THE EFFECTS OF NICKEL ON THE COMPLETELY MIXED ACTIVATED SLUDGE PROCESS

by

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DEDICATION

To my parents

And to my wife

For Their Love and Encouragement

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I. INTRODUCTION

Urbanization and industrialization have provided mankind with many material and social benefits. At the same time they have brought many material and social problems. One of these problems is pollution of the environment. The ecological balance of aquatic ecosystems has been influenced by pollutant discharges. Wastewater treatment processes are used to restore ecological balance. Biological wastewater treatment processes are used to stabilize oxygen demanding organic matter. Knowledge of the means to operate these processes is essential to reducing the pollution load to receiving streams. Whereas knowledge now exists on the procedures to operate treatment processes, little information exerts on the means to operate processes in the presence of toxic compound present in the wastewater. One type of toxic compound that is frequently found in wastewater is heavy metals.

The industries largely responsible for discharge of wastewater containing a high concentration of heavy metals are the electroplating and other heavy metal related industries. These industries tend to discharge their wastewater into municipal sewer systems. Heavy metals are found in domestic sewage at very small concentration. However, combinations of domestic sewage with industrial wastewater contaminated with heavy metals may contain concentration of heavy metals at levels that may impair the efficiency of wastewater treatment processes. The heavy metals nickel, lead, and chromium can react with the microbial enzymes to retard or completely inhibit metabolic activity. Since most domestic treatment plants and many industrial treatment plants employ

biological treatment processes to remove organic materials it is significant to realize the influences of heavy metals on microbial activity in wastewater treatment process.

The purpose of this research was to conduct batch and continuous flow laboratory experiments to determine the influences of nickel on the activated sludge process. Batch reactors and bench scale activated sludge units were operated at various organic substrate and nickel concentrations to study the effects of nickel on organic substrate removal efficiency, degree of nitrification, and on the biokinetic coefficients Y_{max} and k_d.

II. CHEMICAL AND BIOCHEMICAL ASPECTS OF NICKEL IN THE ENVIRONMENT

OCCURRENCE OF NICKEL IN THE ENVIRONMENT

Nickel is a silvery white soft metal that is tenacious, malleable and ductile. It has a specific gravity of 8.9 and a boiling temperature of 1455°C. Nickel occurs naturally throughout the lithosphere. Among the igneous rock in the lithosphere, ultrabasic rocks are the principal sources of nickel ranging from 0.016% in basalt and gabbro to 0.20% in pediotite (1). Rocks high in silica content are relatively high in nickel except for carbonates. Small percentages of nickel are found in petroleum, coal and seawater. Surface and groundwater usually have nickel in relatively low concentration due to the weathering process unless the presence of nickel is due to industrial pollution (2).

Nickel occurs in nature as an oxide or in sulfide ores. Extraction of nickel is dependent on the nature of these ores. Cobalt usually occurs with nickel. The estimated world production of nickel is summarized in Table I. More than 33 percent of nickel production is used in the manufacturing process of nickel stainless steel. The nickel content in stainless steel may range from less than 1 percent to approximately 76 percent.

Electroplating consumes approximately 16 percent of nickel production. Nickel plating is done to improve appearance and to prevent corrosion. Manufacturing of nickel alloys accounts for about 25 percent of total nickel production. The nickel content may range up to 80

TABLE I. ESTIMATED WORLD NICKEL PRODUCTION BY COUNTRY (2)

Country	Nickel Production, tons 1969	1970	1971
Australia (concentrates)	12,324	31,862	34,000
Brazil (ore)	1,900	3,200	3,500
Burma (speiss)	33	23	20
Canada	213,611	305,881	293,947
Cuba			
Oxide	20,400	20,400	40,000
Sulfide	18,400	18,400	
Finland			
Concentrates	3,996	5,634	4,968
Nickel sulfate	211	165	165
Greece (recoverable ore)	9,115	9,500	11,600
Indonesia (ore)	8,404	19,842	29,762
Mexico (ore)	39	49	55
Morocco (nickel ore and cobalt ore)	311	152	220
New Caledonia (recoverable)	99,731	116,164	112,751
Norway (concentrate)	273	360	360
Poland (ore)	1,650	2,200	2,000
Rhodesia, Southern (concentrate)	4,400	12,000	13,000
South Africa, Republic of (electrolytic)	11,000	12,739	14,067
USSR (ore)	115,000	120,000	130,000
United States			
Byproduct of metal refining	2,714	2,909	2,581
Nickel recovered from domestic ore	13,096	12,649	13,073
TOTAL	536,608	694,129	706,069

percent. All other uses amount to approximately 26 percent of nickel production and include ferrous casting, nickel salt, nickel powder, cladding and electronic uses,etc.(3). The amount of nickel consumption in the United States during 1972 is listed in Table II.

Nickel is emitted into the environment largely through industrial operations. The most likely sources of nickel in air appear to be from metallurgical plants using nickel as a raw material, engine burning fuel containing nickel additives, plating plants, as well as from burning of oil and coal and the incineration of nickel products.

Wastewater containing nickel is discharged primarily from metal industries. Plating industry and silver refineries are largely responsible for these discharges (3). Several surveys of metals concentration in influent wastewater have been made. The results of a survey of plants in Michigan shows nickel concentration in wastewater ranging from 0.002 to 880 mg/l (4). Concentrations of nickel in metal processing and plating wastewater is summarized in Table III.

Nickel may be present in wastewater as the soluble ion. Nickel may combine with complexing agents present in wastewater to form soluble nickel complexes. The degree of toxicity of nickel to microbial activity may be dependent on its complexation with ligands.

CHEMICAL ASPECTS OF NICKEL

A knowledge of the solubility of metal ions and their coordination compounds is very important to access the effects of such metal ions on biological activity. Toxicity of heavy metals to microbial activity is

TABLE II. U.S. CONSUMPTION OF NICKEL (EXCLUSIVE OF SCRAP) BY USE AND FORM, 1972 (2)

Use	Form, tons					
	Commercially Pure Unwrought Nickel	Ferronickel	Nickel Oxide	Nickel Sulfate and Other Salts	Other Forms	Total of Figures Shown
Steels						
Stainless and heat-resisting	17,155	16,788	11,196	-	227	45,366
Alloys (excludes stainless)	7,930	5,004	6,408	-	213	19,555
Superalloys	11,536	251	49	-	436	12,272
Nickel-copper and copper-nickel alloys	8,307	-	36	-	199	8,542
Permanent magnet alloys	3,925	221	54	-	-	4,200
Other nickel and nickel alloys	27,873	269	698	4	49	28,894
Cast irons	2,825	272	401	-	938	4,436
Electroplating	25,351	-	31	3,547	107	29,036
Chemicals and chemical uses	906	-	71	204	-	1,181
Other uses	4,614	1	371	183	635	5,804
TOTAL (reported by companies canvassed and estimated)	110,422	22,806	19,315	3,939	2,804	159,286

TABLE III. NICKEL CONCENTRATIONS IN METAL PROCESSING AND PLATING WASTEWATERS (3).

Industry	Nickel Concentration, mg/l	
	Range	Average
Plating Plants		
(4 different plants)	2-205	
Rinse waters	2-205	
Large plants	≤200	25
Metal Finishing		
Mixed Wastes	17-51	
Acid Wastes	12-48	
Alkaline Wastes	2-21	
Tableware Plating		
Silver bearing waste	0-30	5
Acid Waste	10-130	33
Alkaline Waste	0.4-3.2	1.9
Business Machine Manufacture		
Plating Wastes	5.0-35	11
Pickling Wastes	6.0-32	17

mainly attributed to soluble ions. The severity of inhibition is reduced if precipitation of heavy metal ions occurs (5). The important parameters controlling the solubility of metal ions are the pH, type and concentration of complexing inorganic and organic ligands and chelating agents, oxidation state of the mineral components, and the redox potential of the environment in question.

Solubility of Nickel Complexes

Nickel in aquatic environment has a tendency to form soluble complexes with organic and inorganic ligands. In wastewater, nickel complexes are formed by combination with hydroxide, carbonate, ammonia, etc.

The complex formation of nickel hydroxide can be expressed in terms of stepwise formation of nickel hydroxide species as follows:

$$Ni^{2+} + OH^- \rightleftarrows NiOH^+ ; \quad K_1 \tag{1}$$

$$NiOH^+ + OH^- \rightleftarrows Ni(OH)_2 ; \quad K_2 \tag{2}$$

$$Ni(OH)_2 + OH^- \rightleftarrows HNiO_2^- + H_2O ; \quad K_3 \tag{3}$$

The stepwise formation, K_n, and overall formation constant, β_n, are related by

$$\beta_1 = K_1 \tag{4}$$

$$\beta_2 = K_1 \times K_2 \tag{5}$$

$$\beta_3 = K_1 \times K_2 \times K_3 \tag{6}$$

The overall equilibrium reaction of nickel hydroxide complexes can be represented by

$$Ni^{2+} + OH^- \rightleftarrows NiOH^+ ; \quad \beta_1 \tag{7}$$

$$Ni^{2+} + 2OH^- \rightleftarrows Ni(OH)_2 \; ; \quad \beta_2 \tag{8}$$

$$Ni^{2+} + 3OH^- \rightleftarrows HNiO_2^- + H_2O \; ; \quad \beta_3 \tag{9}$$

A mass balance of nickel and nickel hydroxide species must be maintained and can be represented by

$$C = [Ni^{2+}] + [NiOH^+] + [Ni(OH)_2] + [HNiO_2^-] \tag{10}$$

This mass balance equation can be expressed as

$$C = [Ni^{2+}](1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3) \tag{11}$$

The fraction of nickel species, α_n, which is independent of nickel concentration may be calculated as a function of pH as follows:

$$[H^+][OH^-] = K_w = 1 \times 10^{-14} \tag{12}$$

$$pH = 14 - pOH$$

$$\alpha_0 = \frac{[Ni^{2+}]}{C} = \frac{1}{1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH]^3} \tag{13}$$

$$\alpha_1 = \frac{[NiOH^+]}{C} = \beta_1[OH^-]\alpha_0 \tag{14}$$

$$\alpha_2 = \frac{[Ni(OH)_2]}{C} = \beta_2[OH^-]^2\alpha_0 \tag{15}$$

$$\alpha_3 = \frac{[HNiO_2^-]}{C} = \beta_3[OH^-]^3\alpha_0 \tag{16}$$

The distribution diagram of nickel hydroxide species as a function of pH is shown in Figure 1. The values of equilibrium constants used for calculation of the nickel hydroxide distribution diagram are listed in Table IV.

The solubility of nickel hydroxide is governed by the solubility product constant, K_{sp}, and the concentration of nickel hydroxide solid species that is in equilibrium with the soluble free nickel ion or

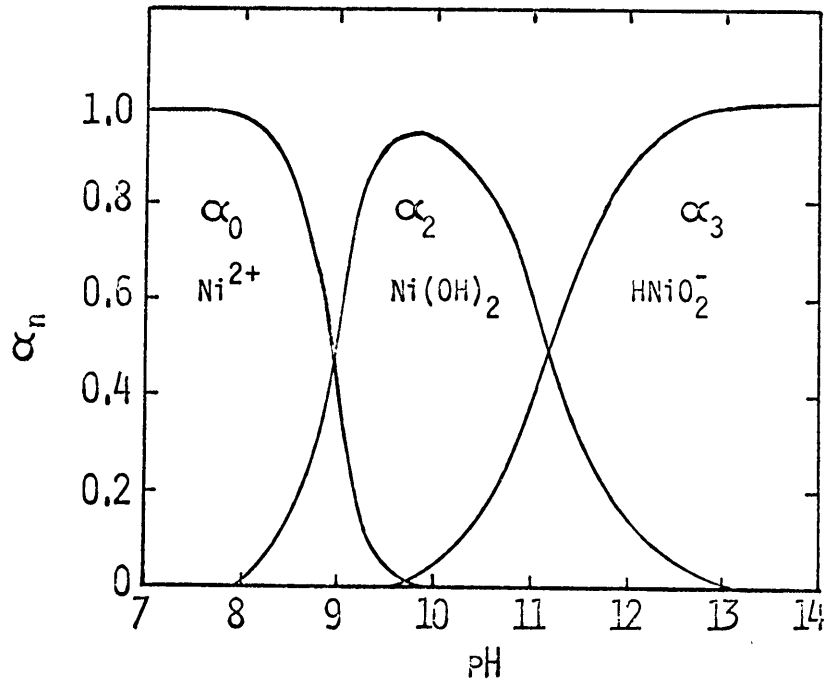

Figure 1. Distribution Diagram for Nickel Hydroxide Complexes.

TABLE IV. EQUILIBRIUM CONSTANTS FOR CALCULATION OF NICKEL DISTRIBUTION DIAGRAMS

	$Log_{(10)}$ of Equilibrium Constant				
Ligand	K_1	K_2	K_3	K_4	Reference
OH^-	3.4	6.8	2.8	-	6
NH_3	2.80	2.24	1.73	1.19	7

	Overall Formation Constants			
Ligand	β_1	β_2	β_3	β_4
OH^-	2.51×10^3	1.58×10^{10}	1.00×10^{13}	-
NH_3	6.31×10^2	1.10×10^5	5.89×10^6	9.12×10^7

nickel hydroxide species.

The equilibrium equation governing the solubility of a divalent nickel hydroxide described by a solubility product constant, K_{sp}, (8):

$$[Ni^{2+}][OH^-]^2 = K_{sp} = 2.00 \times 10^{-15} \quad (17)$$

However, this equilibrium relationship is valid to about pH 8.5. The solubility of nickel is affected by nickel hydroxo-complexes formation above pH 8.5. The complex formation of nickel must be taken into account for nickel solubility consideration.

Substitution of equation [17] into equation [10] yields the solubility of nickel, S, in terms of the solubility product constant, K_{sp}, the overall formation constant, β_n, and hydroxide concentration as:

$$S = \frac{K_{sp}}{[OH^-]^2}(1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3) \quad (18)$$

The solubility diagram of nickel-hydroxy complexes is shown in Figure 2.

Jenkins, and coworkers (9, 10) investigated the solubility of heavy metal hydroxides in water, sewage and sewage sludge. The results showed that nickel hydroxide had a solubility of 1 part per million in pure water at a pH of approximately 7. However, the solubility was increased several fold as the solution was exposed to the air.

Precipitation of nickel hydroxide was observed to occur almost instantaneously, i.e. after a period of contact of only 30 seconds in the sewage. The amount of precipitation was not greatly effected by lowering the pH to 5 or 3.

In aqueous systems containing both hydroxide and carbonate, the

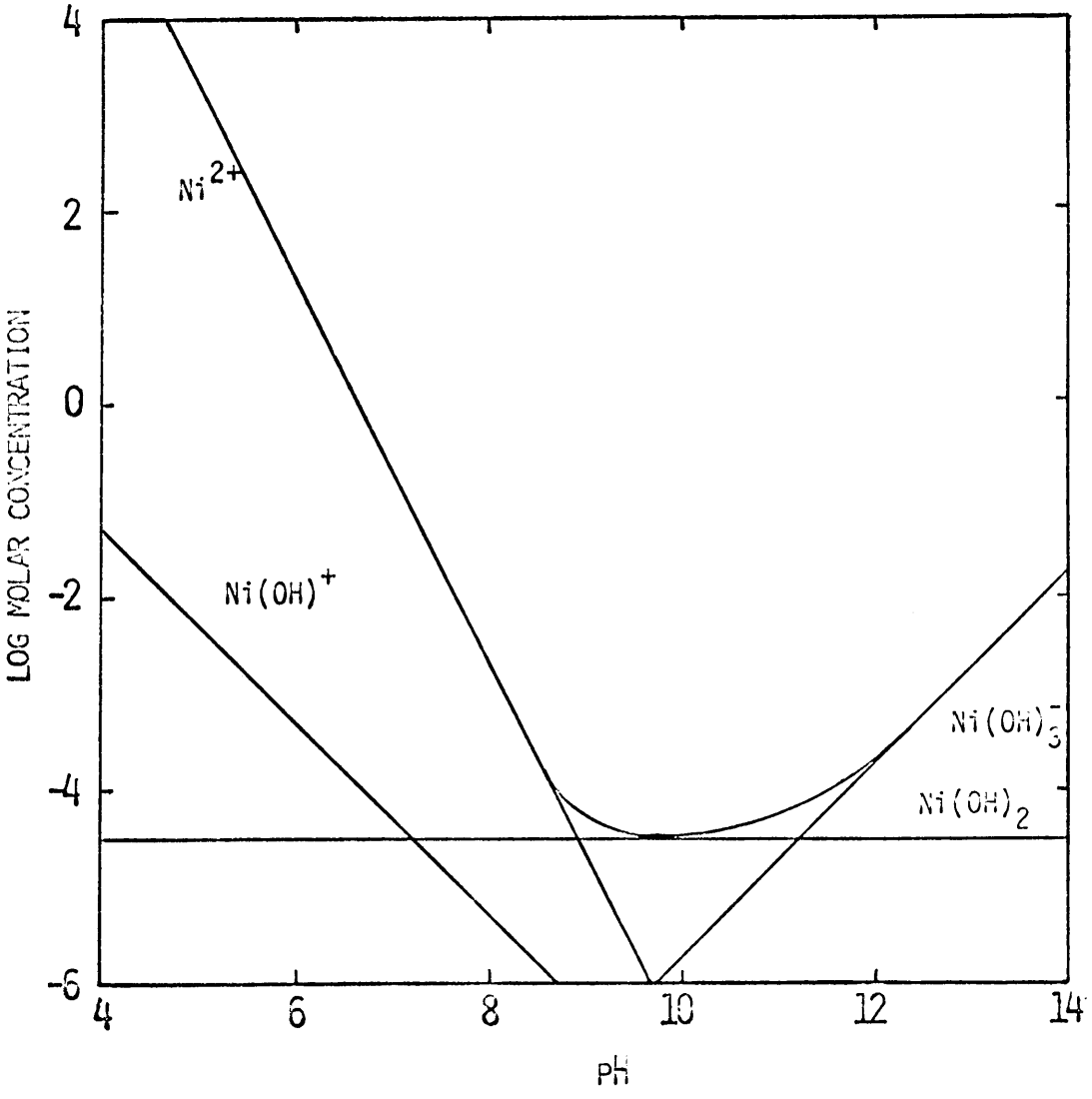

Figure 2. Theoretical Solubility Diagram for Nickel Hydroxide.

solubility of nickel is governed by either hydroxide or carbonate, depending on pH and total carbonate concentration of the system.

The equilibrium equation for nickel carbonate expressed in terms of the solubility product constant (8) is

$$[Ni^{2+}][CO_3^{2-}] = K'_{sp} = 6.31 \times 10^{-9} \quad (19)$$

For aqueous systems where two or more precipitation reactions are competing, the "ion-ratio" method may be employed to determine the order of precipitation of solids (11). However, this method may be overruled by kinetic factors under nonequilibrium conditions. Division of the hydroxide solubility product by the carbonate solubility product yields the ratio, R as

$$R = \frac{[OH^-]^2}{[CO_3^{2-}]} = 3.17 \times 10^{-7} \quad (20)$$

Hydroxide solubility controls the solubility of the system if $R \geq 3.17 \times 10^{-7}$ and if $R < 3.17 \times 10^{-7}$ solubility of the system is controlled by carbonate solubility.

The equilibrium concentration of carbonate, C_T, is expressed as

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad (21)$$

where

$$[CO_2^*] = [H_2CO_3] + [CO_2] \text{ (aq)}$$

The equilibrium equations for carbonic acid are given as

$$K_{a_1} = \frac{[H^+][HCO_3^-]}{[CO_2^*]} = 4.4 \times 10^{-7} \quad (22)$$

$$K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11} \quad (23)$$

By substitution of equations [22], [23] and [12] into equation [21] and rearranging the expression of $[CO_3^{2-}]$ in terms of total carbonate concentration, C_T, pH and equilibrium constants becomes

$$[CO_3^{2-}] = \frac{C_T}{\frac{Kw^2}{[OH^-]^2 K_{a_1} \cdot K_{a_2}} + \frac{Kw}{[OH^-] K_{a_2}} + 1} \qquad (24)$$

The solubility of the carbonate system can be determined by:

$$S = \frac{K'_{sp}}{[CO_3^{2-}]} (1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3) \qquad (25)$$

The theoretical solubility diagram of nickel hydroxide and nickel carbonate for the system having total carbonate concentration of $10^{-1.2}$ M is shown in Figure 3.

Patterson et.al. (12) investigated the behavior of nickel carbonate precipitation compared to a nickel hydroxide system. The data for the nickel carbonate system were identical to those for the nickel hydroxide system which indicated that the nickel hydroxide system controlled the precipitation of the nickel carbonate system. Nickel removal by carbonate precipitation offered no advantage over the hydroxide system at the same operational pH range. A comparison of nickel hydroxide and nickel carbonate experimental data is shown in Figure 4.

Complex Formation of Nickel

Formation of nickel complexes involves competition between water molecules in the hydration shell and the complexing agent or ligand. The tendency of the metal ion to form complexes with various ligands is

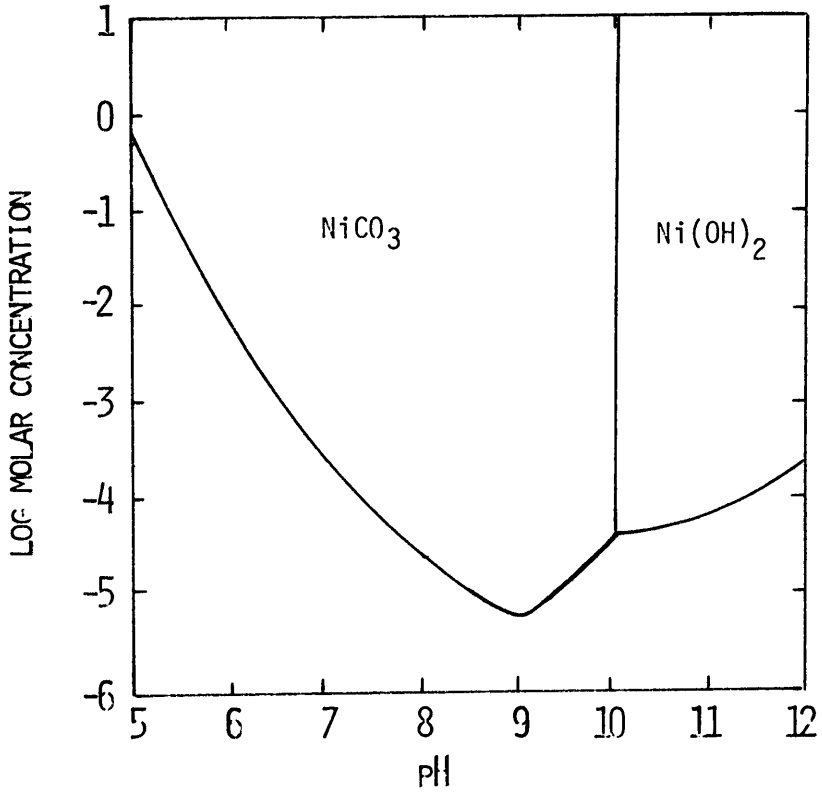

Figure 3. Theoretical Phase Diagram for Nickel Hydroxide and Nickel Carbonate ($C_T = 10^{-1.2}$ M).

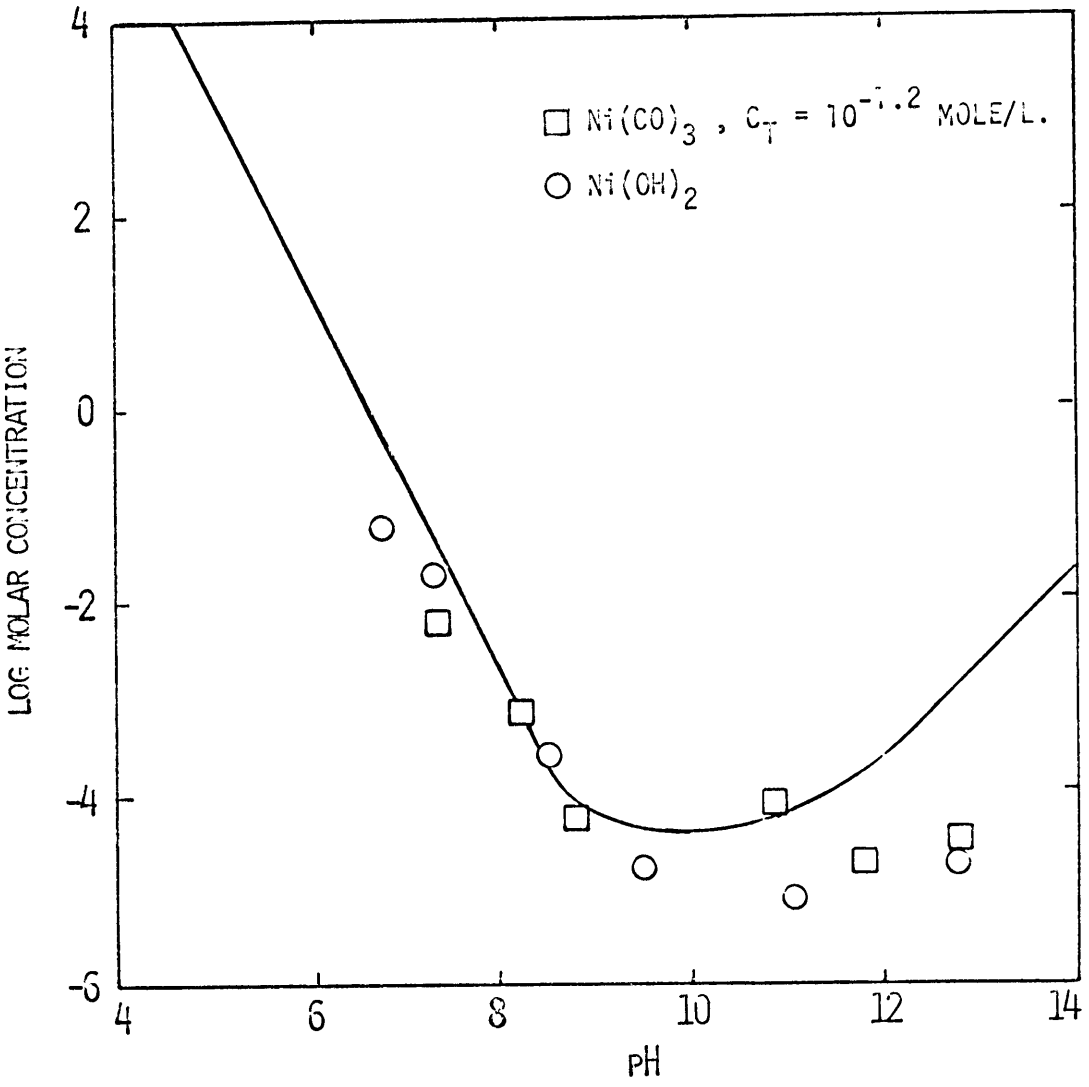

Figure 4. Comparison of Nickel Hydroxide and Nickel Carbonate Data with Theoretical Nickel Hydroxide Solubility Diagram (8).

dependent on the details of the atomic structure of individual metal ions. For a given metal, some complexes are more toxic to microbial populations.

Complexation of nickel with ammonia is stronger than chloride. For a biological treatment process, ammonia complexation can become significant. Inhibition of nitrification due to the presence of metal ions in wastewater can cause an increase in ammonia due to deamination of amino acid in the process. High ammonia concentration can complex with metal ion and affect the toxicity of metal ions.

The chemical equilibrium of nickel-amine complexes can be expressed as follows:

$$Ni^{2+} + NH_3 \rightleftarrows NiNH_3^{2+} \quad ; \quad K_1 = 1 \times 10^3 \tag{26}$$

$$NiNH_3^{2+} + NH_3 \rightleftarrows Ni(NH_3)_2^{2+} \quad ; \quad K_2 = 1.51 \times 10^2 \tag{27}$$

$$Ni(NH_3)_2^{2+} + NH_3 \rightleftarrows Ni(NH_3)_3^{2+} \quad ; \quad K_3 = 43.7 \tag{28}$$

$$Ni(NH_3)_3^{2+} + NH_3 \rightleftarrows Ni(NH_3)_4^{2+} \quad ; \quad K_4 = 14.5 \tag{29}$$

The values of stepwise formation constants were taken from reference 7.

The stepwise equilibrium relationship for the above equations is:

$$\frac{[NiNH_3^{2+}]}{[Ni^{2+}][NH_3]} = K_1 \tag{30}$$

$$\frac{[Ni(NH_3)_2^{2+}]}{[Ni(NH_3^{2+})][NH_3]} = K_2 \tag{31}$$

$$\frac{[Ni(NH_3)_3^{2+}]}{[Ni(NH_3)_2^{2+}][NH_3]} = K_3 \quad (32)$$

$$\frac{[Ni(NH_3)_4^{2+}]}{[Ni(NH_3)_3^{2+}][NH_3]} = K_4 \quad (33)$$

Expressing the equilibrium equations above in logarithmic forms the above equations become

$$\log[NiNH_3^{2+}] = \log[Ni^{2+}] + \log K_1 + \log[NH_3] \quad (34)$$

$$\log[Ni(NH_3)_2^{2+}] = \log[NiNH_3^{2+}] + \log K_2 + \log[NH_3] \quad (35)$$

$$\log[Ni(NH_3)_3^{2+}] = \log[Ni(NH_3)_2^{2+}] + \log K_3 + \log[NH_3] \quad (36)$$

$$\log[Ni(NH_3)_4^{2+}] = \log[Ni(NH_3)_3^{2+}] + \log K_4 + \log[NH_3] \quad (37)$$

A logarithmic concentration diagram of nickel-amine complexes is shown in Figure 5.

The mass balance of all nickel species can be described as:

$$C = [Ni^{2+}] + [NiNH_3^{2+}] + [Ni(NH_3)_2^{2+}] + [Ni(NH_3)_3^{2+}] + [Ni(NH_3)_4^{2+}] \quad (38)$$

where C is the total molar concentration of nickel species.

The fraction of nickel species, α_n, can be determined by:

$$\alpha_0 = \frac{[Ni^{2+}]}{C} \quad (39)$$

$$\alpha_1 = \frac{[NiNH_3^{2+}]}{C} \quad (40)$$

$$\alpha_2 = \frac{[Ni(NH_3)_2^{2+}]}{C} \quad (41)$$

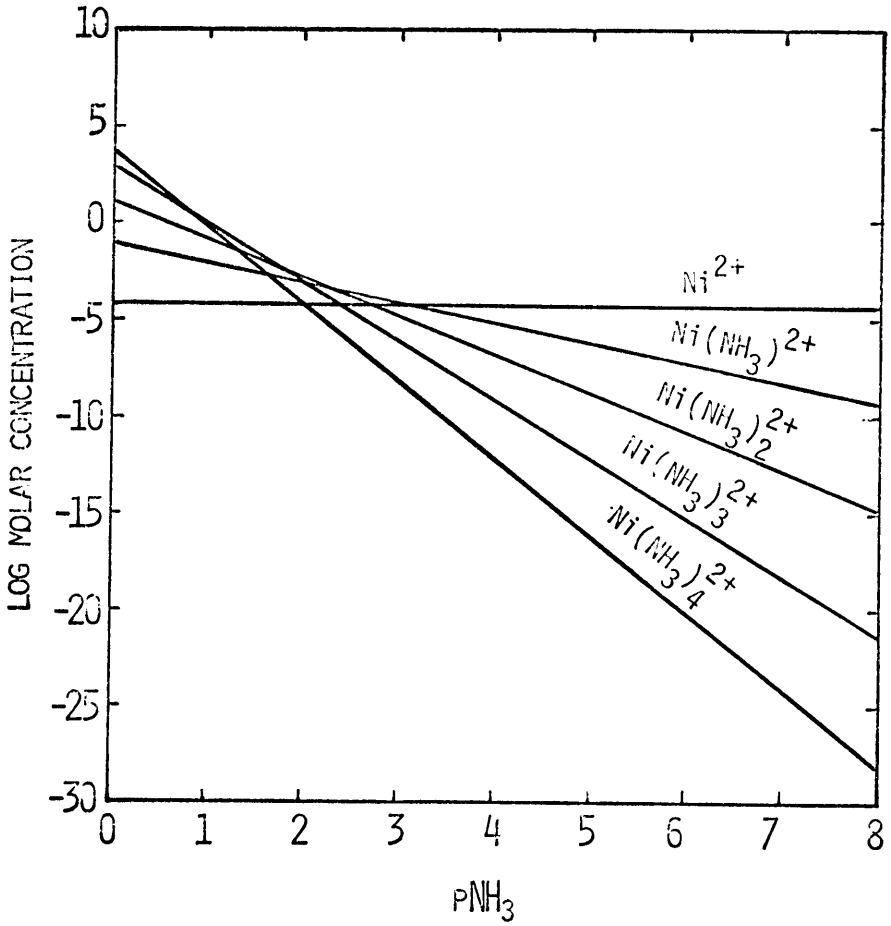

Figure 5. Log Concentration Diagram for Nickel Amine Complexes.
(Ni^{2+} = 8.5 x 10^{-5} M)

$$\alpha_3 = \frac{[Ni(NH_3)_3^{2+}]}{C} \tag{42}$$

$$\alpha_4 = \frac{[Ni(NH_3)_4^{2+}]}{C} \tag{43}$$

Figure 6 shows the distribution diagram of nickel-amine complexes as a function of ammonia concentration expressed as $-\log[NH_3]$.

Cheng et al.(13) studied the uptake of heavy metals by activated sludge. The heavy metal uptake at low metal ion concentration was due to the formation of metal-organic complexes. However, precipitation of heavy metals occurred at higher metal ion concentrations in addition to biological uptake. The results indicated that the order of biological uptake of heavy metals was lead>copper>cadmium>nickel. The rate of uptake depended on metal ion concentration, pH, and organic concentration.

Adams et al. (14) concluded that heavy metals at low concentration tended to form organic-metallic complexes with certain essential extracellular materials and thereby inhibited microbial metabolism. These extracellular materials furnished substantial functional groupings present as polysaccharides, lipids, and nucleic acids in microbial protoplasm (15).

Removal of metal ions from polluted water through complex formation of metal ions was investigated by Jellinek and Sangal (16). Polygalacturonic acid, a natural polyelectrolyte was an efficient complexation agent for Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}. The metal-polyelectrolyte complex-formed was precipitated and the metal ions could be recovered.

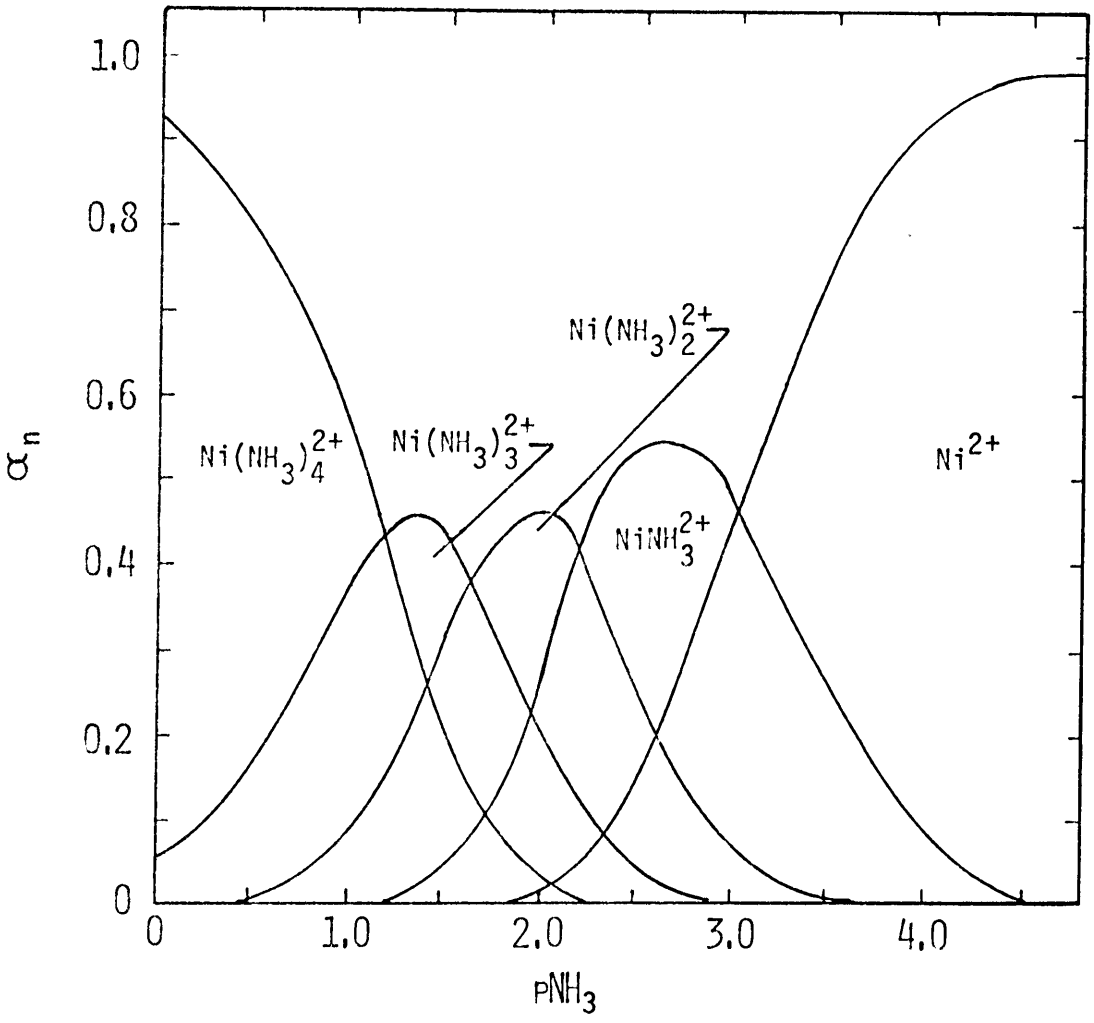

Figure 6. Distribution Diagram for Nickel Amine Complexes.

