THE UNIVERSITY OF MICHIGAN
DEPARTMENT OF CIVIL ENGINEERING

ENVIRONMENTAL CHEMISTRY OF CADMIUM IN AQUEOUS SYSTEMS

Hans S. Posselt
and
Walter J. Weber, Jr.

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I. INTRODUCTION

The adverse effects of trace amounts of cadmium on human health were pointed out almost a decade ago (1,2,3), but only recently, beginning with the identification of the incontestable ecological impact of mercury, has significant attention been given to the role and toxicity of heavy metals in the aquatic, terrestrial and atmospheric environment. Heavy metals of present public concern include barium, arsenic, lead, cobalt, nickel, copper, zinc, cadmium, mercury, chromium and manganese (4).

In contrast to its relatively more abundant sister element zinc, cadmium is a trace element, which is non-essential to man, and its presence in human tissue is regarded abnormal (2). Relatively little is known with respect to the chemical and physiological behavior of cadmium in the soil-plant-animal chain. There is sufficient evidence in the literature to conclude that cadmium tends to accumulate in biological tissues (5). Moreover, cadmium appears to displace - and compete with - the essential element zinc for binding sites within certain protein complexes (6). Accumulation of the metal in human tissues seems to depend more on the molar distribution ratio of Cd:Zn than on the absolute concentrations of the individual elements to which such tissues are subjected.

A. Occurrence, Relative Distribution and Uses of Cadmium

Cadmium occurs naturally as greenochite (CdS) and $CdCO_3$

in combination with zinc- or lead ores, from which it is usually recovered as a by-product. It is one of the least abundant elements of the lithosphere with an estimated concentration of 0.1 - 0.5 ppm, or 10^{-5} - $5{\cdot}10^{-5}$% (7). In soil the weight ratio of cadmium to zinc varies from 0.0002 to 0.002 (or 0.00016 to 0.0016 moles Cd/mole of Zn), depending on geographical location (8).

The cadmium content of seawater is of the order of 1 ppb, with observed variations probably due in part to analytical techniques as well as to differences in geographical distribution. Samples taken from the Caribbean Sea show 0.3 ppb Cd and 24 ppb Zn corresponding to a molar Cd/Zn ratio of 0.0074 (9), whereas Mason gives a molar ratio of 0.006 for seawater in general (10). The fact that the seawater concentration of cadmium falls far below its actual solubility tends to rule out the possibility of a simple equilibrium with cadmium carbonate, which would likely represent the solubility-governing solid phase for the seawater system.

Cadmium data for fresh waters are subject to great variation. To a large extent this may be attributed to variability in industrial discharges and mine leaching phenomena superimposed on steady-state low level leaching from cadmium bearing soils. Table 1 shows selected data on cadmium and zinc concentrations determined in natural fresh and municipal water samples (1).

TABLE 1

Zinc and Cadmium Concentrations of Selected Water Samples (after Perry et al. (1))

Sample Description and Location	Cadmium ppb	Zinc ppb	$\frac{\text{moles Cd}}{\text{moles Zn}}$[a]
Connecticut River, Vermont	14.6[b]	5	1.69
Brook, Vermont	0.5	14	0.021
Brook, Vermont	0.6	3.5	0.098
Spring, New Hampshire	2.5	177	0.0081
Sea water, Caribbean	0.3	24	0.0074
Brattleboro, Vermont:			
inlet (reservoir)	2.1	3.5	0.41
main (town)	14 - 21[b]	-	-
tap hospital:			
cold running	8.3	160	0.030
stagnant	15 - 77[b]	1830	0.00054 to 0.0028
Bridgeport, Conn. (tap)	14	-	-
White Plains, N. Y. (tap)	14	-	-
Private Dwellings:			
Lake N. H.	1.1	3.5	0.18
tap (plastic pipe)	14[b]	20	0.41
Spring, Vt.	3.8	-	-
tap, iron pipe	3.5	-	-
Spring, Vt.	-	-	-
copper pipe	8.3	770	0.0064
Spring, Vt.	2.2	13	0.098
tap, iron pipe	3.8	660	0.0033
Spring, S. C.	-	-	-
iron pipe	8	18	0.26

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a) Weight ratio (Cd : Zn) x 0.58 = molar ratio.
b) Cause for rejection of water supply exceeding allowable limits of 10 ppb (12).

Note: Iron pipes were galvanized, said to contain 140 - 400 ppm cadmium. Two copper pipes, dissolved in acid, contained 57 and 2.76 ppm cadmium (1).

The concentration of cadmium in drinking waters in the U.S. ranges from 0.4 - 60 ppb with a mean of 8.2 ppb (11). Seepage of cadmium from plating shops into ground water has resulted in concentrations ranging from 10 to 3,200 ppb as Cd (12). Corrosive dissolution of galvanized pipes containing cadmium in unspecified amounts is believed to be a significant source of cadmium in drinking waters (1,11,12). This assumption is strongly supported by the analytical data presented in Table 1 (1). It is to be noted that the 1962 drinking water standard recommends an allowable limit of 10 ppb for cadmium (12).

Cadmium and zinc are found in a variety of food products. Oysters, canned fish, oils, grains, gelatin, and meats are good sources of cadmium; vegetables, nuts, and fruits are poor sources (1). Both elements tend to be taken up preferentially by certain grains from superphosphate fertilized soils. Enrichment of cadmium is also indicated in the marine environment. While concentrations of cadmium in seawater are generally less than 1 ppb, marine plants contain approximately 400 ppb, and marine animals exhibit cadmium concentrations ranging from 150 to 3,000 ppb (5).

Although the absolute concentration of cadmium in many foods is by far greater (approximately 200 ppb as Cd) than that found in natural waters and drinking water supplies, the molar ratio Cd:Zn seldom exceeds a value of 0.02 in most food products (1). Molar ratios determined for some water samples (Table 1) tend to vary widely and may assume relatively large values. In addition to competitive effects between Zn and Cd, which would be governed mainly by the molar distribution and the ratio of the equilibrium constants for a certain complex (6), the uptake and accumulation of cadmium in body tissues may also be influenced by specific effects. It has been proposed that equivalent concentrations of cadmium in water are more toxic than equivalent food concentrations because of the antagonistic effect of certain food components (13).

Relatively low availability and high price appear to be the major deterrents to the use of cadmium on a large industrial scale. Its use has increased, however, in recent years, largely in the area of electroplating of steel and as a neutron absorber in nuclear reactors. Other important industrial uses of cadmium are: in alkaline batteries, in pigments (CdS), in ceramics, for photography, and as a component of alloys with copper, lead, silver, aluminum and nickel (7). Cadmium salts are occasionally employed in certain insecticides and antihelminthics (5). The world production of cadmium has risen from 4800 tons in 1947 to 8500 tons in 1957 (14).

B. Toxic Effects

Biologically, cadmium is considered non-essential and non-beneficial (12); it is said to be "moderately toxic" to all organisms and a cumulative poison in mammals (5). Furthermore, cadmium is recognized as an element of "serious toxic potential" when ingested directly, and is of great concern to industrial toxicologist (12,15). Serious forms of acute and chronic diseases, such as:"itai-itai"(18), kidney damage, emphysema, hypertension, and testicular atrophy have been directly associated with cadmium poisoning among workers in the metals industry (16). General cadmium poisoning was found to result from consumption of foods stored in cadmium plated containers (17). Ingestion of cadmium has been responsible for a number of human deaths; in one case only 8.9 mg of $CdCl_2$ caused the death of a child within 1.5 hours (17). Reports have been made of human beings having been sickened by ingestion of 13 - 15 mg/kg of cadmium in popsicles, 67 mg/l in punch, 300 mg/l in a cold drink and 530 mg/kg in gelatin (17). Long term exposure to small amounts of cadmium in drinking water and rice diets has been associated with "itai-itai", a serious and often fatal disease of the bones (18). Recent epidemiologic studies by Schroeder have produced appreciable evidence for linking minute quantities of cadmium in drinking water with incidents of cardiovascular disease in man (for a summary see reference 19). These findings constitute significant grounds for the present study, and are discussed in detail in a subsequent section.

During the course of the "itai-itai" disease cadmium was found to displace calcium within the bone structure as well as to concentrate in soft body tissue (18). However, the usual observation from man and animal studies points towards primary accumulation and retention of cadmium in the liver, kidneys, pancreas and thyroid (1,15,20). Aside from the direct role cadmium plays in human and mammalian toxicology, its adverse effects on fish and other forms of aquatic life are also of vital importance, particularly, considering its preferential uptake and substantial cumulative effects in the food chain.

Literature data indicate that the acute lethal level for fish ranges from 0.01 to about 10 ppm of cadmium, depending on species, exposure times, water composition and temperature (5). Mortality of salmon fry, for example, was caused by 0.03 mg/l of Cd in combination with 0.15 mg/l of Zn derived from corrosive deterioration of galvanized screen (21). The medium tolerance limits, TL_m, for fatheads and bluegills in soft water are 1.09 and 4.56 mg/l for 24 hours of exposure (22). In several instances cadmium and zinc tolerances of fish were reported higher in hard waters than in soft waters (17,24). Inspection of the experimental conditions of these studies reveals, however, that the Cd concentrations employed for study were in excess of actual solubilities, suggesting greater removal of active cadmium via precipitation and settling in the hard waters. Cadmium tends to accumulate in the gills of fish, and a method has been proposed for the detection of cadmium poisoning by gill tissue analysis (23). Most investigators agree in attributing acute cadmium poisoning in fish to coagulation of the mucus secreted by the gills (see reference 23). This effect has been demonstrated with many other heavy metals (eg.: Cu, Zn, Hg, Pb) and suggests non-specific toxicity of cadmium as well as additive or synergistic effects towards fish (5).

Immobilization of Daphnia magna in Lake Erie water has been observed in the presence of 2.6 ppb Cd, and river water studies have shown threshold concentrations of 0.1 - 0.15 ppm Cd for Daphnia magna, Scenedesmus and Escherichia coli (17). Among these and many other accounts of cadmium toxicity in the literature, there is no indication of the existence of higher toxic forms of the element other than the normal ionic species (see Chapter II) obtained upon dissociation of simple cadmium salts in aqueous solution (17). In the absence of such evidence, magnifying effects, as are observed in the case of mercury-methylmercury, can be no more than speculated upon.

C. Cadmium in Drinking Water and its Relationship to Cardiovascular Disease

Numerous investigations have been undertaken in an effort to correlate potable water quality, particularly hardness, and the incidence rate of cardiovascular death rates (for a summary see reference 25). Schroeder in the United States (26) and Morris in the United Kingdon (27), among other investigators, have shown significant negative correlations between water hardness and death rates from cardiovascular diseases. Schroeder (26) pointed out, however, that there were notable exceptions, suspecting that other factors, possibly related to hardness, might play a more important role than the ordinary hardness ions omnipresent in natural and drinking water systems. The following discussion represents an account of the scientific evidences in support of the hypothesis that cadmium in drinking water constitutes a significant factor in relation to incidents of cardiovascular diseases in man.

1. Hypertension is readily induced in rats given trace amounts of cadmium in drinking water (3,28). Cadmium is preferentially accumulated in renal tissues of rats (29) and man (30) with molar renal Cd:Zn ratios in normotensive and hypertensive rats being 0.35 ± 0.18 and 1.02 ± 0.11, respectively. It is common knowledge that the kidney is of primary importance to the regulation of blood pressure.

2. While renal Cd:Zn ratios in infants are near zero (no Cd present) a considerable increase is observed with age, reaching a maximum of approximately 0.7 (3000 ppm of Cd in ash of human kidney tissues) at the age of 50 - 60 years, and subsequently declining at a somewhat lower rate (1,9). More importantly, high renal Cd:Zn ratios in man have been associated with deaths from arterial hypertension and cardiovascular diseases (9,31,32), and Cd concentrations in urine of hypertensive patients have been found to be 40 times higher relative to normotensive persons (33).

3. Hypertension induced in rats may be reversed with a concurrent lowering of the renal Cd:Zn ratio by feeding of the test animals with a zinc complex ($Na_2ZnCDTA$)*

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*disodium-zinc salt of trans-cyclohexane-1,2-diamine-N,N,N'-tetra acetic acid exhibiting a higher affinity for cadmium than for zinc (34).

4. As cadmium tends to compete with zinc for the same binding sites (presumably thiol groups) on metallothionein, an essential protein-complex found in renal tissues of equine and human origin (6), its behavior can be understood as that of an antimetabolite to zinc. In fact, the displacement of zinc by cadmium has been demonstrated in small mammals, while the reverse - cadmium displacement by zinc - could not be verified (9). Under otherwise identical conditions, competitive uptake of cadmium from a binary Cd-Zn system would be governed by the molar ratio of the two metals in solution and the magnitude of the individual metal complex stability constants. As for example, the logarithms of the complex stability constants for the glutathione complexes of Cd^{2+} and Zn^{2+} are 10.5 and 8.3, respectively, indicating that the cadmium complex is thermodynamically favored (35). It has been shown in studies with rats, at least (Table 2), that calcium does not influence the renal uptake of Cd^{2+} from water containing both elements, a result which tends to rule out any direct correlation between water hardness and cadmium induced hypertension (29).

TABLE 2

Cadmium Up-take by Renal Tissues in Rats as Function of Water Hardness (after Schroeder et al. (29)).

Water Quality	Renal Zn μg/g	Renal Cd μg/g
hard	46.8 ± 10.6	42.8 ± 14.61
soft	48.2 ± 10.08	43.1 ± 8.82

5. Cadmium may enter drinking water (5,9,12) via corrosion of (cadmium containing) galvanized zinc and copper pipes. Under such conditions molar Cd:Zn ratios of the elements in solution may assume values much greater than normally found in natural waters or food products. Further indication of the "water factor" is the observation that the incidence rate of cardiovascular diseases is much less in primitive nations, where water pipes of this type are uncommon (32). It must certainly be realized that other factors (eg.: urban stress, crowding, etc.), differentiating civilized from primitive nations, may be of equal or greater importance in determining the statistical difference.

A negative correlation between water hardness and cardiovascular death rate appears more plausible if the hypothesis that cadmium is the causative factor is valid, since it is generally recognized that soft waters tend to be more corrosive than hard waters under comparable conditions. An in-depth discussion of this aspect is presented in conjunction with the interpretation of corrosion data (Chapter V).

D. General Aspects of Cadmium Chemistry

While specific topics of primary interest to water pollution by cadmium will be treated in connection with the interpretation of the presented data, it is appropriate to briefly examine some general aspects of cadmium chemistry preceding this discussion. In view of lacking documentation with respect to the occurrence and significance of organometallic forms of cadmium in the aqueous environment, both the experimental and theoretical treatment of this investigation will be limited to inorganic chemical interactions.

Cadmium belongs to the "zinc-family", or group IIb (Zn, Cd, Hg) of the periodic system. All members of this family have the $(n-1)\ d^{10}\ ns^2$ electron configuration; that is, 2 electrons beyond a completed d-subshell. Although the existence of $Zn^{(+I)}$ and $Cd^{(+I)}$ has been proposed (36), both metals occur predominantly in the (+II) oxidation state. Only mercury is known to form important compounds within the (+I) oxidation state.

Whereas mercury is considered a "noble" metal (E^o (Hg) = +0.85 volts), cadmium and zinc are thermodynamically unstable (E^o (Cd) = -0.4 volts, E^o (Zn) = -0.76 volts) in non-oxidizing acids and waters (37). The "relatively" high corrosion resistance of both metals is due to the formation of slightly soluble or insoluble surface films. In spite of unfavorable potentials, both metals are readily deposited from acid solutions, a phenomenon, which is explained in terms of "overvoltage effects". Cadmium metal is more readily dissolved in dilute nitric acid than in hydrochloric or sulfuric acid and, in contrast to zinc, is not readily soluble in alkali (14). The latter fact demonstrates that cadmium is more basic than zinc, as is also evident from its lesser tendency to form hydroxo-complexes.

A large number of soluble salts of cadmium of the type $A^{(2+)}X_2^{(1-)}$ and $A^{(2+)}X^{(2-)}$ are known (38,39); examples are $Cd(ClO_4)_2$, $CdCl_2$, $Cd(NO_3)_2$, $Cd(CH_3COO)_2$ and $CdSO_4$. Both elements, cadmium and zinc, form a variety of complexes. The most common ligands are probably OH^-, Cl^-, Br^-, I^-, CN^- and NH_3, with a maximum coordination number of 6 rather than 4. The existence of the hexammine complex, $Zn(NH_3)_6^{2+}$, is well documented and salts with $CdCl_6^{4-}$ as anion have been described (36). In aqueous solution the Cd^{2+} ion exists in a state of hydration (38). However, evidence for the formation of polynuclear hydroxide complexes, of the types described for iron (III), bismuth(III), tin(II) and beryllium(II) (40), has not been brought forth.

The solubility of cadmium in aqueous solution, particularly in natural waters, is usually governed by the solubility of cadmium carbonate ($K_{sp} = 5.2 \cdot 10^{-12}$) and hydroxide ($K_{sp} = 2.2 \cdot 10^{-14}$), and to a limited extent by cadmium sulfide ($K_{sp} = 7.0 \cdot 10^{-27}$) (35,41). Higher solubilities, in all cases considering equilibrium conditions, must be expected in waters with relatively high concentrations of anions capable of forming soluble complexes with cadmium. While chloride may be the only anion of significance for natural and potable waters, ammonia and cyanide are of definite importance in industrial waste waters. Because solubility equilibria are vitally important to the aqueous environmental chemistry of cadmium, a detailed and quantitative treatment of this subject is provided in a subsequent chapter (Chapter II).

E. Analysis of Cadmium

Several methods suitable for the precise quantitative determination of cadmium in the ppm and higher concentration range have been described in the literature (38,41). Most of these methods are straightforward, but are usually inapplicable to the range of concentration (sub-ppm) representative of natural waters and drinking waters. Analytical techniques capable of determination of trace amounts of cadmium are few in number and, expectedly, fairly involved.

Polarographic methods are particularly suited for cadmium determination in water because of the selectivity of electrode processes and considering the advantage of simultaneous determination of several metals (42). Sensitivities for cadmium of the order of 10^{-5} $\underline{M}$ ($\approx$1 ppm) have been achieved with direct conventional polarography employing a dropping mercury electrode; when preceded by extraction with dithizone, the sensitivity of this method can be increased to the range of 10^{-7} $\underline{M}$ ($\approx$0.01ppm). Higher increases in sensitivity employing direct methods are realized with linear sweep voltammetry ($\approx 10^{-7}$ $\underline{M}$ Cd) and anodic stripping polarography, which permits sensitivities of better than 10^{-9} $\underline{M}$ ($\approx$0.1 ppb) of the metal (42). Another useful and relatively rapid method of quantitative cadmium analysis in aqueous samples is that of atomic absorption. The usual detection limit of 10 ppb for Cd may be improved by a factor of 12 by extraction of cadmium with sodium diethyl-dithio carbamate in methyl isobutyl ketone (43). The gain in overall sensitivity is due to the concentrating effect and to specific contribution by the solvent selected.

In the absence of other interfering metals, cadmium in the range of approximately 50 ppb may also be determined colorimetrically using dithizone (11). In a recent survey conducted by the "Analytical Reference Service", a voluntary association of 302 private and institutional laboratories, the method revealed "excellent accuracy but poor precision" for cadmium (44). Mallory has demonstrated that spectrographic interference by other metals can be circumvented and sensitivity increased by quantitative precipitation with thioacetamide of metals including cadmium prior to spectrographic analysis (45). Complete separation by precipitation in the range of 5-232 ppb cadmium has been accomplished by this technique, which appears to be fairly independent of the subsequent analytical method employed.

A fairly rapid and new analytical method superior to atomic absorption or flame emission spectroscopy is that of atomic fluorescence flame photometry (46). A comparison of detection limits for cadmium by atomic absorption, flame emission and atomic fluorescence shows 10, 50 and 0.2 ppb as Cd, respectively (45). Even though it is not quite as sensitive as anodic stripping and cannot accomodate simultaneous determination of several metals, the method has the definite advantage of being more rapid.

One serious dilemma commonly encountered in trace metal analysis is that of losses of the metal by adsorption on container surfaces. Mc Farren and Lishka make mention of observing this phenomenon during the analysis of traces of heavy metals including cadmium, and have developed one procedure for minimizing losses during handling of the samples in boro-silicate bottles (44). A more detailed discussion of the phenomenon with respect to cadmium and the precautions taken to minimize the problem in this work is presented in Chapter III.

F. Significance and Scope of Study

The uncontrolled presence of cadmium in the aquatic environment constitutes a serious potential health hazard, particularly in view of the fact that its fate and behavior with respect to the soil-plant-animal chain is not well understood. Any arbitrary dispersal of cadmium into the environment following extraction from naturally stabilized deposits can be regarded as an undesirable distortion of the ecosystem. Ignorance of the role and chemical behavior of toxic trace metals such as cadmium in the aqueous environment may have consequences of unforeseen magnitude, as has been experienced recently in the case of mercury.

The general objective of this investigation has been to gain qualitative and quantitative insight into factors governing the removal of cadmium from industrial effluents and natural waters processed for human consumption and those responsible for the entrance of the element into drinking water distribution systems by corrosion of pipe materials. A primary purpose underlying all phases of this research has been to search for and establish conditions and procedures which afford control over the distribution of cadmium in the aqueous environment.

II. CADMIUM SOLUBILITY EQUILIBRIA

A thorough understanding of solubility equilibria - the thermodynamic relationships between solid and solute species - is of import in many sanitary applications. With respect to heavy metals in the aqueous environment, solubility considerations are invaluable aids for comprehension of mechanisms and design of conditions for processes effecting the removal of these metals, such as adsorption, precipitation, ion exchange and complexation. The leaching of heavy metals from soils, natural deposits or sediments is further example of a phenomenon for which the ultimate magnitude or extent of reaction is governed by thermodynamic laws.

Although the magnitude of equilibrium is a quantity most often required for an adequate description and experimental investigation of a chemical system, its specific applicability is often overestimated by ignoring kinetic factors.

The sluggishness of the precipitation of cadmium carbonate (Chapter III) is a typical example of the primary importance of the rate of attainment of chemical equilibrium. In fact, the literature reveals numerous examples of chemical reactions, for which rates are shown to increase over a range of conditions, under which the thermodynamic spontaneity tends to decrease concurrently. This observation implies, of course, that the considered reactions are thermodynamically favorable throughout the range of these respective conditions.

A. Distribution Diagrams

Cadmium in aqueous solution forms a number of complex species. Of particular interest to natural and industrial wastewater systems are those formed by combination of cadmium with hydroxide, chloride and - to some degree - with ammonia. These systems have been extensively investigated from a thermodynamic point of view, to the extent that the predominance of individual species can be numerically calculated as a function of ligand concentrations (distribution diagrams).

The following discussion presents the mathematical formulation of the Cd-OH-distribution diagram, which applies methodologically as well to the Cd-Cl and Cd-NH_3 systems. According to thermodynamic data for the mononuclear hydroxide complexes of cadmium, the Cd-OH system can be described by four other species in addition to the dipositive cadmium ion (47). The pertinent equilibria are represented in form of a stepwise formation of these species:

$$\mathrm{Cd^{2+} + OH^- \rightleftharpoons CdOH^+} \qquad [\mathrm{CdOH^+}] = K_1[\mathrm{Cd^{++}}][\mathrm{OH^-}] \qquad (1)$$

$$\mathrm{CdOH^+ + OH^- \rightleftharpoons Cd(OH)_2} \qquad [\mathrm{Cd(OH)_2}] = K_2[\mathrm{CdOH^+}][\mathrm{OH^-}] \qquad (2)$$

$$\mathrm{Cd(OH)_2 + OH^- \rightleftharpoons HCdO_2^- + H_2O} \qquad [\mathrm{HCdO_2^-}] = K_3[\mathrm{Cd(OH)_2}][\mathrm{OH^-}] \qquad (3)$$

$$\mathrm{HCdO_2^- + OH^- \rightleftharpoons CdO_2^{2-} + H_2O} \qquad [\mathrm{CdO_2^{2-}}] = K_4[\mathrm{HCdO_2^-}][\mathrm{OH^-}]; \qquad (4)$$

in which $K_1 \ldots K_4$ are the "stepwise" formation constants (Table 3). For reasons of convenience it is appropriate to replace the stepwise formation by "overall" formation reactions; however, one should realize that the latter are mathematical representations only and do not depict elementary reaction steps. Stepwise formation constants $K_1 \ldots K_4$ and overall formation constants $\beta_1 \ldots \beta_4$ are related by $\beta_1 = K_1$, $\beta_2 = K_1 \cdot K_2$, $\beta_3 = K_1 \cdot K_2 \cdot K_3$ and $\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$.

$$Cd^{2+} + OH^- \rightleftharpoons CdOH^+ \qquad [CdOH^+] = \beta_1[Cd^{2+}][OH^-] \tag{5}$$

$$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2 \qquad [Cd(OH)_2] = \beta_2[Cd^{2+}][OH^-]^2 \tag{6}$$

$$Cd^{2+} + 3OH^- \rightleftharpoons HCdO_2^- + H_2O \qquad [HCdO_2^-] = \beta_3[Cd^{2+}][OH^-]^3 \tag{7}$$

$$Cd^{2+} + 4OH^- \rightleftharpoons CdO_2^{2-} + 2H_2O \qquad [CdO_2^{2-}] = \beta_4[Cd^{2+}][OH^-]^4 \tag{8}$$

The species $Cd(OH)_2$ corresponds to the soluble form, also described as $Cd(OH)_{2(aq)}$, and not to precipitated cadmium hydroxide, which will be represented as $Cd(OH)_{2(s)}$ throughout the text. A mass balance on cadmium for a system containing a total of C moles/l as Cd is then given by

$$C = [Cd^{2+}] + [CdOH^+] + [Cd(OH)_2] + [HCdO_2^-] + [CdO_2^{2-}]. \tag{9}$$

Substituting in terms of the formation constants from Equations 5 - 8 gives

$$C = [Cd^{2+}](1+\beta_1[OH^-]+\beta_2[OH^-]^2+\beta_3[OH^-]^3+\beta_4[OH^-]^4). \tag{10}$$

If α is defined as the fraction of a particular species relative to the total analytic concentration, then

$$[A] = \alpha_A \cdot C \tag{11}$$

and the sum of α's over all species is one:

$$\sum_{i=0}^{n} \alpha_i = \alpha_o + \alpha_1 \ldots + \alpha_n = 1 \tag{12}$$

The fractions of the individual solute species of cadmium then may be calculated as a function of hydroxide concentration. Thus, α_n is independent of the cadmium concentration in solution.

$$\alpha_o = \frac{[Cd^{2+}]}{C} = \frac{1}{1 + \beta_1[OH^-]+\beta_2[OH^-]^2+\beta_3[OH^-]^3+\beta_4[OH^-]^4} \tag{13}$$

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

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

$$\alpha_3 = \frac{[HCdO_2{}^-]}{C} = \beta_3[OH^-]^3\alpha_o \tag{16}$$

$$\alpha_4 = \frac{[CdO_2{}^{2-}]}{C} = \beta_4[OH^-]^4\alpha_o \tag{17}$$

Because the OH^- ion concentration is related to pH by

$$[H^+][OH^-] = 10^{-14} \tag{18}$$

$$\log [H^+] + \log [OH^-] = -14 \text{ and} \tag{19}$$

$$pH = 14 + \log [OH^-]; \tag{20}$$

the distribution of species (Figure 1) can be conveniently calculated as a function of pH. It must be noted that the ligand concentrations in distribution diagrams computed by this method correspond to the equilibrium - and not total analytic - concentrations. The latter, in the case of hydroxide as a ligand, is given by the mass balance for hydroxide ions in the system:

$$C_{OH} = [OH^-]+[CdOH^+]+2[Cd(OH)_2]+3[HCdO_2^-]+4[CdO_2^{2-}]. \qquad (21)$$

Thus, calculation of C_{OH} at a given pH is possible only when the total analytic concentration of cadmium is known. The distribution diagrams for the systems Cd-OH (Figure 1), Cd-Cl (Figure 2) and Cd-NH_3 (Figure 3) were calculated on a digital computer, IBM System 1360-Model 67, using the equilibrium constants listed in Table 3 without individual activity corrections.

An example of the calculation of distribution diagrams on a digital computer is given for the Cd-OH system in Computer Program I (Appendix A). The same general technique was employed for the Cd-Cl and Cd-NH_3 systems. The variables β_1, β_2, ...β_n are designated by B1, B2, ...BN and α_1, α_2, ...α_n by A1, A2, ...AN in the program. Variation in OH^- ion concentration (X) is generated by a power series set up in a "DO-LOOP" and then converted to pH according to Equation 20. A "Fortran" subroutine (STPLT 2) was used for a simple graphical representation of the diagrams. In all other respects, the computer program is self-explanatory.

TABLE 3

Equilibrium Constants Used for Calculation of Cadmium Distribution and Solubility Diagrams

Ligand	Log(10) of Equilibrium Constants						Conditions	Ref.
	K_1	K_2	K_3	K_4	K_5	K_6		
OH^-	4.16	4.23	0.69	-0.32	----	----	zero ionic strength, 25°C	(47)
Cl^-	1.32	0.90	0.09	-0.45	----	----	4.5 M $NaClO_4$, 25°C	(35)
NH_3	2.65	2.10	1.44	0.93	-0.32	-1.66	2 M NH_4NO_3, 25°C	(47)

Ligand	Overall Formation Constants						Conditions	Ref.
	β_1	β_2	β_3	β_4	β_5	β_6		
OH^-	$1.45 \cdot 10^4$	$2.46 \cdot 10^8$	$1.20 \cdot 10^9$	$5.76 \cdot 10^8$	----	----	zero ionic strength, 25°C	(47)
Cl^-	21.0	166.0	204.0	71.5	----	----	4.5 M $NaClO_4$, 25°C	(35)
NH_3	$4.47 \cdot 10^2$	$5.63 \cdot 10^4$	$1.55 \cdot 10^6$	$1.32 \cdot 10^7$	$6.31 \cdot 10^6$	$1.38 \cdot 10^5$	2 M NH_4NO_3, 25°C	(47)

1. Discussion. The distribution diagram for cadmium hydroxide complexes (Figure 1) shows Cd^{2+} as the only stable form of cadmium in the range $pH < 8$. The other two species of interest to water treatment applications (i.e. pH 5-11.5) are the monovalent $CdOH^+$ and the neutral molecule $Cd(OH)_{2(aq)}$. As discussed in the next section, the increase in solubility between pH 8 and 11.5 over that calculated from the $Cd(OH)_2$ solubility product, is largely due to the existence of the latter two species. The relatively weak acidity of cadmium is reflected by the fact that species of the type $HCdO_2^-$ and CdO_2^{2-} tend to form in a region of high pH only. There is also some information of analytical importance revealed by distribution diagrams. In the case of cadmium, Cd^{2+} is shown to be the species of predominance at $pH < 8$, $[Cl^-] < 10^{-3}$ $\underline{M}$ (Figure 2) and in the absence of other complexing ions. The presence of ammonia seems to be less critical as it tends to form the non-complexing NH_4^+ ion in acid solution. Often, the precision of analytical methods depends on the existence of one species only. For cadmium, acidification offers a convenient way of circumventing this difficulty.

Complexation by chloride ion becomes a significant factor in solubility considerations at chloride levels $> 10^{-3}$ $\underline{M}$ (35 mg/l), as can be seen from the distribution diagram for cadmium chloride complexes (Figure 2). However, only the two species $CdCl^+$ and $CdCl_{2(aq)}$ need be considered in most water treatment applications.

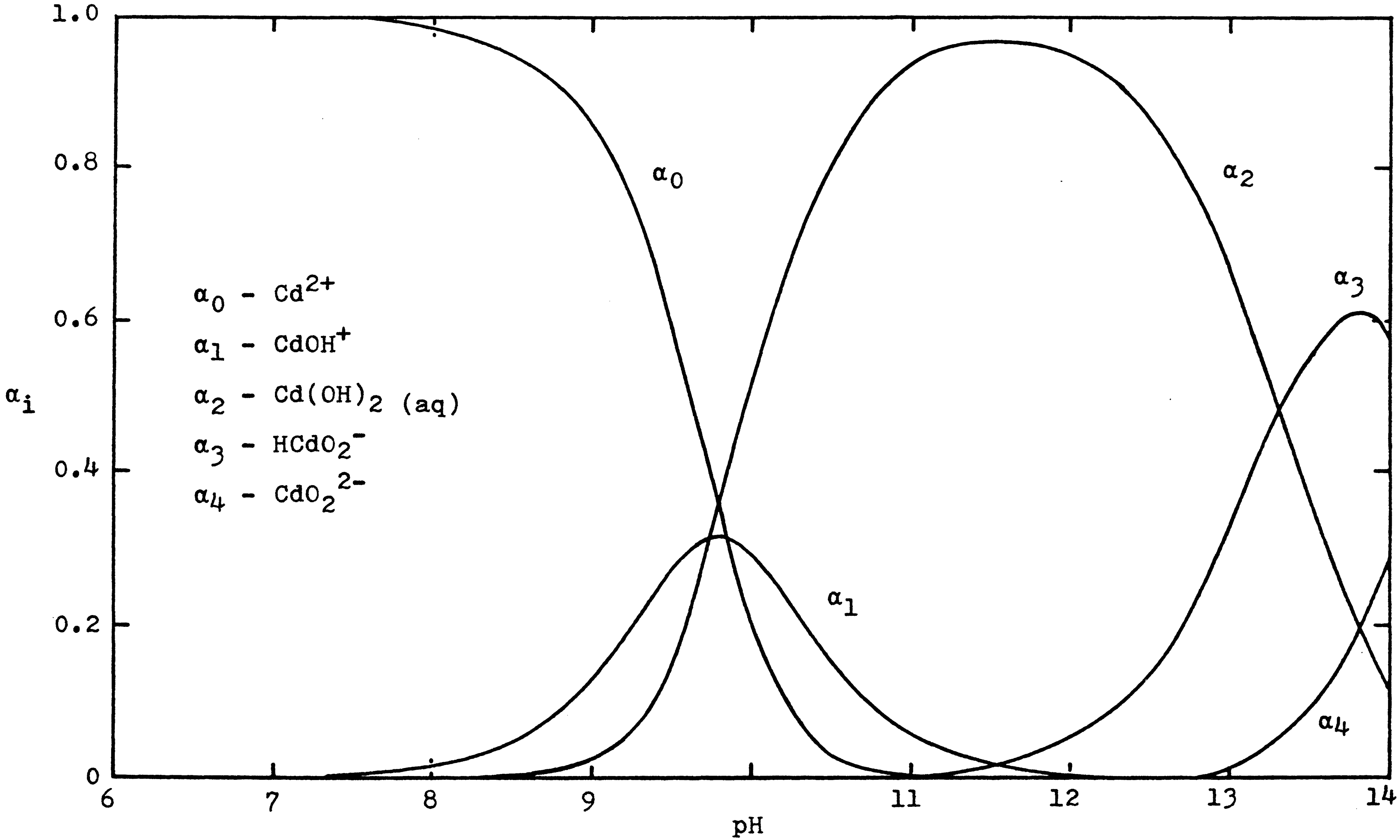

FIGURE 1. DISTRIBUTION DIAGRAM FOR CADMIUM HYDROXIDE COMPLEXES.

