04 University of Plymouth Research Theses

https://pearl.plymouth.ac.uk

01 Research Theses Main Collection

1982

THE INTERACTION OF PHOSPHATE WITH IRON OXYHYDROXIDES IN SIMULATED ESTUARINE CONDITIONS

Crosby, Stuart Arthur

http://hdl.handle.net/10026.1/2117

http://dx.doi.org/10.24382/4989 University of Plymouth

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

S. A. CROSEY

THE INTERACTION OF PHOSPHATE WITH IRON OXYHYDROXIDES IN SIMULATED ESTUARINE CONDITIONS

Ph.D. 1982

store

Attention is drawn to the fact that the copyright of this thesis rests with the author and that no quotation from the thesis and no information derived from it may be published without the prior written consent of the author.

This thesis may be made available for consultation within the Plymouth Polytechnic Library and may be photocopied or lent to other libraries for the purpose of consultation.

Signed Storky



DECLARATIONS

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other CNAA or University award. None of the material herein has been used in any other submission for an academic award.

A programme of advanced study was undertaken in partial fulfilment of the requirements, including guided reading in marine chemistry and estuarine chemical processes (under the direction of Dr. G. Millward); development and supervision of undergraduate practical work, for both the Polytechnic and the Open University; attendance at relevant conferences and seminars at other research establishments. Briefly these consisted of: Conferences

Marine Chemistry Discussion Group Meeting: "Geochemical Cycling". Held at Department of Chemistry, University of Bristol, January 1979.

Marine Chemistry Discussion Group Meeting: "The Chemistry of the Air-Sea Interface". Held at the Department of Environmental Sciences, University of East Anglia, July 1979.

Estuarine and Brackish Waters Sciences Association Conference: "Transfer Processes in Cohesive Sediment Systems". Held at the Freshwater Biological Association, Windermere. Paper presented by S.A. Crosby entitled "Kinetics of Phosphate Adsorption onto Iron Oxyhydroxides". September 1981.

External Visits

Department of Physical Chemistry, University of Bristol for discussions with Dr. D. Thompson and colleagues on iron and manganese oxyhydroxides surface characterisation. January 1980 and December 1980.

Freshwater Biological Association, Windermere for discussions with Dr. E. Tipping and Dr. W. Davison on redox systems and adsorption mechanisms. January 1980 and July 1981.

Department of Oceanography, University of Southampton to attend a joint seminar on marine chemistry between Plymouth Polytechnic and Southampton University. S.A. Crosby presented a paper entitled "Phosphate Adsorption onto Fe^{3+}/Fe^{2+} Precipitates from Aqueous Solution". February 1981.

Programme of Studies

5-day course in transmission electron microscopy. Participant in an ll-day course entitled "School of Marine and Estuarine Chemistry" held at the Marine Biological Association, Plymouth. March 1979. Lecture course in colloid chemistry, including practical tuition of surface area measurement and X-ray diffractometry, given by Dr. D.R. Glasson, Department of Environmental Sciences, Plymouth Polytechnic. October 1978, February 1979. Lecture course in Mössbauer spectrometry given by Dr. A.H. Cuttler, Department of Environmental Sciences, Plymouth Polytechnic. November 1980.

THE INTERACTION OF PHOSPHATE WITH

IRON OXYHYDROXIDES IN SIMULATED

ESTUARINE CONDITIONS

· by

Stuart Arthur Crosby B.Sc. (Hons)

Submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Submitted February 1982

Department of Marine Science Faculty of Maritime Studies Plymouth Polytechnic Plymouth Devon, U.K. In collaboration with: Marine Biological Association of the United Kingdom The Laboratory The Hoe Plymouth Devon, U.K.

(i)

ACKNOWLEDGEMENTS

I gratefully acknowledge the help of all those who contributed to the completion of this work, particularly the following:-

The Natural Environmental Research Council for the provision of a research studentship.

Staff of the Marine Biological Association, in particular Professor E.J. Denton for providing the use of his excellent facilities, Drs. Whitfield and Turner and Mr. E.I. Butler for continued guidance and enthusiastic supervision over the last 3 years and Mr. M.I. Liddicoat and Mrs. S. Knox for assistance with analytical and sampling techniques. The author is indebted to Plymouth Polytechnic for providing a temporary Research Assistantship and the primary resources for carrying out this study. In particular the author would like to thank Dr. D.H. Moreby and colleagues in the Faculty of Maritime Studies for help and advice and Mr. B. Davis for making sampling equipment.

Brian Lakey and Christine Jocelyn at Plymouth Polytechnic Electron Microscopy Unit. Dr. D.R. Glasson for support in the iron oxyhydroxide characterisation studies and Dr. A.H. Cuttler for help with the Mössbauer spectrometry. Peter Davis for assistance with the X-ray diffraction studies.

Dr. E. Tipping of the Freshwater Biological Association and Dr. W. Thompson of the University of Bristol for

(ii)

helpful discussions during the course of the study. Gloria Day for typing the manuscript. Finally, many thanks to Dr. Geoff Millward for considerable encouragement, guidance and discussion throughout an enjoyable 3 years.

THE INTERACTION OF PHOSPHATE WITH IRON OXYHYDROXIDES IN

SIMULATED ESTUARINE CONDITIONS

by STUART ARTHUR CROSBY, B.Sc. (Hons)

ABSTRACT

The uptake of phosphate onto Fe(II) and Fe(III) derived iron oxyhydroxides was examined as a function of time using conditions similar to those encountered in natural waters. The freshly precipitating Fe(III) oxyhydroxide was very active and its adsorption behaviour was independent of pH, temperature and ionic strength. The adsorption onto freshly precipitating Fe(II) derived oxyhydroxide was strongly dependent on all three factors as the rate of uptake was limited by the rate of oxidation and hydrolysis of Fe(II). The aged (20 h) Fe(III) precipitate was identified as am-FeOOH and its adsorption behaviour was dependent on pH and ionic strength but independent of temperature in seawater. The adsorption appears to be chemisorption in distilled water and physical adsorption in seawater. Kinetic analyses were done on these adsorption profiles and a reversible second order reaction was postulated to explain the data. This yielded rate constants that were dependent upon $[PO_4]_0$ and the analyses gave a pH dependence of the rate constants which was useful for comparisons of both model and natural adsorption phenomena. A similar analysis was also carried out for adsorption onto fresh Fe(II) derived material in seawater. Activation energies were calculated whose values supported the physical/chemical adsorption hypothesis. The aged Fe(II) derived precipitate was identified as Y-FeOOH by various techniques and this material did not adsorb phosphate in the natural pH range due to the low pHZ.P.C.

The rate of colloid/particle formation was investigated using a nephelometric technique which revealed that the uptake of phosphate onto freshly forming precipitates was strongly linked to the rate of particle formation. This led to a simple nomograph being developed to show the expected time scales for phosphate removal under varying conditions. Good agreement was found with adsorption onto some precipitates formed from natural waters indicating the importance of this work to the understanding of estuarine adsorption phenomena and to water quality control.

CONTENTS

	Page		
Title			
Acknowledgements			
Abstract			
Contents			
List of Plates			
1. INTRODUCTION			
1.1 Preliminary Remarks	1		
1.2 Environmental Chemistry of Iron	4		
1.2.1 Hydrolysis of Iron and Iron			
Oxyhydroxides	4		
1.2.2 Redox Reactions of Iron	8		
1.2.3 Adsorption Models	11		
1.2.4 Iron in Natural Waters	13		
1.3 Environmental Chemistry of Phosphate	17		
1.3.1 Phosphate Chemistry	17		
1.3.2 Soil/Phosphate Interactions	18		
1.3.3 Water Treatment	20		
1.3.4 Phosphate in Natural Waters	21		
1.4 Aims of Present Work	25		
2. EXPERIMENTAL METHODS	26		
2.1 Nephelometry	27		
2.2 Surface Area Measurements	32		
2.3 Precipitate Identification	36		
2.3.1 Transmission Electron Microscopy	36		
2.3.2 X-ray Diffraction	37		
2.3.3 Mössbauer Spectroscopy	37		

•

.