Adsorption of Nickel

Adsorption of nickel is a significant phenomenon in the removal of nickel ions in water and wastewater treatment process.

Studies made by Dugan and Pfister (17) showed that Zoogloea ramigera was capable of adsorbing nickel, iron, cobalt and copper to as high a value as 34 percent by weight. The adsorption of metal ions onto microbial cells was attributed to extracellular polysaccharides excreted by microorganisms which had a very high affinity for various metal ions (18,19)

Neufeld et al. (20) investigated the kinetics of metal adsorption by activated sludge. The results indicated that the overall affinity of biomass for heavy metals decreased in the order of Pb>Cd>Hg>Cr(III)> Cr(VI)>Zn>Ni.

Distribution of nickel in wastewater treatment processes depended on complex formation, precipitation and adsorption of nickel. The highly complex environment in wastewater treatment imposes difficulty for accurate prediction of nickel distribution in the system. However, a knowledge of nickel behavior in aqueous systems is important to assess the toxicity of nickel in the activated sludge process.

BIOCHEMICAL ASPECTS OF HEAVY METALS

The activated sludge environment is an aquatic environment. The microorganisms which are commonly found in the system are bacteria, fungi, protozoa, rotifers, algae, crustaceans and viruses. These microorganisms for the most part grow and obtain energy through bio-

chemical reactions mediated and directed by enzyme systems. These reactions provide the energy necessary for the various functions of the cell and support the synthesis of material upon which the cell depends for maintenance, growth, and multiplication.

Enzymes are protein molecules. Their function is to catalyse biochemical reactions in living organisms. An enzyme reaction can be represented by the following equation:

$$\underset{\text{Enzyme}}{[E]} + \underset{\text{Substrate}}{[S]} \rightarrow \underset{\substack{\text{Enzyme}\\\text{Substrate}\\\text{Complex}}}{[E][S]} \rightarrow \underset{\text{Product}}{[P]} + \underset{\text{Enzyme}}{[E]}$$

The enzyme combines with substrate to form an enzyme substrate complex and converts it to a product and the original enzyme. The rate of biochemical reactions catalysed by enzymes is dependent on pH, temperature and substrate concentration.

For many enzymes the presence of a specific metal ion is necessary for the reaction to proceed. Mg^{2+}, Mn^{2+}, Zn^{2+} and Fe^{2+} are commonly required and are termed "activators" or "cofactors". The functions of a cofactor (21, 22) are: 1) complexing with the enzyme protein to provide optimum conformation for interaction of enzyme with the substrate, 2) coordinating themselves between substrate and the enzyme, thus positioning the two in spacial alignment, 3) maintaining physiological control by antagonizing the activating of some other metal on the enzyme system or 4) participating in the overall reaction as an active agent that accepts a chemical group from the primary substrate and subse-

quently transfers it to a second substrate in the same or a different reaction.

The stimulatory effects of metal ions are dependent on its ability to perform a nutritional function. As the concentration of metal ions increase, more and more enzyme is activated and the reaction rate increases. However, the excess of metal ions can react with an enzyme which is not a metallic activator and results in a decrease in the reaction rate. Lower concentration of metal ions than the toxic level have been found to produce a stimulatory effect.

Although many metal ions are required for enzymatic activities, some metal ions are powerful inhibitors of enzymatic reactions. The examples of these metal ions are chromium, zinc, copper and nickel. These metal ions tend to form stable complexes with the functional group present as polysaccharide, lipids and nucleic acids in biological protoplasm. These stable complexes can block the active sites and thus decrease the rate of biochemical reaction.

The presence of two or more metal ions in the enzyme system may influence the effects of metal ions on enzymatic activity. Synergism is a phenomenon where the presence of one metal ion will increase the inhibitory effect of the other metal ion. Antagonism is a situation where the presence of one metal ion will decrease the inhibitory effect of another metal ion. Antagonism is achieved by another metal ion if it can reactivate the inactivated enzyme or speed up the blocked enzyme in another manner, such as activation of the enzyme through alternate enzyme pathways. Thus, antagonism is the stimulatory effect of one

metal ion which overcomes the toxic effect of the other.

STIMULATION AND INHIBITION BY NICKEL

Nickel has not yet been found as an intrinsic ingredient of any enzyme. However, stimulation of enzymatic activity by nickel has been reported by many investigators. Eggleston (23) investigated the effects of cations on amino acid decarboxylation in Escherichia coli and Clostidium welchii. Results showed that the activity of amino acid decarboxylase in the microorganisms acting upon L-arginine, L-lysine, L-ornithine and L-glutamate was increased up to 45% by addition of nickel. Webster (24) studied the synthesis reaction of acetyl-CoA in relation to cations. Formation of acetyladenylate was stimulated by nickel when the requirement for a metal cofactor was satisfied.

Some enzymes are associated with a specific metal ion in their native state. The metal cofactor can sometimes be removed and replaced by another metal ion. A study made by Coleman and Valle (25) indicated that the activity of carboxypeptidase was lost on removal of zinc but the activity was resumed when nickel was added to the apoenzyme.

Inhibition of an enzyme by a heavy metal implies a decrease in the rate of biochemical reactions. The inhibition of nickel may have an effect on one biochemical reaction while the others may remain unaffected or may actually increase. In oxidative phosphorylation, the formation of ATP is inhibited by inhibitor molecules while the oxidation of substrate, oxygen uptake and product formation are actually increased (2). Formation of ATP is extremely important in many energy producing

and enzymatic biological processes and is inhibited by nickel.

Joo' et al. (26) reported that ATPase activity in the brain capillaries of rats was lost after injection of $NiCl_2$. However, nickel inhibition of ATP can be reversed by amino acids due to complex action sequestering of nickel ions and prevention of it from exerting any effect on the enzyme (2). Nickel can activate or inhibit various enzymatic reactions. The degree of effect depends on environmental conditions such as pH, nickel ion concentration, the specificity of enzymes, etc.

The activated sludge process contains a mixed microbial population that metabolizes numerous substrates. Many biochemical reactions occur at the same time and prevent any accurate determinations of the effects of nickel at an enzymatic level.

III. THE ACTIVATED SLUDGE PROCESS

The activated sludge process utilizes a culture of microorganisms to metabolize the organic and inorganic substances in wastewater. The process can be best described as a continuous flow process with cellular recycle which allows a greater microorganism residence time than the hydraulic residence time. A common bacterium found in the activated sludge population is Zoogloea ramigera. The important characteristic of this organism is its ability to synthesize a polysaccharide gel and to agglomerate into a biological floc (27).

The biochemical reaction which occurs during oxidation of organic materials by bacteria may be expressed stoichiometrically as (28):

$$\text{Organics} + \text{Nutrients} + O_2 + \text{Bacteria} \rightarrow \text{New Bacteria} + CO_2 + H_2O + \text{Organic and Inorganic End Product} + \text{Heat} \quad (44)$$

Proper environmental conditions must be maintained during the operation of the process. These environmental conditions include pH, temperature, dissolved oxygen and absence of toxic materials.

MICROBIAL GROWTH

General Bacterial Growth Cycles

Bacteria in the proper environmental conditions, containing an excess of food supply and inorganic nutrients necessary for growth, can reproduce by binary fission. However, the growth of bacteria is limited by various environmental conditions, such as substrate concentration,

nutrient concentration, etc. The general growth pattern of bacteria in a batch culture is shown in Figure 7. As illustrated in Figure 7, the general growth pattern has four distinct phases called the lag phase, exponential phase, stationary phase, and death phase or endogenous phase.

When the bacterial population is placed into a new environment, growth usually begins after a period of time called the lag phase. This is because the cells are usually depleted of various essential coenzyme or other cell constituents and time is required for their synthesis. This lag phase is also observed when the population is transferred from a rich culture medium to a poorer one because the cell must have a complete complement of enzymes for the synthesis of the essential metabolites not present in that medium.

Under optimal conditions maximum growth rate occurs in the exponential phase. The growth rates of different organisms vary widely depending upon inherent genetic limitations. For a given organism, the growth rate is dependent on environmental conditions and the composition of culture medium. The constant maximum growth rate is a characteristic of the exponential growth phase. As the food supply or essential nutrient is depleted or the presence of toxic metabolic end product has accumulated, deviations from the exponential growth phase arise. The growth rate decreases until the stationary phase is reached. The bacterial population remains stationary because the cells have exhausted the substrate or nutrients necessary for growth and the growth of new bacterial cells is offset by the death of old bacterial cells. As the

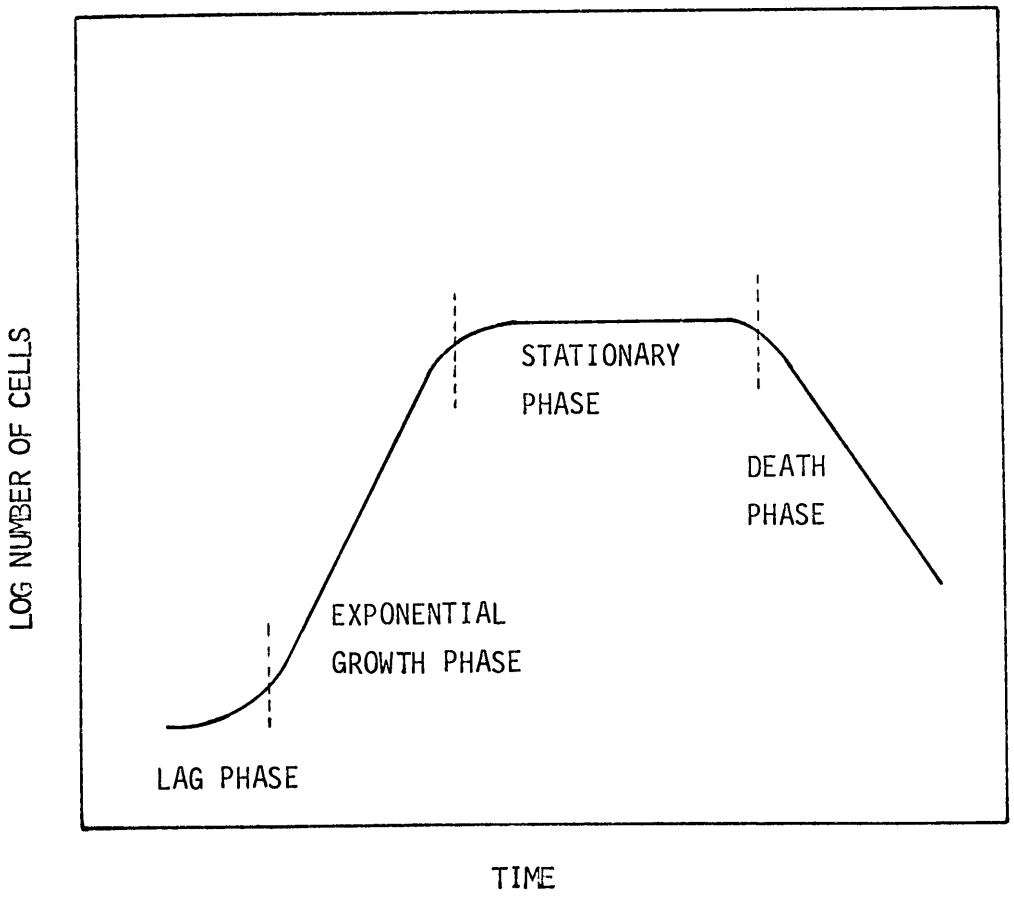

Figure 7. General Microorganisms Growth Pattern (29).

food supply continues to deplete, the microorganisms are forced to metabolize their own protoplasm without replacement. Often the dead cells lyse and the amino acids, carbohydrates, and other components freed from the lysed cell are used as nutrients by the remaining living organisms (cryptic growth). Due to nutrient depletion and toxic-product build up, the microbial population can not sustain itself and the endogenous or death phase begins.

Microbial Growth Kinetics

For a continuous flow reactor microbial growth has been shown to be expressed mathematically as (42):

$$R_g = -Y_{max}R_{su} - k_dX \qquad (45)$$

where R_g = net growth rate of microorganisms, mass/volume-time

Y_{max} = maximum microorganism cell yield coefficient, mass/mass

R_{su} = rate of substrate utilization, mass/volume-time

k_d = endogenous respiration coefficient or maintainance energy coefficient, $time^{-1}$, and

X = concentration of microorganisms, mass/volume.

This equation has been used to describe microbial growth in biological wastewater treatment processes. The rate of substrate utilization, R_{su}, is a negative term. In a batch biological reactor where the microorganisms grow in the presence of excess substrate, the growth of microorganisms is in the exponential phase where the maintainance energy requirement is very small and may be neglected. For maximum logarithmic growth equation [45] becomes:

$$R_g = -Y_{max} R_{su} \tag{46}$$

Thus, the maximum microorganism cell yield coefficient can be defined as

$$Y_{max} = -\frac{R_g}{R_{su}} \tag{47}$$

KINETICS OF THE ACTIVATED SLUDGE PROCESS

The activated sludge process can be modelled as a completely mixed reactor with cellular recycle. A schematic diagram of the process is shown in Figure 8. Kinetic models for this process can be developed based on materials balance equations written around a system boundary (Figure 8).

An operating parameter, mean cell residence time, Θ_c is related to the microbial growth rate, R_g, for the system and is defined as

$$\Theta_c = \frac{VX}{Q_w X + (Q-Q_w)X_e} \tag{48}$$

in which

Θ_c = mean cell residence time, time

V = volume of total reactor, volume

Q_w = wasted sludge volumetric flow rate, volume/time

Q = influent volumetric flow rate, volume/time

X = microorganism concentration in total biological reactor, mass/volume

X_e = microorganism concentration in the effluent, mass/volume.

Mean cell residence time, Θ_c can be used as the basis for comparing

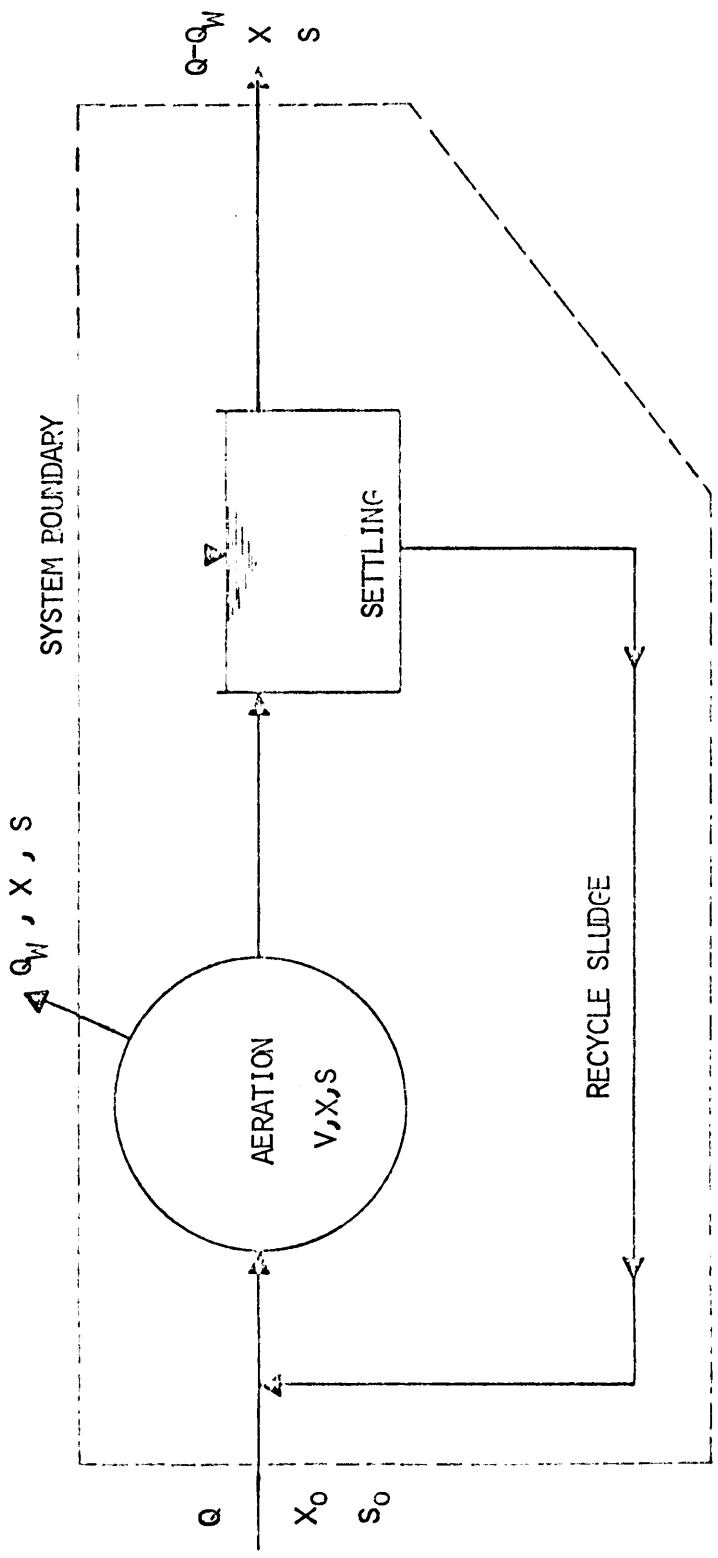

Figure 8. Completely Mixed Activated Sludge Process (31).

process parameters under different operating conditions. The effluent organic concentration, treatment efficiency, microorganism concentration, sludge production and sludge settling characteristics are all functions of mean cell residence time (32).

A mass balance equation written to describe microbial growth for the system shown in Figure 8 is as follows:

$$\begin{bmatrix}\text{Rate of change of microorganism concentration in reactor}\end{bmatrix} = \begin{bmatrix}\text{Rate of microorganism inflow to reactor}\end{bmatrix} + \begin{bmatrix}\text{Net rate of microorganism growth in the reactor}\end{bmatrix} - \begin{bmatrix}\text{Rate of microorganism outflow from reactor}\end{bmatrix}$$

$$V\left(\frac{dX}{dt}\right) = QX_o + (-YR_{su} - k_dX)V - [Q_wX + (Q-Q_w)X_e] \qquad (49)$$

Assuming microorganisms are absent in the influent wastewater (X_o=0) and steady state conditions prevail ($\frac{dX}{dt}$ = 0), equation [49] can be rearranged to yield:

$$\frac{1}{\Theta_c} = -Y_{max}\frac{R_{su}}{X} - k_d \qquad (50)$$

The term ($-\frac{R_{su}}{X}$) is the specific utilization rate, U, which can be defined as:

$$U = \frac{S_o-S}{\Theta X} \qquad (51)$$

in which U = specific utilization rate, $time^{-1}$

Θ = hydraulic residence time, time

= volume of total reactor/influent volumetric flow rate.

Substituting equation [51] into equation [50] yields

$$\frac{1}{\Theta_c} = Y_{max}U - k_d \qquad (52)$$

By plotting $1/\Theta_c$ versus U, a graph similar to that shown in Figure 9 is obtained. From the slope and intercept of this graph, values for Y_{max} and k_d can be calculated.

The value of microorganism cell yield, Y_{max}, has been assumed to be constant by sanitary engineers. Ribbons(33) concluded that the value of cell yield is dependent upon 1) oxidation and reduction state of the carbon source and nutrients, 2) degree of polymerization of the substrate, 3) metabolic pathway, 4) growth rate and 5) various physical parameters of cultivation.

For continuous culture growth Sherrard (34) proposed an alternate approach toward analysing the net microbial growth rate by including the effects of endogenous respiration into a variable microorganism cell yield coefficient. This cell yield coefficient is termed the observed yield, Y_{obs}, that varies with mean cell residence time, Θ_c. The net microbial growth rate can be expressed in terms of Y_{obs} as follows:

$$R_g = -Y_{obs}R_{su} \qquad (53)$$

where

Y_{obs} = observed yield, mass/mass.

Rearranging equation [54], the following equation is obtained:

$$Y_{obs} = -\frac{R_g}{R_{su}} \qquad (54)$$

By substituting equation [54] into equation [52] and rearranging, the following relationship is obtained:

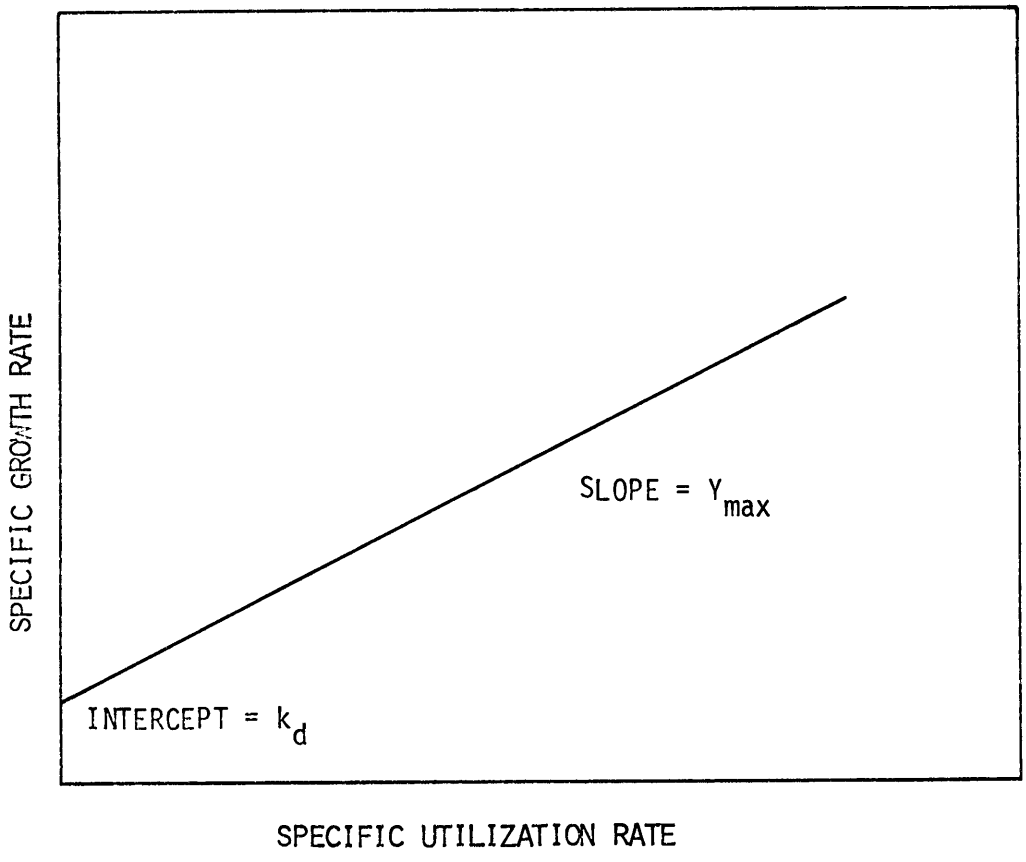

Figure 9. Plot of Specific Growth Rate versus Specific Utilization Rate.

$$Y_{obs} = \frac{Y_{max}}{1+k_d\Theta_c} \tag{55}$$

Rearrangement of this relationship yields

$$\frac{1}{Y_{obs}} = \frac{1}{Y_{max}} + \frac{k_d\Theta_c}{Y_{max}} \tag{56}$$

Sherrard (35) investigated the variation of cell yield in the completely mixed activated sludge process. The results indicated that the value of observed yield decreased as the operating Θ_c increased.

By plotting $1/Y_{obs}$ versus Θ_c on an arithmetic graph paper, value of k_d/Y_{max} and $1/Y_{max}$ can be obtained from the slope and intercept, respectively. Thereby the value of Y_{max} and k_d can also be calculated.

Waste sludge production may be obtained from the expression

$$P_x = \frac{Y_{max}Q(S_o-S)}{1+k_d\Theta_c} \tag{57}$$

$$= \frac{VX}{\Theta_c} \tag{58}$$

where P_x = waste sludge production, mg/day.

For the activated sludge receiving wastewater containing the reactant, i.e., heavy metal, nitrogen, organic material, etc. a general mass balance equation written to describe a reactant for the system previously shown in Figure 8 is as follows:

[Mass of reactant inflow to reactor] + [Mass of reactant converted in the reactor] = [Mass of reactant outflow from reactor] + [Accumulation of reactant in the reactor]

$$QC_o + VR_c = (Q-Q_w)C_e + Q_wC_w + V(\frac{dC}{dt}) \quad (59)$$

where

C_o = reactant concentration in the influent, mass/volume

C_w = reactant concentration in the wasting line, mass/volume

C_e = reactant concentration in the effluent, mass/volume

R_c = rate of reactant convertion, mass/volume - time.

At steady state conditions there can be no accumulation of mass if reactant in the reactor, i.e., dC/dt = 0.

Rearranging of equation [59] yields

$$VR_c = \frac{(Q-Q_w)C_e + Q_wC_w}{QC_o} \quad (60)$$

Equation [60] can be used as a basis to describe a change in concentration of heavy metals, nitrogen concentration or substrate concentration as they pass through the activated sludge process.

NITRIFICATION IN ACTIVATED SLUDGE PROCESS

The activated sludge process is primarily designed to stabilize organic carbonaceous material in wastewater. It is, however, desirable to stabilize those inorganic compounds that can exert an oxygen demand. The most important inorganic compound is ammonia. The presence of ammonia in a receiving stream can lower the dissolved oxygen in the stream due to nitrification.

Nitrification may be achieved in a biological wastewater treatment process. The extent of nitrification depends on the process environment. Parameters such as pH, temperature, dissolved oxygen, presence of

toxic substances and mean cell residence time are important (36). Another important factor is the BOD_5:TKN ratio.

Under proper environmental conditions the activated sludge process is capable of supporting nitrifying organisms which are responsible for the oxidation of ammonia to nitrite and nitrite to nitrate. These nitrifier organisms consist of the genus Nitrosomonas and Nitrobactor. Neglecting the nitrogen incorporated into cellular tissue, Nitrosomonas oxidizes ammonia to nitrite according to the reaction:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2\ NO_2^- + 2H_2O + 4H^+ \qquad (61)$$

and Nitrobactor converts nitrite to nitrate according to the reaction:

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobactor}} 2NO_3^- \qquad (62)$$

The overall reaction for nitrification can be written as follows:

$$NH_4^+ + 2O_2 \xrightarrow{\text{Nitrifiers}} NO_3^- + 2H^+ + H_2O \qquad (63)$$

Nitrification can be achieved in either the one stage activated sludge process or two stage activated sludge process. Downing et al. (37) have postulated that for the nitrification to occur the growth rate of total activated sludge microorganisms must be less than the maximum growth rate of nitrifying microorganisms. The effects of environmental conditions such as dissolved oxygen, temperature, pH and concentration of inhibitor can be predicted from their effects on the growth rate of nitrifying bacteria.

Lawrence and McCarty (38) and Jenkins and Garrison(39) have proposed that mean cell residence time or sludge age is the applicable

parameter for the design and control of nitrification in the activated sludge process. Lawrence and McCarty (38) suggested that to insure nitrification at a high efficiency, the value of mean cell residence time for the activated sludge process must be greater than the largest value of the minimum mean cell residence time of nitrifying bacteria that can be maintained in the system. Jenkins and Garrison (39) and other investigators(38,40) have indicated that a mean cell residence time of approximately 3 days was the point of onset of nitrification and nearly complete nitrification occurs at approximately 10 day θ_c at normal wastewater temperature. No nitrification occurs at mean cell residence time less than 3 days at normal wastewater temperature (41).

The BOD_5:TKN ratio also affects the rate of nitrification due to its impact on the fraction of nitrifiers in the activated sludge process. A high BOD_5:TKN ratio increases the fraction of heterotrophic bacteria and thereby reduces the nitrifier fraction and the rate of nitrification. The rate of nitrification can be increased by lowering the BOD_5:TKN ratio (42).

Certain heavy metals are toxic to nitrifying bacteria. Nickel, silver, chromium, copper and cadmium are among those metals which are capable of inhibiting nitrification. Tomlinson et al. (43) and other investigators (44), investigated the inhibition of nitrification in the activated sludge process. The results indicated that the salts of heavy metals, such as nickel, chromium, and copper inhibited the growth of Nitrosomonas europaea and nitrifying activated sludge. However, a greater concentration of metals were required to reduce the nitrifying

ability of activated sludge to the same extent as those for the pure culture of N. europaea. They concluded that the presence of heavy metals such as copper, mercury and chromium appeared to affect Nitrosomonas in mixtures of activated sludge and sewage very much less than in pure culture. They reasoned that this is likely to be due to the chemical complexes or physical interactions between the metal and organic matter in the sewage or sludge. Barth et al. (45, 46, 47) and McDermott et al. (48, 49, 50) studied the effects of heavy metals on biological wastewater treatment processes. Results indicated that nitrification in the process was inhibited by the presence of heavy metals at low concentration and there was no evidence of acclimation of nitrifying organisms to heavy metals. Weber (51) and Bagby (52) studied the effects of cadmium and nickel-cadmium on the activated sludge process. The degree of nitrification decreased as the influent metal concentration increased. Higher mean cell residence times were required to prevent washout of nitrifying organisms at higher influent metal concentration.

Slug dosages of nickel and zinc retard the rate of nitrification at concentrations greater than 0.5 mg/l as reported by Beckman et al. (53). However, slug dosages of copper and chromium at 1.0 mg/l did not effect the rate of nitrification.

The stoichiometric equation for nitrification previously expressed by equation [63] implies that the biological oxidation of 1 mg/l of NH_3-N to NO_3^--N will destroy 7.14 mg/l of alkalinity as $CaCO_3$ and that 4.57 mg/l of oxygen is required.

Benninger and Sherrard (54) investigated nitrification and alkalinity destruction in the activated sludge process. The results indicated that the theoretical value of 7.14 mg/l of alkalinity as $CaCO_3$ destroyed per mg/l of NH_3-N oxidized was not obtained. The results from these studies were investigated further by Scearce et al. (55). The latter results also showed that the theoretical value of alkalinity destruction was not obtained. It was then concluded that the theoretical value of 7.14 mg/l of alkalinity destroyed per mg/l of NO_3^--N formed was only valid for a wastewater in which no NH_3-N was produced from mineralization or deamination of organic nitrogen in the process. An equation was formulated to predict the change in alkalinity as mg/l $CaCO_3$ in the activated sludge process. This equation is expressed as follows:

$$\Delta Alk = 3.57[(\Delta \text{filtrate Org-N}) - (\text{Synthesized-N})] - 7.14(\Delta NO_3^-\text{-N}) \quad (64)$$

This equation indicates that 3.57 mg/l of alkalinity as $CaCO_3$ will be produced for every 1 mg/l of organic nitrogen mineralized to ammonia nitrogen. However, incorporation of 1 mg/l of ammonia nitrogen into microbial cell will result in the destruction of 3.57 mg/l of alkalinity as $CaCO_3$. The oxidation of 1 mg/l of ammonia nitrogen to nitrate nitrogen will destroy 7.14 mg/l of alkalinity as $CaCO_3$. Scearce et al. (55) compared the predicted alkalinity based on equation [64] with the measured alkalinity obtained from several laboratory experiments. Figure 10 represents the comparison of the measured alkalinity and the alkalinity predicted by equation [64].

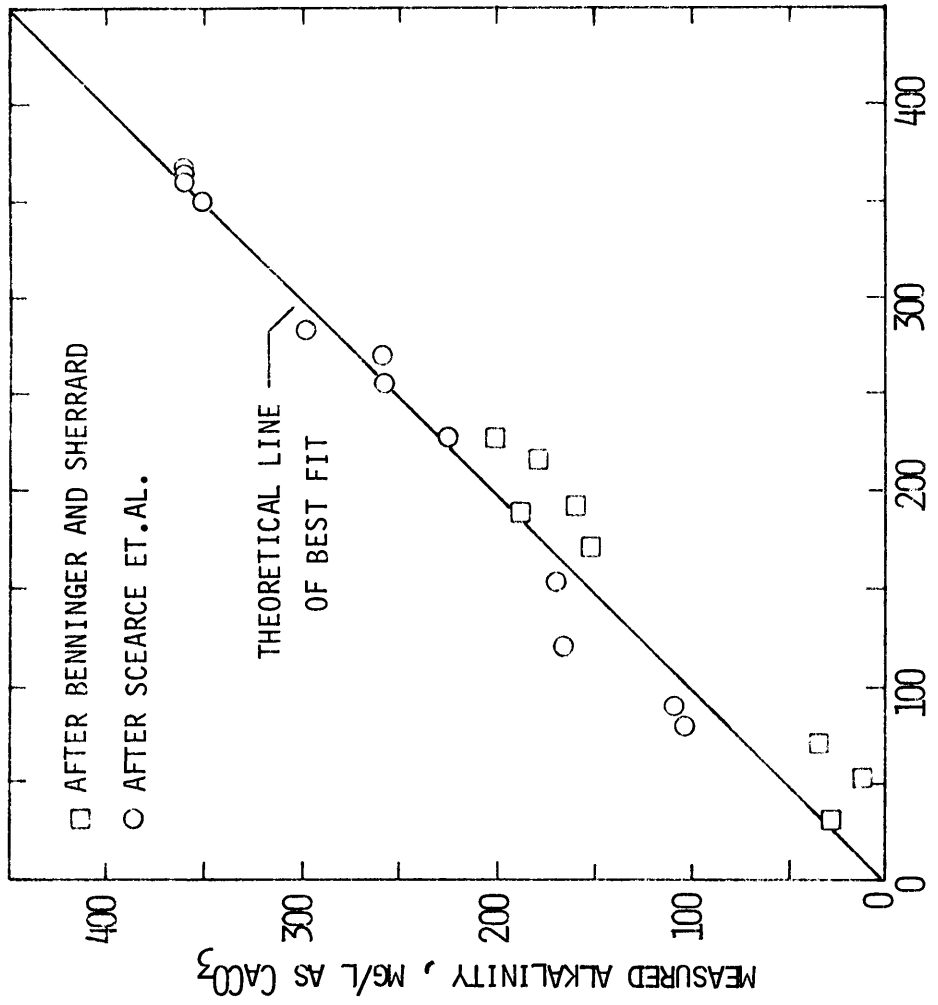

Figure 10. Test of Equation [64], Data from Reference (55).

IV. THE EFFECTS OF HEAVY METALS ON BIOLOGICAL WASTEWATER TREATMENT PROCESSES

The presence of heavy metals in wastewater results from wide usage in metal finishing industries with subsequent discharge of significant quantities of heavy metals. The wastewater being discharged into municipal sewer systems without pretreatment may contain high levels of heavy metals that can cause adverse affects on the biological wastewater treatment process.

With increasing stringent effluent quality requirements, heavy metals have received considerable attention with respect to their toxic effects on aquatic and human life at relatively low concentration. Low concentration of these metals are allowed in the effluent discharges to receiving water. Since practically all municipal wastewater treatment plants and a majority of industrial wastewater treatment facilities utilize biological wastewater treatment processes for stabilization of organic and inorganic substances in their waste stream, it is significant to realize the effects of heavy metal on biological wastewater treatment processes.

Metal ions present in a biological process can be separated into two groups, namely "indispensable" and "dispensable". The indispensable metals may be separated into two classes as "bulk" and "trace" metals. The bulk metals are necessary for life process to function and are found in high concentrations of several grams per kilogram of tissue. The trace elements are found in tissue in the amount of 1-2 mg/kg. The dispensable metallic elements are separated into toxic and non-toxic

elements. The difference between the bulk metals and the trace metals is that the trace metals are transition elements. These transition elements have unfilled inner electron shells which favor stable complex formation. Nickel, copper, chromium and zinc all are examples of transition elements. These metal ions tend to form stable complexes with functional groups such as the polysaccharides, lipids and nucleic acids present in biological protoplasm and, thereby, inhibit normal biological activities.

The toxic effects of nickel in man and animal have been studied by many investigators (2). Toxicity studies have demonstrated that nickel and nickel salts have a relatively low toxicity in various species of animals when administered orally. However, parenteral injections of nickel salts are much more toxic. Major signs of acute nickel toxicity consist of hyperglycemia and gastrointestinal and central nervous system effects. Nickel carbonyl is the organic nickel compound that has been recognized as a cause of human systematic toxicity. The immediate symptoms of nickel carbonyl poisoning are fatigue, headache, nausea, vomiting and irritability (2). Exposure of nickel carbonyl for a period of 3-14 days can cause death which has been attributed to respiratory failure. The effects of specific heavy metal on fish and other aquatic organisms are readily observable based on the concentration which can cause death of the organisms.

Toxicity studies of heavy metals on biological wastewater treatment processes are not as straightforward and simple as studies with human beings or animals. The effects of heavy metals on animals are readily

observable as life versus death. The studies deal with one genus and limited species over the short period of their life span. The life of organisms studied are individually identifiable. Biological wastewater treatment processes contain diverse groups of life forms. The organisms in the process have short generation times and the acclimation of organisms to the toxicant is significant. A shift of predominant species in the process may occur upon receiving a metal bearing wastewater. The degree of toxicity is dependent on the diversity of life forms in the process. The effects of heavy metals on aerobic wastewater treatment processes are different from those on anaerobic treatment processes. Due to the diversity of life form in aerobic wastewater treatment processes, several organism species may be adversely affected without losing total capacity for wastewater stabilization. Anaerobic treatment processes, however, contain a narrow spectrum of life forms and therefore are more susceptible to the toxicity of heavy metals than the aerobic treatment processes. Figure 11 illustrates the responses of aerobic and anaerobic wastewater treatment processes to the dosage of heavy metals.