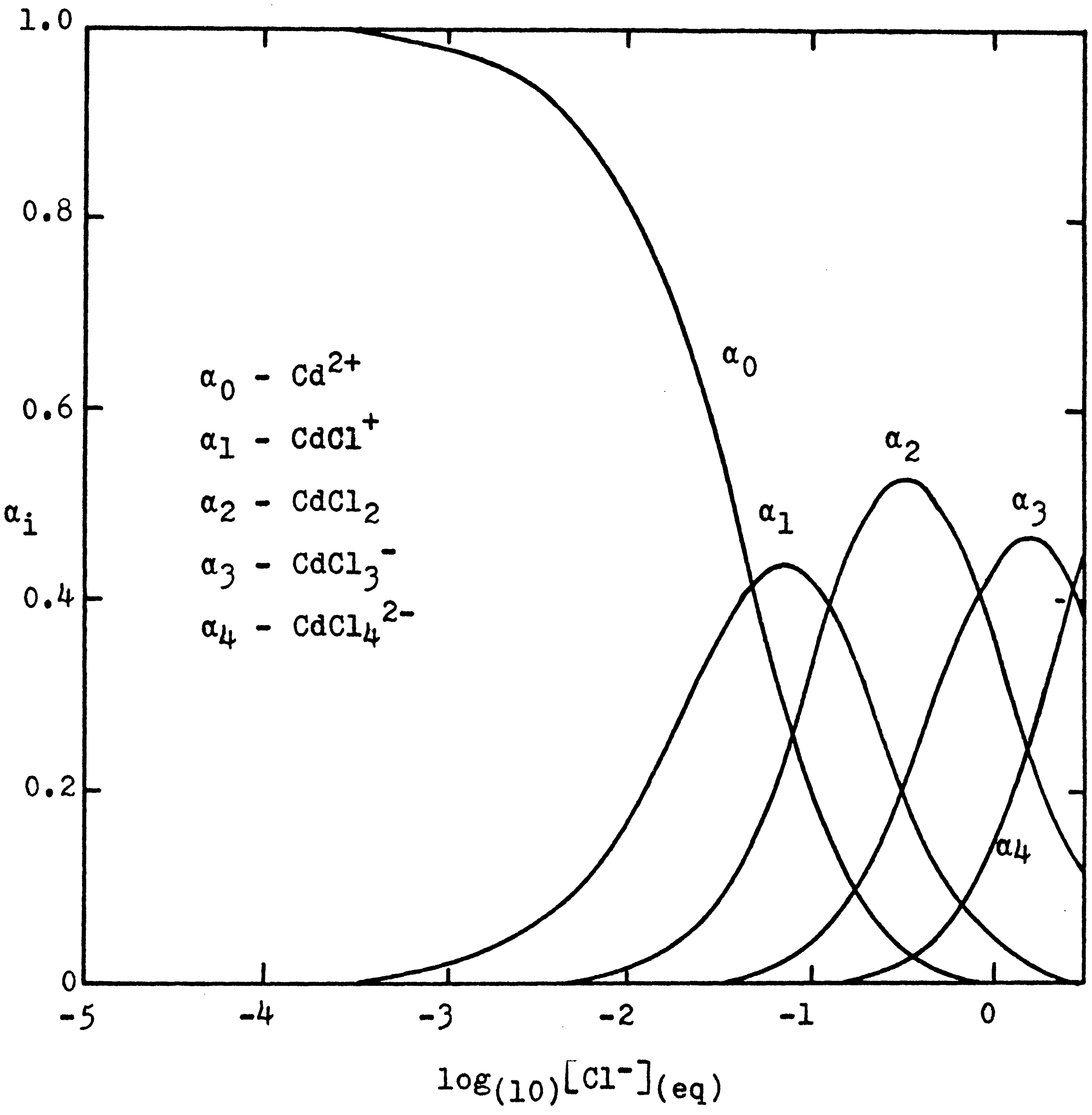

FIGURE 2. DISTRIBUTION DIAGRAM FOR CADMIUM CHLORIDE COMPLEXES

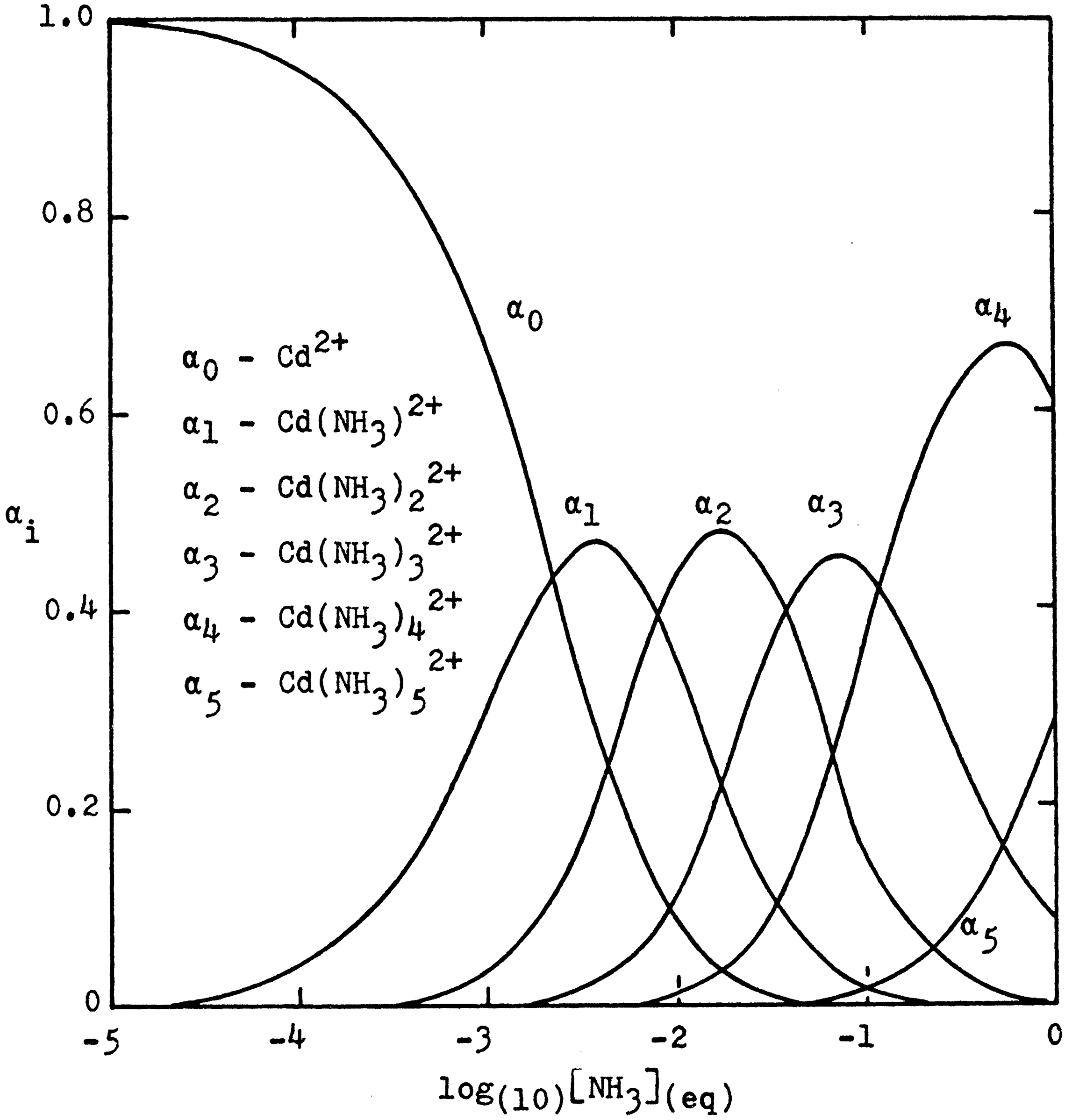

FIGURE 3. DISTRIBUTION DIAGRAM FOR CADMIUM AMMINE COMPLEXES

Ammonia is usually present in only minute concentrations in natural waters and should be largely removed from wastewaters before discharge into receiving bodies. In view of this and its relatively weak complexing tendency for cadmium (Figure 3), it may be concluded that the contribution of ammonia to the solubility of cadmium is negligible in most natural waters and water supplies. In the course of precipitating cadmium from certain industrial wastes with higher concentrations of ammonia, ($> 10^{-2}$ M as NH_3), complexation may become a significant solubility factor, but can be minimized by adding higher doses of carbonate (see Chapter III). It is of interest to note that the hexammine complex of cadmium, $Cd(NH_3)_6^{2+}$, does not exist at a concentration < 1 M of NH_3.

B. The Hydroxide-Carbonate-System

The solubility of cadmium in solutions containing alkali in the form of hydroxide or carbonate is of major importance to water treatment technology for several of the following reasons:

1. Both, OH^- and CO_3^{2-} are omnipresent in natural waters and, by virtue of the corresponding solubility products, govern the solubility of cadmium in most circumstances.
2. With regard to the removal of cadmium from wastewaters the use of alkali hydroxide or carbonate is relatively inexpensive and applicable to a large number of heavy metals.

3. Excess of OH^- or CO_3^{2-} is easily destroyed by neutralization with suitable acids.

Cadmium hydroxide, $Cd(OH)_{2(s)}$ forms as a white precipitate, when solutions containing sufficient amounts of dipositive cadmium ions are made alkaline.

$$Cd^{2+}_{(aq)} + 2OH^- \rightleftharpoons Cd(OH)_{2(s)} \qquad (22)$$

According to some investigations, precipitation is incident at pH > 7.5 and at an $[OH^-]/[Cd^{2+}]$ ratio of 0.05 or greater, but may be suppressed or completely inhibited by the presence of relatively large concentrations of alkali iodide, bromide or chloride, the effectiveness decreasing in that order (48).

The values for the solubility product of cadmium hydroxide at 25°C:

$$K^o_{sp} = [Cd^{2+}][OH^-]^2 \qquad (23)$$

in the literature range from $2.4 \cdot 10^{-15}$ to $5.84 \cdot 10^{-14}$ depending largely on the method of determination, age of precipitate and method used for activity corrections (35,38). Within the context of this discussion, a value of $2.2 \cdot 10^{-14}$, recently published for active $Cd(OH)_{2(s)}$, will be used (47).

The common method for calculating the solubility of sparingly soluble salts is based on direct application of the solubility product, provided that the equilibrium concentration of the anion is known. A more convenient way is that of graphical representation using logarithmic diagrams (49). The following treatment exemplifies the derivation of a straight-line equation for cadmium hydroxide solubility in a saturated system at 25°C.

$$[Cd^{2+}][OH^-]^2 = 2.2\cdot 10^{-14} = K_{sp} \qquad (24)$$

$$[H^+][OH^-] = 10^{-14} = K_w \qquad (25)$$

$$pH + pOH = 14 \qquad (26)$$

$$\log[Cd^{2+}] = \log K_{sp} - 2\log[OH^-]$$

$$\log[Cd^{2+}] = \log K_{sp} - 2(14-pH)$$

$$= -13.66 + 28 - 2pH$$

$$\log[Cd^{2+}] = 14.34 - 2pH \qquad (27)$$

In accord with Equation 27, a plot of $\log[Cd^{2+}]$ versus pH yields a straight line (see also Figure 4) with a slope of -2. Information obtained on the basis of a solubility product is accurate only in the absence of other solubility contributing species. For cadmium hydroxide, the valid range for Equation 27 ceases at pH > 9. Between pH 9 and 12 equilibria of the type shown in Equations 5, 6 and 7 should be included (Computer Program II, Appendix B).

Because the solubility of cadmium carbonate is generally lower under comparable conditions than that of the hydroxide, formation of a solubility model which includes carbonate equilibria is desirable. Apart from the solubility product for $CdCO_3$ (35,41,50)

$$[Cd^{2+}][CO_3^{2-}] = K'_{sp} = 5.2\cdot 10^{-12}, \tag{28}$$

the existence of other pertinent equilibria involving species of the type $CdHCO_3^+$ and $CdCO_{3(aq)}$ has not been established. This and other factors discussed throughout this chapter are reasons for not incorporating activity corrections into the solubility model for cadmium hydroxide and carbonate systems. A formulation of the model is presented below.

In the absence of carbonate and at pH 7-12, the mass balance for cadmium, C, in accordance with the distribution diagram (Figure I) is given by Equation 29.

$$C = [Cd^{2+}]+[CdOH^+]+[Cd(OH)_{2(aq)}]+[HCdO_2^-] \tag{29}$$

It should be noted that the species CdO_2^{2-} is not included in Equation 29, because it does not exist in this pH range. In terms of the equilibria (Equations 5, 6 and 7) discussed previously, Equation 29 yields:

$$C = [Cd^{2+}]+\beta_1[Cd^{2+}][OH^-]+\beta_2[Cd^{2+}][OH^-]^2+\beta_3[Cd^{2+}][OH^-]^3 \tag{30}$$

and, substitution of the solubility product relation for $[Cd^{2+}]$, gives an expression for C, which is independent of the cadmium concentration as long as the system remains saturated with respect to solid cadmium hydroxide. Under these conditions, C is equivalent to the solubility and is, therefore, designated as S.

$$S = \frac{K_{sp}}{[OH^-]^2} + \frac{\beta_1 \cdot K_{sp}}{[OH^-]} + \beta_2 \cdot K_{sp} + \beta_3 \cdot K_{sp}[OH^-] \qquad (31)$$

For solubilities, i.e. saturation conditions, the constants $\beta_1 \cdot K_{sp} \ldots \beta_3 \cdot K_{sp}$ are usually replaced by $K_{s1} \ldots K_{s2}$ giving:

$$S = \frac{K_{sp}}{[OH^-]^2} + \frac{K_{s1}}{[OH^-]} + K_{s2} + K_{s3}[OH^-]. \qquad (32)$$

In aqueous systems containing both hydroxide and carbonate, the ratio of the concentrations of these ions and of their respective solubility products will determine which of the corresponding K_{sp} values applies to the particular case. Thermodynamically it is required that the relationship yielding the lower concentration of Cd^{2+} is governing. Division of the two solubility products

$$[Cd^{2+}][OH^-]^2 = 2.2 \cdot 10^{-14} = K_{sp} \qquad (33)$$

$$[Cd^{2+}][CO_3^{2-}] = 5.2 \cdot 10^{-12} = K'_{sp}, \qquad (34)$$

gives the ratio

$$R = \frac{[OH^-]^2}{[CO_3^{2-}]} = 0.00423, \qquad (35)$$

which is a suitable parameter for comparision of system conditions. If $R > 0.00423$, Equation 33 applies and if $R < 0.00423$, S is calculated in accordance with the carbonate solubility product. For the case that $R = 0.00423$

either relationship holds. The "ion-ratio" method has also been employed as a rule for predicting the order of precipitation of solids in cases where two or more precipitation reactions are competing (50). Because this rule is based on thermodynamic considerations, it will most likely be affected by kinetics and thus apply directly only to reactions with similarly fast rates, whereas it may be overruled by kinetic factors in other circumstances.

Again, it must be realized that the term $[CO_3^{2-}]$ in Equation 34 and subsequent relations corresponds to the equilibrium concentration of CO_3^{2-}, which strongly depends on pH and on the total analytic concentration of carbonic acid species in solution. Carbonate is obtained from the mass balance

$$C_T = [CO_2^*]^{(1)} + [HCO_3^-] + [CO_3^{2-}] = [CO_3]_{TOT} \qquad (36)$$

and the ionization equilibria for carbonic acid (47) and water, all at 25°C

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2^*]} = 4.4 \cdot 10^{-7} \qquad (37)$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \cdot 10^{-11} \qquad (38)$$

$$K_w = [H^+][OH^-] = 10^{-14}. \qquad (39)$$

Substitution of the appropriate expressions for the

---

1) $[CO_2^*] = [CO_{2(aq)}] + [H_2CO_3]$

carbonic acid species from Equations 37 and 38 into the mass balance yields:

$$C_T = \frac{[H^+][HCO_3^-]}{K_{a1}} + \frac{[H^+][CO_3^{2-}]}{K_{a2}} + [CO_3^{2-}] \qquad (40)$$

and by resubstitution

$$C_T = \frac{[H^+]^2[CO_3^{2-}]}{K_{a1}\cdot K_{a2}} + \frac{[H^+][CO_3^{2-}]}{K_{a2}} + [CO_3^{2-}]$$

an expression in terms of $[H^+]$ and $[CO_3^{2-}]$. Further simplification and substitution finally leads to

$$[CO_3^{2-}] = \frac{C_T}{\dfrac{K_w^{\,2}}{[OH^-]^2\cdot K_{a1}\cdot K_{a2}} + \dfrac{K_w}{K_{a2}[OH^-]} + 1}\,; \qquad (41)$$

the desired term relating $[CO_3^{2-}]_{eq}$ with pH and total analytic concentration of carbonic acid species in solution. Thus, if $R < 0.00423$, the concentration of soluble cadmium according to the mass balance (Equation 30),

$$S = [Cd^{2+}]+\beta_1[Cd^{2+}][OH^-]+\beta_2[Cd^{2+}][OH^-]^2+\beta_3[Cd^{2+}][OH^-]^3$$

$$= [Cd^{2+}](1+\beta_1[OH^-]+\beta_2[OH^-]^2+\beta_3[OH^-]^3)$$

and, substitution of Equation 34 gives

$$S = \frac{K_{sp}'}{[CO_3^{2-}]}(1+\beta_1[OH^-]+\beta_2[OH^-]^2+\beta_3[OH^-]^3); \qquad (42)$$

wherein the right side of Equation 41 represents the equilibrium carbonate concentration.

The calculation of the solubility of cadmium at 25°C, between pH 7 and 12 and as function of the total soluble concentration of carbonic acid species is listed in Computer Program II (Appendix B). Variation of pH is generated in the same fashion as in Computer Program I (Appendix A), whereas the total carbonate concentration (TCA) can be varied according to needs (supplied on data cards). If TCA = 0 and/or if $R \geqslant 0.00423$, Equation 32, corresponding to the statement,

```
18     S = CS0/HO2 + CS2 + CS3/HO + CS4*HO;
```

is employed, and if $R < 0.00423$, Equation 42, corresponding to the statement,

```
       S = C8/CO3*(1.0 + C9*HO + C10*HO2 + C14*HO3);
```

is used for calculating the total molar concentration of cadmium. Computation of $[CO_3^{2-}]_{(eq)}$ from pH and TCA in accord with Equation 41 is accomplished by the statement

```
       CO3 = TCA/(C6/HO2 + C7/HO + 1.0),
```

whereby C6 and C7 correspond to $K_w^2/(K_{a1} \cdot K_{a2})$ and K_w/K_{a2}, respectively. The "Fortran" subroutine STPLT 2 is again used for graphical representation of the diagrams.

Discussion.- Figure 4 shows the logarithmic concentration diagram for cadmium at 25°C and at different concentrations of total soluble carbonate species. The dotted line is a representation of Equation 27 indicating that the solubility calculated from this equation, or from the cadmium hydroxide solubility product, is valid only at $pH < 9$. The contribution of the species $CdOH^+$, $Cd(OH)_{2(aq)}$ and - to a minor extent - $HCdO_2^-$ to the solubility becomes increasingly important as pH increases from 9 - 12, above which the ion CdO_2^{2-} must also be taken into account.

The effect of carbonate on the solubility is dramatic, suggesting that removal via carbonate precipitation appears promising provided that attainment of equilibrium proceeds at a practical rate. Conversely, the equilibrium solubilities of cadmium relative to hydroxide would result in effluents much more concentrated than tolerable with regard to fish toxicities, let alone standards for drinking water supplies.

The solubility curves for different carbonate concentrations remain reasonably parallel up to $pH \approx 11$ with a displacement of one logarithmic unit for each factor of 10 in the total molar carbonate concentration, as is postulated thermodynamically. This affords a quick calculation of solubility at different carbonate levels, once that at one level and at the same pH and temperature is known. Calculations of solubility of cadmium in carbonate systems at $pH > 9$ using the solubility product, Equation 34, lead to values corresponding to extrapolation of the respective

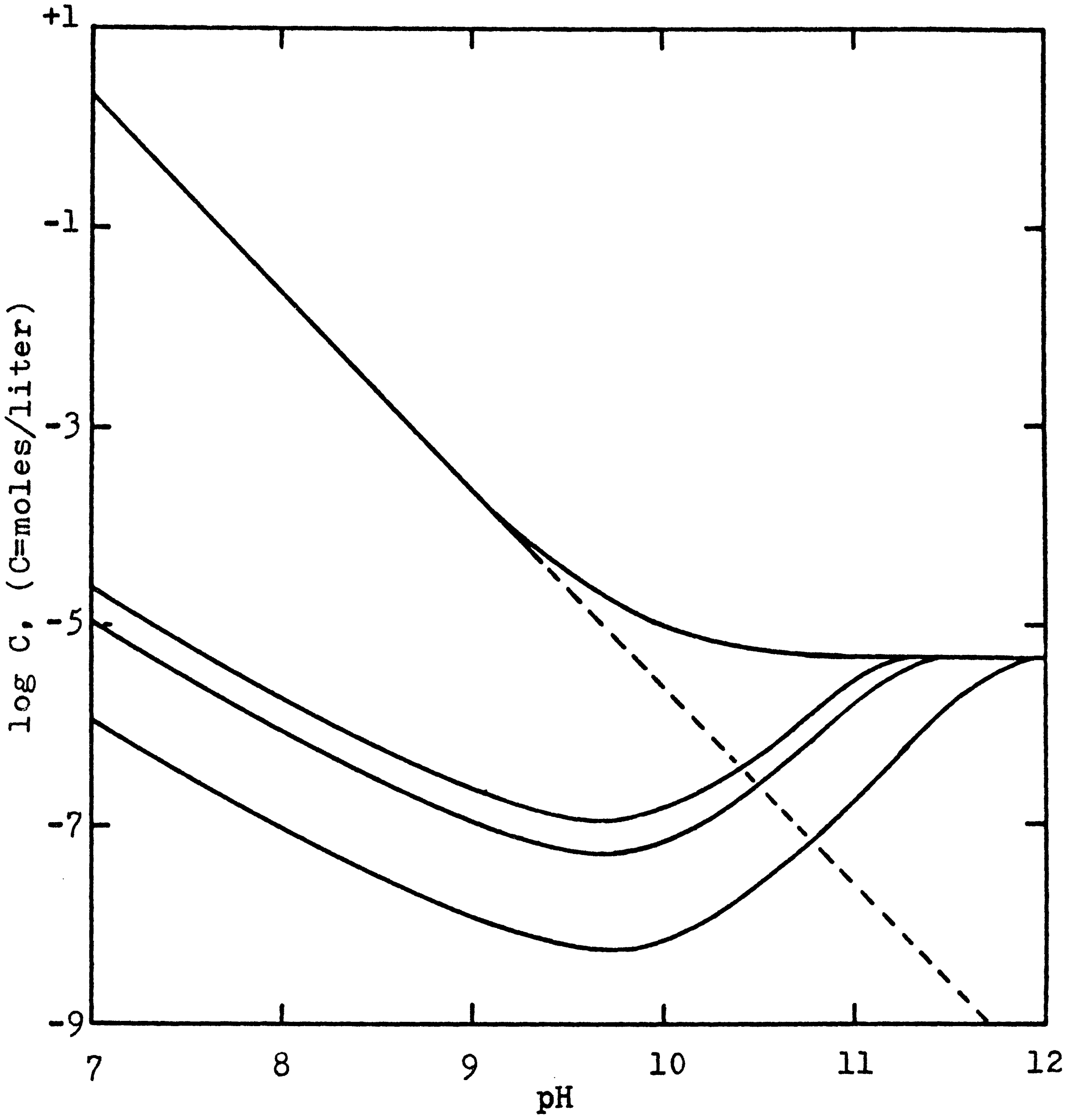

FIGURE 4. SOLUBILITY OF CADMIUM AS FUNCTION OF pH AND AT DIFFERENT CONCENTRATIONS OF CARBONIC ACID SPECIES.

The dotted line represents the solubility corresponding to the solubility product of cadmium hydroxide. The solid lines from top to bottom correspond to: $C_T = [CO_2]+[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}] = 0, 5\cdot10^{-4}, 10^{-3},$ and 10^{-2} M, respectively.

curves beyond pH 9, as illustrated (dotted line in Figure 4) for the carbonate-free system. The actual curvatures shown beyond this pH region arise from the contribution of species other than the dipositive cadmium ion.

C. Complexation by Chloride and Hydroxide

In the range of chloride concentration $[Cl^-]_{(eq)} < 0.1$ <u>M</u> only the species $CdCl^+$ and $CdCl_{2(aq)}$ need be considered. Because of the increasing complexity of the system and insignificant contribution of $HCdO_2^-$ (see Figure 1), this species has been omitted in addition to the ion CdO_2^{2-}, which is unstable at pH < 12. Thus, the mass balance on soluble cadmium for pH 8 - 12 is:

$$S = [Cd^{2+}]+[Cd(OH)_{2(aq)}]+[CdOH^+]+[CdCl^+]+[CdCl_{2(aq)}]. \qquad (43)$$

By substitution of the appropriate equilibrium constants, Equation 43 becomes

$$S = \frac{K_{sp}}{[OH^-]^2} + K_{s2} + \frac{K_{s1}}{[OH^-]} + \frac{21K_{sp}[Cl^-]}{[OH^-]^2} + \frac{166K_{sp}[Cl^-]^2}{[OH^-]^2}. \qquad (44)$$

While the equilibrium concentration of OH^- ions (pH + pOH = 14) is usually known, that of Cl^- ions is not and must be calculated from the total analytic chloride concentration. The mass balance for chloride is given by

$$\begin{aligned} C_{Cl} &= [Cl^-] + [CdCl^+] + 2[Cd(Cl)_{2(aq)}] \\ &= [Cl^-] + 21[Cd^{2+}][Cl^-] + 2\cdot 166[Cd^{2+}][Cl^-]^2, \qquad (45) \end{aligned}$$

or after substituting the cadmium hydroxide solubility product expression by

$$C_{Cl} = [Cl^-] + \frac{21K_{sp}[Cl^-]}{[OH^-]^2} + \frac{332K_{sp}[Cl^-]^2}{[OH^-]^2}. \qquad (46)$$

For systems containing carbonate (with the requirement that $R < 0.00423$), Equations 43 and 45 must be expressed in terms of the cadmium carbonate solubility product, as was shown for the hydroxide-carbonate system. After appropriate substitution, the mass balances for cadmium and chloride are:

$$S = \frac{K'_{sp}}{[CO_3{}^{2-}]}(1+\beta_1[OH^-]+\beta_2[OH^-]^2)+\frac{K'_{sp}}{[CO_3{}^{2-}]}(21[Cl^-]+166[Cl^-]^2) \qquad (47)$$

$$C_{Cl} = [Cl^-] + \frac{21K'_{sp}[Cl^-]}{[CO_3{}^{2-}]} + \frac{332K'_{sp}[Cl^-]^2}{[CO_3{}^{2-}]} \qquad (48)$$

Solving for S in Equation 44 (or 47) is laborious since it involves the solution of a quadratic equation to obtain $[Cl^-]_{(eq)}$ and calculation of $[CO_3{}^{2-}]_{(eq)}$ according to Equation 41. For computation of S as a function of pH - and for a wide range of concentration of total chloride and carbonic acid species - on a digital computer (Computer Program III, Appendix C), Equations 46 and 48 are converted into the general form

$$UZ^2 + VZ - TC = 0 \qquad (49)$$

and solved for Z, ($[Cl^-]_{eq}$), employing Newton's method.

Discussion.- The molar solubility of cadmium as a function of total chloride concentration and at a series of pH values is shown in Figure 5. An analogous plot for a solution with a total carbonate species concentration of 10^{-3} M is given in Figure 6. The slopes of the curves in both cases decrease with increasing pH and approach zero at pH > 10.5, demonstrating that complexation by chloride is important only in the pH range below 10.5. The influence of total carbonate species is of the same magnitude as shown for the hydroxy-carbonate system and independent of chloride concentration. Thus, the solubility of cadmium as function of chloride at other carbonate levels can be easily calculated from that shown for $C_T = 10^{-3}$ M. Again, a tenfold decrease in solubility is obtained for a tenfold increase in C_T and vica versa.

Complexation by chloride is relatively weak and appears to be relevant to industrial waste treatment only, but not to natural water systems, for which the total chloride concentration is usually in the order of less than 150 ppm as Cl^-. For example, the solubility for 0, 175 and 3500 ppm Cl^- and 10^{-3} M of carbonate species at pH 8, is 110, 124 and 520 ppb of cadmium, respectively.

D. Complexation by Ammonia and Hydroxide

Mathematical treatment of systems containing several ligands simultaneously competing for a central ion becomes

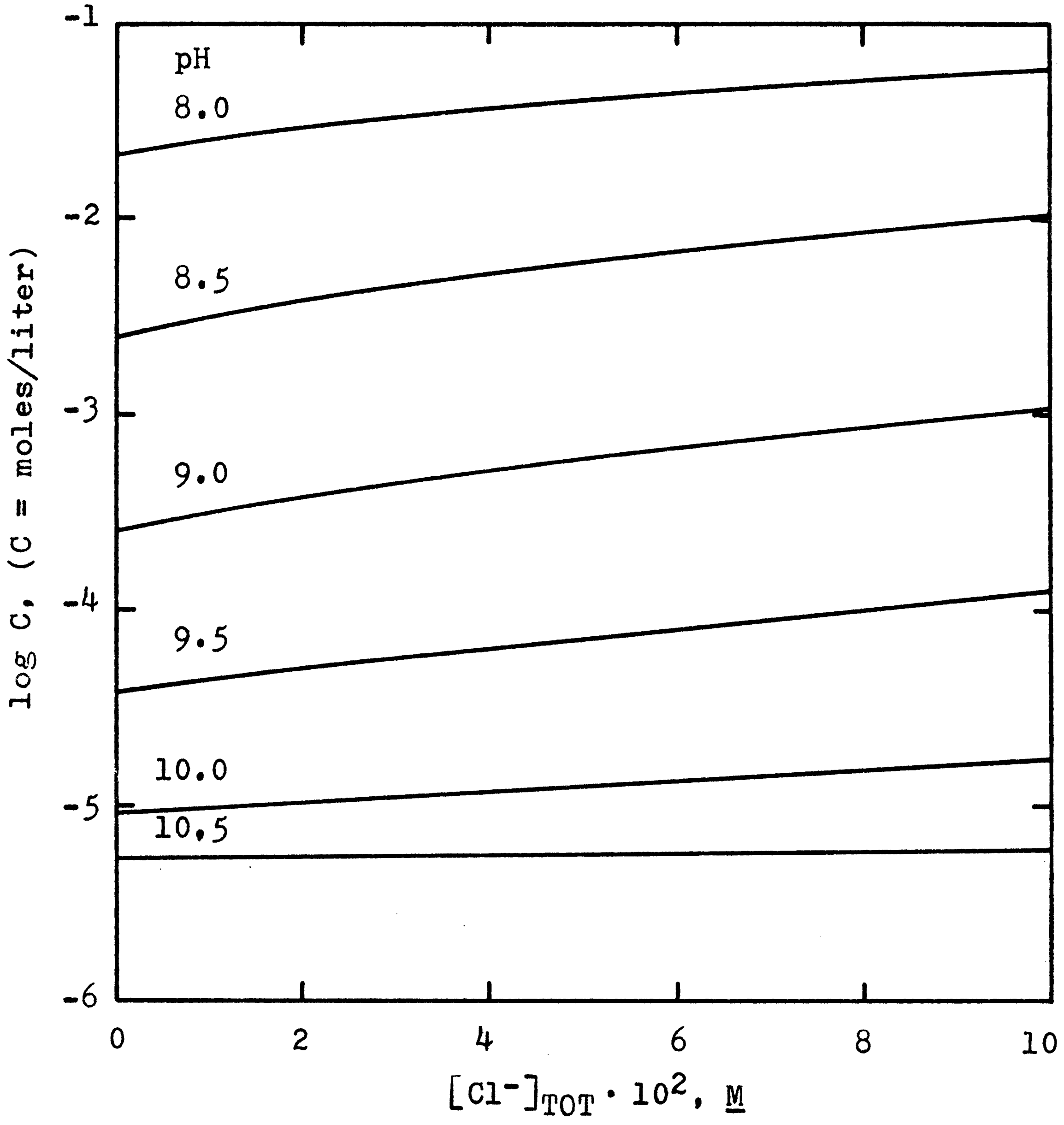

FIGURE 5. SOLUBILITY OF CADMIUM AS FUNCTION OF TOTAL ANALYTIC CHLORIDE CONCENTRATION AT DIFFERENT pH VALUES.

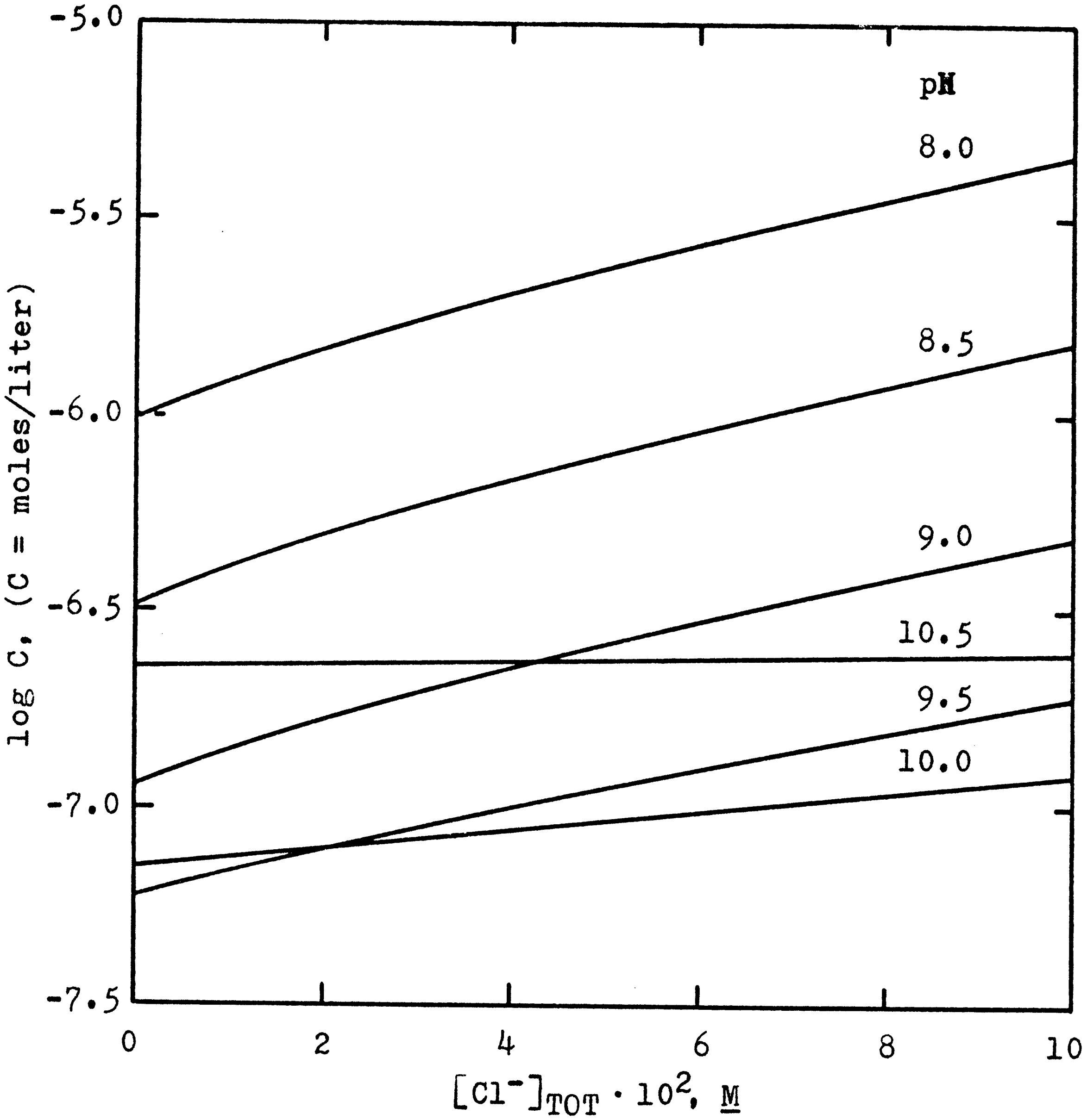

FIGURE 6. SOLUBILITY OF CADMIUM AS A FUNCTION OF TOTAL ANALYTIC CHLORIDE CONCENTRATION AT DIFFERENT pH VALUES IN A SYSTEM CONTAINING 10^{-3} M TOTAL CARBONIC ACID SPECIES.

increasingly complex. An additional degree of difficulty arises from ligand-ligand interactions. This will be demonstrated for the OH^--NH_3-system. In the range of $[NH_3]_{(eq)} < 0.01$ M, the distribution diagram for ammonia (Figure 3) reveals the predominance of the complex species $Cd(NH_3)^{2+}$, $Cd(NH_3)_2{}^{2+}$ and $Cd(NH_3)_3{}^{2+}$ in addition to Cd^{2+} and those formed by combination with hydroxide. Accordingly, the mass balance for soluble cadmium in the range pH < 12 is

$$S = [Cd^{2+}]+[Cd(OH)_{2(aq)}]+[CdOH^+]+[Cd(NH_3)^{2+}] +[Cd(NH_3)_2{}^{2+}]+[Cd(NH_3)_3{}^{2+}], \qquad (50)$$

where (NH_3) designates the molar concentration of ammonia at equilibrium. A further equation required to describe this system is the mass balance for ammonia

$$C_{NH_3} = [NH_3]+[NH_4{}^+]+[Cd(NH_3)^{2+}]+2[Cd(NH_3)_2{}^{2+}] +3[Cd(NH_3)_3{}^{2+}]. \qquad (51)$$

The concentrations of NH_3 and $NH_4{}^+$ as functions of OH^- are given by the equilibrium

$$[NH_4{}^+][OH^-] = K_b[NH_3], \qquad (52)$$

with $K_b = 1.78\cdot10^{-5}$ at 25°C. After a series of familiar substitutions, the two system equations (50 and 51) take the form

$$S = \frac{K_{sp}}{[OH^-]^2} + K_{s2} + \frac{K_{s1}}{[OH^-]} + \frac{\beta_1' K_{sp}[NH_3]}{[OH^-]^2} + \frac{\beta_2' K_{sp}[NH_3]^2}{[OH^-]^2} + \frac{\beta_3' K_{sp}[NH_3]^3}{[OH^-]^2} \qquad (53)$$

$$C_{NH_3} = [NH_3] + \frac{K_b[NH_3]}{[OH^-]} + \frac{\beta_1' K_{sp}[NH_3]}{[OH^-]^2} + \frac{2\beta_2' K_{sp}[NH_3]^2}{[OH^-]^2} + \frac{3\beta_3' K_{sp}[NH_3]^3}{[OH^-]^2}$$

$$= [NH_3]\left(1 + \frac{K_b}{[OH^-]} + \frac{\beta_1' K_{sp}}{[OH^-]^2}\right) + [NH_3]^2 \frac{2\beta_2' K_{sp}}{[OH^-]^2} + [NH_3]^3 \frac{3\beta_3' K_{sp}}{[OH^-]^2} \qquad (54)$$

where $[NH_4^+]$ is calculated according to Equation 52. The mass balance for ammonia (Equation 54) is a cubic equation of the form

$$AX^3 + BX^2 + CX - TA = 0, \qquad (55)$$

which is solved by Newton's method (Computer Program III, Appendix C).

With carbonate governing the solubility of cadmium the two mass balances for the ammonia system are

$$S = \frac{K'_{sp}}{[CO_3{}^{2-}]}\left[(1+\beta_1[OH^-]+\beta_2[OH^-]^2)+(\beta'_1[NH_3]+\beta'_2[NH_3]^2+\beta'_3[NH_3]^3)\right] \quad (56)$$

$$C_{NH_3} = [NH_3]\left(1+\frac{K_b}{[OH^-]}+\frac{\beta'_1K'_{sp}}{[CO_3{}^{2-}]}\right)+\frac{[NH_3]^2 2\beta'_2K'_{sp}}{[CO_3{}^{2-}]}$$

$$+\frac{[NH_3]^3 3\beta'_3K'_{sp}}{[CO_3{}^{2-}]} \quad (57)$$

Discussion.- Complexation of cadmium by ammonia (Figures 7 and 8) is somewhat stronger than by chloride. Since ammonia is rarely present in more than minute amounts in natural waters and usually occurs in industrial wastes at levels much lower than chloride, the difference between the ligand strengths is probably more than compensated by concentration differences. As evident from the slopes of curves in Figures 7 and 8, the effect of the total molar concentration of ammonia on cadmium solubility reaches a maximum between pH 8.5 and 10 and then levels off at both ends of this pH range. By inspection of the appropriate distribution diagrams, this behavior can be directly attributed to formation of $NH_4{}^+$ ions in the acid range and increasing predominance of the non-complexing neutral molecule, $Cd(OH)_{2(aq)}$ at pH > 10.5. The same consideration discussed (II. C.) for chloride applies to ammonia complexation with respect to the effect of total carbonate on the solubility of cadmium.

