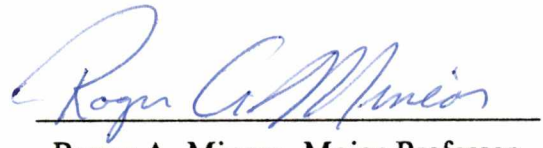


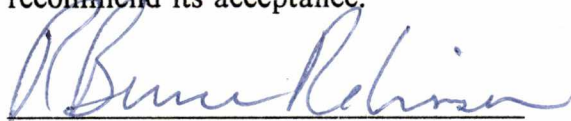
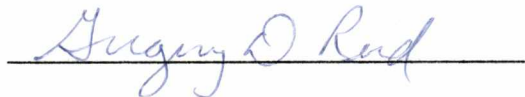
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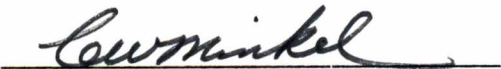
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Date

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**DESTRUCTION OF CADMIUM CYANIDE WASTE BY
ALKALINE CHLORINATION TREATMENT**

**A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville**

Byron T. Butcher

August 1985

To the Lord Jesus Christ
To my wife, Martina

ACKNOWLEDGEMENTS

I am indebted to a number of individuals who have generously assisted me during the course of my research. In particular, I wish to express my gratitude to Professors Roger Minear, Bruce Robinson, and Greg Reed who served as my director and committee, respectively. Their consultation, direction, and assistance enabled me to achieve results otherwise impossible.

Special thanks are due to Mr. Rod Kimmitt for the generous contribution of his personal computer, and Ms. Sharon Hale for her invaluable assistance in the laboratory.

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ABSTRACT

Sludge characteristics and supernatant quality were studied in laboratory-scale tests on alkaline chlorination treatment of cadmium cyanide solutions. Jar tests were conducted at pH values ranging from 7 to 11, utilizing two forms of hypochlorites as oxidants. In addition, synthetic solutions were prepared without cyanide to study the precipitation process independently of the oxidation step in alkaline chlorination. Jar tests were evaluated in the general areas of supernatant and filtrate quality, sludge settling and filterability characteristics, and precipitate mineral characteristics.

Results of the study indicate that at high initial cadmium concentrations calcium hypochlorite treatments yield sludges with better dewatering characteristics than sodium hypochlorite treatments. However, sludge volume is greater in calcium hypochlorite treatments due to coprecipitation of calcium and cadmium carbonate sludges.

Distinctly different types of sludge settling behavior were found as a function of pH. In high pH solutions gelatinous sludges were typically obtained. For $\text{pH} < 10$, dense, grainy sludges were formed containing significantly less volume.

Projections from this work indicate that full-scale treatment at pH 9 would be advantageous. At this pH, cadmium levels are in the region of minimum solubility. In addition, dense, grainy sludges appear to be kinetically favored. Calcium hypochlorite treatment may offer advantages, but pH control problems and excessive sludge volumes must be handled.

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CHAPTER I

INTRODUCTION

1. INDUSTRIAL SOURCES

Cadmium is a component in a variety of industrial materials and processes. Products containing cadmium include rustproofed steels, inorganic pigments, plastics stabilizers, fatigue resistant alloys and nickel cadmium storage batteries (18). An estimated 45–60% of annual cadmium use is in the electroplating industry (16).

Cyanide is also widely used in industry. Major industrial cyanide uses include ore extraction, photographic processing, synthetic fiber production, steel pickeling and case hardening, electroplating, and industrial gas scrubbing. The uses for cadmium and cyanide converge in the electroplating industry where cyanide is typically used to hold cadmium in solution for the electroplating of common metals.

Cyanide is commonly employed as a complexing agent for a number of metals used in the electroplating industry. Concentrated cyanide baths are used to hold metallic ions in solution while immersing the part into the plating solution. Following plating, the part is removed and rinsed of residual plating chemicals. This rinse, commonly known as "drag-out", typically contains between 15 and 100 mg/l of the metal-cyanide complex. Conventional rinsing techniques produce a large amount of drag-out which must meet effluent limitation guidelines before discharge.

The Environmental Protection Agency has promulgated industrial effluent limitation guidelines on the electroplating of common metals (26). The

expected cadmium and cyanide effluent values from a common metals facility discharging 38,000 liters or more are as follows:

	Cd, mg/l	CN, mg/l (a)
One day maximum =	1.2	1.9
Four day average =	0.7	1.0
30 day average (b) =	0.5	0.55

(a) Total cyanide

(b) For integrated facilities only

2. TREATMENT TECHNOLOGY

Treatment technologies for cadmium cyanide destruction include alkaline chlorination, electrolytic decomposition, ozonation and other oxidation processes (18). The most common method employed is alkaline chlorination treatment. This method combines oxidation (chlorination) for the destruction of the cadmium cyanide complex and free cyanide radical, with precipitation for removal of the uncomplexed cadmium ion.

Various forms of chlorine can be used in the alkaline chlorination process including chlorine gas, and sodium and calcium hypochlorite. The oxidizing capability of each form is identical, however, little information is available on the relative benefits of each in the precipitation process.

Alkaline chlorination treatment is commonly conducted in two stages. Solution pH is first raised above 10 where the initial reaction process is most rapid. In the second stage, pH is reduced to 8.0–8.5 where conditions are most favorable to complete cyanide destruction. Conventional two stage treatment has the following advantages:

- Safety. Cyanogen chloride is a volatile and toxic intermediate product of alkaline chlorination treatment. Rapid conversion to cyanate reduces the potential for its release.
- Speed. Reaction rates are maximized under the conditions of two stage treatment.

The primary disadvantage of this method is the production of cadmium hydroxide sludge. Metal hydroxide sludges are typically gelatinous and difficult to dewater (22). In addition, optimum cadmium removals are limited to the pH region above 10. Second stage pH adjustment requires additional chemicals, and in the case of continuous treatment processes, a second tank of reactor vessel to provide for complete cyanide destruction (18).

Alternatively, alkaline chlorination can be conducted at a single intermediate pH (8.5–10) to produce a cadmium carbonate sludge. Metal carbonate sludges are reportedly more dense and exhibit better filterability characteristics (16). In addition, heavy metal removal by carbonate precipitation has been examined and offers advantages over hydroxide precipitation in reduced metal solubilities (16). Another advantage is that treatment and removal of residual, soluble cadmium is theoretically most effective in the pH region 8.5–10.

In single stage chlorination, reaction efficiency and solubility behavior are known to be dependent upon the selection of pH and amount of available chlorine added. The objective of this research was to determine whether the physical characteristics of sludge (volume, density and filterability), produced by alkaline chlorination of a cadmium cyanide waste, were significantly

affected by the selection of pH and chlorine compound used. In addition, experimental cadmium solubility was compared to theoretical values.

The scope of this investigation was to examine sludge characteristics and solubility behavior following alkaline chlorination, with either sodium or calcium hypochlorite additions, at five different pH's between 7 and 11. The alkaline chlorination process is one of oxidation followed by precipitation. Ideally, the precipitation process can be studied independently of the oxidation step with similar results. Based on alkaline chlorination stoichiometry synthetic solutions were prepared, without cyanide, to simulate the end products and precipitation process following alkaline chlorination. In this way, reactions were limited, and dynamics of the system simplified for the purpose of studying its behavior and characteristics. In the second phase of experimentation, cadmium cyanide solutions were prepared and tested to examine the combined effects of oxidation and precipitation.

CHAPTER II

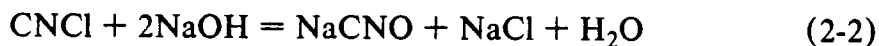
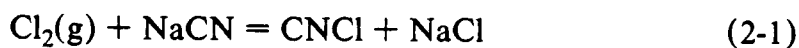
LITERATURE REVIEW

1. ALKALINE CHLORINATION CHEMISTRY

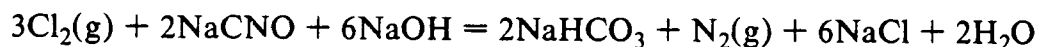
Stoichiometry

The most commonly employed method in the treatment of cyanide plating baths and rinses is the addition of elemental chlorine or hypochlorites under alkaline conditions. This method is a destructive process resulting in the breakup of the metal cyanide complex and precipitation of metal hydroxide or carbonate sludge. The end products of alkaline chlorination treatment are dependent upon the type and amount of oxidant added, and solution pH.

The addition of chlorine gas under alkaline conditions can produce the following reaction sequence for simple (uncomplexed) cyanides (15):

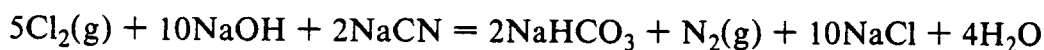


(2-3)



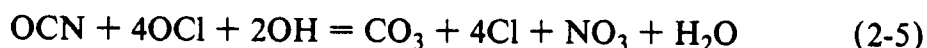
For the overall reaction:

(2-4)



The same reaction mechanisms hold true for complexed cyanides amenable to chlorination. Equation 2-1 and 2-2 represent the first stage of alkaline chlorination treatment. The oxidation step in the first equation is followed by hydrolysis of cyanogen chloride to cyanate in equation 2-2. In the second stage, represented by equation 2-3, cyanate is oxidized to end products.

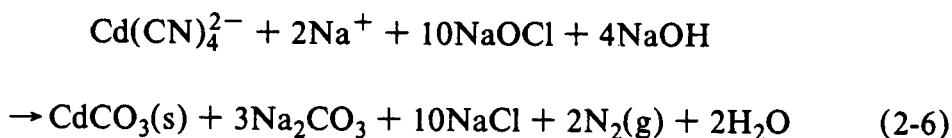
Cyanate oxidation actually absorbs hypochlorite in excess of the stoichiometric requirements of equation 2-3. Oxidation of cyanate to various secondary products such as nitrogen trichloride, nitrous oxide and nitrates have been suggested to account for excess chlorine demand. Strong evidence has been presented (14) indicating that nitrate formation accounts for most of this additional chlorine requirement as shown below:



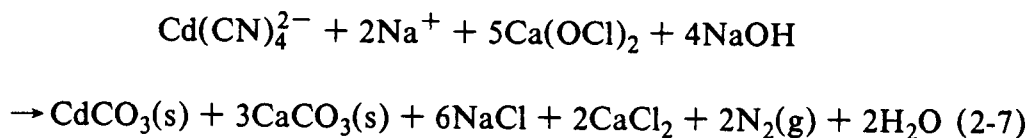
Sodium or calcium hypochlorites are often used in place of chlorine gas due to the hazard in handling the latter. Stoichiometry is the same in terms of equivalents of chlorine added, but base additions required to maintain pH will vary with the form of oxidant used. The term (available) chlorine will be used throughout the text to refer to both elemental chlorine (Cl_2) and hypochlorites (OCl) except when referring to specific reactions.

The behavior of a metal-cyanide complex with alkaline chlorination treatment is a function of its stability. Nickel and ferric cyanide are examples of extremely stable complexes. Both resist rapid and complete oxidation in alkaline solutions containing excess chlorine. In contrast, both cadmium and zinc cyanide are rapidly oxidized under the same conditions.

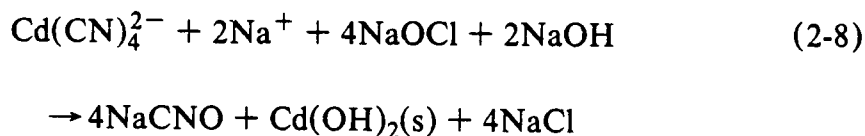
Solution pH is a factor in determining the end products of alkaline chlorination treatment. pH controls cadmium solubility behavior and solid phase mineral characteristics in cadmium carbonate/cadmium hydroxide systems approaching equilibrium (see section on Theoretical Solubility Behavior in this chapter). The type of chlorine compound added also determines end products formed. For cadmium cyanide solutions treated with sodium or calcium hypochlorite the following overall reactions are possible. For addition of sodium hypochlorite:



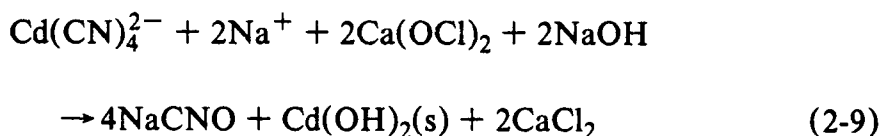
For addition of calcium hypochlorite:



If pH conditions are inadequate, or the amount of chlorine insufficient to carry reactions through to completion, partial oxidation of the cadmium cyanide complex will produce the following reactions for addition of sodium hypochlorite:



For addition of calcium hypochlorite:



The oxidation of cyanide to cyanate (equation 2-2) theoretically requires only one equivalent of chlorine as compared to 2.5 equivalents for complete destruction of the cyanide radical.

Rate Factors

Rate factors play an important role in practical alkaline chlorination treatment. Solution pH not only controls theoretical cadmium solubility behavior, but influences reaction rates as well. Excess available chlorine is also an important rate factor, serving as both a catalyst and oxidizer.

The formation of cyanogen chloride is extremely rapid at all pH levels while hydrolysis of cyanogen chloride to cyanate occurs at a measurable rate (6) given by

$$-d[\text{CNCl}]/dt = k_1[\text{CNCl}][\text{OH}] \quad (2-10)$$

The rate equation indicates hydrolysis to be pH dependent. The reaction has been found experimentally to be most rapid above pH 10. In this region, hydrolysis of cyanogen chloride is 80-90% complete within two minutes.

Hydrolysis of cyanogen chloride is greatly accelerated in the presence of available chlorine. It is apparently a catalytic effect as no chlorine is actually taken up by the reaction. The effect of excess chlorine is reflected in the rate constant which is approximately proportional to hypochlorite concentration within a limited range at constant temperature.

Cyanate oxidation is most rapid below pH 8.5. The reaction rate is proportional to cyanate and chlorine but inversely proportional to hydroxide (14):

$$-d[\text{CNO}]/dt = k_2[\text{OCl}][\text{CNO}]/[\text{OH}] \quad (2-11)$$

Competition between cyanogen chloride and cyanate for excess hypochlorite may result in incomplete hydrolysis of cyanogen chloride at low pH values (<8.5). Alternatively, at high pH values (>10), hydrolysis of cyanogen chloride is essentially complete before significant cyanate oxidation ever occurs (7). Figure 2.1 is a qualitative illustration of the competition between cyanate and cyanogen chloride for excess chlorine for both high and low pH conditions.

Practical Considerations

When alkaline chlorination is conducted in two stages an hour is normally allowed for complete cyanide destruction. Alternatively, if an intermediate pH is selected for conducting treatment, the time required will depend upon the selection of pH and amount of chlorine added. Generally, if pH is maintained between 8.5–10, a 10% hypochlorite excess will ensure sufficiently rapid and complete hydrolysis of cyanogen chloride and oxidation of cyanate for practical treatment (15).

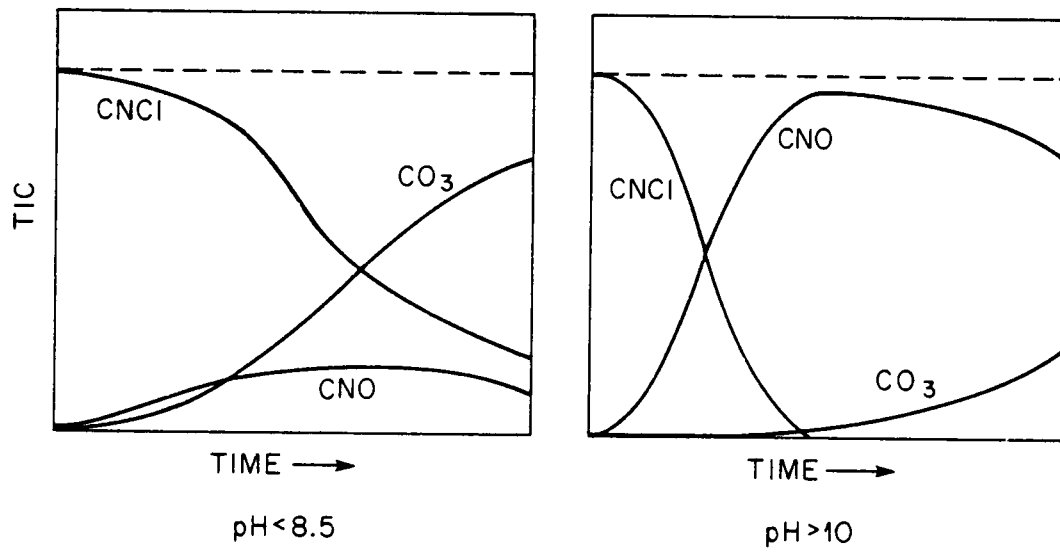


Figure 2.1. Alkaline Chlorination Rate Factors.

Often oxidizable impurities are introduced when solutions from various plating and rinse operations are mixed. This additional chlorine demand must be determined experimentally.

As cyanide decomposition progresses, partially oxidized metal-cyanide complexes may become insoluble or become enveloped in metal hydroxide/carbonate floc. To prevent precipitation and produce the contact necessary to complete oxidation, adequate mixing should be maintained during reaction.

2. INVESTIGATION OF CONDITIONS FOLLOWING CYANIDE DESTRUCTION

Theoretical Solubility Behavior

The stoichiometry and rate factors in cyanide destruction by chlorination have been researched and thoroughly reported in the literature. However, little information is available on the characteristics of sludges and supernatant quality following cyanide destruction and precipitation.

One of the objectives of this investigation was to compare experimental solubilities with theoretical values. The 'fit' of experimental data to the theoretical solubility curve is an indication of whether the experimental system (i.e., solution plus solid phase) is approaching equilibrium within the time frame of treatment. Theoretical solubility relationships can be used to predict heavy metal removals in systems that have reached thermodynamic equilibrium. As is often the case, however, deviations from theoretical solubility behavior occur when there is insufficient time allowed to establish equilibrium

between the soluble metal species and precipitated metal (22). Under these conditions, solubility relationships can only provide boundary conditions for actual solubility behavior.

Cadmium hydroxide solubility is defined by its solubility product and the equilibrium established between the solid phase and various soluble cadmium hydroxide species (22). These relationships can be plotted graphically in a pC-pH diagram as shown in Figure 2.2. Upon the introduction of a sufficient level of carbonate to a system (as in alkaline chlorination), solubility behavior is modified in the region where cadmium carbonate precipitate predominates. The resulting equilibrium expressions can be superimposed on the hydroxide solubility curve to form a cadmium carbonate/cadmium hydroxide phase diagram as shown in Figure 2.3. From this diagram one can determine at any pH the theoretical cadmium solubility and the solid phase controlling equilibrium. The line delineating phase change occurs at the pH where the solubility of cadmium carbonate and cadmium hydroxide are equal.

In addition to soluble cadmium hydroxide species, other anions can complex cadmium and modify solubility behavior. Chlorides in solution will form soluble chlorocadmium complexes (23). Chlorides are produced from the reduction of hypochlorites during alkaline chlorination. Figure 2.3 also shows the effect of chlorocadmium complexes on cadmium carbonate solubility.