Acclimation of microorganisms to heavy metals has been reported by many investigators. Kugelman and McCarty (56) studied the toxic effects of cations in anaerobic waste treatment. The results indicated that the two major phenomena which microorganisms mitigate the toxic effect of cation were antagonism and acclimation. The process of acclimation involved in readjustment of the enzyme balance in the cell to provide extra enzymes to replace the damaged enzyme or the construction of short

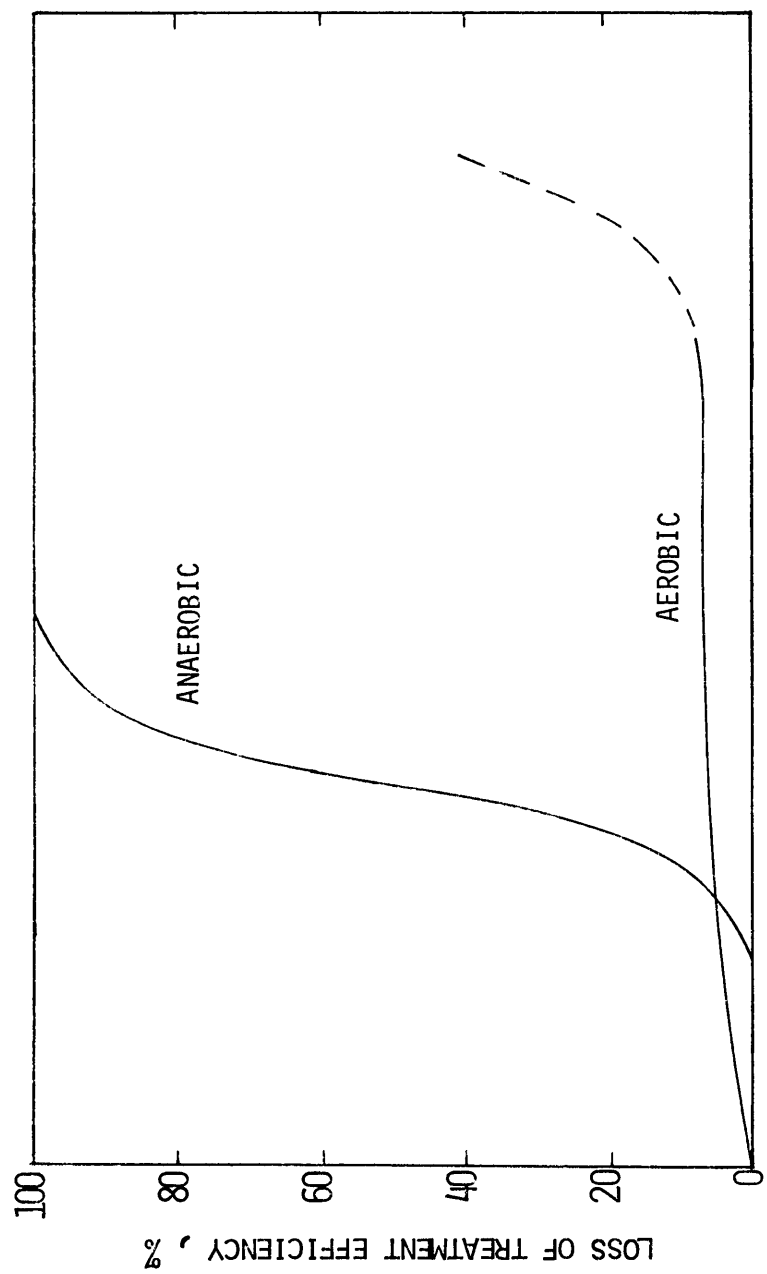

Figure 11. Patterns of Performance Depreciation in Sewage Treatment Processes (15).

pathways around the inhibited enzyme. However, the microorganisms had a certain capacity for acclimation to toxicants and thereby unlimited acclimation is impossible. Combination of antagonism and acclimation resulted in a smaller susceptability than that achieved by either process alone. Kugelman and McCarty (56) reasoned that antagonism could aid acclimation by 1) reducing the strain on the organism by overcoming a portion of the inhibitive effects of toxic cations and thus the organisms can deal with metabolic areas of the cell where the antagonistic cation could not act, and 2) the presence of an antagonistic cation could protect the cell from a toxic cation during the lag time required for acclimation. The acclimation phenomenon is significant to assess the toxicity of heavy metals on biological wastewater treatment processes.

ANAEROBIC WASTEWATER TREATMENT PROCESSES

The responses of each biological treatment process toward receiving heavy metal bearing wastewater are different dependent upon organism species present. As previously shown in Figure 11, the effect of heavy metal doses on anaerobic wastewater treatment processes was greater than that on aerobic wastewater treatment processes. This is due to a narrow spectrum of life forms present in anaerobic wastewater treatment processes.

The toxicity of a heavy metal in anaerobic digestion depends upon the metal complex species which are formed under anaerobic conditions at near-neutral pH values. Precipitated heavy metals are of little conse-

quence with regard to toxicity. McDermott et al. (50) investigated the effects of nickel on the anaerobic digestion process. Results indicated that the anaerobic digestion process was very resistant to the presence of nickel. Slug doses of nickel as high as 200 mg/l did not produce a noticeable effect. They concluded that anaerobic digestion could tolerate high concentrations of nickel due to the soluble nickel introduced with the feed sludge was converted to an insoluble form during digestion. The long mean cell residence time, high alkalinity, hydroxyl ion concentration and sulfide content could cause precipitation of nickel compounds.

McCarty (57) has studied the effects of various cations on anaerobic digestion and found that metal sulfates have very little effect on digester performance in terms of gas production. However, the performance of the digester was significantly decreased by metal chloride salts due to the absence of sulfide which could complex with metal ions and precipitate from the sludges. High concentration of heavy metals present in an anaerobic digester can be tolerated if sufficient sulfide is available to precipitate heavy metals.

Bailey et al. (58) researched the effects of heavy metals on anaerobic digestion. The results indicated that the aceto-bacteria that converted organic complexes to fatty acid were relatively unaffected by the concentrations of chromium. However, the methano-bacteria were unable to convert the fatty acids to methane gas at the same rate and thus a buildup of fatty acids resulted. High concentration of fatty acids in digestion decreased the pH. Methano-bacteria which are very

sensitive to pH were affected and caused a complete breakdown of the process. Operated digesters with high mean cell residence times can tolerate higher concentrations of heavy metal as reported by Bailey et al. (58). For a digester operated at mean cell residence time greater than 20 days, the safe level of trivalent chromium was in excess of 300 mg/l. However, the safe concentration decreased to 100 mg/l and 50 mg/l as the operating mean cell residence time decreased to 17 days and 14 days respectively.

Hayes and Theis(59) studied the removal mechanisms and the distribution of heavy metals among the soluble, precipitated, extracellular and intracellular components of anaerobic digesters. The results indicated that the order of decreasing toxicity was Ni>Cu>Pb>Cr>Zn. Cadmium produced no toxic effects on the digester. Removal of heavy metals in the digester was greater than 95 percent. The mechanism of heavy metal removal was controlled by the solubility of inorganic precipitates, sorption onto digester biomass and incorporation of metals into the biomass. Inhibitory effects of heavy metal on digester organisms occurred near maximum uptake of heavy metals by the organisms. The effects of heavy metals on anaerobic digestion can be minimized by reducing the degree of metal association with the digester biomass. Operation of the digester at the maximum allowable pH and addition of chelating agents or precipitating ligands should increase the tolerance to heavy metal present in the sludges.

Barth et al. (45) investigated the effects of metal bearing sludges on anaerobic digesters. The results showed that the response of anaero-

bic digestion to metal dosage does not exhibit a plateau region as does the aerobic treatment process. The effects of metal on the anaerobic treatment processes could be described as all or nothing reaction. Digestion either proceeded normally or ceased entirely.

AEROBIC WASTEWATER TREATMENT PROCESSES

Most municipal wastewater treatment plants and almost all of the industrial wastewater treatment facilities employ aerobic biological wastewater treatment process to stabilize the organic and inorganic substances in wastewater. An assessment of the response of the processes to receiving metal bearing wastewater is very important to the design and operation of aerobic biological treatment processes.

As can be seen in Figure 11 the response of aerobic treatment is small over a wide range of soluble heavy metal concentration. However, the acclimation of organisms to the heavy metal is limited to certain concentrations. Increasing concentrations of heavy metal beyond a certain limit will cause failure of the process. Barth (15) has reasoned that the aerobic treatment process can tolerate a wide range of heavy metal concentrations because of the high diversity of organisms present in the process. Heavy metals may adversely affect several organism species without significantly affecting total biological treatment efficiency.

McDermott et al. (50) investigated the effects of nickel on the activated sludge process. The results showed that the COD removal efficiency of the activated sludge was significantly affected by con-

tinuous doses of nickel concentration of 2.5, 5 and 10 mg/l. However, the effect of continuous doses of nickel at 1 mg/l was insignificant. The COD removal efficiency of this nickel-fed unit was not significantly different from the control unit. The activated sludge unit studied could tolerate slug doses of nickel up to 200 mg/l. They concluded that the heterotrophic phase of activated sludge process can tolerate, without reduced efficiency, the continuous doses of nickel at concentrations no greater than 1 mg/l, and thus nickel concentration of 1 mg/l can be considered near the threshold limit of nickel toxicity. Barth et al. (45, 46) studied organic loading in relation to the toxicity of heavy metals in the activated sludge process. It was shown that the increase in organic load increased the effluent COD concentration. However, variations of organic loading did not significantly affect the toxicity of copper to the activated sludge process under the conditions studied. Increasing organic loading affected the distribution and form of metal and resulted in high metal removal efficiency at a high organic concentration. Heavy metals removal by the activated sludge was studied by Oliver and Cosgrove (60). They have pointed out that the removal of heavy metals by the sludges occur in two stages. Firstly, by primary settling of insoluble metals or metal sorption to particulates. Secondly, by sorption of dissolved metals or fine particulate metals to the biological floc in the aeration tanks with the subsequently settling out of the biological floc in the secondary clarifier. Stones (61, 62, 63, 64, 65) reported that nickel, iron, lead, copper and zinc were removed by the activated sludge process up to 90 percent. Mechanisms of heavy metal

uptake in the activated sludge process were investigated by Cheng et al. (11). Results have indicated that the uptake of heavy metal by activated sludge can be characterized by a short term, rapid metal uptake phase followed by a long term, slow phase uptake. The uptake of heavy metal at low concentration is due to the formation of metallo-organic complexes. At high heavy metal concentrations, however, the metal ions precipitate from solution in addition to the uptake of heavy metal by the activated sludge. Metal uptake by biological solids depends on several factors including solubility of metal ions, metals concentration, pH,concentration of organic matter and amount of biomass present in the system. The order of metals uptaken by activated sludge was found to be in the sequence of lead>copper>cadmium>nickel. Neufeld et al. (18) have developed kinetic and equilibrium relationships describing the accumulation of various heavy metals in activated sludge. These results showed that the overall affinity of biomass for heavy metals decreased in the order of Pb>Cd>Hg>Cr(+3)>Cr(+6)>Zn>Ni.

One factor that affects the performance of an activated sludge process is separation of sludge solids from the effluent in the secondary clarifier (66). Deflocculation is usually the result of a presence of toxic materials present in the process. Neufeld (67) studied activated sludge deflocculation caused by the presence of heavy metal in the process. Deflocculation occurred almost immediately upon receiving an influent containing mercury. Neufeld (67) indicated that in the operation of the activated sludge process receiving metal bearing wastewater, a potential problem may arise with regard to the possibility

of substantial loss of biomass in the form of pinpoint discrete solids over the effluent weir of the secondary clarifier. This problem, however may be overcome through the use of polyelectrolytes or other types of liquid solid separators such as a sand filter or centrifuge for cell separation in conjunction with cellular recycle. Parsons and Dugan (19) have also reported that settleable activated sludge microorganisms exist as discrete cell enmeshed in a web of extracellular polysaccharides. Heavy metals present in the system could bind to these polymers and result in sludge deflocculation. On the other hand, the studies made by Moulton and Shumate (68) have indicated that the release of bacterial cells into the effluent is due to the effect of heavy metals on biological reactions rather than the chemical interference of heavy metals.

Current effluent quality standards requires wastewater treatment processes capable of removing both organic and inorganic substances that cause adverse effects on receiving water. An important inorganic substance that can deplete the dissolved oxygen in receiving stream is ammonia nitrogen. Ammonia nitrogen can be removed from wastewater through nitrification processes. As previously discussed, the nitrification in activated sludge process may be inhibited by the presence of heavy metals at relatively low concentrations.

FACTORS AFFECTING THE INFLUENCE OF HEAVY METALS ON BIOLOGICAL WASTEWATER TREATMENT PROCESS

The toxicity of heavy metals to biological wastewater treatment process depends on various factors such as organic loading, mean cell

residence time, heavy metal concentration, pH and microorganism concentration, etc. The toxicity of heavy metal is due to the reaction between heavy metals and the active cellular component such as respiratory enzyme to form inactive complexes.

Salotto et al. (69) investigated the effects of organic loading on the toxicity of copper to the activated sludge process. At 5 mg/l of copper concentration, the results indicated that the percent COD removal and distribution of copper in the process was influenced by high organic loading. The high organic loading produced a low soluble copper content in primary and secondary effluents which could be attributed to the stronger wastewater containing a larger concentration of complexing agents than the diluted wastewater. Copper content of the sludge from the high organic loading unit was higher than that from the low organic loading unit, and consequently, the efficiency of copper removal was higher in the high organic loading unit. It was therefore suggested that control of organic loading and microorganism concentration is necessary to assess the toxicity of the heavy metals on biological wastewater treatment processes.

Bailey et al. (58) reported that varying the operating mean cell residence time in an anaerobic digester affected the toxicity of a heavy metal in the process. The safe level of trivalent chromium in anaerobic digestion was increased from 50 mg/l to greater than 300 mg/l as mean cell residence time increased from 14 days to greater than 20 days respectively.

Directo (70) studied the influences of microorganism concentration

and COD concentration on the toxicity of copper to the activated sludge process. The results indicated that, at constant copper concentration, an increase in microorganism concentration decreased the inhibitory effects of copper. The microorganism concentration, however, is controlled by various factors such as mean cell residence time, influent substrate concentration and hydraulic residence time (34). Adams et al. (14) have concluded that the degree of toxicity of the heavy metal on the biological treatment processes is related to the overall metal equilibrium in the aeration tank. The equilibrium of heavy metal is dependent on heavy metal concentration, microorganism concentration and organic concentration. The concentration of these variables affects the proportion of active components which are tied up in metal ligand complexes and, subsequently, affect the extent of metal toxicity. However, the metabolically inactive cellular components which have been complexed by metal ions present in the process may be reinstated by addition of a complexing agent or by dilution. The respiratory enzymes and other cellular materials may revert to the active form upon addition of a strong chelating agent. Consequently, a decrease in heavy metal dosage, an increase in organic loading or an increase in microorganism concentration should decrease the proportion of active cellular components which are tied up as metal ligand complexes and thereby improve the performance of the activated sludge process.

SUMMARY

The toxicity of heavy metals to biological wastewater treatment

process depends on various factors including heavy metals concentration, organic loading, operating mean cell residence time, species of microorganisms, mixed liquor suspended solids concentration, etc. Acclimation of microorganisms to heavy metals is a very important phenomenon for a biological wastewater treatment process receiving metal-laden wastewater.

V. EXPERIMENTAL PROCEDURES

To investigate the effects of nickel on the activated sludge process, a slug fed batch biological reactor system and a continuous flow with internal cell recycle system (CFSTR) were utilized. These biological reactor systems were operated at 21±2°C in a controlled temperature room. For convenience of presentation, each reactor system is presented separately.

SLUG FED BATCH REACTOR SYSTEM

The effects of nickel on microbial growth rate and substrate utilization rate in relation to substrate and nickel concentrations, were studied by utilizing seven batch reactors. Six batch reactors were subjected to acclimated and shock doses of nickel. One reactor was utilized for a control batch reactor. The parameters monitored for this experiment were chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), mixed liquor volatiled suspended solids (MLVSS) and soluble nickel concentration.

Laboratory Apparatus

The reactors were made of glass and each had a total volume of 3.8 liters. The initial operating volumes were 2.0 liters. Air was introduced into each reactor through a porous stone diffuser to maintain dissolved oxygen concentrations greater than 2.0 mg/l and to provide vigorous mixing. Compressed air entered through a water trap and was followed by a cotton air filter to prevent contaminants from enter-

ing the reactors. A manifold with adjustable air valves equalized the air into each reactor. A mechanical mixer was attached to each reactor to further provide adequate mixing conditions at all times. Samples were taken through sampling tubes which extended into the reactor contents. These were kept at a fixed position during the experiments. A schematic diagram of the batch laboratory apparatus is shown in Figure 12.

Feed Solution

The chemical composition of the feed solution is listed in Table V. Feed solutions were designed to have an initial chemical oxygen demand of 400 mg/l in each reactor. Nickel chloride was added to each of three reactors to provide nickel concentrations of 1, 5 and 10 mg/l. One reactor received no nickel and served as the control reactor.

System Operation and Sampling Techniques

The activated sludge microorganisms for seeding a 10 liter reserve batch reactor were obtained from the wasted mixed liquor suspended solids of an operating continuous flow bench scale reactor. This reactor was fed a basic nutrient solution without nickel and served as a reserve reactor. The reserve reactor was operated on a fill and draw basis for a period of 1 week to allow a build-up of microorganisms to a concentration of approximately 710 mg/l.

For the shock load experiment, two liters of mixed liquor suspended solids, MLSS, were transferred to each of the experimental batch reactors. The feed solution was added into each reactor, and nickel was

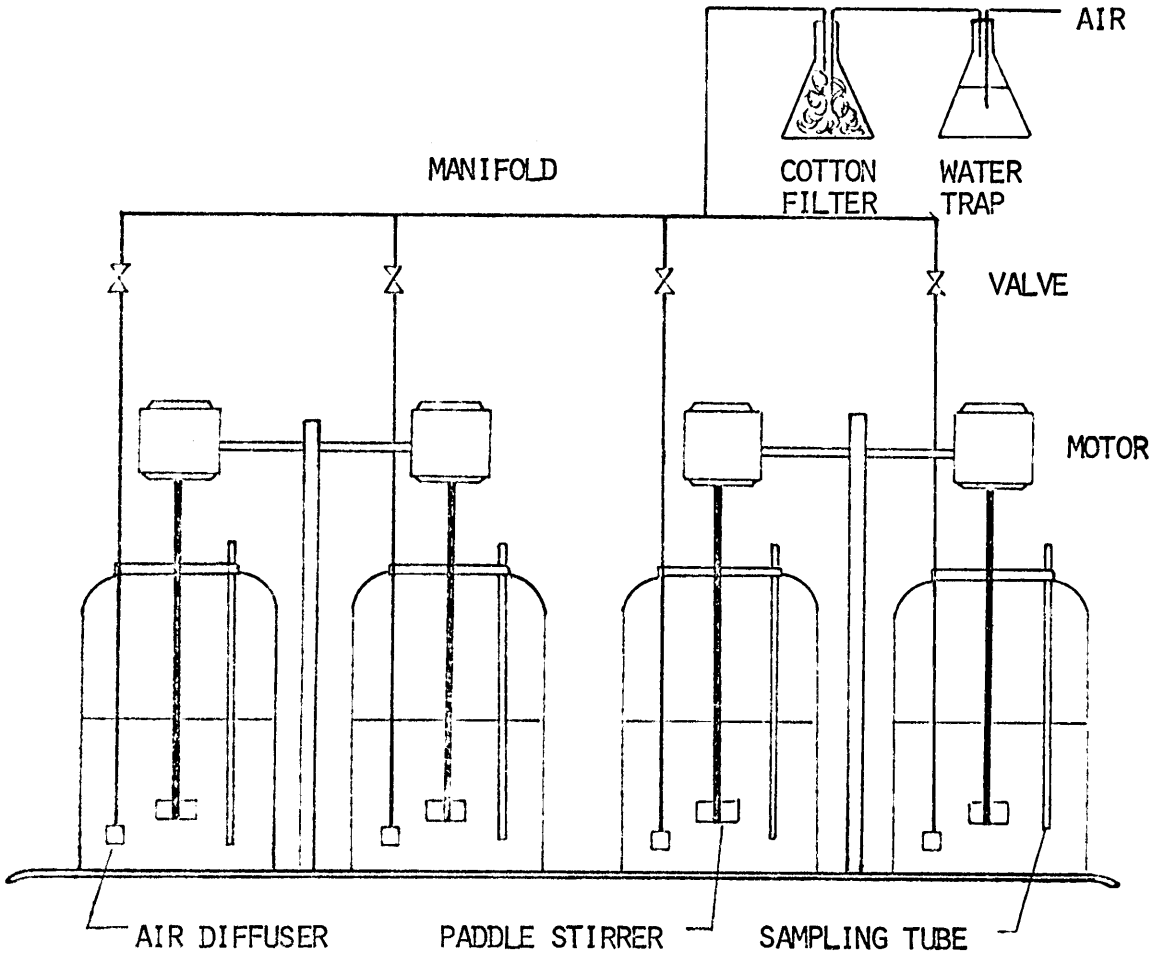

Figure 12. Completely Mixed Batch Reactor System.

TABLE V. COMPOSITION OF FEED SOLUTION FOR SLUG FED BATCH REACTOR EXPERIMENTS.

Chemical	Stock Conc. (gms/2 liters)		Quan. Used (ml/2 liters)	Final Conc. (mg/l)
Bacto-Peptone	129.00		11.0	354.75
$MgSO_4 \cdot 7H_2O$	20.00		10.0	50.00
$MnSO_4 \cdot H_2O$	2.00		10.0	5.00
$FeCl_3 \cdot 6H_2O$	0.25		10.0	0.63
$CaCl_2$	1.50		10.0	3.75
$(NH_4)_2SO_4$	200.00		5.3	265.00
KH_2PO_4	104.50	**	13.0	339.00
K_2HPO_4	214.00		13.0	695.00
$NiCl_2 \cdot 6H_2O$	8.10		*	*

* Dependent on Concentration Utilized
** Phosphate Buffer Solution

introduced into each reactor, except for the control reactor. Then two 80 ml samples were collected from each reactor at 0, 1, 3, 5, 7, 9, 11 and 13 hours. Two 25 ml samples were filtered for solids determinations. Filtrate samples were acidified to pH$\leq$2.0 and stored at 4°C for chemical oxygen demand and soluble nickel concentration determinations.

For the reactors which were acclimated to nickel, approximately 133 ml of mixed liquor from 2 liter batch reactors was wasted daily to give a 15 day mean cell residence time. The feed solution added to each reactor is shown in Table V. After adding the feed to each reactor, tap water was added to give a volume of 2 liters. The batch reactors were operated on this basis for a period of one and one-half months before sampling began. Sampling procedures were identical to the shock loading experiments discussed previously.

Analytical Techniques

Mixed liquor suspended solids, MLSS, and mixed liquor volatile suspended solids, MLVSS, determinations were performed in accordance with Standard Methods for the Examination of Water and Wastewater (71), and were obtained by using 36x22 mm. Gooch crucibles with 2.1 centimeters glass fiber filters (Reeve Angel Type 934 AH, Whatman Inc.). An analytical balance (Model H10, Mettler Instrument Corp.) was used to weigh the samples in solids determinations.

Dissolved oxygen concentration in the mixed liquor was measured with an oxygen meter (Model 54 ARC, Yellow Spring Instrument Co., Inc.).

Determinations of chemical oxygen demand concentration, soluble

nickel concentration and pH measurement are presented later in this chapter.

CONTINUOUS FLOW REACTOR SYSTEM WITH CELL RECYCLE

To investigate the influences of nickel on the continuous flow activated sludge process, two bench scale continuous flow reactors with internal cell recycle were employed to conduct 15 steady state continuous flow experiments. The objectives of these experiments were to determine the effect of nickel on the efficiency of treatment, biokinetic constants, and nitrification of the activated sludge process in relation to organic substrate and nickel concentrations.

Laboratory Apparatus

A schematic diagram of the continuous flow reactors used is shown in Figure 13. The total reactor volume utilized was 8.5 liters. An adjustable baffle plate separated the aeration basin and sedimentation basin into two compartments. The aeration chamber contained 6.0 liters and the sedimentation chamber 2.5 liters.

Air was supplied to each reactor through 2 porous stone diffusers. The position of these diffusers was adjusted to obtain optimum mixing and sludge recirculation. A water trap followed by a cotton air filter were employed to prevent oil and other contaminants from entering the reactor through the compressed air flow line.

Two calibrated 19 liters "Nalgene" carboys were used to prepare the feed solution daily. These feed solutions were fed to each reactor at a

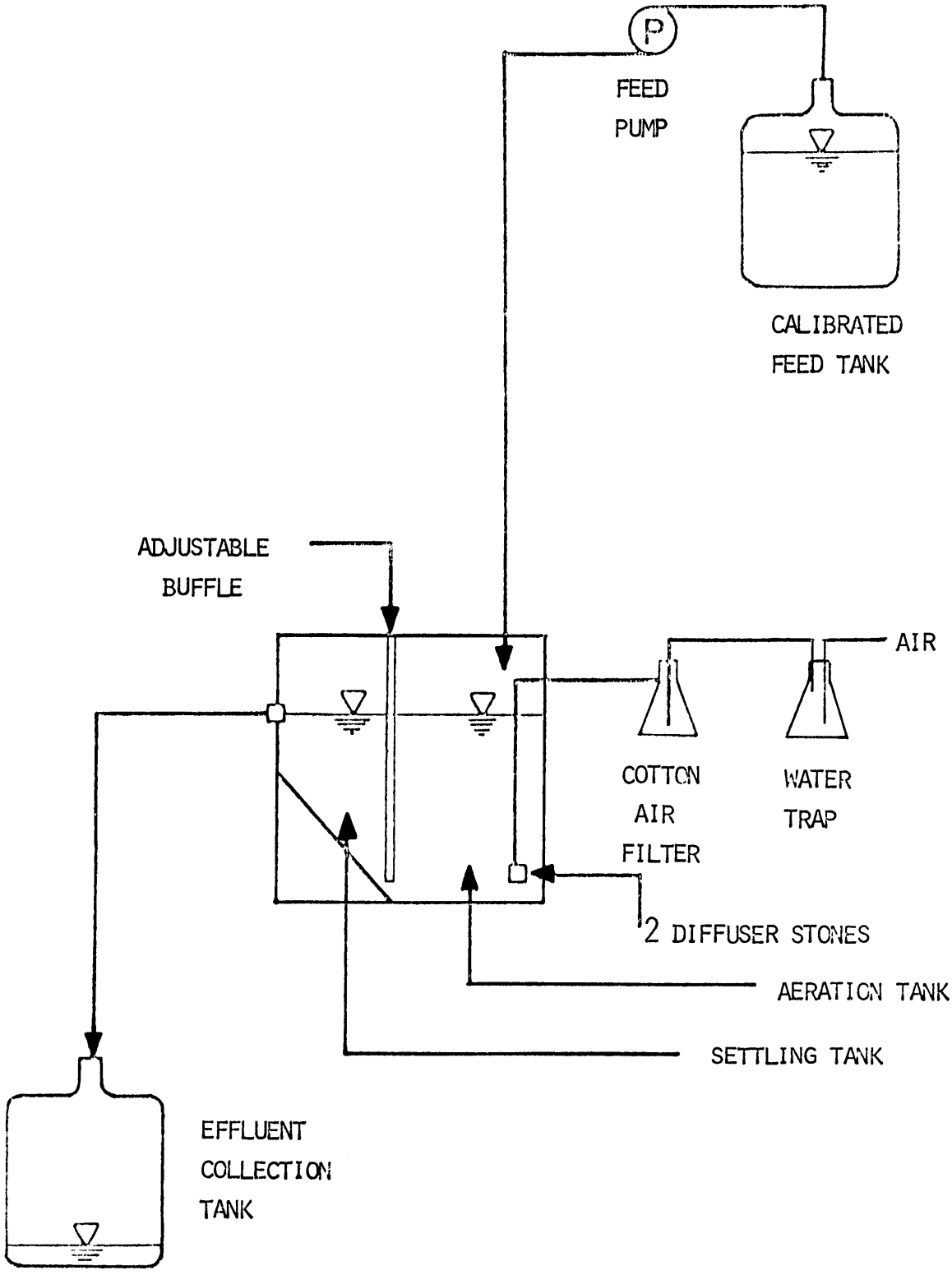

Figure 13. Continuous Flow Reactor with Internal Cell Recycle.

constant flow rate of 14.54 liters per day by means of a variable speed peristaltic pump (Model 1201, Harvard Apparatus Co., Inc.) through latex tubing of size 1/4" x 1/16" (OD x wall thickener) connected to 1/4" x 1/16" polyethylene tubing. Glass tubing was used to suction off waste mixed liquor suspended solids from the total reactor each day.

OPERATING PROCEDURES

Initial Start Up

The activated sludge microorganisms for this study were obtained from the extended aeration activated sludge process treating domestic sewage at the Radford Rest Stop area off Interstate 81 near Radford, Virginia. The microorganisms were acclimated to the feed solution by feeding them continuously a combination of domestic sewage and the feed solution. The amount of domestic sewage was gradually decreased until only the feed solution was used. Two continuous flow reactors were operated for a period of one month for acclimation of microorganisms to the feed solution.

Feed Solution

To assess the influence of nickel concentration and substrate concentration on the activated sludge process, two reproducible soluble synthetic wastewaters with known nickel concentrations were utilized.

The feed solutions containing 394 mg/l COD had Bacto-peptone as a carbon source. A nickel chloride solution was added to the feed solution to provide nickel concentration of 1 and 5 mg/l as Ni(II). No nickel

was added to the feed solution for the control reactor. Supplemental nitrogen was added to the feed solution using an ammonium sulfate solution. A phosphate buffer was added to control pH of the systems and to serve as a source of phosphorus. Other inorganic nutrients were also added to the feed solutions to satisfy microbial growth requirement.

Two calibrated 19 liter carboys were used to prepare the feed solution daily. The carboys were filled with tap water to approximately 10 liters, the feed solutions were added into the carboys according to the amounts given in Table VI. Then each carboy was filled to 16 liters with tap water and mixed thoroughly before connecting to the feed lines.

The influence of substrate concentration on nickel toxicity was investigated by increasing the substrate concentration to 787 mg/l COD. Nickel concentration in the feed solution was 1 mg/l as Ni(II). As shown in Table VII the constituents comprising the feed solution were doubled in concentration with the exception of nickel. A 19.0 liter calibrated carboy was used to prepare the feed solution according to the amounts listed in Table VII and the preparation procedure previously described.

System Operation

Two continuous flow biological reactors were operated on a daily basis for 12 months. Total system mean cell residence time was used as the operational control parameter. Microorganisms were wasted daily to achieve desired mean cell residence times. The baffle was removed to allow complete mixing of mixed liquor in the reactor before wasting of

TABLE VI. CHEMICAL COMPOSITION OF THE FEED SOLUTION FOR CONTINUOUS FLOW REACTOR WITH CELL RECYCLE (COD = 394 mg/l)

Constituent	Stock Conc. (gms/2 liters)	Quantity Used (ml/16 liters)	Final Conc. (mg/l)
Bacto-Peptone	129.00	87.50	352.73
$MgSO_4 \cdot 7H_2O$	20.00	80.00	50.00
$MnSO_4 \cdot H_2O$	2.00	80.00	5.00
$FeCl_3 \cdot 6H_2O$	0.25	80.00	0.50
$CaCl_2$	1.50	80.00	3.75
$(NH_4)_2SO_4$	200.00	42.70	267.88
KH_2PO_4 *	105.40	107.00	349.40
K_2HPO_4 *	214.00	107.00	715.40
$NiCl_2 \cdot 6H_2O$	8.10	**	**

* Phosphate Buffer Solution
** Dependent on Concentration Utilized

TABLE VII. CHEMICAL COMPOSITION OF THE FEED SOLUTION FOR CONTINUOUS FLOW REACTOR WITH CELL RECYCLE (COD = 787 mg/l)

Constituent	Stock Conc. (gms/2 liters)	Quantity Used (ml/16 liters)	Final Conc. (mg/l)
Bacto-Peptone	129.00	175.00	705.46
$MgSO_4 \cdot 7H_2O$	20.00	160.00	100.00
$MnSO_4 \cdot H_2O$	2.00	160.00	10.00
$CaCl_2$	1.50	160.00	2.00
$FeCl_3 \cdot 6H_2O$	0.25	100.00	7.50
$(NH_4)_2SO_4$	200.00	85.40	535.76
KH_2PO_4 *	105.40	214.00	698.80
K_2HPO_4 *	214.00	214.00	1431.12
$NiCl_2 \cdot 6H_2O$	8.10	16.00	1.00**

* Phosphate Buffer Solution

** Expressed as mg/l Ni(II)

mixed liquor suspended solids. The baffle was replaced after wasting of microorganisms. The amount of mixed liquor suspended solids being wasted largely depended on the concentration of solids in the reactor and solids concentration in the effluent.

After replacing of baffle into position, the new feed solution was connected to the feed line and was fed into the reactor. The latex tube on the feed line was replaced and the flow rate was checked periodically. The feed solution carboys, the effluent carboys and the feed lines were disinfected daily with chlorine solution and chromic acid solution.

Total reactor microorganism concentration was used as the indicator of steady state conditions. As the system reached equilibrium, monitoring of parameters listed in Table VIII were performed for approximately 7 days to obtain an average value for a single steady state data point. The time required for the system to reach equilibrium varied ranging from one week to two months.

Sampling Procedure

The samples were collected daily for each steady state condition studied. Approximately 500-800 ml samples were taken from the feed solution carboys and effluent carboys. Each carboy was mixed thoroughly before sampling. Alkalinity and pH determination of these samples were performed immediately after sampling.

A 50 ml MLSS sample was taken from the wasted MLSS in which 25 ml was used for total reactor microorganism concentration and 25 ml was

TABLE VIII

PARAMETERS MONITORED DAILY

INFLUENT FEED

- Chemical Oxygen Demand
- Ammonia Nitrogen Concentration
- Total Kjeldahl Nitrogen Concentration
- Nickel Concentration
- pH
- Alkalinity as mg/l $CaCO_3$

FILTERED EFFLUENT

- Chemical Oxygen Demand
- Ammonia Nitrogen Concentration
- Total Kjeldahl Nitrogen Concentration
- Nickel Concentration
- Nitrate Nitrogen Concentration

UNFILTERED EFFLUENT

- Chemical Oxygen Demand
- Ammonia Nitrogen Concentration
- Total Kjeldahl Nitrogen Concentration
- Nickel Concentration
- pH
- Alkalinity as mg/l $CaCO_3$
- Suspended Solids Concentration

BIOLOGICAL REACTORS

- Mixed Liquor Suspended Solids Concentration
- Nickel Concentration

preserved with acid at pH≤2.0 and stored at 4°C for nickel determination.

A 50-100 ml sample was taken from the effluent sample for effluent microorganism concentration determination. The filtrate was preserved with acid to pH≤2.0 for soluble chemical oxygen demand and soluble nickel concentration determination. The feed solutions and effluent samples being left were acidified to pH≤2.0 and stored at 4°C for further analysis. Nitric acid was used to preserve the sample for nickel determination and sulfuric acid was used to preserve the samples for other analyses.

ANALYTICAL TECHNIQUES

The analytical techniques used in these experiments were as follows:

Chemical Oxygen Demand. The unfiltered feed solution and effluent and filtered effluent samples chemical oxygen demand determinations were made in accordance with Standard Methods (71).

pH. The pH of unfiltered feed solution and effluent were measured as described in Standard Methods (71) using a Fisher Accumet Model 230 pH meter.

Alkalinity. Fifty ml of unfiltered feed solution and effluent were collected for alkalinity determinations in accordance with Standard Methods (71). A calibrated pH meter was used to indicate the end point of titration.

Microorganism concentration. Microorganism concentrations in the reactor and effluent samples were determined on a dry cell weight basis as described in Standard Methods (71) using 0.45 μ membrane filters (Type HA, Millipore Filter Corp.).

Ammonia Nitrogen. Ammonia nitrogen determination was performed on the feed solution and effluent samples by distillation followed by acidimetric titration technique as described in Standard Methods (71).

Total Kjeldahl Nitrogen. The feed solution and effluent samples were digested in accordance with Standard Methods (71) for total Kjeldahl nitrogen determination. Acidimetric titration technique was used as a method of determination.

Nitrate Nitrogen. The Brucine technique, as outlined in Standard Methods (71), was used to determine nitrate nitrogen concentration in the filtered effluent.

Nickel. Nickel concentration in the feed solution and in filtered effluent was determined using an Atomic Absorbtion Spectrophotometer (Model 403, Perkin-Elmer).

Digestion of samples was performed on total reactor MLSS and unfiltered effluent samples as outlined by Krishnamurty et al. (72). The digested sample was filtered through a 0.45 μ membrane filter (Type HA, Millipore Corp.) to remove any insoluble matter. The filtrate was diluted to a known volume and nickel concentration was measured by an Atomic Absorbtion Spectrophotometer (Model 403, Perkin-

-Elmer).

FATE OF NICKEL AND NITROGEN DISTRIBUTION ANALYSIS

The percentage of influent nitrogen leaving the system as particular nitrogen species may be calculated based on a mass balance as described by equation [60] as follows:

$$\%NH_3\text{-}N = \frac{100[Q_w NH_3\text{-}N_f + (Q-Q_w)NH_3\text{-}N_u]}{Q\ TKN} \quad (65)$$

where

$\%NH_3\text{-}N$ = percentage of influent nitrogen leaving system as ammonia nitrogen, percent,

$NH_3\text{-}N_f$ = ammonia nitrogen concentration of filtered effluent, mass/volume,

$NH_3\text{-}N_u$ = ammonia nitrogen concentration of unfiltered effluent, mass/volume,

TKN = total Kjeldahl nitrogen concentration of influent, mass/volume.

$$\%Org\text{-}N = \frac{100[Q_w(\%NX + Org\text{-}N_f)+(Q-Q_w)(Org\text{-}N_u)]}{Q\ TKN} \quad (66)$$

where

%Org-N = percentage of influent nitrogen leaving system as organic nitrogen, percent,

%N = percent nitrogen of microbial solids, mass N/mass cell,

$Org\text{-}N_f$ = organic nitrogen concentration of filtered effluent,

mass/volume,

$Org\text{-}N_u$ = organic nitrogen concentration of unfiltered effluent, mass/volume,

$$\%NO_3^-\text{-}N = \frac{100(NO_3^-\text{-}N_f)}{TKN} \quad (67)$$

where

$\%NO_3^-\text{-}N$ = percentage of influent nitrogen leaving system as nitrate nitrogen, percent,

$NO_3^-\text{-}N_f$ = nitrate nitrogen concentration of filtered effluent, mass/volume.

