soluble nickel	Residual total nickel	Residual soluble nickel	Residual total nickel
$S_T = 0$	11	0.1	1.2	0.1	0.5	0.05	0.2	0.05	0.15
	10	0.2	0.6	0.05	0.3	0.12	0.4	0.1	0.3
	9	4.0	7.7	1.6	2.0	2.3	2.8	6.4	8.0
	8	6.8	7.5	8.3	9.0	8.9	9.7	8.7	9.3
	7	9.5	10.0	7.8	8.7	8.8	9.5	9.6	9.3
	6	8.2	8.7	7.3	7.8	9.8	9.9	9.7	10.0
$S_T = 5$	11	0.05	0.4	0.05	0.4	0.05	0.2	0.05	0.3
	10	0.1	0.4	0.3	0.5	0.1	0.2	0.15	3.5
	9	1.5	2.2	3.2	3.9	4.8	5.2	4.8	5.6
	8	7.8	10.0	8.8	10.0	9.2	9.8	9.1	9.0
	7	9.4	10.0	8.4	9.5	9.5	10.0	9.4	9.9
	6	7.0	9.9	8.7	9.2	10.0	10.0	9.2	9.9

$S_T = 10$	11	0.05	0.60	0.05	0.3	0.05	0.2	0.05	0.2
	10	0.1	0.6	0.1	0.4	0.9	1.3	0.1	0.4
	9	4.6	4.9	4.5	5.4	6.8	7.3	6.6	7.3
	8	7.7	8.5	8.1	9.0	8.6	9.5	8.5	9.3
	7	7.6	8.2	7.8	9.0	9.2	9.5	8.8	9.3
	6	9.1	10.0	8.9	9.5	9.1	9.8	9.2	9.5
$S_T = 20$	11	0.05	0.4	0.1	0.2	0.05	0.2	0.05	0.1
	10	0.1	0.5	0.15	0.3	0.15	0.2	0.3	0.7
	9	3.1	3.3	2.8	3.6	3.4	3.8	5.4	6.1
	8	1.0	8.4	5.2	5.8	9.1	10.0	8.8	9.1
	7	8.2	8.8	6.1	7.2	9.2	9.9	9.0	9.0
	6	9.7	10.0	9.3	10.0	9.5	9.6	8.5	8.9

TABLE 3

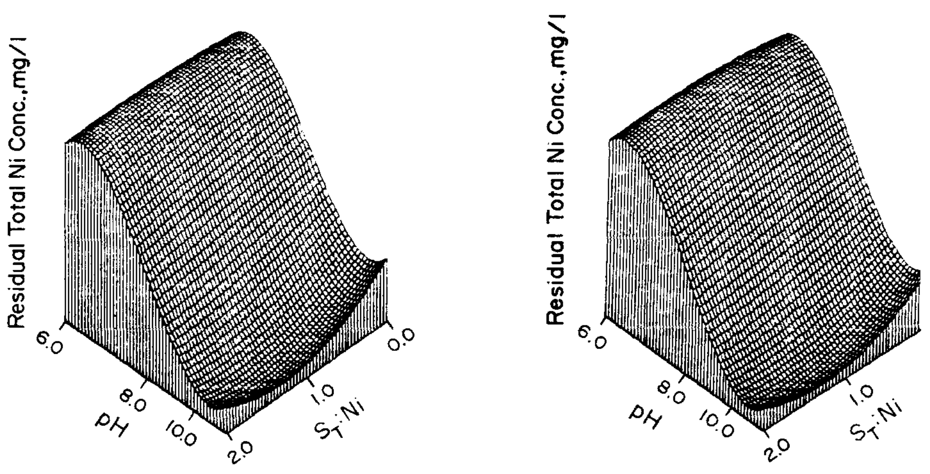
Stepwise Regression Analysis (utilizing maximum R^2) for the Residual Total Nickel Concentrations in the Synthetic Wastewater ($R^2 = .922$)

Parameter[a]	Significance level of parameter in the entire equation
pH	0.0001
$(\mathrm{pH})^2$	0.0001
C	0.0868
$(C)^2$	0.0001
$(\mathrm{pH})^3$	0.0001
$(S)^2$	0.0001
$(C)^3$	0.0001
$(\mathrm{pH})^2(S)$	0.0022
$(\mathrm{pH})^3(S)$	0.0001
$(\mathrm{pH})(S)^2$	0.0001
$(\mathrm{pH})^2(S)^2$	0.0001
$(\mathrm{pH})(C)$	0.0001
$(\mathrm{pH})^2(C)$	0.0333
$(\mathrm{pH})^3(C)$	0.0123
$(\mathrm{pH})^2(C)^2$	0.0096
$(\mathrm{pH})(S)(C)$	0.0443
$(\mathrm{pH})^2(S)^2(C)$	0.0001
$(S)^2(C)$	0.0001
$(S)(C)^2$	0.0001
$(S)^2(C)^2$	0.0001

[a] $C = C_T$:Ni weight ratio. pH = pH of water. $S = S_T$:Ni weight ratio.