Kinetics of Precipitation

Frequently in precipitation reactions, the solid formed is not the thermodynamically stable phase, but a kinetically favored intermediate form. In a process known as ageing, the intermediate (transitional) form slowly converts

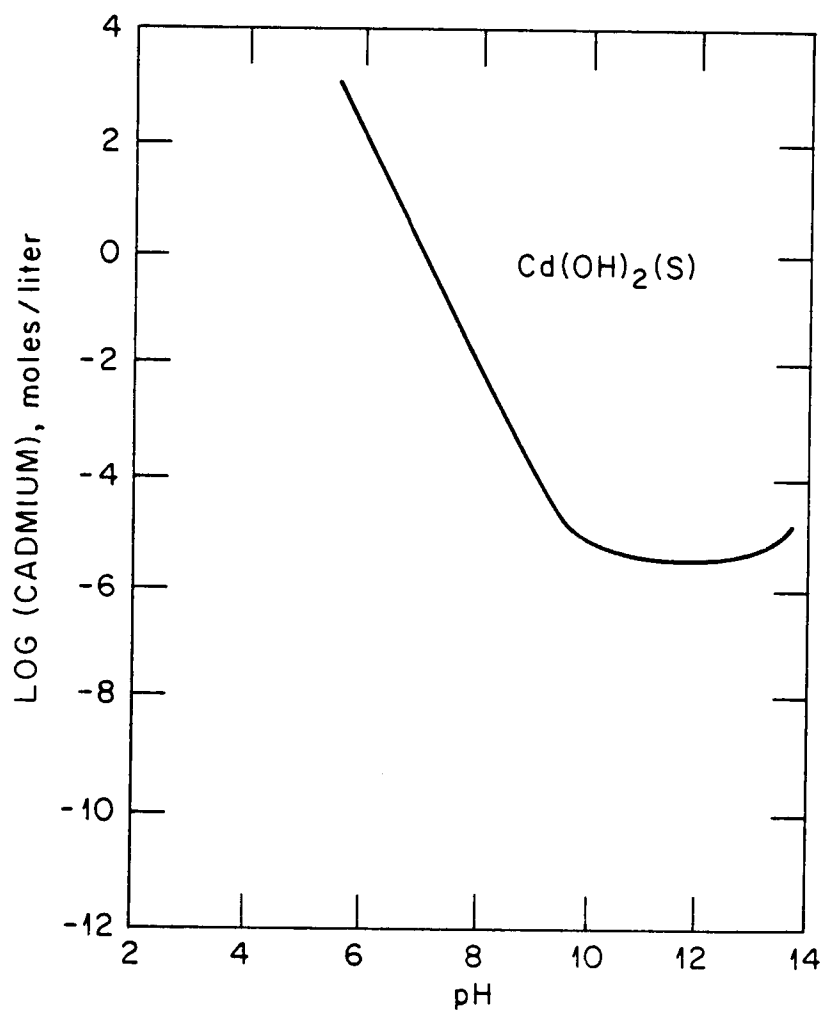


Figure 2.2. Theoretical Cadmium Hydroxide Solubility Curve.

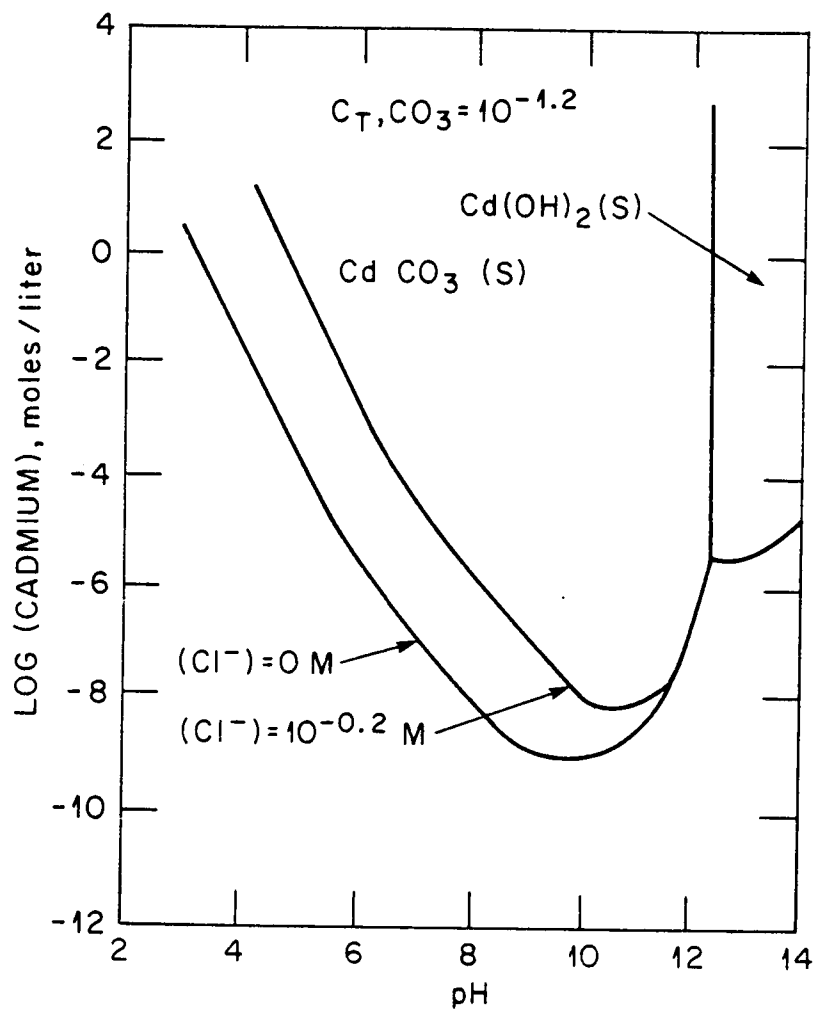


Figure 2.3. Theoretical Cadmium Carbonate/Cadmium Hydroxide Phase Diagram.

to the thermodynamically stable solid phase. To more accurately reflect system behavior, a range of solubility constants have been reported in the literature (19) for "fresh" and "aged" metal hydroxide sludges. Values reported for fresh cadmium hydroxide sludge were used in this investigation (see Appendix A. Basic Program).

The physical characteristics of a fresh sludge (volume, density and filterability) are largely determined by conditions in solution during the initial stages of precipitation. Aged sludges, on the other hand, are primarily affected by recrystallization processes. During crystal formation, precipitates may become contaminated with ions foreign to the particular mineral compound. Such contamination may lead to an entirely new stable solid phase with its own unique solubility characteristics.

Crystal Formation

During the initial stages of precipitation the processes of nuclei formation and crystal growth compete for available solution ions. The rate of formation of nuclei is enhanced by highly supersaturated solutions. Crystal growth, on the other hand, is predominant under conditions of slight supersaturation. When the rate of nuclei formation dominates, a large number of nuclei are formed and the average crystal size declines. When the rate of crystal growth is controlling the opposite is true.

The structure of a precipitate can range from a well ordered crystal to a completely irregular amorphous solid. Precipitate aggregation and structural orientation occur simultaneously during formation of precipitates. Initial conditions of high supersaturation enhance the aggregation velocity over the orientation velocity (13). This generally produces precipitates with disordered lattice

structures. The orientation velocity is independent of the degree of supersaturation but specific for the compound being precipitated (13).

Recrystallization Processes (Ageing)

Following precipitation the aggregation velocity rapidly falls off while structural orientation and recrystallization processes continue. Recrystallization corrects imperfections in crystal structure through dissolution and subsequent re-formation or deposition of new crystal growth. Recrystallization processes are more orderly than initial crystal formation in that earlier precipitation has reduced the amount of excess present in solution. The collection of irreversible changes occurring upon precipitation are generally known as "ageing" processes (13).

The character of "fresh" and "aged" precipitates depends upon the final treatment of the precipitate. Since recrystallization requires a solution as a medium, precipitates agitated or left standing in their mother liquor tend to develop more highly ordered crystalline structures than those removed immediately following precipitation. However, precipitates formed under the conditions of slight supersaturation have well organized crystalline structures initially and therefore are not significantly altered upon aging.

Impurities incorporated into the crystal by adsorption have been found to enhance recrystallization. In a process known as Ostwald Ripening (13), foreign ions are released back into solution due to solubility requirements. Electrostatic forces on adjacent lattice ions are subsequently reduced and the remaining surface ions are lost to larger and more perfect crystals (recrystallization). A second layer is now exposed to solution and the process repeated.

Through successive recrystallizations the precipitate is purified and average particle size increased.

Surface Adsorption

A kinetic exchange exists between the surface of the precipitate and solution. In a fashion similar to the dynamic exchange of molecules at a gas-liquid interface, lattice ions from the precipitate surface are continually dissolving and returning to solution and vice versa. When equilibrium exists these opposing rates become equal. However, during the initial stages of precipitation the rate of deposition of ions from solution controls, resulting in crystal formation and growth (13).

Ions in the lattice at the surface of a precipitate exhibit forces due to their free residual valences. These residual valence forces attract not only ions common to the lattice (carrier) but other ions from solution (contaminants) as well. Foreign anions or cations attracted to the surface may form readily soluble compounds with ions found in the lattice. If too soluble, these ions will probably retain their shell of hydration and remain in the diffuse double layer at the solid-liquid interface (12). (Totally different laws apply to ions in this condition. The ionic valence is an important factor here.) However, those ions capable of forming slightly soluble compounds with lattice ions may be incorporated into the solid through an exchange adsorption at the surface. As an example, when barium sulfate (solid) is mixed in a dilute solution of lead perchlorate the following reaction takes place:



This exchange occurs even though the solubility limit of lead sulfate has not been exceeded (13).

Most adsorption phenomena are a combination of different types of adsorption processes. The primary driving forces for adsorption processes are the hydrophobic nature of the solute and its high affinity for the solid phase. Solutes are generally attracted to a solid surface. Adsorption can range from accumulation of solute ions in the diffuse double layer to actual incorporation of the solute into the surface of the solid. The latter may lead to internal contamination of a precipitate through occlusion or mixed crystal formation while the former generally does not (12). The adsorption factors discussed below generally apply to the adsorption processes leading to contamination of the precipitate.

Compatibility of the Adsorption Compound. Readily soluble adsorption compounds will generally remain in the diffuse double layer. Contaminant ions capable of shedding their shell of hydration and forming slightly soluble adsorption compounds with lattice ions are readily incorporated into the surface of the precipitate (12).

In addition to solubility requirements, the physical size and deformability of the adsorbed ion will also determine the extent of adsorption. Foreign ions with large space requirements may not fit into available adsorption sites unless capable of being sufficiently deformed. Since ions are not rigid structures, electrical forces at the precipitate surface are often capable of deforming the outer shell electrons into more compact arrangements for incorporation of the solute into the crystal surface (13).

Surface Area and Crystalline Defects. Adsorption is enhanced by precipitates with large surface areas. As available adsorption sites decrease, further adsorption can occur only as new surface is formed by additional crystal growth. Contaminants added to a solution containing a "preformed" precipitate will exhibit significantly slower adsorption as crystal growth is essentially complete prior to adding the contaminant.

Precipitation under conditions of high supersaturation produces precipitates with large surface areas and disordered crystal lattice structures. Imperfections or defects in the surface structure provide "active sites" for adsorption (9). As spaces provided by crystal imperfections are filled, surface adsorption decreases. However, during the initial stages of precipitation contaminants can become enclosed or "occluded" by rapidly forming crystal surfaces. Due to a lack of compatibility with the precipitate, contaminants adsorbed at active sites are usually rejected during subsequent recrystallization processes.

Surface Charge and Polarity. Adsorption can be enhanced by the addition of a salt containing ions which "charge" the surface of the precipitate. This additional attraction will statistically increase the amount of time a solute spends in the vicinity of the precipitate, presenting more opportunities for surface adsorption (12).

The polarity of the adsorbent cannot be overlooked as a factor in adsorption. Foreign ions which tend to polarize the surface lattice ions will be more strongly adsorbed than those which do not.

Mixed Crystal Formation

Compounds involved in exchange adsorption at the surface of a precipitate are generally capable of forming mixed crystals. Mixed crystal formation describes the development of a distinctly new solid phase from the coprecipitation of two or more compounds. In other terminology, the contaminant and carrier (precipitate) are respectively identified as the solute and solvent in a solid solution formation. The miscibility of the two (or more) compounds in solid solution may be partial or complete depending upon their degree of isomorphism.

Isomorphism. Isomorphous compounds have closely similar crystalline structures, dimensions and composition. Two compounds are considered isomorphous if one incorporates more than about five percent of the other in mixed crystal formation. Compounds generally exhibit isomorphism in their crystalline structure when atoms occupy like positions within the crystal unit cell and lattice spacings are similar. Similarity in the cation-anion radius ratios are also necessary (20).

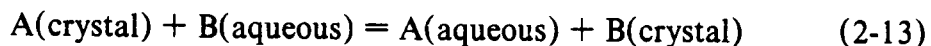
The chemical composition of compounds forming mixed crystals, although generally similar, do not have to be identical. However, in isomorphous substitution the electrostatic neutrality of the crystal must be maintained. If the chemical composition of the compounds involved are dissimilar (i.e. valence charge on ions differ), the electrostatic neutrality is disturbed and must be re-established in one of the following ways (20):

1. An ion of different charge is simultaneously substituted into the crystal surface,

2. Additional ions are incorporated outside the structural framework of the lattice, or
3. A position within the lattice structure is left vacant.

Calcium and cadmium carbonate exhibit isomorphic characteristics. Cadmium carbonate has a rhombohedral structure while calcium carbonate can be hexagonal, rhombohedral, or monoclinic. The rhombohedral structure meets the criteria for closely similar crystalline structures. In addition, calcium and cadmium have similar ionic radii (0.99 Å and 0.97 Å, respectively) and identical charge valences.

Distribution Laws for Homogenous Mixed Crystals. Homogeneous mixed crystal formation is relatively independent of the conditions of precipitation as it represents a state of thermodynamic equilibrium (9). However, under normal conditions of precipitation, a homogeneous distribution of contaminant within the precipitate is rare. As coprecipitation takes place the various (two or more) compounds will distribute themselves between solid and solution. The initial distribution of the contaminant within the precipitate may be quite random or may exhibit a concentration gradient. As recrystallization and diffusion processes take place an orderly arrangement of contaminant within the crystal is ultimately achieved (9). For the system represented by the equation



the equilibrium or distribution constant is given by

$$D = A(\text{aqueous}) * B(\text{crystal}) / \{B(\text{aqueous}) * A(\text{crystal})\} \quad (2-14)$$

which upon rearrangement gives

$$(B/A)_{\text{crystal}} = D^*(B/A)_{\text{aqueous}} \quad (2-15)$$

A series of homogenous mixed crystals of differing composition can be formed based upon the initial ratio of contaminant to carrier in solution. The distribution shown in equation 2-15 represents true thermodynamic equilibrium for the system in which sufficient digestion time has been allowed to eliminate all concentration gradients and to establish homogeneous distribution within the crystal.

Distribution Laws for Heterogeneous Mixed Crystals. Mixed crystals are capable of many heterogeneous arrangements of the contaminant within the crystal. The most widely studied heterogeneous arrangement is the mixed crystal exhibiting a radial concentration gradient. In this distribution the contaminant concentration continuously varies from center to periphery of the crystal. The mechanism responsible for such a distribution was proposed by Doerner and Hoskins (5) to be that "each crystal layer as it forms is in distribution equilibrium with the particular concentration of solution existing at that time." In this system a state of equilibrium exists for an infinitesimal crystal layer but not for the crystal as a whole. Therefore the homogeneous distribution law written for the entire crystal must be differentiated by crystal layers. Integrating such over the entire crystal we obtain the logarithmic distribution law:

$$\log(B_i/B_f) = \lambda \log(A_i/A_f) \quad (2-16)$$

where B_i and A_i represent initial concentrations in solution and B_f and A_f final solution concentrations. λ represents the heterogeneous distribution constant.

Conditions of Precipitation. The length of time a heterogeneous mixed crystal will remain in its metastable state depends upon the conditions of precipitation. Under ordinary conditions of rapid precipitation (large supersaturation) crystal formations tend to have disoriented crystalline structures. Heterogeneous mixed crystals formed under these conditions undergo rapid recrystallizations. As equilibrium conditions are approached the mixed crystal is reorganized into a uniform (homogeneous) distribution arrangement.

Large, well-ordered crystals formed under conditions of slight supersaturation are not subject to significant recrystallization processes upon aging. Contaminants heterogeneously incorporated into such mixed crystals remain locked in the solid until reorganized or expelled by slow recrystallization or diffusion processes (9).

3. SLUDGE HANDLING CHARACTERISTICS

Settleability

One of the functions of a sedimentation basin is to collect sludge solids in as small a volume of water as possible in order to facilitate solids handling. Typically, additional sludge thickening is practiced such as filtration, centrifugation or chemical conditioning (27). To design a settling basin requires laboratory settling analysis of the mixed liquor, which provides information on the rate of settling. Sludge settling analyses were not conducted in this investigation. However, the sludge volume index (SVI) which was

calculated provides some information on the degree of settling at any point in time.

$$SVI = \frac{\text{Sludge Volume at Time, } t \text{ (ml/l)}}{\text{Mixed Liquor Suspended Solids (mg/l)}} \quad (2-17)$$

SVI can be used to compare the relative efficiency of sludges with similar solids concentrations and settling characteristics. However, the SVI gives no information as to the settling rate. The SVI is obtained by placing a sample of mixed liquor in a one liter graduated cylinder or imhoff cone and allowing to settle. After a period of settling (usually 1/2 hour) the sludge volume is recorded and divided by the mixed liquor suspended solids.

Filterability

Precipitates formed by alkaline chlorination have generally been identified as metal hydroxide sludge. Metal hydroxide precipitates are typically voluminous and difficult to dewater. Efforts to obtain a sludge with better handling characteristics led to the development of the Kastone process by Dupont de Nemours and Co (2). Kastone is a proprietary formulation containing hydrogen peroxide which reportedly favors production of metal oxides over hydroxide following destruction of the metal cyanide complex. Dupont claims their sludges can be removed by ordinary filtration equipment.

A standard filtration test is used to evaluate sludge dewatering properties. A variety of methods have been used to evaluate the results of the sludge filtration test (17). In the past, investigators measured the time required for filter

cakes to crack. However, many sludges contain fibers which increase their cohesive nature during filtration. Next, researchers used the amount of filtrate obtained from a given volume of sludge. This, however, ignored the dry solids concentration of the sludge, and was therefore only applicable to sludges with equal dry solids concentration. Presently, the sludge dewatering properties of a precipitate are determined experimentally by measuring the rate of filtration. The standard filtration equation expresses the rate of filtration as a function of pressure (P), filter area (A), volume of filtrate (V), and various sludge parameters such as unit weight (w), viscosity (η) and specific resistance (r). Specific resistance is a unique property of each sludge which allows for comparisons between sludges with different dewatering characteristics. The standard filtration equation can be expressed as a derivative of filtrate accumulation with time (t):

$$dV/dt = PA^2/\eta(rwV + R_m A) \quad (2-18)$$

R_m is a constant representing the resistance to filtration of the filter medium.