The percentage of nitrogen accounted for may be calculated by the expression

$$N = \%NH_3\text{-}N + \%Org\text{-}N + \% NO_3^-\text{-}N \quad (68)$$

where

N = total influent nitrogen accounted for, percent.

A mass balance of nickel may be calculated utilizing the expression

$$\%Ni(II) = \frac{[Q_w Ni(II)_r + (Q\text{-}Q_w)Ni(II)_u]}{QNi(II)} \quad (69)$$

where

%Ni(II) = percentage of influent nickel accounted for, percent

$Ni(II)_r$ = nickel concentration in the reactor, mass/volume

$Ni(II)_u$ = nickel concentration in unfiltered effluent, mass/volume

Ni(II) = nickel concentration in influent, mass/volume.

VI. RESULTS AND DISCUSSION

EXPERIMENTAL RESULTS

For ease of presentation, the experimental results from each reactor system studied will be presented separately. A summary of results for the slug fed batch reactor experiments is presented in Table IX. Raw data for slug fed batch experiments are presented in Appendix A. Table X to Table XIII summarize the results for the continuous flow reactor experiments. Raw data for the continuous flow experiment are presented in Appendix B.

Slug Fed Batch Reactor

The acclimated and non acclimated batch reactors were subjected to slug doses of nickel. Data from six metal-laden batch reactors were recorded and analyzed to determine the influence of shock doses of nickel on a) COD removal rate, b) COD removal efficiency, c) microorganism cell yield, Y_{max} and d) nickel uptake. A control reactor with no nickel dosage was operated to obtain base line data for the experiments. Table IX summarizes the experimental results for the batch reactor experiments.

Shock doses of nickel affected the effluent COD concentration and thus the COD removal efficiency. The efficiency of COD removal decreased by 2, 8 and 11 percent for the batch reactor receiving shock doses of Ni(II) concentrations at 1, 5 and 10 mg/l respectively. These reductions in COD removal efficiency were obtained through a comparison

TABLE IX. SUMMARY OF EXPERIMENTAL RESULTS FOR SLUG FED BATCH REACTOR EXPERIMENTS

Nickel Conc. (mg/l)	Δ MLVSS (mg/l)	Δ COD (mg/l)	COD Remov. Effic. (%)	Y_{max}	Nickel Remov. Effic. (%)
0	150	320	56.6	0.47	-
Shock Doses					
1	195	320	54.7	0.61	34.0
5	170	290	48.7	0.59	66.4
10	100	265	45.6	0.38	74.4
Acclimated Doses					
1	160	335	57.8	0.48	15.5
5	150	345	63.3	0.43	45.2
10	140	330	56.9	0.42	35.4

with data obtained for the control batch reactor. The effect of nickel on COD removal efficiency was negligible in the acclimated batch reactors receiving 1, 5 and 10 mg/l of Ni(II).

Microorganism cell yield, Y_{max}, was affected by shock doses of nickel. The values of Y_{max} obtained for the batch reactor receiving shock doses of nickel at 1, 5 and 10 mg/l were 0.61 mg/l MLVSS/mg/l COD, 0.59 and 0.38 respectively. The value of Y_{max} for the control batch reactor was 0.47. From these results it can be seen that stimulatory effect of nickel occurs at 1 and 5 mg/l of nickel shock dosages. The value of Y_{max}=0.38 at 10 mg/l of nickel shock dosage indicated an inhibitory effect of nickel on microorganism cell yield. The effect of nickel on the value of Y_{max} under shock doses of nickel, however, was negligible in the acclimated batch reactor. The values of Y_{max} obtained for the acclimated batch reactor were 0.48, 0.43 and 0.42 for the reactors receiving 1, 5 and 10 mg/l of Ni(II), respectively.

The uptake of nickel by biological solids was observed under shock loaded and acclimated loaded conditions. For the shock loaded batch reactors, the rapid uptake of nickel occurred during the first 90 minutes of aeration time. The rate of nickel uptake declined rapidly after the rapid uptake period. The percent of nickel taken up by biological solids or nickel removal efficiency appeared to be dependent on the concentration of nickel in the feed solution. Nickel removal efficiency was 34.0, 66.4 and 74.4 percent for the nickel fed reactors having 1, 5 and 10 mg/l of Ni(II), respectively.

For the nickel acclimated batch reactors, the uptake of nickel was

not as fast as those for the shock loaded batch reactors. The rate of nickel uptake gradually decreased after 3 hours of aeration time. Nickel removal efficiency was 15.5, 45.2 and 35.4 percent for the nickel fed reactor having 1, 5 and 10 mg/l of Ni(II), respectively.

Continuous Flow Reactors with Cell Recycle

The effects of nickel on the completely mixed activated sludge process were studied utilizing the bench scale continuous flow reactors with internal cell recycle. Data obtained from four bench scale activated study units were recorded and analyzed to assess the influence of substrate concentration, nickel concentration and mean cell residence time on a) COD removal efficiency,b) microorganism concentration, c) nitrification and d) biokinetic coefficients.

Four bench scale continuous flow reactors with internal cell recycle were operated for a period of 12 months to obtain 15 steady state experimental data points. Raw data for each steady state period are tabulated in Appendix B.

Control

A control reactor was operated for a period of 6 months to obtain base-line data. Four steady state experimental data points were obtained at mean cell residence times of 5.8, 11.5, 12.3 and 16.4 days. Experimental results obtained are summarized in Table X. The average COD concentration of the feed solution (void of nickel) during the four steady state periods was 394 mg/l. The effluent COD concentration was

TABLE X. SUMMARY OF STEADY STATE DATA FOR CONTROL REACTOR (COD = 394 mg/l)

Observation	Mean Cell Residence Time (days)			
	5.8	11.5	12.3	16.4
Chemical Oxygen Demand				
Feed Solution (mg/l)	386	405	390	396
Effluent (mg/l)	19	23	28	27
COD Removal Efficiency (%)	95.2	94.3	92.9	93.2
Microorganism Concentration				
Total Reactor (mg/l)	1156	1920	2120	2681
Effluent (mg/l)	15	5	30	4
Specific Utilization Rate (day^{-1})	0.546	0.340	0.292	0.236
Specific Growth Rate (day^{-1})	0.173	0.082	0.087	0.061
Observed Yield	0.319	0.256	0.281	0.260
Sludge Production (mg/day)	1701	1417	1477	1392
pH				
Feed Solution	7.2	7.2	7.1	7.2
Effluent	7.5	6.6	6.8	6.6
Alkalinity as $CaCO_3$				
Feed Solution (mg/l)	248	259	228	263
Effluent (mg/l)	297	106	165	102
Net Change (%)	19.8	-59.1	-27.6	-61.2
NH_3-N				
Feed Solution (mg/l)	59.2	54.7	51.0	57.7
Effluent (mg/l)	78.3	48.7	51.2	49.4
Net Change (%)	32.3	-11.0	+0.4	-14.4
Org-N				
Feed Solution (mg/l)	48.7	52.5	51.1	49.6
Effluent (mg/l)	3.8	2.5	3.0	2.8
Net Change (%)	-92.2	-95.2	-94.1	-94.4
NO_3^--N in Effluent (mg/l)	8.8	41.5	30.3	42.2
Predicted Alkalinity (mg/l as $CaCO_3$)	285	89	121	83

nearly constant for all operating θ_c. The COD removal efficiency was found to exceed 92 percent at each θ_c. Total reactor microorganism concentrations were 1156, 1920, 2120 and 2681 mg/l as θ_c increased from 5.8 days to 11.5, 12.3 and 16.4 days respectively. Specific utilization rate decreased as θ_c increased. Specific utilization rate was 0.546 day^{-1} at θ_c = 5.8 days and decreased to 0.236 day^{-1} at θ_c = 16.4 days. Observed yield decreased from 0.319 to 0.260 as θ_c increased. Sludge production was found to decrease from 1701 mg/day to 1392 mg/day as θ_c increased.

Degree of nitrification was found to be dependent on θ_c. The highest degree of nitrification occurred at θ_c = 16.4 days while the lowest was observed at θ_c = 5.8 days. NH_3-N concentration in the system was a function of nitrification and thus θ_c. An increase in NH_3-N of 32.3 percent occurred at θ_c = 5.8 days. At higher θ_c, however, reduction of NH_3-N was observed to be between 11.0 to 14.0 percent, with the exception of θ_c = 12.3 days. High organic nitrogen removal conversion was observed at all θ_c. The effluent NO_3^--N increased from 8.8 mg/l to 42.2 mg/l as θ_c increased.

A 19.8 percent increase in alkalinity was measured at θ_c = 5.8 days. Destruction of alkalinity was measured at higher θ_c ranging from 27.6 to 61.2 percent. The changes in pH of the system paralleled the changes in alkalinity.

Ni(II)= 1 mg/l, COD = 396 mg/l

A continuous flow reactor was operated at mean cell residence time

of 5.2, 10.6 and 14.5 days with an average influent Ni(II) concentration of 0.97 mg/l. The feed solution had an average COD concentration of 396 mg/l. A summary of experimental results is presented in Table XI. The effluent COD concentration increased from 25 to 33 mg/l as θ_c increased from 5.2 days to 14.5 days. The COD removal efficiency was nearly constant and higher than 91 percent for all θ_c. Total reactor microorganism concentration increased from 1106 mg/l to 1475 and 1716 mg/l as θ_c increased. Specific utilization rate was found to decrease as θ_c increased. The rate of specific utilization decreased from 0.573 to 0.365 day^{-1} for θ_c = 5.2, 10.6 and 14.5 days, respectively. Observed yield decreased by 0.339, 0.223 and 0.191 as θ_c increased. Sludge production was observed to decrease from 1819 mg/day at θ_c = 5.2 days to 1014 mg/day at θ_c = 14.5 days.

Nitrification was inhibited at all operating θ_c by the presence of nickel in the feed solution. Effluent NO_3^--N concentration was less than 1.8 mg/l indicated the absence of nitrification. Ammonia nitrogen was found to increase by 54.4, 57.0 and 72.5 percent for operating θ_c of 5.2, 10.6 and 14.5 days, respectively. Organic nitrogen conversion was higher than 84 percent at all operating θ_c.

Alkalinity production was observed at all operating θ_c. This was due to the absence of nitrification at each θ_c studied. Production of alkalinity increased from 39.8 percent to 54.5 percent as θ_c increased. The effluent pH was higher than that for the feed solution at all operating θ_c and was attributed to the alkalinity production observed in the system.

TABLE XI. SUMMARY OF STEADY STATE DATA, Ni(II) = 1 mg/l, COD = 396 mg/l

Observation	Mean Cell Residence Time (days)		
	5.2	10.6	14.5
Chemical Oxygen Demand			
Feed Solution (mg/l)	394	396	399
Effluent (mg/l)	25	29	33
COD Removal Efficiency (%)	93.8	92.6	91.7
Microorganism Concentration			
Total Reactor (mg/l)	1106	1475	1716
Effluent (mg/l)	25	29	33
Specific Utilization Rate (day^{-1})	0.573	0.425	0.365
Specific Growth Rate (day^{-1})	0.194	0.095	0.069
Observed Yield	0.339	0.223	0.191
Sludge Production (mg/day)	1819	1185	1014
pH			
Feed Solution	7.2	7.1	7.0
Effluent	7.7	7.6	7.6
Alkalinity as $CaCO_3$			
Feed Solution (mg/l)	241	232	233
Effluent (mg/l)	337	354	360
Net Change (%)	39.8	52.6	54.5
NH_3-N			
Feed Solution (mg/l)	55.7	56.8	49.4
Effluent (mg/l)	86.0	89.2	85.2
Net Change (%)	54.4	57.0	72.5
Org-N			
Feed Solution (mg/l)	52.9	50.6	53.4
Effluent (mg/l)	3.1	4.1	8.2
Net Change (%)	-94.1	-91.9	-84.6
NO_3^--N in Effluent (mg/l)	1.4	1.7	1.6
Predicted Effluent Alkalinity (mg/l as $CaCO_3$)	344	342	355
Nickel			
Feed Solution (mg/l)	0.99	1.00	0.93
Effluent (mg/l)	0.92	0.86	0.85
Sludge (mg/g)	0.48	0.81	0.85
Nickel Removal Efficiency, (%)	7.1	14.0	8.6

The average nickel concentration in the feed solution was 0.97 mg/l as Ni(II). The effluent nickel concentration was 0.92, 0.86 and 0.85 mg/l at θ_c = 5.2, 10.6 and 14.5 days, respectively. Nickel uptake by biological solids was 0.48 mg of Ni(II)/g of MLSS, 0.81 and 0.85 at θ_c = 5.2, 10.6 and 14.5 days respectively. Nickel removal efficiency was 7.1, 14.0 and 8.6 percent and as θ_c increased.

Ni(II) =5 mg/l, COD = 391 mg/l

Five steady state periods were obtained at mean cell residence time of 5.3, 5.7, 6.2, 10.4 and 13.1 days. A summary of experimental results obtained at each steady state period is presented in Table XII. The feed solution had an average COD concentration of 391 mg/l. The effluent COD concentration was between 29 mg/l and 50 mg/l for all operating θ_c. The COD removal efficiency was higher than 87.1 percent at all operating θ_c. Total reactor microorganism concentration increased from 1135 mg/l to 1574 mg/l as θ_c increased from 5.3 days to 13.1 days. The rate of specific utilization decreased as θ_c increased. Specific utilization rate was 0.190, 0.177, 0.166, 0.097 and 0.077 day^{-1} at operating θ_c = 5.3, 5.7, 6.2, 10.4 and 13.1 days, respectively. Observed yield decreased by 0.349, 0.318, 0.328, 0.263 and 0.196 as θ_c increased. Sludge production was found to decrease from 1833 mg/day at θ_c = 5.3 days to 1024 mg/day at θ_c = 13.1 days.

Nitrification was completely inhibited by the nickel present in the feed solution. Effluent NO_3^--N concentration was lower than 2.8 mg/l at all θ_c. Production of ammonia nitrogen was observed at all

TABLE XII. SUMMARY OF STEADY STATE DATA,

Ni(II) = 5 mg/l, COD = 391 mg/l

Observation	Mean Cell Residence Time (days)				
	5.3	5.7	6.2	10.4	13.1
Chemical Oxygen Demand					
Feed Solution (mg/l)	391	397	392	376	401
Effluent (mg/l)	30	29	50	38	42
COD Removal Efficiency (%)	92.3	92.6	87.2	89.9	89.6
Microorganism Concentration					
Total Reactor (mg/l)	1135	1136	1157	1567	1574
Effluent (mg/l)	27	42	59	63	60
Specific Utilization Rate (day^{-1})	0.545	0.556	0.506	0.369	0.391
Specific Growth Rate (day^{-1})	0.190	0.177	0.116	0.097	0.077
Observed Yield	0.349	0.318	0.328	0.263	0.196
Sludge Production (mg/day)	1833	1701	1632	1294	1024
pH					
Feed Solution	7.1	7.2	7.1	7.2	7.1
Effluent	7.5	7.6	7.7	7.6	7.6
Alkalinity as $CaCO_3$					
Feed Solution (mg/l)	252	262	270	254	245
Effluent (mg/l)	356	350	383	332	336
Net Change (%)	41.3	33.6	41.9	30.7	37.1
NH_3-N					
Feed Solution (mg/l)	60.2	57.4	62.7	56.0	54.8
Effluent (mg/l)	88.2	84.0	91.8	82.3	83.4
Net Change (%)	46.5	46.3	46.4	47.0	52.2
Org-N					
Feed Solution (mg/l)	44.8	43.4	55.4	48.2	43.1
Effluent (mg/l)	7.0	4.2	5.0	4.5	4.0
Net Change (%)	-84.4	-90.3	-91.0	-90.7	-90.7
NO_3^- - N in Effluent (mg/l)	1.9	1.7	2.4	2.3	2.7
Predicted Effluent Alkalinity (mg/l as $CaCO_3$)	345	351	365	340	337

TABLE XII. SUMMARY OF STEADY STATE DATA,

Ni(II) = 5 mg/l, COD = 391 mg/l (Continued)

Observation	Mean Cell Residence Time (days)				
	5.3	5.7	6.2	10.4	13.1
Nickel					
Feed Solution (mg/l)	5.19	4.90	5.00	4.94	5.52
Effluent (mg/l)	4.00	3.96	4.34	4.25	4.56
Sludge (mg/g)	6.11	6.2	7.90	5.49	11.66
Nickel Removal Efficiency (%)	22.9	19.2	13.2	14.0	17.4

operating θ_c. The increase of ammonia nitrogen in the system was found to be 46.5, 46.3, 46.4, 47.0 and 52.2 percent at θ_c = 5.3, 5.7, 6.2, 10.4 and 13.1 days, respectively. Organic nitrogen conversion was nearly constant at all θ_c with the exception of θ_c = 5.3 days. An increase in alkalinity was obtained at all operating θ_c. Alkalinity in the system increased by 41.3, 33.6, 41.9, 30.7 and 37.1 percent at θ_c = 5.3, 5.7, 6.2, 10.4 and 13.1 days, respectively. The effluent pH increased at all θ_c due to the increase in ammonia nitrogen concentration.

The average nickel concentration present in the feed solution was 5.11 mg/l as Ni(II). The effluent nickel concentration was found to be 4.00, 3.96, 4.34, 4.25 and 4.56 mg/l at θ_c = 5.3, 5.7, 6.2, 10.4 and 13.1 days respectively. Uptake of nickel by biological solids was 6.11 mg of Ni(II)/g of MLSS, 6.20, 7.90, 5.49 and 11.66 as θ_c increased from 5.3 days to 13.1 days. Nickel removal efficiency was found to be higher than those in the previous nickel fed reactor (Ni(II) = 1 mg/l, COD = 396 mg/l). Nickel removal efficiency was independent of mean cell residence time.

Ni(II)= 1 mg/l, COD = 787 mg/l

A reactor was operated to obtain 3 steady state data points at θ_c of 7.1, 10.0 and 16.9 days. A summary of results obtained from 3 steady state periods is presented in Table XIII. The feed solution contained an average COD concentration of 787 mg/l and average Ni(II) concentration of 1.09 mg/l. The effluent COD concentration was higher than all of the previous reactor runs. The COD concentration in the effluent was

TABLE XIII. SUMMARY OF STEADY STATE DATA,
Ni(II) = 1 mg/l, COD = 787 mg/l

Observation	Mean Cell Residence Time (days)		
	7.1	10.0	16.9
Chemical Oxygen Demand			
Feed Solution (mg/l)	790	788	783
Effluent (mg/l)	80	61	53
COD Removal Efficiency (%)	90.0	92.3	93.2
Microorganism Concentration			
Total Reactor (mg/l)	2426	3490	4314
Effluent (mg/l)	123	39	33
Specific Utilization Rate (day^{-1})	0.501	0.357	0.290
Specific Growth Rate (day^{-1})	0.143	0.101	0.060
Observed Yield	0.285	0.283	0.206
Sludge Production (mg/day)	2942	2987	2186
pH			
Feed Solution	7.1	7.1	7.1
Effluent	7.5	7.2	6.7
Alkalinity as $CaCO_3$			
Feed Solution (mg/l)	457	436	461
Effluent (mg/l)	555	452	249
Net Change (%)	21.4	3.7	-46.0
NH_3-N			
Feed Solution (mg/l)	114.5	110.7	112.4
Effluent (mg/l)	159.8	154.0	125.2
Net Change (%)	39.5	39.1	11.3
Org-N			
Feed Solution (mg/l)	102.2	121.5	106.1
Effluent (mg/l)	9.8	7.4	10.6
Net Change (%)	-90.4	-93.9	-90.0
NO_3^--N in Effluent (mg/l)	21.3	34.7	65.0
Predicted NO_3^--N Concentration (mg/l)	17.8	35.1	69.6
Predicted Alkalinity (mg/l as $CaCO_3$)	543	467	275
Nickel			
Feed Solution (mg/l)	1.09	1.11	1.08
Effluent (mg/l)	0.65	0.69	0.67
Sludge (mg/g)	2.87	3.08	2.79
Nickel Removal Efficiency (%)	40.4	37.8	38.0

80, 61 and 53 mg/l at θ_c = 7.1, 10.0 and 16.9 days, respectively. An increase in COD removal efficiency as θ_c increased was obtained. The COD removal efficiency was 90.0, 92.3 and 93.2 percent as θ_c increased. Total reactor microorganism concentration increased from 2426 mg/l to 4314 mg/l as θ_c increased from 7.1 days to 16.9 days. Specific utilization rate decreased from 0.501 day^{-1} to 0.290 day^{-1} as θ_c increased. Observed yield was found to decrease as θ_c increased. The values of observed yield was 0.285, 0.283 and 0.206 at θ_c = 7.1, 10.0 and 16.9 days, respectively. Sludge production was 2942 mg/day at θ_c = 7.1 days and decreased to 2186 mg/day at 16.9 days.

Nitrification was observed in the system at all operating θ_c. The presence of NO_3^--N in the effluent indicated the presence of nitrifying organisms. Effluent NO_3^--N concentration was 21.3, 34.7 and 65.0 mg/l at θ_c = 7.1, 10.0 and 16.9 days, respectively. An increasing concentration of ammonia nitrogen in the system was observed at all operating θ_c. Production of ammonia nitrogen was 39.5, 39.1 and 11.3 percent at θ_c = 7.1, 10.0 and 16.9 days, respectively. Production of alkalinity was also observed at θ_c = 7.1 days and 10.0 days. However, destruction of alkalinity occurred at θ_c = 16.9 days. Organic nitrogen removal was higher than 89.9 percent at all operating θ_c. Effluent pH was increased and decreased according to the change of alkalinity in the system.

Effluent nickel concentration was lower than that in the other nickel-laden reactors studied. The effluent nickel concentration was 0.65, 0.69 and 0.67 mg/l as Ni(II). Nickel removal efficiency was

highest at all operating θ_c when compared to other metal-laden reactors. Percent nickel removal efficiency was 40.4, 37.8 and 38.0 percent at θ_c = 7.1, 10.0 and 16.9 days, respectively.

DISCUSSION OF RESULTS

The experimental data and results presented previously are discussed in this section. The results for the slug fed batch reactors and continuous flow reactors are discussed separately below.

Slug Fed Batch Reactors

COD Removal

The effect of nickel on COD removal is shown in Figure 14. The COD removal rate decreased as the concentration of shock doses of nickel increased. The reduction in COD removal efficiency also decreased as the concentration of nickel increased as illustrated in Figure 15. Decrease in COD removal rate and COD removal efficiency can be attributed to the inhibitory effect of nickel on the utilization of substrate. The reduction in COD removal efficiency, however, was not a linear decrease with increasing concentration of nickel. The reduction in COD removal efficiency was approximately 11 percent. Thus it can be concluded that a shock dose of 10 mg/l or less of nickel does not greatly affect the substrate utilization rate and substrate removal efficiency.

Figure 15 and Figure 16 illustrate the influence of nickel on COD removal rate and COD removal efficiency for the reactor acclimated to

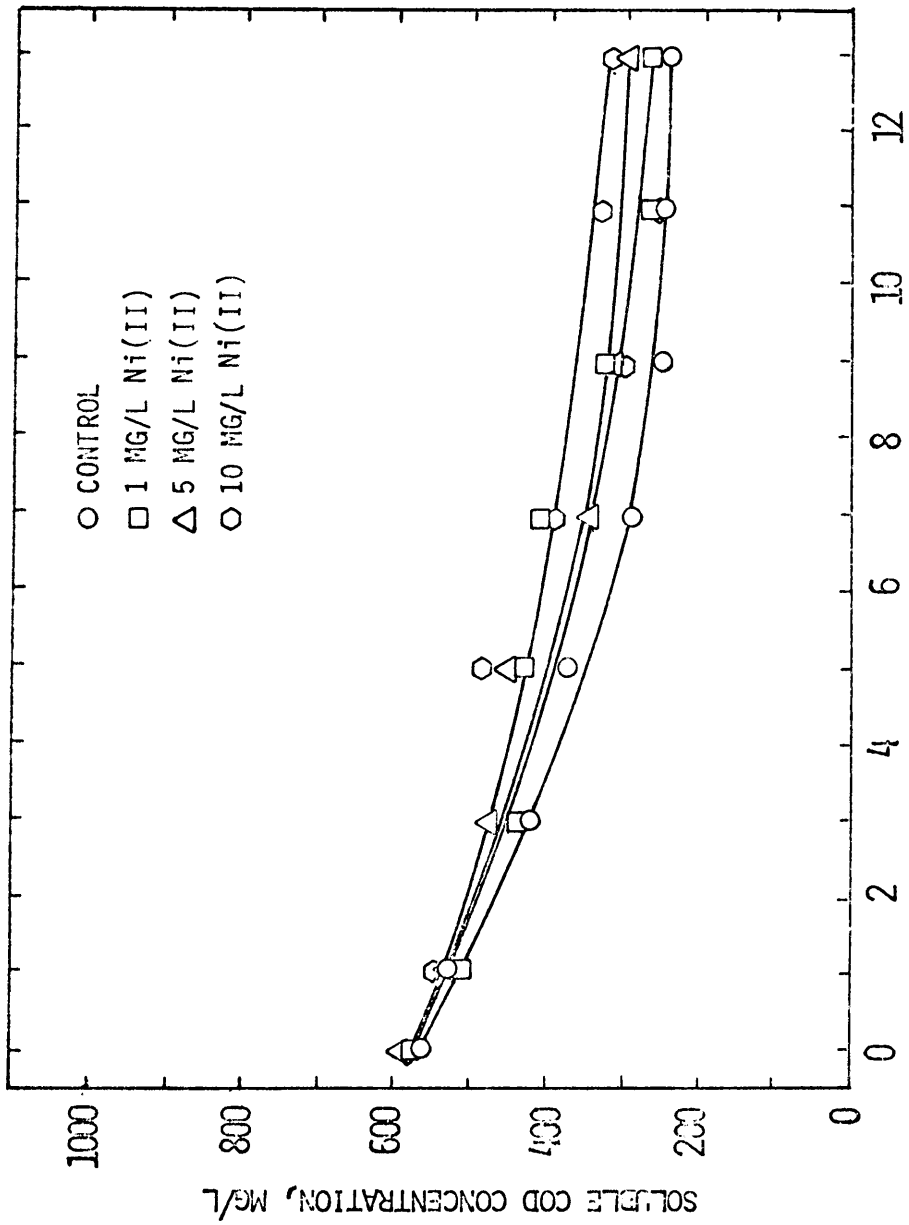

Figure 14. Effect of Nickel on Soluble COD Removal Rate for Shock Loaded Batch Reactors.

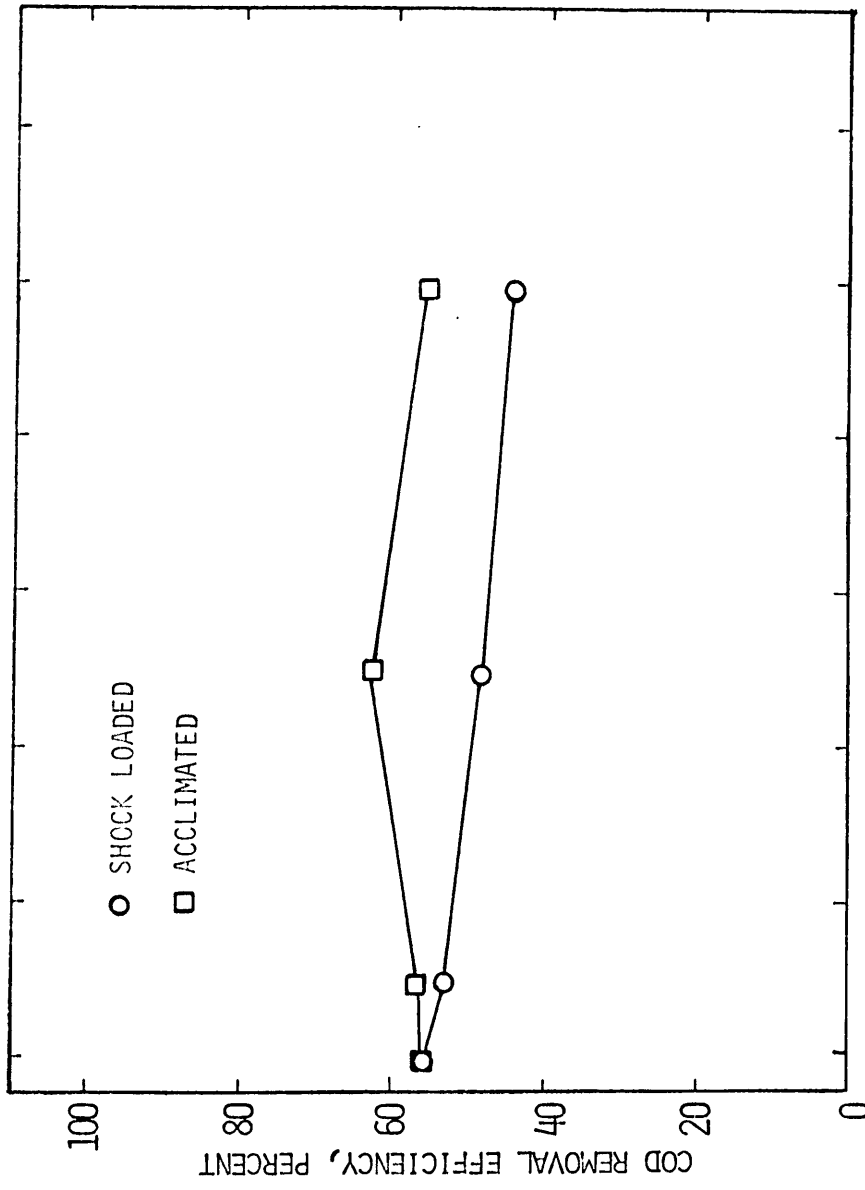

Figure 15. Effect of Nickel on COD Removal Efficiency for Shock Loaded and Acclimated Batch Reactors.

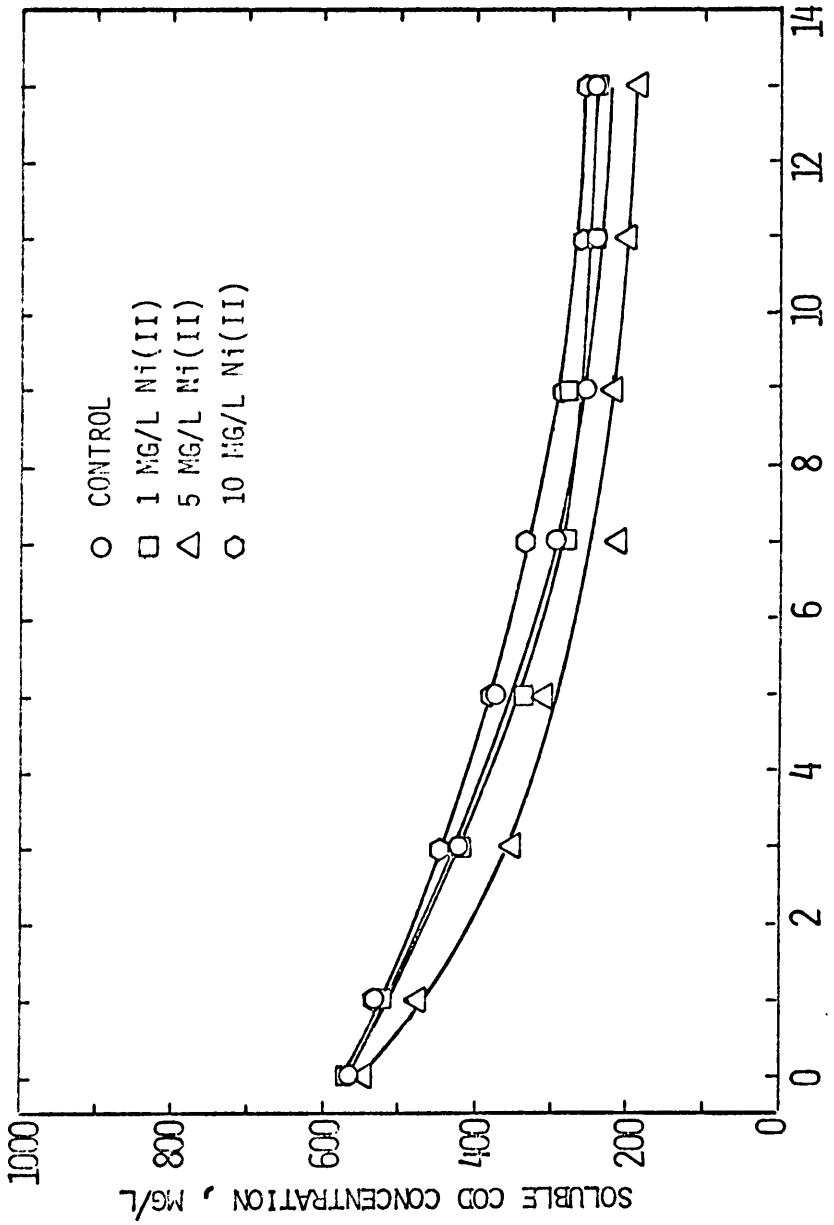

Figure 16. Effect of Nickel on Soluble COD Removal Rate for Acclimated Batch Reactors.

nickel. The effects of acclimated doses of nickel on COD removal rate and COD removal efficiency were insignificant for the nickel-fed reactors having 1 and 10 mg/l of Ni(II). However, COD removal rate and COD removal efficiency for the nickel fed reactor having 5 mg/l of Ni(II) were higher than those for the control reactor. This can be attributed to the stimulatory effect of nickel on substrate utilization which increased the rate of COD removal and COD removal efficiency. The stimulatory effects of toxic metal ions at concentrations below those where toxicity was produced has also been recognized by many investigators (73). The stimulatory effects of nickel may occur on specific enzymes involved in metabolism of amino acids present in the substrate used for these studies. As reported earlier that the activity of amino acid decarboxylation in Escherichia coli increased up to 45 percent upon addition of nickel (23).

Microorganism Cell Yield Coefficient

The effect of nickel on microorganism cell yield under shock loaded and acclimated load conditions is illustrated in Figure 17. Microorganism cell yield coefficients for the batch reactor receiving 1 and 5 mg/l of shock doses of nickel were higher than that for the control reactor. These are due to the stimulatory effect of nickel on the microbial cell synthesis as described earlier. At 10 mg/l of shock doses of nickel, however the microorganism cell yield coefficient was lower than that for the control. This can be attributed to the inhibitory effect of shock doses of nickel occurring on microbial cell synthesis at 10 mg/l.

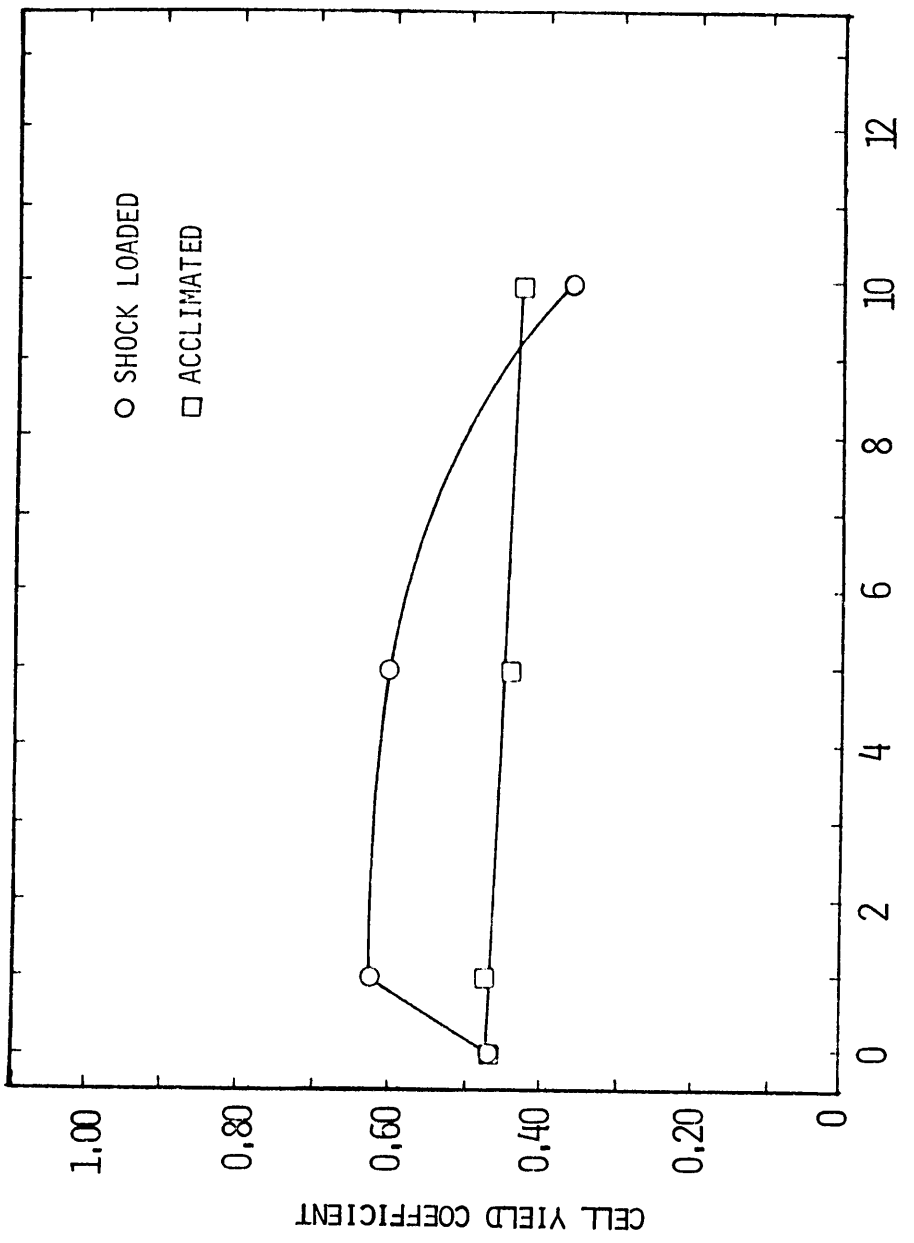

Figure 17. Effect of Nickel on Microorganism Cell Yield Coefficient.