•			-	<u>Page</u>
		2.3.4	Additional Techniques	38
	2.4	Phosph	nate Adsorption	40
		2.4.1	The Design of the Chemical Models	40
		2.4.2	Analytical Methods	42
	2.5	Collec	ction of Natural Samples	45
		2.5.1	Sample Sites and Field Operations	45
		2.5.2	Analytical Methods	49
		2.5.3	Preparation of Models and	
			Precipitates	50
з.	RESU	LTS AND	DISCUSSION	53
	.3.1	Precip	oitate Characterisation	54
		3.1.1	Surface Area Measurements	54
		3.1.2	Electron Microscopy	78
		3.1.3	X-ray Diffraction	99
		3.1.4	Mössbauer Spectroscopy	110
		3.1.5	Infra-red Spectroscopy	126
		3.1.6	Summary of Characterisation of	136
			Precipitates	
	3.2	Precip	itate Formation	141
		3.2.1	Nephelometry	141
		3.2.2	Fe(III) Derived Precipitates	146
		3.2.3	Fe(II) Derived Precipitates	154
		3.2.4	Kinetic Analysis of Nephelometry	163
		3.2.5	Summary of Precipitate Formation	173
	3.3	Phosph	ate Adsorption	175
		3.3.1	Discussion of Chemical Modelling	175
		3.3.2	General Discussion on Aged	177
			Precipitates in Model Solutions	

		3.3.3	General Discussion on Fresh	
			Precipitates in Model Solutions	193
		3.3.4	Kinetic Analysis of the Uptake	
			onto Aged Precipitates	207
		3.3.5	Kinetic Analysis for Uptake	
			onto Fresh Precipitates	229
		3.3.6	Summary of Phosphate Adsorption	244
4.	<u>SUMM</u>	ARY AND	CONCLUSIONS	247
•	4.1	Surfac	e Characteristics and Phosphate	
		Uptake		247
	4.2	A Meth	od for Predicting the Behaviour	
		of Pho	sphate in the Presence of	
		Iron i	n Estuarine Media	251
	4.3	Conclu	sions from Complete Study	257
	4.4	Recomm	endations for Future Work	261
	REFE	RENCES		263
	APPEN	IDIX 1 P	ublished Work	A1

<u>Page</u>

LIST OF PLATES

-

T	he pla	tes are numbered by reference to the fa	cing
p	age.		
			<u>Page</u>
Plate	2.1	The iron-rich stream draining from Lady Bertha Mine	45
Plate	3.1	General view of am-FeOOH precipitated from seawater (Mag. = 45,000x)	80
Plate	3.2	Electronmicrograph showing particle size range for am-FeOOH precipitated from seawater	80
Plate	3.3	General view of γ -FeOOH precipitated from seawater (Mag. = 2,700x)	82
Plate	3.4	Electronmicrograph showing structure for γ -FeOOH precipitated from seawater	82
Plate	3.5	High magnification of γ -FeOOH showing crystalline laths and amorphous areas (Mag. = 200,000x)	82
Plate	3.6	Electronmicrograph showing similar structure of Y-FeOOH precipitated from distilled water in the presence of phosphate	82
Plate	3.7	High magnification of precipitate shown in Plate 3.6	85
Plate	3.8	View of another y-FeOOH sample precipitated from seawater	85
Plate	3.9	Scanning electronmicrograph of am-FeOOH showing large particle with smooth surface	85
Plate	3.10	Scanning electronmicrograph of γ-FeOOH showing granular texture of large particles	85
Plate	3.11	Electronmicrograph of well crystallised synthetic γ -FeOOH showing variation in particle size and shape	88
Plate	3 .12	Higher magnification of γ -FeOOH showing layering of crystalline material (Mag. = 68.000x)	88

•

<u>Page</u>

•

Plate	3.13	High magnification of single crystal of γ-FeOOH showing well ordered structure (Mag. = 100,000x)	88
Plate	3.14	General view of Lady Bertha Mine stream sediment showing variation in particle size and shape	88
Plate	3.15	Iron oxyhydroxide particles from Lady Bertha Mine stream sediment (Mag. = 6,300x)	88
Plate	3.16	Iron oxyhydroxide particles plus unidentified "crystalline" particle from Lady Bertha Mine stream sediment	88
Plate	3.17	Mass of iron oxyhydroxide particles precipitated from Carnon River	92
Plate	3.18	Electronmicrograph showing particle size of iron oxyhydroxide precipitated from Carnon River (Mag. = 56,000x)	92
Plate	3.19	High magnification of Carnon River precipitate showing amorphous nature of iron oxyhydroxide spheres (Mag. = 100,000x)	92
Plate	3.20	General view of iron oxyhydroxide precipitated from interstitial water	92
Plate	3.21	Particles of iron oxyhydroxide precipitated from interstitial water showing evidence of organic coating (Mag. = $100,000x$)	92
Plate	3.22	High magnification showing density of iron oxyhydroxide particles precipitated from interstitial waters with organic coatings present (Mag. = 160,000x)	92

-

•

1.1 Preliminary Remarks

The understanding of the geochemical cycling of trace constituents in natural waters is of importance to the development of predictive models. especially those related to the fate of anthropogenic inputs into the environment. Each trace constituent follows a complex pathway through the natural system which is determined by its chemical and physical properties. The clarification of the behaviour of trace constituents and the extraction of the rates for natural processes is extremely difficult. This is due mainly to the complexity of the system and the need to separate chemical and physical time scales, plus the continuing and increasing contamination of the system by man. Attempts at understanding a system with such variability can only succeed if environmental measurements are coupled with detailed studies of simple chemical systems, which are related to the natural waters under investigation. This study is designed along those lines, so that the known behaviour of a trace constituent is modelled using simple solutions in order that both mechanistic and kinetic information is obtained which can then be used in quantitative models.

Phosphorus is an important trace element in the environment due to its role in biological systems, and its limited availability. The major reservoir of phosphorus

is as calcium phosphate $[Ca_3(PO_4)_2]$ in sedimentary rocks. Both this and other calcium phosphates have very low solubilities (1) so that the levels of phosphorus in natural waters are very low, usually $<1.0 \mu mol 1^{-1}$. However, large quantities of soluble phosphorus compounds are being added to streams, lakes, estuaries and coastal waters in the forms of fertilizers, sewage and detergents, all resulting from man's activities. The need to predict the fate of these inputs has important implications for water quality. The behaviour of phosphorus in these waters is thought to be linked to the presence of iron in the water column, although the mechanisms and rates of this interaction are not well understood.

Iron is the fourth most abundant element in the earth's crust, and makes up approximately 5% of the crust by weight (2). It is a vital biological element forming porphyrin complexes used in respiration by many animals (3, 4). The chemical behaviour of iron in natural waters is known to be the key to the interpretation of many processes involving trace constituent cycles. The transformation of Fe(III) in fresh waters and fresh waters entering marine systems in the neutral to alkaline pH range usually involves the appearance of a solid phase which may have a high sorptive capacity for trace constituents such as phosphate. The situation may be further complicated by the presence of Fe(II) which can oxidise and precipitate under conditions commonly found

in water systems to give solid phases with different surface activities.

This study attempts to investigate in some detail the nature of the iron solids and their interactions with phosphate. Both natural waters and simple chemical analogues have been used to elucidate the mechanisms and kinetics of the interaction. What follows in this first chapter is a review of the environmental chemistry of iron and phosphate, but due to the vast literature on both these topics, only those aspects relevant to this study are included. The chapter is concluded with a detailed listing of the specific objectives of the work.

1.2 Environmental Chemistry of Iron

1.2.1 Hydrolysis of Iron and Iron Oxyhydroxides

The hydrolysis of iron (5-11) and the subsequent precipitate formation (7, 12-14) have been intensively studied for a number of years. The reactions are complex and important, not only for their intrinsic value, but also for soil component interactions (15-21), their occurrence and behaviour in natural aquatic environments (22-27), and as a valuable tool in water quality control (28-30).

The hydrolysis of Fe(III) has been reviewed by Sylva (6) and the reaction can be represented by: $x[Fe(H_2O)_6]^{3+} + y H_2O \longrightarrow [Fe_x(OH)_y(H_2O)_n]^{(3x-y)+} + y H_3O^+$... Eq. (1.1)

where n = the degree of hydration.

For Fe(III) hydrolysis can go beyond the uncharged species $[Fe(OH)_3(H_2O)_3](s)$ to form anions (31), such as $[Fe(OH)_4 (H_2O)_2]^-$. The reactions have been shown to be dependent on pH, temperature, ionic strength and concentration of Fe(III) (16), with precipitate formation and character also depending on age (32). Isolation of the precipitates for further study is also difficult as the character and/or surface activity may be altered by the isolation and subsequent treatment (7). The majority of the studies of the hydrolysis are carried out at low pH ranges so that the rates of hydrolysis

reactions can be measured more easily (7, 13, 16, 33). Much discussion centres on the possible formation of dimers and polymer chains made up from $[Fe(OH)]^{2+}$ units (9, 31, 34) by a condensation reaction as shown in Eq. (1.2).

$$2[Fe(H_2O)_5 OH] \xrightarrow{2+} [(H_2O)_4 Fe + 2H_2O] \xrightarrow{OH} Fe(H_2O)_4 \xrightarrow{4+} + 2H_2O$$

The second major difference between pure chemical studies of the hydrolysis and this work, as well as the low pH range, is the low concentrations of iron that are used compared with those in the pure chemical studies (7-14). This is to model the system on the natural environment, and all variables such as pH, temperature and ionic strength are controlled so that they are close to an estuarine like system.

... Eq. (1.2)

Very few studies on the hydrolysis of iron in estuarine systems have been carried out, but it has been found that the presence of suspended particles will increase the rate and extent of coagulation of hydrolysis products, and the same effect is observed for increasing salinity (35).