Integrating and rearranging:

$$t/V = (\eta rw/2PA^2)V + R_m/PA \quad (2-19)$$

which has the form of a straight line equation ($y = mx + b$), where

$$m = \eta rw/2PA^2 \quad \text{and,} \quad r = 2mPA^2/\eta W \quad (2-20)$$

This equation is obtained experimentally by measuring the rate of filtration for a constant pressure (or vacuum) (27). Results of a typical filtration test are shown in figure 2.4 for calcite sludge.

Shortcomings of the Standard Filtration Equation

The influence of the filter medium (R_m term in equation 2-18) on the resistance of a sludge to filtration depends upon the nature of the sludge. When the average particle size of the precipitate is equal to or less than the pore size of the filter, the filter medium becomes clogged during filtration. For sludges with the minimum particle size greater than the pore size of the filter medium, a sludge "mat" forms over the filter. In this case, the filter medium does not significantly contribute to the total resistance (cake + filter). In a test comparing an unused filter with one clogged by solids from a previous sludge filtration test, the unclogged filter exhibited a filtration rate 136 times faster than the clogged medium rate (17).

The specific resistance of a sludge (r term in equation 2-20) is not necessarily constant, but depends upon the particle size distribution. Sludges with heterogeneous particle sizes generally exhibit variable specific resistances. This phenomenon is a result of smaller particles progressively clogging the voids formed by larger particles in the filter cake (or pores in the filter medium). In order to derive the standard filtration equation one must assume that particles are deposited in the most recently formed layer of the filter cake, and that porosity is solely a function of the applied pressure drop. When clogging occurs due to the deposition of heterogeneous particles, smaller particles are deposited in previously formed layers of the filter cake or within the filter medium itself.

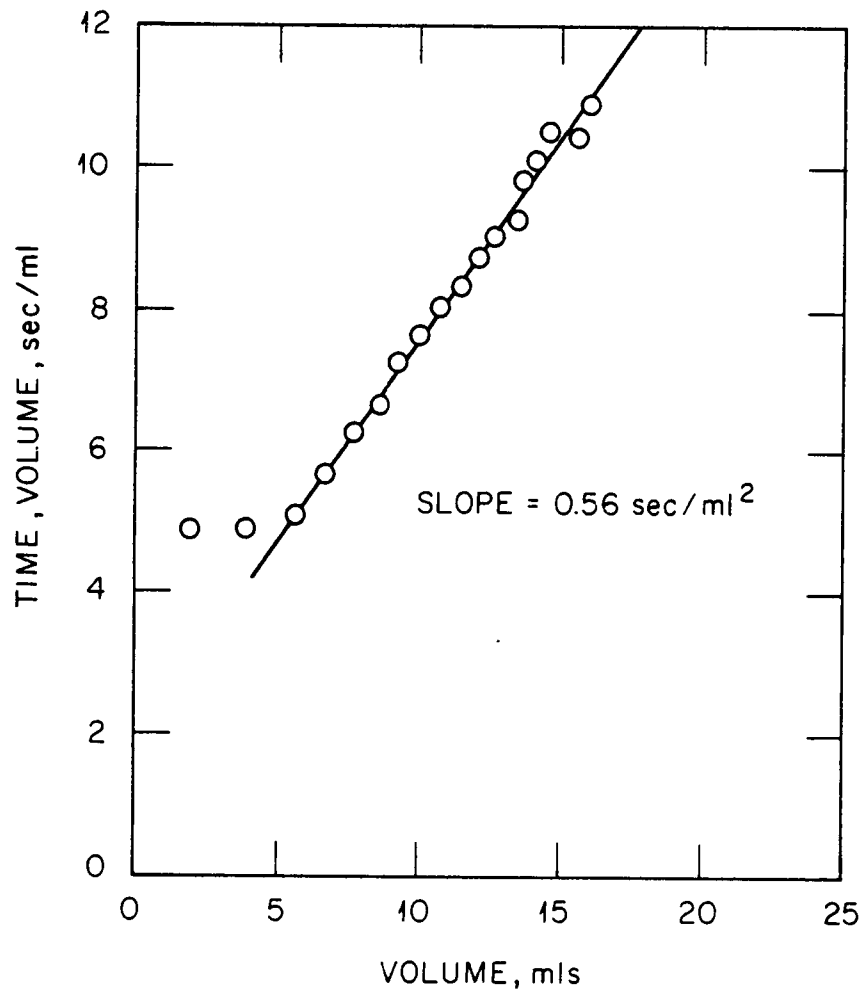


Figure 2.4. Filtration Curve for a Calcium Carbonate Sludge.

Consequently, one obtains a curve instead of a straight line when plotting the standard filtration equation. Taking the log of the standard filtration equation one obtains

$$\log T = \log m + 2 \log V \quad (2-21)$$

where

$$m = r'w/2PA^2 \quad (2-22)$$

and r' is the total specific resistance of cake plus filter medium. This is the equation of a straight line with a slope of two and a y-intercept of $\log m$. When clogging occurs, the slope of this line will increase or decrease as a function of the particle size distribution with respect to the pore size of the filter medium. Notebaert et al. (17) has demonstrated that if the particle size distribution in a heterogeneous sludge is in the range of the pore size of the filter medium, the slope of this line will be less than two and, conversely, for a range of particle sizes greater than the pore size of the filter medium this value is greater than two. Sludges with homogeneous particle size will register a value of two.

Capillary Suction Time Test

The capillary suction time (CST) test is another method of evaluating relative sludge dewatering properties. With CST it is possible to obtain information quickly with a minimum amount of sludge (3–5 mls). This method is

primarily useful as it empirically relates to the specific resistance obtained from filtration tests (27). Once this relationship has been established for a particular sludge, it can be used in place of filtration tests as an indication of sludge dewatering properties.

The CST method is based upon the capillary attraction between filter paper and filtrate. Sludge is placed in the center of an absorbent filter pad causing filtrate to spread outward. The rate at which filtrate drains from the sludge is measured by a timer actuated by probes on the filter paper. The probes measure movement of liquid across the filter paper. The time required for the liquid front to move between the two probes is the capillary suction time. Smaller CST values correlate with lower specific resistance values (27).

CHAPTER III

EXPERIMENTAL PROCEDURE

1. NON-CYANIDE PHASE

The initial experimental phase involved simulating the results of alkaline chlorination and precipitation, by preparing a non-cyanide solution containing the end products of cadmium cyanide destruction. To this end, a series of two liter jar tests were conducted on cadmium nitrate solutions containing carbonate and either sodium or calcium chloride. Precipitation was initiated by adjusting pH between 7 and 11 with sodium hydroxide base additions. The variables in this initial phase were the chloride salt used and test pH. Duplicate jar test were run for each condition.

Electroplating rinses typically contain between 15–100 mg/ℓ of the metal being plated (25). Preliminary jar tests conducted in this concentration range did not yield sufficient sludge for filtration tests. Therefore, non-cyanide jar tests were conducted with initial concentrations of both 100 and 3000 mg/ℓ cadmium. Although not representative of dilute drag-out rinses, 3000 mg/ℓ cadmium is typical of concentrated plating baths (16). Initial solution concentrations for jar test are shown in Table 3.1.

Following precipitation, solutions were mixed for one hour on a Phipps and Byrd jar tester before being transferred to two-liter graduated cylinders for settling. Mixed liquor samples were withdrawn for solids analysis. Following two hours of settling, supernatant samples were taken for solids, total inorganic carbon and residual metals analyses. In the dilute (100 mg/ℓ) cadmium system

Table 3.1.
Initial Solution Concentrations in Non-Cyanide Jar Tests.⁽¹⁾

Constituents	Concentrated ⁽²⁾				Dilute ⁽²⁾			
	NaCl ⁽³⁾		CaCl ₂ ⁽³⁾		NaCl		CaCl ₂	
	mg/l	M	mg/l	M	mg/l	M	mg/l	M
Cd ²⁺	3,000	0.0267	3,000	0.0267	100	8.90E-4	100	8.90E-4
Ca ²⁺	0	0	12,700	0.318	0	0	420	0.0105
Na ⁺	18,200 ⁽⁴⁾	0.792	3,700(4)	0.161	562	0.0244	82	3.57E-3
Cl	22,400	0.632	22,400	0.632	742	0.0209	742	0.0209
CO ₃ ²⁻	6,430	0.107	6,430	0.107	213	3.55E-3	213	3.55E-3
NO ₃ ⁻	1,670	0.0269	1,670	0.0269	111	1.179E-3	111	1.79E-3

⁽¹⁾Prior to pH adjustment.

⁽²⁾Concentrated or dilute cadmium jar tests.

⁽³⁾Jar tests with either sodium or calcium chloride additions (typical).

⁽⁴⁾Average concentration.

only, selected samples of supernatant were filtered and identical analyses run on filtrates.

Sludges were collected for solids analyses and filtration tests. Sludge dewatering characteristics were studied using both the standard filtration test and the capillary suction time (CST) test. Finally, the mineral content of precipitates was identified by X-ray diffraction, atomic absorption (AA) and total inorganic carbon (TIC) analyses.

In the AA analysis of sludges, samples were prepared by dissolving a weighed amount of dried precipitate in a known volume of acid. Since acids drive off carbonate as carbon dioxide gas, TIC samples were prepared with distilled water instead.

Figure 3.1 is a diagram of experimental procedure followed in the non-cyanide phase.

2. CYANIDE PHASE

In the last phase of the experiment, alkaline chlorination jar tests were performed on laboratory prepared cadmium cyanide solutions at pH's 7-11, using both sodium and calcium hypochlorite as oxidants. The test variables were solution pH and form of hypochlorite oxidant. Duplicates were run at each pH and for each form of oxidant tested.

Alkaline chlorination treatment was conducted at a single pH instead of in two stages. Solution pH was adjusted and maintained at the test pH value until destruction of the cadmium cyanide complex was complete.

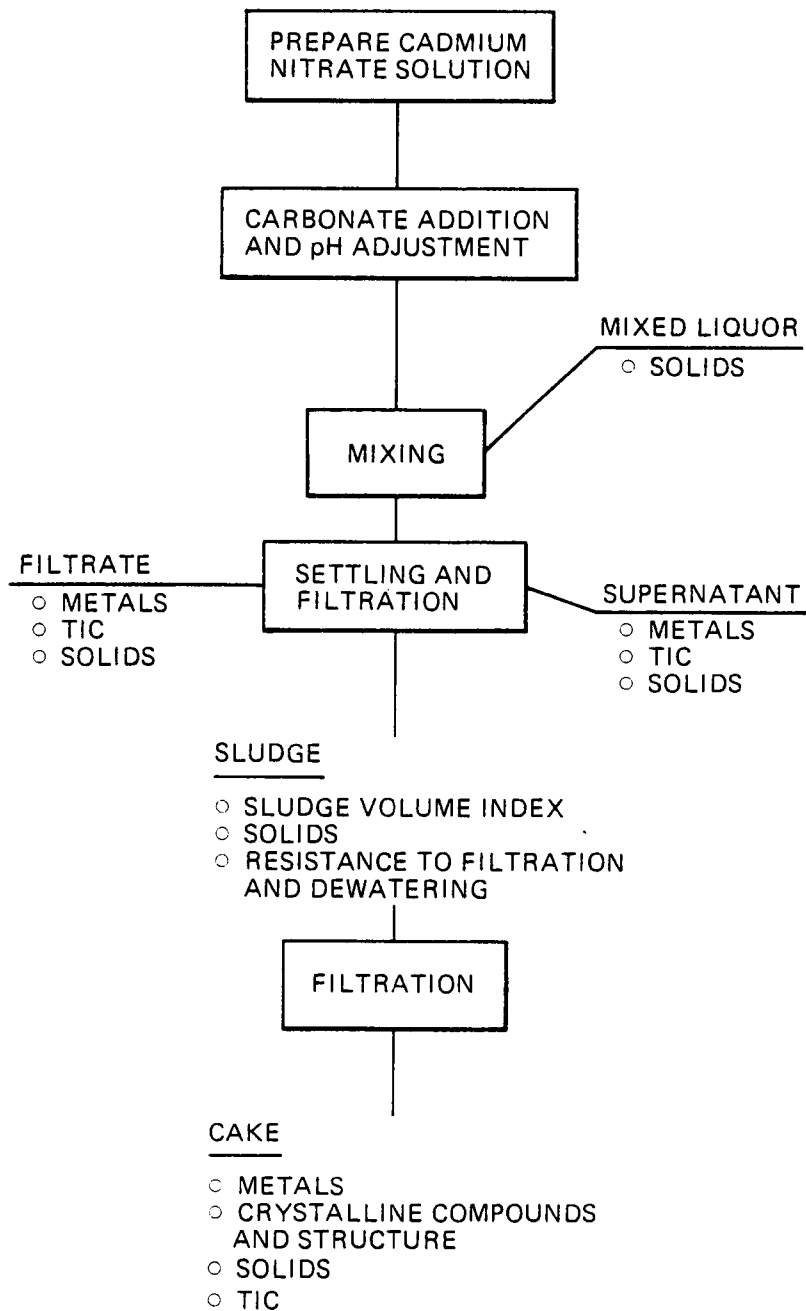


Figure 3.1. Experimental Design, Non-Cyanide Phase.

The impact of the hypochlorite compound added on solution conditions was also investigated. "Chlorox" bleach was used as the source of sodium hypochlorite. Reagent grade calcium hypochlorite was added to solutions as a powder. Both were standardized by the Iodometric method (24). Chlorine gas was not used as its dissolution and conversion to the hypochlorite form is nearly instantaneous in basic solutions (21).

All jar test solutions were prepared at 100 mg/l cadmium and 97 mg/l cyanide. The molar ratio of CN: Cd was 4:1 with a 5% cyanide excess to ensure complete complexation of cadmium. Sodium hydroxide base additions were used to bring solutions to test pH. Next, standardized sodium or calcium hypochlorite was added, while mixing, to react with the cadmium cyanide complex. A 10% hypochlorite excess was added to account for any secondary reactions. Small base additions were generally required to maintain pH during initial stages of mixing. This was due to both consumption of hydroxides during reaction, and removal of carbonate alkalinity through precipitation. Following destruction of the cadmium cyanide complex, no further pH adjustments were made. Spot test screening was used as a quick method of determining approximate cyanide (and cyanogen chloride) levels (24). In each case, cyanides were reduced from their initial concentration to less than 1 mg/l within 10 minutes of hypochlorite addition. Table 3.2 lists the constituents and initial solution concentrations prepared for cadmium cyanide jar tests.

Test solutions were mixed on a Phipps and Byrd jar tester for a one hour period. Mixed liquor samples were withdrawn, following mixing, for solids and cyanate analysis. Test solutions were then transferred to Imhoff cones for a

Table 3.2.
Initial Solution Concentrations in Cadmium Cyanide Jar Tests.⁽¹⁾

Constituents	NaOCl ⁽²⁾		Ca(OCl) ₂ ⁽²⁾	
	mg/l	M	mg/l	M
Cd ²⁺	100	8.90E-4	100	8.90E-4
Ca ²⁺	0	0	331	8.28E-3
Na ⁺	(3)		86	3.74E-3
CN ⁻	97	3.73E-3	97	3.73E-3
OCl ⁻	778	0.0219	778	0.0219
NO ₃ ⁻	110	1.77E-3	110	1.77E-3

⁽¹⁾Prior to pH adjustment.

⁽²⁾Jar tests treated with either sodium or calcium hypochlorite.

⁽³⁾Sodium concentration of chlorox unknown.

two hour settling period. Following settling, samples were taken for solids, residual metals, alkalinity and cyanate analyses. Solutions were filtered, and filtrates tested for dissolved solids, metals, and alkalinity. Suspended and soluble cadmium, calcium, and sodium were determined by atomic absorption spectrometry.

Cyanate and alkalinity samples were collected with as little headspace as possible to minimize volatilization and equilibrium with the atmosphere. Cyanate samples were preserved with the addition of sodium thiosulfate to prevent further oxidation of cyanate to end products. Both alkalinity and cyanate samples were refrigerated.

Precipitates ranged from the immeasurable to 100 ml sludge per liter of solution. However, most precipitates averaged between one and three ml per liter of solution. Where volumes permitted, sludge dewatering characteristics were evaluated. Filtration tests required a minimum of 15 ml of sludge. Only the sodium hypochlorite jar test at pH 10 had sufficient sludge for this test. As stated earlier, the Capillary Suction Time (CST) test requires only three to five ml of sludge. This test was run on most of the sludges generated.

Precipitates were dried in a vacuum desiccator and crushed into powder. The dried powders were identified by X-ray diffraction using the powder diffraction technique. X-ray diffraction uses the principle that X rays are of the same order of magnitude as the distances between atoms in crystalline materials. Since planes of atoms (lattices) are duplicated in all crystalline compounds, X rays are diffracted at predominant angles. The diffracted angles are a function of the kind, size and arrangement of atoms present. By

comparing diffraction patterns of known compounds with unknown ones, identification of the unknown compound or phase is possible.

Finally powders were dissolved in acid, and cadmium, calcium and sodium metals determined by atomic absorption spectrometry. Figure 3.2 is a flowchart of the experimental and analytical work performed.

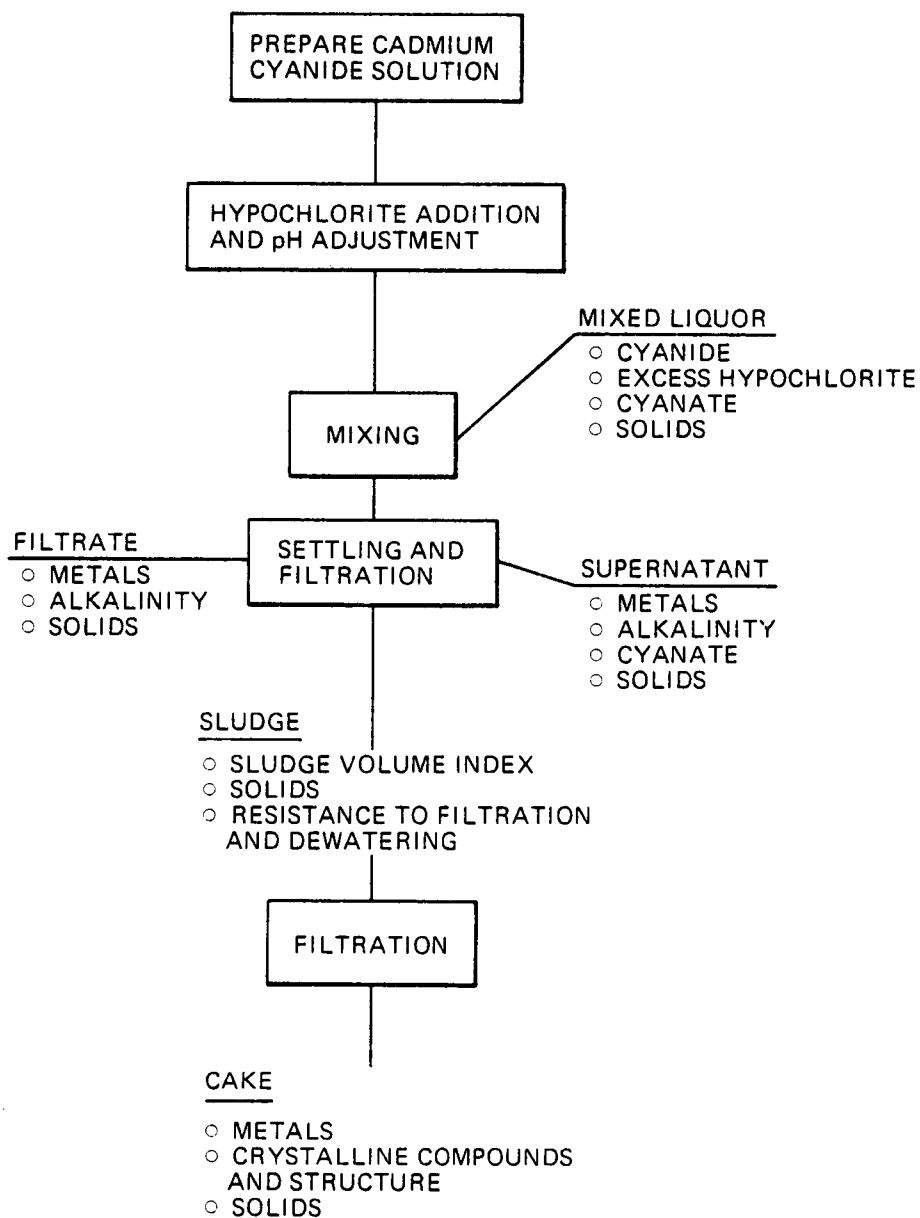


Figure 3.2. Experimental Design, Cyanide Phase.