As can be seen from Figure 17, the effects of nickel on the microorganism cell yield for the acclimated batch reactor was negligible. This may be attributed to a change in microbial species in the batch reactors during the acclimation period. The microorganisms that were susceptible to the nickel may have been replaced by nickel resistant microorganisms. These nickel resistant microorganisms may eventually have approximately the same microorganism cell yield coefficient as the microorganisms in the control batch reactor.

It can be concluded that the effects of nickel on the batch reactor are more noticeable under shock doses of nickel than those under acclimated doses of nickel. The degree of influence of nickel is dependent on nickel concentration and how the microorganisms are exposed to the nickel.

Nickel Uptake

The uptake of nickel on biological surfaces under shock loaded conditions is graphically presented in Figure 18. It can be seen that for the nickel concentration of 1, 5, and 10 mg/l, the rapid uptake of nickel by biological solids occurred within 90 minutes and leveled off after approximately 90 minutes. The degree of nickel uptake is dependent on the concentration of nickel in the batch reactors. The rate of nickel uptake declined after 90 minutes and can be attributed to a near saturation of biological floc surface by nickel and thus less biological floc surface is available for nickel affinity. The rapid initial uptake rate was due to the physical, chemical and surface

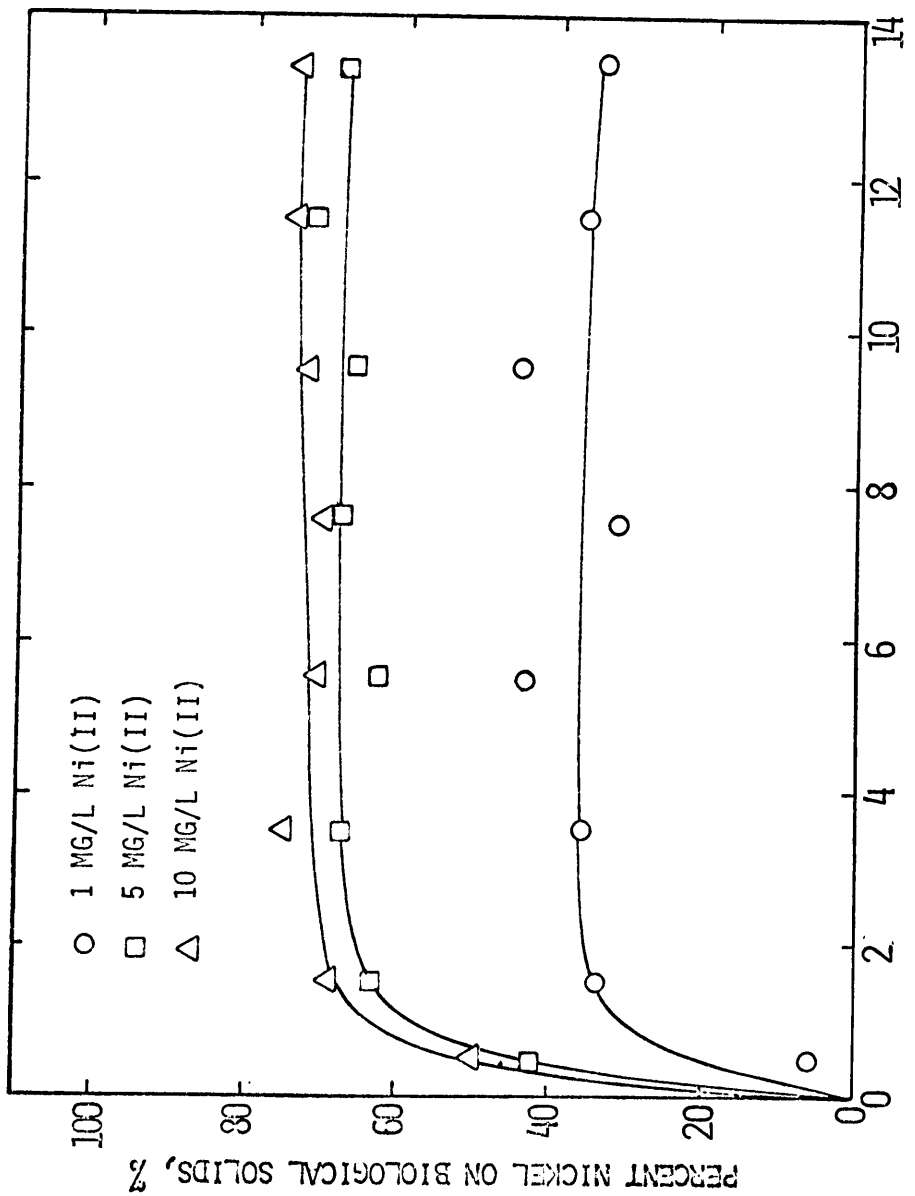

Figure 18. Nickel Uptake by Biological Solids in the Shock Loaded Batch Reactors (pH = 7.7±0.5).

properties of biological solids rather than a biological property of microbial cell, i.e. incorporation of nickel into the cell. Cheng et al.(13)have postulated that the uptake of heavy metals at low concentration by biological solids is due to the formation of metallo-organic complexes while the uptake of heavy at high concentration by biological solids is due to precipitation of heavy metals from solution in addition to heavy metal uptake by the biological solids. Metal uptake by biological solids is dependent on heavy metal concentration, pH, solubility of heavy metals and concentration of the biomass present in the system.

Figure 19 shows the uptake of nickel by biological solids in the acclimated batch reactors. As can be seen, the rate of nickel uptake is gradually increased with aeration time. This can be attributed to the nickel already occupying the biological floc surface during the acclimation period. The rate of nickel uptake appeared to be dependent upon the new microbial mass being synthesized during the aeration time studied and nickel ions being precipitated out from solution due to the high concentration accumulated during the acclimation period. Figure 20 illustrates the effect of nickel concentration, nickel removal efficiency for shock loaded and acclimated load conditions. It can be concluded that nickel removal efficiency is a function of nickel concentration and the nickel loading method. In addition, pH, biological solids concentration and solubility are also important factors affecting nickel removal efficiency by the activated sludge.

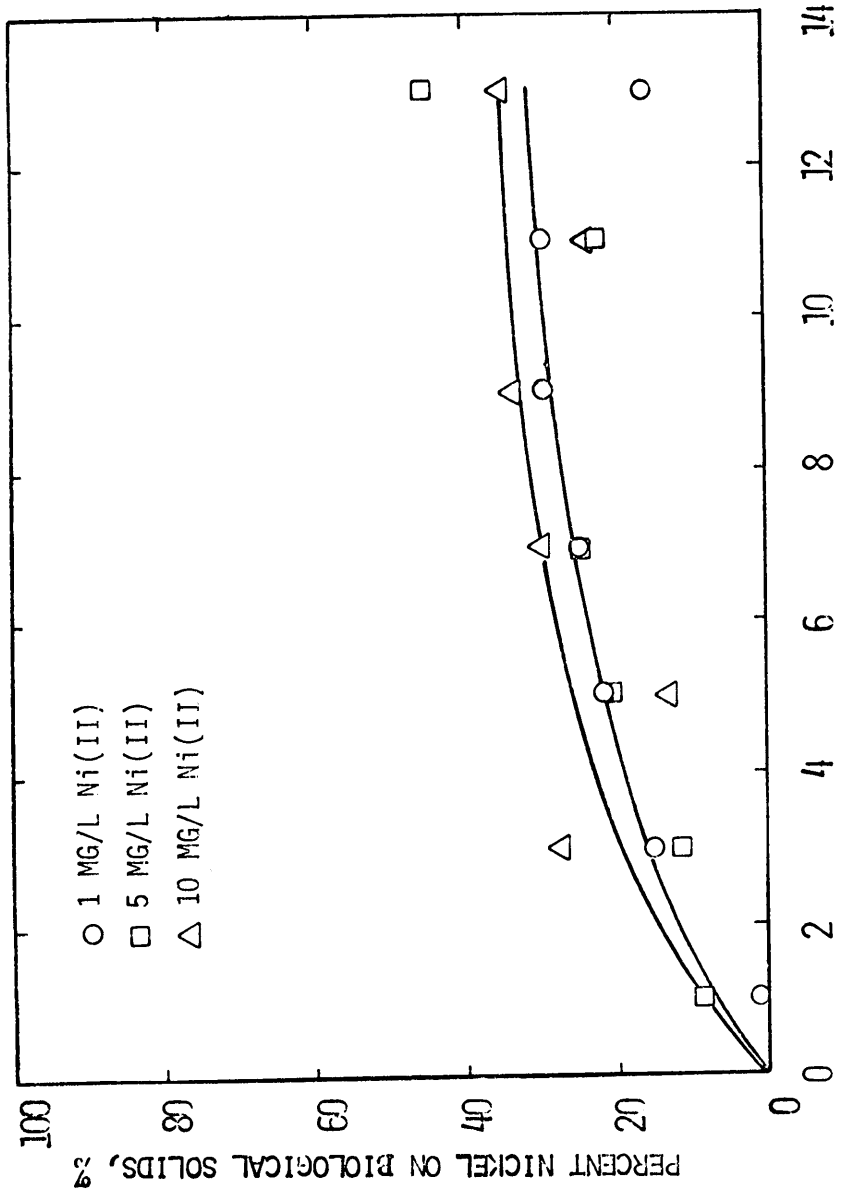

Figure 19. Nickel Uptake by Biological Solids in the Acclimated Batch Reactors. (pH = 7.7±0.5)

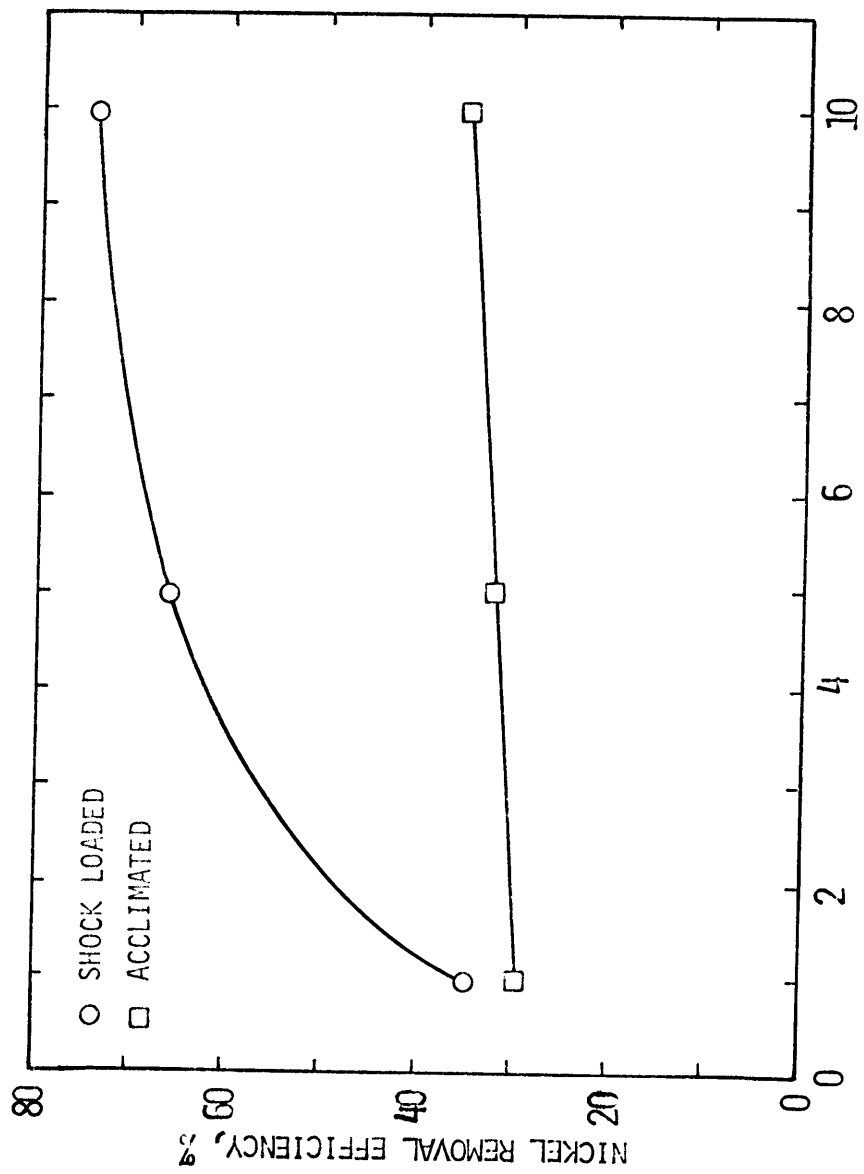

Figure 20. Effect of Nickel Concentration on Nickel Removal Efficiency for Shock Loaded and Acclimated Batch Reactors.

Continuous Flow Reactor with Cell Recycle

COD Removal Efficiency

Figure 21 illustrates the effect of nickel on COD removal efficiency at various mean cell residence times. Slight reductions in COD removal efficiency were observed in the nickel fed reactors as compared to the control reactor. The effect of nickel on COD removal efficiency increased with the concentration of nickel present in the feed solution having the same COD concentration. However, the difference in COD removal efficiency was not significant for the nickel concentrations studied. McDermott et al (50) observed a 5 percent reduction of substrate removal in the activated sludge process receiving wastewater containing 2.5, 5 and 10 mg/l of nickel. By increasing the COD concentration to 787 mg/l while maintaining 1 mg/l of nickel concentration in the feed solution the COD removal efficiency for the reactor operated at a θ_c of 15 days was approximately the same as that obtained for the control reactor. This can be attributed to the high organic substrate present in the feed solution that is available to complex with nickel present in the feed solution and thus reduce the amount of free nickel ion which can adversly effect the substrate utilization of microorganisms in the activated sludge process. In addition the increase in substrate concentration increased microorganism concentration in the reactor and decreased the proportion of active cellular components that are bound as nickel organic complexes and thus allowed more substrate utilization and thereby increased COD removal efficiency.

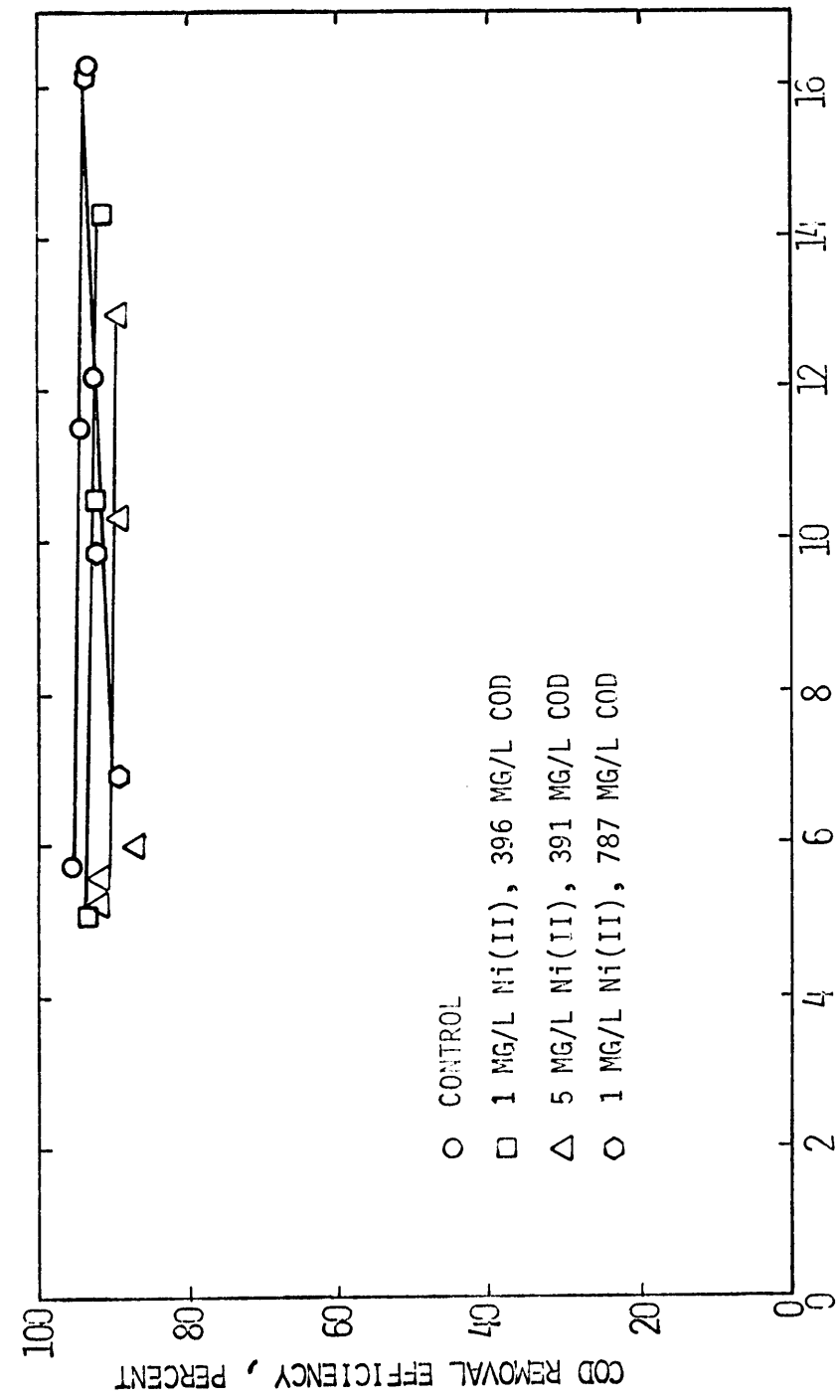

Figure 21. Effect of Nickel on COD Removal Efficiency at Different Mean Cell Residence Times.

Total Reactor Microorganism Concentration

The effect of nickel on microorganism concentration at various mean cell residence time is graphically presented in Figure 22. Mixed liquor suspended solids for the control reactor were higher than those for the nickel fed reactors with the exception of the reactor receiving the feed solution having 1 mg/l of Ni(II) and 787 mg/l COD. This is attributed to the presence of nickel in the feed solution causing stress on the microorganisms. The stressed microorganisms may require more energy for cellular maintainance and thus less energy is available for cell synthesis. For the reactor receiving the feed solution having 1 mg/l Ni(II) and 787 mg/l COD, the microorganism concentration in the total reactor volume was approximately doubled that in the control reactor. This is because more substrate is available for cell synthesis. It is also indicated that the microbial growth kinetics for the nickel fed reactor receiving 1 mg/l Ni(II) and 787 mg/l COD is similar to that for the control reactor. This is due to the high ratio of organic to nickel which decreased the toxic effects of nickel.

Specific Utilization Rate

The effect of nickel on specific utilization rate at various operating mean cell residence times is illustrated in Figure 23. As can be seen, the rates of specific utilization for the nickel fed reactor receiving the feed solution containing 1 mg/l Ni(II) and 396 mg/l COD, and 5 mg/l Ni(II) and 391 mg/l COD were higher than those for the

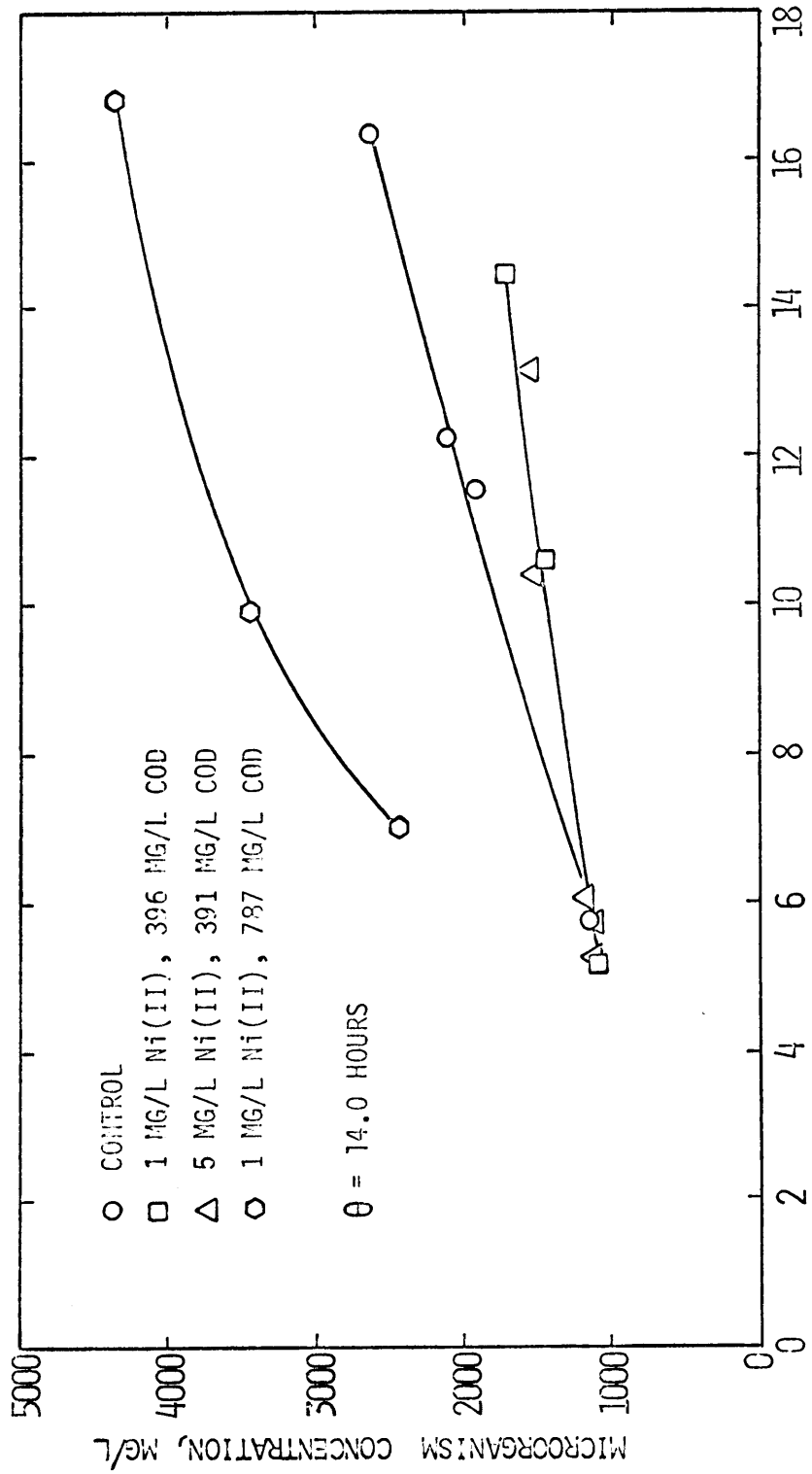

Figure 22. Effect of Nickel on Microorganism Concentration in Total Reactor Volume at Different Mean Cell Residence Times.

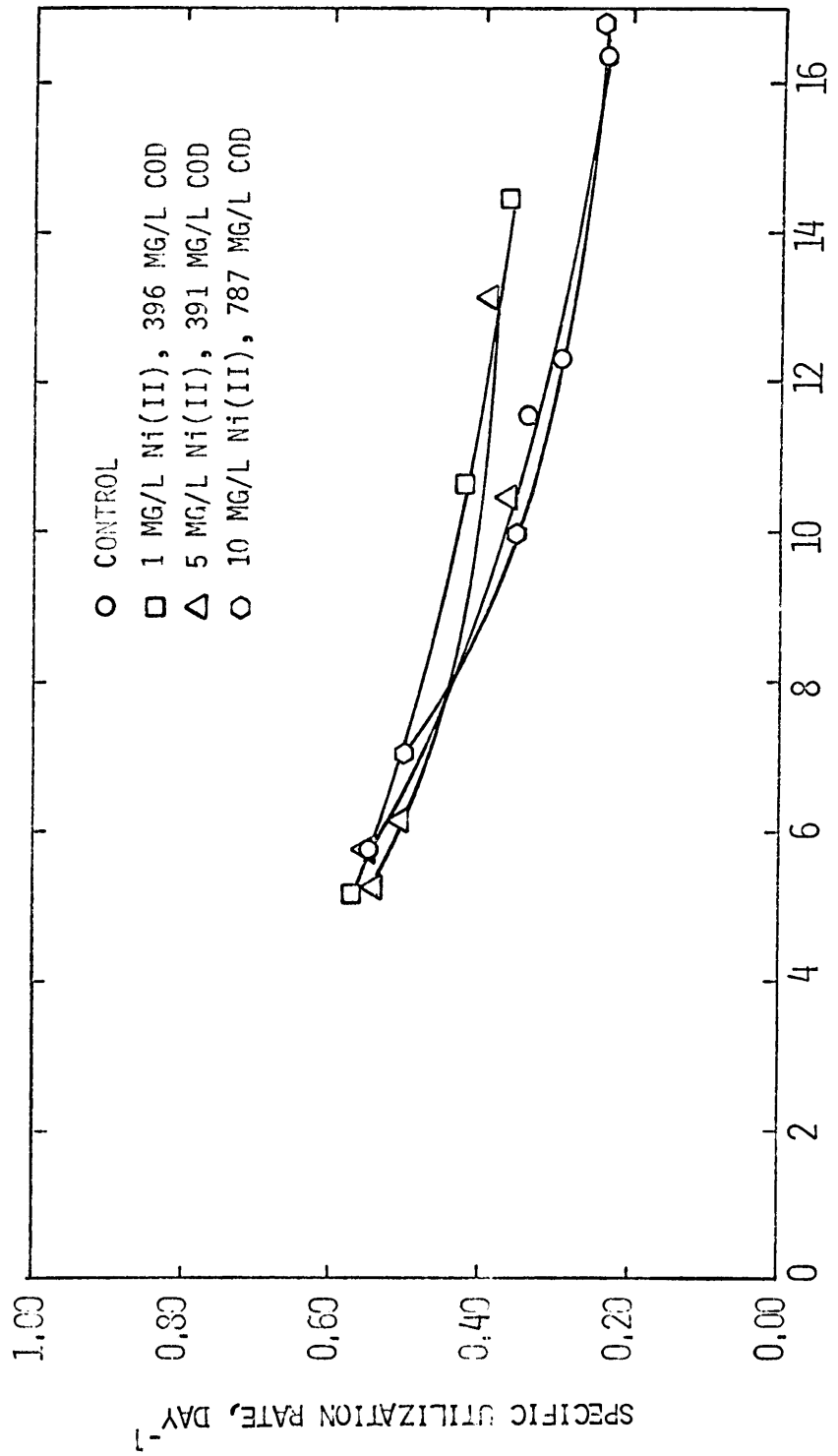

Figure 23. Effect of Nickel on Specific Utilization Rate at Different Mean Cell Residence Times.

control reactor and the reactor receiving the feed solution having 1 mg/l Ni(II) and 787 mg/l COD. This may be attributed to less substrate available for biomass synthesis in the reactors receiving the 1 mg/l Ni(II), 396 mg/l COD and the 5 mg/l Ni(II), 391 mg/l COD feed solution. For the nickel fed reactor receiving 1 mg/l Ni(II), 787 mg/l COD feed solution, the amount of substrate being utilized by microorganisms was higher than that in the control reactor. However, this nickel fed reactor contained higher microorganism concentrations. Thus, the rate of substrate utilization was approximately the same as the control reactor.

Biokinetic Coefficients

The microorganism cell yield coefficient and maintainance energy requirement were determined according to the linear relationship between specific growth rate and specific utilization rate as described by equation [52]

$$\frac{1}{\Theta_c} = Y_{max}\, U - k_d \qquad (52)$$

It can be seen from this linear equation that the slope of the straight line represents Y_{max} and the intercept represents k_d. Figure 24 illustrates the plots of specific growth rate versus specific utilization rate for all experimental runs. A least squares method was utilized to linearize the plotted experimental data. The values for Y_{max} and k_d obtained from each reactor are listed in Table XIV.

The values of Y_{max} and k_d for the reactors receiving the feed solutions having 1 mg/l Ni(II), 396 mg/l COD and 5 mg/l Ni(II), 391 mg/l

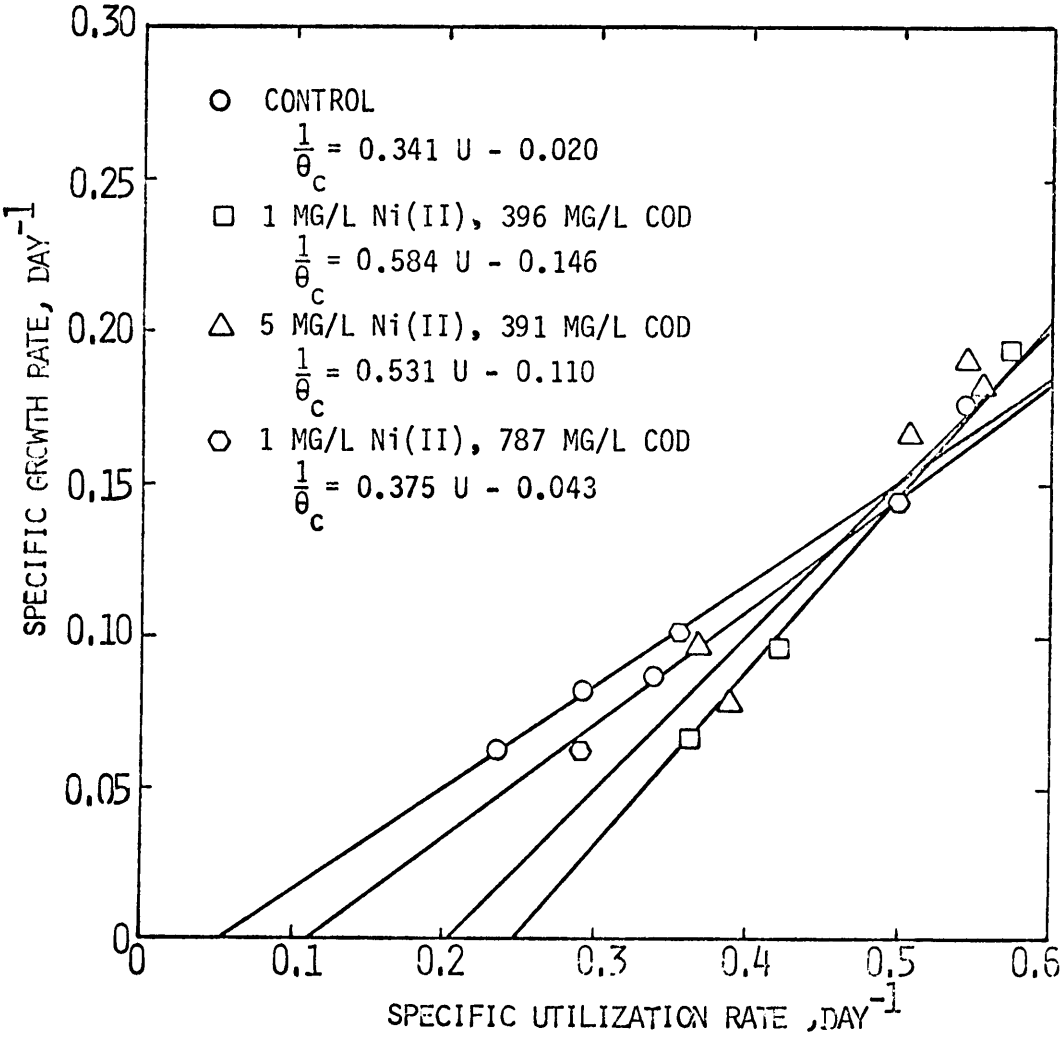

Figure 24. Specific Growth Rate versus Specific Utilization Rate.

TABLE XIV. BIOKINETIC EQUATIONS AND COEFFICIENTS

Reactor	Linear Equation	Y_{max}	k_d (day^{-1})
Control	$\frac{1}{\theta_c} = 0.341\ U - 0.020$	0.341	0.020
Ni(II) = 1 mg/l, COD = 396 mg/l	$\frac{1}{\theta_c} = 0.584\ U - 0.146$	0.584	0.146
Ni(II) = 5 mg/l, COD = 391 mg/l	$\frac{1}{\theta_c} = 0.531\ U - 0.110$	0.531	0.110
Ni(II) = 1 mg/l, COD = 787 mg/l	$\frac{1}{\theta_c} = 0.375\ U - 0.043$	0.375	0.043

COD are higher than those obtained for the control reactor. The high value of Y_{max} observed in these nickel fed reactors may be attributed to the influence of nickel on the activated sludge process causing a shift in microbial species and these nickel tolerant organisms in these reactors may eventually have higher cell yield coefficients. It may also be attributed to the stimulatory effect of nickel on microbial activity (i.e. nickel has been found to increase amino acid decarboxylation in Escherichia coli (23) and thus increases the synthesis of cellular structure. However, the microorganisms in these nickel fed reactors were stressed by the presence of nickel in the reactors which was indicated by higher values of k_d than that for the control reactor. The high k_d value obtained for these nickel fed reactors may be due to stressed microorganisms requiring higher maintainance energy for their biological activities.

The values of Y_{max} and k_d for the nickel fed reactor receiving 1 mg/l Ni(II) 787 mg/l COD, however, are approximately the same as those obtained for the control reactor. This indicates that the increase in COD concentration can reduce the toxicity of nickel on microbial activity. This may be attributed to more organic substrate available to complex with nickel or the increase in ammonia in the feed solution (to maintain constant COD:TKN) may complex with nickel and reduce the toxicity of nickel. The increase in COD concentration can also increase the microorganism concentration in the reactor and thus decrease the ratio of nickel to biomass and thereby decrease the toxicity of nickel. The high microorganism concentration can increase the amount of

extracellular polysaccharide which is responsible for microbial aggregation. This extracellular polysaccharide can form organic-nickel complexes and can settle out in secondary clarifier or be removed through the daily wasting of sludge. The soluble nickel species present in the reactor decrease and thereby its toxicity decreases. As pointed out by Busch (74) and Adams et al (14), an increase in micro-organism concentration or increase in sewage strength and a decrease in metal dosage should decrease the toxicity of metal in the biological wastewater treatment process.

Sludge Production

As illustrated in Figure 25, low sludge production was observed in the reactors receiving 1 mg/l Ni(II),396 mg/l COD feed solution and 5 mg/l Ni(II) 391 mg/l COD feed solution when compared to the control reactor. The low sludge production in these nickel fed reactors can be attributed to the higher maintainance energy requirement, k_d, than that for the control reactor. Sludge production for the reactor treating the feed solution having 1 mg/l Ni(II), 787 mg/l COD was higher than that for the control reactor even though the values of Y_{max} and k_d for these reactors were similar. This is due to the higher amount of substrate available for cellular synthesis in the nickel fed reactor. The sludge production for all reactors decreased as operating mean cell residence time increased.

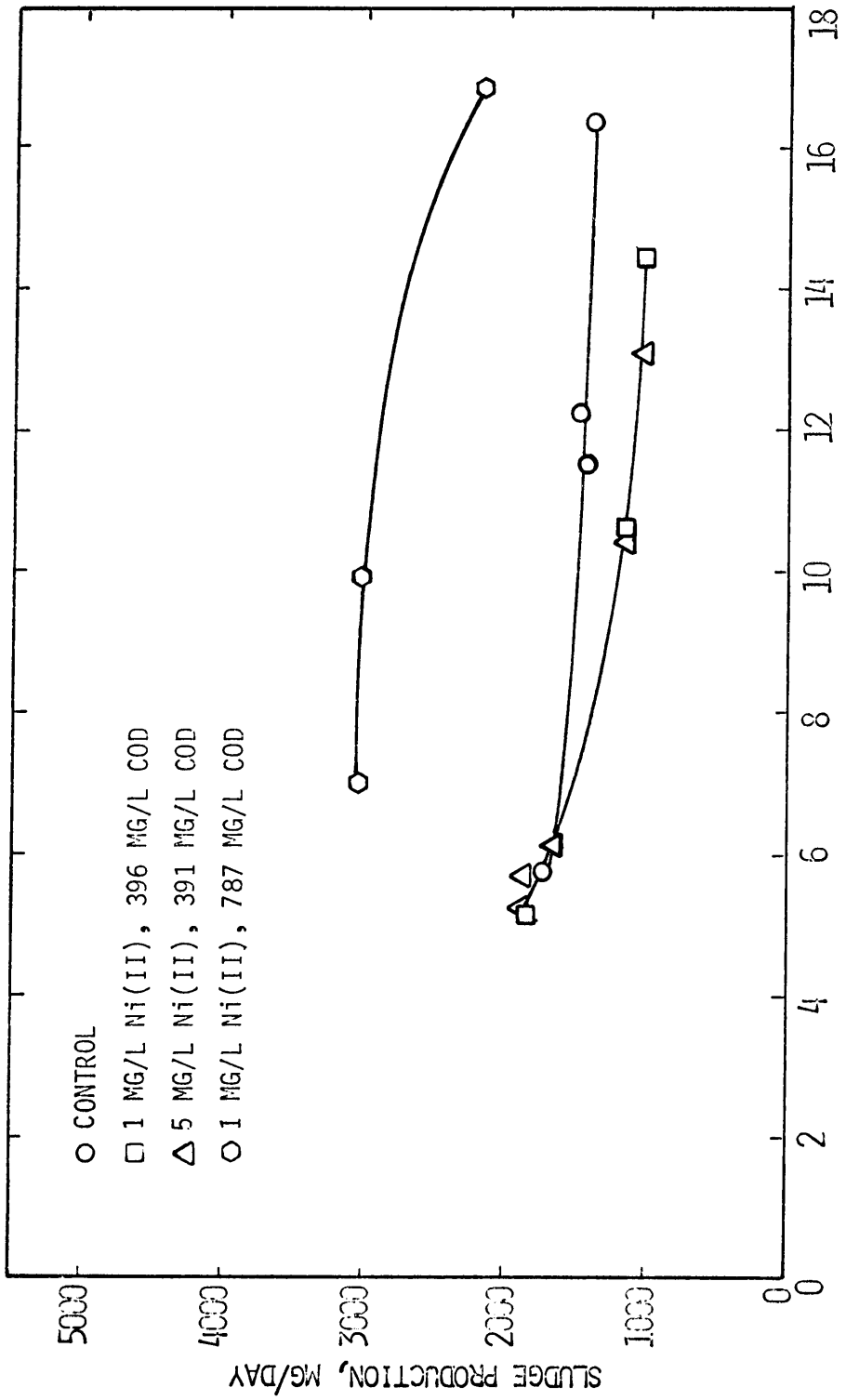

Figure 25. Effect of Nickel on Sludge Production at Different Mean Cell Residence Times.