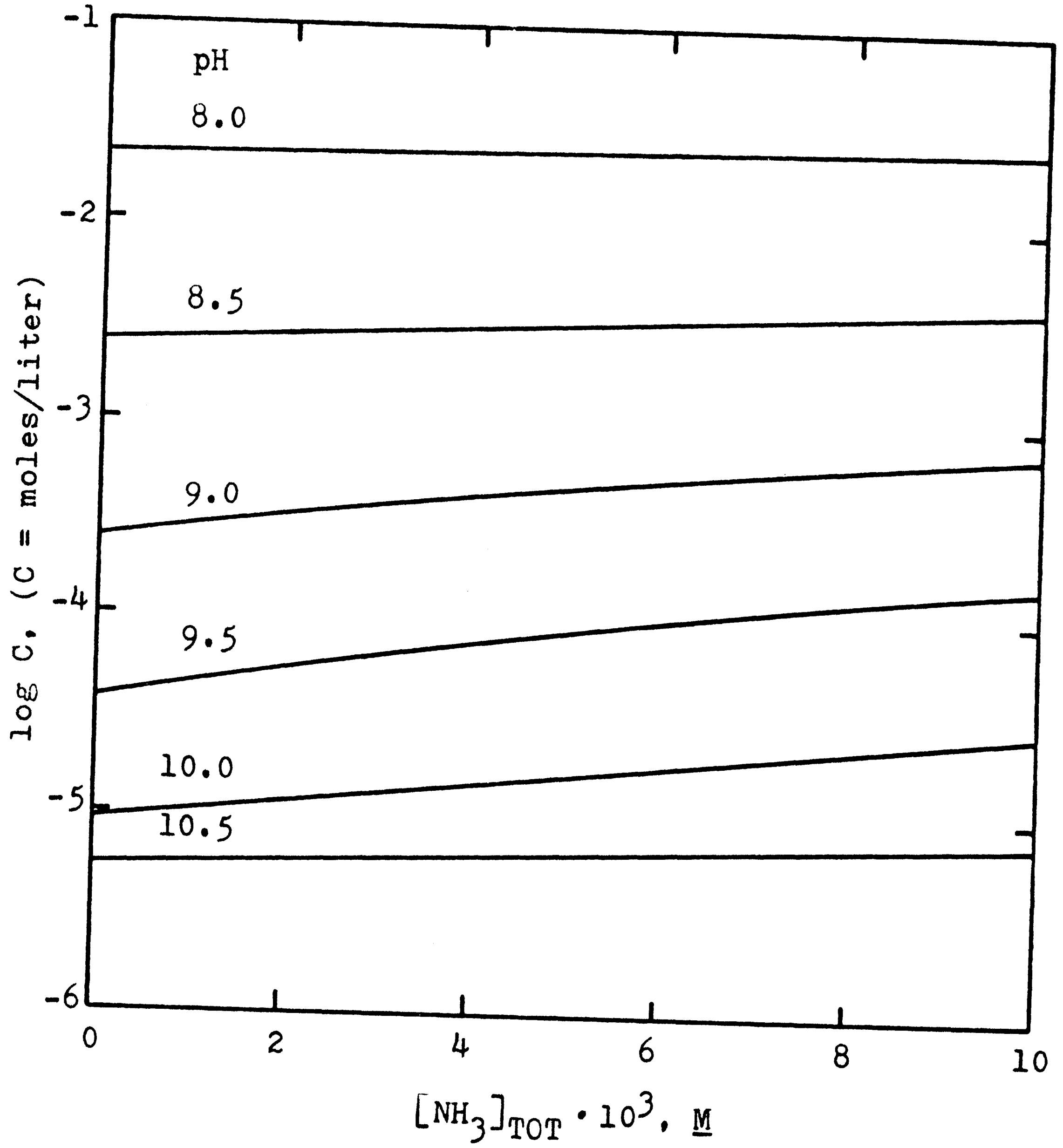

FIGURE 7. SOLUBILITY OF CADMIUM AS FUNCTION OF TOTAL ANALYTIC AMMONIA CONCENTRATION AT DIFFERENT pH VALUES.

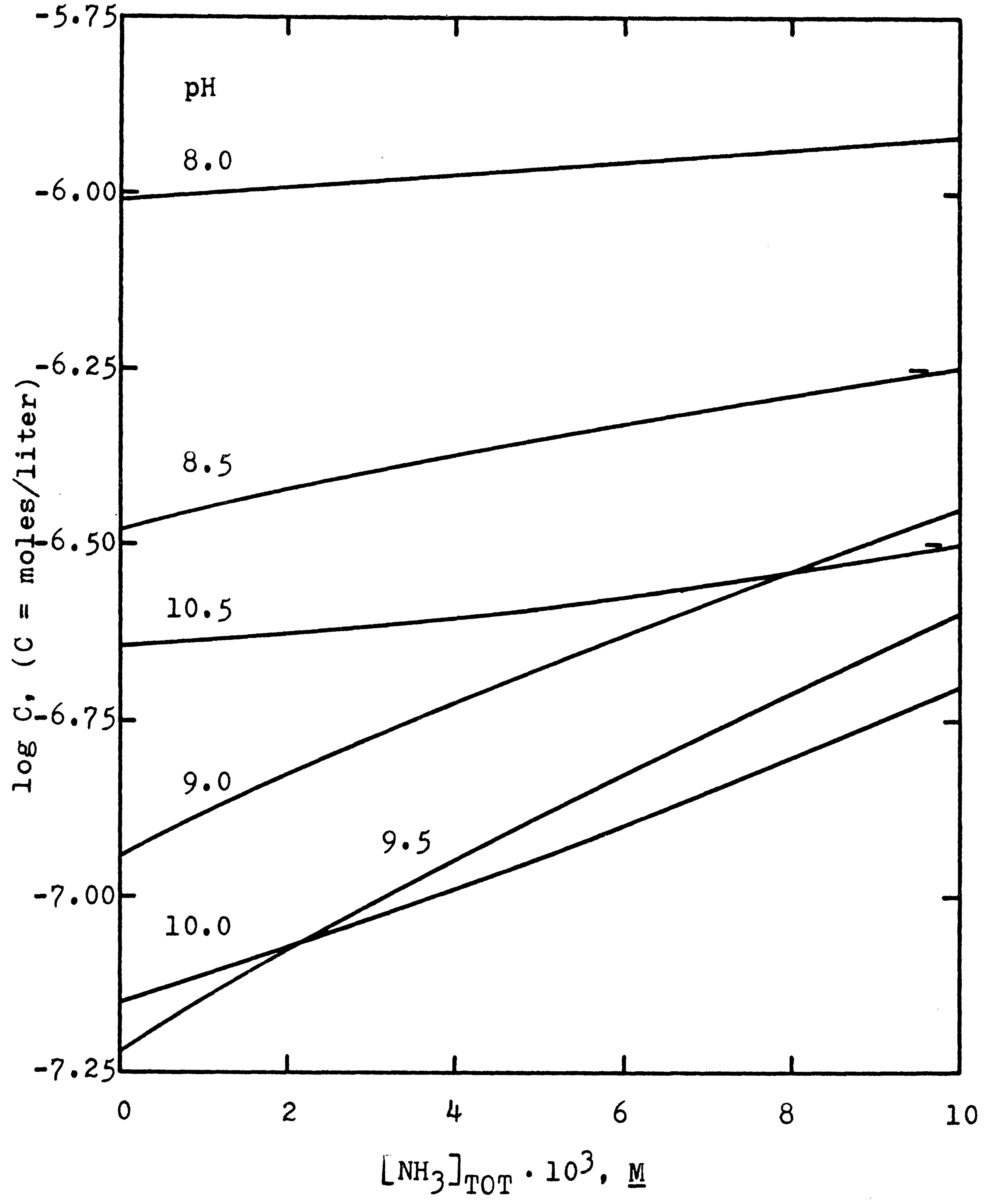

FIGURE 8. SOLUBILITY OF CADMIUM AS A FUNCTION OF TOTAL ANALYTIC AMMONIA CONCENTRATION AT DIFFERENT pH VALUES IN A SYSTEM CONTAINING 10^{-3} M TOTAL CARBONIC ACID SPECIES.

E. Complexation by Chloride, Ammonia and Hydroxide

Because chloride ion and ammonia are independent entities in aqueous solution, their interaction with cadmium with respect to complexation is additive. The solubility models developed for the systems Cd-OH-CO_3-Cl and Cd-OH-CO_3-NH_3 may, therefore, be combined in an additive fashion. For demonstration, the solubility of cadmium at pH 9 and at $[CO_3]_{TOT}$ = 0.001 M, $[Cl^-]_{TOT}$ = 0.1 M and $[NH_3]_{TOT}$ = 0.005 M are calculated in an additive way from the solubility obtained for the individual cases (Table 4).

TABLE 4

Solubility Computations at pH 9 and $[CO_3]_{TOT} = 10^{-3}$ M

Case #	$[Cl^-]_{TOT}$ M	$[NH_3]_{TOT}$ M	Log [S]	[S] M·10^7	Method
1	0	0	-6.94	1.15	from Figure 4
2	0.1	0	-6.31	4.90	from Figure 6
3	0	0.005	-6.67	2.14	from Figure 8
4a	0.1	0.005	-6.23	5.89	additive calculation
4b	0.1	0.005	-6.23	5.89	Computer Program III, Appendix C

Addition of [S] for cases 2 and 3 and subtraction of case 1 yields [S] for case 4. The same result was obtained by a computer program (Appendix C), designed to simultaneously accomodate a wide range of all variables (pH, $[CO_3]_{TOT}$, $[Cl^-]_{TOT}$, $[NH_3]_{TOT}$) discussed. The program requires as input the total analytic concentrations of carbonate, chloride and ammonia species, and calculates the solubility of cadmium as a function of pH between 8 and 12. The pH range may be easily extended to the acid region by changing the last number in the statement "DO 20 I=1,4", however, the species $HCdO_2^-$ and CdO_2^{2-} should be included for expansion beyond pH 12. A listing of the symbol designations used in the program is shown in Table 5 (Appendix C). Solution of the quadratic (Equation 49) and cubic (Equation 55) equations for the respective equilibrium concentrations of chloride and ammonia is performed by Newton's method, provided as the subroutine "RTNI". In addition to the inputs TC, ($[Cl^-]_{TOT}$), and TA, ($[NH_3]_{TOT}$), the subroutine requires a first guess (ZST and XST) for the roots $[Cl^-]_{(eq)}$ and $[NH_3]_{(eq)}$ and a statement of the desired accuracy (EPS2 and EPS) in terms of the difference between results of two iterations. The subroutine "STPLT 2" is again used for plotting of the solubility of cadmium (log [S]) as function of pH.

F. Validity of Equilibrium Models

The models developed for the solubility of cadmium in complex chemical systems are based on the present knowledge of relevant equilibria and of their respective thermodynamic constants. Under the assumptions that the list of species described is exhaustive, that activity corrections are made for individual cases, and that equilibrium constants are numerically factual, the models should accurately predict the solubility of cadmium for a given set of conditions at equilibrium.

There is some uncertainty, however, with regard to the existence of polynuclear hydroxide complexes and of the species $CdHCO_3^+$ and $CdCO_{3(aq)}$. Further, in systems containing multiple ligands there is a possibility for the formation of mixed ligand species. The solubility product for cadmium hydroxide has been found to vary by as much as an order of magnitude, depending on a variety of factors, but without any apparent consistency (35,38). It is not uncommon to find large discrepancies for solubility products of sparingly soluble salts, depending on the direction of approach to equilibrium (50). Data measured en route of the dissolution of well defined crystals may differ substantially from those obtained via precipitation from solution. Phenomena such as phase transitions, aging, colloid formation, and differences in particle size are frequently found to obscure solubility measurements subsequent to precipitation reactions (50,51).

Slow attainment of equilibrium is probably the most significant limiting factor in many applications of thermodynamic solubility relationships, particularly in precipitation reactions. While fair agreement with theory was observed (Chapter III, Table 6) for presumably equilibrium conditions, the precipitation of cadmium in alkaline carbonate systems was found to proceed at a relatively slow rate.

In light of this, an investigation of factors controlling the kinetics of precipitation of cadmium under conditions similar to practical applications, particularly industrial waste treatment, appears more meaningful for the present study than does any attempt at further refinement of thermodynamic equilibrium relationships.

III. REMOVAL OF CADMIUM BY PRECIPITATION IN ALKALINE CARBONATE SYSTEMS

Electroplating - or more generally, metal finishing - constitutes perhaps the largest single industrial and/or domestic use of cadmium, primarily for corrosion protection of metal parts (7). By nature of these operations, large volumes of water are used and must be treated by this industry. Cooling and rinsewaters, on the whole, represent the two largest volumes of spent waters in the United States (54). With certain exceptions, such as with chromium, the general approach to heavy metal removal from industrial wastes is that of precipitation at elevated pH (52,53,54). There is no further information in the pertinent literature of other more specific chemical treatments for the removal of cadmium or similar heavy metals.

The solubility calculations carried out in Chapter II show substantial differences between the solubilities of cadmium hydroxide and carbonate. For example, at pH 9 the solubilities are 28.8 and 0.008 ppm as Cd, for systems containing 0 or 10^{-3} $\underline{M}$ carbonate, respectively. Because equilibrium is probably rarely attained under practical conditions, heavy metal levels in industrial effluents may often be much higher than expected. Dobson (55) reported that effluents from chlorine treated cyanide wastes contained as much as 60 ppm of cadmium. The extent of pollution by these elements may further be increased by complexation reactions and colloid stabilization.

The primary pollutant in most metal finishing wastes is the extremely toxic cyanide, which is used as a complexing agent for a variety of metals for electroplating in basic solutions. Alkaline chlorination is the method of choice for detoxification of cyanides (52). This includes the direct application of chlorine gas as well as the use of pre-formed hypochlorites. Cyanide oxidation with hypochlorite at pH > 10 yields in the first stage the much less toxic cyanate (56),

$$CN^- + ClO^- \longrightarrow CNO^- + Cl^-. \qquad (58)$$

The process is both quantitative and fairly rapid for most cyanide complexes, with some exceptions. Ferrocyanide, $[Fe(CN)_6]^{4-}$, is converted to $[Fe(CN)_6]^{3-}$ only, whereas the oxidation of $[Ni(CN)_4]^{2-}$ according to Equation 58 proceeds at a rather slow rate.

In some instances, the discharge of cyanate, which readily hydrolyses to yield ammonia,

$$CNO^- + H_3O^+ + HOH \longrightarrow NH_3 + H_2CO_3 \qquad (59)$$

is not permissible, and secondary oxidation to elemental nitrogen is required

$$2CNO^- + 3ClO^- + H_2O \rightarrow N_2 + 2HCO_3^- + 3Cl^-. \quad (60)$$

The first oxidation step (Equation 58) requires a relatively higher pH to prevent formation of toxic cyanogen chloride gas

$$CN^- + HOCl \longrightarrow ClCN + OH^- \qquad (61)$$

and evolution of hydrogen cyanide, while the second reaction (Equation 60) proceeds most favorably in the pH range 7.5-9.

Heavy metal removal by alkaline precipitation may be - and most commonly is - regarded as coincidental to cyanide. oxidation. In these circumstances carbonate levels and pH may vary substantially, depending on the degree of oxidation (Equations 58 and 60) and subsequent chemical operations. Differences in physical treatment conditions, such as agitation and sedimentation, must also be expected and taken into consideration.

A. Analytic Technique

The study of reactions with equilibrium concentrations of cadmium in the ppm and sub-ppm range calls for a precise and rapid analytic technique. The methods capable of the desired precision (Chapter I. D.) were ruled out on the basis of time involvement and, above all, the lack of appropriate instrumentation. Employment of a suitable radioisotope and subsequent counting of activity appeared as the most promising approach. The tracer found useful for this purpose is ${}_{48}Cd^{115m}$ with a half-life of 43 days (58). It is commercially available* in 99+ % radiopurity in form of $CdCl_2$ in 0.5 N hydrochloric acid. The decay process for ${}_{48}Cd^{115m}$ yields ${}_{49}In^{115}$ by emission of a 1.63 MeV β^--particle. The high specific activity of Cd^{115m} affords direct measurement in aqueous solution based on Cerenkov radiation (57).

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*New England Nuclear, No. NEZ-012

Light emission in the wavelength band between 3000 and 7000 Å is produced when β-particles of sufficient energy (> 260 keV) pass through aqueous solution at a speed greater than that of light. Since the photon yield is relatively low, the practical range of Cerenkov counting requires β-emission energies of ≈1 Mev and greater. Detection efficiencies for Cerenkov radiation depend strongly on β-energies. Typical values for absolute counting efficiencies are: 25 % for P^{32} (E_{max} = 1.71 MeV (100 %)) and 14 % for K^{40} (E_{max} = 1.32 MeV (89 %)). With $_{48}Cd^{115m}$ (E_{max} = 1.63 MeV (97 %)), a Cerenkov counting efficiency of ≈ 35 % has been realized in the technique described using the Beckman Model CPM-200 liquid scintillation counter. Light emission in Cerenkov radiation is relatively weak in intensity and has a continuous energy mainly concentrated in the ultraviolet region. Thus, the majority of events were measurable in the low energy, or tritium channel (cut-off point at ≈0.018 MeV), of the instrument used.

In spite of low photon yields and relatively weak emission energies characteristic for Cerenkov counting, the method offers several advantages over conventional liquid scintillation techniques. Sample preparation is simple and no scintillation "cocktail" is required. Volumes of up to approximately 20 ml may be counted, which tends to compensate for the apparent loss in efficiency. Furthermore, the efficiency is unaffected by chemical quenching (57).

The weak decay energy of $_{49}In^{115}$ (E_{max} = 0.6 MeV), relative to the requirements for Cerenkov counting,rules out the possibility for interference by subsequent radiation events from the decay product of $_{48}Cd^{115m}$. This assumption has been verified experimentally by repeated counting checks made against the decay curve for the cadmium isotope.

Within the range of 15-21 ml, volume effects on counting efficiency were found negligible, however, for reasons of consistency, viles were usually filled to a volume of approximately 20 ± 1 ml. By nature of the counting technique, losses in efficiency are also to be expected due to light absorption by solids or colored components present in the sample. While colored solutions were not encountered, the occurrence of solids was eliminated by acidification of all samples with HNO_3 (to pH < 2) prior to radioassay. This procedure proved advantageous also with respect to minimizing wall adsorption of the tracer and the consequent difficulties of cleaning of the sample viles for re-use. For the same reason, viles made of polyethylene were preferred over those made of glass. Acidified aqueous samples stored in polyethylene viles showed excellent counting stability over weeks, taking into account their normal decay pattern.

The CPM-200 is a highly automatic, ambient temperature soft-beta spectrometer, which can accomodate 200 samples. It provides electronic computation (2 Sigma, statistical error) and print-out results programmed on a preset-time or preset-error basis, among other features. By use of the new Beckman RCA bialkali photomultiplier tubes, the system achieves a very high quantum efficiency and a negligible thermoionic noise background up to 40°C. Background counts with empty well or washed viles were found in the order of 30-50 counts per minute (cpm), which was ordinarily considered negligible in view of the high count rates ($> 10{,}000$ cpm) of most samples measured.

The general technique used in most phases of this study for handling and measuring of solutions labelled with ${}_{48}Cd^{115m}$ is summarized below. Variations of these procedures are discussed in the appropriate sections.

A stock solution of 500 ml was prepared in a polyethylene bottle by dilution of 2 mc of ${}_{48}Cd^{115m}$ with 0.01 N nitric acid resulting in approximately 10^{-4} moles/l of isotope, depending on the radiometric purity of the $CdCl_2$ supply. Transfers of radioactive solutions and other solutions containing minute amounts of cadmium were done with labware made of teflon, polypropylene or polyethylene, since these materials were found to have the lowest adsorptive properties relative to aqueous species of cadmium. Sample volumes in viles were always determined by weight with consideration of the specific gravity of individual solution systems. All samples were acidified to $pH < 2$ with small amounts of ≈ 4 $\underline{N}$ HNO_3 prior to counting. In most cases the statistical counting error was set to ± 2 %, or better, depending on specific activities. Corrections for decay during counting were not made in view of the short times elapsed and the relatively long half-life of the radioisotope. The linearity between tracer concentration and count-rate per unit amount of tracer was established repeatedly and over a wide range of activities. Thus, only a limited number of standards were run with each sample batch for purposes of calibration.

B. Preliminary Explorations

Initial efforts of this study were directed towards verification of the solubility models presented in Chapter II under a variety of conditions. Because in most water treatment applications cadmium solubility considerations pertain to aspects of removal - rather than to dissolution of well defined crystals - it is more meaningful from a practical applications standpoint to approach equilibrium via precipitation.

In the range pH 8.5 - 11, $[CO_3]_{TOT} = 10^2\text{-}10^{-3}$ $\underline{M}$, $\mu = 0.01\text{-}0.05$ and $[Cd]_o = 10^{-3}\text{-}10^{-4}$ $\underline{M}$, the formation of precipitates was observed to occur almost instantly under moderate mixing conditions. The magnitude of the initial drop in soluble cadmium varied greatly with physical conditions in addition to chemical factors. Moreover, it was found that rates of attainment of equilibrium after the initial phase, measured in terms of residual cadmium in solution, were rather slow and highly irreproducible. Investigation of kinetic parameters of influence on the rate of precipitation was therefore considered of primary significance, particularly with respect to industrial waste treatment.

Serious difficulties were encountered during handling, especially filtration of cadmium containing solutions, due to losses of the metal by adsorption on container walls. The effect is most pronounced in systems of low concentration ($< 10^{-7}$ $\underline{M}$ as Cd) and at pH > 7, as prevail after initial precipitation in alkaline solutions. Semiquantitative studies revealed that sorption of cadmium at pH > 7 occurs on pyrex glass, stainless steel, Nalgene TPX (polycarbonate), plexiglass, linear polyethylene and polypropylene, given in the order of decreasing affinity. No losses were observed due to sorption on teflon, and those found for polypropylene and linear polyethylene were considered minimal. The latter two materials were chosen for handling and storage of acid cadmium solutions, under which conditions they exhibited no sorptive properties towards cadmium.

Membrane filtration was used for separation of solids from the liquid phase. Here, it was found necessary to replace all components of the filter holder by parts made of teflon. There was little choice with respect to the membrane filters of microporosity (100 - 450 mμ). Glass fibre and paper filters were found inferior due to sorption, and membrane filters made of polyethylene or teflon were not available in the desired porosities.

Sorptive uptake by the conventional cellulose base millipore filters* was found relatively small, but became negligible by employing larger pore sizes (450 mμ) with faster filtration rates and by discarding a substantial portion of the filtrate. In several cases it was shown that the sorptive uptake of cadmium by membrane filters approached equilibrium after filtration of a given volume of solution, but that the equilibrium value was independent of pore size between 100 and 450 mμ. At least for these conditions, the presence of particles of a size between this range (colloidal range) can be ruled out.

In contrast to the rigorous and relatively simple conditions employed in the study of mechanisms for nucleation and crystal growth (59), those characteristic for practical applications of precipitations are usually not suited for mechanistic interpretation. Precipitation by direct mixing of reactants has been called the most complicated process for which kinetic analysis is attempted (60). Much of this dilemma arises from the strong influence of physical conditions (i.e. rate of addition, rate of mixing, vessel geometry etc.) on the nucleation - and subsequently the crystal growth process - a phenomenon with poor reproducibility. Kinetic experiments performed in closed polyethylene bottles, which were kept mixed using a mechanical shaker, have demonstrated these effects beyond doubt. Since simulation of

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* Metricel GA-6; Gelman Instrument Company, Ann Arbor, Michigan

widely varying physical conditions found in actual treatment plants is a fruitless endeavor, the focus in this study was placed mainly on the influence chemical factors exert on the kinetics of cadmium precipitation. In view of the foregoing, the design of physical conditions for these experiments was - to a large extent - guided by the objective of optimum reproducibility and consistency.

Some further attempts were made to check the validity of the solubility diagrams presented in Chapter II. However, equilibrium - though closely approached (Table 6) - was not attained after shaking of the solutions in closed polyethylene bottles for a period of four weeks. In view of the lower priority of these experiments, and the uncertainty of long-term stability of aqueous carbonate solutions, further investigations of this type were not undertaken. Table 6 shows residual cadmium concentrations obtained by radioassay of membrane filtered systems after shaking in sealed polyethylene bottles for four weeks at room temperature.

TABLE 6

Comparison of Equilibrium Solubilities for Cadmium with Values Obtained Experimentally*

pH	Cd found ppb	Solubility of Cd at 25°C corrected for μ = 0.05 ppb
9.0	8.9	5.4
9.45	10.0	2.9
9.95	5.6	3.3
10.45	9.5	9.6

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* Experimental Conditions: $\mu = 0.05$ ($NaClO_4$), $[Cd]_o = 10^{-4}$ M, $[CO_3]_{TOT} = 10^{-2}$ M, time: 4 weeks; ambient temperature.

C. Experimental Details

1. Chemicals and Solutions

All chemicals used were of standard reagent grade unless otherwise specified. Stock solutions of 10^{-2} $\underline{M}$ $Cd(NO_3)_2$ and 10^{-2} $\underline{M}$ HNO_3 were prepared by dissolution of reagent grade cadmium metal in appropriate amounts of 2 $\underline{M}$ nitric acid and distilled water. The preparation of the stock solution of the radioisotope (${}_{48}Cd^{115m}$) has been described in section III.A.. All other reagent solutions used in the experiments were made and standardized according to well established procedures (11). Frequent titrations of the distilled water used revealed a CO_2 level of 10^{-4} $\underline{M}$ or less.

2. Equipment

Measurement of pH was performed using a Beckman Zero-Matic pH-meter with a calomel/glass electrode couple. Precipitation reactions were carried out in vessels (Figure 9) made of 3/8 inch plexiglass. The solutions were kept agitated with pyrex-stirrers (Figure 9) by means of synchronous motors. Stirrer speeds were regulated by adjustable power-stats with primary voltage stabilization and measured with a stroboscope, calibrated in rpm. A Thermostated waterbath was employed for temperature control. Suction, provided by an aspirator pump, was applied to facilitate filtration of samples. Further details on

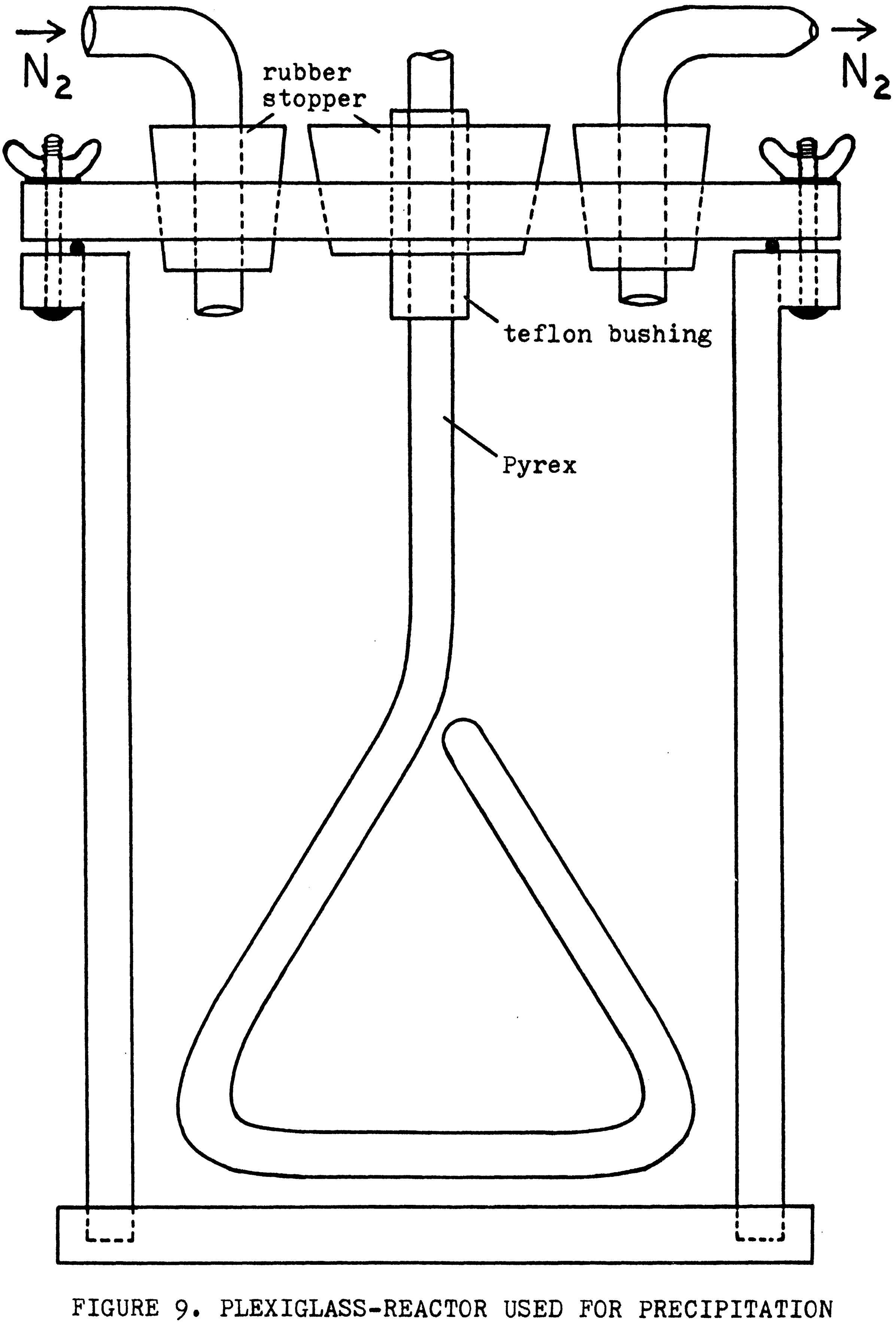

FIGURE 9. PLEXIGLASS-REACTOR USED FOR PRECIPITATION EXPERIMENTS (Scale: 1:1).

filtration and measurement of samples have been given in preceding sections. Standard laboratory glassware was used except for handling of solutions containing cadmium, for which containers and devices made of teflon, polyethylene and polypropylene were employed. These are further described in the discussion of procedures.

3. Procedures

Rates of precipitation of cadmium from alkaline carbonate solution were followed by the disappearance of soluble cadmium from solution. All runs were performed in a closed plexiglass vessel (Figure 9), at controlled agitator speed, constant temperature, and under a blanket of chemically pure nitrogen. Aside from experimental variations to determine the influence of one specific variable on the rate of precipitation, the following conditions were employed:

volume at $t = 0$: 800 ml
temperature : $27 \pm 0.5^{\circ}C$
agitator speed : 400 rpm
$\mu = 0.05\ (NaClO_4)$
$[CO_3]_{TOT} = 10^{-2}\ \underline{M}$
$[Cd]_o = 10^{-4}\ \underline{M}$
$[{}_{48}Cd^{115m}]_o \approx 10^{-6}\ \underline{M}$

Initially, a volume of 780 ml was prepared by mixing predetermined quantities of the reagents, except for Cd and ${}_{48}Cd^{115m}$, with distilled water (containing $[H_2CO_3] < 10^{-4}\ \underline{M}$), to a given pH. An additional quantity of NaOH was included for neutralization of the acid solutions of cadmium, which were added at a later time. After closing, the vessels were set in the waterbath and stirred at 400 rpm for ≈ 30 mim under a flow of ≈ 0.5 l/min of nitrogen until reaction temperature was reached.

Solutions containing either radioactive or stable cadmium were transfered with polyethylene pipettes into a 100 ml teflon beaker and mixed with distilled water to give a total volume of 20 ml of the reactant solution. At time zero, the reactant solution was added to the vessels by pouring the total beaker content into an open polyethylene syringe (no needle attached, capacity : 30 ml), positioned over the nitrogen outlet of the vessel. This method gave reproducible reactant flow, and losses of the solution by adhesion on the walls were not observed. Plexiglass was found appropriate for use as reactor material, since cadmium losses by adsorption on this material were negligible relative to the high concentration (10^{-4} $\underline{M}$ as Cd) employed.

Sample portions of ≈ 20 ml were drawn from the vessel by means of a polyethylene syringe (30 ml), to which a polyethylene tube had been attached. These were directly transfered into the filter funnel (teflon) and filtered through a 450 mμ membrane under slight negative pressure provided by an aspirator pump. The first portion of ≈ 20 ml was discarded, whereas the second was directly filtered into the vile attached to the filter assembly. Usually, two identical systems were run in parallel: thus, filter cleaning or replacement was not necessary when duplicate samples were taken in succession. Otherwise, the membranes were treated with ≈ 1 N HNO_3 and thoroughly washed with distilled water before a new sample was filtered. The membranes were discarded after each batch. Soluble cadmium in the filtrate was determined by radioassay as discussed in section A. of this Chapter.

D. Treatment of Data

As mentioned in section III. B., the bulk of the precipitate was found to form almost instantly (see also Figure 10) under a wide range of conditions investigated. From the standpoint of practical applications, it is of considerable interest to know the extent of bulk removal as well as the rate of secondary growth as functions of operational parameters.

In view of the complex nature of the systems under study and of the limitations of the experimental technique with respect to studying nucleation in detail, it was found appropriate, to treat both phases of the precipitation separately. This practice seems very common in the study of complex precipitation reactions (60).

Figure 10 shows a representative plot for residual cadmium (logarithmic scale) versus time for a given set of conditions. The rapid initial fall-off in solute species

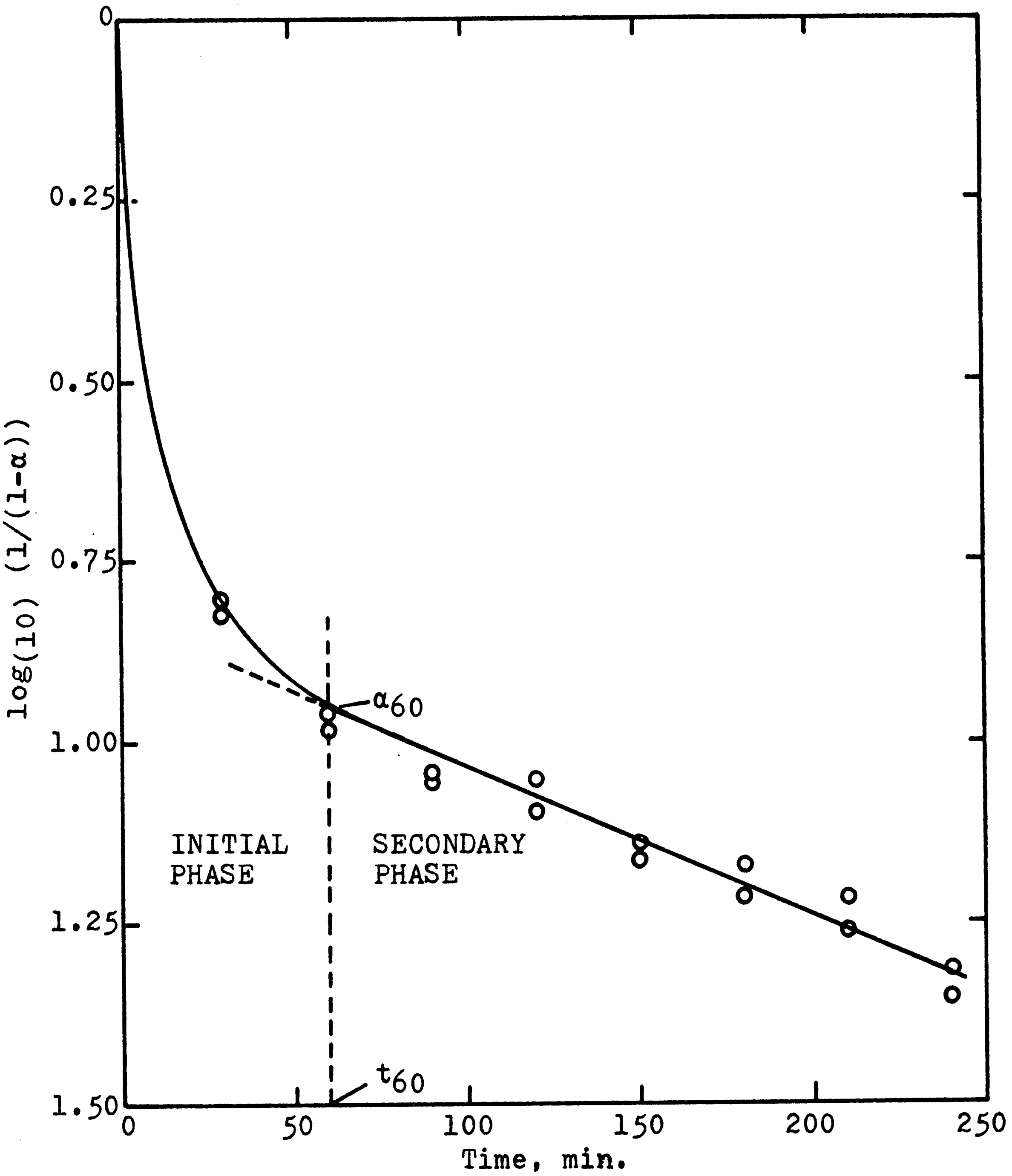

FIGURE 10. GRAPHICAL REPRESENTATION OF CADMIUM PRECIPITATION DATA.