CHAPTER IV

RESULTS

1. NON-CYANIDE EXPERIMENTAL PHASE

The purpose of the non-cyanide experimental phase was to accurately represent the precipitation characteristics of cadmium cyanide destruction by alkaline chlorination. This subchapter is organized into an analysis of experimental technique and presentation of results. The analysis section examines the problems and short-coming of various methods and techniques, their impact on results, and what was done to correct them. Presentation of results is divided into subsections on concentrated and dilute cadmium jar tests. Each subsection explains tables and figures in the general categories of supernatant and filtrate quality, sludge settling and filterability characteristics, and precipitate mineral characteristics.

Analysis of Experimental Technique

Early in the experimental work, a number of problems with laboratory technique or procedure were identified which limited data collection or potentially biased results. In most cases, corrective actions were taken to either improve technique or substitute other, more reliable methods. Those significant events which impacted the quality of results are reported below:

1. Unfiltered supernatant did not accurately reflect cadmium solubility behavior in jar tests. Preliminary jar tests at the 3000 mg/l level revealed

that suspended solids accounted for less than one percent (by weight) of the total solids found in supernatants. It was (incorrectly) assumed that suspended solids could be ignored, thereby eliminating the need for filtration. What was not taken into account was that the dissolved and suspended solids consisted of different mineral composition due to differences in the relative solubilities of various constituents in solution. Soluble cadmium was effectively swamped by suspended cadmium. For example, 100 mg/l TSS consisting of cadmium carbonate precipitate represents 65 mg/l cadmium as compared to 0.01–0.1 mg/l soluble cadmium obtainable in this system at optimum pH. Consequently, comparison of residual cadmium in the unfiltered supernatant with theoretical solubility values is tenuous at best. Experimental data are of value, however, in evaluating efficiency of the precipitation process. Filtered samples were later obtained in the dilute cadmium jar tests and cadmium cyanide experimental phase.

2. Poor technique in preparing multiple sample dilutions for AA work biased sodium results in the concentrated cadmium jar tests. Micropipetting techniques were later used to improve accuracy and reduce the number of dilutions.
3. Precise measurements were difficult using the total carbon analyzer (TCA) for measuring the inorganic carbon content of precipitates. As previously discussed, dried precipitates were mixed with distilled water and injected into the TCA furnace. Several factors probably contributed to the lack of precision:

- It was difficult to maintain a homogeneous mixture in solution.
- Some particles may have been too large to pass through the syringe.
- The TCA instrument used was marginally reliable due to problems with the furnace.

This method, however, did provide data for comparison of results on a relative scale. Inorganic carbon analysis was abandoned in later (dilute) work in favor of more extensive mineral characterization by X-ray diffraction.

4. Mechanical mixing at 50–60 RPM typically resulted in floc breakup. This contributed to the resuspension of solids, resulting in increased cadmium levels in solution. In addition, the physical properties of the sludge (volume, density, and filterability) were probably modified due to the change in the particle size distribution. Since this phenomenon was (mistakenly) attributed to recrystallization processes by the author, no attempt was made to reduce paddle speed on the mixer.
5. Unwashed precipitates in concentrated cadmium jar tests were found to be contaminated with sodium chloride. Contamination was only found in those jar test originally prepared with sodium chloride. The degree of contamination was greatest for voluminous sludges, indicating contaminated interstitial water was responsible. Precipitates were lightly washed in the subsequent experimental phases.
6. Two-liter jar tests prepared at 3000 mg/ℓ initial cadmium concentration did not produce sufficient sludge to run filtration tests. A filtration apparatus was subsequently assembled which substantially reduced sludge

requirements for the filtration test. The following subsection presents details of the modified filtration test.

Modified Filtration Test

One of the first problems encountered in design of the experiment was generating enough sludge to run filtration tests. Preliminary jar tests showed that two liters of a 3000 mg/l cadmium solution did not produce sufficient sludge to run repetitive Buchner funnel filtration tests. Consequently, a filtration system was designed using the Gooch crucible as the receptacle for sludges. Sludge requirements were reduced from 100 to 15 ml by use of the Gooch crucible. Figure 4.1 is an illustration of the filtration apparatus used.

Theoretically, specific resistance is directly proportional to both the slope of the filtration curve and the square of the filter area (see equation 2-20). Therefore, all other values being constant (i.e. vacuum, sludge viscosity and percent solids in sludge and cake), a reduction in filtration area should result in a corresponding increase in the slope of the filtration curve. This was tested experimentally on a calcium carbonate sludge using both the Buchner funnel and Gooch crucible sludge receptacles. The Buchner funnel and Gooch crucible used had diameters of 2.1 and 4.25 cms., respectively. Results of the tests are shown in table 4.1. Filtration area apparently does affect specific resistance. The specific resistance values obtained from Gooch crucible filtration tests were approximately 70% of the values recorded for Buchner funnel tests. This phenomenon may be related to the difference in diameter and sidewall effects. Therefore, caution should be observed when comparing filtration results using different sized sludge receptacles.

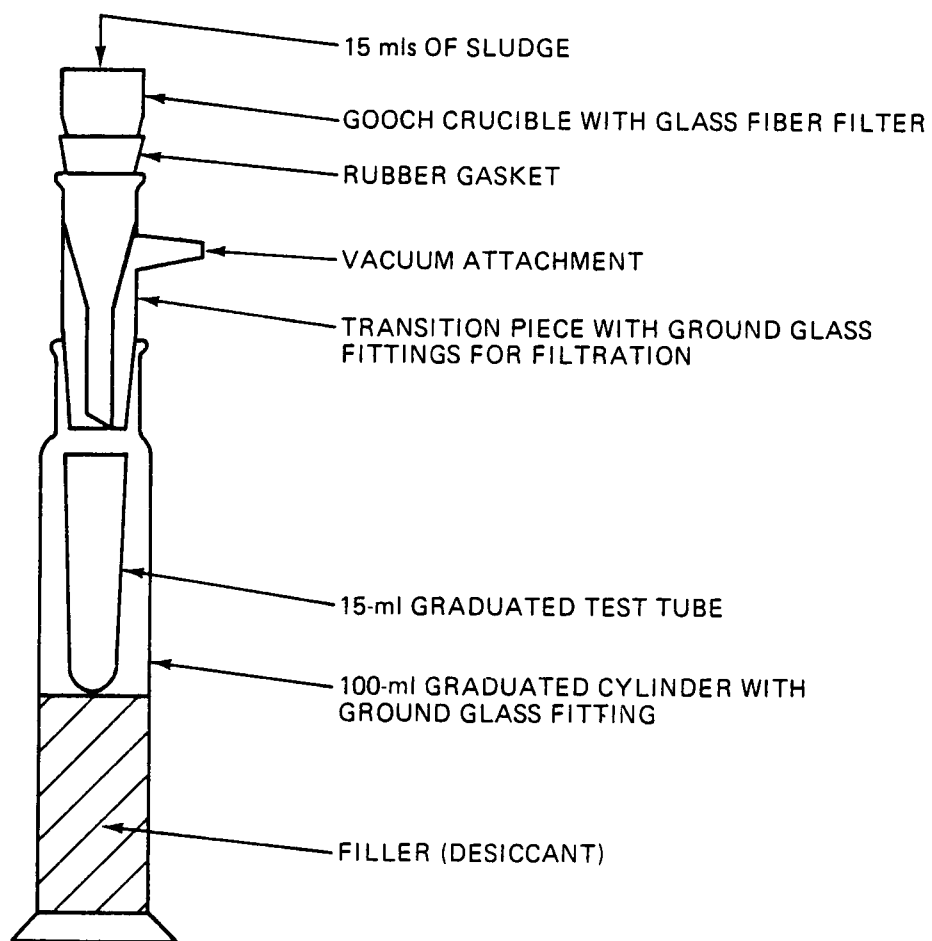


Figure 4.1. Sludge Filtration Apparatus.

Table 4.1.
Sludge Filtration Tests. Gooch Crucible
Versus Buchner Funnel.

Parameter	Buchner Funnel				Gooch Crucible	
	1	2	3	4	1	2
Slope, sec/cm ⁶	0.46	0.56	0.60	0.62	12.2	13.3
Vacuum, gm/cm ²	518	518	518	518	518	518
Area ² , cm ⁴	241	241	241	241	8.12	8.12
Viscosity, gm-sec/cm ²	9.18	9.18	9.18	9.18	9.18	9.18
Cake Solids, gm/cm ³	0.78	0.78	0.78	0.78	0.79	0.79
Specific Resistance, cm/gm	16,100	19,600	21,000	21,700	14,200	15,500
Average, cm/gm	19,600				14,850	

Presentation of Results

Concentrated Cadmium Solutions

Supernatant Quality (Tables 4.2 and 4.3, and Figures 4.2 and 4.3). Results on the efficiency of the precipitation process are presented in the tables and figures of this part. Unfiltered supernatant samples were examined for residual metals, total inorganic carbon, and total solids content. Residual cadmium levels were compared with theoretical solubility values in Figures 4.2 and 4.3.

A number of considerations went into construction of the theoretical solubility curves:

1. The equilibrium soluble cadmium concentration is dependent upon the final total inorganic carbon level ($C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) in equilibrium with the solid phase. Solubility curves representing three different C_T values were plotted in Figures 4.2 and 4.3. The solubility curves selected were representative of the range of C_T values found in jar tests over the pH region studied. Also plotted was the cadmium hydroxide solubility curve ($C_T = 0$).
2. In a more direct comparison, the equilibrium cadmium solubility concentration corresponding to each individual jar test C_T and pH value (+ symbol in figures) was calculated and plotted with experimental data. A computer program written to handle the simultaneous solution of stability and solubility expressions for each jar test condition is shown in Appendix A, along with tabulated output in Appendix B.
3. Due to the relatively high ionic strength of solutions tested (average 0.9) the resulting activities in solution could not be ignored. An empirical

Table 4.2.
Results of Analyses on Supernatant in Concentrated Cadmium
Jar Tests with Sodium Chloride Additions.

Jar Test pH ⁽¹⁾	Solids ⁽²⁾ mg/ℓ	Cadmium mg/ℓ	Calcium mg/ℓ	Sodium ⁽³⁾ mg/ℓ	Carbonate ⁽⁴⁾ mg/ℓ
NaCl	54,000	3000	0	Initial-Final	6400
11	57,200	0.86	0	20,300-22,200	7830
11	61,100	0.50	0	21,100-24,000	9250
10	49,500	17.0	0	19,000-18,600	4420
10	54,900	30.0	0	19,400-21,600	7420
10	50,000	18.0	0	20,900-20,400	5340
9	47,900	31.0	0	18,200-18,000	4270
9	47,300	25.0	0	18,700-22,000	5130
8	46,500	26.0	0	17,700-17,600	3710
8	47,100	3.0	0	18,300-18,400	4980
7	45,700	9.0	0	17,100-18,000	3360
7	46,200	7.0	0	17,800-18,600	4270

(1)Initial pH values (typical).

(2)Total solids. First entry in column is the average initial concentration.

(3)Initial sodium concentration varied with base additions.

(4)Total inorganic carbon expressed as CO₃.

Table 4.3.
Results of Analyses on Supernatant in Concentrated Cadmium
Jar Tests with Calcium Chloride Additions.

Jar Test	Solids ⁽¹⁾	Cadmium	Calcium	Sodium ⁽²⁾	Carbonate ⁽³⁾
pH	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ
CaCl ₂	52,000	3000	12,580	Initial-final	6400
11	45,900	13.0	9,250	5080-5050	15.3
11	43,300	15.0	6,950	5740-8000	14.2
10	45,200	13.0	7,550	5370-7550	20.3
10	42,200	32.0	7,750	5250-6750	11.7
9	44,000	104.	9,700	3630-4900	16.3
9	46,000	58.0	7,950	5320-6800	12.2
8	55,500	145.	10,000	5010-5000	31.5
8	43,500	139.	9,600	6820-4950	18.3
7	49,300	114.	10,150	7100-4900	55.9
7	46,800	115.	10,250	6600-4900	61.5

⁽¹⁾Total solids. First entry in column is the average initial concentration.

⁽²⁾Initial sodium concentration varied with base additions.

⁽³⁾Total inorganic carbon expressed as CO₃.

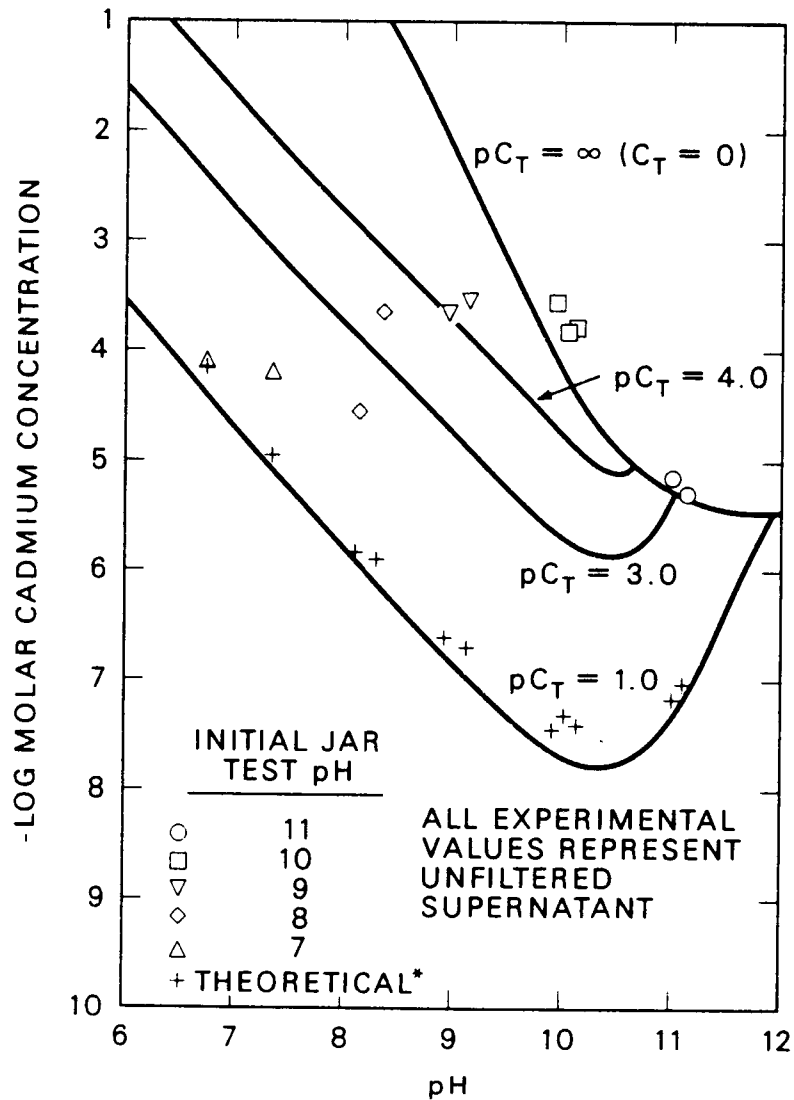


Figure 4.2. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Concentrated Cadmium Jar Tests with Sodium Chloride Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

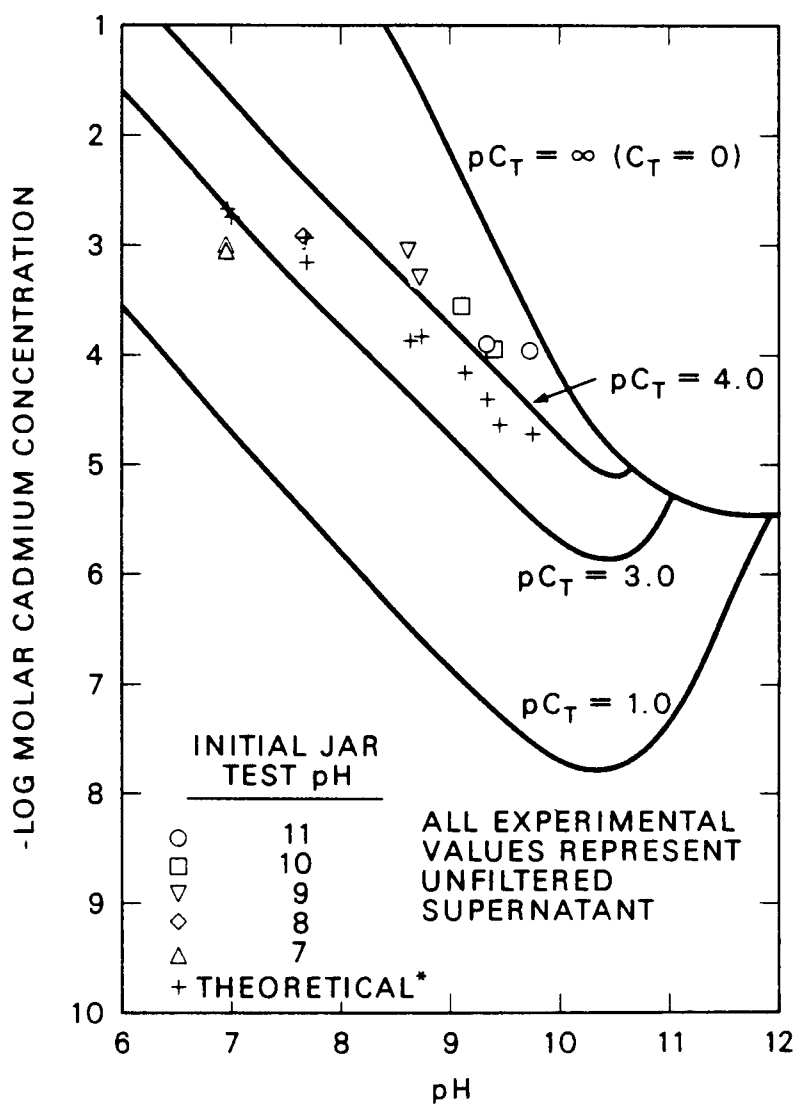


Figure 4.3. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Concentrated Cadmium Jar Tests with Calcium Chloride Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

extension of the Debye-Huckel theory proposed by Davies was used to calculate activity coefficients for modifying solubility and stability constants (3). The Davies equation:

$$-\log \gamma = Az^2[\sqrt{I}/(1 + \sqrt{I}) - 0.2I] \quad (4-1)$$

was thought to be the best approximation of the various activity expressions investigated.