Observed Yield

The effect of nickel on cellular synthesis based on the same amount of substrate utilized can be examined by inspecting the variation of the observed yield with θ_c. Figure 26 illustrates the effect of nickel on observed yield at various operating mean cell residence times. As can be seen from this figure, the observed yield for the nickel fed reactor receiving the feed solutions having 1 mg/l Ni(II), 396 mg/l COD and 5 mg/l Ni(II), 391 mg/l COD were higher than those for the control reactor. The low observed yield for these nickel fed reactors can be explained by the fact that the maintainance energy required by the microorganisms in these reactors is greater than that in the control reactor. Thus less energy is available for cellular synthesis. This indicates that cellular synthesis of microorganisms can be depressed by the presence of nickel in the feed solution. The values of observed yield for the reactor receiving the feed solution having 1 mg/l Ni(II), 787 mg/l COD were approximately the same as those obtained for the control reactor. This can be attributed to the decrease in toxicity of nickel resulting from the increase in substrate concentration.

Nitrification and Alkalinity Relationship

Nitrification occurs to some extent in an activated sludge process operated at θ_c greater than 3 days provide that there is no toxic material presence and environmental conditions are suitable for nitrifying bacteria. Nitrification may be inhibited by the presence of nickel

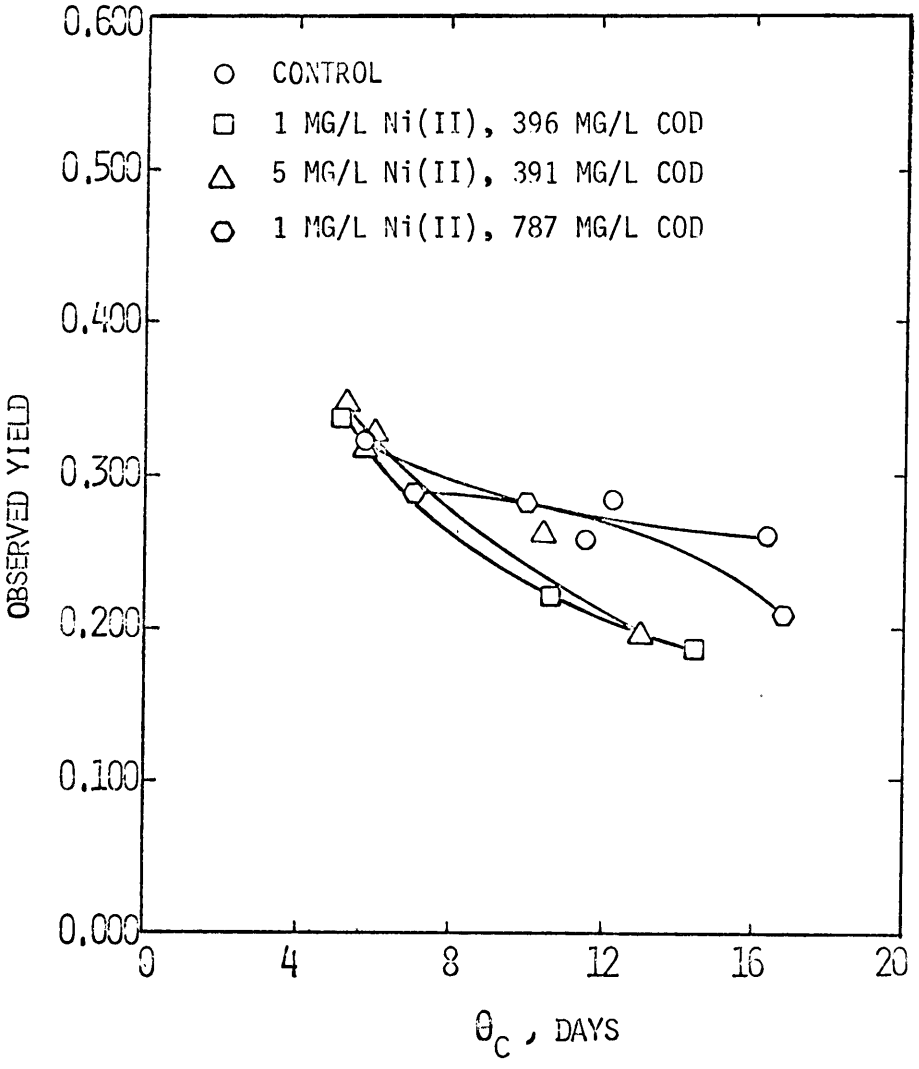

Figure 26. Effect of Nickel on Observed Yield at Different Mean Cell Residence Times.

in wastewater at relatively low concentrations. A threshold toxicity of nickel on nitrification has been reported to be 0.5 mg/l (75).

The results obtained from these experimental studies have indicated that the degree of nitrification is dependent on operating mean cell residence time, substrate concentration and nickel concentration in the feel solution. The degree of nitrification in turn influences the distribution of nitrogen in the activated sludge process. Figure 27 to Figure 30 demonstrate the effects of mean cell residence time, nickel concentration and substrate concentration on the distribution of nitrogen species in the activated sludge process. Equations [62], [63], [64] and [65] were utilized to generate the plotted data for these graphs. Organic nitrogen being incorporated into microbial cell was assumed to be 14 percent by weight of the total microbial mass. As illustrated in Figure 27, nitrification in the control reactor was found to be dependent on operating mean cell residence time. As mean cell residence time increased, the percent NH_3-N in the system decreased and the percent NO_3^--N in the system increased. This can be attributed to the larger nitrifier populations at high mean cell residence time than those at low mean cell residence time. Although nitrification in the control reactor was evident at θ_c = 5.8 days, NH_3-N and alkalinity were produced in the system. This is due to the fact that at this low mean cell residence time, the population of nitrifying bacteria is not very high and thus the oxidation rate of NH_3-N to NO_3^--N is offset by the deamination rate of organic nitrogen to NH_3-N.

As can be seen in Figure 28 and 29 the percent of NH_3-N in these

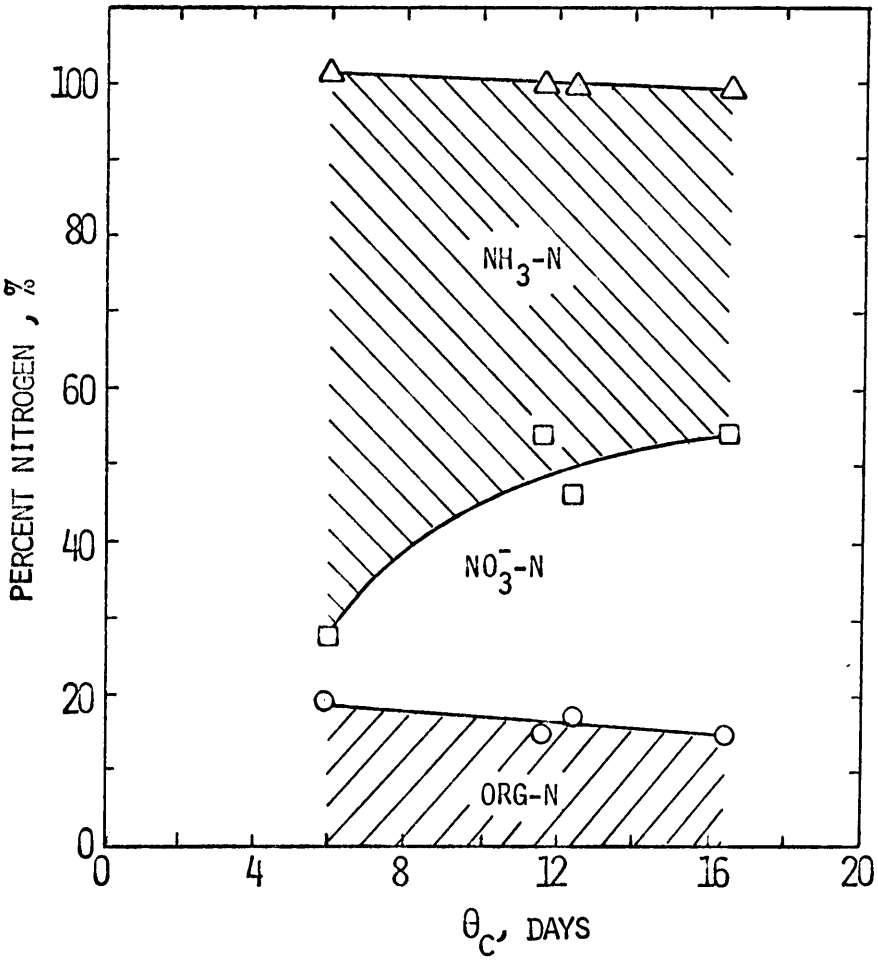

Figure 27. Nitrogen Distribution in Effluent and Wasted Nitrogen as a Function of Mean Cell Residence Time for Control Reactor (COD = 394 mg/l).

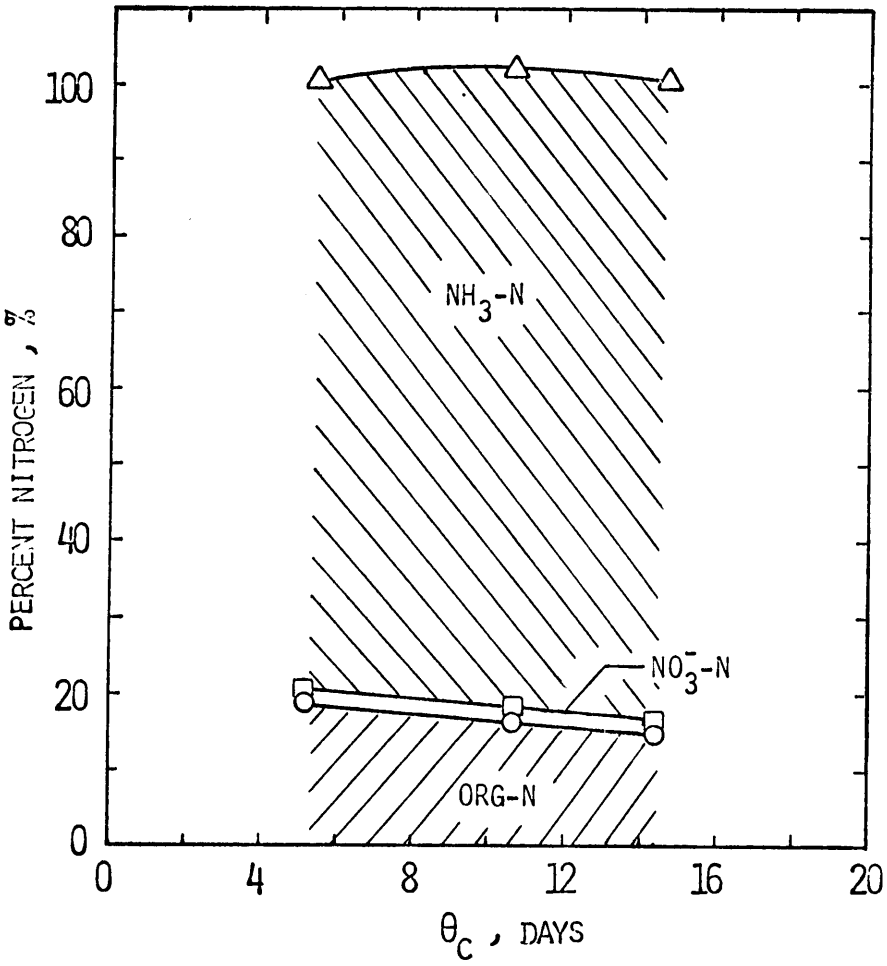

Figure 28. Nitrogen Distribution in Effluent and Wasted Nitrogen as a Function of Mean Cell Residence Time for Ni(II) = 1 mg/l, COD = 396 mg/l.

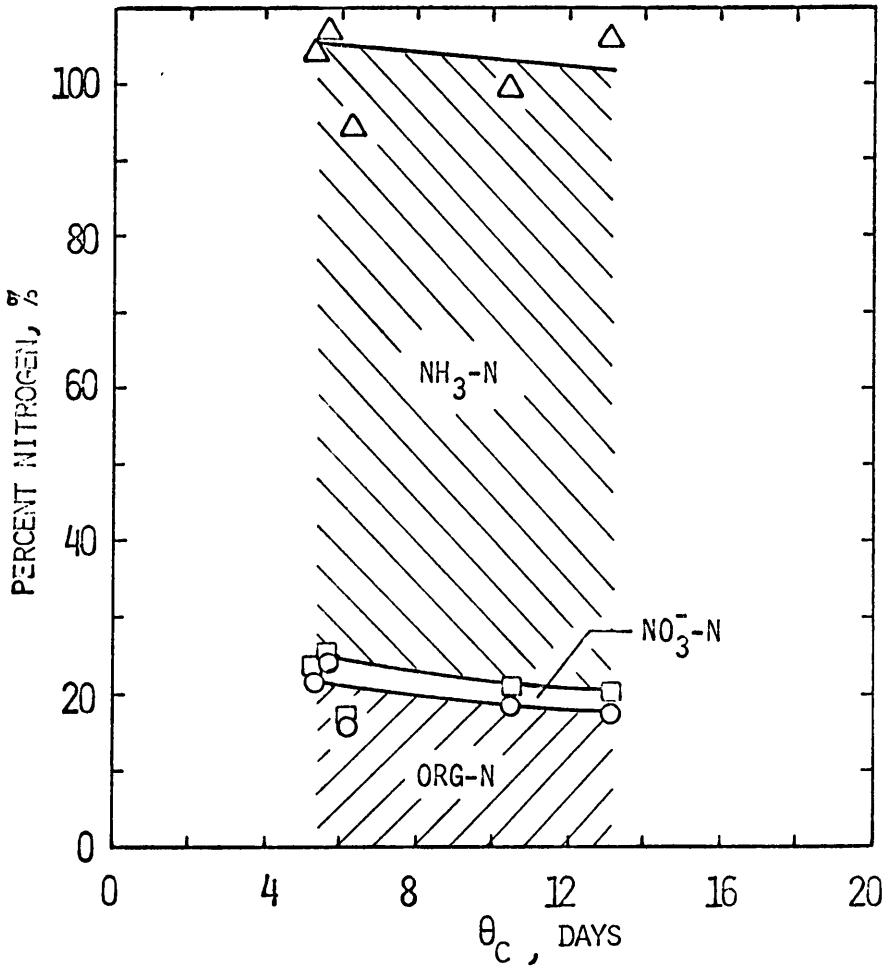

Figure 29. Nitrogen Distribution in Effluent and Wasted Nitrogen as a Function of Mean Cell Residence Time for NI(II) = 5 mg/l, COD = 391 mg/l.

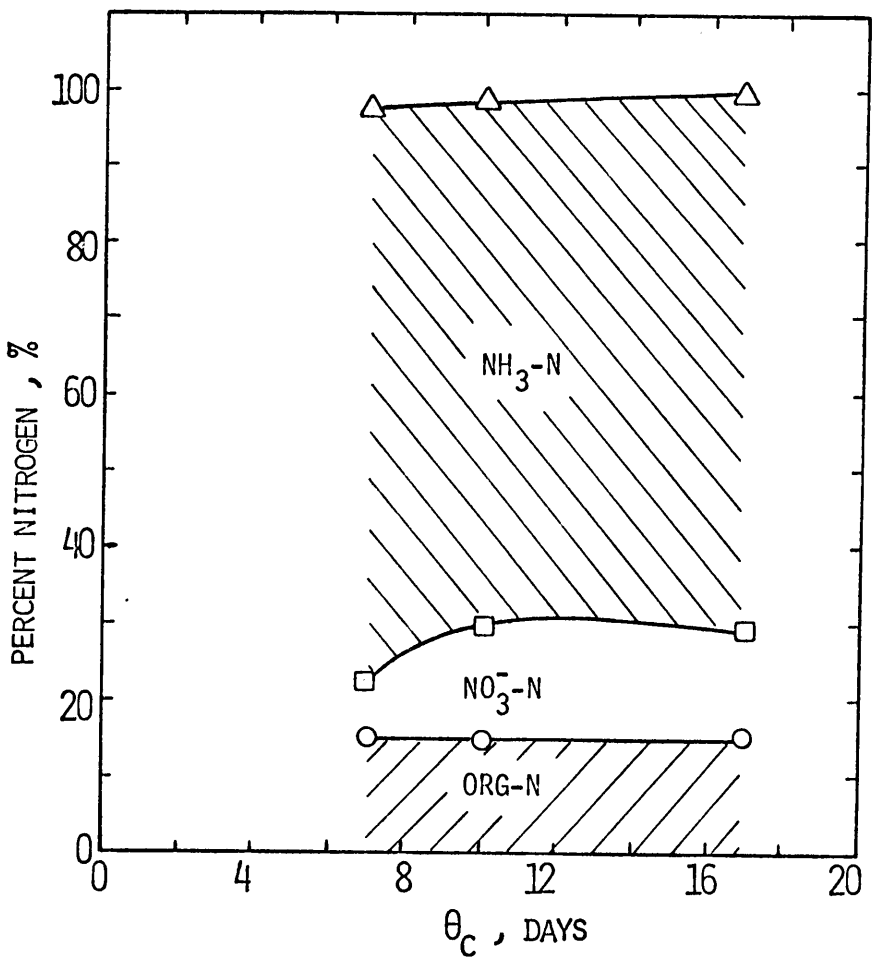

Figure 30. Nitrogen Distribution in Effluent and Wasted Nitrogen as a Function of Mean Cell Residence Time for Ni(II) = 1 mg/l, COD = 787 mg/l.

nickel fed reactors was high and nearly constant over the range of operating mean cell residence time. The production of NH_3-N and alkalinity were observed at all mean cell residence time. The increase in NH_3-N and alkalinity in the process is due to the inhibition of nitrifying bacterial activity by the presence of nickel and deamination of amino acids in the feed solutions. These feed solutions having 1 mg/l Ni(II),396 mg/l COD and 5 mg/l Ni(II), 391 mg/l COD. The percent of NO_3^--N distribution in the system was insignificant and appeared to be independent of mean cell residence time. This indicated the absence of nitrification in the system and was responsible for the rise in the NH_3-N and alkalinity in the system. Figure 30 illustrates the influence of mean cell residence time on the distribution of nitrogen species in the nickel fed reactor receiving the feed solution having 1 mg/l Ni(II) and 787 mg/l COD. The results indicated that the percent distribution of NH_3-N in the system decreased as θ_c increased. The percent distribution of NO_3^--N increased as θ_c increased. Production and destruction of alkalinity were observed as operating θ_c increased from 7.1 days to 16.9 days. This can be attributed to the rate of nitrification increasing as θ_c increases.

Figure 31 shows the effect of nickel concentration and substrate concentration on nitrification at various operating mean cell residence times. As can be seen from this Figure, nitrification was absent in the nickel fed reactor receiving the feed solutions having 1 mg/l Ni(II) 396 mg/l COD and 5 mg/l Ni(II), 391 mg/l COD. By increasing the COD concentration to 787 mg/l COD while maintaining 1 mg/l of Ni(II) in the

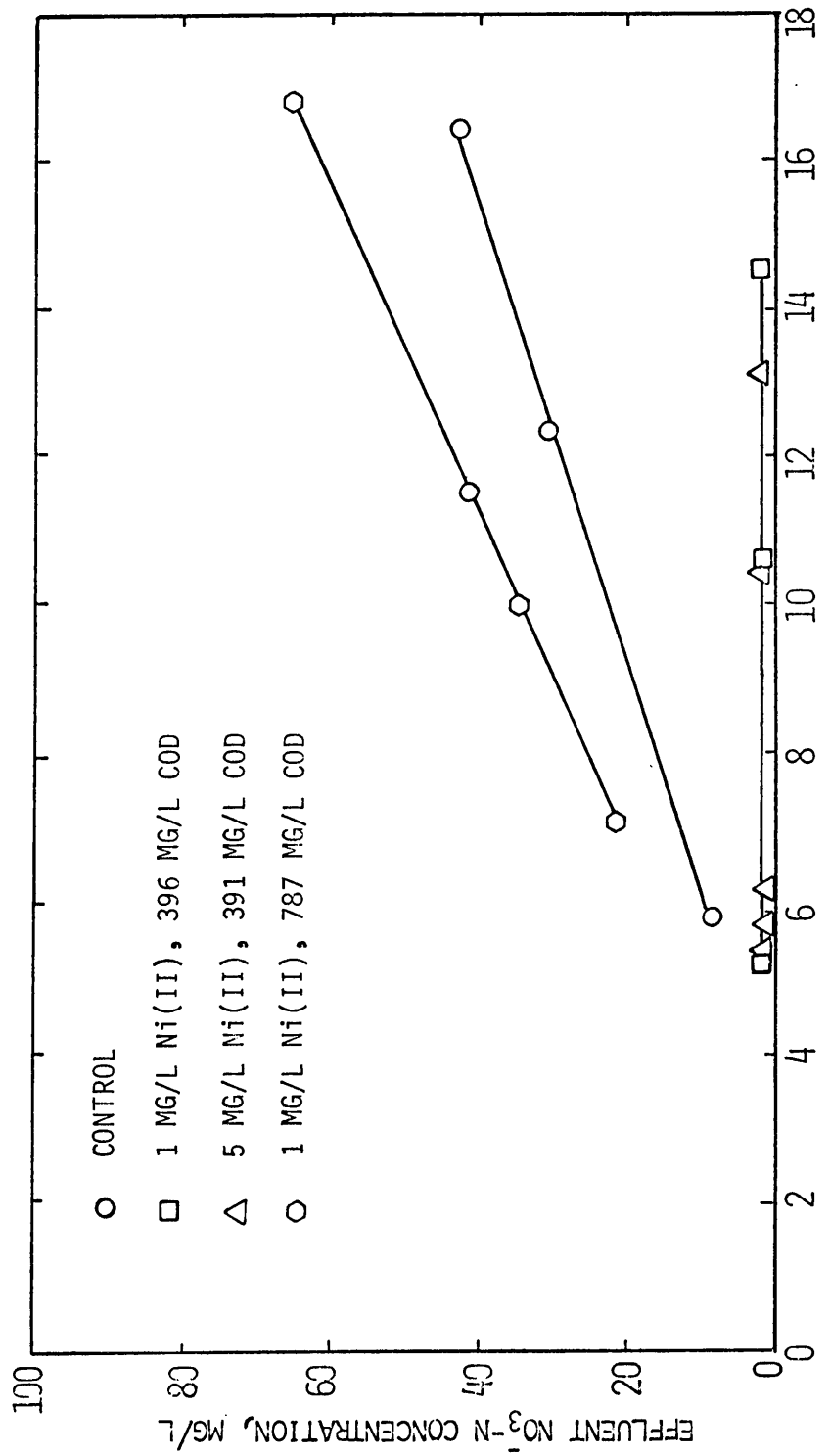

Figure 31. Effect of Nickel on Nitrification in the Activated Sludge Process Operated at Different Mean Cell Residence Times.

feed solution, nitrification was not as affected by the nickel presented in the feed solution. The effluent NO_3^--N concentration was higher than that for the control reactor. Higher NH_3-N concentration in the feed solution increased the nitrifying population in the reactor oxidize and subsequently increased the NO_3^--N in the system. The degree of nitrification in this nickel fed reactor and the control reactor was dependent on Θ_c.

The inhibition of nitrification in the nickel fed reactor receiving the feed solution having 1 mg/l Ni(II), 396 mg/l COD and the noninhibition of nitrification in the nickel fed reactor receiving the feed solution having 1 mg/l Ni(II), 787 mg/l COD indicates that the toxicity of nickel on microbial activity is not a function of nickel concentration alone. The concentration of substrate in the feed solution is another important factor that influences the toxicity of nickel. This may be explained by the fact that increasing the substrate concentration enhances the formation of nickel complexes such as nickel-organic complexes and nickel-amine complexes and subsequently decreases the toxicity of nickel present in the system. In addition the increases in substrate concentration increased the microorganism concentration in the system and thereby decreases the proportion of active cellular components that are bound as nickel organic complexes (14). Figure 32 illustrates the effect of MLSS to Ni(II) ratio on nitrification. It is clearly indicated that the toxicity of nickel is also a function of the ratio of microorganism concentration presence in the reactor to the soluble nickel presence in the feed solution.

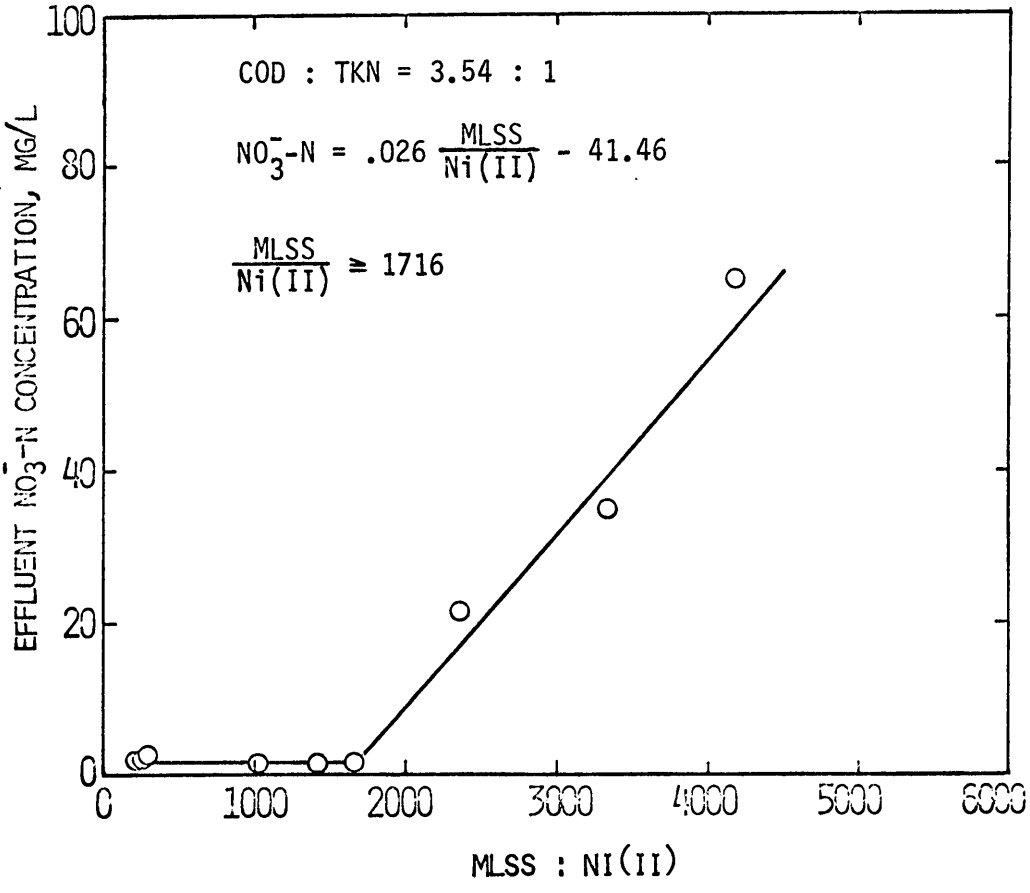

Figure 32. Effect of MLSS:Ni(II) on Nitrification in Activated Sludge Process.

For the activated sludge process treating nickel bearing wastewater, the concentration of NO_3^--N in the effluent as the function of MLSS:Ni(II) ratio can be predicted by the following empirical equation for a COD:TKN of 3.53:1 at 14.0 hours total system hydraulic detention time.

$$NO_3^-\text{-}N = .026 \frac{X}{Ni(II)} - 41.46 \qquad (70)$$

This empirical equation can be related to the ratio of influent substrate concentration and influent nickel concentration as follows:

$$NO_3^-\text{-}N = 0.00026 \left(\frac{S_o}{Ni(II)}\right)(\theta_c)\left(\frac{Y_{max}}{1+k_d\theta_c}\right)\left(\frac{E}{\theta}\right) - 41.46 \qquad (71)$$

A value of NO_3^--N = 0 indicates the absence of nitrification. All the terms being used in equation (70) and (71) have been defined previously.

Nitrification is related to the alkalinity in such a way that oxidation of 1 mg/l of NH_3-N to NO_3^--N destroyed 7.14 mg/l of alkalinity as $CaCO_3$. The ratios of mg alkalinity destroyed per mg of NH_3-N oxidized in the nitrified activated sludge process have been reported to be between 6.0 to 7.1 (76). However, increases of alkalinity were observed in these experimental studies. The increasing alkalinity in the system can be attributed to the deamination or mineralization of organic nitrogen to free NH_3-N at a rate higher than the oxidation of NH_3-N to NO_3^--N. Deamination or mineralization of 1 mg/l of Org-N to free NH_3-N imparts 3.57 mg/l of alkalinity as $CaCO_3$ into the system. Incorporation of 1 mg/l of NH_3-N into microbial cell destroys 3.57 mg/l of alkalinity as $CaCO_3$. The changes of alkalinity in the activated

sludge process can be predicted by equation [64]. Figure 33 compares the predicted alkalinity and the measured alkalinity of the systems studied. As can be seen, the alkalinity in the activated sludge process can be closely predicted by this equation.

Nickel Removal

Figure 34 shows nickel removal efficiency for each reactor studied. Nickel removal efficiency increased as nickel concentration increased for the nickel fed reators receiving the feed solution having approximately the same COD concentration. This may be attributed to the precipitation of nickel in addition to the uptake by biological solids. For the nickel fed reactor receiving the feed solution having 1 mg/l Ni(II),787 mg/l COD, the efficiency of nickel removal was higher than that for the nickel fed reactor receiving 1 mg/l Ni(II),396 mg/l COD. This can be explained by the fact that the increase of COD concentration in the feed solution causes increasing of microorganism concentration in the reactor. These microorganisms produce extracellular polysaccharide that can bind with nickel present in the system. Thus, higher influent COD concentration increases nickel removal efficiency in the system. Figure 35 illustrated the uptake of nickel by the activated sludge for each nickel fed reactor. A comparison between the nickel fed reactors receiving the feed solutions having 1 mg/l Ni(II),396 mg/l COD and 5 mg/l Ni(II), 391 mg/l COD indicates that the degree of nickel uptake is dependent on nickel concentration in the feed solution. It can also be seen that the uptake of nickel in the nickel fed reactor

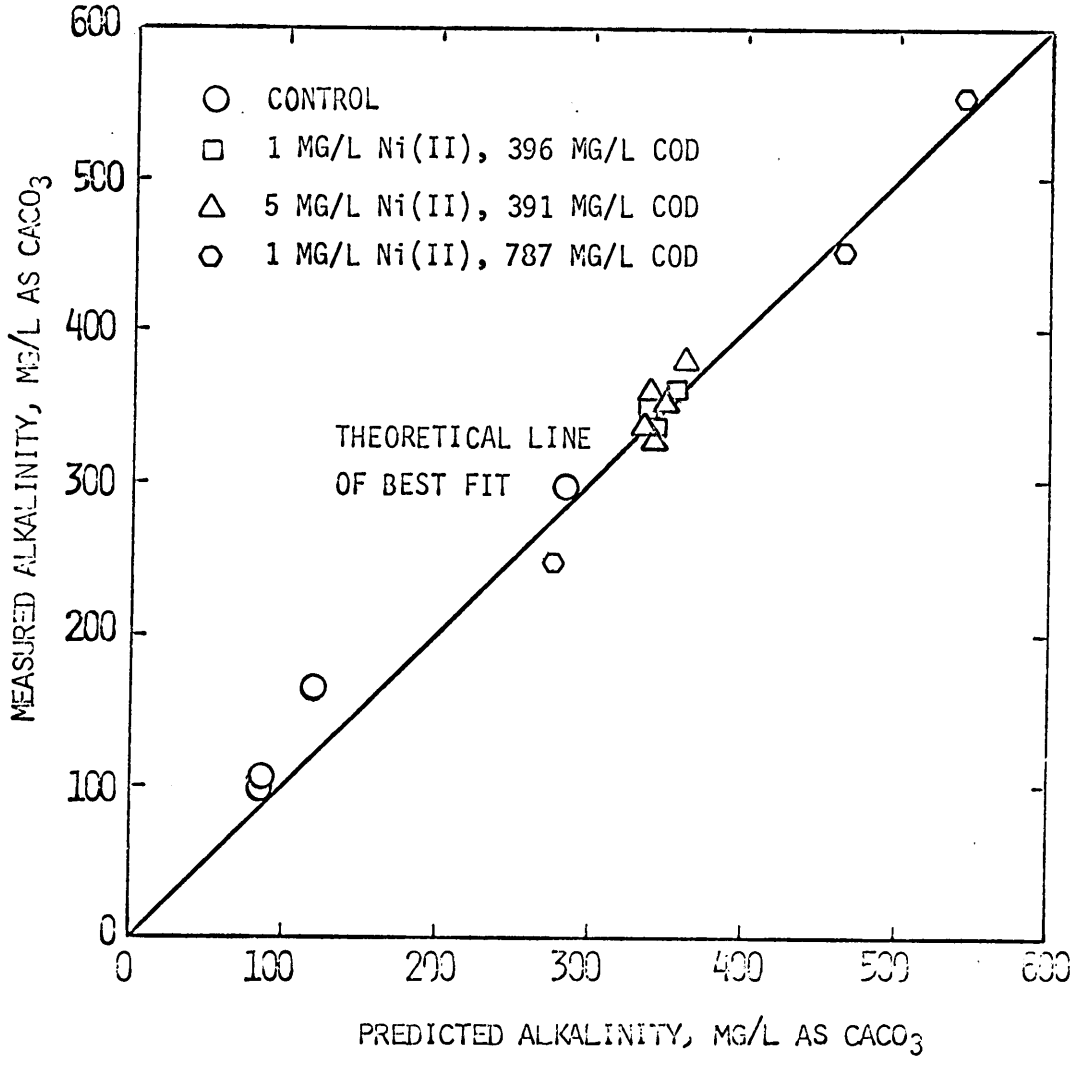

Figure 33. Comparison of Predicted Alkalinity with Measured Alkalinity.

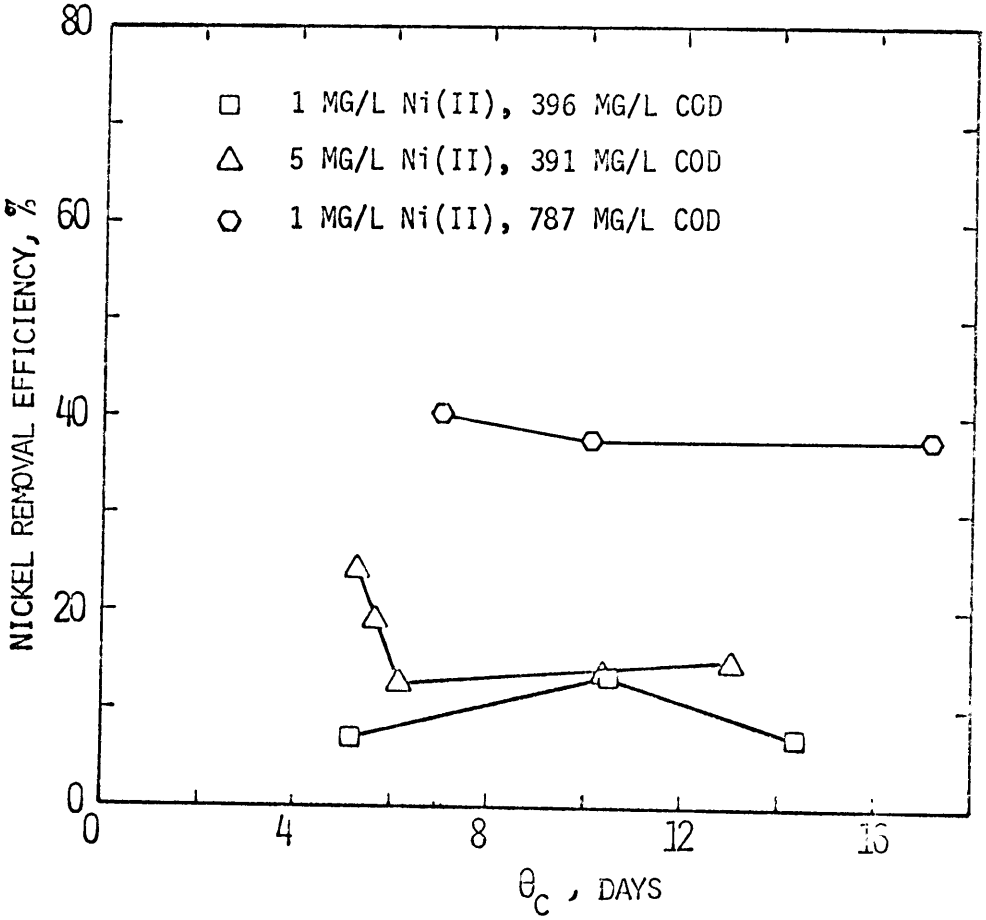

Figure 34. Nickel Removal Efficiency at Differrent Mean Cell Residence Times.