Experimental Conditions: pH 9.5, t = 27±0.5 °C, 400 rpm, $[CO_3]_{TOT} = 3.5 \cdot 10^{-3}$ $\underline{M}$, $[Cd]_o = 10^{-4}$ $\underline{M}$, $\mu = 0.05$ ($NaClO_4$). $\alpha = ([Cd]_o - [Cd]_t)/[Cd]_o$ = fraction of cadmium precipitated.

followed by a steady rate of secondary precipitation or precipitate growth is apparent from this figure and was found qualitatively typical for all experiments. The reproducibility of independent runs is also shown by the duplicate data points on the figure. In order to examine the influence of specific variables on the secondary precipitation rate, an empirical rate expression was needed, which would accomodate all data under a wide range of conditions.

Several empirical equations have been employed for fitting of kinetic data for precipitation reactions, but theoretical interpretation and justification leaves much to be desired (51,59,60). This is true even for the treatment of classical examples of precipitation, such as that of $BaSO_4$ under well defined reaction conditions.

Purely chemical consideration of a system containing the species: OH^-, H_3O^+, CO_2^*, HCO_3^-, CO_3^{2-}, Cd^{2+}, $CdOH^+$ and $Cd(OH)_{2(aq)}$ with their relative distribution changing as a function of pH, suggests a very complex kinetic pattern for cadmium precipitation. Apart from the strong possibility for simultaneous operation of several mechanisms under one given set of conditions, variations in mechanisms, and consequently in rate laws, must be expected for different pH values.

A general equation used for empirical treatment of precipitate growth phenomena is

$$\frac{d\alpha}{dt} = k^n (1-\alpha)^p, \qquad (62)$$

in which n is usually a fractional power, k is the rate constant and p an integer ranging from 0 - 4, depending on the order of the reaction (60). The term α designates the fraction precipitated and can assume values from 0 - 1 only. By this definition, α in terms of concentrations

$$\alpha = \frac{C_o - C_t}{C_o - C_s} \qquad (63)$$

is a dimensionless reaction variable. In Equation 63, C_o and C_t stand for the concentrations at time zero and t, respectively, while C_s is the solubility limited concentration (saturation concentration) of the same species for a specific system. In relation to cadmium, the terms C_o, C_t and C_s are equivalent to the concentration terms $[Cd]_o$, $[Cd]_t$ and S, respectively.

As shown in Figure 10, a plot of $\log_{(10)}(1/(1-\alpha))$ versus time yields a fairly linear trace for the secondary growth phase, that is, for the time range beyond 60 minutes. Of several other rate expressions, a first-order representation was found the most reasonable approximation for fitting of the data obtained under a wide range of experimental conditions for the secondary phase. Because a gradual transition between the initial and secondary phase of the reaction can be reasonably assumed, a definite separation of the two rate components is neither justified nor is it easily accomplished in view of insufficient data for the initial phase (Figure 10). The demarcation line of 60 minutes was chosen, because it represents the minimum time required for accomodation of all experimental data. While this boundary between the two reaction phases affords a convenient comparison and quantitative treatment of the data, it should not be interpreted as a theoretical dividing line between two independent rate components.

In terms similar to Equation 62, the rate expression used for description of data for the secondary growth phase is

$$\frac{d\alpha}{dt} = k\ (1-\alpha). \tag{64}$$

Since the solubility of cadmium, S, is negligible relative to the initial concentrations, C_o, ($C_o >> S$) the fraction precipitated can be closely approximated by

$$\alpha = \frac{C_o - C_t}{C_o}, \tag{65}$$

or in terms of cadmium by

$$\alpha = \frac{[Cd]_o-[Cd]_t}{[Cd]_o}. \tag{66}$$

The first-order rate coefficients, k values, for the data presented were obtained by graphical evaluation of plots of log $(1/(1-\alpha))$ versus time (Figure 10), in which the slope is equal to k/2.303. Information on the extent of precipitation at a time of 60 minutes (α_{60}) obtains from the intersection of the secondary growth-line with the "60 minute" line as shown in Figure 10. For convenient calculation of the extent of precipitation under experimental conditions from the data, presented in terms of α_{60} and k, equation 64 is integrated between the limits (α_{60}, 60) and (α_t, t), and rearranged:

$$\log (1-\alpha_t) = \log (1-\alpha_{60}) - \frac{k\ (t_2-60)}{2.303} \qquad (67)$$

with the condition that $t_2 > 60$ minutes.

The mathematical form of the rate expression used (Equation 64) implies that the rate of secondary growth is proportional to the unprecipitated fraction present in solution. This requires that k be independent of the initial cadmium concentration, C_o, which indeed was found experimentally to be the case. From the foregoing discussion it should be evident that the mathematical representation of the second phase precipitation data by a first-order rate expression is strictly empirical and has, in view of the complexity of the system and general lack of understanding of precipitation phenomena, no theoretical meaning. The first-order rate expression of cause does not even apply to the initial precipitation data.

E. Results and Discussion

Nucleation and crystal growth are generally strongly affected by the rate and mode of agitation. Poor reproducibility, settling and deposition of crystals are problems observed in lower mixing regimes (< 200 rpm), while distortion of the boundary layer at the crystal surface and subsequently poor growth frequently occurs at very high agitator speeds (60). For these reasons and for mechanical stability, a speed of 400 rpm was chosen for the experiments. In this range and in view of small agitator speed variations during runs (< 5 %), the influence of agitation on the data obtained is considered minimal and essentially constant. Under otherwise identical conditions, variations in growth rates, expressed in terms of k values, for 325, 400 and 500 rpm, were found to be 0.0172, 0.0181 and 0.023 min^{-1}, respectively.

1. Effect of Cadmium Concentration

The validity of the first-order rate relationship (Equation 64) for description of the secondary precipitation rate data was verified with three different initial cadmium concentrations. Furthermore, it was confirmed by the linearity of logarithmic rate representations (e.g. Figure 10) for a wide range of cadmium concentrations and experimental conditions.

Table 7 shows kinetic data for the precipitation of cadmium at different initial cadmium concentrations under the following conditions:

$$\text{pH } 9.5;\ t = 27 \pm 0.5^{\circ}\text{C};\ 400 \text{ rpm};$$
$$[CO_3]_{TOT} = 10^{-2}\ \underline{M};\ \mu = 0.05\ (NaClO_4).$$

TABLE 7

Effect of Initial Cadmium Concentration on Rate of Precipitation of Cadmium

$[Cd]_0 \cdot 10^5$ M	α_{60}	$\log\left(\frac{1}{1-\alpha_{60}}\right)$	k min^{-1}
5.0	0.946	1.27	0.0179
10.0	0.960	1.40	0.0181
20.0	0.980	1.70	0.0182

Most runs were followed to a final cadmium concentration in solution in the range of $\approx 10^{-7}$ M. Thus, from the data presented in Table 7, it may be concluded that the secondary precipitation rate for cadmium under the conditions studied can be represented by a first-order relationship with respect to cadmium for a range of [Cd] from 10^{-7} to 10^{-4} M.

The initial extent of the reaction, expressed in terms of α_{60}, tends to increase slightly with increasing initial cadmium concentration (Table 7) in the range of $5\text{-}20 \cdot 10^{-4}$ M Cd. While this observation may - at least in part - be attributed to nucleation phenomena, the constancy of k suggests that the secondary growth rate is fairly independent of the number of nuclei and thus limited by a different process. In the net-deposition of solute material on nuclei one must also consider the influence of back reactions (51), that is the dissolution of pre-formed crystals, which may proceed via various paths, e.g.:

$$(A_nB_n)_{(solid)} \longrightarrow (A_{n-1}\ B_{n-1})_{(solid)} + AB_{(aq)} \qquad (68)$$

$$(A_nB_n)_{(solid)} \longrightarrow (A_{n-1}\ B_n)^-_{(solid)} + A^+_{(aq)} \qquad (69)$$

$$(A_nB_n)_{(solid)} \longrightarrow (A_n\ B_{n-1})^+_{(solid)} + B^-_{(aq)} \qquad (70)$$

The rates of these reaction steps are very likely influenced by the solubility of the salt (AB) and the degree of supersaturation in solution, among other factors (60).

2. Effect of Carbonate Concentration

The concentration of total carbonic acid species, $[CO_3]_{TOT}$, governs the equilibrium solubility of cadmium (i.e., when $R < 0.00423$) and, as shown in Figure 11, is also of strong influence on the overall rate of precipitation.

The effect of carbonate concentration on the initial extent of the precipitation (α_{60} values) compares well with that observed for cadmium concentration (Table 7), and is probably also related to the nucleation process, because both cadmium and carbonate are "common ions".

The acceleration of the secondary rate of precipitation by carbonate species appears unrelated to nucleation in view of the constancy of k values over a wide range of cadmium concentrations, and considering the advanced stage of the reaction. The kinetic behavior is consistent, however, with the operation of reverse reactions (Equations 68 - 70), because these are expected to decelerate with increasing concentration of carbonate species. An alternative interpretation of the effect of carbonate can be made on the basis of variations in the composition of nuclei. At constant pH,

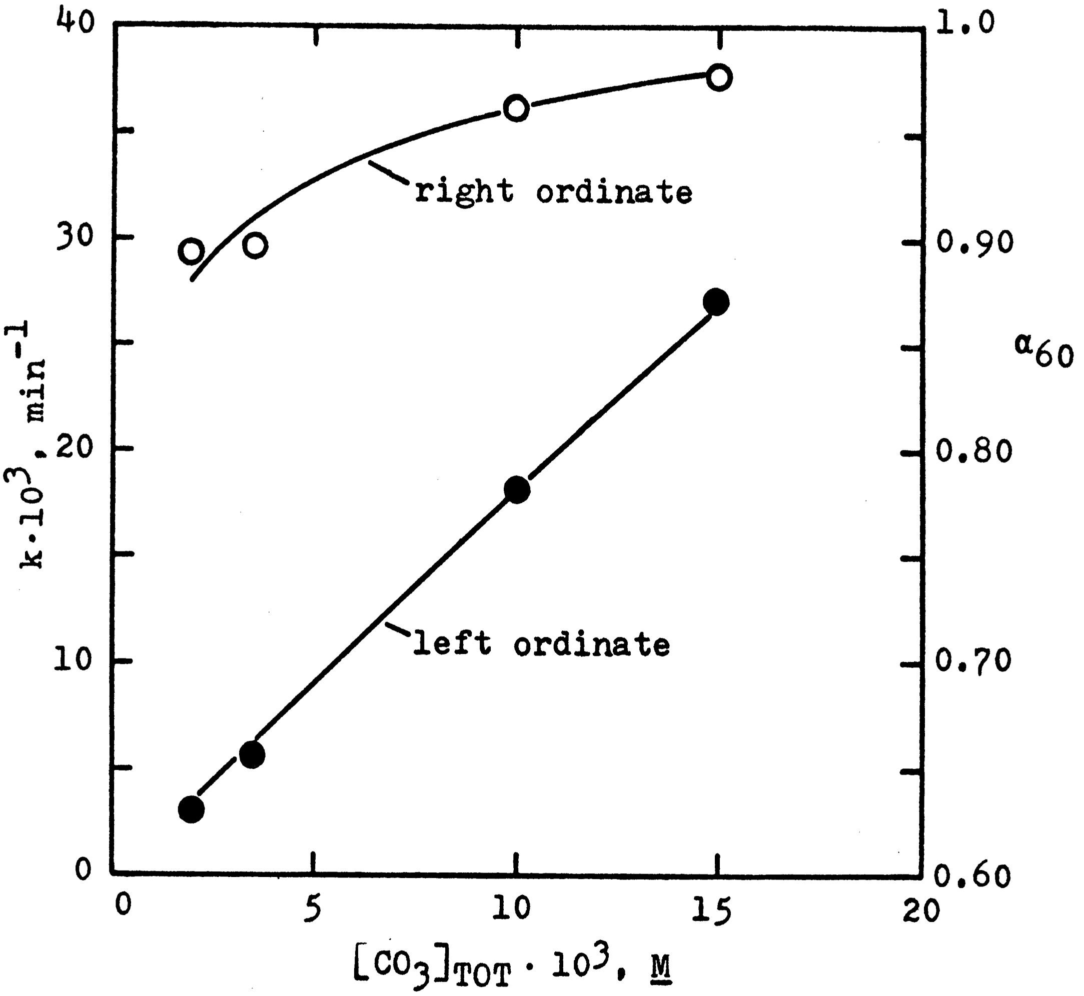

FIGURE 11. EFFECT OF CONCENTRATION OF CARBONATE ON RATE OF PRECIPITATION OF CADMIUM.

Experimental Conditions: pH 9.5, t = 27±0.5 °C, 400 rpm, $[Cd]_0 = 10^{-4}$ M, $\mu = 0.05$ ($NaClO_4$). In the graph, open circles (right-hand scale) and solid circles (left-hand scale) represent α_{60} and k values, respectively.

the carbonate/hydroxide ratio increases in proportion to the carbonate concentration. Because the solubilities of both cadmium carbonate and hydroxide are exceeded under these experimental conditions, the composition of initially formed crystals is expected to vary with the ratio of the respective anions. In this light, the secondary growth of $CdCO_3$ crystals at low carbonate levels would be greatly distorted and probably involve the re-dissolution of $Cd(OH)_2$, while this tendency would decrease in magnitude at higher carbonate/hydroxide ratios.

More definite information on precipitation mechanisms for cadmium carbonate systems would be obtained by study of nucleation and growth kinetics at lower pH, where the solubilities of $Cd(OH)_2$ and $CdCO_3$ are not exceeded concurrently. By the nature of carbonate equilibria, these systems would require controlled carbon dioxide pressure and, consequently, sealing against the atmosphere.

As discussed in the following section, both species, HCO_3^- and CO_3^{2-} can lead to formation of cadmium carbonate, and since the rates for carbonate-bicarbonate equilibria are extremely rapid, a kinetic and mechanistic differentiation in terms of cadmium carbonate formation is extremely difficult.

3. Effect of pH

The variation of solute species and solubility of cadmium as function of pH suggests a direct and strong influence of this parameter on the kinetics of precipitation of cadmium from alkaline carbonate solutions. Experimental evidence for this is presented in Figure 12, which shows the effect of pH on the initial reaction extent (α_{60} values) and on the rate of the secondary phase (k values) of cadmium precipitation in the presence of 10^{-2} M total carbonic acid species.

The equilibrium concentration of $CO_3^{=}$ increases from $\approx 5.3 \cdot 10^{-3}$ M at pH 9 to $\approx 8.5 \cdot 10^{-3}$ M at pH 11, however, the rate of secondary growth decreases over this pH range, while the initial extent of the reaction (α_{60}) goes through a minimum.

A better understanding of this behavior is gained from inspection of the appropriate distribution diagrams and of possible elementary reactions leading to the reaction products. The following reaction schemes appear of interest in this light:

$$Cd^{2+} + HCO_3^- \longrightarrow CdHCO_3^+ \tag{71}$$

$$CdHCO_3^+ + OH^- \longrightarrow CdCO_{3(s)} + HOH \tag{72}$$

$$CdOH^+ + HCO_3^- \longrightarrow CdCO_{3(s)} + HOH \tag{73}$$

$$Cd^{2+} + CO_3^{2-} \longrightarrow CdCO_{3(s)} \tag{74}$$

$$CdCO_{3(aq)} \longrightarrow CdCO_{3(s)} \tag{75}$$

$$CdOH^+ + OH^- \longrightarrow Cd(OH)_{2(s)} \tag{76}$$

$$HCdO_2^- + HOH \longrightarrow Cd(OH)_{2(s)} + OH^- \tag{77}$$

$$Cd(OH)_{2(aq)} \longrightarrow Cd(OH)_{2(s)} \tag{78}$$

Although the relative role and contribution of these reactions to the net-rate of cadmium precipition is unknown, a

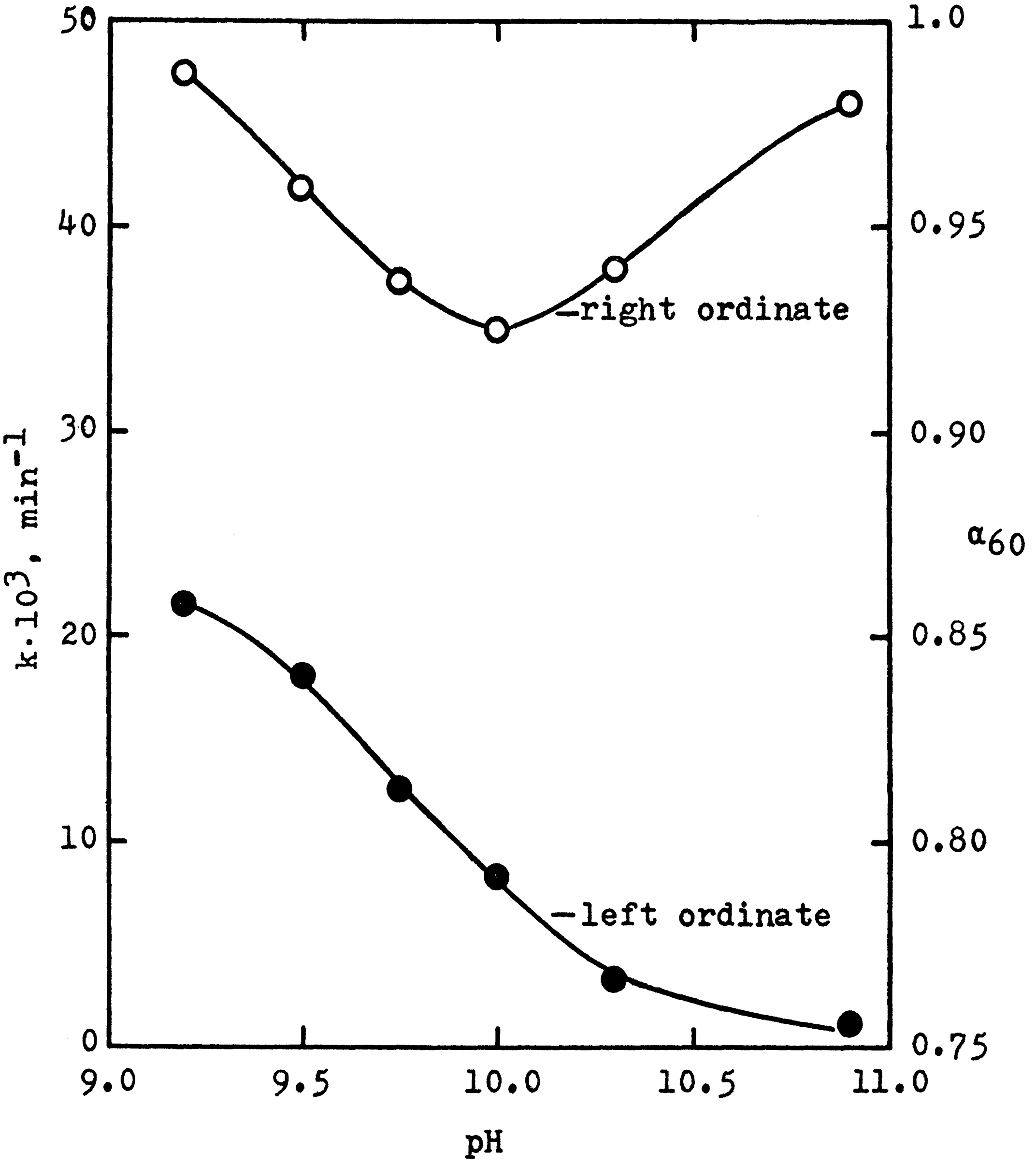

FIGURE 12. EFFECT OF pH ON RATE OF CADMIUM PRECIPITATION.

Experimental Conditions: $t = 27 \pm 0.5$ °C, 400 rpm, $[CO_3]_{TOT} = 10^{-2}$ M, $[Cd]_0 = 10^{-4}$ M, $\mu = 0.05$ ($NaClO_4$).
In the graph, open and solid circles represent α_{60} and k values, respectively.

relationship between this chemistry and the observed reaction rates as functions of pH seems to exist. Two types of mechanisms are indicated both by the kinetics and by the nature of the products. In the lower pH range, the formation of $CdCO_3$ by reactions of the types shown in Equations 71-75, appears to predominate, whereas the other extreme would be represented by the production of cadmium hydroxide (Equations 76-78) at the high end of the pH scale. In this perspective it must be realized that Cd^{2+} and $CdOH^+$ are the only reasonable species leading to $CdCO_3$, and that their existence ceases beyond pH 12.

Precipitates obtained at pH 9.5 and in the presence of 10^{-2} $\underline{M}$ carbonate (as $[CO_3]_{TOT}$) exhibited a neutral reaction in water, and an acid titration pattern and behavior characteristic of carbonates. Those formed at pH 10.9 under otherwise identical conditions, however, show evidence for both carbonate and hydroxide. A quantitative characterization of the chemical composition of these precipitates has not been undertaken, because of the inherent experimental difficulties. It must also be realized that the chemical composition and morphologies of carbonates and hydroxides tend to change with age and rate of precipitation (61). The formation of basic carbonates of the kind $(CdCO_3)_x \cdot (Cd(OH)_2)_y$ has been observed under similar reaction conditions (38,39), and frequent inclusion of large amounts of anions in cadmium precipitates seems a common phenomenon (62).

The observed rate variation with pH would therefore be consistent with a gradual transition between the formation of cadmium carbonate and hydroxide, whereby the simultaneous and/or transient occurrence of cadmium hydroxide cannot be ruled out for the lower pH range, since the solubility of both reaction products is exceeded under the experimental conditions.

The increase observed for the initial reaction extent (α_{60}) beyond pH 10 may in part be explained by rapid formation of cadmium hydroxide,

$$Cd(OH)_{2(aq)} \rightarrow Cd(OH)_{2(s)},$$

which is superimposed on a very slow precipitation of cadmium carbonate; the latter represents the therodynamically favored compound. This process is followed by slow crystal growth (k), with a rate dependent on various factors, including species availability at the solid surface, re-dissolution of cadmium hydroxide, phase transformation of the crystals and other related phenomena.

From the standpoint of practical applications, both, the solubility limit and the rate pattern for precipitation should be considered with respect to cadmium removal. In this perspective, the beneficial effect of carbonate is certainly evident. While bulk removal of cadmium in the presence of sufficient carbonate is relatively fast (α_{60} values in Figure 12) between pH 9.2 and 10.9, optimum conditions for secondary growth tend to coincide with the pH range of minimum solubility (Figure 4). This conclusion derives from rate data and solubility calculations. For purposes of illustration, the times for 99.9 % cadmium removal ($\alpha_{99.9}$) at different pH values have been calculated from the data presented in Figure 12 in accord with a modified form of Equation 67:

$$t_{99.9} = \frac{6.909 + 2.3 \log(1-\alpha_{60})}{k} + 60. \qquad (79)$$

These 99.9 % removal times are given in Table 8.

TABLE 8

Calculated 99.9 % Removal Times for Cadmium as Function of pH

pH	9.2	9.5	9.75	10.0	10.3	10.9
$t_{99.9}$, min	177	264	360	590	1360	2460

Note: Conditions cited under Figure 12

Thus, at pH > 10, conditions for cadmium removal are not favorable, as indicated by a rapid increase in the required time ($t_{99.9}$) and by the corresponding solubility. A similar situation exists in the range of pH < 9.3. The solubility increases rapidly, and the net-rate of precipitation is expected to fall off concurrent with the decreasing stability of the species $CO_3^=$ and HCO_3^- when pH is lowered.

4. Ionic Strength and Anion Effects

Small amounts of soluble impurities are known to alter both, the growth rate and crystal habit of precipitates (60). Growth usually tends to be inhibited by foreign ions, mainly due to distortion of the crystal lattice via adsorption on growth sites. Certain ionic or molecular species may also exert specific effects, such as complexation or participation in the growth of crystals. Also, coprecipitation of several salts, as has been discussed for cadmium carbonate and hydroxide, is frequently observed in multicomponent systems. This effect is especially pronounced, when the solubility of all reaction products is exceeded.

Unless otherwise specified, all precipitation experiments were carried out at a constant ionic strength of 0.05, which was adjusted by addition of appropriate amounts of sodium perchlorate. In order to examine specific anion effects, the variation of the rate of precipitation was studied over a range of concentrations of different anions representative for natural and wastewaters. As shown by a plot of the initial reaction extent (α_{60} values) and that of the secondary growth rate (k values) versus the perchlorate-ionic strength in Figure 13, the anion concentration tends to effect nucleation to a higher degree than it does the secondary growth phase within the investigated range of ionic strength. In view of lattice distortions by minute amounts of foreign ions (60), higher rates of precipitation

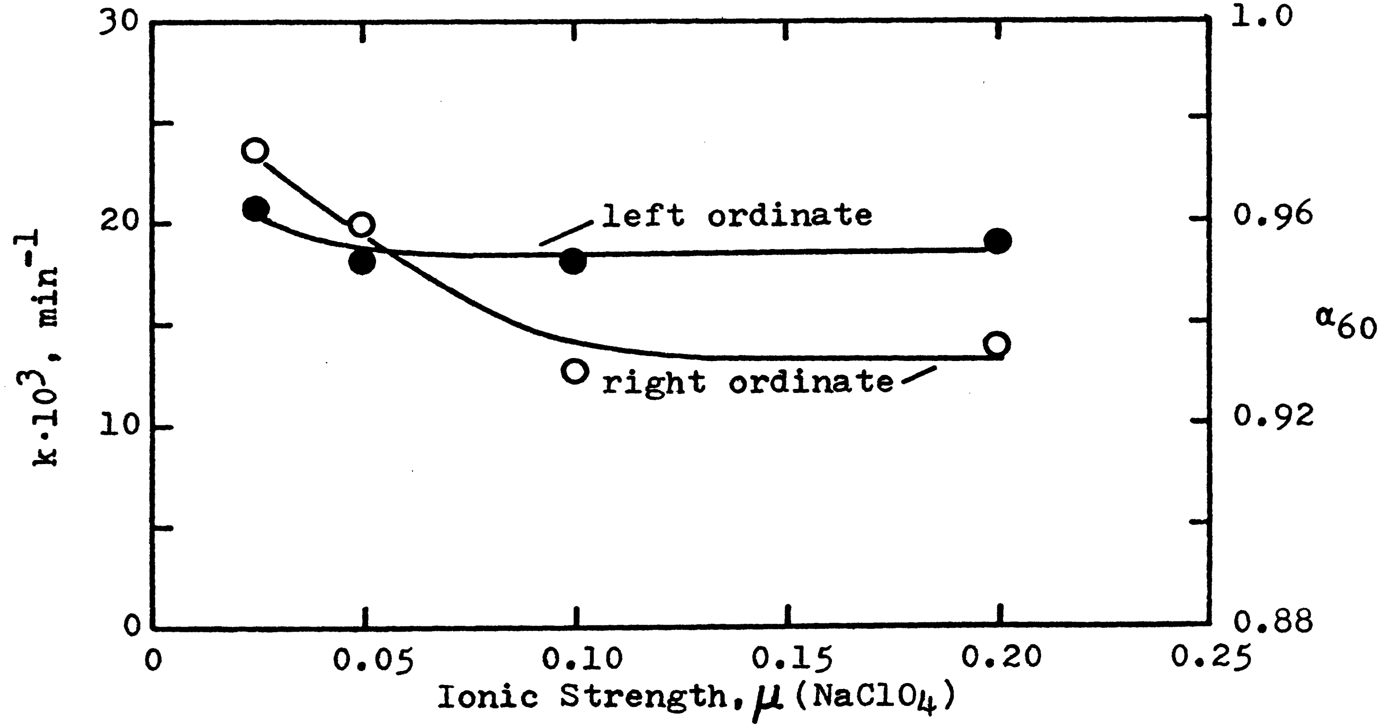

FIGURE 13. EFFECT OF IONIC STRENGTH ON THE RATE OF CADMIUM PRECIPITATION.

Experimental Conditions: pH 9.5, t = 27±0.5 °C, 400 rpm, $[CO_3]_{TOT} = 10^{-2}$ M, $[Cd]_o = 10^{-4}$ M.
In the graph, open and solid circles represent α_{60} and k values, respectively.

are expected, when such ions are completely excluded from the experimental systems (e.g.: $[NaClO_4] = 0$); however, these conditions are of little practical significance.

Other ions of interest, in addition to hydroxide and carbonate, are chloride and sulfate, which are - though in relatively low concentrations - omnipresent in natural water systems. At a constant ionic strength of 0.1, chloride ion, in the range of $0\text{-}8 \cdot 10^{-2}$ $\underline{M}$ as NaCl, does not appear to alter the overall rate of cadmium precipitation (Figure 14) under the experimental conditions (pH 9.5, $[CO_3]_{TOT} = 10^{-2}$ $\underline{M}$, $[Cd]_o = 10^{-4}$ $\underline{M}$) investigated. The effect of chloride ion complexation on the solubility of cadmium (Figure 6) is negligible in view of the high initial concentration of cadmium, and is thus of no measurable consequence on the rate in terms of α, the rate variable

$$\alpha = \frac{[Cd]_o - [Cd]_t}{[Cd]_o - S}$$

$$\alpha = \frac{[Cd]_o - [Cd]_t}{[Cd]_o} \qquad ([Cd]_o >> S) \qquad (66)$$

Thus, the anions ClO_4^- and Cl^- exhibit similar effects on the precipitation of cadmium within the range of experimental conditions investigated.

In contrast to monovalent ions, sulfate has a notable effect on the overall rate of cadmium precipitation, as indicated by the data in Figure 14. The influence exerted on the secondary growth rate (k) is relatively small and its

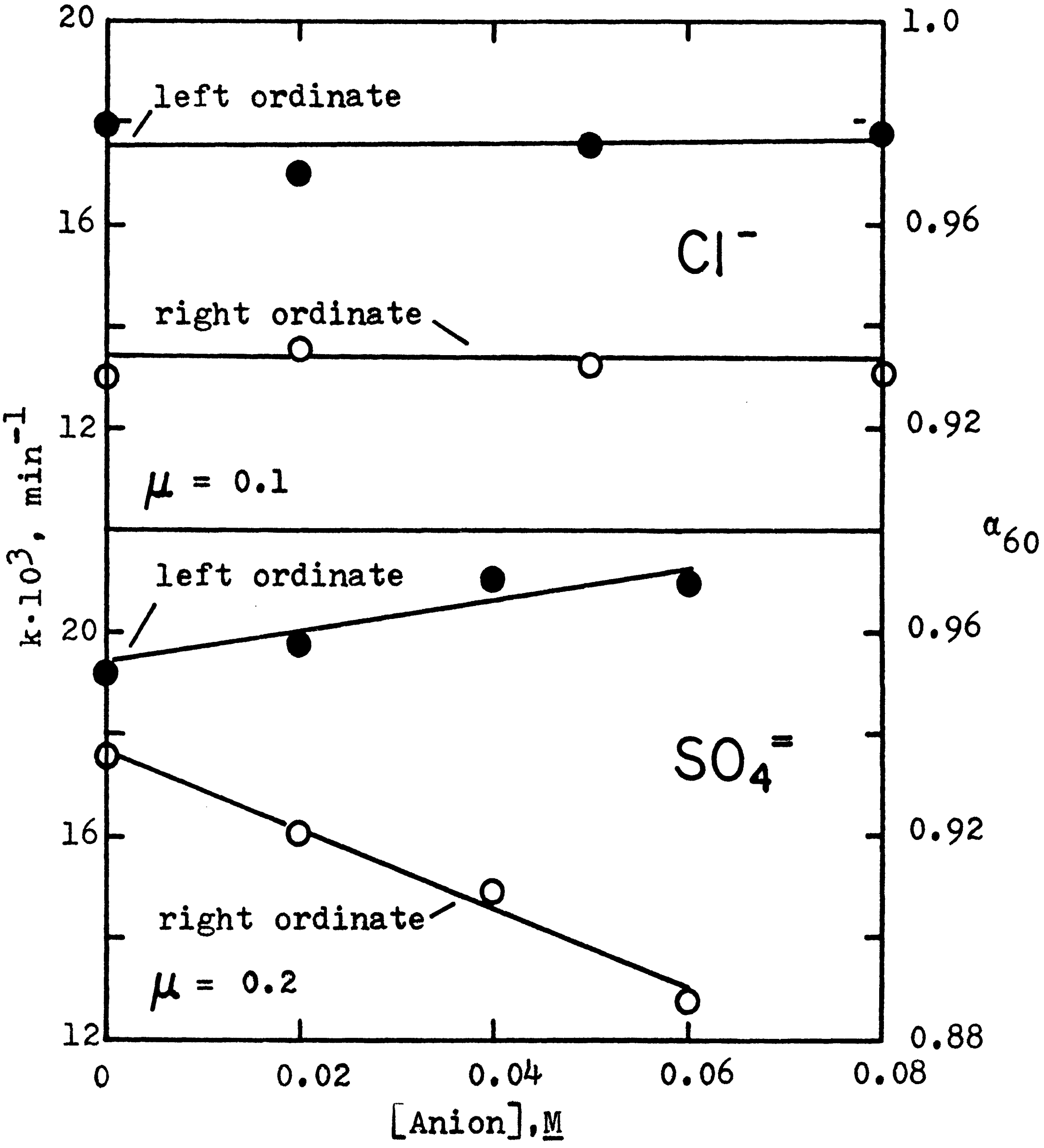

FIGURE 14. EFFECT OF CHLORIDE AND SULFATE ON THE RATE OF CADMIUM PRECIPITATION.

Experimental Conditions: pH 9.5, t = 27±0.5°C, 400 rpm, $[CO_3]_{TOT} = 10^{-2}$ M, $[Cd]_o = 10^{-4}$ M. In the graph, open and solid circles represent α_{60} and k values, respectively.

significance thereto is questionable. The strong dependence of the initial extent of the reaction on the sulfate ion concentration points toward a more pronounced distortion of the crystal lattice by sulfate in the nucleation phase, but alternative explanations cannot be ruled out in the absence of confirmative evidence.

5. Effect of Seeding

Because flexibility with respect to manipulation of the chemistry and, more particularly, mechanical parameters is often limited in large scale applications of precipitation reactions in water treatment, other approaches to enhancing reaction rates are often more attractive.

In chemical precipitation, the method of "seeding" appears very promising in several respects. It obviates the formation of nuclei with the usual induction period, but, more importantly, it tends to accelerate the rate by propagation of growth of higher ordered and more stable crystals. This implies that negative growth factors, such as dissolution of small crystals and phase transitions, may be minimized or completely eliminated when seed crystals are employed. In highly saturated systems, both the propagation of seed crystals and formation of new particles capable of growth, are expected to occur simultaneously. Also, the effect of age and morphology of the seed crystals used must be considered as important rate variables.

With respect to industrial water treatment applications of precipitation processes, recirculation of "sludge" containing pre-formed crystals would constitute the more practical version of seeding. This method is most feasible in continuously operating systems, but may also be used in batch operations.

To examine the feasibility of sludge recirculation, seed crystals were grown under the same conditions (pH, μ, $[CO_3]_{TOT}$) as the precipitation experiments. They were prepared approximately 24 hours before the precipitation experiments and were added from well stirred suspensions prior to the addition of cadmium.

The effect of seeding with previously precipitated cadmium carbonate on the rate of precipitation is shown in Figure 15. Both rate components, particularly however, the initial extent of precipitation (α_{60}), were found to increase considerably with increasing seed concentration. In view of the high initial effect followed by a relatively fast rate of secondary growth, addition of seed crystals - in both batch or continuous mode - appears to be a very promising and feasible method of attaining high efficiency for cadmium removal by precipitation in industrial wastewaters. In this connection it should be mentioned that addition of precipitated calcium carbonate of up to 10^{-4} $\underline{M}$ was found to have no measurable effect on the rate of cadmium precipitation under similar conditions.