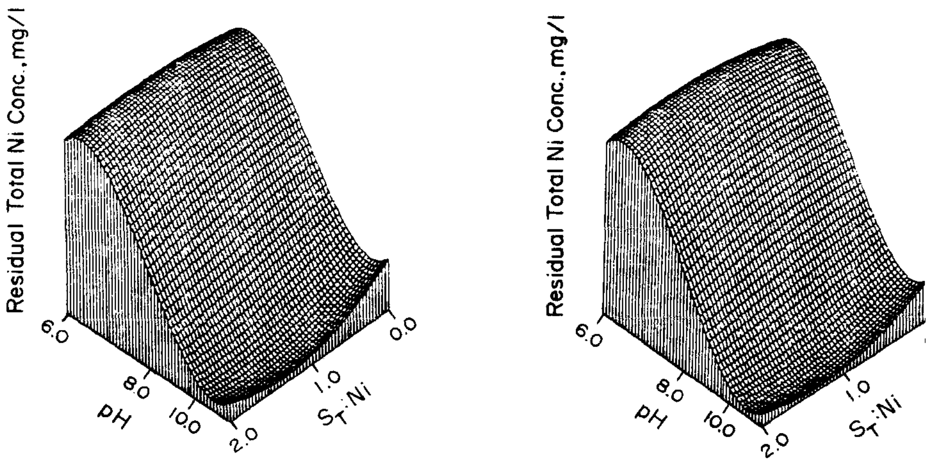
$$
\begin{aligned}
N = {} & -174.061 + 29.802(S) + 69.334(\mathrm{pH}) - 8.437(\mathrm{pH})^2 + 0.325(\mathrm{pH})^3 \\
& + 9.240(S)^2 - 0.489(S)^3 - 0.001(C)^3 - 12.478(\mathrm{pH})(S) \\
& + 1.628(\mathrm{pH})^2(S) - 0.068(\mathrm{pH})^3(S) - 1.928(\mathrm{pH})(S)^2 \\
& + 0.114(\mathrm{pH})^2(S)^2 - 0.021(\mathrm{pH})(C) + 0.006(\mathrm{pH})(C)^2 \\
& - 0.0003(\mathrm{pH})^2(C)^2 + 0.139(\mathrm{pH})(S)(C) - 0.008(\mathrm{pH})^2(S)(C) \\
& - 0.324(S)(C) - 0.182(S)^2(C) - 0.001(S)(C)^3 + 0.009(S)^2(C)^2
\end{aligned}
\tag{5}
$$

The results are presented in Table 4. All terms are highly significant in the 21-term model. Again pH is found to exert the greatest effect on soluble nickel removal. The $(\mathrm{pH})^2$ term alone accounted for 85.5% of the data



a. C_T: Ni = 0.0

b. C_T:Ni = 0.5



c. C_T: Ni = 1.0

d. C_T: Ni = 2.0

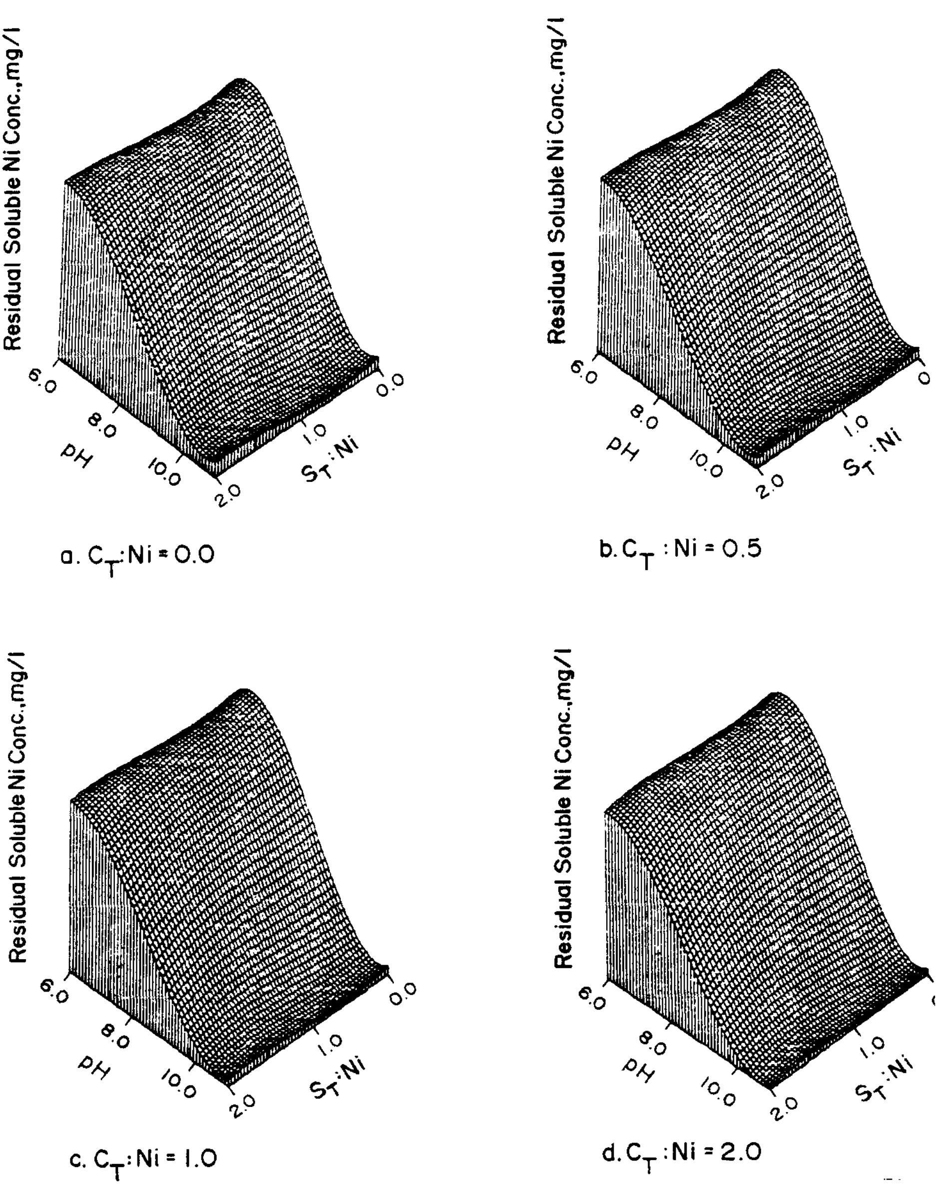
FIG. 11. Surface response plots for the residual total nickel concentration in the synthetic wastewater vs pH and S_T:Ni weight ratios at C_T:Ni weight ratios of 0.0, 0.5, 1.0, and 2.0.