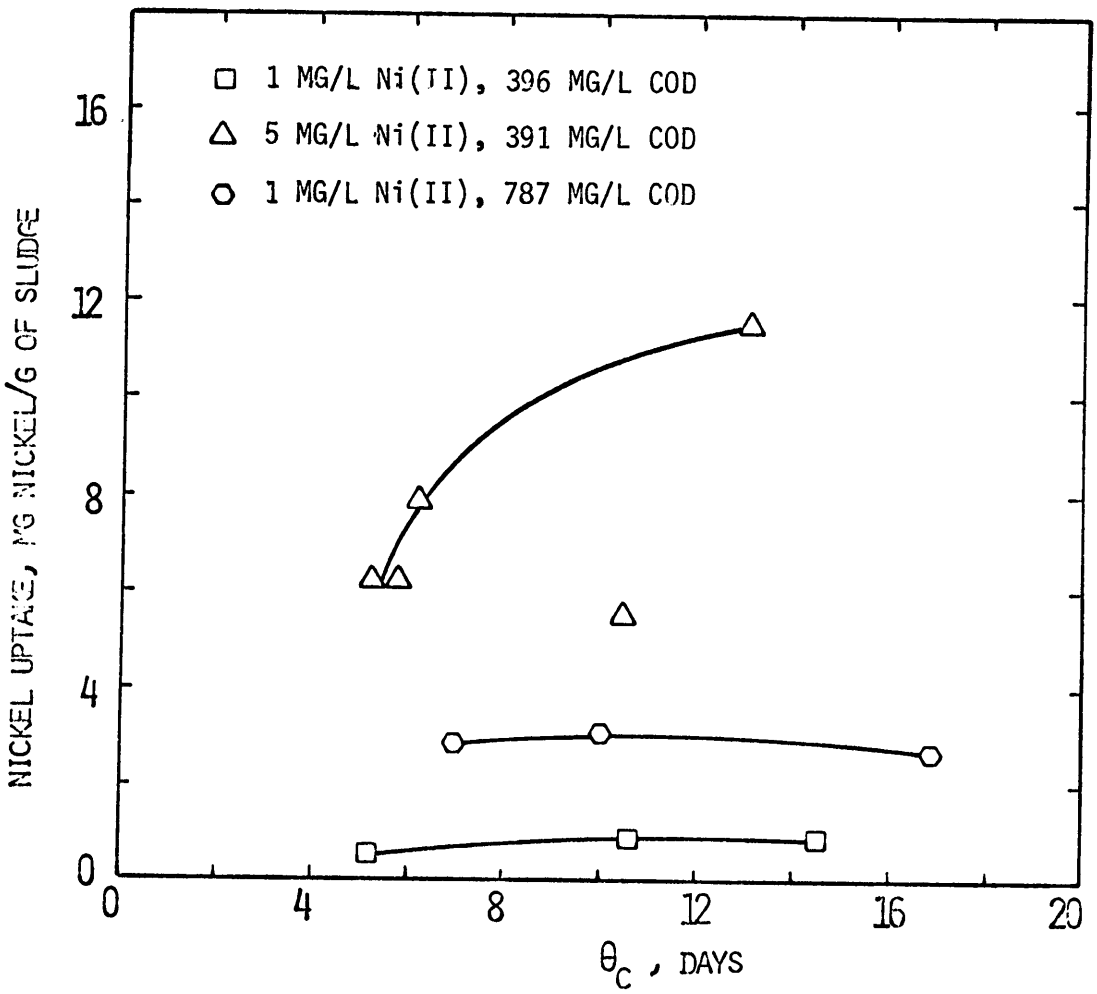

Figure 35. Nickel Uptake by the Activated Sludge at Different Mean Cell Residence Times.

receiving 1 mg/l Ni(II),787 mg/l COD is higher than that in the nickel fed reactor receiving 1 mg/l Ni(II),396 mg/l COD. This indicated that the uptake of nickel by activated sludge was dependent on substrate concentration in the wastewater.

Toxicity of Nickel to the Activated Sludge Process

The results obtained from these experimental studies have indicated that the degree of nickel toxicity in the activated sludge process depends on several factors other than the concentration of nickel present in the wastewater. High operating mean cell residence times can reduce the toxicity of nickel in the activated sludge process due to the fact that high microorganism concentrations in the process occur at high mean cell residence times. The concentration of substrate in the wastewater can greatly reduce the toxicity of nickel in the activated sludge process due to the fact that the high organic substrate concentration increases the microorganism concentration in the process. In addition, organic substrate and inorganic substrate present in the wastewater can also function as nickel ligands. Since only soluble nickel species can be actively transported across the cell membrane and affects the enzyme activity, the formation of nickel complexes with various ligand (i.e. organo-nickel complexes, nickel-amine complexes) can reduce the toxicity of nickel in the activated sludge process significantly. The results obtained from these experimental studies, however,have been found to agree with the theory postulated by Busch (74) and Adams et. al. (14). Busch (74) has postulated that

the toxicity of toxic ion on microorganisms depends on the ratio of toxic ion to biomass rather than the concentration of toxic ion alone. Adams et. al. (14) have also postulated that an increase in microorganism concentration, or increase in sewage strength and a decrease in metal dosage should decrease the proportion of active cellular component which are complexed with heavy metal and thus decrease the inhibitory effects of metal on the biological treatment process.

The results from the experimental studies have indicated that the COD concentration, nickel concentration in the wastewater and operating mean cell residence time are very important factors to assess the toxicity of nickel on the activated sludge process.

VII. ENGINEERING APPLICATIONS

The experimental results obtained from these studies are significant to the design and operation of the activated sludge process treating nickel bearing wastewater. The purpose of this section is to illustrate the practical applications of the experimental results.

DESIGN

The biokinetic coefficients, Y_{max} and k_d are helpful when designing an activated sludge process. The values of Y_{max} and k_d are affected by nickel ions presence in the wastewater. The effects of nickel on these biokinetic coefficients are dependent upon the COD to nickel ratio. Design engineers must be aware of the significance of the COD to nickel ratio in the wastewater. Altering COD concentration in the wastewater is not always practical, however, varying nickel concentrations in the wastewater can be accomplished by separation of nickel bearing wastewater from wastewater void of nickel. Certain COD to nickel ratios in wastewater can be achieved by proportioning these wastewaters in an equalization tank. Pretreatment of nickel bearing wastewater is required to reduce nickel concentration down to the desired concentration. Chemical precipitation or adsorption processes can be utilized to remove nickel from wastewater.

The activated sludge process with nitrification usually utilizes two stages of treatment processes. The first stage of treatment is to remove or stabilize the organic substrate in the wastewater while the second stage of treatment is utilized for nitrification. Although

nickel can be removed to some extent in the first stage of treatment, nitrification can be inhibited by low concentration of nickel in the effluent from the first stage. As discussed earlier, an increase in COD to nickel ratio can reduce the toxicity of nickel and reduce the effluent nickel concentration and may prevent failure of nitrification in the second stage.

In the design of the activated sludge process treating nickel bearing wastewater, it is feasible to know the threshold toxicity of nickel based upon the ratio of COD to nickel concentration in the wastewater.

OPERATION

To operate the activated sludge process treating nickel bearing wastewater a certain ratio of COD to nickel concentration in wastewater entering the process must be maintained to prevent any adverse effects on treatment efficiency. Operating the activated sludge at high operating θ_c will result in high microorganism concentration available for nickel and substrate removal and less susceptibility to any variation in wastewater characteristics including nickel concentration. The presence of nickel complexing reagents can reduce the toxic effects of nickel substantially. A knowledge of nickel complexing reagents and ligands is helpful for treatment plant operator when faced with a nickel bearing wastewater problem.

VIII. CONCLUSIONS

From these experimental studies, the following conclusions can be drawn:

Slug Fed Batch Reactors

1. COD removal rate and COD removal efficiency were reduced by shock doses of nickel of 1, 5 and 10 mg/l of Ni(II). These reductions in COD removal rate and COD removal efficiency were not very significant. The effect of nickel on COD removal rate and COD removal efficiency in acclimated batch reactors was also negligible.
2. Shock doses of nickel at 1 and 5 mg/l Ni(II) increased the value of the microorganism cell yield coefficient. This indicated a stimulatory effect of shock doses of nickel at these concentrations. A shock dose of nickel at 10 mg/l decreased the value of microorganism cell yield which indicated an inhibitory effect of nickel at high concentrations. The effect of nickel on the cell yield coefficient of acclimated batch reactors was negligible.
3. The rate of nickel uptake and nickel removal efficiency were high in the shock loaded batch reactor and were found to be dependent on nickel concentration and time after applying the shock load. The rate of nickel uptake and nickel removal efficiency for the acclimated batch reactor were lower than those for the shock loaded batch reactors.

4. The stimulatory effects and inhibitory effects of nickel on the microorganism cell yield coefficient can be observed in the shock loaded batch reactor.

Continuous Flow Reactor with Cell Recycle

5. COD removal efficiency was not significantly affected by the presence of nickel as high as 5 mg/l at a θ_c of greater than 5 days.
6. The introduction of 1 and 5 mg/l of Ni(II) to the feed solution having 396 mg/l COD and 391 mg/l COD respectively resulted in inhibition of heterotrophic and autotrophic activity. By increasing COD concentration to 787 mg/l while maintaining 1 mg/l Ni(II) in the feed solution, microbial growth approached that of the feed solution containing no Ni(II).
7. A continuous feed of nickel-bearing wastewater to the activated sludge process may result in either a replacement of organisms species in the process or a stimulatory or inhibitory response of microbial activities in the process as indicated by a change in biokinetic coefficients, Y_{max} and k_d. The values of Y_{max} and k_d appeared to be dependent on the ratio of COD to Ni(II) in the feed solution.
8. Observed yield and sludge production were affected by nickel present in the feed solution. Lower sludge production and observed yield than those in the control reactor was

observed in the nickel fed reactors receiving the feed solutions having 1 mg/l Ni(II), 396 mg/l COD and 5 mg/l Ni(II), 391 mg/l COD as a result of high k_d for these nickel fed reactors. By increasing COD concentration to 787 mg/l while maintaining 1 mg/l Ni(II) concentration in the feed solution, the influences of nickel on observed yield and sludge production were negligible.

9. Nitrification was inhibited by 1 and 5 mg/l Ni(II) present in the feed solution having 396 mg/l and 391 mg/l COD, respectively. Nitrification proceeded by increasing the COD concentration to 787 mg/l while maintaining 1 mg/l of Ni(II) concentration in the feed solution. The degree of nitrification appeared to be dependent on the COD to Ni(II) ratio and thereby MLSS to Ni(II) ratio.

10. Degree of nitrification in the activated sludge process treating a nickel bearing wastewater having a COD to TKN ratio of 3.54:1, was found to be predicted by

$$NO_3^-\text{-}N = .00026\left(\frac{S_o}{Ni(II)}\right)(\Theta_c)\left(\frac{Y_{max}}{1+k_d\Theta_c}\right)\left(\frac{E}{\Theta}\right) - 41.46$$

11. The toxicity of nickel to nitrification appears to be based on the COD to nickel ratio rather than the concentration of nickel alone.

12. Production of alkalinity can occur in the activated sludge process.

13. The influences of nickel on the activated sludge process depend on organic substrate to nickel ratio, microorganism concentration to nickel ratio and operating mean cell residence time.

IX. RECOMMENDATIONS FOR FUTURE STUDY

Based on the experimental results, the following topics are suggested for future study:

Slug Fed Batch Reactor

1. A study to determine the response of activated sludge when receiving shock doses of nickel at a wider range of substrate concentrations.
2. An investigation to determine the mechanisms of nickel removal in shock loaded and acclimated batch reactors. The kinetics of nickel uptake should also be studied.

Continuous Flow Reactor With Cell Recycle

3. An investigation to determine the influences of other COD to Ni(II) ratio on the activated sludge process. The effects of the COD to Ni(II) ratios on the sludge characteristics, i.e.; settling, dewatering and nickel content could also be studied.
4. An analysis to determine the influences of NH_3-N to Ni(II) ratio on nitrification in the activated sludge process.
5. A study to determine the optimal and economic procedure for treatment and disposal of nickel bearing sludge. Methods to recover nickel from sludge should also be considered.

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APPENDIX A.

Raw Data for Slug Fed Batch Reactors.

TABLE A-I

Growth Curve and Substrate Utilization Data for Control Batch Reactor.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	960	708	968	716	964	712	567
1	1020	784	1104	848	1062	816	533
3	1148	844	840	800	994	822	425
5	1132	872	1064	836	1098	854	375
7	1128	876	1168	940	1148	908	293
9	1124	856	1124	900	1124	878	257
11	1088	848	1056	860	1072	854	248
13	1084	864	1080	856	1082	860	249

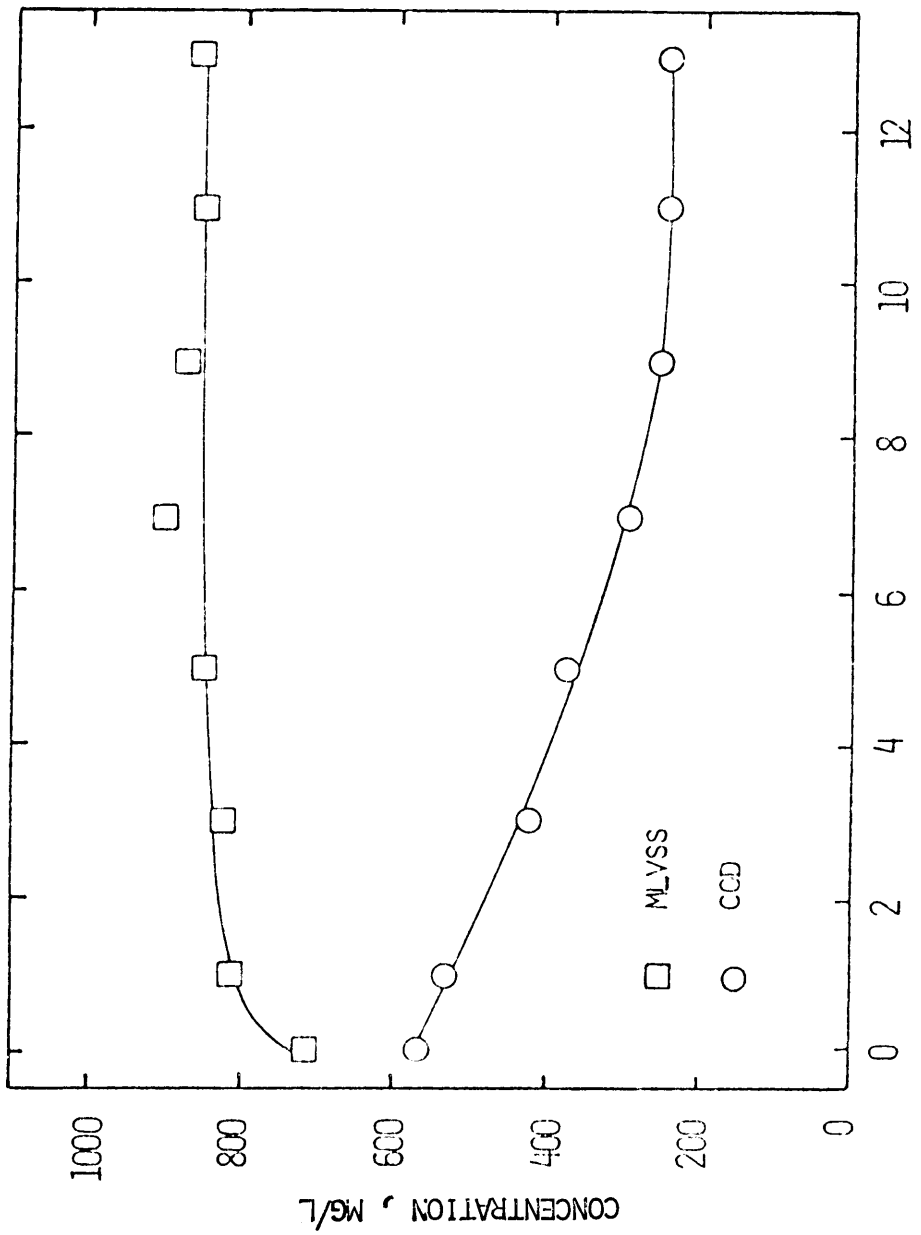

Figure A-1. Microbial Growth and Substrate Utilization in Control Batch Reactor.

TABLE A-II

Growth Curve and Substrate Utilization Data for Shock Loaded Batch Reactor, Ni(II) = 1 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	1108	804	1104	820	1106	812	583
1	1012	764	828	624	920	694	436
3	1156	876	1076	780	1116	828	443
5	1284	964	1118	892	1201	928	432
7	1180	884	1212	896	1196	890	417
9	1188	896	1236	920	1212	908	332
11	1188	892	1148	900	1168	896	261

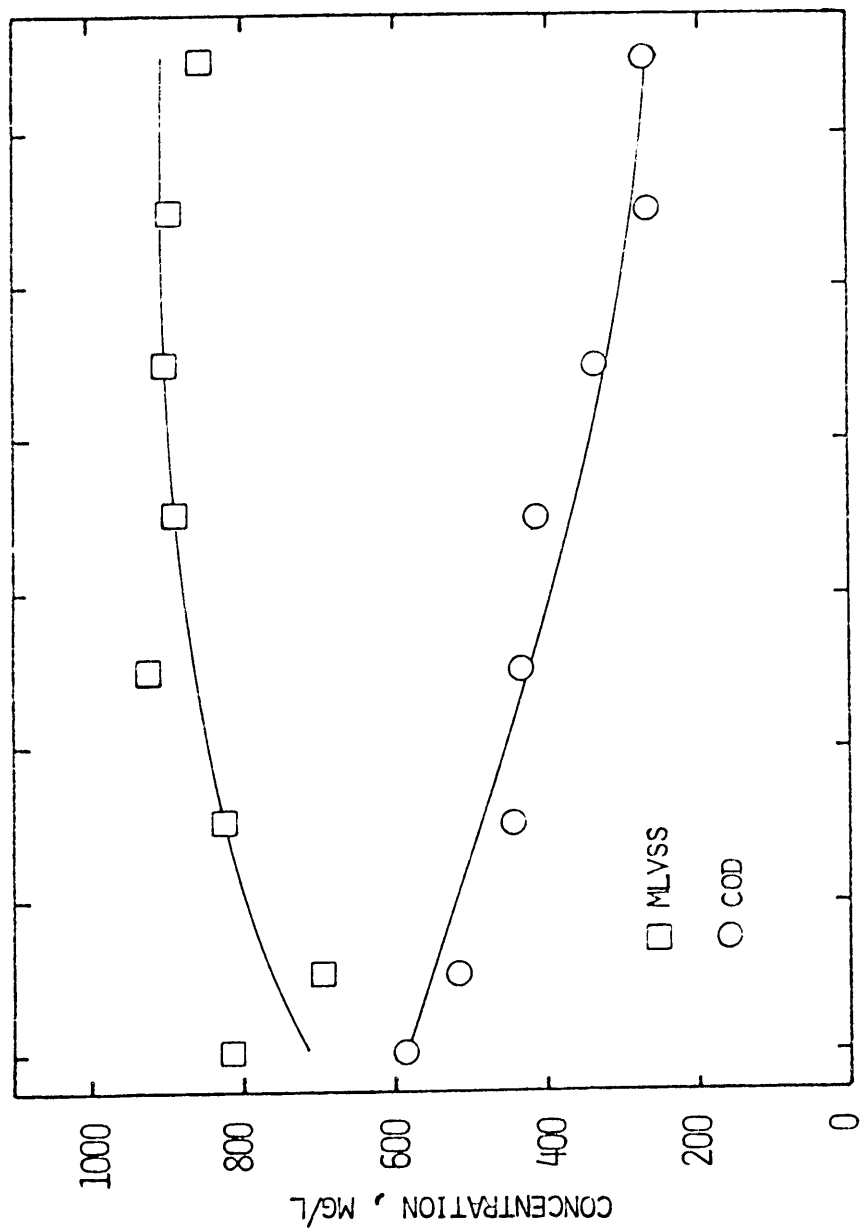

Figure A-2. Effect of 1 mg/l of Ni(II) on Microbial Growth and Substrate Utilization in Shock Loaded Batch Reactor.

TABLE A-III

Growth Curve and Substrate Utilization Data for Shock Loaded Batch Reactor, Ni(II) = 5 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	1024	752	1128	812	1076	782	598
1	1004	736	1056	764	1030	750	538
3	1096	784	1100	792	1098	788	482
5	1176	892	1148	844	1162	868	458
7	1060	792	1132	876	1096	834	347
9	944	720	1100	804	1022	762	333
11	1120	808	1156	900	1138	884	267
13	1128	876	1168	940	1148	908	301

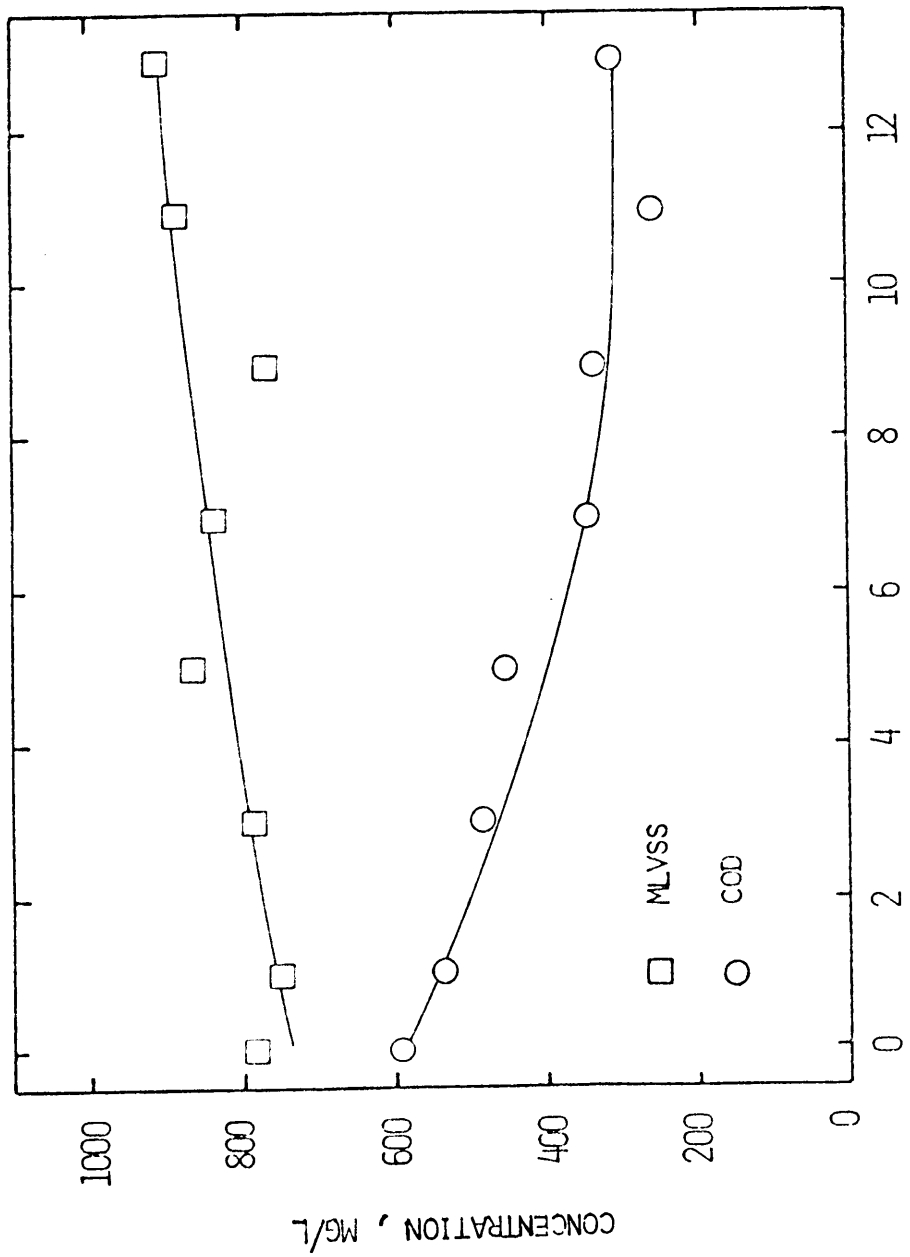

Figure A-3. Effect of 5 mg/l of Ni(II) on Microbial Growth and Substrate Utilization in Shock Loaded Batch Reactor..

TABLE A-IV

Growth Curve and Substrate Utilization Data for Shock Loaded Batch Reactor, Ni(II) = 10 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	1084	772	1060	792	1072	782	583
1	980	728	1036	736	1008	732	544
3	1128	832	1088	776	1108	804	434
5	1032	764	1048	796	1040	780	490
7	1123	832	1068	828	1096	830	392
9	1088	848	1088	824	1088	836	322
11	1064	800	1088	836	1076	818	330
13	1228	860	1124	800	1176	830	317

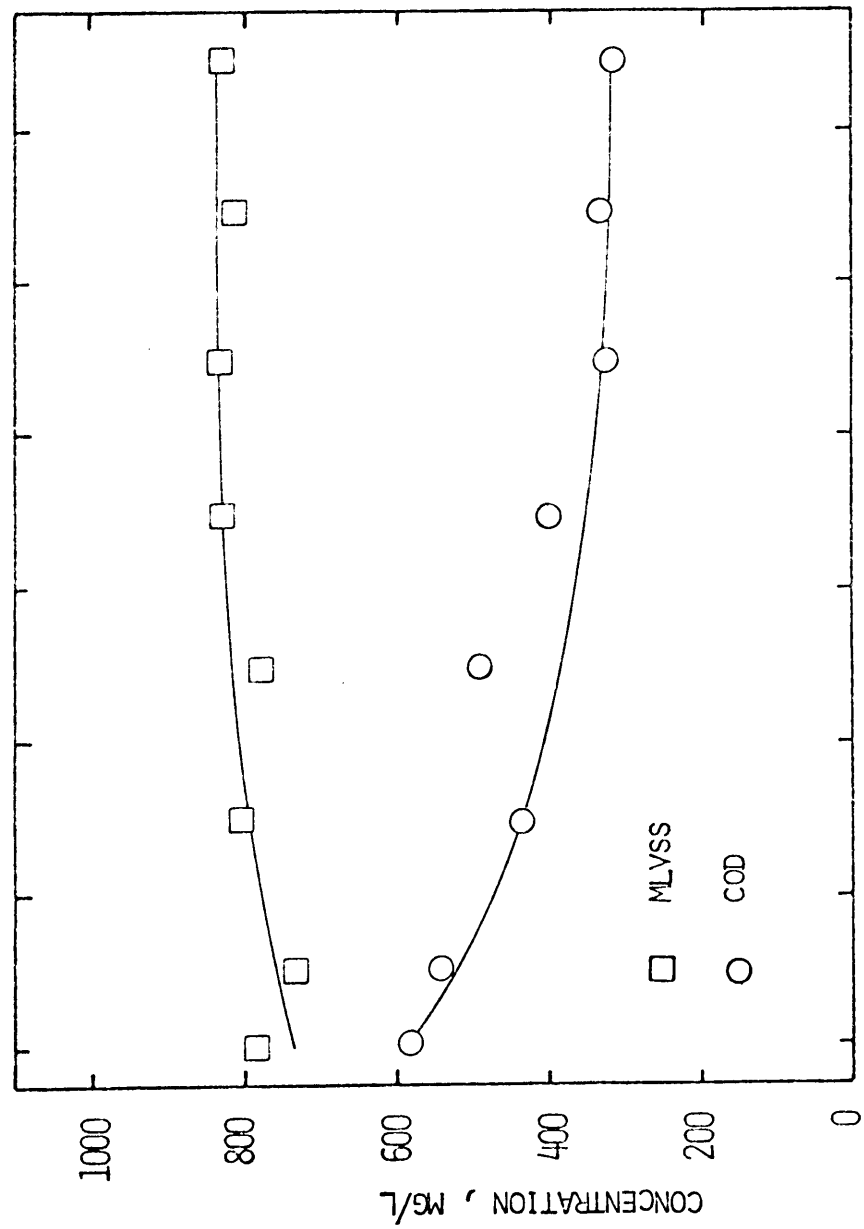

Figure A-4. Effect of 10 mg/l of Ni(II) on Microbial Growth and Substrate Utilization in Shock Loaded Batch Reactor.

TABLE A-V

Growth Curve and Substrate Utilization Data for Acclimated Batch Reactor, Ni(II) = 1 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	988	704	1340	816	1164	760	581
1	948	716	856	644	902	680	515
3	1048	808	1056	740	1052	774	413
5	1108	832	1020	776	1064	804	339
7	1128	840	1128	848	1128	844	275
9	1152	860	1096	800	1124	830	283
11	1196	892	1224	840	1210	866	246
13	--	--	1088	812	1088	812	244

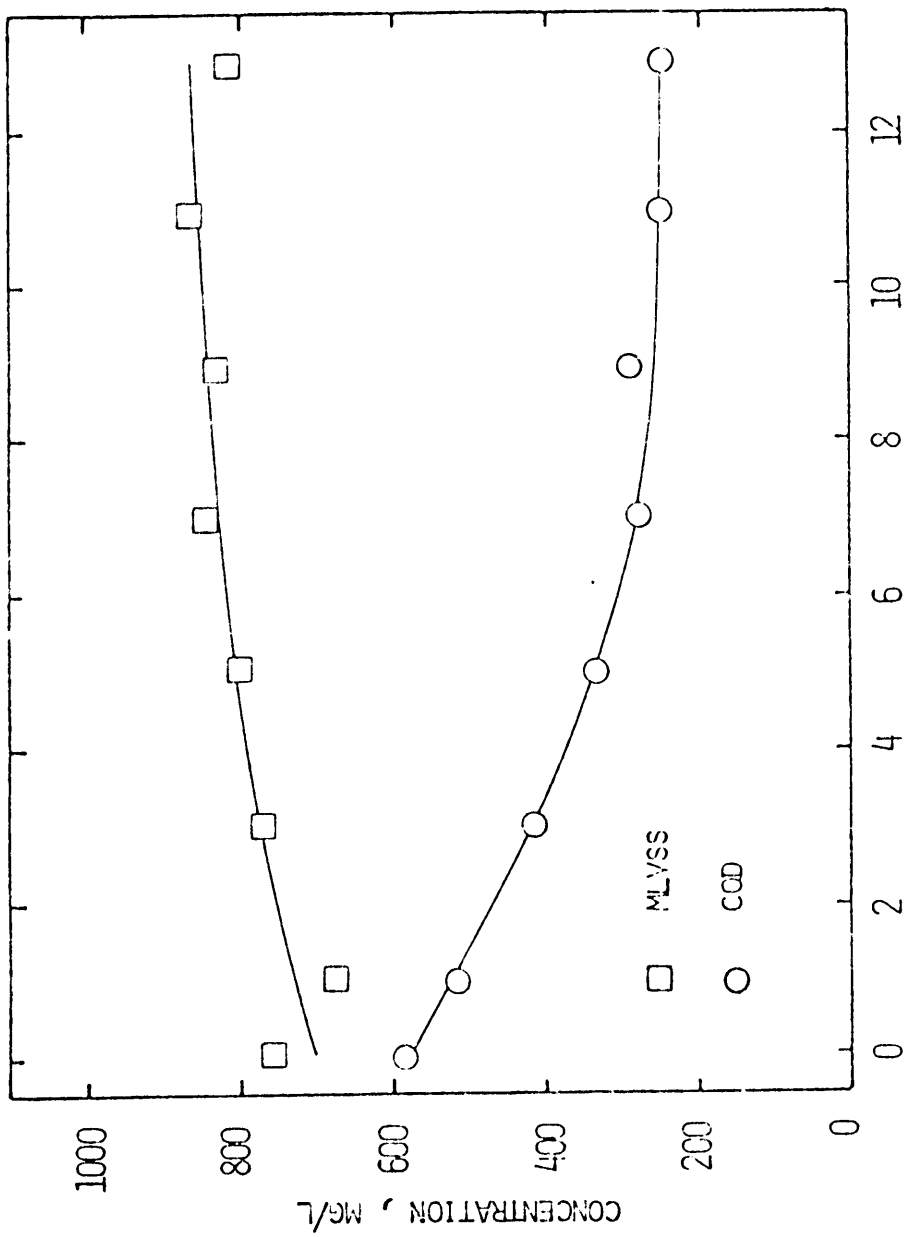

Figure A-5. Effect of 1 mg/l of Ni(II) on Microbial Growth and Substrate Utilization in Acclimated Batch Reactor.

TABLE A-VI

Growth Curve and Substrate Utilization Data for Acclimated Batch Reactor, Ni(II) = 5 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	1252	788	1152	772	1202	780	547
1	1232	856	1228	836	1230	846	479
3	1460	888	1452	876	1456	882	345
5	1136	892	1224	840	1180	866	259
7	1272	848	1496	988	1384	918	212
9	1452	924	1424	924	1438	924	228
11	1576	992	1410	888	1493	940	206
13	1480	884	1496	988	1488	936	198

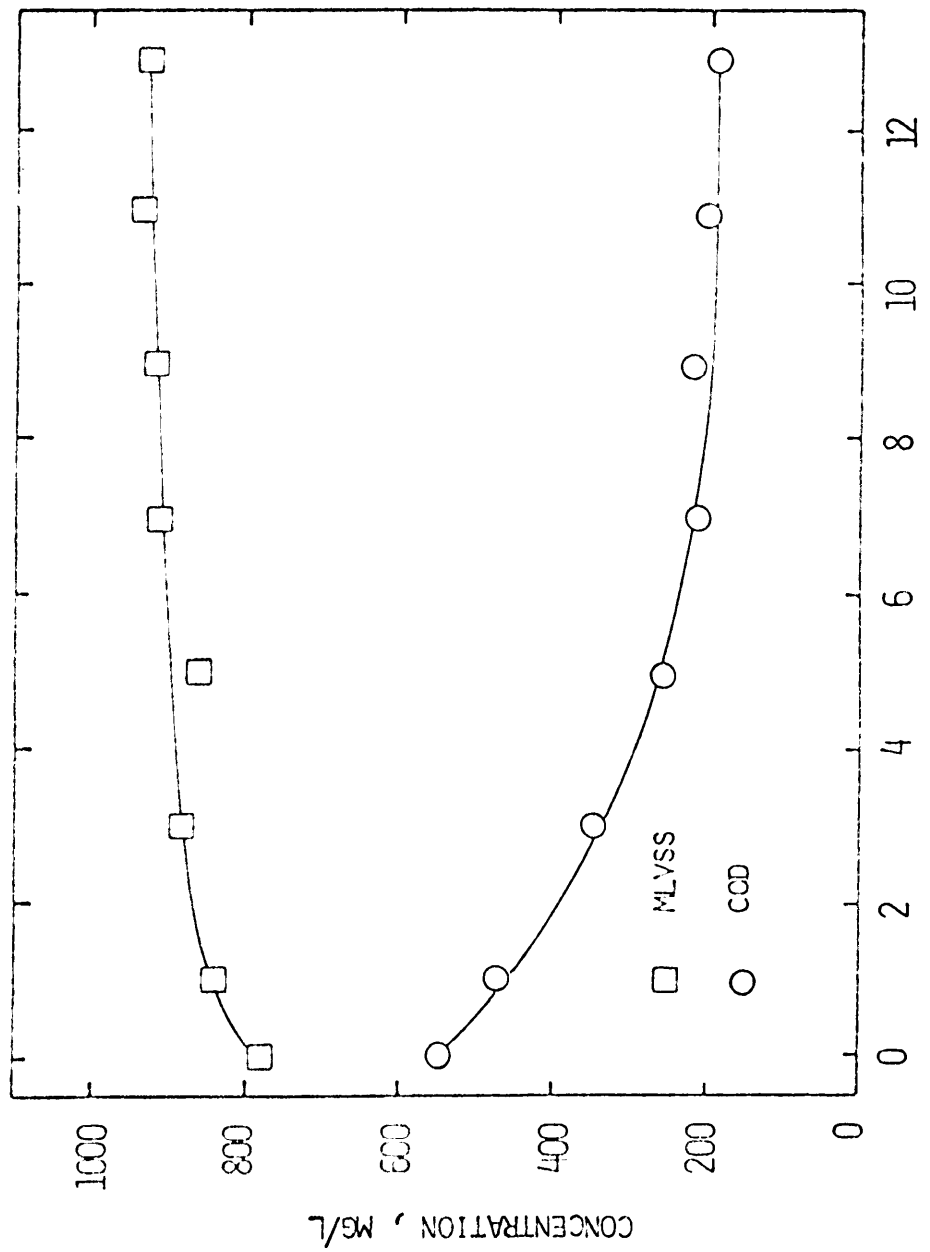

Figure A-6. Effect of 5 mg/l of Ni(II) on Microbial Growth and Substrate Utilization in Acclimated Batch Reactor.

TABLE A-VII

Growth Curve and Substrate Utilization Data for Acclimated Batch Reactor, Ni(II) = 10 mg/l.