The introduction of Fe(II) from the sediments, mine streams etc. into an estuarine water column can occur and may then participate in different reactions compared to

- 13

Item on Hold

Interaction of phosphate with iron oxyhydroxides in simulated estuarine conditions / by Stuart Arthur Crosby. Crosby, Stuart Arthur. Thesis 546.6212 CRO





13/07/2011 LIBRARY.



those of Fe(III). Consideration of the solubility products of Fe(OH), and Fe(OH), which are approximately $K_{so} = 10^{-36}$ and $K_{so} = 10^{-17}$ respectively, can give information on the rate of nucleation for each species. For example, at pH = 8 the maximum solubility of the two hydroxides can be calculated thus: $[Fe^{3+}]OH^{-}]^{3} = 10^{-36}$ and $[Fe^{2+}]OH^{-}]^{2} = 10^{-17}$ At $pH = 8 [OH] = 10^{-6}$... $[Fe^{3+}] = 10^{-18} \text{ mol. } 1^{-1} \text{ and } [Fe^{2+}] = 10^{-5} \text{ mol. } 1^{-1}.$ The rate of nucleation of the precipitate R is:= $R = \frac{k(S' - S)}{S}$... Eq. (1.3) where k = Rate constantS = Maximum solubility S' = Instantaneous concentration, which in this work is 5×10^{-5} mol. 1^{-1} . . . R for Fe(OH)₃ = $\frac{k(5 \times 10^{-5} - 10^{-18})}{10^{-18}} = 5 \times 10^{13}$ k. R for Fe(OH)₂ = $\frac{k! (5 \times 10^{-5} - 1 \times 10^{-5})}{1 \times 10^{-5}} = 4 k!$.

For this rough calculation k and k' can be assumed to be equivalent so that the rate of nucleation for $Fe(OH)_3$ is very much faster than for $Fe(OH)_2$ (36). This suggests that the precipitates derived from these two sources will have different morphologies and possibly different surface characteristics.

There are numerous crystalline forms of iron oxyhydroxides (37), some of which have well defined and understood crystal structures, while others have only recently been identified (17) and in some cases the postulated structures have not gained complete acceptance (38). The iron oxyhydroxides are important in aquatic environments as they are thought to control trace element partitioning between the dissolved and solid phases (39). The commonest oxyhydroxide formed by the precipitation of iron from natural waters is amorphous ferric hydroxide, but this will age to Goethite (α -FeOOH) (40). Other crystalline forms are found in aquatic environments such as Lepidocrocite (γ -FeOOH) (41) and Ferroxyhite (δ '-FeOOH) (42) although these usually occur as mixtures (43-44). The removal from solution of the dissolved iron can occur by either inorganic (45) or bacterial precipitation (46) and the conditions under which precipitation occurs will also affect the oxyhydroxide formed. When precipitation occurs in multicomponent media as in an estuary, the presence of dissolved organic matter may inhibit crystal formation (47-48). The ageing to Goethite will also be retarded, and consequently the dominant form for iron oxyhydroxides precipitated in situ will be amorphous, whereas the oxyhydroxides transported by rivers into an estuary resulting from crustal weathering will be the crystalline form.

The adsorption behaviour of both the amorphous and

crystalline oxyhydroxides is dependent on their surface characteristics. Most importantly, the pH of zero point of charge $(pH_{Z,P,C})$ is different for each oxyhydroxide (49), so the adsorption behaviour for two oxyhydroxides may be completely opposite at the same pH, with one being an anion adsorber whilst the other adsorbs This is a very simple picture, and care must be cations. taken to ensure that the model is not extended too far. Other factors such as chemical bonding may be more important than surface charge effects so that adsorption may occur against electrostatic repulsion (50). The surface areas for each oxyhydroxide are also different (41-43) with amorphous oxyhydroxides having larger surface areas than the more crystalline forms (42). The degree and type of porosity is another surface characteristic that may vary, but how porosity affects the adsorption in solution is not known. Therefore it is important to characterise and identify the oxyhydroxides formed in model solutions to aid the explanation of varying adsorption phenomena, and then to examine natural precipitates to seek similar behaviour.

1.2.2 Redox reaction of Iron

It is important to study the oxidation and reduction of iron as either the ferric Fe(III) or the ferrous Fe(II) form can exist in natural systems depending on the pH and the redox potential Eh (51) Figure 1.2.1. The oxidation of Fe(II) to Fe(III) occurs rapidly at the pH

and Eh of most natural waters but the presence of organic matter has been shown to retard the oxidation (52-53) which may lead to increased concentrations of dissolved iron. Conversely the rate of oxidation has been found to be increased by relatively high concentrations of phosphate, and the mechanism for this reaction is thought to be the formation of a more reactive complex between the Fe(II) and the phosphate (54). These factors show how complex the reaction can be, and the oxidation of Fe(II) has been studied both for its intrinsic value as well as for water quality control in both natural (45, 53, 55-56) and waste water (57, 58) systems. The rate of oxidation is dependent on pH, temperature and ionic strength (57) and autocatalysis on ferric oxide surfaces becomes important above pH = 7 (56). However there is still a wide range in the values for the rate constants and it is vital that all possible variables are controlled when measuring the kinetics of Fe(II) oxidation.

Redox reactions are important in the natural environment, and Fe(II) is present in the anoxic layers of stratified lakes and fjords (59-60), in acid mine streams (45, 61-62) and in the interstitial pore water of anoxic estuarine and marine sediments (63-65). The oxidation of the Fe(II) in pore waters may alter other components in the solution (66) and the reduction of Fe(III) may act as an electron acceptor for arsenite (As(III)), although the kinetics of this reaction appear to be slow

(67). Reduction of Fe(III) will occur in the sediment pore water after the dissolved oxygen has disappeared and nitrate and manganese oxides have been reduced (68). It is known that the Eh must fall below Eh = +100 mV before iron oxyhydroxides are reduced (68), but this is a difficult parameter to measure precisely as the system is not at equilibrium and the Eh will be changing as the iron oxyhydroxides are reduced (69). The reduction of the iron leads to enrichment of dissolved iron in the pore water up to several orders of magnitude higher than that in the overlying water (68), and this may be remobilised if the sediment is disturbed. This is an important input of dissolved iron into estuarine systems which has not received the attention it deserves.

1.2.3 Adsorption Models

Adsorption phenomena are vital in controlling the distribution of trace components between the solid and dissolved phases (39). Numerous papers have been published on the behaviour of the iron oxide/solution interface (18, 70-74) and adsorption of cations (75-81) and anions (72, 82-84) at this interface. Two types of absorption mechanism have been proposed, one emphasising specific chemical interactions (85) and the other concentrating on the well defined electrical double layer and charge on oxide surface and adsorbant (70, 78).

Recently both these concepts have been combined into a single, and perhaps more realistic model which describes

anionic and cationic adsorption plus the surface characteristics of the oxyhydroxide (71, 80-82, 86). A comparison of five of the adsorption models has been made (87), and it concludes that all of the models examined are a good fit to the experimental data. However, no model will give an unambiguous description of the adsorption energies so that separation into electrostatic and chemical components is not possible. The study of adsorption onto iron oxides is complex due to the variation in the surface properties of the oxide with pH and ionic strength, and also the fact that porosity almost certainly exists, while models assume a smooth surface with well defined surface groups. The possible effects of porosity have been examined for Haematite $(\alpha - Fe_2O_3)$ (18) and two possible mechanisms of uptake are proposed, one dependent on the ability of an ion to penetrate the pores, and the other based on an ion's affinity towards the solid. The specific adsorption of phosphate and sulphate is considered to be too large for penetration of the pores found in a Haematite (18). This oxide had been degassed at 85°C and this type of pretreatment has been shown to affect the surface characteristics of oxyhydroxides (88) and decrease the porosity of clays (89). Also the connection between the porosity of an iron oxyhydroxide in solution and the same oxyhydroxide collected and dried is not known. Macroporosity may well be increased as the precipitate is concentrated and dried into large masses while micro-

porosity may be decreased.

Adsorption models are still in the formative stage, and the complexity of a system that a model can describe is still limited although improvements are being made all the time. A recent advance involves the effect of major seawater ions on the surface of Goethite (73-74) and their effect on the adsorption of heavy metals (90). The effect of adsorbed humic acids on the surface properties of Goethite has also been investigated (91) but all these studies are still a long way from obtaining a model to fit the adsorption phenomena in a complex environment such as an estuary. A more simplified approach has been used to obtain information, in which models are used to describe adsorption phenomena and which do not involve detailed specific mechanisms at the oxide/water interface. These adsorption isotherms summarize the adsorption behaviour of a system, and the equations used can be modified to fit the experimental data. A more detailed discussion of these adsorption isotherms is given in Section 1.3.2.

1.2.4 Iron in natural waters

Iron is found in all types of natural water both as dissolved and particulate forms. Its presence in seawater has been studied for a number of years (22), and iron oxyhydroxides were suggested as controls for heavy metal partitioning in seawater over twenty-five years ago (39). Most of the early research on iron in the

aquatic environment concentrated on distribution and simple speciation studies (92-101), and methods for improving the analytical techniques for measuring dissolved iron in seawater are still being investigated. Using solubility data for iron oxyhydroxides the calculated dissolved iron concentration should be less than 10 ug 1^{-1} at the pH and Eh of most natural waters. However, the world average concentration of dissolved iron in river water is 670 μ g 1⁻¹ (102), and despite the arbitrary definition of dissolved being that which passes through a 0.45 $\mu\,\text{m}$ filter, this represents a substantial apparent supersaturation. Considerable concentrations of dissolved and particulate iron and other heavy metals are found in rivers and estuaries draining from areas of intensive and prolonged mining activity (61-62). The concentration of dissolved iron in seawater is much lower, and closer to the expected concentration, with 5.5-32 μ g 1⁻¹ being found in coastal waters (24), and an average concentration of 2.7 μ g 1⁻¹ found for marine waters (103). If the oceanic residence time for iron is calculated using the average river concentration as the rate of input of dissolved iron, a residence time of only a few hundred years is found. If the removal of riverborne dissolved iron in the estuarine mixing zone is taken into account a longer oceanic residence time would be found (104), but consideration of the residual flux of particulate iron has given a residence time of only 30 years (105).