4. Finally, adding to the solubility of cadmium carbonate was the formation of chlorocadmium complexes. Stability expressions for the various chlorocadmium complexes were included in the calculation of theoretical cadmium carbonate solubilities. Chlorocadmium complexes increased free cadmium ion solubility 19 times in concentrated cadmium solutions.

Sludge Settling and Filterability Characteristics (Tables 4.4 and 4.5, and Figure 4.4). The tables and figures in this part represent the results of solids analyses, CST measurements and sludge filtration tests. Figure 4.4 is a graphical representation of the relationship between specific resistance and capillary suction time. A unique relationship was established for each system. Extrapolation of curves through the zero specific resistance value reveals good agreement with the CST value expected for pure distilled water (8–10 seconds).

Precipitate Mineral Characteristics (Tables 4.6 and 4.7). Sludge handling behavior is a function of the mineral characteristics of the precipitate. Analyses of precipitates for metals and inorganic carbon were supplemented by X-ray diffraction for identification of the types and forms of minerals present. X-ray

Table 4.4.

Results from Solids Analyses and Sludge Filtration Tests in Concentrated Cadmium Jar Tests with Sodium Chloride Additions.

Jar	Sludge				Specific		
Test	MLSS	Vol. ⁽¹⁾	SVI	W _s ⁽²⁾	W _c ⁽³⁾	Resis.	CST
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	(4)	773.		(4)	(4)	(5)	8.9
11	4800	580.	121.	0.0665	0.165	(5)	8.5
10	6900	27.9	4.0	0.254	0.708	2380	
10	1800	5.0	2.8	0.329	0.611	1500	
10	5300	27.5	5.2	0.210	0.689	1500	28.7
9	5600	25.0	4.5	0.241	0.701	2320	39.6
9	4700	18.9	4.0	0.256	0.713	1800	34.0
8	5000	22.2	4.4	0.228	0.690	3070	47.4
8	5700	25.1	4.4	0.233	0.707	2800	44.8
7	6600	32.5	4.9	0.229	0.687	1200	24.5
7	5100	40.0	7.8	0.182	0.687	1800	25.3

(1) Measured at 2 hours (typical).

(2) Mass of dry solids per unit mass of sludge.

(3) Mass of dry solids per unit mass of cake.

(4) Weighing errors. Weighing procedure modified in subsequent runs.

(5) Variable specific resistance.

Table 4.5.

Results from Solids Analyses and Sludge Filtration Tests in Concentrated
Cadmium Jar Tests with Calcium Chloride Additions.

Jar	Sludge				Specific		
Test	MLSS	Vol.	SVI	$W_s^{(1)}$	$W_c^{(2)}$	Resis.	CST
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	13,600	75.5	1.27	0.198	0.579	400	17.6
11	20,600	82.9	1.30	0.248	0.590		17.4
10	25,000	80.8	1.15	0.309	0.609	620	39.3
10	19,400	71.8	1.17	0.266	0.598	210	18.2
9	12,200	44.6	0.794	0.267	0.611	190	16.9
9	12,300	66.3	1.14	0.220	0.593	170	17.5
8	12,000	55.6	0.824	0.234	0.617	210	22.0
8	11,300	49.7	0.907	0.239	0.600	360	18.6
7	12,800	40.0	0.644	0.302	0.675	98	19.5
7	14,000	32.5	0.535	0.385	0.706		16.1

⁽¹⁾Mass of dry solids per unit mass of sludge.

⁽²⁾Mass of dry solids per unit mass of cake.

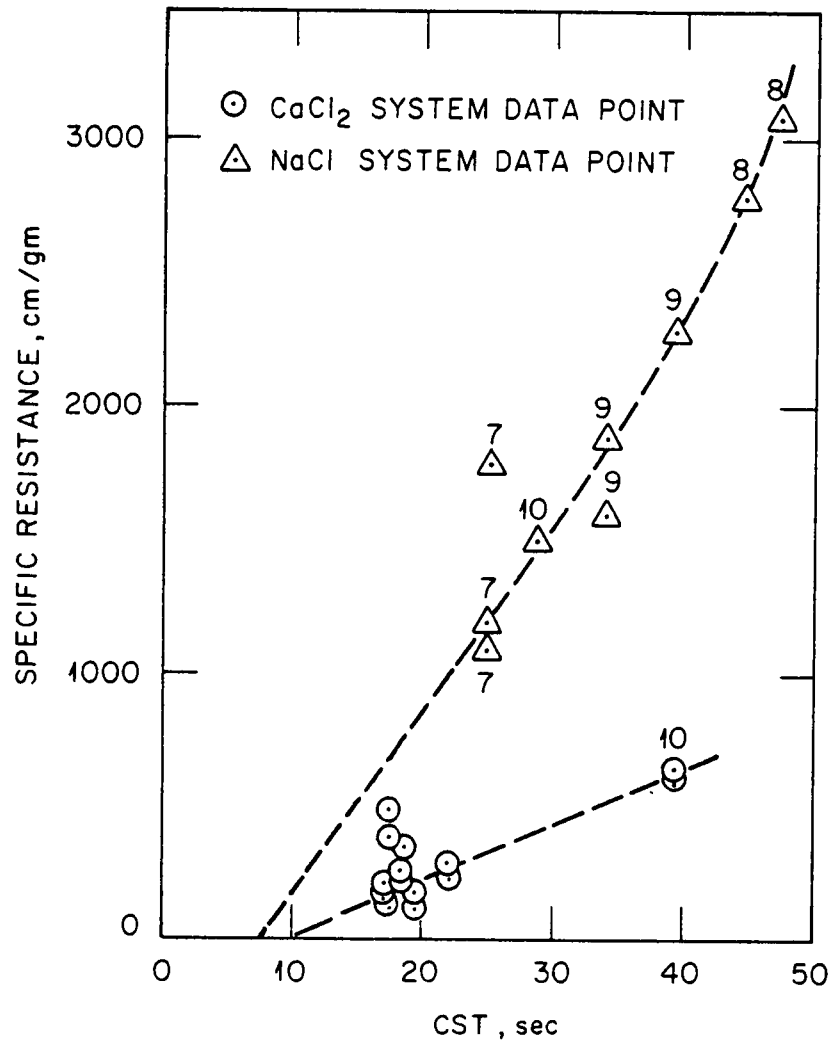


Figure 4.4. Sludge Dewatering Properties. Capillary Suction Time Versus Specific Resistance in the Concentrated Cadmium Phase.

Table 4.6.
Results of Analyses on Precipitates from Concentrated Cadmium
Jar Tests with Sodium Chloride Additions.

Jar					Eq CAT ⁽²⁾	X-ray Diffraction Patterns	
Test	% ⁽¹⁾	%	%	%	÷		
pH	Cadmium	Calcium	Sodium	Carbonate	Eq CO ₃	1st	2nd
11	34.8	0.017	21.0	13.3	1.40		
11	41.4	0.085	16.0	15.0	1.48	Halite ⁽³⁾	Otavite ⁽⁴⁾
10	60.0	0	2.0	27.5	1.17		
10	60.0	0.080	2.3	29.3	1.10		
10	62.0	0.111	1.25	30.2	1.10	Otavite	Halite
9	59.0	0.023	1.6	27.0	1.17		
9	61.0	0.016	1.1	29.3	1.11	Otavite	Halite
8	60.0	0	1.6	30.0	1.07		
8	62.0	0	1.0	30.0	1.10	Otavite	Halite
7	62.0	0	0.75	30.5	1.09		
7	62.0	0.078	1.05	30.5	1.09	Otavite	Halite

⁽¹⁾Percent by weight in dried precipitate (typical).

⁽²⁾Equivalents of cadmium and calcium cations per equivalent of carbonate.

⁽³⁾Halite is the crystalline form of sodium chloride.

⁽⁴⁾Otavite is the crystalline form of cadmium carbonate.

Table 4.7.
Results of Analyses on Precipitates from Concentrated Cadmium
Jar Tests with Calcium Chloride Additions.

Jar					Eq CAT	X-ray Diffraction Patterns	
Test	%	%	%	%	÷		
pH	Cadmium	Calcium	Sodium	Carbonate	Eq CO ₃	1st	2nd ⁽¹⁾
11	21.2	26.0	0.4	31.2	1.61		
11	15.2	30.0	0.5	43.0	1.23	Calcite ⁽²⁾	
10	14.7	29.0	0.4	40.2	1.28		
10	16.8	30.0	0.4	45.0	1.20	Calcite	
9	21.5	25.0	0.3	38.5	1.27		
9	16.4	29.1	0.6	43.8	1.20		
8	22.0	23.2	0.3	37.5	1.24		
8	21.8	25.6	0	38.3	1.31		
7	22.2	25.5	0	30.0	1.67	Calcite	
7	22.5	25.7	0.2	30.0	1.68		

⁽¹⁾Otavite may be present but masked by the calcite peaks.

⁽²⁾Calcite is one crystalline form of calcium carbonate.

diffraction was performed on selected precipitates thought to be representative of mineral composition over the pH range examined.

The ratio of +2 cations (cadmium and calcium) to the carbonate anion found in precipitates was calculated and presented in the tables. A value of one would indicate metal carbonate ($M^{2+} CO_3^{2-}$) stoichiometry exclusively. However, problems with the TIC analysis of precipitates biased results (see section on Analysis of Experimental Technique).

Dilute Cadmium Solutions

Supernatant and Filtrate Quality (Tables 4.8 and 4.9, and Figures 4.5 and 4.6). Filtered and unfiltered samples of supernatant were analyzed for solids, total inorganic carbon, and residual metals content. Filtration was conducted on those samples with visible, colloidal suspensions. Filtered cadmium results provided true metal solubilities (as compared to unfiltered sample results) for comparison with theoretical solubility curves.

The figures in this part were prepared in the same manner as the solubility curves presented earlier for the concentrated cadmium system. However, ionic strength was substantially less (average 0.03) in the dilute system, reducing the impact of activity coefficients on stability and solubility constants. The impact of chlorocadmium complexes in the dilute system was relatively minor, increasing free cadmium ion solubility by 26%.

Sludge Settling and Filterability Characteristics (Tables 4.10 and 4.11). Sludge volumes were insufficient to run CST and filtration tests in most jar tests. Consequently, the relationship between CST and specific resistance was not established in either sodium or calcium chloride treated jar tests.

Table 4.8.
Results of Analyses on Supernatant and Filtrate in Dilute Cadmium
Jar Tests with Sodium Chloride Additions.

Jar Test		Solids ⁽²⁾	Cadmium	Calcium	Sodium	Carbonate ⁽³⁾
pH	Phase ⁽¹⁾	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ
NaCl		1740	100.	0	Initial-Final	218
11	S	1820	0.39	0	726-603	282
11	S	1578	0.39	0.21	714-698	193
10	S	1624	1.00	0	638-634	202.
10	S	1550	1.32	0	638-614	192
9	S	1554	1.69	0	615-574	178
9	F	1388	0.07	0.21	599-571	160
	S	1420	9.6	0.21	599-596	181
8	F	(4)	0.14	0	592-548	156
	S	(4)	13.7	0	592-568	156
8	S	1610	9.3	0	595-561	158
7	F	(4)	10.9	0	585-543	110
	S	(4)	51.	0	585-555	118
7	S	1554	53.	0	572-549	120

⁽¹⁾Supernatant (S), Filtrate (F).

⁽²⁾Measured total dissolved solids in filtrate and total solids in supernatant.

⁽³⁾Total inorganic carbon expressed as CO₃.

⁽⁴⁾Weighing errors. Weighing procedure modified in subsequent runs.

Table 4.9.
Results of Analyses on Supernatant and Filtrate in Dilute
Cadmium Jar Tests with Calcium Chloride Additions.

Jar Test		Solids	Cadmium	Calcium	Sodium	Carbonate ⁽¹⁾
pH	Phase	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ
CaCl ₂		1680	100.	424	Initial-Final	218
11	S	1704	10.49	298	262-220	3.55
11	F	1500	0.01	279	250-230	3.75
	S	1562	2.76	297	250-220	3.00
10	S	1674	0.73	313	195-192	10.2
10	S	1564	1.02	310	193-189	6.60
9	S	1692	1.68	342	156-148	40.3
9	F	1710	0.93	321	170-164	8.80
	S	1420	1.13	310	170-168	9.40
8	F	(2)	0.42	353	138-134	64.
	S	(2)	1.92	362	138-134	66.
8	S	1836	1.54	386	121-119	100.
7	F	(1)	32.3	409	138-132	91.
	S	(1)	63.	407	138-131	143.
7	S	2120	37.2	402	98-94	72.

⁽¹⁾Total inorganic carbon expressed as CO₃.

⁽²⁾Weighing errors. Weighing procedure modified in subsequent runs.

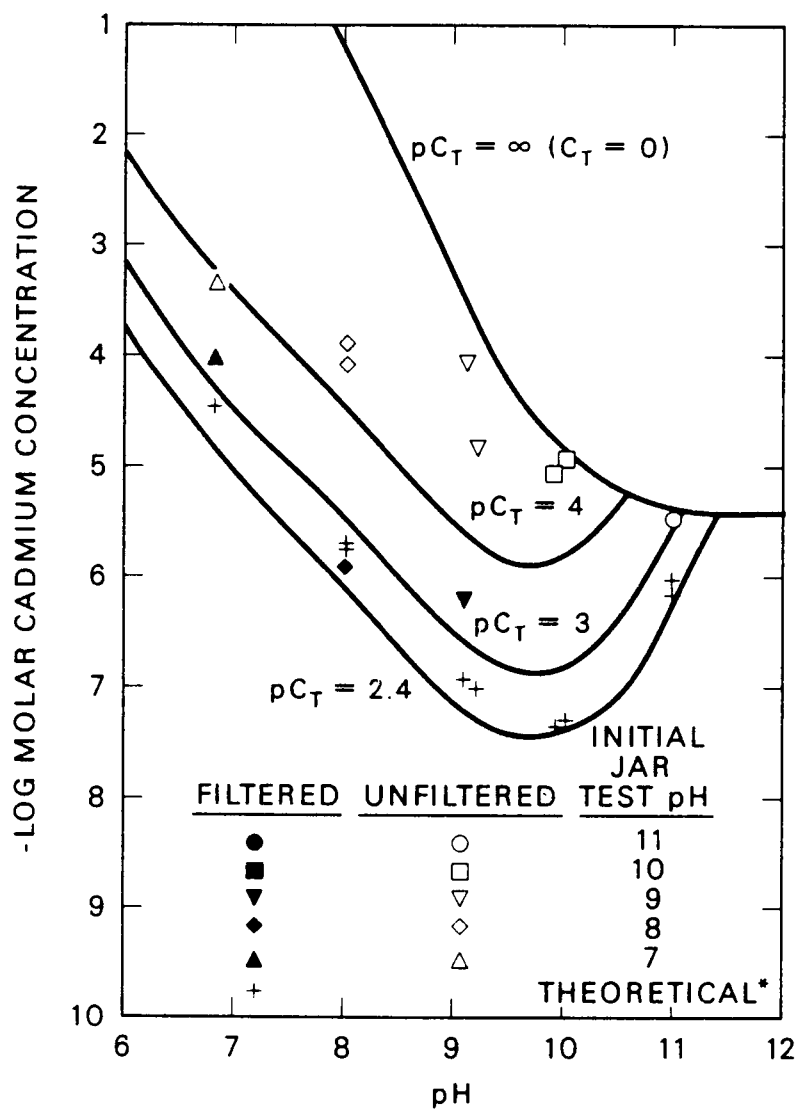


Figure 4.5. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Dilute Cadmium Jar Tests with Sodium Chloride Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

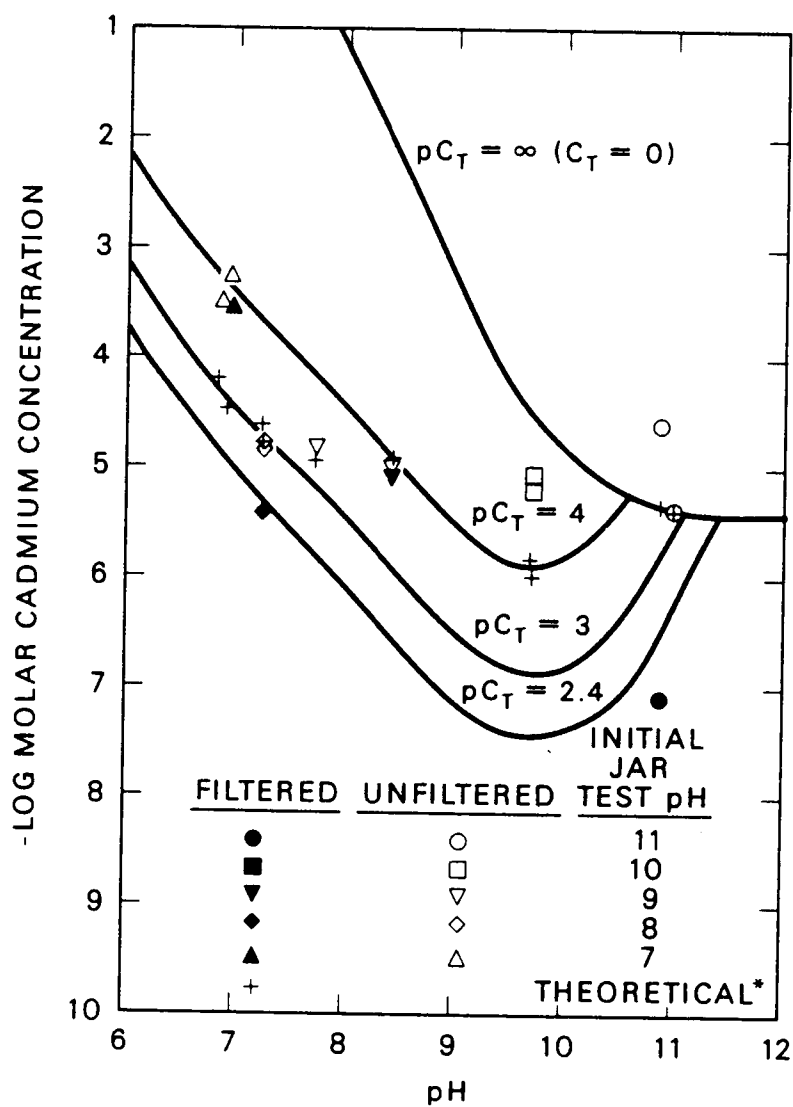


Figure 4.6. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Dilute Cadmium Jar Tests with Calcium Chloride Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

Table 4.10.