	SAMPLE A		SAMPLE B		AVERAGE		
TIME (hour)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	COD (mg/l)
0	988	728	1340	828	1164	778	576
1	1352	808	1364	768	1358	788	531
3	1460	884	1448	870	1454	877	445
5	1428	924	1292	808	1360	866	386
7	1572	936	1532	912	1552	924	334
9	1460	876	1440	820	1450	848	281
11	1544	904	1528	936	1536	920	259
13	1488	880	1488	924	1488	902	252

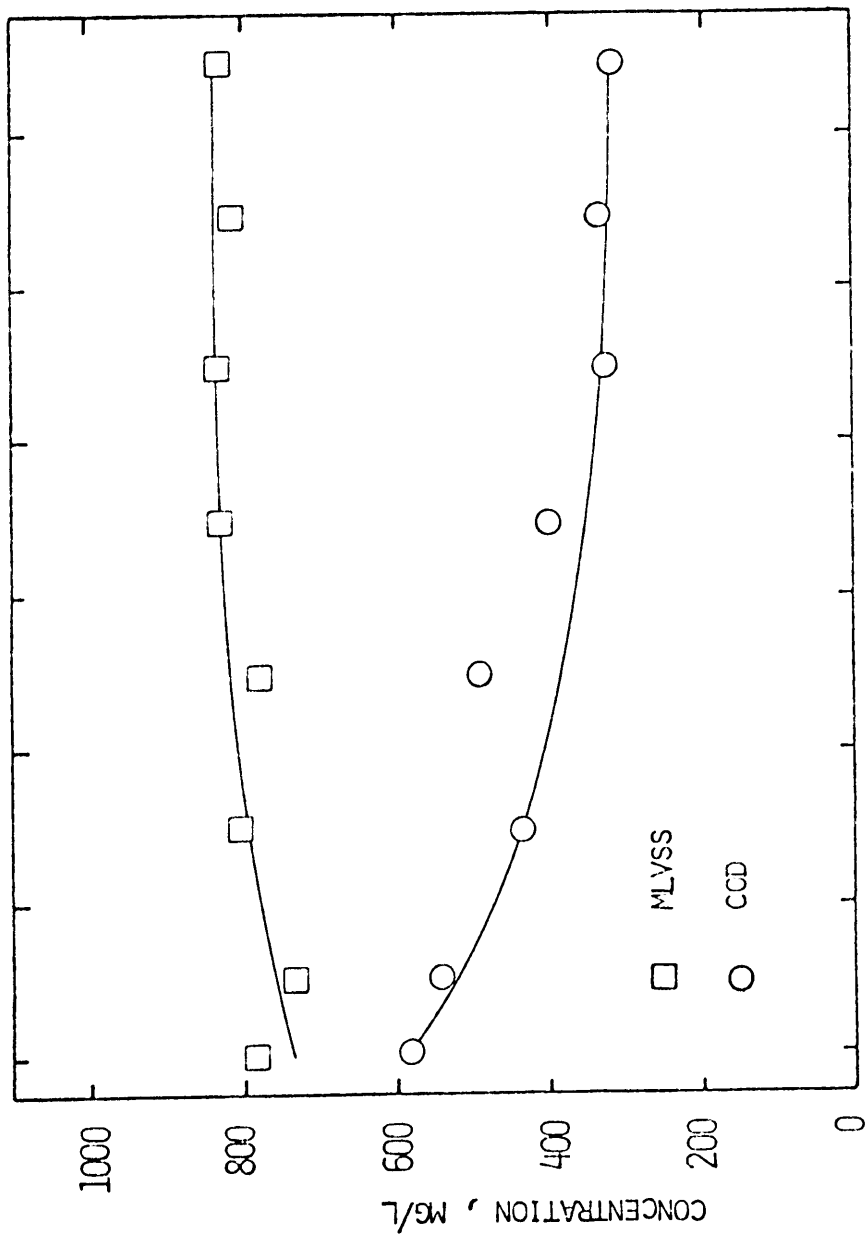

Figure A-7. Effect of 10 mg/l of Ni(II) on Microbial Growth and Substrate Utilization for Shock Loaded Batch Reactor.

TABLE A-VIII

Nickel Removal in Shock Loaded

Batch Reactor. (pH = 7.7 ± 0.5)

Time	Ni(II)=1 mg/l		Ni(II)=5 mg/l		Ni(II)=10 mg/l	
(hour)	Ni(II) (mg/l)	%Ni(II) Remov.	Ni(II) (mg/l)	%Ni(II) Remov.	Ni(II) (mg/l)	%Ni(II) Remov.
0	1.00	0	5.00	0	10.00	0
1/2	0.94	6.0	2.94	41.2	4.96	50.4
1	0.66	34.0	1.82	63.6	3.04	69.6
3	0.64	36.0	1.62	67.6	2.47	75.3
5	0.56	44.0	1.86	62.8	2.86	71.4
7	0.68	32.0	1.66	66.8	3.22	67.8
9	0.56	44.0	1.74	65.2	2.77	72.3
11	0.64	36.0	1.48	70.4	2.56	74.4
13	0.66	34.0	1.68	66.4	2.56	74.4

TABLE A-IX

Nickel Removal in Acclimated

Batch Reactor. (pH = 7.7 ± 0.5)

Time	Ni(II)=1 mg/l		Ni(II)=5 mg/l		Ni(II)=10 mg/l	
(hour)	Ni(II) (mg/l)	%Ni(II) Remov.	Ni(II) (mg/l)	%Ni(II) Remov.	Ni(II) (mg/l)	%Ni(II) Remov.
0	5.80	0	9.40	0	14.70	0
1	5.80	0	8.65	8.0	---	---
3	4.88	15.5	8.351	11.2	10.70	27.2
5	4.57	21.2	7.50	20.2	12.70	13.6
7	4.39	24.1	7.10	24.5	10.80	30.7
9	4.10	29.3	12.80	-36.2	9.80	33.3
11	4.05	30.2	7.30	22.3	11.20	23.8

APPENDIX B.

Raw Data for Continuous Flow Reactors with Cell Recycle.

TABLE B-I

Raw Data for Control Reactor, COD = 390 mg/l, θ_c = 12.3 Days.

Date	COD				MLSS			pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effl.
		Unfil.	Fil.	Effic.	Reac.		θ_c		
(1978)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(days)		
3-9	391	59	31	92.1	2164	28	12.5	7.1	7.0
3-10	385	50	27	93.0	2144	25	12.8	7.0	6.9
3-11	372	46	27	92.7	2056	24	12.8	7.1	6.8
3-12	391	65	28	92.8	2152	15	14.2	7.1	6.8
3-13	387	59	23	94.1	2072	36	11.4	7.1	6.7
3-14	400	61	35	91.3	2104	44	10.7	7.1	6.7
3-15	402	59	23	94.3	2148	36	11.6	6.9	6.8
AVE.	390	57	28	92.9	2120	30	12.3	7.1	6.8

TABLE B-I (continued)

Date	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Effl.
	Feed	Effl.	Net Change	Feed	Effluent		Net Change	Feed	Effluent		Net Change	NO_3^--N
					Unfil.	Fil.			Unfil.	Fil.		
(1978)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)
3-9	218	132	-16.5	44.8	51.5	51.5	15.0	50.4	9.0	1.7	-96.6	13.3
3-10	221	172	-22.2	47.6	54.9	55.3	17.7	52.6	5.2	2.2	-95.8	26.6
3-11	232	156	-32.8	49.3	53.8	52.6	6.7	51.5	7.5	3.9	-93.4	26.6
3-12	243	155	-36.2	55.4	57.1	57.1	3.1	51.8	5.6	2.2	-95.7	55.8
3-13	232	141	-39.2	59.9	58.0	57.1	-4.7	48.7	8.1	3.4	-93.0	28.3
3-14	232	132	-43.1	49.8	54.9	54.9	10.2	52.1	9.5	3.4	-93.5	37.5
3-15	220	218	-0.9	51.0	55.1	30.2	-40.8	51.1	7.5	4.5	-85.3	24.2
AVE.	228	165	-27.3	51.0	55.0	51.2	-1.8	51.1	7.5	3.0	-93.3	30.3

TABLE B-II

Raw Data for Control Reactor, COD = 386 mg/l, θ_c = 5.8 Days.

Date	COD				MLSS		θ_c	pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Efflu.
		Unfil.	Fil.	Effic.	Reac.				
(1978)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(days)		
3-29	375	64	20	94.7	1212	18	5.7	7.1	7.5
3-30	382	28	16	95.8	1128	14	5.8	7.2	7.5
3-31	390	40	24	93.9	1132	12	5.9	7.2	7.5
4-1	378	62	20	94.7	1204	18	5.7	7.1	7.5
4-2	398	36	16	96.0	1012	9	6.1	7.2	7.6
4-3	392	40	16	95.9	1248	19	5.7	7.2	7.5
AVE.	386	45	19	95.2	1156	15	5.8	7.2	7.5

TABLE B-II (continued)

Date (1973)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Effl. NO_3^--N
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	(mg/l)
3-29	228	305	33.8	62.7	79.5	79.5	26.8	45.9	7.9	3.9	-91.5	7.5
3-30	241	288	19.5	58.2	79.0	78.4	33.6	51.0	7.2	4.5	-91.2	7.0
3-31	250	293	17.2	56.0	79.5	78.4	40.0	50.4	5.6	1.1	-97.8	3.5
4-1	255	294	15.3	59.4	78.7	78.4	32.0	50.4	8.7	3.9	-92.3	12.5
4-2	264	304	15.2	60.5	80.6	77.3	28.6	48.1	7.6	5.1	-85.4	10.5
4-3	249	298	19.7	58.2	79.5	77.3	32.3	46.5	7.9	4.5	-90.3	7.0
AVE.	248	297	20.1	59.2	79.5	78.3	32.3	48.7	7.0	3.8	-91.4	8.8

TABLE B-III

Raw Data for Control Reactor, COD = 405 mg/l, θ_c = 11.5 Days

Date	COD				MLSS			pH	
	Feed	Effluent		Remov.	Total	Effl.	θ_c	Feed	Efflu.
		Unfil.	Fil.	Effic.	Reac.				
(1978)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(days)		
6-4	427	38	32	92.5	1952	2	11.9	7.3	6.5
6-5	399	40	30	92.5	1956	2	11.9	7.2	6.6
6-6	383	32	18	95.3	1956	2	11.9	7.3	6.7
6-7	403	40	24	94.0	1952	8	11.2	7.2	6.6
6-8	427	34	22	94.9	1852	14	10.6	7.3	6.7
6-9	399	40	18	95.5	1896	2	11.9	7.3	6.6
6-10	395	38	18	95.4	1876	7	11.3	7.2	6.6
AVE.	405	37	23	94.3	1920	5	11.5	7.2	6.6

TABLE B-III (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
6-4	269	88	-67.3	53.8	47.6	49.3	-8.4	56.0	4.2	1.1	-98.0	46.5
6-5	258	107	-58.5	54.3	50.4	48.2	-12.0	52.2	5.6	2.2	-95.8	40.5
6-6	257	117	-54.4	53.3	50.4	48.2	-10.4	49.8	2.8	3.3	-93.4	40.5
6-7	259	106	-59.1	56.0	51.8	49.3	-12.0	52.6	2.0	2.2	-95.8	41.5
6-8	254	111	-56.3	56.0	51.8	50.4	-10.0	54.9	4.2	3.4	-93.8	38.0
6-9	251	107	-57.4	54.9	49.0	49.3	-10.2	50.4	3.6	1.1	-97.8	41.5
6-10	268	107	-60.1	53.8	47.6	46.5	-13.6	51.5	6.2	4.5	-91.3	42.0
AVE.	259	106	-59.0	54.7	49.8	48.7	-10.9	52.5	4.1	2.5	-95.1	41.5

TABLE B-IV

Raw Data for Control Reactor, COD = 396 mg/l, θ_c = 16.4 Days

Date	COD				MLSS		θ_c	pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Efflu.
		Unfil.	Fil.	Effic.	Reac.				
(1978)	(mg/l)	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)			
7-26	399	21	12	97.0	2620	6	16.0	7.2	6.7
7-27	413	21	35	91.5	2644	2	16.7	7.3	6.7
7-28	396	16	29	92.7	2668	2	16.7	7.3	6.6
7-29	393	29	29	92.6	2724	2	16.7	7.2	6.6
7-30	403	25	27	93.3	2692	1	16.8	7.2	6.5
7-31	396	30	26	93.4	2772	4	16.3	7.2	6.5
8-1	374	31	35	90.6	2776	0	17.0	7.2	6.5
8-2	395	30	26	93.4	2656	4	16.3	7.2	6.6
8-3	401	47	37	90.8	2636	10	15.4	7.2	6.5
8-4	387	49	12	96.9	2620	6	16.0	7.2	6.5
AVE.	396	30	27	93.2	2681	4	16.4	7.2	6.6

TABLE B-IV (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
7-26	264	136	-48.5	55.4	49.7	50.4	-9.0	51.6	3.5	2.8	-94.6	38.4
7-27	276	128	-53.6	66.1	50.4	50.4	-23.8	47.6	2.1	2.8	-94.1	31.5
7-28	264	108	-59.1	57.7	50.4	49.0	-15.1	49.6	3.5	2.8	-94.4	40.0
7-29	261	102	-60.9	54.9	50.4	50.4	-8.2	51.5	2.8	2.8	-94.6	37.0
7-30	263	88	-66.5	52.5	49.0	49.0	-6.7	50.5	2.8	2.8	-94.5	40.0
7-31	254	101	-60.2	57.7	48.6	49.3	-14.6	49.6	3.4	2.8	-94.4	42.2
8-1	260	99	-61.9	57.1	50.4	50.4	-11.7	47.1	3.5	2.8	-94.1	53.0
8-2	256	96	-62.5	58.2	48.6	49.3	-15.3	51.6	3.4	2.8	-94.6	42.2
8-3	264	84	-68.2	58.2	47.0	46.5	-20.1	48.7	4.4	4.5	-90.8	45.9
8-4	264	82	-68.9	59.4	41.3	49.3	-17.0	47.0	4.5	1.1	-97.7	51.5
AVE.	263	102	-61.0	57.7	48.6	49.4	-14.2	49.6	3.4	2.8	-94.4	42.2

TABLE B-V

Raw Data for COD = 399 mg/l, Ni(II) = 0.93 mg/l, θ_c = 14.5 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
2-22	402	61	34	91.5	1736	6	15.5	0.85	--	0.79	7.1	0.67	7.1	7.7
2-23	412	61	46	88.8	1704	12	14.2	1.00	--	0.90	10.0	0.56	6.9	7.7
2-24	410	61	38	90.7	1684	8	15.0	0.95	--	0.83	12.6	0.62	7.1	7.5
2-25	402	58	42	89.6	1648	17	13.2	0.86	--	0.81	5.8	0.72	7.1	7.7
2-26	395	58	30	92.4	1704	4	16.0	0.98	--	0.79	19.4	0.79	7.1	7.5
2-27	385	58	34	91.2	1732	8	15.1	0.94	--	0.87	7.5	0.66	7.1	7.7
2-28	370	53	27	92.7	1768	16	13.6	0.88	--	0.90	-2.3	0.55	7.0	7.5
3-1	393	53	23	94.2	1672	14	13.8	0.93	--	0.87	6.5	0.59	7.0	7.6
3-2	431	65	27	93.7	1808	20	13.0	1.00	--	0.90	10.0	0.53	7.0	7.6
3-3	393	691	31	92.1	1702	6	15.5	0.89	--	0.88	1.1	0.62	7.0	7.6
AVE.	399	60	33	91.7	1716	11	14.5	0.93	--	0.85	7.8	0.62	7.0	7.6

TABLE B-V (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
2-22	222	352	58.6	47.0	87.4	84.0	78.7	44.8	10.0	10.0	-77.7	1.4
2-23	218	344	57.8	47.0	87.4	86.2	83.4	53.8	10.0	6.8	-87.4	1.6
2-24	230	346	50.4	52.1	87.4	84.0	61.2	49.8	12.3	9.0	-81.9	1.4
2-25	222	352	58.6	38.1	87.4	84.0	120.5	61.6	5.6	9.0	-85.4	1.4
2-26	274	350	27.7	53.8	84.0	84.0	56.1	61.6	9.0	6.7	-89.1	1.6
2-27	232	356	53.4	52.1	80.6	85.1	63.3	49.8	12.4	7.9	-84.1	1.5
2-28	246	354	43.9	53.8	87.4	84.0	56.1	48.1	6.7	6.7	-86.1	1.6
3-1	272	388	42.6	49.3	86.2	81.8	65.9	52.6	5.6	10.0	-81.0	1.6
3-2	240	384	60.0	51.0	86.2	90.7	77.8	57.6	14.6	7.9	-86.3	2.2
3-3	225	371	64.9	49.8	86.2	88.4	77.5	54.4	11.2	7.9	-85.5	1.7
AVE.	233	360	51.8	49.4	86.0	85.2	74.1	53.4	9.7	8.2	-84.5	1.6

TABLE B-VI

Raw Data for COD = 396 mg/l, Ni(II) = 1.00 mg/l, θ_c = 10.6 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
3-10	406	64	36	91.1	1480	12	10.5	1.01		0.85	15.8	0.81	7.1	7.6
3-11	414	50	28	93.2	1512	4	11.5	1.03		0.70	32.0	0.94	7.1	7.8
3-12	398	48	28	93.0	1564	6	11.3	1.00		0.95	5.0	0.67	7.2	7.7
3-13	387	56	32	91.7	1488	14	10.2	1.02		0.90	11.8	0.71	7.1	7.6
3-14	387	52	28	92.8	1448	5	11.4	0.99		0.77	22.2	0.89	7.0	7.6
3-15	375	84	28	92.5	1396	24	9.1	0.96		1.00	-4.2	0.70	7.1	7.6
3-16	402	54	24	94.0	1436	12	10.4	0.98		0.84	14.3	0.97	7.1	7.5
AVE.	396	58	29	92.6	1475	11	10.6	1.00		0.86	13.8	0.81	7.1	7.6

TABLE B-VI (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
3-10	236	356	50.8	56.0	85.1	82.9	48.0	48.7	6.7	5.3	-89.1	1.9
3-11	229	362	58.1	52.6	89.6	85.7	62.9	53.2	15.7	3.3	-93.8	1.7
3-12	224	352	57.1	56.0	91.8	89.0	58.9	53.8	7.3	4.0	-92.6	1.8
3-13	229	356	55.5	57.1	91.8	92.4	61.8	51.5	4.6	4.2	-91.8	1.8
3-14	230	354	53.9	57.1	96.3	95.2	66.7	52.1	5.6	5.6	-89.3	1.9
3-15	236	361	53.0	52.7	94.1	94.1	50.1	45.9	10.1	3.3	-92.8	1.5
3-16	242	340	40.5	56.0	86.4	85.2	52.1	51.5	4.3	3.3	-93.6	1.6
AVE.	232	354	52.7	56.8	90.7	89.2	57.2	50.6	7.7	4.1	-91.9	1.7

TABLE B-VII

Raw Data for COD = 394 mg/l, Ni(II) = 0.99 mg/l, θ_c = 5.2 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
5-2	410	61	24	94.2	1124	20	5.5	1.00		0.92	8.0	0.60	7.1	7.7
5-3	396	69	28	92.9	1120	30	5.1	0.96		0.80	16.7	0.66	7.1	7.7
5-4	383	65	32	91.6	1116	27	5.3	0.98		0.91	7.1	0.58	7.2	7.6
5-5	396	65	20	95.0	1120	36	4.9	1.00		1.03	-3.0	0.29	7.0	7.6
5-6	400	65	24	94.0	1036	32	5.0	1.01		1.05	-4.0	0.45	7.3	7.7
5-7	389	57	24	93.8	1112	28	5.2	0.97		0.89	8.2	0.31	7.2	7.7
5-8	387	57	20	94.8	1112	29	5.2	1.00		0.84	16.0	0.50	7.2	7.7
AVE.	394	63	25	93.8	1106	29	5.2	0.99		0.92	7.0	0.48	7.2	7.7

TABLE B-VII (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu. NO_3^--N
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	(mg/l)
5-2	238	330	38.7	58.2	88.5	87.9	51.0	54.3	6.7	3.4	-93.7	1.3
5-3	244	338	38.5	52.6	86.8	86.2	63.9	52.6	7.8	2.2	-95.8	0.7
5-4	246	326	32.5	60.5	87.4	86.2	42.5	52.1	7.8	2.8	-94.6	2.0
5-5	236	336	42.4	60.5	91.3	90.7	49.9	52.1	6.2	1.7	-96.7	1.5
5-6	237	344	45.1	53.8	88.5	87.4	62.5	53.2	7.3	2.2	-95.9	1.6
5-7	239	340	42.3	50.4	83.4	82.9	64.5	53.2	6.7	3.4	-93.6	1.1
5-8	244	344	41.0	53.8	82.3	80.6	49.8	52.6	6.6	6.2	-88.2	1.3
AVE.	241	337	40.1	55.7	86.9	86.0	54.9	52.9	7.0	3.1	-94.1	1.4

TABLE B-IIX

Raw Data for COD = 376 mg/l, Ni(II) = 4.94 mg/l, θ_c = 10.4 Days.

Date	COD				MLSS			Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.	θ_c	Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
7-21	375	140	45	88.0	1540	46	12.6	4.80		4.15	13.5	4.64	7.1	7.6
7-22	375	136	37	90.1	1500	64	9.9	5.35		4.35	18.7	5.30	7.2	7.6
7-23	371	128	33	91.1	1544	58	10.8	4.85		4.30	11.3	5.50	7.2	7.6
7-24	379	107	37	90.2	1560	78	8.8	4.80		4.25	11.5	5.87	7.2	7.6
7-25	375	109	41	89.1	1612	68	10.0	4.90		4.40	10.2	5.96	7.2	7.6
7-26	387	115	37	90.4	1604	54	11.6	4.95		4.15	16.2	5.49	7.1	7.6
7-27	371	111	37	90.0	1608	74	9.4	4.95		4.15	16.2	5.69	7.2	7.5
AVE.	376	127	38	89.9	1567	63	10.4	4.94		4.25	13.9	5.49	7.2	7.6

TABLE B-IIX (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
7-21	250	334	33.6									2.4
7-22	254	332	30.7									2.2
7-23	260	332	27.7									2.3
7-24	251	327	30.3	54.9	82.3	81.3	49.0	47.0	9.6	6.4	-86.4	2.7
7-25	250	332	32.8									2.4
7-26	242	324	33.9									2.0
7-27	272	342	25.7									2.4
AVE.	254	332	30.7	56.0*	82.8*	82.3*	48.2	15.2*	4.5*	4.5*	-90.7	2.3

* Composite Sample

TABLE B-IX

Raw Data for COD = 401 mg/l, Ni(II) = 5.52 mg/l, θ_c = 13.1 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
8-7	386	94	32	91.7	1504	60	12.6	5.40	--	6.30	-16.7	7.18	7.1	7.5
8-8	421	112	43	89.8	1560	54	14.2	5.55	3.38	4.35	21.6	13.58	7.2	7.6
8-9	417	104	43	89.7	1556	62	12.6	5.55	4.48	4.60	17.1	3.32	7.1	7.6
8-10	413	133	43	89.6	1656	58	14.0	5.40	3.38	4.25	21.3	13.03	7.2	7.6
8-11	398	167	45	88.7	1660	66	12.6	5.52	4.93	4.05	26.6	15.65	7.1	7.6
8-12	382	173	43	88.7	1500	66	11.6	--	5.60	4.15	--	16.79	7.1	7.7
8-13	390	131	43	89.0	1584	54	14.8	5.70	4.35	4.25	25.4	--	7.2	7.7
AVE.	401	131	42	89.6	1574	60	13.1	5.52	4.35	4.56	17.4	11.66	7.1	7.6

TABLE B-IX (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Effluent NO_3^--N (mg/l)
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	
8-7	241	310	28.6									2.0
8-8	240	331	37.9									2.7
8-9	237	334	40.9	57.1	84.0	82.6	44.7	48.2	11.0	6.0	-87.6	2.7
8-10	244	344	41.0									3.3
8-11	244	338	38.5									2.7
8-12	260	342	31.5									2.4
8-13	251	351	39.8									2.8
AVE.	245	336	36.9	54.8*	84.1*	83.4*	52.2	43.1*	15.6*	4.0*	-90.7	2.7

* Composite Sample

TABLE B-X

Raw Data for COD = 391 mg/l, Ni(II) = 5.19 mg/l, θ_c = 5.3 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
9-11	384	70	28	92.7	1184	18	5.7	5.85	4.50	3.30	43.6	7.33	7.0	7.6
9-12	388	70	26	93.3	1172	20	5.6	5.20	4.26	4.35	16.3	6.11	7.0	7.5
9-13	404	54	34	91.6	1128	20	5.5	4.85	4.18	4.40	9.3	5.34	7.0	7.5
9-14	384	50	34	91.2	1140	18	5.6	5.00	3.94	3.62	27.6	5.79	7.1	7.5
9-15	408	62	34	91.7	1084	44	4.6	5.00	4.14	3.76	24.8	6.37	7.1	7.5
9-16	380	58	26	93.2	1104	42	4.7	5.25	4.26	4.00	23.8	5.74	7.1	7.6
AVE.	391	61	30	92.3	1135	27	5.3	5.19	4.21	3.91	24.2	6.11	7.1	7.5

TABLE B-X (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
9-11	244	348	42.6									2.1
9-12	248	352	41.9									2.4
9-13	260	358	37.7	51.5	84.0	84.0	63.1	53.8	11.8	16.1	-70.1	2.1
9-14	254	354	39.4									2.0
9-15	250	360	44.0									1.5
9-16	256	364	42.2									1.1
AVE.	252	356	41.3	60.2*	85.4*	88.2*	46.5	44.8*	21.0*	7.0*	-84.4	1.9

* Composite Sample

TABLE B-XI

Raw Data for COD = 399 mg/l, Ni(II) = 4.90 mg/l, θ_c = 5.7 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
9-17	371	76	25	93.3	1196	28	6.5	5.07	3.86	3.96	21.9	6.94	7.0	7.6
9-18	411	92	25	93.9	1276	52	5.5	4.77	3.90	4.30	9.9	6.08	7.1	7.5
9-19	397	108	28	92.9	1084	40	5.7	4.37	3.86	3.85	11.9	6.50	7.1	7.6
9-20	409	156	42	89.7	1064	72	4.4	4.72	4.30	3.71	21.4	8.19	7.2	7.6
9-21	409	106	28	93.2	1136	32	6.2	5.07	4.10	3.68	27.4	--	7.2	7.5
9-22	397	102	25	93.7	1080	40	5.7	5.35	4.10	3.96	21.9	3.50	7.3	7.6
9-23	394	76	32	91.9	1116	28	6.3	5.22	4.26	4.25	18.6	5.99	7.2	7.6
AVE.	399	102	29	92.6	1136	42	5.7	4.90	4.05	3.96	19.0	6.20	7.2	7.6

TABLE B-XI (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
9-17	261	372	42.5									1.0
9-18	257	346	34.6									1.0
9-19	253	352	36.4									--
9-20	268	342	27.6	52.6	31.8	31.2	54.4	56.5	17.9	6.5	-88.5	2.0
9-21	264	352	33.3									0.8
9-22	264	340	28.8									--
9-23	264	349	32.2									3.6
AVE.	262	350	33.6	57.4*	32.6*	34.0*	46.3	43.3*	14.0*	4.2*	-90.3	1.7

* Composite Sample

TABLE B-XII

Raw Data for COD = 392 mg/l, Ni(II) = 5.00 mg/l, θ_c = 6.2 Days.

	COD				MLSS			Nickel Concentration					pH	
Date	Feed	Effluent		Remov.	Total	Effl.	θ_c	Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
9-27	400	116	50	87.5	1176	74	5.4	5.10	4.70	4.00	21.6	7.47	7.1	7.7
9-28	392	104	57	85.5	1032	52	6.1	5.25	4.78	4.35	17.1	7.90	7.1	7.6
9-29	398	--	42	89.5	1148	80	5.1	4.75	4.35	4.05	14.7	7.37	7.1	7.7
9-30	392	106	46	88.3	1204	76	5.4	4.85	4.38	5.60	15.5	8.72	7.1	7.7
10-1	404	98	48	88.1	1164	42	7.1	5.00	3.38	4.40	12.0	8.06	7.2	7.7
10-2	380	88	57	85.0	1180	58	6.2	5.00	4.14	3.90	22.0	8.19	7.1	7.7
10-3	376	78	50	86.7	1196	34	7.8	4.90	4.74	4.10	16.3	7.58	7.1	7.6
AVE.	392	98	50	87.2	1157	59	6.2	5.00	4.35	4.34	17.0	7.90	7.1	7.7

TABLE B-XII (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Effl.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
9-27	265	361	36.2									1.9
9-28	324	400	23.5									1.9
9-29	254	413	62.6	56.0	96.6	95.8	17.5	46.5	18.2	10.5	-77.4	2.0
9-30	266	412	54.9									2.4
10-1	266	384	44.4									2.4
10-2	264	368	39.4									3.6
10-3	248	344	38.7									2.8
AVE.	270	383	42.8	62.7*	90.7*	91.8*	47.0	55.4*	11.2*	5.0*	-90.7	2.4

* Composite Sample

TABLE B-XIII

Raw Data for COD = 790 mg/l, Ni(II) = 1.09 mg/l, θ_c = 7.1 Days.

	COD				MLSS			Nickel Concentration					pH	
Date	Feed	Effluent		Remov.	Total	Effl.	θ_c	Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
8-24	787	185	78	90.1	2344	122	6.9	0.98	1.09	0.63	35.7	2.72	7.2	7.4
8-25	771	207	78	89.9	2368	140	6.4	1.05	0.89	0.63	40.0	2.74	7.1	7.4
8-26	787	201	72	90.9	2364	132	6.6	1.12	0.61	0.65	42.0	2 88	7.2	7.5
8-27	787	177	66	91.6	2452	142	6.5	1.06	0.73	0.65	38.7	2.45	7.2	7.5
8-28	795	141	66	91.7	2440	96	8.1	1.16	0.57	0.58	50.0	2.88	7.2	7.6
8-29	811	129	133	83.6	2592	100	8.2	1.11	0.50	0.59	46.8	2.71	7.1	7.5
8-30	790	167	64	91.9	2424	130	6.8	1.17	0.73	0.81	30.8	3.73	7.1	7.5
AVE.	790	172	80	90.0	2426	123	7.1	1.09	0.73	0.65	35.5	2.87	7.1	7.5

TABLE B-XIII (continued)

Date	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Effiu.
	Feed	Effl.	Net	Feed	Effluent		Net	Feed	Effluent		Net	NO_3^--N
(1978)	(mg/l)	(mg/l)	Change (%)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Change (%)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Change (%)	(mg/l)
8-24	440	504	43.6	113.1	156.8	162.4	43.6	103.0	3.4	9.8	-90.5	28.0
8-25	454	548	20.7	113.7	165.2	163.8	44.1	104.7	18.2	2.8	-97.3	28.0
8-26	456	546	19.7	105.3	148.4	168.0	59.5	114.2	39.9	12.6	-89.0	24.0
8-27	440	536	21.8	105.6	166.7	161.3	52.5	104.2	18.2	1.4	-98.6	22.0
8-28	460	548	19.1	119.3	165.2	158.2	32.6	99.1	18.2	11.2	-88.7	20.0
8-29	460	584	27.0	109.2	148.4	141.4	29.5	110.6	30.8	21.0	-81.0	5.0
8-30	492	620	26.0	135.5	168.7	163.8	20.9	79.5	16.1	9.8	-87.7	22.4
AVE.	457	565	21.3	114.5	159.9	159.8	40.4	102.2	21.4	9.8	-90.4	21.3

TABLE B-XIV

Raw Data for COD = 788 mg/l, Ni(II) = 1.11 mg/l, θ_c = 10.0 Days.

	COD				MLSS			Nickel Concentration					pH	
Date	Feed	Effluent		Remov.	Total	Effl.	θ_c	Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
9-29	788	115	62	92.1	3528	30	10.4	1.07	1.26	0.61	43.0	3.42	7.1	7.5
9-30	788	115	66	91.6	3616	32	10.3	1.12	0.70	0.63	43.8	3.00	7.1	7.4
10-1	821	113	50	93.9	3540	32	10.3	1.12	0.58	0.74	33.9	3.60	7.2	7.4
10-2	760	121	66	91.3	3424	44	9.7	1.23	0.70	0.68	44.7	2.77	7.1	7.3
10-3	807	109	58	92.8	3440	34	10.2	1.09	0.81	0.74	32.1	2.90	7.1	7.3
10-4	764	115	62	91.9	3392	64	8.8	1.05	0.81	0.71	32.4	2.76	7.1	7.2
AVE.	788	115	61	92.3	3490	39	10.0	1.11	0.81	0.69	38.3	3.08	7.1	7.2

TABLE B-XIV (continued)

Date	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed	Effl.	Net	Feed	Effluent		Net	Feed	Effluent		Net	NO_3^--N
					Unfil.	Fil.			Unfil.	Fil.		
(1978)	(mg/l)	(mg/l)	Change (%)	(mg/l)	(mg/l)	(mg/l)	Change (%)	(mg/l)	(mg/l)	(mg/l)	Change (%)	(mg/l)
9-29	460	624	35.7	111.3	170.3	--	---	135.1	16.1	7.4	-94.5	33.3
9-30	484	572	18.2	114.8	176.4	176.4	51.2	140.0	3.5	3.4	-94.0	35.0
10-1	460	562	22.2	112.0	144.9	142.3	27.5	100.2	9.1	7.4	-93.2	26.7
10-2	445	534	13.3	106.4	159.3	156.8	47.4	126.0	3.4	7.0	-94.4	38.7
10-3	430	436	1.3	109.0	156.8	148.4	35.0	115.5	9.5	8.4	-92.7	36.7
10-4	466	472	1.3	109.9	152.6	148.4	35.0	102.3	10.5	5.6	-94.6	40.0
AVE.	436	452	15.3	110.7	160.2	154.0	39.2	121.5	9.5	7.4	-93.9	34.7

TABLE B-XV

Raw Data for COD = 783 mg/l, Ni(II) = 1.08 mg/l, θ_c = 16.9 Days.

Date	COD				MLSS		θ_c	Nickel Concentration					pH	
	Feed	Effluent		Remov.	Total	Effl.		Feed	Effluent		Remov.	Sludge	Feed	Effl.
(1978)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	Reac. (mg/l)	(mg/l)	(days)	(mg/l)	Unfil. (mg/l)	Fil. (mg/l)	Effic. (%)	(mg/g)		
10-7	784	87	46	94.1	4388	30	17.1	1.10	1.06	0.92	16.4	2.78	7.1	6.8
10-8	798	122	40	95.0	4420	54	14.8	1.09	0.94	0.76	30.3	2.73	7.1	6.8
10-9	800	121	48	94.0	4260	40	16.0	1.09	0.78	0.71	34.9	2.66	7.1	6.9
10-10	760	99	64	91.6	4204	18	18.5	1.05	0.54	0.59	43.8	2.87	7.1	6.7
10-11	781	99	56	92.8	4420	40	16.1	1.09	0.54	0.53	51.4	---	7.1	6.7
10-12	770	75	50	93.5	4300	22	17.7	1.07	0.55	0.50	53.3	2.73	7.1	6.6
10-13	790	107	66	91.7	4208	24	17.7	1.09	0.74	--	--	2.97	7.1	6.7
AVE.	783	102	53	93.2	4314	33	16.9	1.08	0.74	0.67	38.4	2.79	7.1	6.7

TABLE B-XV (continued)

Date (1978)	Alkalinity as $CaCO_3$			NH_3-N Concentration				Org-N Concentration				Efflu.
	Feed (mg/l)	Effl. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	Feed (mg/l)	Effluent Unfil. (mg/l)	Effluent Fil. (mg/l)	Net Change (%)	NO_3^--N (mg/l)
10-7	466	328	-29.6	110.6	130.9	128.8	16.5	107.8	10.5	8.4	-92.2	66.7
10-8	468	316	-32.5	113.4	129.5	123.2	8.6	105.0	11.2	14.0	-86.7	46.7
10-9	460	324	-29.6	113.4	123.1	120.4	6.2	111.3	9.8	12.6	-88.7	60.0
10-10	468	296	-36.8	114.1	121.8	121.8	6.7	102.9	8.4	5.6	-94.6	70.0
10-11	468	272	-41.9	112.7	124.6	119.0	5.6	103.6	8.4	11.2	-89.2	83.3
10-12	456	256	-43.9	112.0	122.5	120.4	7.5	103.6	4.9	7.0	-93.2	--
10-13	444	268	-39.6	110.9	122.1	113.1	2.0	108.2	8.9	15.7	-85.5	63.3
AVE.	461	249	-36.3	112.4	125.6	125.2	7.5	106.1	8.9	10.6	-90.0	65.0

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THE EFFECTS OF NICKEL ON THE COMPLETELY MIXED ACTIVATED SLUDGE PROCESS

by

Suthirak Sujarittanonta

(ABSTRACT)

The purpose of this investigation was to conduct batch and continuous flow laboratory experiments with bench scale activated sludge units to determine the effects of nickel on the completely mixed activated sludge process. The model units were located in a constant temperature room maintained at 20°±2°C. The batch reactors were operated under acclimated and shock loaded condition with various nickel concentration to determine its effects on the rate of COD removal. The continuous flow units were operated until steady state conditions were obtained at each mean cell residence time studied and then data were recorded for an approximate 7 days period and averaged to obtain one steady state data point. Nickel was added to the wastewater at various concentration to determine its effects on COD removal efficiency, degree of nitrification and on the biokinetic constants Y_{max} and k_d.

Based on the results obtained, it is clearly possible to see the influence of nickel on the biokinetic constants Y_{max} and k_d. Nitrification was inhibited at low nickel concentrations, however, it was possible to remove this inhibition by increasing the wastewater strength and allow nickel concentration to remain constant. As a result, it was possible to describe nickel toxicity with respect to nitrification in

terms of COD to nickel ratio. From these results, meaningful data have been obtained to assist the design engineer and treatment plant operator when faced with an influent heavy metal problem.