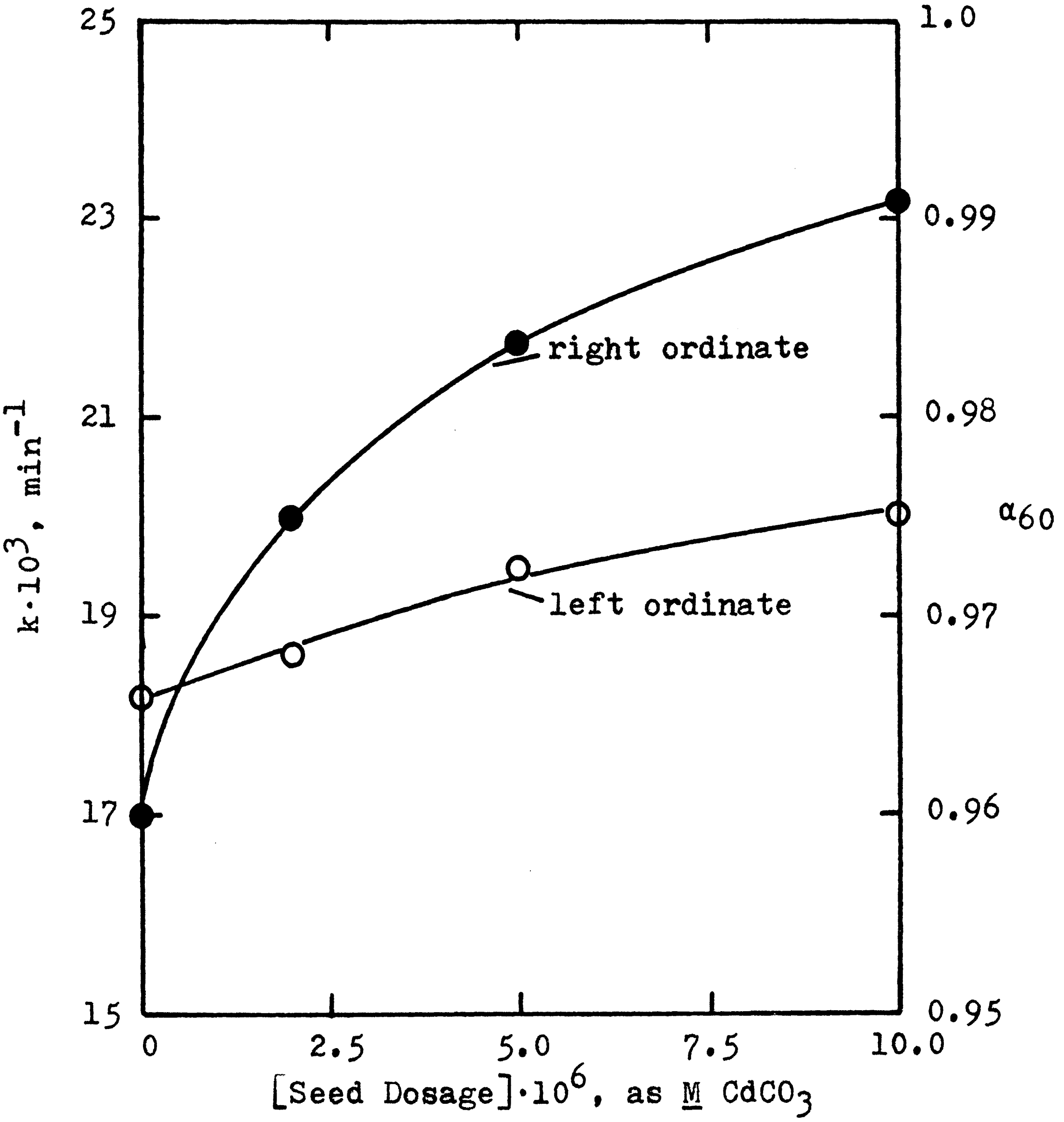

FIGURE 15. EFFECT OF SEEDING ON THE RATE OF CADMIUM PRECIPITATION.

Experimental Conditions: pH 9.5, 400 rpm, t = 27±0.5 oC, $\mu = 0.05$ ($NaClO_4$), $[CO_3]_{TOT} = 10^{-2}$ M, $[Cd]_o = 10^{-4}$ M.
In the graph, open and solid circles represent k and α_{60} values, respectively.

F. Conclusion

The rate of precipitation of cadmium in alkaline carbonate solutions exhibits a rapid initial and a slower secondary rate component. The secondary precipitation rate is reasonably well described by a first-order expression over a wide range of ionic strength, pH and initial concentrations of cadmium, carbonate species, chloride and sulfate. The beneficial effect of carbonate on cadmium removal is indicated by increasing overall rates as well as by decreasing solubility of cadmium with increasing carbonate concentration. The variation of rates with pH suggest changes in reaction mechanisms and products to occur as function of OH^- and possibly $CO_3^=$ ion concentration. Optimum pH conditions for high and rapid cadmium removal tend to coincide with the pH range (9.3 - 10) of minimum cadmium solubility in carbonate controlled systems.

The initial extent of precipitation was found to decrease with increasing ionic strength (0.025 - 0.2) and increasing sulfate (at $\mu = 0.2$ and from 0 - 0.06 $\underline{M}$ $SO_4^=$) concentration, whereas the secondary rate was not appreciably affected. Chloride ion (at $\mu = 0.1$ and from 0 - 0.08 $\underline{M}$ Cl^-) did not exert measurable effects on any of the two rate components. A substantial acceleration of the overall rate was observed due to seeding of the precipitation process with pre-formed cadmium carbonate particles.

Theoretical interpretation of the precipitation process studied under more practical and consequently more complex conditions is extremely difficult. The variations in species distribution and in rate patterns as functions of pH are indicative of simultaneous interactions of several chemical steps leading to reaction products. Further complication is expected to arise from foreign-ion-induced lattice distortion and possible phase transitions during crystal growth. The overall rate may, therefore, be regarded as the reflection of a process with several chemical and physical mechanistic elements.

More detailed information on the role of mechanistic parameters should become available from a separate study of the nucleation - and crystal growth phase in "pure" and physically well defined systems. With respect to cadmium carbonate as the sole reaction product, a lower pH range must be chosen to eliminate coprecipitation of cadmium hydroxide. For reasons of carbonate stability, these systems require controlled CO_2 pressures and, consequently, sealing against the atmosphere.

IV. REMOVAL OF CADMIUM BY SORPTION ON HYDROUS METAL OXIDES

A. General

The removal of traces of cadmium and certain other heavy metals present in the aqueous environment is of primary import to the production of potable waters. With increasing shortages of water resources and increased emphasis on re-use, it may also find useful application as a secondary treatment method for industrial wastes.

In accordance with the recommendations of the USPHS, a water supply containing more than 0.01 mg/l of cadmium ($\approx 10^{-7}$ M), should not be considered as a source for drinking water production (12). In view of the cumulative toxicity of cadmium (Chapter I) and the fact that drinking water standards serve merely as guidelines, it is of considerable interest to examine the feasibility of methods for removal of traces ($< 10^{-6}$ M) of cadmium.

Ion exchange has been successfully employed for the removal and subsequent reclamation of metals in process waters (63). The economic feasibility of this method for treatment of large water volumes is, however, questionable considering the relatively large concentrations of ordinary competing cations (e.g. Ca^{2+}, Mg^{2+}, Na^{+}) in contrast to trace amounts of heavy metals.

A more promising approach to selective removal of certain heavy metals is that of sorption on suitable solid materials (51,64,65,66). High sorptive affinities of hydrous oxides of iron(III) and manganese(IV) for heavy metal ions have been observed in a number of investigations. A similar behavior should be expected with hydrolyzed products of Al(III) and probably some other solids which exhibit similar surface-chemical properties. Hydrous oxides of Al(III), Fe(III) and Mn(IV) are commonly employed or encountered in water treatment operations. Their general sorptive properties for cations, low price and established use in water treatment technology suggest certain promises for cadmium removal via sorption.

1. Hydrous Manganese Dioxide

It has been proposed that naturally occurring oxides of Mn(IV) and Fe(III) control the fixation of Mn, Fe, Co, Ni, Cu, and Zn in soils and in the aqueous environment (64).

A rather amorphous but very active form of hydrous oxide of manganese(IV)* is formed by oxidation of divalent manganese and/or by reduction of manganate(VII) in permanganate treated waters (56). Hydrous manganese dioxide prepared in situ exhibits a very high surface area (e.g. 300 m^2/gr.; see reference 67) and a varied chemical composition ($MnO_{1.1}$ - $MnO_{1.95}$) depending on the conditions and mode of its formation. Under certain conditions, hydrous manganese dioxide may occur in a colloidal state of relatively high and long-

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[*] generally referred to as hydrous manganese dioxide or often as δ-MnO_2

term stability. The protonic acidity of MnO_2 has been sufficiently evidenced (51), but there is less certainty with respect to the value for the pH of zero point of charge (ZPC). Recent investigations show ZPC values from pH 1.5 for δ-MnO_2, pH 1.8 for Mn(II)manganite, pH 4.5 for α-MnO_2, pH 5.5 for γ-MnO_2, and pH 7.3 for β-MnO_2 (68). In situ preparations of hydrous and low ordered MnO_2 show ZPC values close to 2 and a higher sorptive affinity compared with well ordered oxides of manganese(IV) (67,69,70). Sorptive uptake of cations by hydrous MnO_2 is accompanied by proton release and generally increases in magnitude with increasing pH in the range $pH > pH_{ZPC}$ (67,69). Consistent with this behavior is the colloid stability of hydrous MnO_2, which was found to increase over the same pH range, but is reduced concurrent with an increase in cation concentration in solution (70).

The sorptive affinity of hydrous MnO_2 for cations is in fair agreement with Hofmeister's rule (67). That is, the affinity tends to increase with increasing positive charge and decreasing ionic radius of metal cations.

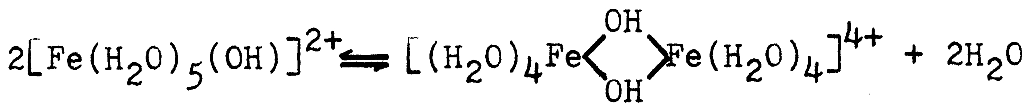
2. Hydrolysis Products of Fe(III) and Al(III)

Ferric and aluminum salts are the most commonly used primary coagulants in water treatment (54). The main objective of coagulation in these applications is the removal of colloids (including suspended matter), colored compounds and similar impurities by agglomeration and subsequent sedimentation.

The trivalent ions Fe^{3+} and Al^{3+} or their respective aquo-complexes are unstable under the pH conditions (pH 5 to 11) representative for water treatment operations and a number of hydrolysis species are formed, as illustrated for iron:

$$Fe(H_2O)_6^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+ \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + 2H^+ \rightleftharpoons$$
$$[Fe(H_2O)_3(OH)_3]_{(s)} + 3H^+ \rightleftharpoons [Fe(H_2O)_2(OH)_4]^- + 4H^+. \qquad (80)$$

The neutral species $[Fe(OH)_3(H_2O)_3]$ predominates in the neutral pH range, but there is also evidence for the existence of polynuclear complexes; for example:



$$2[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [(H_2O)_4Fe\langle{}^{OH}_{OH}\rangle Fe(H_2O)_4]^{4+} + 2H_2O \qquad (81)$$

and other species capable of colloid formation. The coagulant effect of ferric and aluminum salts derives from positively charged hydrolysis species and not from the ions Fe^{3+} and Al^{3+} as was earlier believed. There is little consistency with respect to the ZPC values for Fe(III) and Al(III) sols. The reason for this is probably related to aging and polymerization phenomena most often observed with these compounds. Coagulation studies and electrophoretic measurements show that the ZPC values for both compounds fall in the range of pH 5-8.5 (70,71).

Cation sorption on Fe(III) and Al(III) polymers has been observed but capacities are less than those reported for hydrous MnO_2 under similar pH conditions (51,65,66).

B. Experimental Details

1. Preparation of Hydrous MnO_2 Sols

Formation of hydrous MnO_2 by oxygenation of divalent manganese is known to yield products of varied degree of oxidation ($MnO_{1.1}$ - $MnO_{1.95}$) depending largely on experimental conditions (69). This result is not surprising in view of the high sorption capacity of MnO_2 towards Mn^{2+} ions and a similar behavior - though much less in degree - must be expected under the conditions of the Guyard reaction (67):

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+. \qquad (82)$$

Sorption concurrent with oxidation can be generally minimized by maintaining an excess of the oxidant over the entire period of the reaction. This is achieved by observing the sequence of reactant additions. Thus, the reductant should be slowly added to a slight excess of the oxidant.

The problem of sorptive interference can be avoided by choosing a more suitable reducing agent, such as hydrogen peroxide. In moderate alkaline solution (pH 8-10) the reaction

$$3H_2O_2 + 2KMnO_4 \longrightarrow 2H_2O + 3O_2 + 2MnO_2 + 2KOH \qquad (83)$$

is fairly rapid and quantitative. Slow addition of H_2O_2 to a slight excess of permanganate in dilute solution and at pH > 10 showed a stepwise reduction of permanganate to

MnO_2. The green manganate(VI), formed as an intermediate product, undergoes disproportionation according to:

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^- \qquad (84)$$

yielding permanganate and manganese dioxide.

Sols of $2 \cdot 10^{-4}$ M of hydrous MnO_2 were prepared in accordance with these reactions (Equations 83 and 84) as described below.

A 20-ml portion of a standardized (11) solution of 0.02 M $KMnO_4$ was pipetted into a beaker containing 900 ml of distilled water (pH ≈ 8). About 98 % of the stoichiometrically required hydrogen peroxide was mixed with the permanganate by dropwise addition from a ≈ 0.03 M solution of H_2O_2. The resulting solution (pH ≈ 10) was kept for approximately 24 hours, then adjusted to the desired pH level by addition of nitric acid and filled to a volume of 2000 ml in a volumetric flask.

Residual permanganate in these solutions was determined by the following method. One ml of a solution of ≈ 2 M $Ca(NO_3)_2$ was added to a portion of 50 ml of the MnO_2 sol. Coagulation of MnO_2 was observed after 15 minutes of rapid mixing. The coagulated MnO_2 was separated by filtration through a 100 mμ membrane filter. The concentration of permanganate in the filtrate was obtained by spectrophotometric analysis at 526 mμ and comparison with a known standard. These analyses showed residues of less than 1 % of the original permanganate used for the formation of the MnO_2 sol.

2. Fe(III and Al(III) Stock Solutions

The aforementioned hydrolysis reactions of Fe(III) and Al(III) give rise to changes in the composition of solutions containing these salts unless they have been stabilized by acidification. Stock solutions were made ≈ 10^{-2} M in $HClO_4$ and 10^{-1} M in $Al(ClO_4)_3$ or $Fe(ClO_4)_3$. Standardization of the reagent grade salts $Fe(ClO_4)_3 \cdot 6H_2O$ and $Al(ClO_4)_3 \cdot 9H_2O$ was done by alkalimetric titration (72).

The stock solutions exhibited good stability with respect to precipitation over the entire period of their usage. Secondary stock solutions, usually of $2 \cdot 10^{-4}$ M, were made by dilution of the stock solutions with distilled water prior to the sorption experiments.

3. Chemicals

All chemicals used in the course of the sorption experiments were of standard reagent quality. The preparation of stock solutions of stable and radioactive cadmium has been described in the experimental section of Chapter III.

4. Equipment

The reactants were mixed in teflon beakers with a magnetic stirrer. Capped polyethylene bottles (125 ml capacity) were used for equilibration. A mechanical laboratory shaker*

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*Made by the Arthur Thomas Co., Philadelphia, Pa.

was used to provide for agitation. The shaker was operated at ≈ 400 displacements/min and with a horizontal displacement of ≈ 1 inch. A description of the instrumentation for pH-measurement, radioassay and of the filtration apparatus has been given in Chapter III. Standard laboratory glassware was employed except for polyethylene pipettes, which were used for transfer of the radioisotope and of dilute solutions of cadmium.

5. Procedures

Predetermined volumes of the standard reagent and adsorbent stock solutions (except for cadmium) were mixed with distilled water in a teflon beaker to yield (100-x) ml of the buffered and pH-adjusted solution of the adsorbent. A known quantity of the radioisotope and stable cadmium were mixed with distilled water. Of this, a predetermined quantity was added, under rapid mixing, to the adsorbent solution to yield 100 ml of the experimental medium, specifically defined in terms of pH, ionic strength and concentration of all reagents. Since the concentration of the adsorbent was varied while that of the sorbate remained constant, the pH variation within the determination of one particular isotherm was usually less than 0.05 pH units. This has been verified repeatedly prior and after filtration of sorption systems.

The well mixed solutions were poured into polyethylene bottles, capped and mechanically shaken for approximately

60 minutes (except for sorption rate studies) at ambient temperature.

Between pH 5 - 7 the solutions were buffered with 0.001 M sodium acetate, and with 0.001 M sodium tetraborate at higher pH conditions. The usefulness of both buffer systems was established by comparisons with unbuffered experiments.

The samples were filtered according to the technique described in Chapter III, section C.3, using 100 mμ membrane filters. Filters were cleaned with acid and washed with distilled water after each individual filtration. For MnO_2 experiments, a mixture of dilute H_2O_2 and H_2SO_4 was used to dissolve the filter cake, while $\approx$ 3 N HCl was found more suitable for dissolving precipitated Al(III) and Fe(III) products.

Equilibrium concentrations of the sorbate were determined by radioassay of the acidified filtrates as discussed in detail in Chapter II, section A. The small excess of permanganate applied in the MnO_2 experiments was rarely noticeable after final filtration of the samples. This is very likely due to decomposition, which is catalyzed by MnO_2. Filtrates discolored by residual permanganate were decolorized by small additions of acidic hydrogen peroxide after weighing of the viles.

C. Treatment of Data

The sorptive uptake of cations on hydrous oxides of manganese(IV) and iron(III) has usually been presented in terms of the Langmuir equation for adsorption (67,69).

$$X = \frac{X_m \cdot b \cdot C_{eq}}{1 + b \cdot C_{eq}} \tag{85}$$

In this equation, X represents the quantity sorbed per unit amount of sorbent, X_m the limiting value for X ("mono layer" capacity), C_{eq} the equilibrium concentration of the sorbate in solution and b is a constant related to the energy of sorption. By rearrangement, Equation 85 yields a linear form of Langmuir's equation

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{X_m \cdot b \cdot C_{eq}} , \tag{86}$$

which is more convenient for the evaluation of sorption data and calculation of the constants X_m and b. In accordance with Equation 86, a plot of $1/X$ versus $1/C_{eq}$ should give a linear trace with a slope of $1/X_m \cdot b$ and an intercept of $1/X_m$ (Figure 16).

The conceptual basis for the Langmuir adsorption model includes the assumptions that:

a) adsorption is limited to a monolayer of the sorbate on the solid surface,

b) the heat of adsorption is independent of the degree of surface coverage, and

c) sorbate species are localized.

However, a fair mathematical agreement of experimental data with the Langmuir equation does not imply that the proposed

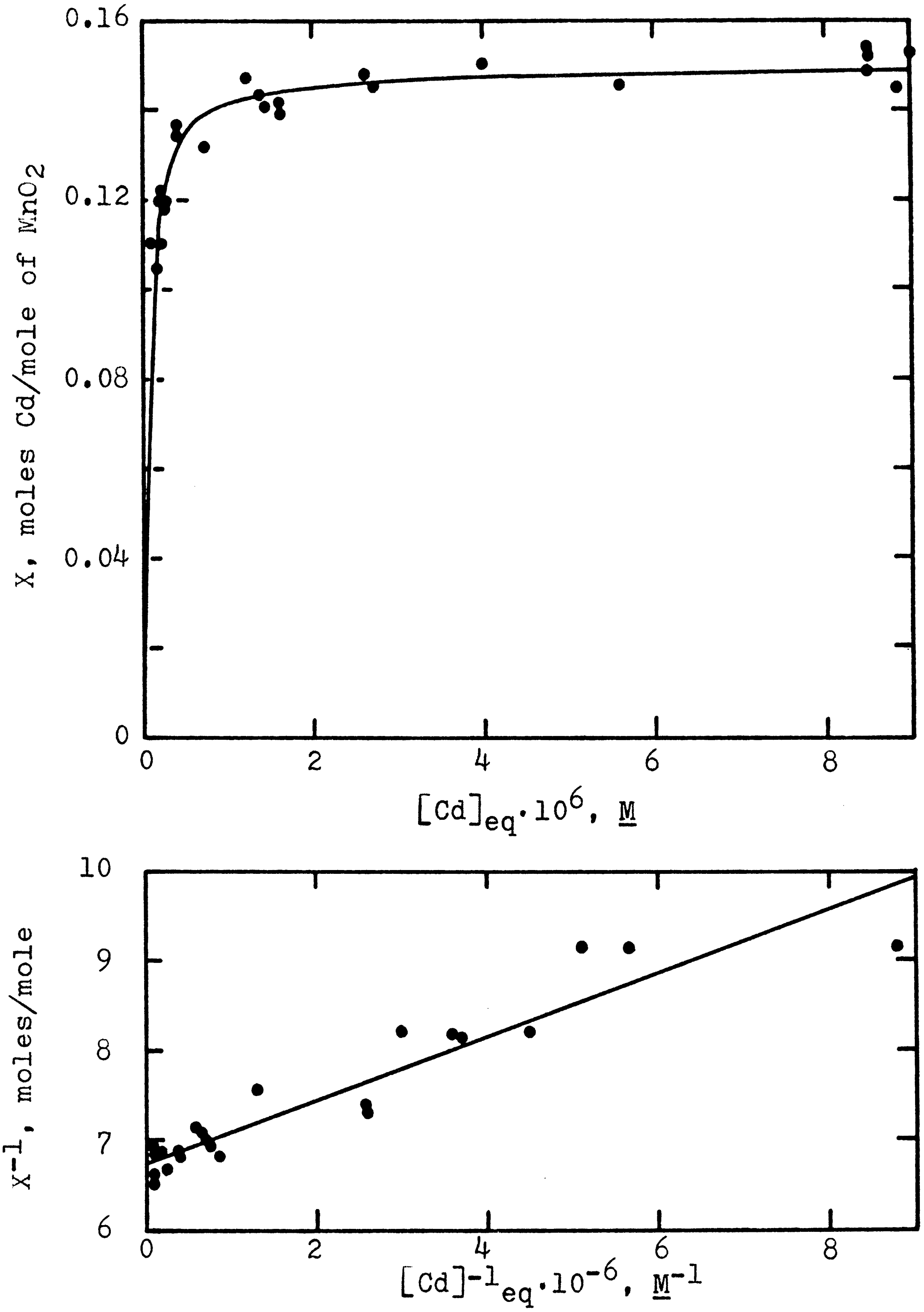

FIGURE 16. SORPTION OF CADMIUM ON HYDROUS MANGANESE DIOXIDE AT pH 5.

Experimental Conditions: $\mu = 0.01$, pH 5, ambient temperature. Lower graph shows Langmuir plot fitted by method of least squares. Curve in upper graph is calculated Langmuir isotherm.

model is valid for that particular system. Nevertheless, the equation has been found very useful for a quantitative description and comparison of sorption data for many systems.

A typical representation of the obtained data is shown in Figure 16 for the sorption of cadmium on hydrous manganese dioxide at pH 5 and at an ionic strength of 0.01. The data were fitted in accord with Equation 86 by the method of least squares, from which the monolayer capacity, X_m (moles/mole), and the Langmuir constant, b (l/mole), were obtained. The curve in the upper plot of Figure 16 was then calculated for different equilibrium concentrations of cadmium using Equation 85. Subsequent results are usually presented in terms of X_m (or X) and b values as a function of systemic variables of interest. For calculation of sorption equilibria under a given set of conditions from the presented constants X_m and b; X in Equation 85 must be expressed in terms of the respective concentrations of the sorbate and sorbent species.

$$X = \frac{C^o - C_{eq}}{m} \tag{87}$$

In this equation, C^o and C_{eq} stand for the initial and equilibrium concentration of the sorbate, respectively; and m is the concentration of the sorbent, all given in moles per liter.

D. Results and Discussion

1. Sorption Rates

It has been observed previously that the rates of attainment of sorption equilibria for cation uptake on freshly prepared hydrous oxides of Mn(IV) and Fe(III) are very rapid (67,69). The kinetics of sorption with these oxides have been followed by the disappearance of the sorbate in solution (67,69), as well as by the concurrent release of protons (51), which are displaced by cations of sufficient sorptive - or ion exchange - affinity. In these cases, equilibrium was usually established within 10 minutes or less. It is noteworthy to mention that sorption rates with well ordered (most often aged) crystals may be much slower compared to freshly precipitated or highly dispersed forms of these oxides. For example, contact times of 15 hours were required for equilibrium uptake of zinc on γ-MnO_2 at pH 7 and an ionic strength of 2.0 (2 M NH_4Cl) (73).

Apart from the possible influence of crystal habit and modification on sorption rates, one must also consider the contribution of particle size and its effect on the transport of the solute to the solid surface site. Indications for this are given by the observation that the rate of Mn^{2+} uptake on hydrous manganese dioxide tends to decrease at higher ionic strength, at which particle aggregation of the sorbent is predominant (69).

Rate studies within the context of this work were performed with the aim of establishing certainty of sorption equilibrium within the experimental contact times. This requirement seems to be sufficiently met by a contact period of 60 minutes as indicated by the rate studies for the oxides used (Figure 17) and by similar results of other relevant investigations (67,69).

2. Effect of pH on the Sorption of Cadmium on Hydrous Manganese Dioxide

In most water treatment operations including sorption and colloid-destabilization, pH is a very important variable. In the process of sorptive uptake of cations by hydrous metal oxides, one must consider that pH exerts direct influence on the chemical and often physical structure of both the sorbate and sorbent species.

The distribution of cadmium species as a function of pH has been shown in Figure 1, but there is much less certainty with respect to the influence of pH on the structural chemistry and physical morphology of hydrous oxides of Mn(IV). Manganese dioxide is generally regarded as insoluble under the pH conditions of natural waters (51). The possibility for structural changes (e.g. particle size, polymerization etc.) of MnO_2 is indicated by the observation of reversible color changes induced by variation of pH of hydrous manganese dioxide sols. Furthermore, as discussed in Chapter IV, section A.1., the charge of colloidal hydrous manganese dioxide becomes increasingly negative as pH in-

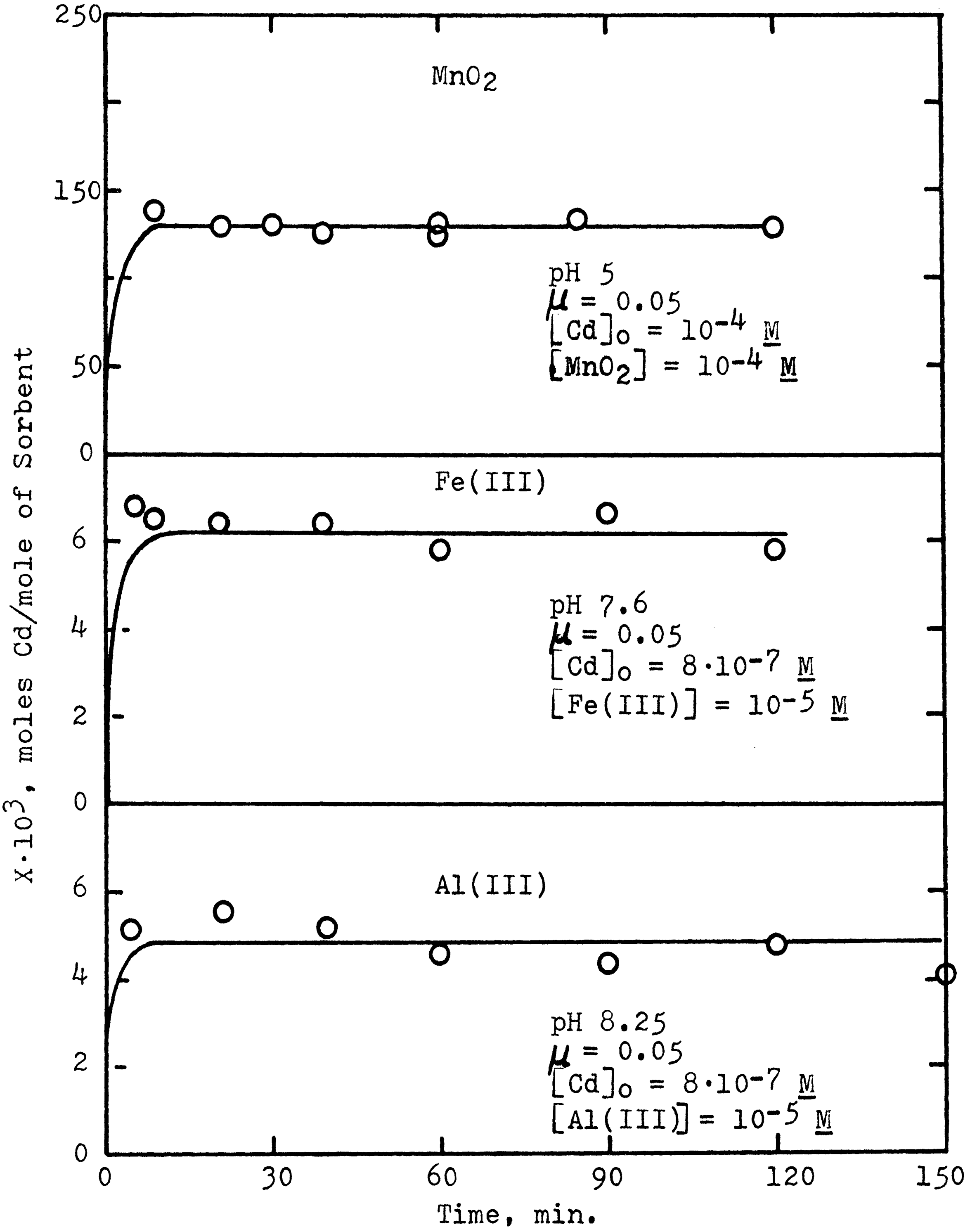

FIGURE 17. RATES OF SORPTION OF CADMIUM ON HYDROUS OXIDES OF Mn(IV), Fe(III) AND Al(III).

ceases beyond the pH of zero point of charge. The simultaneous increase of the cation exchange capacity within the same pH range points toward a structurally related linkage between the colloid-chemical and sorptive behavior of hydrous MnO_2 (67,69). An analogous situation is expected to exist with other hydrous heavy metal oxides, which exhibit similar structural and chemical properties.

While other mechanistic interpretations for cation sorption on hydrous MnO_2 cannot be ruled out, the present concepts of the chemical behavior of highly dispersed forms of the oxide in the presence of relatively low concentrations of cations (67,69), suggests a mechanism of exchange sorption. The fact that proton release concurs with sorptive uptake of cadmium upon mixing of isoprotic solutions of hydrous MnO_2 and cadmium, shows that the same qualitative interpretation may be extended to this study.

Individual sorption isotherms for cadmium were determined for a pH range of 5-8.3 and at an ionic strength of 0.05 and ambient temperature. A plot of the limiting sorption capacities and Langmuir constants versus pH is shown in Figure 18. The increase of X_m values with increasing pH is qualitatively in good agreement with sorption data for other cations on hydrous MnO_2, however, the quantitative effect of pH on the extent of cadmium sorption is less pronounced than has been reported for manganese (69). This difference may in part be explained by a high specific affinity of manganese compared with other cations studied (69),

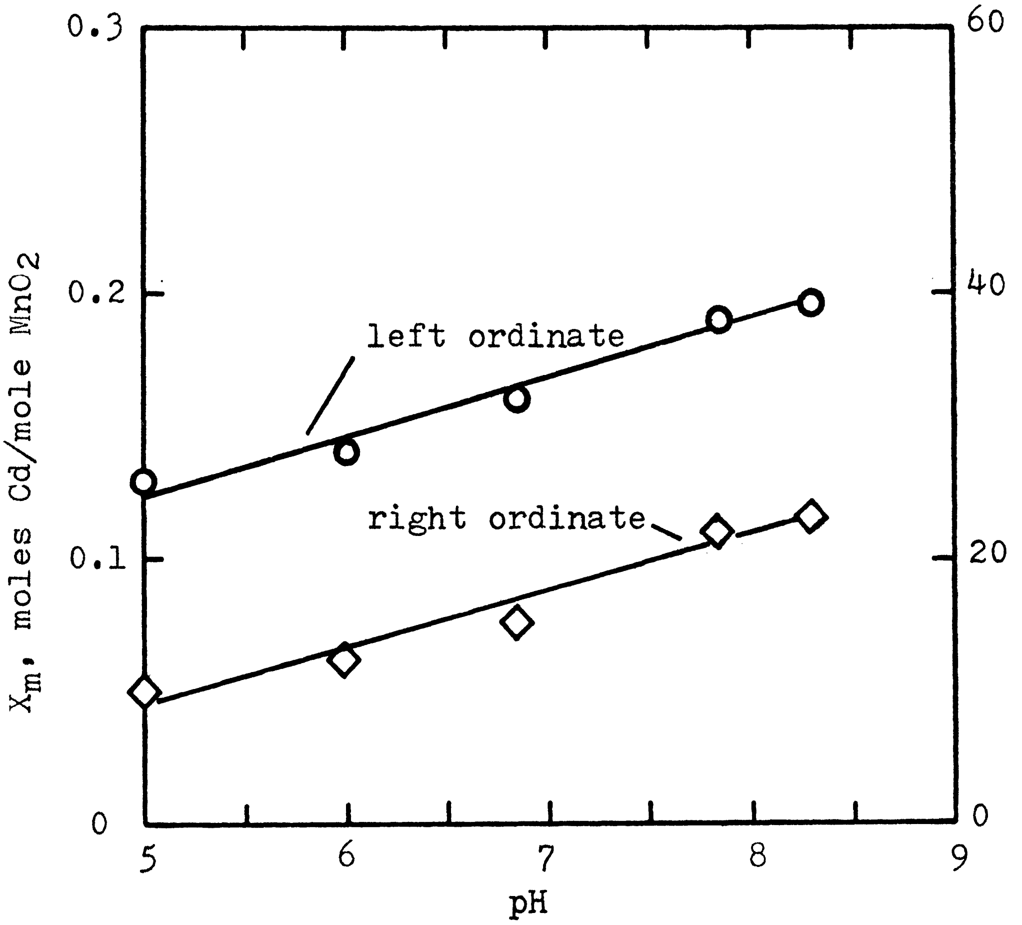

FIGURE 18. EFFECT OF pH ON SORPTION OF CADMIUM ON HYDROUS MANGANESE DIOXIDE.

Experimental Conditions: $\mu = 0.05$, ambient temperature.
pH 5-7: $[Cd]_o = 10^{-5}$ M, $[MnO_2] = (10\text{-}140) \cdot 10^{-6}$ M,
buffer: 10^{-3} M sodium acetate.
pH 7-8.3: $[Cd]_o = 8 \cdot 10^{-7}$ M, $[MnO_2] = (1\text{-}7) \cdot 10^{-7}$ M,
buffer: 10^{-3} M sodium tetraborate.

In the graph, circles represent plot of limiting sorption capacity (left-hand scale), diamonds represent plot of Langmuir constant b (right-hand scale) versus pH.

but may also derive from differences in the distribution of aquo and hydroxy-species of the two metals.

An experimental investigation of the sorption of cadmium at a range higher than pH 8.3 is of questionable value, since extremely low concentrations of the metal must be employed in order to eliminate the possibility of precipitation. Results obtained in such low concentration ranges are obscured by wall adsorption, and the limited range of sorbate concentration is insufficient to determine isothermic parameters with any degree of accuracy.

Since ionic equilibria of the type

$$Cd^{2+} + OH^{-} \rightleftharpoons CdOH^{+} \qquad (88)$$

are considered very rapid, an assessment with respect to which species is preferentially adsorbed, cannot be easily made on the basis of sorption data as a function of pH. In view of the small competitive effect of monovalent cations ((67); also see Figure 19), one is tempted to assume that $CdOH^{+}$ plays a much smaller role than the stronger positively charged Cd^{2+} ion. On the other hand, the less hydrated (51) $CdOH^{+}$ may approach and penetrate surface sites more readily than the more bulky species Cd^{2+}_{aq}; and the process shown in Equation 88 may proceed from right to left in the course of exchange sorption.

While X_m values for cadmium compare well with those obtained for other divalent cations (67,69), the b values found for cadmium are considerably higher. An explanation for the latter result may be sought in specific properties of the sorbate species or in possible differences of the sorbent structure.

The ion Cd^{2+} differs from the corresponding ions of the group IIa-metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+}) in that it possesses 10 electrons in the outer shell and thus has no inert gas configuration as is exhibited by the alkaline earth metal cations. By this definition, cadmium has been classified as a B-metal cation or a so-called soft acid (51). B-metal cations are considered as soft spheres, that is, their electron sheaths are readily deformable under the influence of electric fields. Furthermore, metal ions of this class tend to bind ammonia stronger than water, or prefer CN^- more than OH^- as a ligand among other properties compared to A-metal cations. In light of this theory and supported by differences in basicity constants, Cd^{2+} has a lower tendency towards hydration than Ca^{2+}, or $Cd^{2+}_{(aq)}$ is a stronger acid than $Ca^{2+}_{(aq)}$. Because the crystal ionic radii for both elements are almost identical ($Ca^{2+} = 0.99$ Å, $Cd^{2+} = 0.97$ Å), the electrostatic attraction of the less hydrated, and thus smaller, aqueous ion of cadmium is expected to be greater in comparison with calcium.

A relatively higher sorptive activity of hydrous MnO_2 is expected from its formation by careful reduction of permanganate with hydrogen peroxide in contrast to reduction with divalent manganese (67). A study of the effect of the mode of preparation and age of hydrous MnO_2 sols on their sorptive properties appears worthwhile in this connection.

3. Ionic Strength and Competitive Effects

In terms of electrostatic theory, ionic strength effects on sorption equilibria can be interpreted in a simplified manner by way of cation competition. In accordance with Hofmeister's rule, a cation will be held more strongly by a negatively charged surface site, the higher its charge and the smaller its size (74). Thus, the effect of sodium ion concentration on the sorption of - or cation exchange capacity for - divalent ions is not expected to be very pronounced.

Figure 19 shows the effect of ionic strength ($NaClO_4$) on the Langmuir constants X_m and b for cadmium on hydrous MnO_2 at pH 5 and roomtemperature. Considering the low initial concentration of cadmium (10^{-5} M) in contrast to that of sodium ions, it is apparent that the influence of monovalent cations is rather weak. A stronger ionic strength effect has been previously reported for the sorption of calcium on hydrous MnO_2 at the same pH (67). This fact is quite consistent with the high sorptive affinity of hydrous MnO_2 for cadmium and the relatively small competitive effect of calcium ion on the molar sorption ratio Cd/MnO_2 as shown in Figure 20.