Results of Solids Analyses and Sludge Filtration Tests in Dilute
Cadmium Jar Tests with Sodium Chloride Additions.

Jar	Sludge				Specific		
Test	MLSS	Vol.	SVI	$W_s^{(1)}$	$W_c^{(2)}$	Resis.	CST
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	114	100.	877	0.00290	0.0771	13,400	7.2
11	174	70	400	0.00380	0.110	11,800	6.6
10	246	50.	200	0.00489	0.0824	10,800	7.6
10	96	50.	520	0.00518	0.0854	21,900	7.4
9	186	0.01	0.054				
9	110	0	0				
8	(3)	<7					
8	134	0	0				
7	(3)	<3					
7	116	0	0				

⁽¹⁾Mass of dry solids per unit mass of sludge.

⁽²⁾Mass of dry solids per unit mass of cake.

⁽³⁾Weighing errors. Weighing procedure modified in subsequent runs.

Table 4.11.

Results of Solids Analyses and Sludge Filtration Tests in Dilute
Cadmium Jar Tests with Calcium Chloride Additions.

Jar	Sludge			Specific			
Test	MLSS	Vol.	SVI	W _s	W _c	Resis.	CST
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	396	4.5	11.				14.9
11	432	0.70	1.6				
10	476	80.0	170.	0.00820	0.191	61,100	9.0
10	496	80.0	160.	0.00770	0.244	53,900	9.2
9	440	0.05	0.1				
9	624	0.30	0.48				
8	(1)	<9					
8	80	1.0	12.5				
7	(1)	<5					
7	48	0	0				

(1) Weighing errors made. Weighing procedure changed in subsequent runs.

Two types of settling behavior were evident. At higher pH values (>9), precipitates typically flocculated and settled out quickly. Sufficient sludge to run filtration tests was available under these conditions. Below pH 10, flocs broke up during mixing, or no flocculation occurred at all. Precipitates from these jar tests settled out as discrete particles with very little sludge volume.

Precipitate Mineral Characteristics (Table 4.12). Only those jar tests with enough sludge to be characterized are presented. All available precipitates were characterized by X-ray diffraction. TIC analyses were not obtained.

2. CADMIUM CYANIDE EXPERIMENTAL PHASE

The complete alkaline chlorination process was studied in the final experimental phase. The rate factors which control oxidation (pH and hypochlorite concentration), influence solubility behavior and sludge characteristics as well. Therefore, additional analyses were included in this phase to monitor the oxidation reaction, including spot test screening for cyanide, cyanate determinations and alkalinity measurements.

This subchapter is organized in the same manner as the non-cyanide subchapter before it. The one exception is that only dilute cadmium cyanide ($\text{Cd} = 100 \text{ mg/l}$) jar test results are included, as concentrated cadmium cyanide jar tests were not conducted.

Analysis of Experimental Technique

As in the previous subchapter, several problems with experimental methods or techniques were discovered which limited the amount of

Table 4.12.

Results of Analyses on Precipitates from Dilute Cadmium Jar Tests.

Jar	X-ray Diffraction Patterns					
Test	% ⁽¹⁾	%	%			
pH	Cadmium	Calcium	Sodium	1st	2nd	3rd
NaCl						
11				Otavite ⁽²⁾		
11	61.0	19.5 ⁽³⁾	0.06	Otavite		
10	58.5	0	0.06	Otavite		
10				Otavite		
CaCl ₂						
11	20.6	27.9	0.04	Calcite ⁽⁴⁾	Otavite	(5)
11	21.2	28.5	0.05	Calcite	Otavite	β -Cd(OH) ₂
10	21.8	26.2	0.10	Calcite	Otavite	
10	21.9	26.3	0.09	Calcite	Otavite	
9	23.9	23.9	0.03	Calcite	Otavite	
8	40.7	14.0	0.02	Calcite	Otavite	

⁽¹⁾Percent by weight in dried precipitate (typical).⁽²⁾Otavite is the crystalline form of cadmium carbonate.⁽³⁾Possible contamination of sample from preparing XRD samples.⁽⁴⁾Calcite is one crystalline form of calcium carbonate.⁽⁵⁾This secondary pattern could not be identified. Possibly a form of cadmium hydroxide.

information obtainable or, at worst, biased some of the results obtained. Results are presented in the next section with the following limitations:

1. Alkalinity samples were not adequately preserved against subsequent cyanate decomposition to carbonates. Alkalinity titrations were further complicated by the contribution of residual hypochlorite to alkalinity. The following equilibrium



produces one equivalent of alkalinity when titration is carried out to the methyl orange endpoint. Therefore, carbonate levels determined several days to several weeks later did not necessarily reflect alkalinity levels at the time of treatment.

2. pH measurements were obtained before, but not after, the two hour settling period. This complicated the comparison of experimental data with theoretical solubility curves. Solution pH levels declined as much as 1-3 units in jar test solutions with limited carbonate buffering capacity. As expected, calcium hypochlorite scavenged much more carbonate alkalinity (as calcium carbonate) from solution than did jar tests with sodium hypochlorite additions.
3. Nitrogen gas production from cyanate decomposition resulted in sludge flotation in those jar tests producing flocculate (as opposed to discrete particle settling). Sludge volume measurements were simply estimates when sludge flotation occurred.

4. Insufficient sludge was generated in most cases to run sludge filtration or CST tests. Therefore, sludge handling behavior could not be adequately quantified in the cadmium cyanide jar tests.

Presentation of Results

Supernatant and Filtrate Quality (Tables 4.13, 4.14, 4.15; Figures 4.7, 4.8)

Cyanide and cyanate results are reported in Table 4.13. The extent of reaction was monitored at ten minutes, one hour and six hours following hypochlorite addition. Cyanate levels were monitored in selective jar tests representing the range of pH conditions examined.

Filtered samples of supernatant were obtained for every jar test pH regardless of visible supernatant quality. TIC analysis was abandoned in favor of more accurate alkalinity measurements.

As in the first experimental phase, theoretical solubility curves were prepared illustrating equilibrium conditions over the range of pH and alkalinities tested. An important distinction between the non-cyanide and cadmium cyanide experimental phases was the manner and timing of introducing inorganic carbon into jar tests. In the non-cyanide experimental procedure, sodium carbonate or bicarbonate was added immediately before precipitation and mixing. In the cadmium cyanide experimental phase, the only source of inorganic carbon was through the oxidation of cyanate to end products.

Table 4.13.

Cyanide and Cyanate Results.

Jar Test	[Cyanide], mg/ℓ		[Cyanate], mg/ℓ	
	10 min	1 hr.	1 hr.	6 hrs.
Ca(OCl)₂				
11	1	0.01		
11	1	0.01	160.	149.
10	1	0.01	0	0
9	1	0.01		
8	1	0.01		
7	1	0.01		
7	1	0.01	0	0
NaOCl				
11	1	0.01		
11	1	0.01	164.	151.
10	1	0.01	20.3	18.1
9	1	0.01		
8	1	0.01		
8	1	0.01	0	0
7	1	0.01		
7	1	0.01	0	0
7	1	0.01	0	0

Table 4.14.

Results of Analyses on Supernatant in Cadmium Cyanide
Jar Tests Treated with Sodium Hypochlorite.

Jar Test		Solids	Cadmium	Calcium	Sodium	Carbonate
pH	Phase	mg/l	mg/l	mg/l	mg/l	mg/l
NaOCl		(1)	100.0	0	(1)	224
11	F	2200	0.046	0	765	305
	S	2200	3.58	0	787	296
11	F	2300	0.110	0	804	340
	S	2200	3.36	0	804	324
10	S	2150	3.04	0	809	264
10	F	2150	0.072	0	800	252
	S	2200	1.98	0	796	252
9	S	2200	26.7	0	787	229
9	F	2050	0.078	0	747	194
	S	2050	22.1	0	756	214
8	F	1950	0.284	0	742	190
	S	2100	13.4	0	751	202
8	F	2100	0.847	0	800	206
	S	2100	9.43	0	782	209
7	F	2350	11.5	0	902	145
	S	2600	23.8	0	889	135
7	F	2450	27.1	0	858	146
	S	2350	40.6	0	844	122
7	F	2500	6.30	0	880	146
	S	2550	28.8	0	880	160

⁽¹⁾Initial solids and sodium concentration of chlorox unknown.

Table 4.15.

Results of Analyses on Supernatant in Cadmium Cyanide
Jar Tests Treated with Calcium Hypochlorite.

Jar Test		Solids	Cadmium	Calcium	Sodium	Carbonate
pH	Phase	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ
Ca(OC1) ₂			100.	331		224.
11	F	1400	0.032	186	281	123.
	S	1450	13.3	211	280	169.
11	F	1250	0.038	195	282	134.
	S	1350	9.12	209	282	170.
10	S	1350	15.7	192	238	109.
10	F	1200	0.361	180	238	88.8
	S	1350	6.94	185	237	107.
9	S	1350	9.56	149	268	67.8
9	F	1400	0.668	155	269	59.4
	S	1350	15.7	167	268	96.6
8	S	1450	21.5	206	241	112.
8	F	1300	0.579	182	246	85.8
	S	1300	10.7	188	245	116.
7	F	1350	6.27	242	204	105.0
	S	1550	18.3	242	203	120.
7	F	1400	2.27	237	233	125.
	S	1500	16.5	235	233	144.

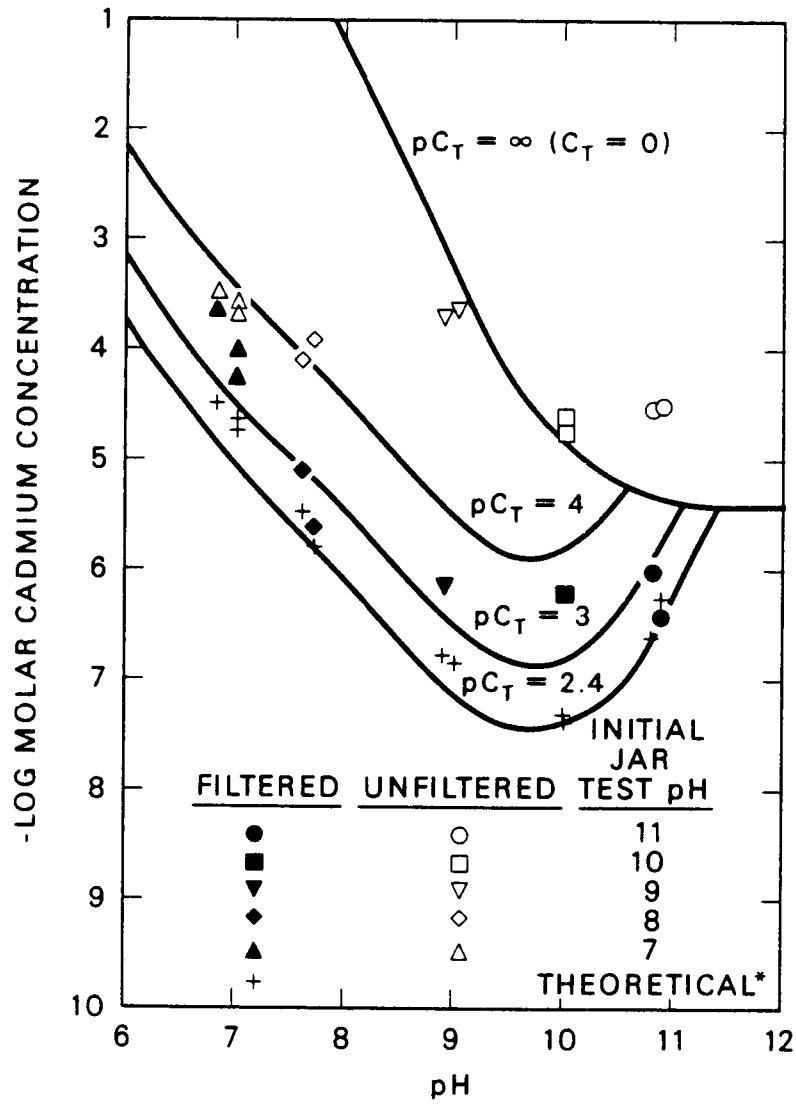


Figure 4.7. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Cadmium Cyanide Jar Tests with Sodium Hypochlorite Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

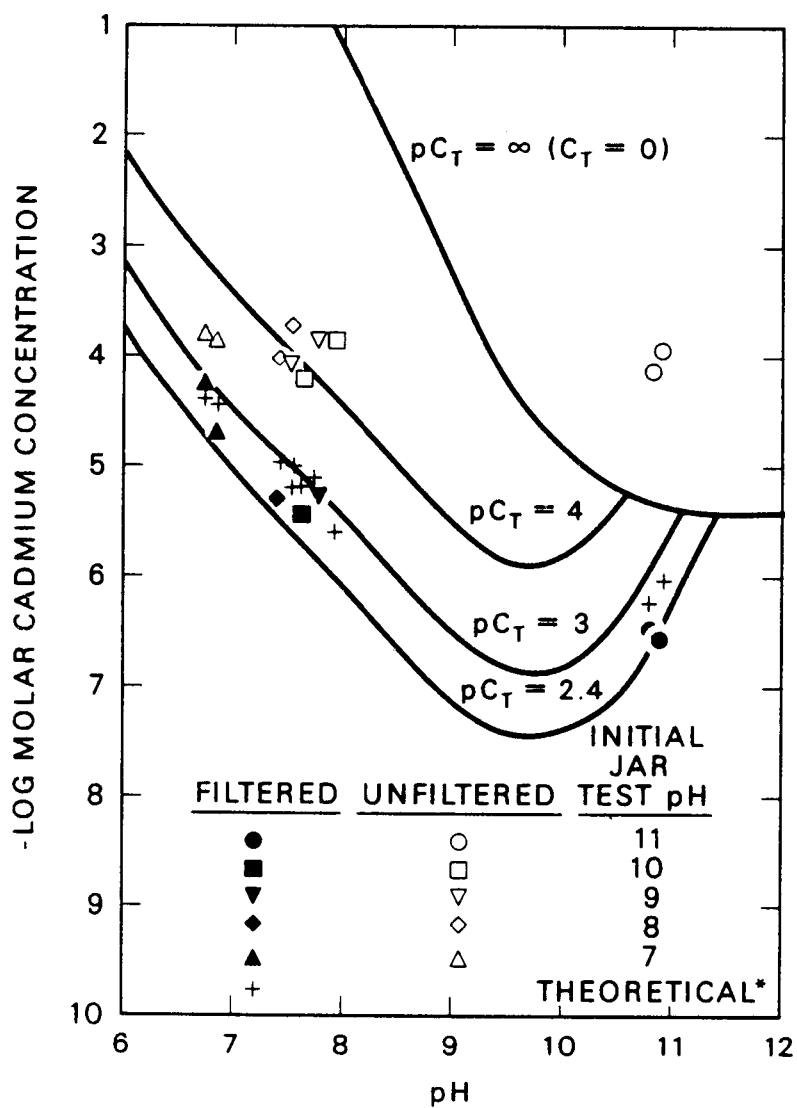


Figure 4.8. Comparison of Theoretical Solubility Values with Experimental Cadmium Data Obtained in Cadmium Cyanide Jar Tests with Calcium Hypochlorite Additions. (*Theoretical Cadmium Concentration Representing Individual Jar Test C_T and pH Values.)

Sludge Characteristics (Tables 4.16, 4.17, and 4.18)

As in dilute cadmium jar tests, two types of settling behavior were observed. Flocculates produced in pH 10 jar tests treated with sodium hypochlorite persisted throughout the mixing stage. No other jar tests produced sufficient sludge volumes for filtration tests. Most jar tests produced enough sludge for mineral characterization of precipitates.

Table 4.16.

Results of Solids Analyses And Sludge Filtration Tests in Cadmium Cyanide Jar Tests Treated with Sodium Hypochlorite.

Jar	Sludge			Specific ⁽³⁾			
Test	MLSS	Vol.	SVI	W _s ⁽¹⁾	W _c ⁽²⁾	Resis.	CST ⁽³⁾
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	50	0.8	16.0				
11	150	0.6	4.0				
10	200	55.0	275.0	0.0042	0.2	45,000	8.0
10	150	15.0	100.0	0.0085	0.49	39,000	9.1
9	50	0.2	4.0				
9	150	0.2	1.3				
8	100	0.2	0.2				
8	200	0.1	0.5				
7	0	<0.1					
7	100	<0.1	1.0				
7	200	0.4	2.0				

⁽¹⁾Mass of dry solids per unit mass of sludge.

⁽²⁾Mass of dry solids per unit mass of cake.

⁽³⁾Insufficient sludge volume generated for these tests except at pH 10.

Table 4.17.

Results of Solids Analyses And Sludge Filtration Tests in Cadmium Cyanide Jar Tests Treated with Calcium Hypochlorite.

Jar		Sludge		Specific ⁽¹⁾			
Test	MLSS	Vol.	SVI	W _s ⁽¹⁾	W _c ⁽¹⁾	Resis.	CST ⁽²⁾
pH	mg/l	ml/l	ml/gm	gm/gm	gm/gm	cm/gm	sec.
11	300	2.0	6.7				59.8
11	250	2.2	8.8				58.2
10	400	0.8	2.0				
10	250	1.0	4.0				43.4
9	350	1.2	3.4				35.5
9	450	1.0	2.4				57.5
8	150	0.6	4.0				
8	400	0.4	1.0				
7	0	0.6					
7	150	0.8	5.3				

⁽¹⁾Insufficient sludge volume for these tests.

⁽²⁾CST values were suspect with <3 ml of sample.

Table 4.18.
Results of Analyses on Precipitates from Cadmium Cyanide Jar Tests.

Jar	X-ray Diffraction Patterns					
Test	%	%	%			
pH	Cadmium	Calcium	Sodium	1st	2nd	3rd
NaOCl						
11	73.0	0	0.072	γ -Cd(OH) ₂	β -Cd(OH) ₂	Otavite
11	71.0	0	0.060	γ -Cd(OH) ₂	Otavite	β -Cd(OH) ₂
10	64.9	0.017	0.345	Otavite		
10	65.6	0.0054	0.135	(1)		
9	65.0	0	0.113	Otavite		
9	65.0	9.0	0.088	(1)		
8	62.4	0	0.086	(1)		
7	62.1	0	0.118	(1)		
Ca(OCl) ₂						
11	37.0	18.2	0.055	Calcite	β -Cd(OH) ₂	Otavite
11	37.2	17.3	0.050	Calcite	β -Cd(OH) ₂	Otavite
10	26.7	23.2	0.088	Calcite	Otavite	
10	26.9	23.0	0.062	Calcite	Otavite	
9	22.5	26.2	0.112	Calcite	Otavite	
9	22.2	25.7	0.073	Calcite	Otavite	
8	29.8	20.8	0.100	Calcite	Otavite	
8	27.5	22.6	0.093	Calcite	Otavite	
7	42.3	12.2	0.099	Calcite	Otavite	
7	42.2	12.8	0.090	Calcite	Otavite	

(1) Insufficient sludge volume to run test.