In river waters the dominant mechanisms for iron transport are thought to be as precipitates and coprecipitate coatings on solids, or incorporated in crystalline matrices (106). A small amount is incorporated in organic coatings, with only 1% in solution. However, this small fraction of the total plays a major part in the chemical and physical reactions that occur when river water mixes with seawater in the estuaries. The physical and especially the chemical changes that may occur to the particulate material as it passes through an estuary are extremely difficult to study and consequently have received little attention until recently (106-111).

The non-conservative behaviour of iron in estuaries is now well known (35, 104, 110-117) and can be explained by the destabilising effect of the seawater cations Mg^{2+} and Ca^{2+} towards the negatively charged iron humic colloids (108), which are stabilised by dissolved organic matter in the river water (104). The fact that the iron is in a colloidal form makes the choice of a 0.45 µm pore size as the cut off inconvenient in studying the removal processes of the dissolved fraction. The phenomenon is now accepted, but further work is required on the mechanism of flocculation and perhaps more importantly the effect of the flocculation on other components such as heavy metals, phosphate and dissolved organic carbon. These three have been examined, and it is known that only a small percentage (less than 20%) (118) of the dissolved organic carbon

(D.O.C.) is removed and manganese appears to behave independently of iron so that it may be a conservative component (116). This can be explained by the oxidation state and hence solubility of manganese as it can exist in the Mn(II) form at the pH and Eh found in an estuary and will be truly dissolved (116). The behaviour of manganese is apparently not consistent from one estuary to another (119-120) and deserves separate study from iron. The interaction of iron and heavy metals in an estuarine environment has also been studied (76, 113, 121) and this important area of research is receiving considerable attention.

The association of iron with humic acids has been studied for a number of years both by soil scientists (122-124) and in all types of natural waters (125-128) and the comparison of adsorption behaviour in the presence of humic acids and in their absence should show the importance of the humic acids. Adsorption studies without humic acids are probably more reproducible due to differences in humic acid samples and mechanisms without this complicating factor are still difficult enough to prove.

1.3 Environmental Chemistry of Phosphate

1.3.1 Phosphate Chemistry

Phosphorus can exist in many forms both in dissolved or solid phases, and some of these have been listed by previous workers (30, 129). The term "phosphates" encompasses orthophosphate, polyphosphates and organic phosphorus compounds but this study is concerned with dissolved orthophosphate species, and the term phosphate will be used to represent all the orthophosphate species unless otherwise stated.

Dissolved phosphate enters the natural water system by crustal weathering, soil erosion and biological transfer, plus the anthropogenic inputs from sewage, detergents, fertilizers and other waste waters (1). Phosphorus is a biolimiting element, and high available phosphorus concentrations can lead to high algal growth which will upset the photosynthetic and respiratory activity balance. This may finally result in eutrophication of the water body due to the consumption of dissolved oxygen in the decomposition of the organic matter produced. Therefore it is desirable to monitor the input of nutrient elements into natural water systems, and to control anthropogenic inputs, so that the system is altered as little as possible. A method for removing dissolved phosphate from waste waters is coprecipitation by Fe(III) or Al(III) salts (130-131), but the oxides from iron and aluminium also play a major role in phosphate fixation in

soils, and the interaction of iron oxides and phosphate in soils is an area of considerable research activity (15, 132-143). Some of the laboratory modelling techniques used by soil scientists are transferable to the aquatic system, but usually both iron and phosphate concentrations are much higher in the soil systems than are found in natural waters.

1.3.2 Soil/Phosphate Interactions

The study of soil/phosphate interactions is centred around the retention of phosphate by soil components, and its availability to plants as a nutrient. Almost all the experiments are of an adsorption and/or desorption type and data is usually analysed by either the Langmuir or Freundlich equations, although the Temkin equation has also been used (138). The use of adsorption isotherms for this type of study has been reviewed by Barrow (140). The simple forms of these equations are: i) Langmuir equation

 $\frac{C}{S} = \frac{1}{k S_{max}} + \frac{C}{S_{max}} \qquad \dots Eq. (1.4)$ where $C = [PO_4]$ in solution at equilibrium $S = [PO_4]$ adsorbed per g adsorbant $S_{max} = Adsorption maximum where a complete$ monolayer is formed

k = Constant related to bonding energy

ii) Freundlich equation $S = kC^{1/n}$... Eq. (1.5) where S. C = Defined for Eq. (1.4)

k and n = Constants

iii) Temkin equation

$$\frac{S}{S_{max}} = \frac{RT}{b} \cos (AC) \qquad \dots Eq. (1.6)$$

where R = Gas constant

T = Temperature S, S_{max} and C = Defined for Eq. (1.4) A and b = Constants

All these models are based on equations derived for gas adsorption onto solid surfaces and have no terms which consider ionic interactions. This is not an ideal situation, and although modifications have been made both to the Langmuir (144) and the Freundlich (137) equations, good correlation between experimental and theoretical data does not mean that the model is correct. Certainly when dealing with the adsorption of phosphate onto a charged oxide surface the Langmuir isotherm is unlikely to be appropriate (143) and a model of ionic adsorption onto charged mineral surfaces has been derived (70).

The nature of phosphate/soil interactions are such that slow long term adsorption is important and the formation of new crystalline phases can occur (133, 145).
This is of much less importance in the more dynamic estuarine environment so different sets of equations are required, and the same applies for the removal of phosphate from waste waters where fast and almost quantitative removal is desired.

1.3.3 Water Treatment

Iron and aluminium hydroxides have been used for a number of years both in waste water treatment and removal of phosphate from treated sewage (131). It is known that these reactions are dependent on pH, phosphate to hydroxide ratio and actual concentration of phosphate and hydroxide, but the removal mechanism is complex, and not yet clearly understood (146). It has been shown that the removal of phosphate is more efficient if the Fe(III) is produced <u>in situ</u> by the addition of a Fe(II) salt to the solution rather than direct addition of Fe(III) (30). The removal by Fe(III) is also found to be more efficient than aluminium although both coagulants follow the same mechanism (29).

In all these studies the phosphate and iron concentrations are far removed from those found in an estuary with mg 1^{-1} of phosphate used compared with µg 1^{-1} phosphate for estuaries and iron concentrations of 10^{-4} M or higher (131).

For natural water systems the interactions of phosphate with sediments and components therein, have only been studied comparatively recently with both model and natural experiments.

1.3.4 Phosphate in Natural Waters

Phosphorus has no naturally occurring volatile compound therefore it is restricted to transfer in and between the lithosphere and the hydrosphere (1). Phosphate in natural waters has been studied for a number of years (147-150) due to its importance in the biological cycles. It is these biological cycles which make field results even more difficult to model in the laboratory. Almost all the research is concentrated on adsorption and desorption reactions connected with the geochemical cycling of phosphorus, and its availability to the biota. Similar results have been obtained between adsorption onto sediments, and adsorption onto soils, with a fast initial uptake of phosphate followed by a slower incorporation into the solid phase (148, 150-151).

The importance of phosphate as regards eutrophication mainly applies to enclosed or stagnant bodies of fresh or brackish water. The sea is generally depleted in phosphate except for localised areas of upwelling (1). Consequently research has concentrated on phosphate exchange reactions with lake sediments (152-157) and iron interactions are often included in these reactions (156-157). The stratification that can occur in lakes during summer months makes the anoxic/oxic boundary easier to examine compared to sediment studies. The reduction of iron that occurs in the anoxic system is thought to be a controlling reaction for phosphate release, while amorphous iron oxides in the oxygenated system are suggested as adsorbers of phosphate.

A similar situation occurs in the sediments where an oxidised surface layer overlies sediment which becomes anoxic and reducing with depth.

Recently, suspended sediment has been used as a mechanism for phosphate buffering in a turbid river (158), and this ties in with work carried out in the estuarine environment where changes in ionic strength add to the complexity of the reactions. Furthermore, the phosphate speciation changes with both pH and salinity. At pH = 7 in distilled water both $H_2PO_4^-$ and HPO_4^{2-} species are present in about equal concentrations, whereas at pH = 8 in seawater, HPO_4^{2-} is the dominant form, and above $pH = 8, PO_4^{3-}$ becomes increasingly important (159).

A considerable amount of research effort has been put into the study of dissolved phosphate in the estuarine environment. Early studies indicated the unusual behaviour of phosphate, in that its concentration remained relatively constant throughout the salinity range found in an estuary (147). Estuarine sediments have been shown to remove phosphate from solution and some separation of the biological and physical/chemical reactions was possible. (148, 150). The exchange of phosphate that occurred was thought to maintain the concentration of phosphate in the water at $\approx 1.0 \ \mu$ mol 1⁻¹, and similar conclusions were drawn from a series of measurements made in the Tamar Estuary (160). It was suggested that the sediment acted as a buffer for the phosphate in solution, adsorbing

when concentrations in the water increased, and desorbing when concentrations were low. Due to the known association of iron with phosphate this element was suggested as a possible controlling factor. The uptake of phosphate on sediments was found to be a two stage reaction (150, 161), with a fast initial uptake as physical/chemical adsorption occurs, followed by a slower incorporation into the sediment. as was found for the reaction with soil components (133, 145). The secondary slow reaction becomes important in the sediments, where iron phosphate minerals may be formed (155, 162). This reaction will tend to immobilise the phosphate but reduction of the iron oxyhydroxides to Fe(II) as the sediment becomes anoxic may release phosphate back into solution (163). Some recent work both in the field and in laboratory simulations has shown some removal of phosphate from solution in the low salinity region of an estuary (114, 164-165). This removal is also associated with the removal of dissolved and colloidal iron so that the behaviour of phosphate in an estuary is closely connected to the behaviour of iron, both in the water and the sediment. There is considerable evidence for phosphate removal, as shown above, but for a true buffer system to exist, desorption must occur, and it is much more difficult to show direct evidence of desorption from sediments to the water column. Laboratory experiments have shown desorption from typical estuarine sediments (148, 161) and further evidence of possible buffering is found in a study of Hong Kong

harbour sediments (166). A decrease in available phosphorus extracted from sediments with increasing salinity is explained as the phosphate being held by an iron organic phosphate complex of limited stability which can lose phosphate as the sediment particles are transported down an estuary (167).