A loss of only about 20 % of the original sorption capacity (at zero calcium) is encountered by addition of $2 \cdot 10^{-3}$ M of calcium nitrate. Relative to the initial con-

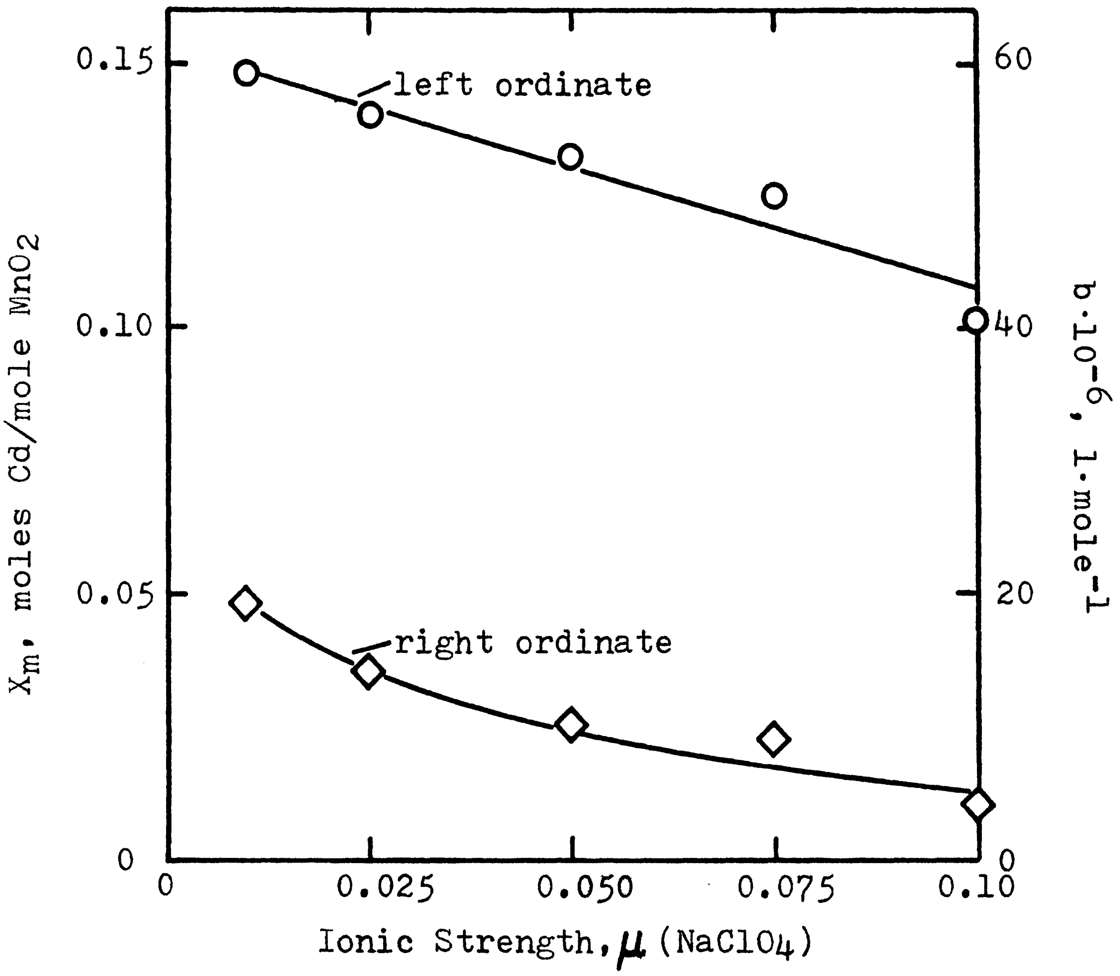

FIGURE 19. EFFECT OF IONIC STRENGTH ON SORPTION OF CADMIUM ON HYDROUS MANGANESE DIOXIDE AT pH 5.

Experimental Conditions: pH 5, ambient temperature, $[Cd]_o = 10^{-5}$ M, $[MnO_2] = (4\text{-}160) \cdot 10^{-6}$ M, buffer: 10^{-3} M sodium acetate.

In the graph, circles represent plot of limiting sorption capacity (left-hand scale), diamonds represent plot of Langmuir constant b (right-hand scale) versus ionic strength.

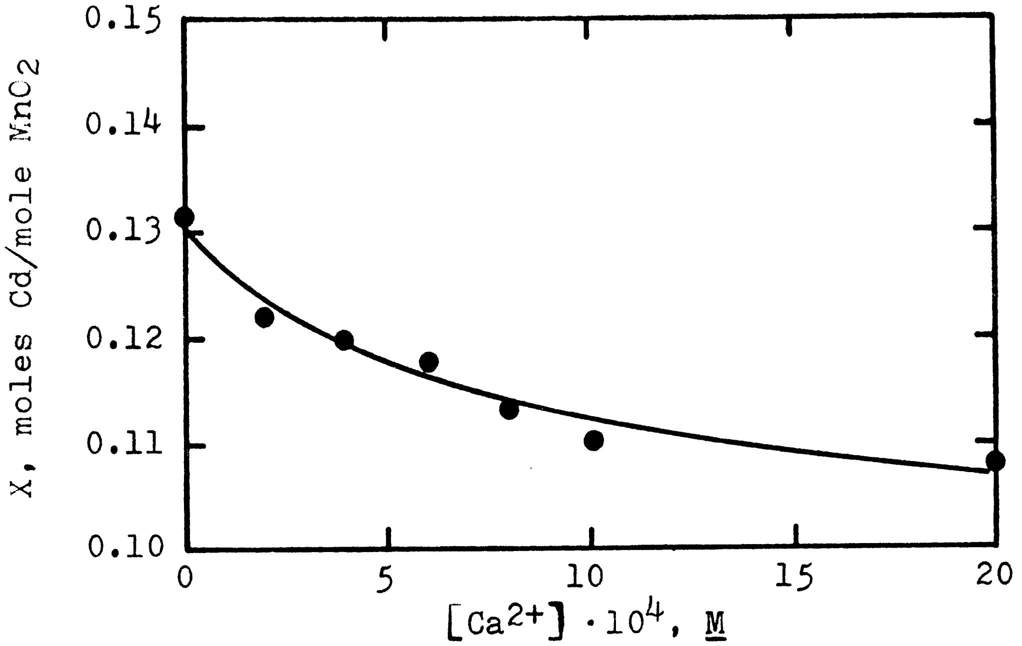

FIGURE 20. EFFECT OF CALCIUM ON SORPTION OF CADMIUM ON HYDROUS MANGANESE DIOXIDE.

Experimental Conditions: pH 5, μ= 0.05, ambient temperature, $[Cd]_o = 10^{-5}$ M, $[MnO_2] = 4\cdot10^{-6}$ M, buffer: 10^{-3} M sodium acetate.

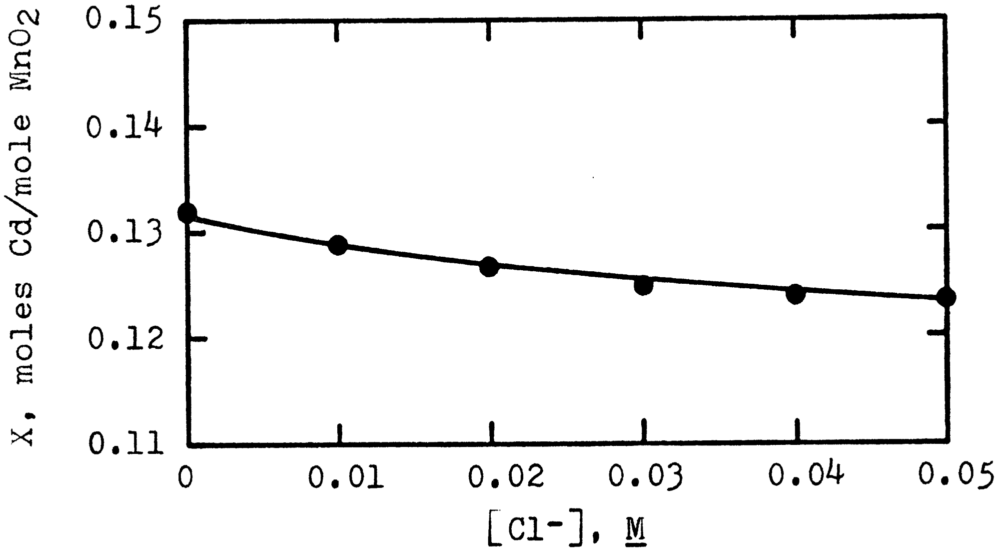

FIGURE 21. EFFECT OF CHLORIDE ON SORPTION OF CADMIUM ON HYDROUS MANGANESE DIOXIDE.

Experimental Conditions: pH 5, μ= 0.05, ambient temperature, $[Cd]_o = 10^{-5}$ M, $[MnO_2] = 4\cdot10^{-6}$ M, buffer: 10^{-3} M sodium acetate.

centration of cadmium, this corresponds to a molar $[Ca^{2+}]/[Cd^{2+}]$ ratio of 200. While the formation of specific surface complexes between the sorbate ion and functional groups cannot be excluded in ion exchange phenomena, the weak competition between calcium and cadmium is reasonably well interpreted in terms of differences in acidity and outer shell configuration, as discussed in the preceeding section.

Complexation of cadmium by chloride ion as a competing process for sorption is similarly weak in magnitude. This is shown by a plot of the chloride ion concentration versus the molar sorption ratio X in Figure 21. The distribution diagram for chloride species of cadmium (Figure 2) reveals that $CdCl^+$ occurs as the only competitor for Cd^{2+} in this concentration range and at pH 5. While the observed effect of chloride and hydroxide on cadmium uptake by hydrous MnO_2 appears insignificant in view of the concentration and pH conditions of water treatment operations, considerable interference with sorption processes may occur in the presence of ligands with stronger complexing capability. This complication is expected due to complexation with certain organic compounds present in many natural and wastewaters. Decomplexation via oxidative degradation of organic ligands prior to sorption appears to be a feasible process to minimize this interference (56).

4. Sorption on Hydrous Oxides of Fe(III) and Al(III)

Several accounts in the literature document sorptive properties of highly dispersed (mostly X-ray amorphous) products of the hydrolysis of Fe(III)* towards cations (51, 64,66,69). From the general chemical resemblance of Fe(III) with Al(III) this behavior is, at least qualitatively, also expected for aluminum hydrolysis products.

Apart from quantitative differences in hydrolysis equilibria, it must be realized that profound qualitative differences in the type of species, degree of polymerization crystal modifications etc. exist between hydrous oxides of Mn(IV), Fe(III) and Al(III).

On a quantitive basis, it is important to consider the fact that hydrous oxides of Al(III) and Fe(III) exhibit ZPC values considerably higher than hydrous forms of MnO_2. As a consequence, the operational range of cation sorption by Al(III) and Fe(III) products is much smaller compared to MnO_2. As shown in Figure 22, sorptive uptake of cadmium begins at approximately pH > 6 for Fe(III) and pH > 6.75 for Al(III), and continues to rise with increasing pH. Assuming Cd^{2+} and $CdOH^+$ as species capable of sorption, and considering the increasing negative charge of the sorbent with pH, one would predict a further increase of sorption capacity for the approximate range pH 8.3-10. Opposing this trend, however, is the increased tendency of these sorbents to form soluble anionic complexes by combination with hydroxide

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* generally referred to as hydrous oxides of Fe(III)

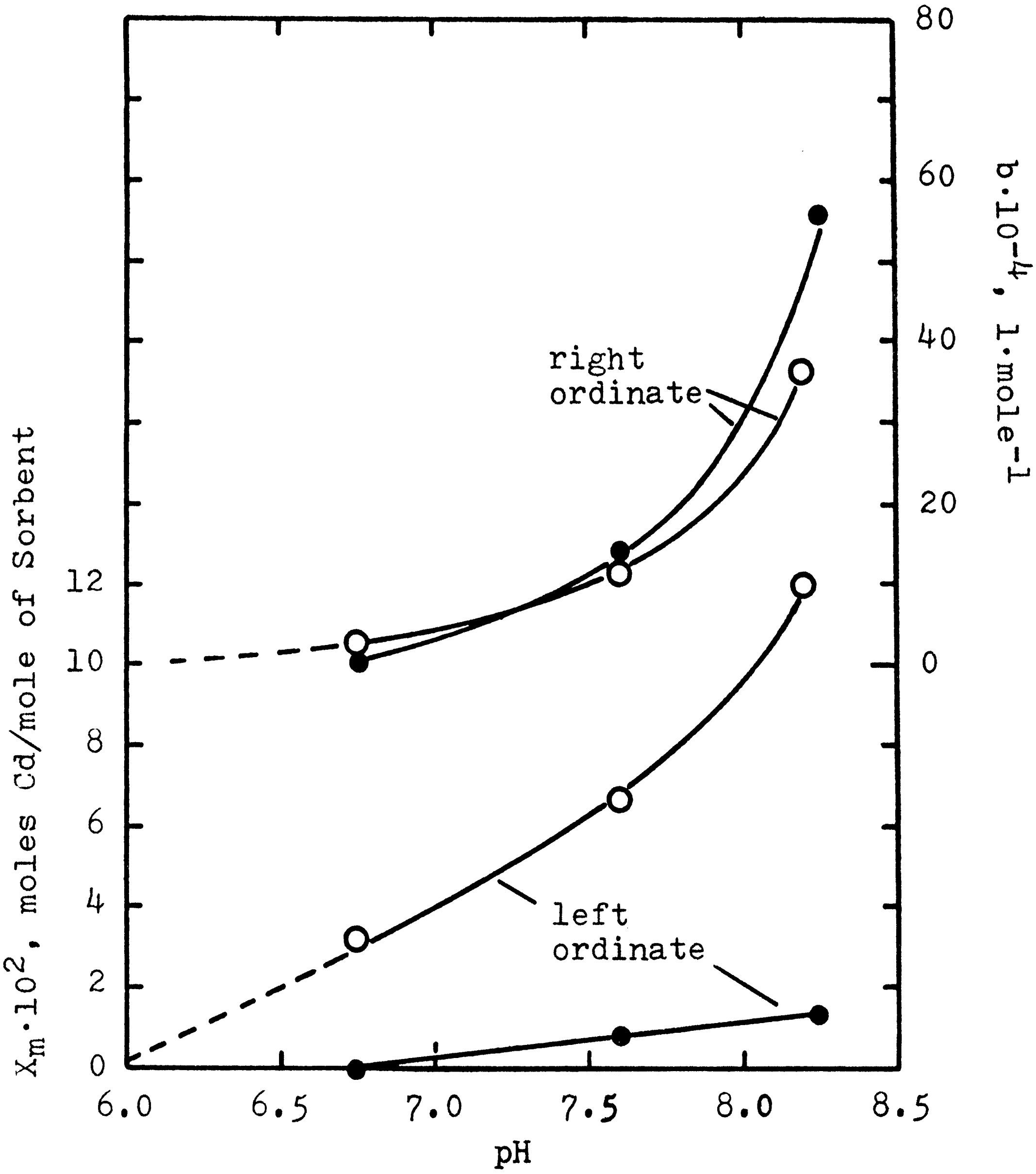

FIGURE 22. EFFECT OF pH ON SORPTION OF CADMIUM ON HYDROUS OXIDES OF Fe(III) AND Al(III).

Experimental Conditions: $\mu = 0.05$, ambient temperature,

<u>pH 6.75:</u> 10^{-3} M sodium acetate, $[Cd]_0 = 10^{-5}$ M, $[Fe(III)] = (5\text{-}50) \cdot 10^{-5}$ M;

<u>pH>6.75:</u> 10^{-3} M sodium tetraborate, $[Cd]_0 = 8 \cdot 10^{-7}$ M, $[Fe(III)] = (4\text{-}140) \cdot 10^{-6}$ M, $[Al(III)] = (1\text{-}50) \cdot 10^{-5}$ M.

In the graph, open and solid circles stand for Fe(III) and Al(III), respectively. Upper two curves (right-hand scale) show plot of Langmuir constant b, lower two curves (left-hand scale) show plot of limiting sorption capacity as function of pH.

ion (71). Formation of ferrate(III) appears insignificant in the practical range of pH and concentration conditions, but solubilization of $Al(OH)_3$ becomes of serious consequences in the range pH > 8 and at $[Al(III)] < 10^{-5}$ M. The very low sorptive capacity of hydrous Al(III) oxide may - at least in part - be attributed to this behavior. In light of these facts and considerations, Al(III) salts cannot be considered feasible for sorptive removal of cadmium and probably other cations.

At comparable pH conditions, hydrous oxides of Fe(III) show a somewhat lower sorption affinity towards cadmium than does hydrous manganese dioxide. This is reflected in the values for limiting sorption capacities as well as in the Langmuir constants. The importance of the magnitude of b values is often overlooked; in fact, some investigators have failed to report these at all.

The following calculation will serve to demonstrate the practical significance of Langmuir constants at comparable values for X_m.

Assume the cadmium content of a given water is $5 \cdot 10^{-7}$ M (56 ppb) and is to be reduced to 10 % of its original level (5.6 ppb) by sorption on hydrous oxides of Fe(III) or Mn(IV) at a pH of 8.25 and otherwise identical conditions ($\mu = 0.05$). The molar concentration, m, of the sorbate is calculated by

$$m = \frac{(C_o - C_{eq})\,(1 + b \cdot C_{eq})}{X_m \cdot b \cdot C_{eq}} \qquad (89)$$

and from the respective constants X_m and b. These are:

Fe(III): $X_m = 0.12$ moles/mole
$b = 3.7 \cdot 10^5$ l/mole
MnO_2 : $X_m = 0.195$ moles/mole
$b = 23 \cdot 10^6$ l/mole.

The calculation of m yields $4.4 \cdot 10^{-6}$ $\underline{M}$ ($\approx$ 0.4 ppm as MnO_2) for Mn(IV) and $2 \cdot 10^{-4}$ $\underline{M}$ ($\approx$ 113 ppm as $Fe_2(SO_4)_3 \cdot 9H_2O$) for the case of Fe(III) as a sorbent.

Cadmium sorption on hydrous oxides of Fe(III) exhibits a very similar response to chloride complexation and calcium competition as shown previously for hydrous manganese dioxide. This is illustrated in Figures 23 and 24, respectively. On a quantitative basis, the effects of both Cl^- and Ca^{2+} ions appear relatively stronger compared to MnO_2, but accounting for the differences in the initial concentrations of cadmium tends to compensate for this apparent behavior.

An interpretation of competitive effects has been given during the discussion of sorption with hydrous MnO_2. On the basis of the data presented, it appears reasonable, to extend this general interpretation also to the sorption of cadmium on hydrous oxides of ferric iron.

E. Conclusion

Equilibrium conditions for the sorptive uptake of cadmium from aqueous suspensions of hydrous oxides of manganese(IV), iron(III) and aluminum(III) can be described in terms

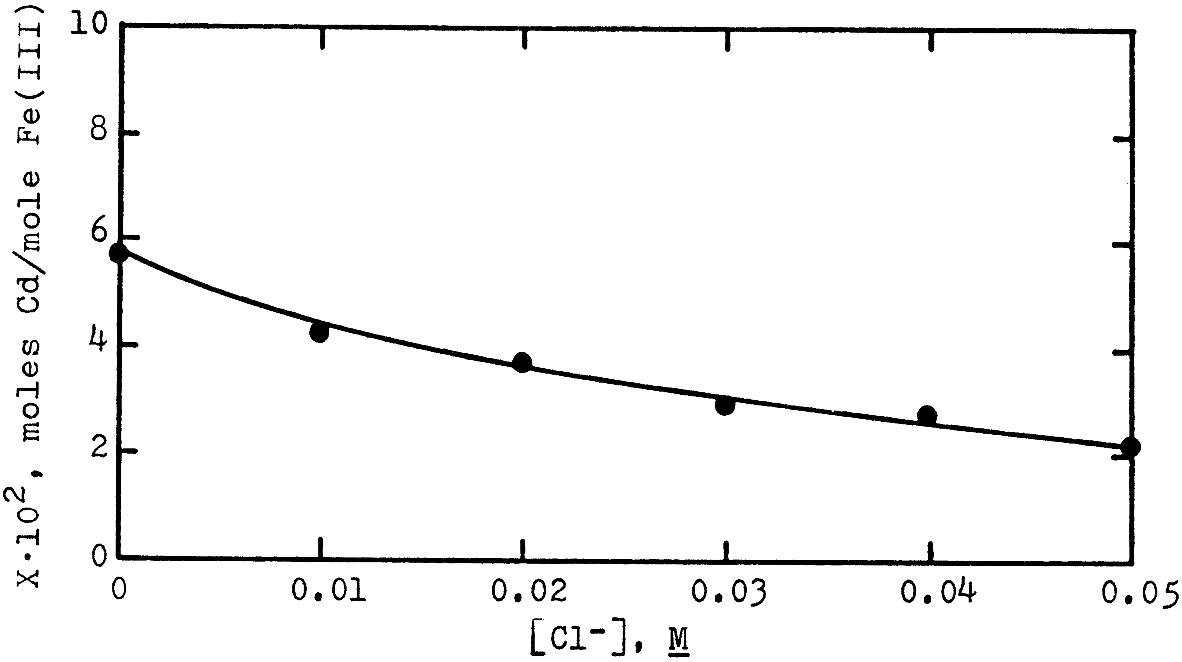

FIGURE 23. EFFECT OF CHLORIDE ON SORPTION OF CADMIUM ON HYDROUS OXIDES OF Fe(III).

Experimental Conditions: pH 7.6, $\mu = 0.05$, ambient temperature, $[Cd]_0 = 8 \cdot 10^{-7}$ M, [Fe(III)] = 10^{-5} M, buffer: 10^{-3} sodium tetraborate.

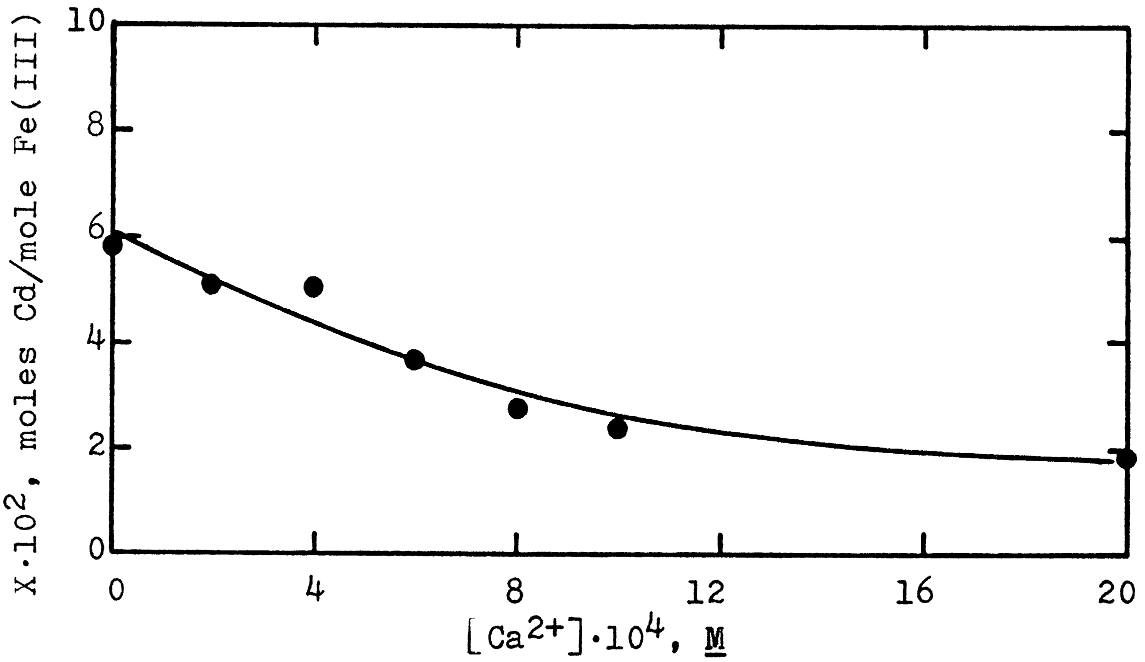

FIGURE 24. EFFECT OF CALCIUM ON SORPTION OF CADMIUM ON HYDROUS OXIDES OF Fe(III).

Experimental Conditions: pH 7.6, $\mu = 0.05$, ambient temperature, $[Cd]_0 = 8 \cdot 10^{-7}$ M, [Fe(III)] = 10^{-5} M, buffer: 10^{-3} M sodium tetraborate.

of the Langmuir sorption equation under the experimental conditions studied. Rates of attainment of sorption equilibrium are very rapid and contact times of ≈ 10 minutes are considered sufficient for equilibrium establishment. The sorption capacity for cadmium has been found to increase with pH in the range $pH > pH_{ZPC}$ for all of the three oxides studied.

Hydrous manganese dioxide formed by controlled reduction of permanganate with hydrogen peroxide exhibits sorption affinities superior to those of the other two hydrous metal oxides. An additional operational advantage of hydrous MnO_2 is the fact that it can be used over a wider range of pH conditions based on the relatively lower pH corresponding to its zero point of charge (ZPC).

Hydrous oxides of Fe(III) show a feasible range for cadmium sorption above ≈ pH 6, but sorption capacities and Langmuir constants are lower compared to MnO_2 products under comparable conditions.

The usefulness of Al(III) salts for sorptive removal of cadmium is very questionable in view of its limited pH range of application and inferior sorption capacity. This behavior of Al(III) in contrast to Fe(III) is probably due to the formation of aluminate in the pH range above that of ZPC.

The relatively weak effect of ionic strength and calcium ions on cadmium sorption equilibria is consistent with a mechanism of exchange sorption and tends to follow Hofmeister's rule. Complexation by chloride as a competing process is considered negligible in view of the experimental data. More serious competition must, however, be expected from organic ligands with stronger complexing capabilities. In these cases, oxidative degradation of the ligand structure prior to the sorption process may be practiced.

From the standpoint of practical applications, the removal of cadmium via sorption on hydrous oxides of Mn(IV) and Fe(III) appears to be a practically feasible approach to the treatment of potable waters and - as a secondary step - to industrial waste treatment.

V. ENTRANCE OF CADMIUM INTO DRINKING WATER DISTRIBUTION SYSTEMS VIA CORROSION OF PIPE MATERIALS

A. General

Corrosion of zinc-galvanized pipes is recognized as a source of cadmium in drinking water supplies (1,5,12). Cadmium is indeed a well known impurity of zinc (14,75), and its concentration in crude grades of zinc commonly used for galvanic coating of steel is not ordinarily specified (1).

The more corrosion resistant copper has gradually displaced galvanized steel as a household plumbing material, but it is very difficult to estimate the relative proportions of these two types of pipe presently in use for household water systems. Although some studies have indicated that copper pipes may also constitute a source of cadmium (1), corrosive attack of these systems probably plays a minor role. A more severe situation, however, is likely to exist in cases where galvanized pipes are coupled to copper or brass pipes or fittings, as this condition enhances the rate of corrosion of the less noble metals.

The eventual answer to the problem of uncontrolled metal leakage into drinking waters by corrosion probably lies in the usage of suitable plastic materials (76). Presently, the trend toward using plastic piping is gaining momentum, but reservations have been made against the use of certain plasticizers, which contain toxic heavy metals, such as cadmium and lead (77).

While under more practical conditions both cadmium and zinc are less noble than steel (75,79), cadmium contained within the microstructure of a zinc surface and exposed to a corrosive medium, is expected to assume the role of the cathode. This would imply that under these conditions, only the less noble zinc is subject to corrosive attack. However, it will be shown that "chemical" attack of cadmium may occur as a simultaneous process superimposed on the galvanic corrosion of zinc in a Zn/Cd couple.

Furthermore, it must be realized that water distribution systems often contain metals of higher cathodic potential, such as copper, brass or even steel (79), which are externally coupled with galvanized zinc. These metals exert a driving force on the corrosion of both, zinc and cadmium. Coupling of metals with dissimilar electrochemical stability is a very prominent source of corrosive attack, but there are other ways by which potential differences may be established (78,79). In water distribution systems, such situations may also arise from differences in temperature, in concentration of dissolved species, and in flow conditions, for example.

The presumably chemical attack of metals by a corrosive environment is usually regarded as a galvanic process on a micro-scale. That is, chemical or physical (e.g.: stress-induced) inhomogeneities may lead to a preferential localization of cathodic and anodic sites within the structure of a single metal (80). Thus, a differentiation between "chemical" and galvanic corrosion is merely operational, and does not necessarily reflect the nature of the mechanism involved in the corrosive process.

The standard electrode potential for cadmium is -0.40 volts (vs. H_2-electrode). Thus, cadmium is thermodynamically unstable in non-oxidizing acids and water under a wide range of conditions. In reality, pure cadmium is quite resistant to non-oxidizing acids, however. This behavior is explained in terms of its hydrogen overpotential, or mechanistically by a relatively high energy of activation for the discharge of H^+ ions at the metal surface. Thus, from a kinetic point of view, pure cadmium is expected to be stable under the pH conditions of natural waters (≈ pH 5-11), and in the absence of other driving forces or attacking species. A higher thermodynamic spontaneity for the oxidation of cadmium

$$Cd \rightarrow Cd^{2+} + 2e^- \qquad (E^o = -0.4\ V) \qquad (90)$$

results from the concomitant reduction of oxygen as a cathodic process.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (E^o = +1.23\ V) \qquad (91)$$

The equivalent cell potential for the oxidation of cadmium via oxygen reduction

$$2Cd + O_2 + 4H^+ \rightarrow 2Cd^{2+} + 2H_2O \qquad (92)$$

is +1.63 volts (at pH = 0) as compared with +0.400 volts for the process via the reduction of hydrogen.

Again, favorable thermodynamic conditions are inconclusive with regard to actual reaction rates, but owing to relatively lower effects of oxygen overpotentials (78), corrosive attack of certain metals by oxygen proceeds usually at measurable rates (75). By rearrangement of the Nernst equation for the oxygen attack of cadmium

$$E = E^{o} - \frac{RT}{nF} \ln \left(\frac{[Cd^{2+}]^2}{P_{O_2} \cdot [H^+]^4} \right) , \qquad (93)$$

and assuming all other variables to remain at standard state conditions, the variation of the cell potential for the overall process as a function of pH is given by

$$E = 1.63 - 0.059 \cdot pH. \qquad (94)$$

This relationship shows that the driving force for the reaction decreases by 0.059 volts for every unit decrease in pH.

Provided that the reaction proceeds at a measurable rate and that the mechanism does not change with pH, the thermodynamic relationship shown in Equation 94 can be used to predict the corrosion rate of cadmium as function of pH, at least on a qualitative basis. Usually, the situation is more complicated, and factors such as the formation of insoluble films and changes in the activation energy with pH, for example, must be taken into account. Kinetic phenomena are in general not readily predictable and must, therefore, be examined by actual experiment. Unfortunately, information on corrosion rates of cadmium in the aqueous environment is almost entirely lacking, and predictions about its kinetic behavior are highly speculative (79).

In addition to pH and oxygen concentration, the driving force for the corrosion of cadmium (Equation 93) is also affected by temperature and, to a minor extent, by the concentration of cadmium in solution. Kinetic temperature effects (e.g. Arrhenius-type dependence) are usually found to outweigh thermodynamic factors under the range of practical conditions in aqueous systems. The fact that oxygen solubility decreases strongly with increasing temperature tends to compensate for temperature effects on corrosion rates in the opposite direction.

One very important aspect of general significance to the corrosive properties of water is that of calcium carbonate saturation, which is governed by the following equilibrium:

$$CaCO_{3(s)} + H^+ \rightleftharpoons HCO_3^- + Ca^{2+}. \tag{95}$$

In quantitative terms, Equation 95 leads to

$$\log[H^+] = \log[HCO_3^-] + \log[Ca^{2+}] - \log K \tag{96}$$

and, substitution of

$$-\log[H^+] = pH, -\log K = pK, etc., \tag{97}$$

gives

$$pH = pHCO_3^- + pCa^{2+} - pK. \tag{98}$$

Further, it can be shown that

$$pK = pK_{sp} - pK_2, \tag{99}$$

in which K_{sp} and K_2 are given by

$$K_{sp} = [Ca^{2+}]\,[CO_3{}^{2-}] \tag{100}$$

and

$$K_2 = \frac{[H^+]\,[CO_3{}^{2-}]}{[HCO_3{}^-]}\,. \tag{101}$$

If the equilibrium pH for the reaction shown in Equation 95 is designated as pH_s and the alkalinity

$$[Alk] = [HCO_3{}^-] + 2[CO_3{}^{2-}] + [OH^-] - [H^+] \tag{102}$$

is substituted for the concentration of bicarbonate, the following expression is obtained:

$$pH_s = (pK_2 - pK_{sp}) + pCa^{2+} + p(Alk. + [H^+] - \frac{K_w}{[H^+]}) - p(1 + \frac{2K_2}{[H^+]}). \tag{103}$$

The difference between the pH of saturation and the actual pH is a measure of the saturation with respect to calcium carbonate, known (54) as the Langelier Index (L.I.):

$$L.I. = pH - pH_s. \tag{104}$$

The relevance of the Langelier Index to corrosion is based on the fact that waters saturated with $CaCO_3$ (L.I. > 0) have a tendency to form scales, whereas conditions of "undersaturation" (L.I. < 0) are regarded as "aggressive". While the corrosion protection of water pipes by scale formation is very desirable, it has the disadvantage of obstructing the flow and reducing the transfer of heat in boilers. The practical approach is usually that of a compromise with only a low degree of saturation being favored.

A discussion of further rate-controlling factors relative to the corrosion of cadmium will be presented in subsequent sections of this Chapter.

B. Experimental Approaches

Methods to study the rate of corrosion of metals are numerous, and may drastically differ in character depending on the purpose of the test and the nature and extent of the process, among other factors and considerations (79).

The objective of this investigation was to evaluate the nature and magnitude of corrosion of cadmium under conditions closely resembling those of drinking water systems and to establish the influence of systemic variables on the kinetic course of corrosive attack. The requirements of control and simulation of the chemical environment for such a study can usually be met, whereas the task of duplicating the physical conditions of a representative galvanized surface is rather difficult. Furthermore, the relatively low cadmium content in zinc, combined with slow kinetics would require long term observations and thus not be practical. For these reasons, the study of corrosion of a pure cadmium surface, which can be physically defined - at least on a macro-scale - appeared a more logical approach. Attempts for a quantitative extrapolation from a pure cadmium surface to more practical conditions will be made, but the validity of such extrapolations must be regarded as tentative in the absence of other experimental evidence. Nevertheless, it seems appropriate to assume that the influence of chemical factors on rates of cadmium corrosion with pure cadmium will be qualitatively similar to those in a cadmium-zinc system, provided appropriate experimental considerations are taken into account.

In view of an established radiochemical technique for trace measurement of cadmium, the kinetics of corrosion may be easily followed by counting of aliquots of the aqueous solution in contact with a solid cadmium surface of known activity. Since cadmium can be readily deposited from aqueous solutions, the preparation of a pure cadmium surface by plating on an inert metal, such as platinum, is a feasible experimental method.

C. Experimental Details

1. Electrolytic Deposition of Cadmium

A cadmium "electrode" was prepared by electroplating cadmium on a smooth sheet of platinum (dimension: $0.1 \cdot 10 \cdot 15$ mm^3) metal from perchloric acid solution containing labelled and stable cadmium (81).

A total amount of $5 \cdot 10^{-4}$ moles as Cd was originally employed by mixing a known quantity of the tracer solution (5.14 mg ${}_{48}\mathrm{Cd}^{115m}$ = 2mc) and a solution of cadmium perchlorate, prepared by dissolution of high grade CdO in $HClO_4$, in a tared teflon beaker. The electrolyte was made 1 M in $NaClO_4$ and adjusted to pH ≈ 1.5 by addition of appropriate quantities of sodium perchlorate, perchloric acid and distilled water. The resulting solution (≈ 70 g) containing $5 \cdot 10^{-4}$ moles of cadmium was calibrated by weighing and by radioassay as described in Chapter III. Prior to plating, the platinum surface was etched by treatment with "aqua regia" and finally it was rinsed with distilled water.

Initially, about 50 % of the total amount of cadmium was deposited by application of a current of ≈ 3 mA for several hours (Figure 25) with mixing provided by a magnetic stirrer. This procedure was repeated for 30 minutes at 2 mA prior to each corrosion experiment. The electrode was then removed, rinsed with distilled water, blotted with lense paper and immersed in the corrosion medium. After corrosion testing, the electrode was rinsed and stored in a dry and shielded bottle.

Occasionally the cadmium content in the plating bath was found depleted as indicated by a fall-off in current. In this case, cadmium was stripped off the surface by current reversal and then redeposited according to the above-mentioned procedures.