CHAPTER V

DISCUSSION AND SUMMARY

1. CONCENTRATED CADMIUM JAR TESTS

Supernatant Quality

A number of general observations are in order. First, cadmium solubility behavior in calcium chloride treated solutions was adequately explained by the cadmium carbonate solubility system in Figure 4.3, p. 49. In sodium chloride jar tests, (unfiltered) cadmium residuals obtained at high pH values were better represented by the cadmium hydroxide solubility system. As pH values decreased, experimental values conformed more to the cadmium carbonate solubility system (Figure 4.2, p. 48). This general behavior was also noted by Minear and Patterson in their work with cadmium cyanide plating wastes (16).

A trend toward improved cadmium removals at higher pH values was observed in the calcium chloride system. However, the best performance was obtained in the sodium chloride system at pH 11, where residual cadmium was an order of magnitude below most other results. Because of the loss of buffering capacity and pH control, no comparable value is available at pH 11 in the calcium chloride system.

Minear and Patterson found that cadmium cyanide wastes treated with calcium hypochlorite, typically provided better cadmium removals than those treated with sodium hypochlorite (16). This same distinction cannot be drawn from the results in Figures 4.2 and 4.3, pp. 48–49. Cadmium residuals in the calcium chloride system were typically an order of magnitude greater than

those obtained by Minear and Patterson, for the equivalent calcium hypochlorite treatment. This phenomena appears to be a result of differences in the final inorganic carbon levels between the two experiments.

Precipitate Mineral Characteristics

Cadmium solubility behavior indicates the presence of cadmium hydroxide precipitates at higher pH values. This is also supported by the cadmium and inorganic carbon levels measured in precipitates (Tables 4.6 and 4.7, pp. 54–55). The ratio of cadmium to TIC (expressed as carbonate) provides an indication of mineral stoichiometry. This ratio generally increased with pH, indicating that cadmium carbonate stoichiometry did not account for all cadmium present in precipitates at high pH values. Conversely, X-ray diffraction analysis of selected precipitates at high pH showed no evidence of cadmium hydroxide formation. Since X-ray diffraction work preceded metals and inorganic carbon analysis, it is inconceivable that changes in the mineral form could account for this phenomena. In addition, precipitates were dried and stored in a vacuum desiccator immediately following sludge filtration tests. Two possible explanations are that filtered residuals present an entirely different picture or, the cadmium hydroxide pattern is masked by other more predominant diffraction patterns.

X-ray diffraction work on precipitates in the CaCl_2 system was inconclusive in showing whether mixed crystal formation was occurring between cadmium and the calcite mineral structure. However, in work by Chang and Peters (4), lime treatment of very dilute hardness solutions

containing cadmium, calcium and inorganic carbon (added as bicarbonate) resulted in adsorption of cadmium on calcite crystal surfaces. Their hypothesis was supported by kinetic information on crystal development, residual calcium levels following precipitation, X-ray diffraction results and scanning electron microscope (SEM) pictures. SEM pictures of calcite crystals inhibited by cadmium impurities exhibited a layered growth structure, while calcite crystals in the absence of impurities exhibited smooth rhombohedral structures. X-ray diffraction work on the cadmium inhibited calcite crystals revealed only a calcite pattern. Similarly, in this author's work, the calcite mineral diffraction pattern was seen to the exclusion of all others in the calcium chloride system. Metals analysis of these precipitates reveal a calcium to cadmium ratio of 3:1 for low and high pH solutions, and 5:1 for those solutions in the range of minimum cadmium solubility. A 3:1 ratio of calcium to cadmium carbonate is predicted by the stoichiometry of equation 2-7.

Calcite is the thermodynamically stable crystalline form of calcium carbonate, while aragonite is the kinetically favored metastable form. According to Chang and Peters, cadmium impurities inhibited the formation of aragonite, allowing the thermodynamically stable calcite to prevail. However, they concluded from SEM pictures and solubility data that calcite contamination was limited to surface adsorption and did not lead to mixed crystal formation (4).

Sludge Settling and Filterability Characteristics

Distinctly different sludge physical behavior was obtained depending upon the type of treatment and pH condition examined. At high pH's a gelatinous

sludge was typically seen in both systems, while at lower pH's a dense, grainy sludge was generally the case. The largest sludge volume (by an order of magnitude) was obtained for the sodium chloride system at pH 11. The SVI for this test was 121 mL/gm, indicating an extremely voluminous precipitate. Below pH 11, the sodium chloride system generally produced less sludge than the calcium chloride system. Roughly twice as much sludge was generated in the calcium chloride system due to calcium carbonate precipitation.

Sludges obtained in the calcium chloride system exhibited the best filtration characteristics over the pH region studied. Specific resistance and CST values are compared for both systems in Figure 4.4, p. 53. Specific resistance values for the calcium chloride system were typically an order of magnitude lower than those for the sodium chloride system. Moreover, pH had little effect on CST and specific resistance values for calcite sludges as evidenced by the "clustering" of points in one region for all pH conditions. The pH 10 jar test was the exception, exhibiting an increase in both specific resistance and CST values. However, a duplicate run at the same pH produced values typical of other jar tests. Sludges in the sodium chloride system exhibited a range of specific resistance and CST values somewhat dependent upon pH. This phenomenon could be the result of changing mineral composition or particle size over the pH region studied.

A projection from these results is that sludges from calcium hypochlorite treatment are more easily filtered than those produced by sodium hypochlorite treatment. However, the larger volume of sludge solids from the calcium hypochlorite system will increase disposal costs.

2. DILUTE CADMIUM JAR TESTS

Supernatant Quality

Cadmium solubility behavior was more accurately represented by filtered sample results in dilute cadmium jar tests. Filtered cadmium residuals in sodium chloride treated solutions conformed more closely to the cadmium carbonate solubility system. This is also supported by X-ray diffraction results which show cadmium carbonate exclusively for all pH conditions. Improved cadmium removals point out the need for filtration in full scale treatment.

There appears to be some advantage in filtered cadmium removals in the pH region 8-10 for the sodium chloride system. However, insufficient filtered data are available to establish a trend. Final TIC levels for the calcium chloride system were generally between 10^{-3} to 10^{-4} M, as found in concentrated cadmium jar tests. Final TIC levels in the sodium chloride system were not significantly reduced from their initial level at $10^{-2.4}$ M. Filtered cadmium levels show a trend towards improved removals in the region of minimum cadmium solubility (pH 9-10). The filtered data point at pH 11 in the calcium chloride system appears to be an aberration from the theoretical cadmium value.

Precipitate Mineral Characteristics

Both calcite (calcium carbonate) and otavite (cadmium carbonate) were identified in precipitates from calcium chloride jar tests for all pH conditions examined. This is in contrast with results in concentrated cadmium jar tests which identified only calcite. However, samples from concentrated cadmium

jar tests were prepared with a greater degree of compaction than samples from dilute cadmium jar tests. A higher level of compaction exposes more crystals to X rays, resulting in stronger diffraction patterns. Since calcite and otavite patterns are very similar, otavite may have been masked by the presence of the more abundant calcite. The ratio of calcium to cadmium in the precipitate ranged from 3.8 at pH 11 to 1.0 at pH 8 indicating the possibility of a pH related surface adsorption.

In the calcium chloride system at pH 11, precipitates consisted of a mixture of cadmium hydroxide, cadmium carbonate and calcium carbonate. A cadmium hydroxide solid phase is predicted by cadmium solubility data at this pH.

Sludge Settling and Filterability Characteristics

Two distinctly different types of setting behavior were observed in jar tests as a function of pH. Generally, at high pH's (≥ 10) solids coagulated to generate significant sludge volume and clear supernatants. Low pH conditions produced dense, grainy precipitates with very little settled volume. A cloudy suspension remained following precipitation. Sludges in the sodium chloride system were more voluminous than in the calcium chloride system as indicated by the SVI.

Filtration tests showed sludges in the sodium chloride system to be more filterable than those in the calcium chloride system. Too little data are available to establish a relationship between CST and specific resistance. However, lower specific resistance values are obtained in the sodium chloride system (Tables 4.10 and 4.11, pp. 61–62). This behavior is exactly opposite of

filtration results in the concentrated cadmium tests. Insufficient sludge was available at low pH values to test the filtration characteristics of dense, grainy precipitates.

3. CADMIUM CYANIDE JAR TESTS

Supernatant Quality

Filtered cadmium residuals generally conformed to the cadmium carbonate solubility system for both forms of hypochlorite treatment. Calcium hypochlorite additions resulted in substantial reductions in carbonate alkalinity (buffering capacity), especially in the pH region of minimum cadmium solubility. As a result, pH values declined 1–2 units in pH 9 and 10 jar tests. Residual cadmium levels increased in this lower pH region, as predicted by the cadmium carbonate solubility system. Without some form of buffering capacity, calcium hypochlorite treatment has significant disadvantages over sodium hypochlorite in the lack of pH control and higher residual cadmium levels.

Final inorganic carbon levels following calcium hypochlorite treatments were an order of magnitude higher than in equivalent (calcium chloride) jar tests in the non-cyanide experimental phase. This was determined to be the result of larger calcium additions (reflected in the calcium to cadmium ratio in Tables 3.1 and 3.2, pp. 31, 35) in non-cyanide work. At 10^{-2} to 10^{-3} M, final inorganic carbon levels were more in line with results obtained by Minear and Patterson (16).

The extent of reaction was monitored by sampling for cyanide and cyanogen chloride (spot test screening), and cyanates at various stages during each jar test (Table 4.13, p. 67). Spot test screening indicated that destruction of the cadmium cyanide complex and hydrolysis of cyanogen chloride was complete within ten minutes of alkaline chlorination. In all but the pH 10 and 11 jar tests, cyanate levels were undetected in mixed liquors following one hour of mixing. Cyanate oxidation was inhibited by excess hydroxide in high pH solutions. Six hours following treatment, cyanate oxidation was still less than 5% complete in pH 11 jar tests.

Cyanate oxidation produces an equivalent amount of inorganic carbon as an end product (equation 2-4). Consequently, in high pH jar tests, precipitation was carbonate limited in the early stages. The absence of carbonate alkalinity inhibited otavite (cadmium carbonate) growth, causing cadmium hydroxide to prevail. This hypothesis is supported by cyanate levels, solubility behavior and X-ray diffraction results.

Precipitate Mineral Characteristics

X-ray diffraction work identified cadmium hydroxide as the predominant cadmium mineral form in pH 11 jar tests (Table 4.18, p. 75). Two forms of cadmium hydroxide were found. $\gamma\text{-Cd(OH)}_2(\text{s})$ is one of two metastable forms of cadmium hydroxide (8). It appears to be the kinetically favored form obtained in sodium hypochlorite treatment. $\gamma\text{-Cd(OH)}_2(\text{s})$ ultimately converts to $\beta\text{-Cd(OH)}_2(\text{s})$ the thermodynamically stable form. The stable solid phase is found in both sodium and calcium hypochlorite systems at pH 11.

Precipitates from calcium hypochlorite jar tests contained mixtures of calcite and otavite. The ratio of calcium to cadmium in precipitates again reveals a sensitivity to pH conditions. This ratio decreases from a high of 3.3 at pH 9, to 0.8 at pH 7, and 1.4 at pH 11. A reduction of calcium in precipitates at high pH is possibly explained by the relative stoichiometric requirements of the carbonate limited reaction (equation 2-9), and overall reaction (equation 2-7). The low pH behavior may be a surface adsorption phenomenon. Chang and Peters found that adsorption of cadmium onto calcite surface increased calcium solubility as a function of pH. The largest increases in calcium solubility were obtained at low pH values (4).

Sludge Settling and Filterability Characteristics

Dense, grainy precipitates were obtained for all but one jar test pH condition (Tables 4.16 and 4.17, pp.73–74). The exception was at pH 10 in the sodium hypochlorite system which produced the voluminous sludges typical of high pH jar tests. In all other cases, sludge volumes were typically less than 2 mL/L.

Filtration tests were conducted on the pH 10 sludge. The specific resistance values obtained were somewhat higher than values reported in the equivalent (sodium chloride) system of the previous subchapter.

CST tests were conducted where sufficient precipitate was available. Relatively high CST values were obtained, indicating larger specific resistance values may be expected. However, insufficient data is available to adequately explain sludge dewatering behavior.

CHAPTER VI

CONCLUSIONS

Results of this study indicated the following trends in sludge characteristics and cadmium solubility behavior for the treatments and pH conditions examined:

1. At high initial cadmium levels, sludges produced in calcium chloride (simulated calcium hypochlorite) treated solutions exhibited significantly better dewatering characteristics than in the corresponding sodium chloride system.
2. Sludge dewatering characteristics in the calcium chloride system were not affected by initial jar test pH conditions. A pH related trend was seen in the correlation of specific resistance and CST values for sludges in the sodium chloride system. Optimum filtration characteristics were obtained at pH 7 and 10.
3. Sludge volume in the calcium chloride system was much greater due to calcite precipitation.
4. In dilute cadmium work, two distinctly different types of sludge settling behavior were found as a function of pH. Minimum sludge volume was obtained at low pH's where dense, grainy sludges were evident. Insufficient sludge volumes were available to establish filterability characteristics. At high pH's, precipitates coagulated to form gelatinous sludges with high specific resistances.

5. The need for filtration in full scale treatment to reduce cadmium residuals to discharge limits was evident.
6. In the cadmium cyanide experimental phase, pH control was necessary in calcium hypochlorite treatments to maintain pH in the region of minimum cadmium solubility. Use of sodium carbonate in initial pH adjustments would aid in stabilizing pH.
7. Data seemed to indicate adsorption of cadmium onto calcite surfaces. However, mixed crystal formation was not in evidence according to solubility behavior and X-ray diffraction results.

Projections of this work indicate optimum treatment at pH 9 may be advantageous in full scale operations. Below this pH, cadmium solubilities rapidly increase. Above pH 9, the gelatinous form of precipitate appears to be kinetically favored. Calcium hypochlorite treatment may yield sludges with better filterability characteristics for concentrated cadmium plating baths. However, problems with pH control and additional sludge volume must be addressed.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Adamson, A. W., *Physical Chemistry of Surfaces*. 3rd Ed., Wiley, New York, NY (1976).
2. Anonymous, "New Process Detoxifies Cyanide Wastes," *Envr. Sci. Technology*, 5, 496 (1971).
3. Butler, J. N., *Ionic Equilibrium a Mathematical Approach*, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1964).
4. Chang, T., and R. W. Peters, "Removal of Cadmium from Contaminated Groundwaters through Coprecipitation and Adsorption in Lime Softening Operations," Presented at the 17th Mid-Atlantic Industrial Waste Conference, Bethlehem, PA, June 25, 1985.
5. Doerner, H. A., and W. M. Hoskins, "Co-Precipitation of Radium and Barium Sulfates," *Jour. Amer. Chem. Soc.*, 47, 662 (1925).
6. Eden, G. E., and A. B. Wheatland, "Effect of Temperature and Presence of Hypochlorite on the Rate of Hydrolysis of Cyanogen Chloride in Alkaline Solution," *J. Soc. Chem. Ind.*, 69, 166, June, 1950.
7. Eden, G. E., B. I. Hampson, and A. B. Wheatland, "Destruction of Cyanide in Waste Waters by Chlorination," *J. Soc. Chem. Ind.*, 69, 244, August, 1950.
8. Feitknecht, W., and P. Schindler, "Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution," *Pure and Applied Chemistry*, 6, 130 (1963).
9. Gordon, L., M. L. Salutsky, and H. H. Willard, *Precipitation from Homogeneous Solution*. John Wiley and Sons, Inc., New York, NY (1959).
10. Gurnham, *Industrial Wastewater Control*.
11. *Handbook of Chemistry and Physics*. 30th ed., Chemical Rubber Publishing Co., Cleveland, OH (1947).
12. Hahn, O., *Applied Radiochemistry*. Cornell University Press, Ithaca, NY, (1936).

13. Kolthoff, I. M., *Quantitative Chemical Analysis*. The Macmillan Co., London (1969).
14. Lister, M. W., "The Reaction Between Cyanate and Hypochlorite," *Can. Journal Chem.*, 34, 489 (1956).
15. Marin, S., R. B. Tratner, P. N. Cheremisinoff, and A. J. Perna, "Methods for Neutralizing Toxic Electroplating Rinsewater—Part 1," *Manufacturing*, May/June, 50 (1979).
16. Minear, R. A., and J. W. Patterson, "Carbonate Precipitation Treatment for Cadmium," Presented at the 8th WWEMA Industrial Pollution Conference, Houston, TX, June 5, 1980.
17. Notebaert, F. F., D. A. Wilms, and A. A. van Haute, "A New Deduction with a Larger Application of the Specific Resistance to Filtration of Sludges," *Water Research*, 9, 667 (1975).
18. Patterson, J. W., *Wastewater Treatment Technology*. Ann Arbor Science, Ann Arbor, Mich. (1975).
19. Patterson, J. W., H. E. Allen, and J. J. Scala, "Carbonate Precipitation for Heavy Metals Pollutants," *J. Wat. Poll. Cont. Fed.*, 49, 2397 (1977).
20. Rankama, K., and T. G. Sahama, *Geochemistry*. University of Chicago Press, Chicago, IL (1950).
21. Sawyer, C. N., and P. L. McCarty, *Chemistry for Environmental Engineering*. 3rd Ed., McGraw-Hill Book Company, New York, NY (1978).
22. Scala, J. J., *Carbonate Precipitation of Heavy Metals*. MS Thesis, Environmental Engr. Dept., Illinois Institute of Technology (1975).
23. Snoeyink, V. L., and D. Jenkins, *Water Chemistry*. John Wiley and Sons, New York, NY (1980).
24. *Standard Methods for the Examination of Water and Wastewater*. 15th Ed., Amer. Pub. Health Assn., Washington, D.C. (1980).
25. U.S. Environmental Protection Agency, "Control and Treatment Technology for the Metal Finishing Industry," EPA-625/8-82-008, Cincinnati, OH (January, 1982).

26. U.S. Environmental Protection Agency, "Effluent Guidelines and Standards; Electroplating Point Source Category Pretreatment Standards for Existing Sources, " Federal Register 46, 18 (Jan., 1981).
27. Weber, W. J., *Physicochemical Processes for Water Quality Control*. Wiley-Interscience, New York, NY (1972).