TABLE 4
Stepwise Regression Analysis (utilizing maximum R^2) for the Residual Soluble Nickel Concentrations in the Synthetic Wastewater ($R^2 = .936$)

Parameter[a]	Significance level of parameter in the entire equation
S	0.0002
pH	0.0001
$(\mathrm{pH})^2$	0.0001
$(\mathrm{pH})^3$	0.0001
$(S)^2$	0.0001
$(S)^3$	0.0139
$(C)^3$	0.0001
$(\mathrm{pH})(S)$	0.0001
$(\mathrm{pH})^2(S)$	0.0001
$(\mathrm{pH})^3(S)$	0.0001
$(\mathrm{pH})(S)^2$	0.0001
$(\mathrm{pH})^2(S)^2$	0.0001
$(\mathrm{pH})(C)$	0.0001
$(\mathrm{pH})(C)^2$	0.0001
$(\mathrm{pH})^2(C)^2$	0.0001
$(\mathrm{pH})(S)(C)$	0.0001
$(\mathrm{pH})^2(S)(C)$	0.0001
$(S)(C)$	0.0026
$(S)^2(C)$	0.0001
$(S)(C)^3$	0.0001
$(S)^2(C)^2$	0.0001

[a] $C = C_T$:Ni weight ratio. pH = pH of water. $S = S_T$:Ni weight ratio.

variability which is only 8% less than the 21-term model. The consideration of total carbonate as C in the 2-term model only accounted for an additional 1% of data variability. The sulfide concentration did not show an influence until a 5-term model was considered and then (as an S^3 term) it only accounted for an additional 0.2% of the data variability beyond the 4-term model. Figures 12(a)–(d) show the response surface plots for the residual soluble nickel concentrations versus pH and sulfide variations for C_T:Ni weight ratios of 0, 0.5, 1.0, and 2.0. These figures show results which are comparable to the residual total nickel concentrations given in Figs. 11(a)–(d). The greatest combined effect of pH and total carbonate concentration is observed at pH 11 which is expected since that is what occurred for the residual total nickel response. The R^2 value of 0.936 indicates that the model predictions compare quite favorably with the actual data.



a. C_T:Ni = 0.0

b. C_T : Ni = 0.5

c. C_T: Ni = 1.0

d. C_T : Ni = 2.0

FIG. 12. Surface response plots for the residual soluble nickel concentration in the synthetic wastewater vs pH and S_T:Ni weight ratios at C_T:Ni weight ratios of 0.0, 0.5, 1.0, and 2.0.

SUMMARY AND CONCLUSIONS

The results of this study indicate that nickel removal with hydroxide precipitation for the synthetic wastewater was very efficient at pH 10. However, the best removal produced a residual total nickel concentration of 0.1 mg/L. This occurred at pH 11 with a carbonate:nickel (C_T:Ni) ratio of 20:1 and a sulfide:nickel (S_T:Ni) ratio of 2:1. Still, this was not greatly different from other treatment combinations at pH 10 which gave residual concentrations of 0.2 mg/L.

The multiple regression analysis for the synthetic wastewater system produced equations that predicted the relative responses of the true data points quite accurately.

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