Therefore both iron and phosphate are involved in reactions where the fresh water meets the saline; removal of phosphate also occurs on iron oxyhydroxides but may be returned to solution if salinity or phosphate concentration changes allow. Both iron and phosphate may be fixed in the sediments as discrete crystal phases or under anoxic conditions both may be returned to solution. In this study the interactions of well defined iron oxyhydroxides with phosphate under tightly controlled conditions will be examined. The uptake of phosphate will be examined at the fresh water and seawater ends of the estuarine environment and pH, temperature, $[PO_4]$ and [Fe] will be maintained at typical estuarine values.

乱

1.4 Aims of Present Work

The aims of this research can be summarised as follows:

- To study the formation of iron oxyhydroxide precipitates from Fe(II) and Fe(III) in various aqueous media. This aspect to include buffered distilled water, NaCl solutions, seawater and natural fresh waters.
- 2. To characterise and identify the above precipitates by transmission electron microscopy, Mössbauer spectroscopy, X-ray diffraction, infra-red spectroscopy and surface area measurements.
- 3. To study the uptake of phosphate onto these precipitates under strictly controlled conditions typically found at either end of the estuarine range, and to extract kinetic information and mechanistic pathways for these reactions wherever possible.
- 4. To complement the above model studies with examination of precipitates formed from natural sources of dissolved iron and to compare the uptake of phosphate onto these precipitates with the synthetic oxyhydroxides.
- 5. To combine all the above into a semi-quantitative model which may enable predictions to be made on possible reactions between iron and phosphate in an estuarine environment.

2. EXPERIMENTAL METHODS

The experimental work undertaken in this study can be split into two parts; the first is concerned with the behaviour and characterisation of iron precipitates derived from either model or natural sources of iron. The experimental methods for this are outlined below, starting with a study of the precipitate formation, and progressing through precipitate characterisation to identification. The second part is concerned with the interaction of both the synthetic and natural precipitates with dissolved phosphate. This is in order to investigate the possible phosphate adsorption mechanism thought to occur in estuarine waters (160, 166) and it also has important implications for water quality control (30).

2.1 Nephelometry

The formation and short term ageing of Fe(III) and Fe(II) derived precipitates were studied using a nephelometric technique. Nephelometry is the measurement of light scattered by microscopic particles. For most water analyses an angle of scattering 90° to the incident ray is used as this is least sensitive to variation in particle size (168). Turbidity measurements have been used to study precipitation reactions (164, 169-170, 14) but light scattering theory is complicated by such factors as particle size and shape, absorption, concentration and other physical or optical anisotropies which makes the extraction of quantitative information extremely difficult (168).

A recent progression is the use of laser Fraunhofer diffraction to study the particle size characteristics of suspended sediments in the turbidity maximum of an estuary (171). This technique is still in the development stage but the possibility of measuring the changes in particle size distribution as Fe(III) or Fe(II) precipitates and flocculates would add greatly to the understanding of these complex reactions.

In this work, the formation and subsequent flocculation of colloidal iron oxyhydroxides in model and natural waters were studied using a continuous flow system. Initially a batch sampling technique was tried, but the particle formation from Fe(III) was too rapid and so the flow system was developed. This was then used

for all subsequent experiments with Fe(III), Fe(II) and natural forms of iron.

The instrument used was an Aminco Fluoro-Colorimeter with a 4 watt U.V. lamp with maximum emitted energy at 36Onm wavelength. The flow system was constructed from a 250ml polyethylene beaker with 2 P.V.C. tubes set low into opposite sides to act as inlet and outlet points (Figure 2.1.1). The quartz glass lcm.square cells were adapted to decrease dead volume and had glass tubes fixed at either end. A Watson Marlow MHRE 200 Mk 4 peristaltic pump was used to pass, the fluid around the system. The beaker had to be covered with black masking tape as well as the input tube otherwise sensitivity was greatly reduced. Loss of iron to the glass and plastic surfaces was minimised by ageing the system with an iron solution, and not activating the surfaces by acid washing. The system was rinsed several times with distilled water between runs, and after approximately 2 weeks use, the glass cell would be acid washed because the gradual buildup of iron was found to decrease the sensitivity over longer periods. A flow rate of approximately 5 ml s⁻¹ was used which is equivalent to a complete cycling time of 40 seconds. The dead volume was 26ml, and iron entered the sensor within 3 seconds of injection into the beaker.

ε.

A fixed speed mini magnetic stirrer was used to stir the solution/suspension rapidly and pH was measured with an E.I.L. combination glass electrode with an E.I.L. model 7060 digital pH meter. The electrode was calibrated





with pH = 4 and pH = 7 buffers before each experiment, and the pH was plotted alongside the relative intensity of scattered light on a 2 pen chart recorder. The chart speed was varied according to the speed of reaction; a 5mm sec⁻¹ speed was required for the particle formation from FeCl₃ but this could be reduced to 1mm sec⁻¹ or 10mm min⁻¹ for the slower stages of flocculation and the slower particle formation from FeCl₂.

All chemicals used were analytical grade (B.D.H. AnalaR) except for the FeCl, which was a reagent grade chemical 96% FeCl,. The iron concentrations were held close to typical river concentrations (172) by injecting 100 μ l of 0.1M FeCl₃ or FeCl₂ in 0.01M HCl into 200 ml of the model or natural water to give a final concentration of 5×10^{-5} mol 1^{-1} . Model waters used were distilled water (initially without a carbonate buffer but a 2mequivalent buffer was required to curb the pH changes occurring from the addition of the acidic iron solutions) NaCl solutions of 0.1 or 1.0M ionic strength, and artificial seawater as formulated by Kester et al (173). The natural solutions were filtered Tamar river water, filtered seawater collected from the Western Approaches. to the English Channel at station El, or water from iron rich acidic streams near Cadover Bridge on the river Plym and Carnon River, Falmouth. In the latter two cases, the dissolved iron was precipitated by changing the pH and/or ionic strength and no further iron was added.

Although the light scattering properties were not examined in detail, an attempt was made to obtain semi-quantitative information on the relationship between relative intensity and iron remaining in solution. During the first 5 minutes of an experiment 10 ml aliquots would be removed, and immediately filtered through 0.45 um or 0.22 um Millipore membrane filters into standard flasks containing 1 ml of concentrated AristaR HC1 to quench the precipitation. This solution was then analysed for iron on an I.L.151 Atomic Absorption Spectrophotometer in the flame mode. using a lean air acetylene flame. This indicated that all the iron was removed from solution within one minute unless the pH fell below pH = 6. In seawater the pH could fall as low as pH = 5 and the iron would still be rapidly removed from solution showing the strong coagulating nature of the seawater ions. No difference was found between solutions filtered through 0.45 μ m and 0.22 μ m filters, but if the initial rise in relative intensity is due to colloid formation then the sampling technique is too slow to extract suspensions containing the stable colloid. This can be judged from the timescale of the event which was in the order of 5 to 10 seconds whereas the first aliquot was withdrawn in 25 to 30 seconds.

2.2 Surface Area Measurements

To characterise the precipitates formed, and as a comparison between the ferric and ferrous derived material, surface area measurements were carried out. An in situ measurement was thought preferable because the pretreatment required by other methods may alter the surface characteristics, and therefore a dye adsorption technique was tried (174-175). The cationic dye Methylene Blue C.I.52015 was used. 1 g samples of iron oxyhydroxide were precipitated from FeCl₂ by the addition of 1.OM NaOH, and 150 ml of dye solution ranging from 0.8-8.0 g 1^{-1} were added to the suspensions and shaken for 20 hours on an orbital shaker. The pH was maintained between pH = 6and pH = 8 (176) and experiments were done at room temperature. A 20 ml aliquot was removed from each solution and the iron oxyhydroxide centrifuged off. - A 1 ml sample of the supernatant liquid was diluted to a known volume to enable the absorbance to be measured. This was done on a Corning 253 colorimeter at 610 nm using 1 cm plastic cuvettes with distilled water as the blank.

No sensible results were obtained from this method, see Figure 2.2.1. The solubility of the dye was exceeded before a plateau in the adsorption isotherm was reached and it was thought that dye miscelles were being adsorbed rather than single dye molecules (175). The large surface areas that have been found for iron oxyhydroxides



(80, 177) meant that large concentrations of dye had to be used to get complete monolayer coverage and this concentrated dye solution would more easily form miscelles. Therefore this method was abandoned and the more common B.E.T. gas adsorption method (178) was used.