APPENDIXES

APPENDIX A

BASIC PROGRAM

```

10      PROGRAM CALCULATES THEORETICAL CADMIUM
          AND CALCIUM SOLUBILITY
20
30 DEF FNLG(X) = LOG(X)/LOG(10)
40 DIM C(6)
50 DIM Z(6)
60 KW = 10^(-14)
70 K1 = 10^(-6.3)
80 K2 = 10^(-10.3)
90 KSP = 10^(-11.2)
100 KSO = 10^(-13.7)
110 KS1 = 10^(-9.5)
120 KS2 = 10^(-5.4)
130 KS3 = 10^(-4.7)
140 KS4 = 10^(-5)
150 KC1 = 10^(1.32)
160 KC2 = 10^(.9)
170 KC3 = 10^(9.000001E-02)
180 KC4 = 10^(-.45)
190 KSL = 10^(-8.3)
200 KSL1 = 10^(-5.1)
210 KSL2 = 10^(+3.26)
220 KL = 10^(-1.49)
230 PRINT
240 PRINT TAB(2)"TEST PH" TAB(12)"EXP CARB" TAB(22)
          "THEOR CD" TAB(32)"EXP CD" TAB(42)"MIN CD"
          TAB(52)"THEOR CA" TAB(62)"EXP CA" TAB(72)"CDOH2"
250 PRINT
260 LPRINT
270 LPRINT TAB(2)"TEST PH" TAB(12)"EXP CARB" TAB(22)
          "THEO CD" TAB(32)"EXP CD" TAB(42)"MIN CD" TAB(52)
          "THEOR CA" TAB(62)"EXP CA" TAB(72)"CDOH2"
280 LPRINT
290 OPEN "B:CONC.PRN" FOR INPUT AS #1
300 OPEN "B:SOLUB.PRN" FOR OUTPUT AS #2
310 FOR I = 1 TO 50
320 IF EOF(1) THEN CLOSE #1: GOTO 540
330 INPUT #1, ID#,PH,C(1),Z(1),C(2),Z(2),C(3),Z(3),
          C(4),Z(4),C(5),Z(5),C(6),Z(6)
340 H = 10^(-PH)
350 GOSUB 1490
360 IF PH > 6.3 AND PH < 10.3 THEN GOSUB 1780
370 IF PH > 10.3 THEN GOSUB 1880
380 GOSUB 750
390 IF PH > 6.3 AND PH < 10.3 THEN GOSUB 560
400 IF PH > 10.3 THEN GOSUB 660

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410 GOSUB 1090
420 TOT = 10^L + 10^LOH + 10^LOH2 + 10^LOH3 + 10^LOH4
      + 10^LCL + 10^LCL2 + 10^LCL3 + 10^LCL4
425 CDTOT = 10^LCD + 10^LCDOH + 10^LCDOH2 + 10^LCDOH3
      + 10^LCDOH4 + 10^LCL + 10^LCL2 + 10^LCL3
      + 10^LCL4
430 DEF FNROUND(X) = INT(X*100 + .5)/100 'ROUNDS TO
      TWO DECIMAL PLACES
440 GOSUB 1170
450 GOSUB 1390
460 PRINT ID$, "IONIC STRENGTH = ";FNROUND(I)
470 PRINT USING " ##.##      ";PH,FNLG(C(1)),FNLG(TOT),
      FNLG(C(2)),FNLG(MINCAD),FNLG(CATOT),FNLG(C(3)),
      FNLG(CDTOT)
480 PRINT
490 LPRINT ID$, "IONIC STRENGTH = ";FNROUND(I)
500 LPRINT USING " ##.##      ";PH,FNLG(C(1)),FNLG(TOT),
      FNLG(C(2)),FNLG(MINCAD),FNLG(CATOT),FNLG(C(3)),
      FNLG(CDTOT)
510 LPRINT
520 WRITE #2, ID$,PH,FNROUND(FNLG(C(1))),
      FNROUND(FNLG(TOT)),FNROUND(FNLG(C(2))),
      FNROUND(FNLG(CATOT)),FNROUND(FNLG(C(3)))
530 NEXT I
540 END
550 '
560 '      SUBROUTINE CALCULATES CADMIUM SOLUBILITY
      FOR PK1<PH<PK2
570 '
580 HCO3 = C(1) * H * CK1 / (CK1*CK2 + H*CK1 + H^2)
590 L = LK4 - FNLG(HCO3) - PH
600 LOH = LK7 - FNLG(HCO3)
610 LOH2 = LK10 - FNLG(HCO3) + PH
620 LOH3 = LK13 - FNLG(HCO3) + 2*PH
630 LOH4 = LK16 - FNLG(HCO3) + 3*PH
640 RETURN
650 '
660 '      SUBROUTINE CALCULATES CADMIUM SOLUBILITY
      FOR PH>PK2
670 '
680 CO3 = C(1) * CK1 * CK2 / (CK1*CK2 + H*CK1 + H^2)
690 L = LK5 - FNLG(CO3)
700 LOH = LK8 - FNLG(CO3) + PH
710 LOH2 = LK11 - FNLG(CO3) + 2*PH
720 LOH3 = LK14 - FNLG(CO3) + 3*PH
730 LOH4 = LK17 - FNLG(CO3) + 4*PH

```

```

740 RETURN
750 '
760 '     SUBROUTINE CALCULATES SOLUBILITY PRODUCT
          CONSTANTS FOR CDC03
770 '
780 LK3 = FNLG(CKSP) - (FNLG(CK2) + FNLG(CK1))
790 PRINT "LOG K3 = ";LK3
800 LK4 = FNLG(CK1) + LK3
810 PRINT "LOG K4 = ";LK4
820 LK5 = FNLG(CK1) + FNLG(CK2) + LK3
830 PRINT "LOG K5 = ";LK5
840 LK6 = FNLG(CKW) + FNLG(CKS1) + LK3 - FNLG(CKS0)
850 PRINT "LOG K6 = ";LK6
860 LK7 = FNLG(CKW) + FNLG(CKS1) + LK4 - FNLG(CKS0)
870 PRINT "LOG K7 = ";LK7
880 LK8 = FNLG(CKW) + FNLG(CKS1) + LK5 - FNLG(CKS0)
890 PRINT "LOG K8 = ";LK8
900 LK9 = 2*FNLG(CKW) + FNLG(CKS2) + LK3 - FNLG(CKS0)
910 PRINT "LOG K9 = ";LK9
920 LK10 = 2*FNLG(CKW) + FNLG(CKS2) + LK4 - FNLG(CKS0)
930 PRINT "LOG K10 = ";LK10
940 LK11 = 2*FNLG(CKW) + FNLG(CKS2) + LK5 - FNLG(CKS0)
950 PRINT "LOG K11 = ";LK11
960 LK12 = 3*FNLG(CKW) + FNLG(CKS3) + LK3 - FNLG(CKS0)
970 PRINT "LOG K12 = ";LK12
980 LK13 = 3*FNLG(CKW) + FNLG(CKS3) + LK4 - FNLG(CKS0)
990 PRINT "LOG K13 = ";LK13
1000 LK14 = 3*FNLG(CKW) + FNLG(CKS3) + LK5 - FNLG(CKS0)
1010 PRINT "LOG K14 = ";LK14
1020 LK15 = 4*FNLG(CKW) + FNLG(CKS4) + LK3 - FNLG(CKS0)
1030 PRINT "LOG K15 = ";LK15
1040 LK16 = 4*FNLG(CKW) + FNLG(CKS4) + LK4 - FNLG(CKS0)
1050 PRINT "LOG K16 = ";LK16
1060 LK17 = 4*FNLG(CKW) + FNLG(CKS4) + LK5 - FNLG(CKS0)
1070 PRINT "LOG K17 = ";LK17
1080 RETURN
1090 '
1100 '     SUBROUTINE CALCULATES COMPLEXATION
          EFFECTS OF CL ON CAD SOLUBILITY
1110 '
1120 LCL = L + FNLG(C(5)) + FNLG(CKC1)
1130 LCL2 = LCL + FNLG(C(5)) + FNLG(CKC2)
1140 LCL3 = LCL2 + FNLG(C(5)) + FNLG(CKC3)
1150 LCL4 = LCL3 + FNLG(C(5)) + FNLG(CKC4)
1160 RETURN
1170 '
1180 '     SUBROUTINE CALCULATES MINIMUM CADMIUM
          SOLUBILITY AND PH
1190 '

```

```

1200 MINCAD = 1000
1210 FOR MPH = 7 TO 10.2 STEP .1
1220 MH = 10^(-MPH)
1230 MHC03 = C(1) * MH * CK1/(CK1*CK2 + MH*CK1 + MH^2)
1240 MLHC03 = FNLG(MHC03)
1250 ML = LK4 - MLHC03 - MPH
1260 MLOH = LK7 - MLHC03
1270 MLOH2 = LK10 - MLHC03 + MPH
1280 MLOH3 = LK13 - MLHC03 + 2*MPH
1290 MLOH4 = LK16 - MLHC03 + 3*MPH
1300 MLCL = ML + FNLG(C(5)) + FNLG(CKC1)
1310 MLCL2 = MLCL + FNLG(C(5)) + FNLG(CKC2)
1320 MLCL3 = MLCL2 + FNLG(C(5)) + FNLG(CKC3)
1330 MLCL4 = MLCL3 + FNLG(C(5)) + FNLG(CKC4)
1340 MTOT(MPH) = 10^ML + 10^MLOH + 10^MLOH2 + 10^MLOH3
               + 10^MLOH4 + 10^MLCL + 10^MLCL2
               + 10^MLCL3 + 10^MLCL4
1350 IF MTOT(MPH) < MINCAD THEN MINCAD = MTOT(MPH)
1360 IF MTOT(MPH) = MINCAD THEN PHMIN = MPH
1370 NEXT MPH
1380 RETURN
1390 '
1400 '   SUBROUTINE CALCULATES CD(OH)2 SOLUBILITY
1410 '
1420 LCD = FNLG(CKS0) - 2*PH
1430 LCDOH = FNLG(CKS1) - PH + 14
1440 LCDOH2 = FNLG(CKS2)
1450 LCDOH3 = FNLG(CKS3) + PH - 14
1460 LCDOH4 = FNLG(CKS4) + 2*PH - 28
1480 RETURN
1490 '
1500 '   SUBROUTINE CALCULATES ACTIVITY COEFFICIENTS AND
               MODIFIED SOLUB CONSTANTS
1510 '
1520 I = 0
1530 FOR N = 1 TO 6
1540 I = I + .5 * (C(N) * Z(N)^2)
1550 NEXT N
1560 A1 = 10^(-.509 * (I^.5 / (1 + I^.5) - .2 * I))
1570 A2 = 10^(-.509 * 4 * (I^.5 / (1 + I^.5) - .2 * I))
1580 A0 = 10^(.1 * I)
1590 CKC1 = KC1 * A2
1600 CKC2 = (KC2 / A0) * A1^2
1610 CKC3 = KC3 * A0
1620 CKC4 = (KC4 / A2) * A1^2
1630 CKSP = KSP / A2^2
1640 CKS0 = KS0 / A2
1650 CKS1 = KS1 / A1
1660 CKS2 = KS2 / A0

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1670 CKS3 = KS3 / A1
1680 CKS4 = KS4 / A1
1690 CK1 = K1 * A0 / A1
1700 CK2 = K2 * A1 / A2
1710 CKW = KW
1720 CKSL = KSL / A2^2
1730 CKSL1 = KSL1 / A0
1740 CKSL2 = KSL2 / A1
1750 CKL = KL * A1 / A2
1760 CKP = CKSL / CK2
1770 RETURN
1780 '
1790 '   SUBROUTINE CALCULATES DISTRIBUTION OF
        SOLUBLE CALCIUM SPECIES FOR PK1<PH<PK2
1800 '
1810 HCO3 = C(1) * CK1 * H / (CK1*CK2 + H*CK1 + H^2)
1820 LCA = FNLG(CKP) - FNLG(HCO3) - PH
1830 LCACO3 = FNLG(CKSL1)
1840 LCAHCO3 = FNLG(CKSL2) - PH
1850 LCAOH = LCA - FNLG(CKL) + PH - 14
1860 CATOT = 10^LCA + 10^LCACO3 + 10^LCAHCO3 + 10^LCAOH
1870 RETURN
1880 '
1890 '   SUBROUTINE CALCULATES DISTRIBUTION OF
        SOLUBLE CALCIUM SPECIES FOR PH > 10.3
1900 '
1910 CO3 = C(1) * CK1 * CK2 / (CK1*CK2 + H*CK1 + H^2)
1920 LCA = FNLG(CKSL) - FNLG(CO3)
1930 LCACO3 = FNLG(CKSL1)
1940 LCAHCO3 = FNLG(CKSL2) - PH
1950 LCAOH = LCA - FNLG(CKL) + PH - 14
1960 CATOT = 10^LCA + 10^LCACO3 + 10^LCAHCO3 + 10^LCAOH
1970 RETURN

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APPENDIX B

RESULTS OF THEORETICAL CADMIUM CARBONATE SOLUBILITY CALCULATIONS FOR INDIVIDUAL JAR TEST CONDITIONS

Table B.1.
Results of Theoretical Cadmium Carbonate Solubility
Calculations for Individual Jar Test Conditions.

Jar			Experimental (-Log M)			Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
NaCl						
11	S	1.0	11.0	0.97	5.12	7.17
11	S	0.99	11.1	0.97	5.35	7.03
10	S	0.91	10.0	1.14	3.82	7.29
10	S	0.89	9.9	0.97	3.57	7.42
10	S	0.94	10.1	1.06	3.80	7.40
9	S	0.77	9.1	1.15	3.56	6.70
9	S	0.78	8.9	1.08	3.65	6.61
8	S	0.76	8.3	1.22	3.64	5.90
8	S	0.77	8.1	1.09	4.57	5.84
7	S	0.71	6.7	1.26	4.10	4.18
7	S	0.76	7.3	1.15	4.21	4.96

Table B.1 (continued)

Jar			Experimental (-Log M)			Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
CaCl ₂						
11	S	0.91	9.7	3.60	3.94	4.69
11	S	0.81	9.3	3.63	3.88	4.39
10	S	0.84	9.4	3.48	3.94	4.62
10	S	0.84	9.1	3.72	3.55	4.15
9	S	0.91	8.6	3.57	3.03	3.84
9	S	0.85	8.7	3.72	3.29	3.79
8	S	0.95	7.6	3.29	2.89	3.14
8	S	0.93	7.6	3.52	2.91	2.90
7	S	0.96	6.9	3.08	3.00	2.65
7	S	0.96	6.9	3.00	2.99	2.69

Table B.1 (continued)

Jar	Experimental (-Log M)					Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
NaCl						
11	S	0.04	11.0	2.33	5.46	6.17
11	S	0.03	11.0	2.49	5.46	6.02
10	S	0.03	9.9	2.47	5.05	7.34
10	S	0.03	10.0	2.49	4.93	7.29
9	S	0.03	9.2	2.53	4.82	7.02
9	F	0.02	9.1	2.57	6.21	6.91
	S	0.03	9.1	2.52	4.07	6.95
8	F	0.02	8.0	2.59	5.90	5.86
	S	0.02	8.0	2.59	3.91	5.86
8	S	0.02	8.0	2.58	4.08	5.87
7	F	0.02	6.8	2.74	4.01	4.42
	S	0.03	6.8	2.71	3.34	4.45
7	S	0.03	6.8	2.70	3.33	4.46

Table B.1 (continued)

Jar	Experimental (-Log M)					Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
CaCl ₂						
11	S	0.03	11.0	4.23	5.36	4.29
11	F	0.03	10.9	4.20	4.61	4.39
	S	0.03	10.9	4.30	7.05	4.50
10	S	0.03	9.7	3.77	5.19	6.02
10	S	0.03	9.7	3.96	5.04	5.83
9	S	0.03	7.7	3.17	4.83	4.95
9	F	0.03	8.4	3.83	5.08	4.99
	S	0.03	8.4	3.81	5.00	5.01
8	F	0.03	7.2	2.97	5.43	4.62
	S	0.03	7.2	2.96	4.77	4.63
8	S	0.03	7.2	2.78	4.86	4.80
7	F	0.04	6.9	2.82	3.54	4.41
	S	0.04	6.9	2.62	3.25	4.61
7	S	0.03	6.8	2.92	3.48	4.20

Table B.1 (continued)

Jar			Experimental (-Log M)			Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
NaOCl						
11	F	0.04	10.9	2.29	6.39	6.37
	S	0.04	10.9	2.31	4.50	6.36
11	F	0.04	10.8	2.24	6.01	6.59
	S	0.04	10.8	2.27	4.52	6.56
10	S	0.03	10.0	2.36	4.57	7.40
10	F	0.03	10.0	2.38	6.19	7.38
	S	0.03	10.0	2.38	4.75	7.39
9	S	0.03	9.0	2.42	3.62	6.94
9	F	0.03	8.9	2.49	6.16	6.79
	S	0.03	8.9	2.45	3.71	6.83
8	F	0.03	7.7	2.50	5.60	5.62
	S	0.03	7.7	2.47	3.92	5.64
8	F	0.03	7.6	2.46	5.12	5.55
	S	0.03	7.6	2.46	4.08	5.55
7	F	0.03	7.0	2.62	3.99	4.74
	S	0.03	7.0	2.65	3.67	4.71
7	F	0.03	6.8	2.61	3.62	4.51
	S	0.03	6.8	2.69	3.44	4.43
7	F	0.03	6.9	2.61	4.25	4.63
	F	0.03	6.9	2.58	3.59	4.67

Table B.1 (continued)

Jar	Experimental (-Log M)					Theoretical
Test		Ionic				Cadmium
pH ⁽¹⁾	Phase ⁽²⁾	Strength	pH	Carbonate ⁽³⁾	Cadmium	(-Log M)
Ca(OC1) ₂						
11	F	0.03	10.9	2.69	6.55	6.00
	S	0.03	10.9	2.55	3.93	6.13
11	F	0.03	10.8	2.65	6.47	6.21
	S	0.03	10.8	2.55	4.09	6.30
10	S	0.03	7.9	2.74	3.85	5.59
10	F	0.03	7.6	2.83	5.49	5.20
	S	0.03	7.6	2.75	4.21	5.28
9	S	0.03	7.5	2.95	4.07	4.98
9	F	0.03	7.7	3.00	5.23	5.13
	S	0.03	7.7	2.79	3.85	5.34
8	S	0.03	7.5	2.73	3.72	5.19
8	F	0.03	7.4	2.84	5.29	4.97
	S	0.03	7.4	2.71	4.03	5.10
7	F	0.03	6.7	2.76	4.25	4.25
	S	0.03	6.7	2.70	3.79	4.31
7	F	0.03	6.8	2.68	4.69	4.45
	S	0.03	6.8	2.62	3.83	4.51

⁽¹⁾Initial jar test pH value.

⁽²⁾Supernatant (S), filtrate (F).

⁽³⁾Total inorganic carbon expressed as CO₃.

VITA

Byron Thomas Butcher, Jr., was born in Norfolk, Virginia, on July 14, 1955. His family moved to High Point, North Carolina, and from there to Knoxville, Tennessee, where he was graduated from Farragut High School in June 1973. In August 1973 he entered Oral Roberts University in Tulsa, Oklahoma, in their pre-engineering program.

After two years at Oral Roberts University, he came back to complete his education at The University of Tennessee Knoxville. There he graduated with a Bachelor of Science in Civil Engineering in December 1978.

While at The University of Tennessee, Mr. Butcher completed five quarters of engineering co-op experience with Union Carbide Corporation-Nuclear Division, former contractor to the Department of Energy in Oak Ridge, Tennessee. Upon graduation he obtained full-time employment with Union Carbide at their Y-12 Plant. He is currently employed by Martin Marietta Energy Systems, Inc., the new DOE contractor, in the Waste Transportation, Storage and Disposal Department at Y-12.

In January 1979 the author entered the graduate school of The University of Tennessee Knoxville and attended courses through the evening school program. He obtained his Master of Science Degree with a major in Environmental Engineering in August 1985.