Hydrogen evolution was not noticed during electrolysis but was found to commence at currents of ≈ 50 mA and more, as was established by preliminary plating experiments with unlabelled cadmium. Also, it was observed that the cadmium

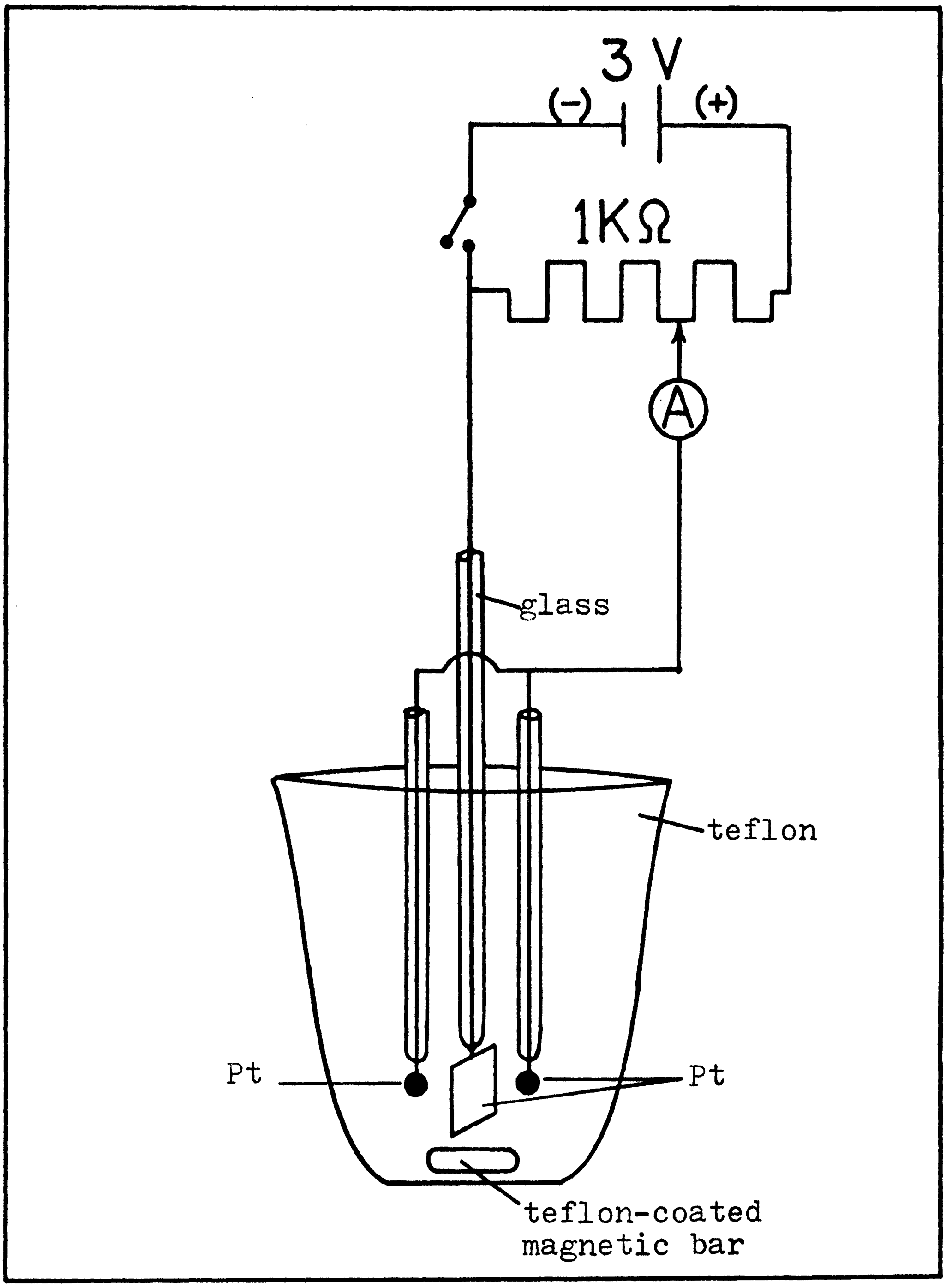

FIGURE 25. SCHEMATIC ASSEMBLY FOR ELECTRODEPOSITION OF CADMIUM ON PLATINUM ELECTRODE.

surface obtained at the low current densities applied was very smooth compared to dendritic growth in the higher current range.

2. Chemicals

Unless otherwise indicated, all chemicals used were of reagent grade. A dry and oil-free grade of compressed air and chemically pure nitrogen were used for atmospheric control of the corrosion experiments. When desirable, carbon dioxide was removed by passage of these gases through a column filled with "Ascarite", an adsorbent largely consisting of solid $Ca(CH)_2$, NaOH and certain minor additives. Calgon, a commercial grade of sodium polymetaphosphate, $(NaPO_3)_x$, was employed in some experiments, since this grade is used in many water treatment applications, including corrosion prevention.

3. Equipment

The instruments used for the measurement of pH, activity (scintillation counter) and the speed of agitation have already been described in Chapter III. A sensitive laboratory-type "VOM"-meter was used to measure the current during electrolytic deposition of cadmium. Direct current was provided by a heavy load dry-cell battery.

Corrosion experiments were performed in the plexiglass vessel shown in Figure 9, with additional openings to accomodate insertion of a thermometer and the cadmium and pH-electrodes. Mixing of the solution was provided for by a teflon coated stirring bar (1.5 inches long), which was rotated by a synchronous motor through a magnetic coupling. A medium porosity gas immersion tube made of polyethylene was used for passage of gases of defined composition through the reaction solution. The desired oxygen content of the atmosphere in contact with the solution was regulated by mixing of nitrogen and compressed air. The O_2 concentration in the gas mixture was measured with a polarographic oxygen sensor coupled with a continuous oxygen analyzer, Model 77700, both manufactured by Beckman Instruments. Air and O_2-free nitrogen were used as reference gases for purpose of calibration of the instrument.

Initial de-gassing of the corrosion medium was achieved by purging with nitrogen followed by evacuation with an aspirator pump.

4. Procedures

Prior to addition of chemicals, a volume of 770 ml distilled water contained in the corrosion reactor was de-gassed by alternate evacuation and purging with CO_2-free nitrogen accompanied by rapid mixing. The removal of CO_2 and O_2 was verified by concurrent pH measurement and continuous monitoring of the O_2 concentration in the effluent gas, respectively. Subsequently, and throughout the entire length of the corrosion experiment, the solution was kept saturated with a gas mixture of defined composition. The purging procedure was omitted in the case of experiments in equilibrium with air (pH 8.3, $[CO_3]_{TOT} = 10^{-3}$ M). In this case air was passed through the solution for 30 minutes prior to corrosion testing.

The desired levels of pH, ionic strength and reagent concentrations were adjusted by addition of appropriate quantities of standardized solutions of the respective chemicals. A total initial volume of 800 ml was prepared for each experiment. Unless otherwise specified, an agitator speed of 450 rpm was maintained during the corrosion experiments. After equilibration of the system, the cadmium "electrode" was immersed in the solution. Its position was fixed such that it would be reproduced in each run.

The rate of corrosion was followed by radioassay of solution aliquots, which were withdrawn from the vessel with a polyethylene syringe and directly transfered into the tared scintillation viles at fixed time intervals.

5. Analytical Method

Basically, the same counting technique, described in Chapter III, section A., was employed for radioassay of aqueous samples from corrosion experiments. Certain modifications became necessary, however, which will be described below.

In order to account for the total amount of cadmium in solution as a function of time, a loss of solution during sample withdrawal had to be avoided. Thus, the syringe was rinsed with the sample medium, emptied into the vessel, and after re-filling, the total sample volume was transfered into the pre-weighed vile until the same procedure was repeated. By subtraction of the sample volume (determined by weight), the remaining volume in the vessel could be calculated with fairly high precision.

Since the plating bath volume was bound to fluctuate over the period of this investigation, a different method for standardization was adopted. Prior to any removal of cadmium by deposition, an aliquot of the weighed electrolyte was removed and counted. This standard was used for initial and subsequent calibrations. Repeated checking of the count rate of the initial standard against the decay law for the cadmium isotope revealed excellent agreement indicating that the instrument efficiency was sufficiently stable. Thus, the concentration of cadmium in solution was calculated from the count rate and the time elapsed from the "time zero" in accordance with the decay law for this isotope. The validity of this procedure was always verified by paralled counting of the initial standard.

D. Treatment of Data

The rate of corrosion of a uniform metal surface in contact with a large excess of attacking species in the solution phase, is expected to be proportional to the surface area of the metal only.

$$-\frac{d[Me]}{dt} = kA \qquad (105)$$

Because the surface area, A, is practically constant, the process of metal corrosion under the above specified conditions should approximate a pseudo zero-order reaction.

$$- \frac{d[Me]}{dt} = k' \qquad (106)$$

This is indeed observed in many corrosion experiments and was found valid also for the corrosion of cadmium in well stirred aqueous media. Accordingly, a plot of the loss of cadmium per unit area of the metal surface versus time should yield a straight line with a slope of k'. Figure 26 shows the rate linearity required by zero-order kinetics, for the corrosion of cadmium in carbonate-free solution at different pH-levels. In accordance with the units used for weight and area, the specific rate constants (slopes of lines shown in Figure 26) for cadmium have the units of $\mu g \cdot cm^{-2} \cdot min^{-1}$. These are used in all presentations of corrosion rates for cadmium and were determined from the data by the method of "least squares" with a digital computer.

The proportionality of the rate of corrosion with respect to the surface area of cadmium has been established independently by experiments with electrodes of different surface areas. The treatment of data with a non-linear rate pattern, as has been observed in the case of film formation, will be discussed in connection with the interpretation of these individual cases.

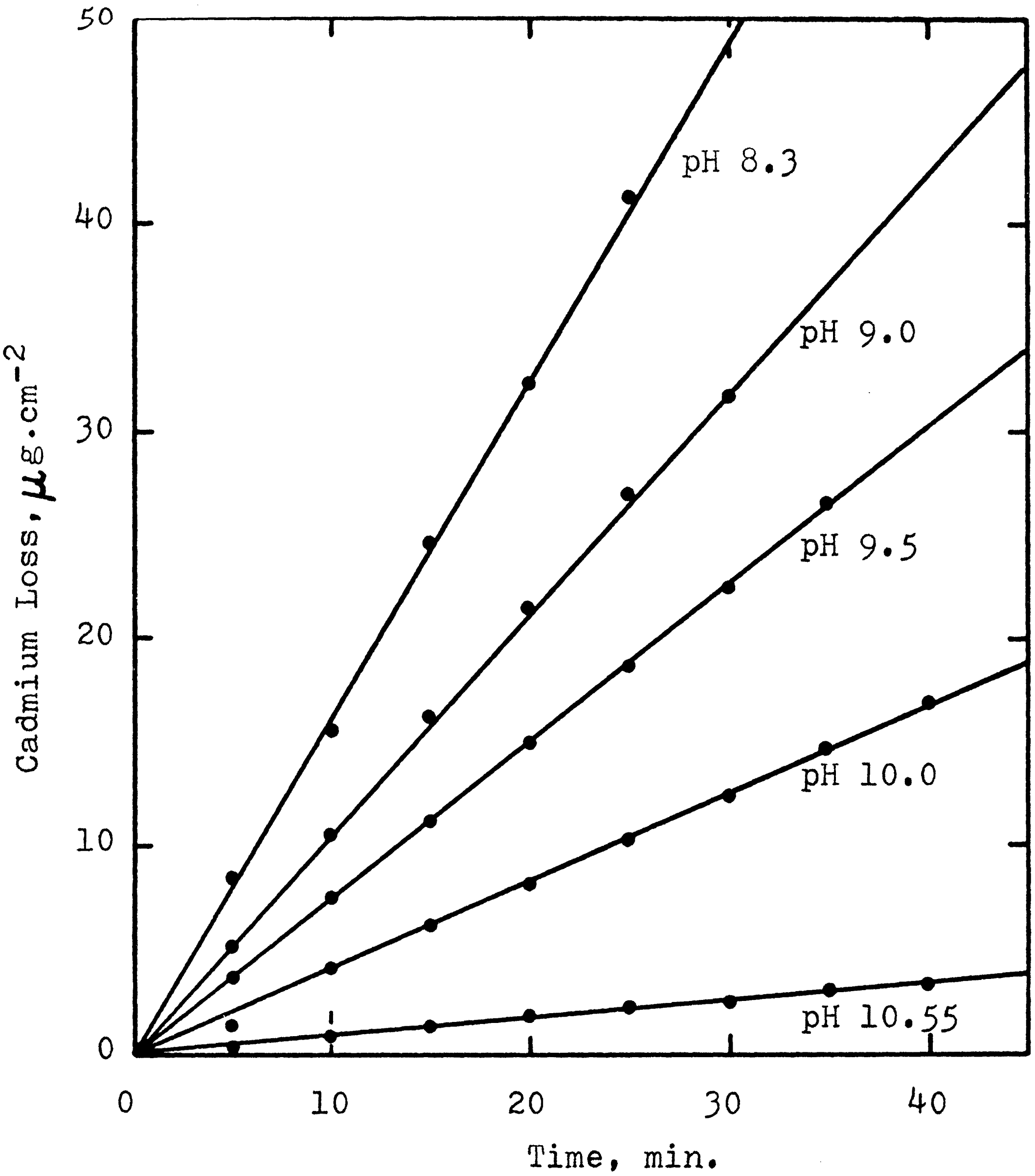

FIGURE 26. CORROSION OF CADMIUM AS FUNCTION OF pH IN CARBONATE-FREE SOLUTIONS.

Experimental Conditions: $t = 25.5 \pm 0.5\ ^{\circ}C$, $\mu = 0.01$ ($NaClO_4$), $P_{O_2} = 0.2$ atm., 450 rpm.

E. Results and Discussion

1. Cathodic Process and Mass Transport

The overall reaction of "chemical" dissolution of a single metal in an aqueous corrosive environment is mechanistically divided into a cathodic and an anodic process. With the exception of certain relatively noble metals (e.g. Cu), anodic reactions of the type

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne^- \qquad (107)$$

are considered very rapid (75). Thus, the corrosion of cadmium is expected to proceed under cathodic control. Evidence for the assumption that the reduction of oxygen constitutes the cathodic and rate-controlling reaction is shown by a plot of the corrosion rate versus the oxygen partial pressure in equilibrium with the solution phase (Figure 27). The rate increases rapidly with increasing concentration of oxygen, after which it tends to approach a limiting value. The rate determining step for the cathodic reaction may be:

a) the diffusion of oxygen at the solution-metal interface,
b) a reaction step during ionization of oxygen,
c) the removal or penetration of diffusion-obstructing solid products, such as $CdCO_3$ or $Cd(OH)_2$ films,

or any combination of these phenomena.

Mass transport control is sufficiently evidenced (see also Figure 28) for the conditions pertinent to Figure 27

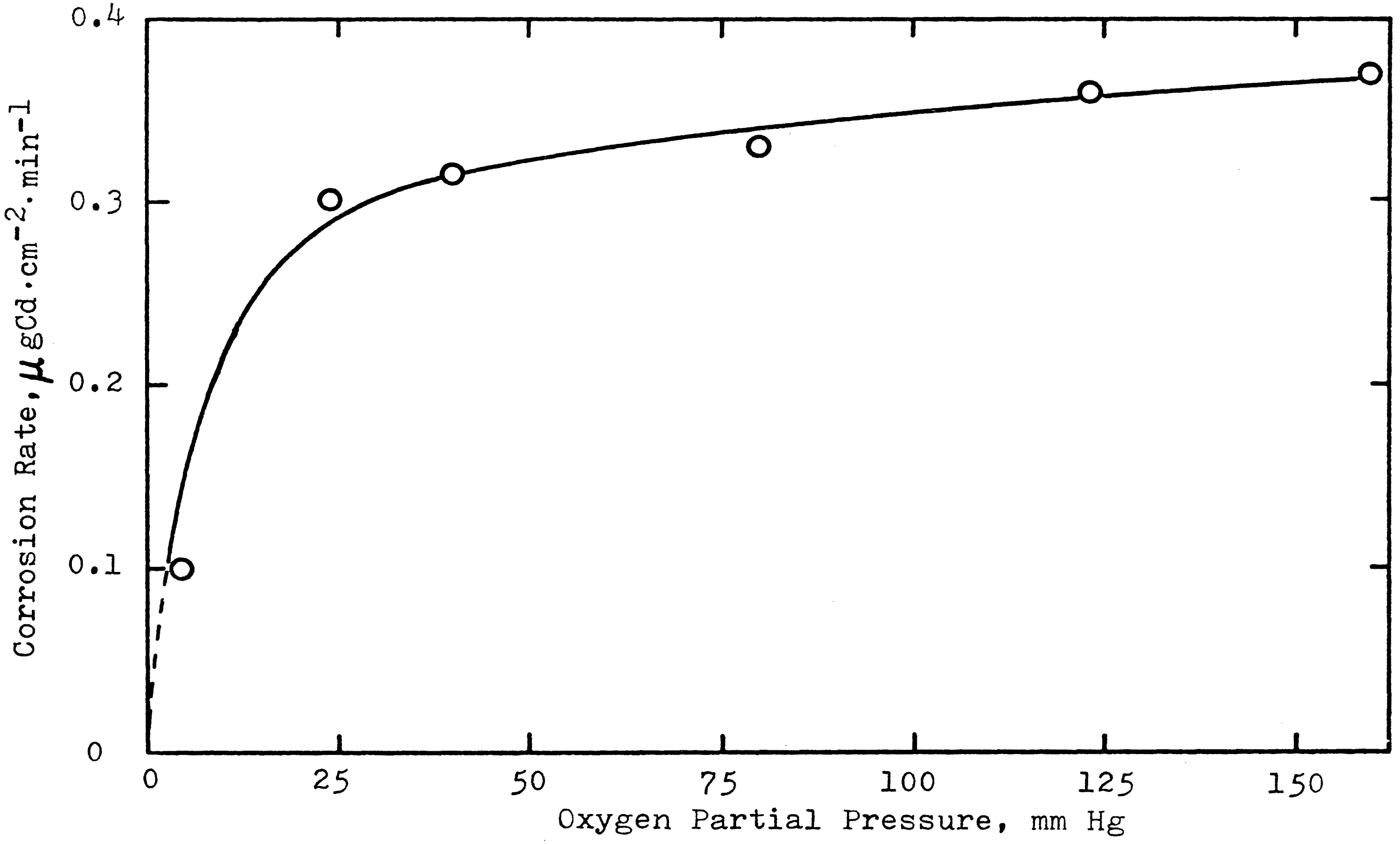

FIGURE 27. EFFECT OF SATURATION PRESSURE OF OXYGEN ON THE RATE OF CORROSION OF CADMIUM.

Experimental Conditions: $t = 25.5 \pm 0.5$ °C, $\mu = 0.01$ ($NaClO_4$), pH 9.5, 450 rpm, $[CO_3]_{TOT} = 10^{-3}$ $\underline{M}$, $P_{N_2} = (760 - P_{O_2})$ mm Hg.

and would, by the above definitions, apply to case a) and c) equally well. Activation control (case b) can be ruled out on the basis of the data shown in Figure 28, because in this case the rate of corrosion should be independent of the rate of agitation beyond a minimum degree of mixing of the solution.

The formation of surface films is indeed indicated by kinetic experiments in carbonate-free and carbonate-containing systems (see Figure 29, 30, and 31), and by the relative rate increase observed with galvanic corrosion experiments (see Section E. 4.) performed under comparable conditions.

The observed dependence of the rate on the oxygen concentration is generally consistent with hindrance of oxygen diffusion through a surface film consisting of cadmium carbonate or cadmium hydroxide. In view of an expectedly higher surface concentration of hydroxide ions in the rate limiting region for oxygen (Figure 27), the variation of the corrosion rate with oxygen may also indicate variable film permeability and composition throughout the entire range of oxygen partial pressures investigated.

As shown in Figure 28, the rate of cadmium corrosion in well oxygenated systems increases with increasing rate of agitation over a fairly wide rpm range without an indication of a plateau region much below ≈ 1000 rpm. A rate of 450 rpm was chosen for all other experiments, for this

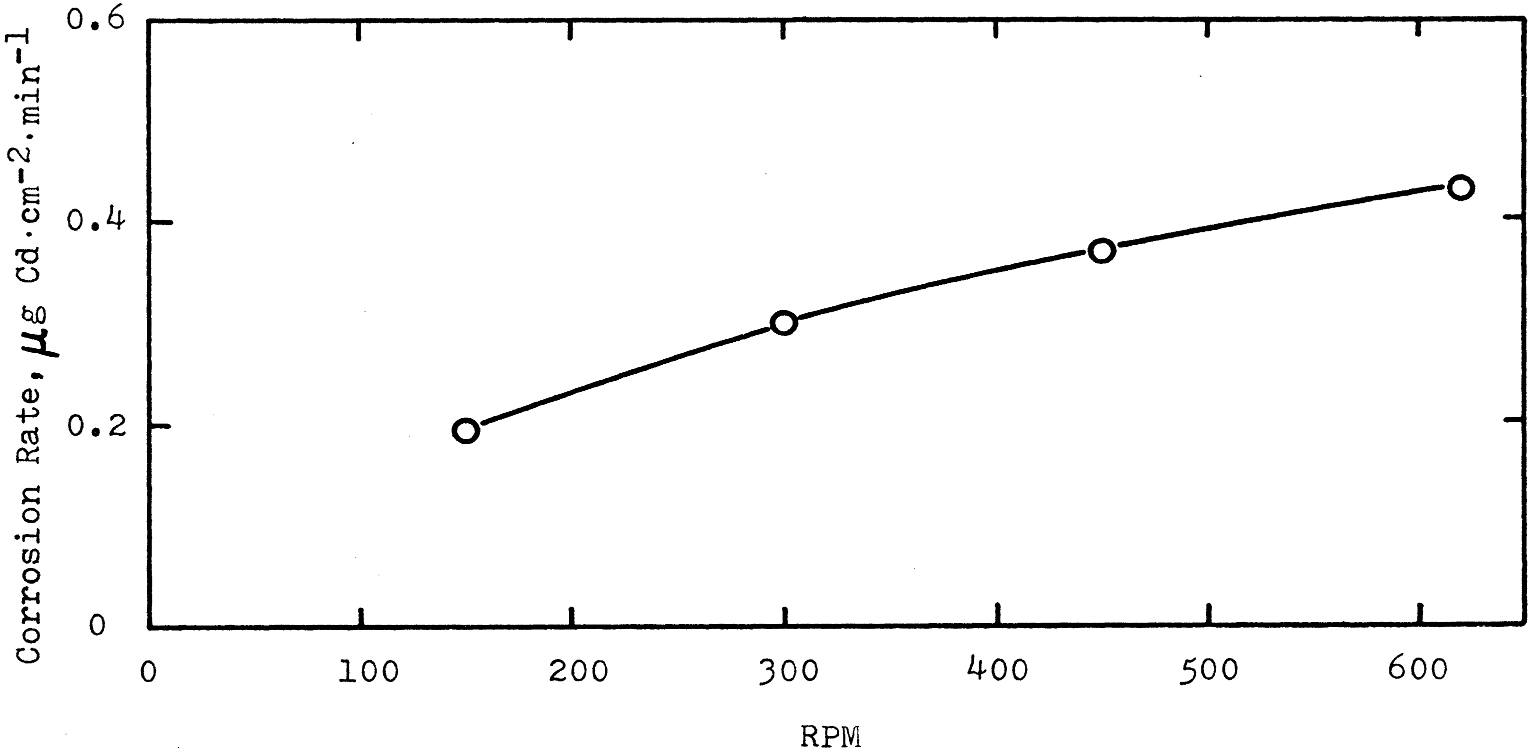

FIGURE 28. RATE OF CORROSION OF CADMIUM AS FUNCTION OF AGITATOR SPEED.

Experimental Conditions: $t = 25.5 \pm 0.5\ ^{o}C$, $\mu = 0.01$ ($NaClO_4$), pH 9.5, $P_{O_2} = 0.2$ atm., $P_{N_2} = 0.8$ atm., $[CO_3]_{TOT} = 10^{-3}$ M.

agitator speed was found most adequate for the desired level of turbulence in the experimental reactor. Although the data indicate that the corrosion rate in quiescent solution is rather slow, it is certainly not expected to become zero in view of convective migration of reactants and products. In fact, convection supported migration in standing pipes may be fairly extensive considering the temperature differences between the incoming water and the environment of its residence.

Cathodic depolarization of cadmium may also be affected by chlorine or hypochlorite ion, which are both present in small concentrations (usually less than 1 ppm as chlorine) in most drinking waters. Corrosion experiments performed with hypochlorite were considered inconclusive because of the observed chemical reduction of chlorine on the vessel walls (plexiglass). Because glass reactors are inadequate for reasons of cadmium adsorption, a study of the corrosive action of chlorine was not further attempted as it would have required the use of a closed teflon vessel, which was not readily accessible.

2. Effect of pH

The corrosion of cadmium has been studied in the pH range 8.3 - 10.55 in carbonate-free systems and in the presence of 10^{-3} $\underline{M}$ total carbonic species at an equilibrium oxygen partial pressure of 0.2 atmospheres. Figure 29 shows the results of these studies in a plot of the corrosion rates

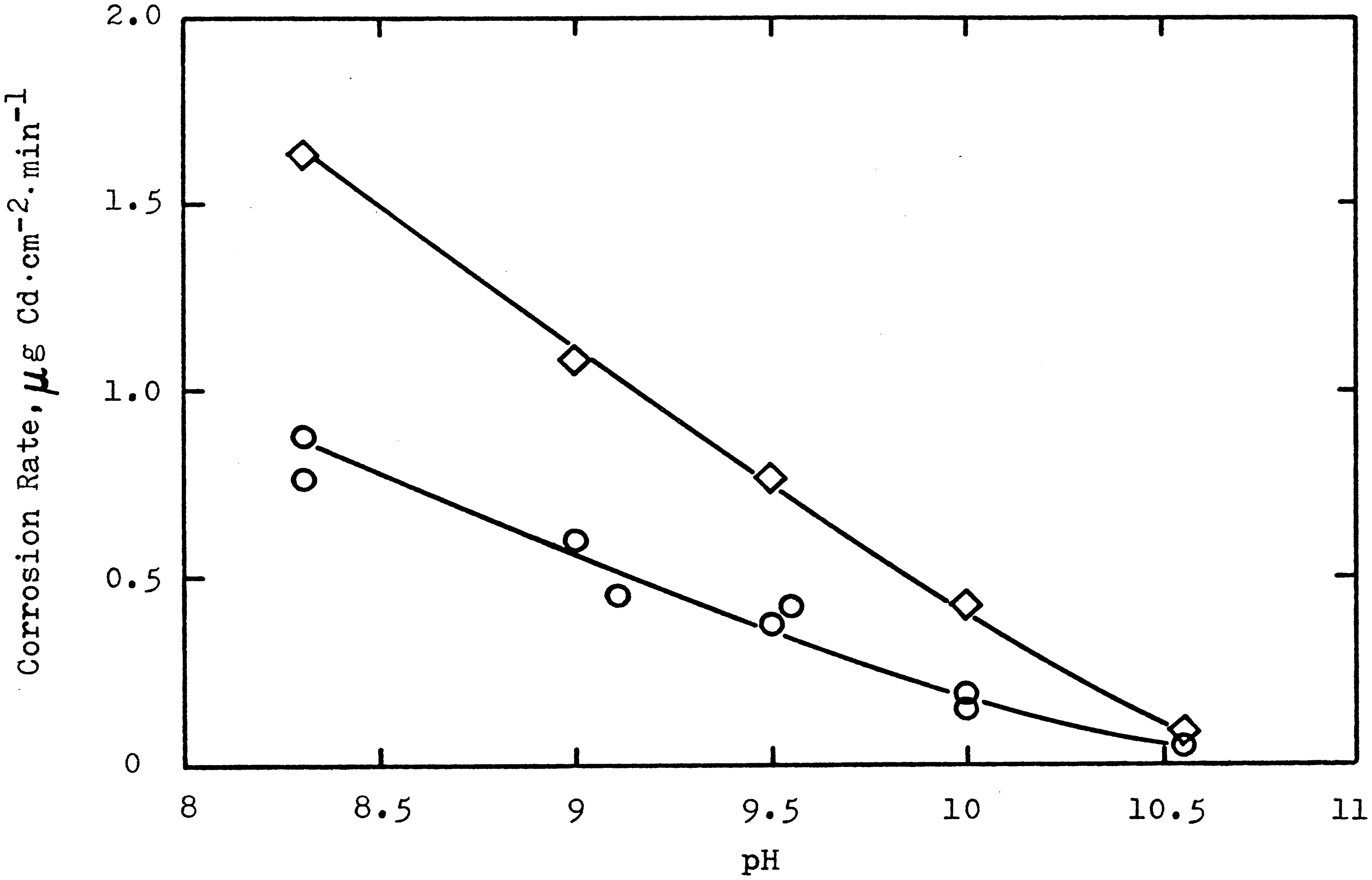

FIGURE 29. RATE OF CORROSION OF CADMIUM AS A FUNCTION OF pH IN CARBONATE AND CARBONATE-FREE SOLUTIONS.

Experimental Conditions: t = 25.5 ± 0.5 °C, μ = 0.01 ($NaClO_4$), 450 rpm, P_T = 1 atm., P_{O_2} = 0.2 atm., $[CO_3]_{TOT}$ = 0 (upper curve), = 10^{-3} M (lower curve).

(k' values) versus the pH. The rates tend to fall off with increasing pH, which is qualitatively consistent with a concurring decrease in the equivalent cell potential (Equations 93 and 94) for the overall process, but may also have mechanistic reasons. An asymptotic course for both curves in the higher pH region is also conspicuous. For the carbonate-free system, the latter behavior may be related to an increased tendency for the removal of films by complexation with hydroxide. The formation of films in carbonate-free systems is indeed indicated, particularly in the range pH >10 by a slight decrease in rates at an advanced stage of the reaction. This phenomenon will be given further consideration (Figure 30) in the following section.

3. Effect of Carbonate on Corrosion Inhibition

Carbonate species, present in low concentrations, decelerate the rate of cadmium corrosion substantially compared to carbonate-free rates. This decelerative effect is most pronounced in the lower pH range and tends to decrease in magnitude when pH increases (Figure 29). The gradual formation of a protective film on the cadmium surface is indicated by the fact that corrosion rates in carbonate systems exhibit a non-linear behavior, that is, the rates were observed to fall off with increasing extent of the reaction. This effect is illustrated in Figure 30, showing the separate average slopes (rates) for the initial and secondary stage of the reaction. The tendency of rates to fall off is found to

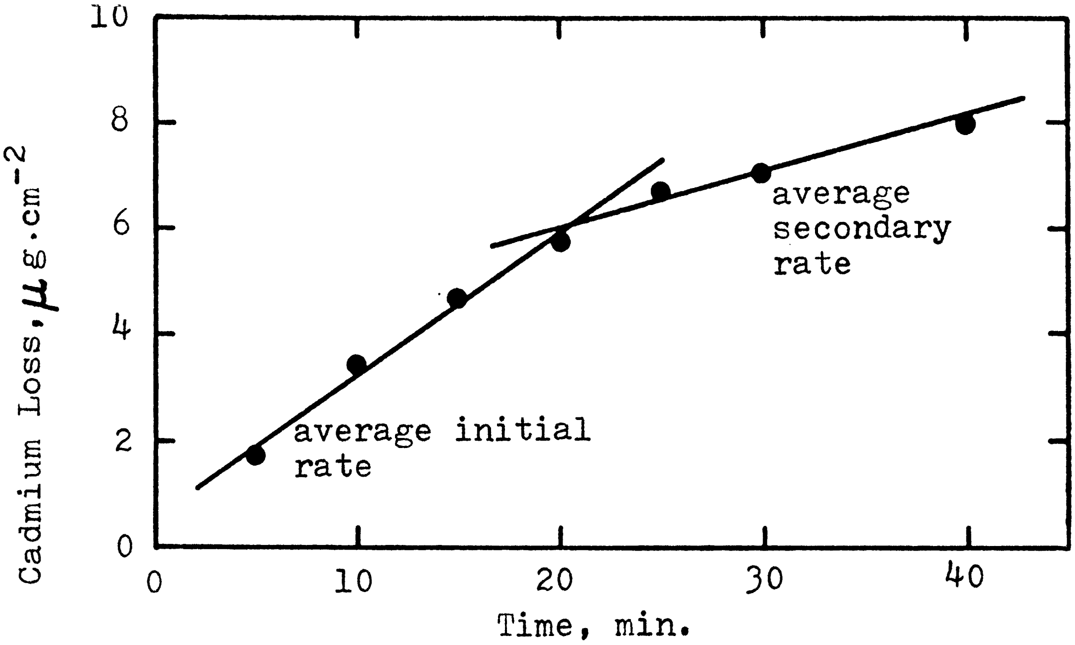

FIGURE 30. CORROSION OF CADMIUM AT pH 9.5 IN THE PRESENCE OF $5 \cdot 10^{-3}$ M CARBONIC ACID SPECIES.

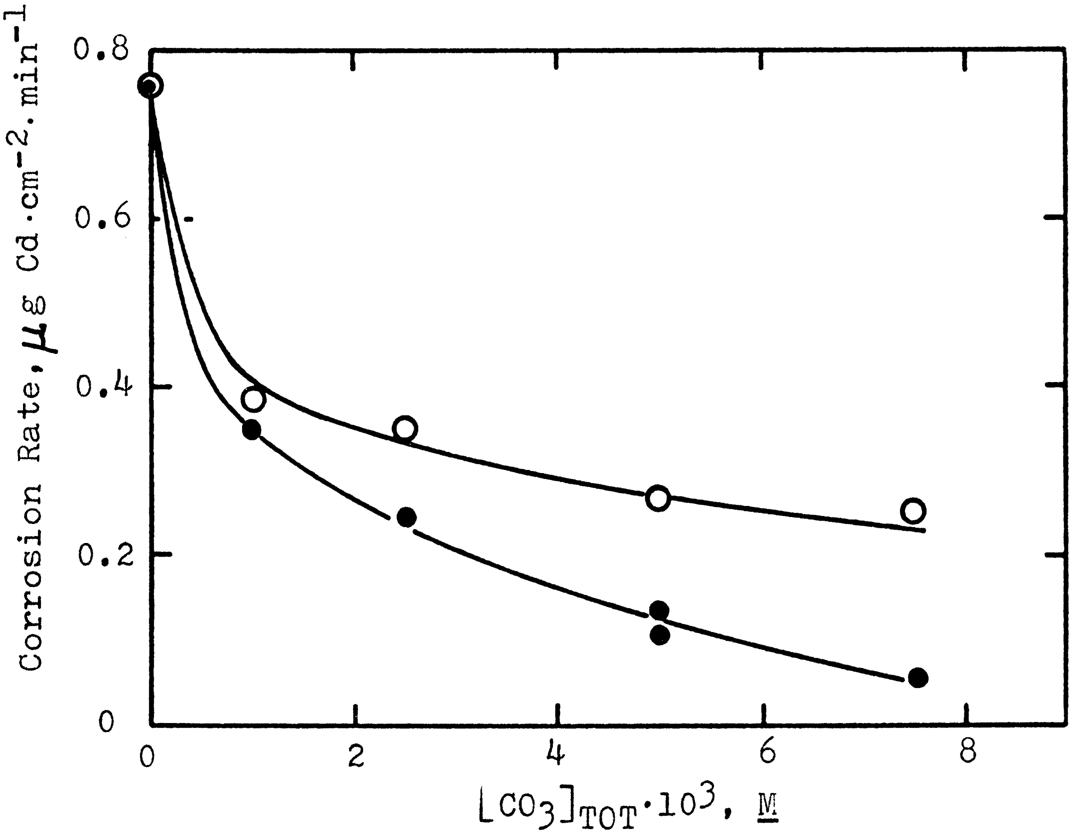

FIGURE 31. EFFECT OF TOTAL CARBONIC SPECIES CONCENTRATION ON RATE OF CADMIUM CORROSION.

Experimental Conditions: $t = 25.5 \pm 0.5$ °C, pH 9.5, $\mu = 0.01$ ($NaClO_4$), $P_{O_2} = 0.2$ atm., 450 rpm.
Upper and lower curve show average initial and average secondary rates, respectively.

increase in magnitude with increasing concentration of carbonate species in solution. This is shown in Figure 31 by a plot of the average initial and secondary corrosion rates at pH 9.5 as function of the carbonate species concentration. The fact that corrosion inhibition by carbonate is quite strong even at pH 8.3 (Figure 29) and that a linear rate pattern for these experiments (pH 8.3-9.5, $[CO_3]_{TOT} = 10^{-3}$ M, Figure 29) is observed, suggests that film formation in these instances must be fast. Furthermore, and in agreement with cadmium carbonate precipitation data (Chapter III.), this behavior suggests that film formation may either operate via combination with bicarbonate or with carbonate ions:

$$Cd^{2+} + OH^- \rightleftharpoons CdOH^+ \qquad (108)$$

$$CdOH^+ + HCO_3^- \longrightarrow CdCO_{3(s)} + HOH \qquad (109)$$

$$Cd^{2+} + CO_3^{2-} \longrightarrow CdCO_{3(s)}, \qquad (110)$$

since all of the reaction steps shown are considered rapid.

A similar reaction scheme can be used to describe formation of $Cd(OH)_2$ films in carbonate-free systems (Figure 29). The tendency for rates to fall off during the extent of the reaction is much less pronounced and observable only at pH > 10 in these cases. Thus, the formation of $Cd(OH)_2$ films is expected to be similarly rapid.

Solidifying evidence in favor of carbonate film formation was obtained by treatment of the cadmium surface with solutions containing 10^{-1} M carbonate species prior to corrosion experiments in 10^{-3} $\underline{M}$ carbonate solutions. The corrosion rate following such treatment was found to be (Figure 32) much reduced compared to the rate observed with an untreated surface.

In light of the present data, it appears that the different rate behavior found for carbonate and carbonate-free systems can be explained in terms of film permeability and/or film thickness, which in turn may be related to solubility phenomena. In this connection it is noteworthy to mention that the extent of corrosion in carbonate systems was usually found to far exceed the solubility limits for cadmium independent of a linear or non-linear rate pattern. Since precipitation of cadmium on vessel walls or in solution has not been observed, the rate fall-off at an advanced stage of the reaction is therefore an indication for progressing growth of the film, which is affected by the number of carbonate species in solution.