The main drawback of this method is it requires the isolation of the precipitate from solution, and exactly what relationship there is between the surface area of the isolated precipitate and that in solution it is impossible to say. However the surface areas measured can be used as a comparison between the Fe(III) and Fe(II) derived precipitates and also the natural precipitates.

The synthetic iron oxyhydroxides were prepared by adding 0.05M FeCl₃ or FeCl₂ to 5 1 of buffered distilled water, to give a final concentration of 1×10^{-4} mol 1^{-1} . This is double the concentration used in the adsorption experiment because this enabled sufficient oxyhydroxide to be collected from 15-20 1 of suspension which was the maximum volume practicable. The precipitates were aged from 1 hour to 12 days in suspension at 15° C. For the short term ageing all the solution was centrifuged at 2000 r.p.m. in a large volume (2.5 1) centrifuge for 10 minutes. The precipitates were washed out of the tube with acetone to remove internal water and thus arrest ageing processes. Finally the precipitates were dried under vacuum at room temperature. Longer ageing times meant that the precipitates were settled out overnight

and approximately half the supernatant liquid was decanted off before centrifugation and collection as above. A similar procedure was used for natural waters, but this is described in detail in Section 2.5.3.

The surface areas of the iron oxyhydroxides were measured for approximately 0.1 g samples using a gravimetric B.E.T. nitrogen adsorption technique. A C.I. Mark 2B vacuum microbalance was used, and this gave μ g to mg sensitivity using samples of 0.25 g or less.

The samples were outgassed on the vacuum microbalance at room temperature for 24 hours after which the adsorption of nitrogen at -196°C was measured in sequential steps. Approximately 6 measurements were made at $\frac{P}{P_o}$ values from O to O.3. P is the pressure of nitrogen in mm Hg and P_o is the atmospheric pressure also in mm Hg. When $\frac{P}{P_o} = 0.3$ complete monolayer coverage of the solid has occurred, and for higher $\frac{P}{P_o}$ values the measurements were more widely spaced.

The porosity of the samples was also investigated by plotting the desorption curve. The extent and type of porosity is indicated from the hysteresis curves, and longer equilibration times, up to one hour, were allowed for the desorption points. The hysteresis curves were normally plotted with the adsorption isotherms so that the presence of porosity was clearly shown.

2.3 Precipitate Identification

Both the phosphate adsorption studies and the surface area measurements revealed considerable differences in the behaviour of Fe(III) derived compared with Fe(II) derived precipitates. To give a positive identification of the oxyhydroxides formed, a variety of analytical techniques had to be used. The main techniques used were transmission electron microscopy (T.E.M.), X-ray diffraction and Mössbauer spectroscopy. In some cases I.R. spectroscopy and scanning electron microscopy (S.E.M.) with an X-ray dispersive energy microprobe were also used.

2.3.1 Transmission Electron Microscopy

A Philips E.M. 300 microscope was used to examine a variety of precipitates, both freshly prepared and aged synthetic oxyhydroxides and natural iron precipitates. An 80 kV accelerating voltage was used for all samples which were mounted on Formovar coated copper grids. Samples were withdrawn using capillary tubes and the water was evaporated off under a high powered lamp. The convection created in the water drop by the heat from the lamp ensured a disperse coverage, but some of the samples had to be ultrasonically treated before extraction. To prevent salt crystallising from samples precipitated in seawater the precipitates were settled out, the seawater was decanted off, and the precipitate washed twice in distilled water.

Aged precipitates were stored in 50 ml or 100 ml plastic bottles for up to 6 months at room temperature. They were aged in the mother liquor or some seawater precipitated oxyhydroxides were aged in distilled water. 2.3.2 X-ray Diffraction

A few milligrammes of the oxyhydroxides isolated for surface area measurements were mounted on glass cover slips using a little Durafix adhesive dissolved in acetone. The powder X-ray diffractograms were taken using a Hilger Watts Y90 X-ray generator with a Solus-Schall diffractometer and a Berthold scaler timer. An Mo K source with a Zirconium filter was used, and the radiation was generated at 36 kV and 18 mA, with 3×10^2 counts per second and a 3 second time constant. The d-spacings were calculated for all visible peaks and then compared with all possible iron oxyhydroxides on the ASTM cards. A reference sample of γ -FeOOH (Lepidocrocite) Sample P23 (179) was used as a comparison for the Fe(II) derived precipitates and the Lady Bertha Mine stream sediment, but the Fe(III) derived and other natural precipitates were almost totally amorphous.

2.3.3 Mössbauer Spectroscopy

Additional 10-20 mg samples (were taken from the oxyhydroxides used for surface area measurements, and placed between polyethylene discs fitted into a perspex holder. Mössbauer spectra were recorded at room temperature (293K) and in liquid nitrogen (77K) on a Mössbauer spectrometer of similar design to that of Clarke <u>et al</u> (180). The source was 25m Ci of 57Co in a

rhodium matrix and measurements were made over 24 hours. The isomer shifts (δ) were measured against iron metal as the zero velocity reference and could be measured to ± 0.1 mm s⁻¹. Quadrapole splitting could be measured to ± 0.05 mm s⁻¹. The spectra were plotted by computer but a line of best fit has not been drawn through the points. 2.3.4 Additional Techniques

Whereas the synthetic oxyhydroxides are likely to be one oxide only, the natural precipitates may include various forms of iron plus other precipitated material. To aid the identification of these more complex precipitates scanning electron microscopy and infra-red (I.R.) spectroscopy have been used.

The scanning electron microscope was a JEOL 35 which was combined with a Link Model 860 X-ray spectrum analyser. This X-ray dispersive energy probe was very useful for identifying the elements present in the single particles under examination and so prove that what was under scrutiny was an iron rich compound. This facility was not available on the transmission microscope and care must be taken that particles examined are representative of that sample and not unusual ones that look "interesting".

Samples for S.E.M. were mounted on Aluminium stubs and coated with a thin layer of gold. An accelerating voltage of 25 kV was used but little additional information could be gained except from the X-ray probe analyses.

The major problem in studying the precipitates on the S.E.M. was an inability to focus clearly on the particles. The T.E.M. clearly showed how small the particles were, and as magnification was increased in the S.E.M. resolution was decreased so that the images became indistinct before the small particles could be seen. Only aggregates could be seen clearly, and so no extra information on the three dimensional aspects of the precipitates could be gained, as was originally hoped.

I.R. spectroscopy was also used to examine some of the precipitates by comparison with crystalline references. One or two milligrammes were dispersed in 400 mg KBr and compressed into a disc. The spectra were recorded on a Perkin Elmer 257 double beam spectrophotometer, from 4000 wavenumbers to 400 wavenumbers.

2.4 Phosphate Adsorption

The removal of phosphate from solution by iron oxyhydroxides was examined under varying conditions closely modelled to those found at either extreme of the estuarine environment. Initial experiments revealed the necessity for tight control of all experimental variables including reactor size, temperature, pH, precipitate age and initial iron and phosphate concentrations. 2.4.1 The Design of the Chemical Models

Initially experiments were carried out in 500 ml glass beakers. This was unsatisfactory due to the volume of liquid withdrawn for analysis leaving less than half the initial volume, and some interaction between the glass surfaces and the iron precipitates. Therefore the experiments were carried out in 1 1 glass beakers to give a larger volume to surface area ratio to reduce the container wall effects without requiring specialised stirring methods on very large volumes of liquid. All the work was carried out in constant temperature rooms fixed at $15^{\circ}C \pm 1^{\circ}C$ or $2^{\circ}C \pm 1^{\circ}C$. Solutions of 0.05M FeCl₃ and FeCl, were made up as for the nephelometric study, and iron oxyhydroxides were produced by adding 1 ml of solution to 1 1 of either seawater filtered through Whatman GF/C filters or distilled water. The latter contained a buffer of approximately 2m equivalents produced by dissolving 1.8 g of NaHCO₂ in 10 1 of distilled water and bubbling air through the solution overnight. Both this solution and the filtered seawater were stored

in 10 1 polyethylene bottles; this reduced the phosphate in the seawater to <0.1 μ mol 1⁻¹. (181).

The pH range examined was pH = 6.5 to pH = 8.4 with the pH altered by addition of 0.1M HCl or NaOH. For low pH values $^{\infty}6.5$ a variable mixture of CO_2 /air was bubbled through the solution, this giving a more stable value than the addition of acid. The maximum variation of pH during the course of an experiment was ± 0.2 pH units in seawater, and ± 0.4 pH units in distilled water. The pH was monitored with an E.I.L. combination glass electrode in conjunction with an E.I.L. model 7060 digital pH meter.

The initial dissolved iron concentration was 5×10^{-5} mol 1⁻¹. The beakers were not acid washed between experiments so that losses of iron to the container walls were reduced. After each experiment the beakers were wiped with a tissue and rinsed thoroughly with distilled water to remove excess iron. Less than 10% of iron was adsorbed for each experiment, and a blank solution to test for phosphate removal in the absence of iron showed losses below the limit of detection (see below) over a 2 hour period.

The precipitates were either freshly formed <u>in situ</u> or aged for 20 hours <u>in situ</u>. Fe(II) solutions were stirred open to the air so that the solution could be considered to be O_2 saturated throughout the course of an experiment. To avoid dust contamination a plastic film was stretched over the beakers. The phosphate was added

from a stock solution of NaH_2PO_4 made up by dissolving O.1361 g of dry NaH_2PO_4 in 1 l of distilled water saturated with chloroform to inhibit biological activity. Initial phosphate concentrations ranged from 0.5 to 10.0 µmol 1⁻¹, with the majority of experiments using 1.0 µmol 1⁻¹ initial concentration, this being typical for natural waters (148, 160, 165).

2.4.2 Analytical Methods

The uptake of phosphate was monitored over 2 hours by withdrawing 25 ml aliquots in a syringe and filtering immediately through 0.45 µm Millipore filters. The dissolved phosphate was measured using the Molybdenum Blue complex single reagant method on a Pye Unicam SP500 spectrophotometer at 850nm using 10 cm cells (182). For initial phosphate concentrations above 5.0 μ mol 1⁻¹ which is the upper limit of the linear range (183) 25 ml of distilled water were pipetted into the conical flasks to dilute the phosphate solution before reagent addition. Equilibrium values for the dissolved phosphate were taken after 20 hours. This was taken as the end point of the adsorption processes under study, before diffusion of adsorbed phosphorus into the bulk of the oxyhydroxide occurs (133).

The coefficient of variation for the Molybdenum Blue method was found by taking 8 replicates of a $1.0 \mu \text{ mol } 1^{-1}$ standard and was found to be 1.9%. Therefore the reproducibility of the sampling method is very good despite

the number of stages involved. The coefficient of variation for the measurements taken during an adsorption experiment was found by taking a sample from 4 separate but identical runs at a fixed time of 10 minutes. The coefficient of variation increased to 6%, only a 3 fold increase over the analytical method despite the added complexity of the system.

The equilibrium concentration of phosphate varied with pH but never fell below 0.09 μ mol 1⁻¹ even after a 20 hour equilibrium time. The limit of detection was 0.02 μ mol 1⁻¹ and blanks of distilled water contained no measurable phosphate. Therefore this very low equilibrium concentration is a real measurable value. and is not below the limit of detection for the analytical method. The phosphate concentrations used were low, therefore care had to be taken at all times to avoid contamination. Solutions were partially covered whenever possible, and all syringes, flasks and filter holders were washed in dilute HCl and rinsed with distilled water before each experiment. Problems involving phosphate desorption and/or adsorption from/to filters have been identified (181), but pretreatment of the filters was impracticable due to the very large numbers used. Experiments were carried out to investigate this problem by measuring the phosphate in filtered and non-filtered solutions. At the phosphate concentrations and pH range used there was no desorption, and less than 5% adsorption

onto the filters was found. This removal is not significant compared to the adsorption onto the iron oxyhydroxides, and the consistancy of replicate runs in the modelling experiments and the coefficient of variation indicates that this removal is a consistent factor in the experiments. Analysing the filtrate for iron either by a colorimetric method (see Section 2.5) or by Atomic Absorption showed that iron was completely removed from solution over the pH range used by the 0.45 μ m filter. The slowly oxidising Fe(II) solutions were an exception to this, as Fe²⁺ remained in solution and so could pass through the filter.

The measurement of phosphate at these levels was a standard procedure in the M.B.A. laboratory, and checks on both blank and calibration factors were carried out regularly. Calibrations were only found to vary significantly when fresh stock solutions of NaH_2PO_4 were made up, and the calibration factor was altered accordingly.

2.5 Collection of Natural Samples

The majority of natural waters examined contained predominantly Fe(II) as it was thought this form of iron would be of importance in an estuary, but as yet had received little attention. Fe(II) oxidises rapidly in aerobic conditions at pH values greater than pH = 3, therefore care was needed in collecting and using samples. The section below outlines the sites, methods of collection and analysis and the experiments carried out using these natural sources of iron.

2.5.1 Sample Sites and Field Operations

Acid mine streams at Cadover Bridge on the river Plym, Lady Bertha Mine (184), Plate 2.1, on the river Tavy, both sites in Devon, and the Carnon river (61) in Cornwall, all S.W. England, Figure 2.5.1 were found to contain high concentrations of dissolved iron, 90% or more as Fe(II). Samples were collected from these streams in acid washed 1 1 plastic bottles filled to overflowing and tightly stoppered to exclude air. These samples were returned to the laboratory within two hours and stored at 2° C. A 1 1 sample was taken, filtered through Whatman GF/C and then 0.45 µm Millipore filters and used in a phosphate adsorption study immediately. Analysis for total dissolved iron and Fe(II) iron, and dissolved phosphate was carried out during the second filtration stage.

The second source of natural samples was interstitial



Plate 2.1



Figure 2.5.1. The S.W. peninsula of the U.K., showing the mineralised catchment area of Dartmoor, the estuarine systems in the Plymouth region and Restronguet Creek into which the Carnon River discharges.

waters taken from either estuarine or mine stream sediments. The latter site gave very high dissolved iron concentrations and together with ease of locating and collecting the samples, this site was favoured over estuarine sites.

Interstitial samples were collected by <u>in situ</u> dialysis using cellulose acetate dialysis bags mounted in perspex holders (185). Each dialysis bag contained approximately 20 ml of deoxygenated distilled water, and they were immersed in the anoxic layer of sediments for between 5 and 8 days, with the object of collecting Fe(II). Very few studies have been made on the sampling of waters by dialysis bags (186) but it proved to be a satisfactory technique for this study as a source of Fe(II) was all that was required.

On retrieving the samplers approximately 2 1 of the sediment were also collected to protect the samples from the air. Beakers containing samplers and sediment were put into a glove bag previously flushed with nitrogen, and returned to the laboratory within two hours. There the bags were quickly transferred from the holders into deoxygenated distilled water, and then the outer surfaces rinsed clean before cutting the bag and emptying the contents into a measuring cylinder. The whole operation after transfer from the holders was done under nitrogen, and the measuring cylinders were tightly stoppered and stored in a fridge. These samples were always used within

48 hours of collection, and were not used if signs of oxidation were apparent, i.e. an orange precipitate collecting at the bottom of the cylinder. Usually 2 or 3 bags were combined in 1 cylinder to give between 40 and 60 mls of sample. A small aliquot of this was analysed (see Section 2.5.2) the rest used in modelling experiments (see Section 2.5.3).

2.5.2 Analytical Methods

The analysis of the natural samples is discussed here under a separate heading as there are additional factors and problems that have to be taken into account when analysing these natural waters rather than the chemically simpler model solutions.

Phosphate was measured using the Molybdenum Blue complex single reagent method (183). There were no additional problems for this method, provided that the very variable phosphate concentrations in the streams and more especially the interstitial samples did not exceed the linear range of the method. When this was the case, the samples were diluted with distilled water prior to analysis, and for some interstitial samples a 25 fold dilution was required.

Dissolved total Fe and Fe(II) were measured using the Ferrozine reagent method (187) on a Pye Unicam SP500 spectrophotometer with 1 cm cells at 560 nm. The measurement of total dissolved iron is straightforward, and for the measurement of iron in some interstitial samples an

80 fold dilution with distilled water was required. The analysis of Fe(II) presents problems both in sample handling and also the specificity of the measurement. Natural waters may contain both Fe(III) and Fe(II) iron, and the complexation of Fe(II) may disturb the Fe(II)/Fe(III) equilibrium (188). However, the Fe(III) is usually in a colloidal form (189) and its conversion to Fe(II) will therefore involve a heterogeneous process that is likely to be slow (190). The dissolved organic matter will also interact with the Fe(II) (52) so that organic matter can reduce Fe(III) even under oxidising conditions (190). From these considerations the Ferrozine method was thought to be suitable for Fe(II) analysis, with the acidification and reduction steps omitted, and absorbance readings taken after 5 minutes of reagent addition. A comparison between the 2,2' Bipyridyl colorimetric and polarographic methods of measuring Fe(II) in natural waters has found good agreement (190) and checks on the measurement of Fe(II) in an excess of Fe(III) showed negligible reduction of the Fe(III) after 10 minutes provided the acidification step was omitted. 2.5.3 Preparation of Models and Precipitates

The natural sources of iron were used both for phosphate adsorption experiments and also precipitate characterisation studies. The most important consideration for these studies was restricting the concentrations to the levels controlled in the models. The solutions were first used in the phosphate adsorption experiments, and then the precipitates formed were examined to compare

with the synthetic precipitates.

The stream waters contained dissolved iron levels close to those used in the model adsorption experiments, and no addition or dilution was carried out. The phosphate levels were variable, but tended to be lower than those used in models so that additional phosphate was added, as in the model experiments, before the iron was precipitated. The pH was increased by adding 0.1M NaOH and the precipitates formed rapidly, and removal of phosphate was monitored as before. Further experiments were carried out by increasing the ionic strength of the sample at the same time as increasing pH. This was done by adding 200 ml of a concentrated solution of NaCl and $MgSO_4$ dissolved in filtered seawater, to 800 ml of stream water. 22 g of NaCl was added directly to 200 ml of seawater and then 8 g of $MgSO_4$ dissolved in a little distilled water was carefully added to this solution. This gave a concentrated seawater analogue with normal concentration of Na⁺, C1⁻, Mg^{2+} and SO_4^{2-} and other ions depleted when added to the stream water.

Almost all the experiments involved freshly forming precipitates but a few were carried out on precipitates aged for 20 hours as a comparison with the model.