Prevention of corrosion by addition of film forming reagents is common practice, but is severely restricted to a few compounds in potable water treatment. The most natural approach of restraining corrosive attack of pipes is that of controlled deposition of calcium carbonate, the theory of which has been presented in a previous section. Other popular corrosion inhibitors used for protection of drinking water distribution systems are sodium metasilicate and sodium metapolyphosphates. The growth of protective layers of these compounds present in small concentrations is usually

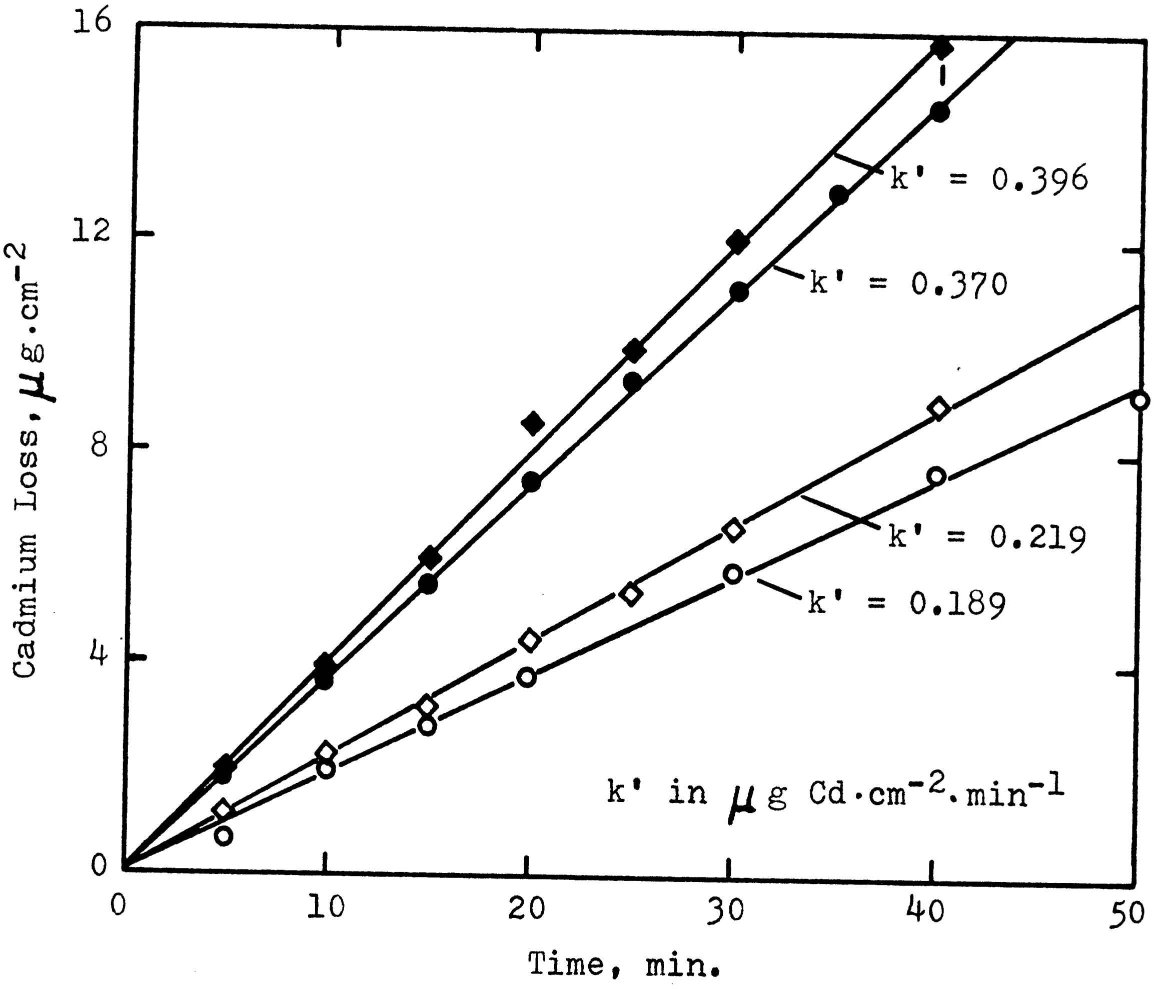

FIGURE 32. EFFECT OF SURFACE TREATMENT WITH INORGANIC COMPOUNDS ON CORROSION RATE OF CADMIUM.

Experimental Conditions: t = 25.5 ± 0.5 °C, pH 9.5, $\mu = 0.01$ ($NaClO_4$), $P_{O_2} = 0.2$ atm., $[CO_3]_{TOT} = 10^{-3}$ M, 450 rpm.

Conditions of surface treatment and further additives to testing medium:

Curve Designation	Pre-treatment Conditions	Additive
solid circles	none	none
solid diamonds	15 min. in solution of 1 g/l of $(NaPO_3)_x$, pH 9.5	$(NaPO_3)_x$ 5 mg/l
open diamonds	15 min. in solution of 1 g/l of Na_2SiO_3, pH 9.5	Na_2SiO_3 5 mg/l
open circles	15 min. in solution of 0.1 M $NaHCO_3/Na_2CO_3$, pH 9.5.	none

a slow process and cannot be easily simulated under laboratory conditions. Frequently, a high initial "shock" dosage followed by continuous application of small concentrations of these inhibitors is practiced. The feasibility of this method may be easier demonstrated on laboratory scale.

In Figure 32, the rates of cadmium corrosion are shown for cases of surface pretreatment with carbonate, sodium metapolyphosphate and sodium metasilicate followed by exposure to small concentrations of these compounds during the corrosion experiment. The results indicate specific film formation for pretreatment with carbonate and metasilicate, whereas no such effect can be claimed for metapolyphosphates. Experiments carried out in the presence of small concentrations of metapolyphosphate (Table 9) are consistent with this result.

TABLE 9

Corrosion of Cadmium in the Presence of Sodium Metapolyphosphate

$(NaPO_3)_x$ ppm	Corrosion Rate $\mu g(Cd) \cdot cm^{-2} \cdot min^{-1}$
0	0.370
2.5	0.350
4.37	0.389
6.25	0.378

Conditions: pH 9.5, $[CO_3]_{TOT} = 10^{-3}$ M,
450 rpm, $\mu = 0.01$,
$t = 25.5 \pm 0.5^{\circ}C$.

While the corrosion inhibiting properties of carbonate and silicate could be readily demonstrated, the apparent response to metapolyphosphates does not appear conclusive in view of the well-documented usefulness of these compounds for corrosion protection (75). Kinetic effects and participation of calcium ions may play a major role in film formation by metapolyphosphates (75).

A more adequate examination of the role of metapolyphosphate and calcium carbonate in the corrosion of cadmium should include long-term exposure of actual galvanized pipe structures. In this context, it must be realized that corrosive attack of a minor component within an alloy structure, such as cadmium, is expected to decrease concurrent with a reduction of corrosion of the overall surface in the presence of protective coatings. Thus, compounds capable of coating the entire surface, without necessarily exerting metal-specific effects, should also be protective towards cadmium.

4. Corrosion with Galvanic Coupling

Polarization of cadmium by external coupling with a nobler metal, such as copper ($E^0 = +0.34$ volts) or brass, provides an additional driving force for the corrosive attack of cadmium. Thermodynamically, the potential difference of a Cu-Cd couple is markedly larger than that established by microscopic short-circuited galvanic couples (microcells or microcouples) on an inhomogeneous cadmium surface. As illustrated in Figure 33, the corrosion rate increases by a factor of ≈ 10 when cadmium is galvanically coupled to copper as compared with "non-coupling" rates. Consideration of the relative increase in surface area for oxygen reduction (area (Cu) = 6 cm^2) and the rates for the Cu/Cd and Cd-systems suggests that the "free" surface area of cadmium under otherwise identical but "non-coupling" conditions is small compared with the geometric surface area employed. This fact is additional evidence for the formation of surface films as proposed for the non-galvanic corrosion of cadmium in oxygenated aqueous systems. The galvanic experiment with copper was observed for 24 minutes. A gradual rate fall-off was found (average rate = 2.66 μg Cd $cm^{-2} \cdot min^{-1}$) beyond a time of ≈ 16 minutes, which again indicates formation of film during an advanced stage of the reaction.

Much of the anodic role of cadmium, but not all, is lost by coupling of the Cu-Cd system to the less noble zinc. This behavior is illustrated (Figure 33) by the corrosion rate of cadmium observed in a Cu-Zn-Cd system. Cadmium continues to corrode fairly rapidly when coupled to the less noble zinc, that is under conditions of cathodic protection. This indicates that microcell-induced corrosion of cadmium may proceed under favorable conditions - though to a lesser degree - in spite of cathodic protection by zinc as an underlying process.

While measured on a quantitative scale, the galvanic experiments were performed to gain some qualitative insight

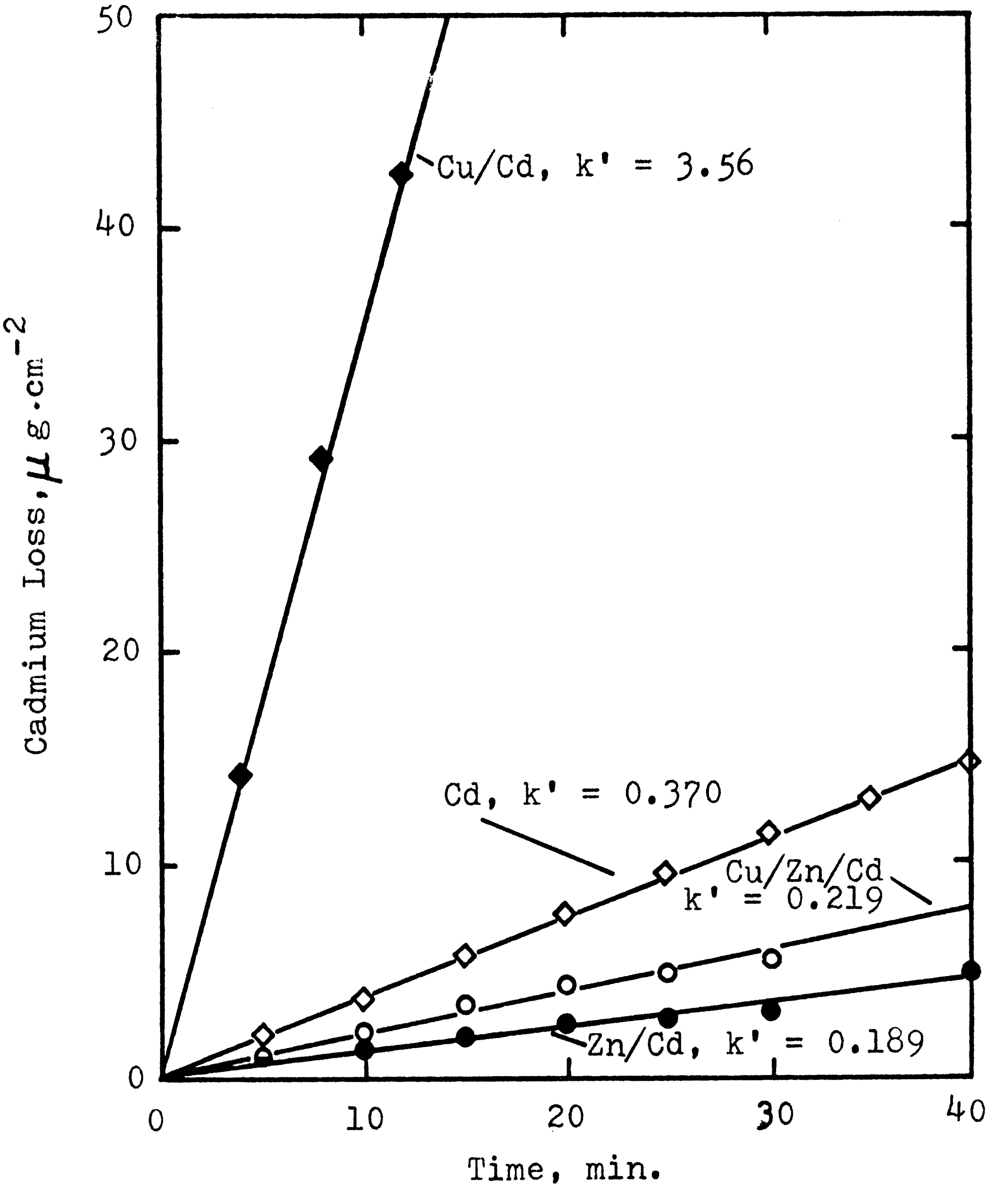

FIGURE 33. EFFECT OF EXTERNAL GALVANIC COUPLING ON RATE OF CADMIUM CORROSION.

Experimental Conditions: t = 25.5 ± 0.5 °C, pH 9.5, μ = 0.01 ($NaClO_4$), 450 rpm, $[CO_3]_{TOT}$ = 10^{-3} M; Surface areas: Cu = 6 cm^2, Cd = 3 cm^2, Zn = 4.5 cm^2. k' values in graph are given in $\mu g\ Cd \cdot cm^{-2} \cdot min^{-1}$.

into the corrosive behavior of cadmium under more complex conditions such as prevail in water distribution systems. The effect of relative areas of anodic and cathodic sites, oxygen accessibility and other factors of influence on the corrosion rate, must also be taken into account when considering more practical metal systems. Cadmium present within the microstructure of galvanized zinc may also become mechanically dislodged during the corrosion of zinc. In view of these possibilities, it will be of interest to examine some properties of zinc relative to corrosion.

Zinc is less noble than cadmium ($E^o = -0.76$ volts) and dissolves readily in non-oxidizing acids. The solubility products for zinc hydroxide and zinc carbonate are $7 \cdot 10^{-18}$ and $2.1 \cdot 10^{-11}$, respectively (50). Thus, owing to the relative difference in the solubility products for zinc in comparison to cadmium (Chapter II), its solubility under most conditions of natural waters will be governed by pH rather than by the concentration of carbonate species. This suggests also that protective films on a zinc surface consist largely of $Zn(OH)_2$ or similar products but not likely zinc carbonate. Furthermore, zinc is less soluble than cadmium under a wide range of conditions (pH 7-11, $[CO_3]_{TOT} < 5 \cdot 10^{-4}$ $\underline{M}$), representative for drinking waters.

Although zinc is known to dissolve under alkaline conditions, this behavior is insignificant under the pH conditions (≈ pH 5-11) of natural, and particularly drinking waters, in view of the magnitude of formation constants for zinc-hydroxide-complexes (47).

Consistent with the thermodynamic properties of zinc is its corrosive behavior in water as reflected by the data in Table 10 (after Bhakalov et al., reference 78).

TABLE 10

Corrosion of Zinc in Distilled Water as Function of pH (78)

pH	Corrosion Rate* $\mu g(Zn)\cdot cm^{-2}\cdot min^{-1}$
4	1.4
6	0.70
8	0.35
10	0.14
12	0.14
13	1.4

Qualitatively, the corrosion properties of zinc resemble those of cadmium in the range pH 8-11, beyond which zinc exhibits less corrosion resistance. While the exact experimental conditions have not been cited, the data found for the corrosion of zinc indicate somewhat slower rates than obtained for cadmium in this study. At least, an agreement in the order of magnitude for corrosion rates of both metals is evident. Thus, the minimum rate for the corrosion of cadmium, present within a galvanized zinc surface, appears to be governed by the rate of corrosion of the less noble zinc, in which case the process may simply be one of mechanical dislodgement.

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* approximate values taken from a graphical presentation by Bhakalov et al. (78)

Increased overall corrosion of both metals is very likely to occur when these are galvanically coupled to elements of lower corrosive potential, such as copper, brass, and passivated steel.

F. Conclusion

The corrosion of cadmium has been investigated under a variety of conditions representative for natural water and drinking water systems. Oxygen reduction appears as the only cathodic process in the corrosion of cadmium between pH 8.3 and 10.55 and cathodic control is indicated throughout the conditions of this investigation. The limiting step in the cathodic reaction appears to be solely associated with the transport of oxygen through surface films formed on the cadmium surface.

The corrosive attack of cadmium was found to decrease with increasing concentration of hydroxide and carbonate species present in solution. These data, supported by additional experimental evidence, suggest that corrosion inhibition by carbonate and hydroxide is attributable to the formation of protective films. A substantial rate reduction has also been observed after initial "shock" treatment of the cadmium surface with carbonate/bicarbonate or sodium metasilicate, but not with sodium metapolyphosphate.

The solubility limits for cadmium in carbonate containing solutions were often found to be far exceeded during corrosion experiments. Thus, the dissolution of cadmium metal in a corrosive environment proceeds to a high degree independent of saturation conditions in the aqueous phase.

As thermodynamically expected, the corrosion of cadmium was found greatly accelerated by galvanic coupling to copper. The high relative rate for a Cu/Cd couple over rates observed with non-galvanic corrosion experiments serves as further evidence for film formation in the corrosive attack of cadmium in oxygenated aqueous systems.

Galvanic coupling to the less noble zinc indicates that corrosive dissolution of cadmium may proceed in spite of cathodic protection by zinc under favorable circumstances. Otherwise, it appears that cadmium, contained within galvanized zinc, becomes mechanically dislodged during the corrosion of zinc, which reveals corrosive properties similar to those obtained for cadmium (78).

Leaching of cadmium into drinking waters may be greatly reduced by appropriate adjustment of pH and alkalinity levels. "Shock" treatment with high dosages of carbonate or sodium metasilicate followed by continuous "low level" feed of these compounds is similarly effective. Controlled deposition of calcium carbonate by chemical manipulation of the saturation index appears highly beneficial, since the transport of oxygen will be considerably restrained.

VI. SUMMARY AND CONCLUSIONS

Specific results and conclusions relative to individual phases of the research are presented in detail in the appropriate sections of each chapter. A summary of the more significant features of this report and suggestions for further research are given below.

1. Models describing the equilibrium solubility of cadmium over a wide range of variable conditions representative for natural waters and wastewaters have been formulated. In accord with these models, the solubility of cadmium in most natural waters should be governed by carbonate, or by hydroxide in systems having very low carbonate concentrations. For example, the solubilities of cadmium at pH 8.3 and at concentrations of 0 and $5 \cdot 10^{-4}$ $\underline{M}$ total carbonic acid species, are 637 mg/l and 0.11 mg/l, respectively. Simple solubility calculations for cadmium are valid only in the range pH < 9, above which formation of hydroxide complexes becomes increasingly important. Complexation by chloride and ammonia seems insignificant in view of the low level occurrence of these ions in the fresh water environment; but such reactions may be of serious consequence in the treatment of certain industrial wastes. The latter systems may suffer from even greater complexity by interaction of cadmium with organic ligands, a recognized tendency of this metal.

2. Isotope techniques, using ${}_{48}Cd^{115m}$ and subsequent Cerenkov counting of aqueous samples are ideally suited for

experimental examination of systems containing trace amounts of cadmium. Complications arising from losses of the metal by sorption on container walls can be circumvented or minimized by acidification and/or employment of polyethylene or teflon labware.

3. The kinetics of precipitation of cadmium in alkaline carbonate solutions has been studied as function of pH, ionic strength and concentration of cadmium, chloride, sulfate and carbonic acid species. The rate of precipitation generally exhibits a rapid initial and slow secondary growth component; the latter is reasonably well described by a first-order rate expression with respect to cadmium.

4. Precipitation of cadmium with carbonate is advantageous in that it results in minimum solubility and faster overall rates, compared with rates and limits of solubility of cadmium in carbonate-free systems. The variation of rate with pH and with the concentration of carbonic acid species is indicative of simultaneous operation of several mechanisms leading to mixed reaction products, such as basic carbonates. High carbonate/hydroxide ratios represent optimum conditions for quantitative and rapid cadmium removal. These conditions tend to coincide with the pH range (9.3-10.0) of minimum cadmium solubility in carbonate controlled systems.

5. The initial extent of the reaction was found to decrease with increasing perchlorate ionic strength and sulfate concentration, while the secondary precipitation rate

was not appreciably affected. Chloride exerts no specific effects on the reaction over that observed with perchlorate ion.

6. Seeding with pre-formed particulate $CdCO_3$ considerably accelerates the overall rate of subsequent precipitation of cadmium in carbonate systems. Experimental results suggest high feasibility for the practice of sludge recirculation in the treatment of cadmium bearing wastes. Pilot studies with actual waste solutions should be conducted to evaluate the performance and practical feasibility of this process on a larger scale. Such an approach should also yield further information on the effect of physical conditions (e.g.: mixing, settling) and on the general compatibility of cadmium precipitation with a simultaneous removal of other heavy metals.

7. If warranted by field data, a study of the complexation of heavy metals by organic compounds, such as are employed in metal finishing operations, deserves consideration. Decomplexation of the metal may be accomplished by oxidative degradation of the organic ligands in such cases, for example.

8. Removal of trace amounts of cadmium ($< 10^{-6}$ $\underline{M}$) from drinking water supplies is highly desirable in view of the low levels at which toxic effects are manifest by this metal (19). Sorptive uptake of cadmium on suitable solid materials would constitute a method easily adaptable to present water treatment technology. Accordingly, the sorption

behavior of hydrous oxides of Al(III), Fe(III), and Mn(IV) towards cadmium was examined over a wide range of variable conditions.

9. The equilibrium uptake of cadmium on the sorbents studied can be described well by the Langmuir equation for sorption. Sorption rates observed with highly dispersed hydrous oxides are extremely rapid, with equilibrium usually being attained in less than 10 minutes.

10. Both the limiting sorption capacity (X_m) and adsorption affinity (b) for cadmium tend to increase over the pH range beyond the pH of zero point of charge (ZPC) for all three oxides studied. Hydrous manganese dioxide, prepared by careful reduction of permanganate, was found superior on the basis of Langmuir parameters and by virtue of its low ZPC value. The practical range for Al(III) salts is rather limited due to the formation of aluminate and a relatively high ZPC for Al(III) hydrolysis products.

11. The sorption of cadmium exhibits a small dependence on ionic strength, and competitive effects from uptake of calcium or from chloride complexation are similarly weak in magnitude. These results suggest that sorption on hydrous oxides of Mn(IV) and Fe(III) is a feasible approach for removal of cadmium in municipal water treatment and in secondary waste treatment operations.

12. This work and related studies (67,68,69) indicate that the sorptive behavior of hydrous oxides is greatly influenced by the age and mode of preparation of these materials. Investigation of these aspects may prove very fruitful from the standpoint of optimizing the efficiency of sorptive processes on separate basis or in combination with coagulation techniques.

Furthermore, the chemical and structural resemblance between hydrous manganese dioxide and "silica" suggests similar sorptive properties for the latter material. Since the use of silica as a coagulant aid in water treatment has already been established, an examination of its role as a potential sorbent for heavy metal ions appears worthwhile.

13. Cadmium may enter drinking waters by corrosion of galvanized pipes (1,5,12). This is presumably a temporary problem in view of the present trend for displacing galvanized steel by copper or even plastic plumbing materials. From the standpoint of the high toxic potential of cadmium to man (19), a study of the corrosion behavior of the metal in representative aqueous systems was felt of immediate importance in order to establish criteria for preventative measures.

14. The corrosion of cadmium in water between pH 8.3 to 10.55 was found to proceed under cathodic control via reduction of oxygen. The cathodic reaction is limited by oxygen transport to the corrosion site under a wide range

of experimental conditions.

15. Corrosion rates were found to decrease substantially with increasing concentration of hydroxide and carbonate species. Pre-coating of the surface with carbonate or sodium metasilicate resulted in greatly reduced rates of attack relative to those when no petreatment was provided. The data suggest that corrosion inhibition by carbonate, metasilicate, and hydroxide is attributable to the formation of protective films.

16. In spite of a film forming tendency observed with solubility governing ions, the corrosion of cadmium may lead to accumulation of the metal in solution far in excess of concentrations corresponding to calculated solubilities in these systems. With respect to drinking water contamination it seems irrelevant, however, whether the metal exists in a dissolved or dispersed solid (precipitated) state.

17. Coupling of cadmium with the more noble copper was shown to result in drastic corrosion of the former, as can be expected thermodynamically. The high relative rate of corrosion of a Cu/Cd couple compared with rates observed for a Cd-system, is further evidence in favor of film formation for the case of non-galvanic attack of cadmium in oxygenated waters.

18. Under favorable conditions, "chemical" corrosion of cadmium coupled to less noble zinc may proceed at measur-

able rates in spite of cathodic protection by zinc. Otherwise, it appears that cadmium,contained within galvanized zinc, becomes mechanically dislodged during corrosion of zinc, which exhibits corrosive properties similar to those obtained for cadmium (78).

19. Corrosion of cadmium contained within galvanized zinc pipes may be minimized or prevented from occurring by:

a) pre-treatment of piping systems with solutions of carbonate or sodium metasilicate followed by low level feed of these compounds,

b) maintaining relatively high pH and carbonate concentration in drinking water,

c) elimination of coupling with more noble metals (e.g. copper, brass),

d) manipulation and control of chemical factors (pH, alkalinity, hardness), such that the solubility of calcium carbonate is slightly exceeded in order to facilitate interior coating of the pipes with calcium carbonate.

20. Inhibition of corrosion by pre-treatment of cadmium metal with, or exposures to aqueous solutions containing small concentrations of sodium metapolyphosphate, has not been observed in this work. In view of the well documented suitability of these compounds for corrosion prevention, the observed results are considered inconclusive. Long term experimentation, possibly on a pilot scale, seems necessary to establish more information on the usefulness of metapolyphosphates for this purpose.

21. In light of recent publications indicating that cadmium in drinking water is a potential factor in cardiovascular disease of man (19), it appears appropriate to initiate further statistical programs with analytical data for cadmium gathered from actual household plumbing systems. Important parameters for meaningful statistical correlations should include the following:

a) incidence rate of disease,
b) concentration of cadmium (and other toxic metals) in standing and running pipe systems,
c) nature of piping materials,
d) water composition: pH, alkalinity, hardness, dissolved oxygen, stability index (Langelier Index), presence and concentration of corrosion inhibitors, and concentration of heavy metals in the finished water at the site of the treatment plant.

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APPENDIX A - COMPUTER PROGRAM I

Calculation of Distribution Diagrams for Cadmium Hydroxide Complexes.

```
      DIMENSION PHHOLD(80),A0HOLD(80),A1HOLD(80),A2HOLD(80),
     2A3HOLD(80),A4HOLD(80),IMAGE(1400)
      B1=1.45*10**4
      B2=2.46*10**8
      B3=1.20*10**9
      B4=5.76*10**8
C
      WRITE(6,50)
C     CALCULATE ALPHA'S AS FUNCTION OF PH
      N=1
      E=1
      DO 15 I=1,8
      E=E-1
      P=1.1
C
      DO 15 J=1,10
      P=P-0.1
      X=P*10**E
      X2=X*X
      X3=X2*X
      X4=X3*X
      A0=1.0/(1.0+B1*X+B2*X2+B3*X3+B4*X4)
      A1=B1*X*A0
      A2=B2*X2*A0
      A3=B3*X3*A0
      A4=B4*X4*A0
      ATOT=A0+A1+A2+A3+A4
      Y=ALOG10(X)
      PH=14+Y
C
      WRITE(6,100) PH,A0,A1,A2,A3,A4,ATOT
C
C     STORE CALC. VALUES IN MATRICES FOR PLOTTER
      PHHOLD(N)=PH
      A0HOLD(N)=A0
      A1HOLD(N)=A1
      A2HOLD(N)=A2
      A3HOLD(N)=A3
      A4HOLD(N)=A4
      N=N+1
15    CONTINUE
C
      WRITE(6,200)
      CALL STPLT 2 (IMAGE,PHHOLD,A0HOLD,80,4,'*',11,
     2'ALPHA  ZERO')
      WRITE(6,150)
```

COMPUTER PROGRAM I (continued)

```
      WRITE(6,250)
      CALL STPLT 2 (IMAGE,PHHOLD,A1HOLD,80,4,'*',11,
     2'ALPHA   ONE')
      WRITE(6,150)
      WRITE(6,300)
      CALL STPLT 2 (IMAGE,PHHOLD,A2HOLD,80,4,'*',11,
     2'ALPHA   TWO')
      WRITE(6,150)
      WRITE(6,350)
      CALL STPLT 2 (IMAGE,PHHOLD,A3HOLD,80,4,'*',11,
     2'ALPHA THREE')
      WRITE(6,150)
      WRITE(6,400)
      CALL STPLT 2 (IMAGE,PHHOLD,A4HOLD,80,4,'*',11,
     2'ALPHA  FOUR')
      WRITE(6,150)
C
50    FORMAT('1',10X,'PH',13X,'ALPHA--ZERO',4X,'ALPHA---ONE',
     24X,'ALPHA---TWO',4X,'ALPHA-THREE',4X,'ALPHA--FOUR',
     34X,'ALPHA-TOTAL')
100   FORMAT('0',6X,7F15.9)
150   FORMAT('0',55X,'PH')
C
200   FORMAT('1',35X,
     2'DISTRIBUTION OF (CD++) AS FUNCTION OF PH')
250   FORMAT('1',35X,
     2'DISTRIBUTION OF (CDOH+) AS FUNCTION OF PH')
300   FORMAT('1',35X,
     2'DISTRIBUTION OF (CD(OH)2) AS FUNCTION OF PH')
350   FORMAT('1',35X,
     2'DISTRIBUTION OF (HCDO2(1-)) AS FUNCTION OF PH')
400   FORMAT('1',35X,
     2'DISTRIBUTION OF (CDO2(2-)) AS FUNCTION OF PH')
      END
```

APPENDIX B - COMPUTER PROGRAM II

Calculation of Solubility of Cadmium as Function of pH in Carbonate and Carbonate-Free Systems.

```
      DATA CS0,CS2,CS3,CS4,C6,C7,C8,C9,C10,C14/
     22.2E-14,4.2E-6,3.2E-10,2.64E-5,3.8E-12,1.8E-4,5.2E-12,
     31.45E+4,2.47E+8,1.2E+9/
3     READ(5,205) TCA
C
      DIMENSION PHHOLD(50),SYHOLD(50),IMAGE(1400)
      N=1
      E=-1
      WRITE(6,25)
      DO 20 I=1,5
      E=E-1
      P=1.1
      DO 20 J=1,10
      P=P-0.1
      HO=P*10**E
      HO2=HO*HO
      HO3=HO*HO2
      IF(TCA.EQ.0.0) GO TO 17
C
      CO3=TCA/(C6/HO2+C7/HO+1.0)
      R=HO2/CO3
      IF(R.GE.0.00423) GO TO 18
      S=C8/CO3*(1.0+C9*HO+C10*HO2+C14*HO3)
      GO TO 19
17    CO3=0.0
      R=-0.0
C
18    S=CS0/HO2+CS2+CS3/HO+CS4*HO
19    SY=ALOG10(S)
      Y=ALOG10(HO)
      PPM=S*112.4*1000
      PH=14+Y
      WRITE(6,50) PH,TCA,CO3,R,S,SY,PPM
      PHHOLD(N)=PH
      SYHOLD(N)=SY
      N=N+1
20    CONTINUE
```

COMPUTER PROGRAM II (continued)

```
C
      WRITE(6,100)
      CALL STPLT 2 (IMAGE,PHHOLD,SYHOLD,50,4,'*',15,
     2'LOG SOL*CADMIUM')
      WRITE(6,150)
      GO TO 3
C
25    FORMAT('1','PH',6X,'T(CO3)',2X,'CO3-EQ',3X,'HO2/CO3',2X,
     2'TOT(CD)M/L',2X,'LG(CD)',7X,'PPM-AS--CD')
50    FORMAT('0',F6.3,2X,F6.4,2X,F7.5,2X,F7.4,2X,E10.4,2X,
     2F7.3,2X,F12.6)
100   FORMAT('1',30X,
     2'TOTAL CD-SOLUBILITY-LOG(M/L) AS FUNCTION OF PH')
150   FORMAT('0',55X,'PH')
205   FORMAT(F6.4)
      END
```

APPENDIX C - COMPUTER PROGRAM III

Calculation of Solubility of Cadmium as Function of pH in Systems Containing Hydroxide, Carbonate, Chloride and Ammonia.

```
      EXTERNAL FCT,FCT2
      COMMON A,B,C,TA,U,V,TC
      DATA CS0,CS2,CS3,CA,C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,
     2C12,C13/2.2E-14,4.27E-6,3.2E-10,1.78E-5,9.8E-12,
     32.48E-9,1.02E-7,4.6E-13,7.3E-12,3.8E-12,1.8E-4,5.2E-12,
     41.45E+4,2.47E+8,4.47E+2,5.63E+4,1.55E+6/
3     READ(5,205) TCA
      READ(5,200) TC,ZST,EPS2
      READ(5,201) TA,XST,EPS
C
      DIMENSION PHHOLD(40),SYHOLD(40),IMAGE(1400)
      N=1
      E=-1
      WRITE(6,25)
      DO 20 I=1,4
      E=E-1
      P=1.1
      DO 20 J=1,10
      P=P-0.1
      HO=P*10**E
      HO2=HO*HO
C
      IF(TCA.EQ.0.0) GO TO 4
      CO3=TCA/(C6/HO2+C7/HO+1.0)
      R=HO2/CO3
      GO TO 6
C
4     R=1.0000
      CO3=0.0000
6     IF(TC.EQ.0.0) GO TO 13
C
      IF(R.GE.0.00423) GO TO 5
      U=332.0*C8/CO3
      V=1.0+21.0*C8/CO3
      GO TO 7
C
5     U=C5/HO2
      V=1.0+C4/HO2
7     IF(V.EQ.1.0) GO TO 12
      CALL RTNI (Z,F2,DERF2,FCT2,ZST,EPS2,20,IER2)
      Z2=Z*Z
      GO TO 14
```

COMPUTER PROGRAM III (continued)

```
12     Z=TC
       Z2=Z*Z
       IER2=4
       GO TO 14
C
13     Z=0.0000
       Z2=0.0000
       IER2=5
C
14     IF(TA.EQ.0.0) GO TO 16
C
       IF(R.GE.0.00423) GO TO 15
       A=3.0*C13*C8/CO3
       B=2.0*C12*C8/CO3
       C=1.0+CA/HO+C11*C8/CO3
       GO TO 151
C
15     A=C3/HO2
       B=C2/HO2
       C=1.+CA/HO+C1/HO2
C
151    CALL RTNI (X,F,DERF,FCT,XST,EPS,30,IER)
       X2=X*X
       X3=X*X*X
       GO TO 17
C
16     X=0.0000
       X2=0.0000
       X3=0.0000
       IER=7
C
17     IF(R.GE.0.00423) GO TO 18
C
       S=C8/CO3*(1.0+C9*HO+C10*HO2)+C8/CO3*(C11*X+C12*X2+C13*X3)+
      6C8/CO3*(21.0*Z+166.0*Z2)
       GO TO 19
18     S=CS0/HO2+CS2+CS3/HO+C1*X/HO2+C2/2.*X2/HO2+C3/3.*X3/HO2
      2+C4*Z/HO2+C5/2.Z2/HO2
C
19     SY=ALOG10(S)
       Y=ALOG10(HO)
       PPM=S*112.4*1000
       PH=14+Y
       WRITE(6,50) PH,TCA,CO3,R,TA,X,IER,TC,Z,IER2,S,SY,PPM
       PHHOLD(N)=PH
       SYHOLD(N)=SY
       ZST=Z
       EPS2=0.01*Z
       XST=X
       EPS=0.01*X
```

COMPUTER PROGRAM III (continued)

```
      N=N+1
20    CONTINUE
C
      WRITE(6,100)
      CALL STPLT 2 (IMAGE,PHHOLD,SYHOLD,40,4,'*',15,
     2'LOG*CADMIUM')
      WRITE(6,150)
      GO TO 3
C
25    FORMAT('1','PH',5X,'T(CO3)',2X,'(CO3)EQ',2X,'HO2/CO3',
     22X,' T(NH3)',2X,'(NH3)EQ',2X,'IER',2X,'T.(CL)',2X,
     3'(CL)EQ',2X,'IER2',2X,'TOT(CD)M/L',2X,'LOG(CD)',2X,
     4'(CD)-PPM')
50    FORMAT('0',F5.2,2X,F6.4,2X,F7.5,2X,F7.5,2X,F6.4,2X,F6.4,
     22X,I3,2X,F6.4,2X,F6.4,2X,I4,2X,E10.4,2X,F7.3,2X,F8.6)
100   FORMAT('1',30X,
     2'TOTAL CD-SOLUBILITY-LOG(M/L) AS FUNCTION OF PH')
150   FORMAT('0',55X,'PH')
200   FORMAT(F6.4,1X,F6.4,1X,F8.6)
201   FORMAT(6X,F6.4,3X,F6.4,3X,F8.6)
205   FORMAT(F6.4)
      END
C
      SUBROUTINE FCT(X,F,DERF)
      COMMON A,B,C,TA,U,V,TC
      F=A*X*X*X+B*X*X+C*X-TA
      DERF=3*A*X*X+2*B*X+C
      RETURN
      END
C
      SUBROUTINE FCT2(Z,F2,DERF2)
      COMMON A,B,C,TA,U,V,TC
      F2=U*Z*Z+V*Z-TC
      DERF2=2.0*U*Z+V
      RETURN
      END
```

TABLE 5

Designations of Symbols Used in Computer Program III

Symbol in Program	Meaning of Symbol and Reference to Equations (E) and Tables (T)
CSO	K_{sp} for $Cd(OH)_2$;(E23); $2.2x10^{-14}$
CS2	$K_{s2} = \beta_2 xK_{sp}$;(E31,32,T3); $4.27x10^{-6}$
CS3	$K_{s3} = \beta_3 xK_{sp}$;(E31,32,T3); $3.20x10^{-10}$
CA	K_b ;(E52); $1.78x10^{-5}$
C1	β_1' xK_{sp} ;(E53,T3(NH_3));$9.8x10^{-12}$
C2	$2\beta_2'$ xK_{sp} ;(E53,T3(NH_3));$2.48x10^{-9}$
C3	$3\beta_3'$ xK_{sp} ;(E53,T3(NH_3));$1.02x10^{-7}$
C4	$21K_{sp}$;(E46,T3(Cl));$4.6x10^{-13}$
C5	$332K_{sp}$;(E46,T3(Cl));$7.3x10^{-12}$
C6	$K_w^2/(K_{a1}xK_{a2})$;(E41);$3.8x10^{-12}$
C7	K_w/K_{a2} ; (E41);$1.8x10^{-4}$
C8	K_{sp}' for $CdCO_3$;(E28);$5.2x10^{-12}$
C9	$\beta_1(OH^-)$; (E42,T3);$1.45x10^4$
C10	$\beta_2(OH^-)$;(E42,T3);$2.47x10^8$
C11	$\beta'_1(NH_3)$;E56,T3);$4.47x10^2$
C12	$\beta'_2(NH_3)$;E56,T3);$5.63x10^4$
C13	$\beta'_3(NH_3)$;E56,T3);$1.55x10^6$
TCA	$[CO_3]_{TOT}$
TC	$[Cl^-]_{TOT}$
TA	$[NH_3]_{TOT}$
HO,Z,X	$[OH^-]_{eq}$;$[Cl^-]_{eq}$;$[NH_3]_{eq}$