The interstitial samples contained high levels of iron and phosphate so that 20 ml could be injected into l l of seawater or buffered distilled water to give comparable iron concentrations. The solutions contained

1.0 or 2.0 μ mol 1⁻¹ of additional phosphate, and the removal was monitored as before with the interstitial phosphate taken into account. Again, the majority of experiments involved freshly forming precipitates but a few experiments examined the uptake onto aged precipitates derived from interstitial waters.

It was not possible to obtain sufficient precipitate from the interstitial samples for surface area analysis, X-ray diffraction or Mössbauer spectroscopy, but the precipitates were examined under the electron microscope.

For the stream waters, 30 l of the iron rich water were collected, filtered and the iron precipitated out by increasing the pH. For one sample which was rich in organic matter the iron was precipitated out by the addition of a concentrated NaCl solution. The total ionic strength was thus raised by 0.07M and the precipitate formed within 36 hours at 15°C. Once the iron had been removed from solution, it was isolated and dried in the same way as for the synthetic precipitates.

3. RESULTS AND DISCUSSION

This, the major chapter of the study, is large in content because of the need to integrate the two interrelated aspects of the study, namely the nature of the iron oxyhydroxide solids and the response of phosphate to those solids. The first section describes the characterisation studies undertaken on both natural and synthetic iron oxyhydroxides. The second section describes their oxidation and precipitation behaviour under simulated natural conditions using nephelometry. This aspect then interfaces with the final section on phosphate adsorption since the appearance and nature of the solid phase controls the chemistry of the dissolved component.

3.1 Precipitate Characterisation

3.1.1 Surface Area Measurements

The surface area of an adsorbant is one of the major variables encountered in adsorption studies. Numerous measurements have been made on the specific surface areas of amorphous and crystalline iron oxyhydroxides and various techniques have been developed and modified to try and improve the accuracy and reproducibility of the measurements. In this study, the difficulties encountered in measuring the surface areas were exemplified by the apparent failure of the dye adsorption method. It was therefore decided that the more commonly used B.E.T. No adsorption technique would be employed to give a comparison between synthetic and natural precipitates formed in this study and also iron oxyhydroxides investigated by other workers. Unfortunately, there is little agreement in surface areas measured by different workers using the same technique for a well defined oxyhydroxide, and the variability between techniques is even greater, as shown in Table 3.1. Some of the variability in the surface areas for Goethite as measured by B.E.T. N₂ adsorption for instance must lie in the oxyhydroxide itself, and will depend on how it was formed and isolated prior to being analysed. It is also apparent that measurements made in situ are much larger than those made on precipitates removed from solution. Studies on the weight loss on outgassing of iron oxyhydroxides have

Table 3.1 Comparison of specific surface areas of

iron oxyhydroxides

Iron Oxyhydroxide	Method of Measurement	Surface area m. ² g ⁻¹	Reference
α – FeOOH	Adsorption of Ethylene Glycol	112	191
17	Geometric Surface Area from Electron Microscopy	118	191
11	Geometric Surface Area from Electron Microscopy	11-18	91
	B.E.T.	87	192
. 11	B.E.T. No	89	193
tt	B.E.T. No	48	84
	B.E.T. N2	71	194
γ - FeOOH	B.E.T.	128	192
	B.E.T. Ar	116 ± 8 ^(a)	146
-		114 [±] 3.6 ^(b)	
**	B.E.T. N ₂	100	195
18	B.E.T. N	171	196
11	B.E.T. N2	97-121	This work
Amorphous Fe(OH) ₃	B.E.T. Ar	$215^{(c)}_{265}^{(d)}$	17
	B.E.T. N.	215	76
n	Adsorption of Phosphate	720	197
n	B.E.T. No	182	81
rt	Negative Adsorption of	270-335	198
. n	B.E.T. N	320	88
n	Calculated from	520	
	Particle Diameter and Density	840	81

ł
Method of Measurement	Surface area m. ² g ⁻¹	Reference
B.E.T.	159	199
Negative Adsorption of Mg ²⁺	≃700	199
B.E.T. N ₂ B.E.T. N ₂	280 159–234	15 This work
	Method of Measurement B.E.T. Negative Adsorption of Mg ²⁺ B.E.T. N ₂ B.E.T. N ₂	Method of MeasurementSurface area $m.^2 g^{-1}$ B.E.T.159Negative Adsorption of Mg2+ ≈ 700 B.E.T. N2 B.E.T. N2280 159-234

t

(a) Measured on manually operated equipment

(b) Measured on automatic equipment

- (c) 1 year old
- (d) 1 month old

shown loss of chemisorbed water (88). This has been shown to occur at room temperature and this results in surface decomposition which may lead to an underestimate of the actual specific surface area. Comparative studies on two clays have shown variations in the surface areas of each clay when air dried, vacuum dried and oven dried (89). However, care must also be exercised when using some of the <u>in situ</u> techniques such as the negative adsorption technique which applies only to smooth nonporous surfaces (200), an assumption that cannot be made for iron oxyhydroxide surfaces.

The results of the specific surface area measurements for synthetic iron oxyhydroxides prepared in this study are included in Table 3.1, and it can be seen that for Lepidocrocite (γ -FeOOH) there is very good agreement with other values and that for amorphous ferric hydroxide the surface area falls within the considerable range of previous values but towards the lower end.

The B.E.T. plots for two of the Lepidocrocite samples and two of the amorphous oxyhydroxides are given to show the reproducibility of the measurements (Figures 3.1.1-3.1.2). The variation in surface areas due to ageing processes is shown in Table 3.2 which includes typical values found for the completely crystalline forms of the oxyhydroxides. The initial increase in the surface area of Fe(III) derived precipitates from 159 m² g⁻¹ to 234 m² g⁻¹ is either due to a disordering of some initial structure





Table 3.2 The surface areas of aged Fe(III) derived and Fe(II) derived oxyhydroxides

Ageing Time	Specific Surface Area $m^2 g^{-1}$ (b)		
	Fe(III) derived	Fe(II) derived	
2	159	121	
48	234	120	
168	-	97	
288	173	-	
ω	87 ^(a)	128 ^(a)	

- (a) As measured for crystalline α -FeOOH and γ -FeOOH by Cabrera <u>et al</u> (192)
- (b) Surface areas calculated from $\frac{P}{P_0}$ against $\frac{P}{x(P_0-P)}$ plots by standard gravimetric method including buoyancy corrections (217)

in the precipitate over a short time, or it may be an artifact in the sampling procedure as the 48 h old precipitate was allowed to settle in the beakers before centrifugation whereas the 2 h old precipitate was not. The decrease in surface area from 234 m² g⁻¹ to 173 m² g⁻¹ is due to some of the amorphous precipitate ageing to Goethite and quantities of this crystalline form were found using the Mössbauer and infra-red techniques described in Sections 3.1.6 and 3.1.5 respectively. If the ageing process reaches completion the surface area would be that for Goethite, approximately 80 m² g⁻¹, although this would have taken many months at the temperature and iron concentration used.

The surface area changes on ageing for the Fe(II) derived precipitates are not as complex, and this is because a crystalline oxyhydroxide is formed almost immediately. The decrease in surface area over 120 h is probably due to an increase in the crystallite size occurring either in solution, or on collection. All three measurements and especially those for the comparatively fresh material are close to the surface areas of Lepidocrocite measured by other workers.

Further information on the precipitates is given by the full adsorption isotherms, and the isotherms with hysteresis loops, where present, are given for each precipitate studied. The isotherms for the 2 h. 48 h and 288 h old precipitates are shown in Figures 3.1.3, 3.1.4



O - Adsorption points. \triangle - Desorption points.



and 3.1.5 respectively and they are all of type IV according to the classification of Brunauer, Deming, Deming and Teller (B.D.D.T.) (201). All three solids are porous as shown by the hysteresis loops which are type E according to the De Boer classification (202), and this type of hysteresis results from narrow necked wide bodied pores commonly called "ink bottle" pores. An indication of the pore size distribution is given by the closure at either end of the hysteresis loop, and this information is given in Table 3.3 for Fe(III) and Fe(II) derived precipitates; the latter will be discussed below. The pore size range for the Fe(III) derived precipitates is in the mesopore range, i.e. between micro and macro, and the changes in the size range may indicate changes in the structure of the oxyhydroxide. Thus the decrease in both the upper and lower limits in ageing for 48 hours support the hypothesis that some original structure formed within 2 h ageing is disrupted so that the precipitate is more closely packed, and pore spaces are smaller. As the precipitate ages the crystal structure begins to form and the upper limit is increased 4 or 5 fold as the precipitate becomes more loosely packed.

Isotherms for the 48 h and 168 h old Fe(II) derived precipitates are shown in Figures 3.1.6 and 3.1.7 respectively. The isotherm for the 2 h old precipitate was identical to that shown in Figure 3.1.6 and is therefore







 \triangle - Desorption points.

not included. The isotherms are type II according to the B.D.D.T. classification with a type D hysteresis loop using De Boers classification. This type of hysteresis is associated with either slit-shaped pores or the space between parallel plates and the isotherm classification means that there is no upper limit for the pore size. Therefore the upper limit given in Table 3.3 is probably low as the oxyhydroxide has a much more open structure than the Fe(III) derived precipitates. The decrease in surface area might occur in the lower pore sizes as the hysteresis loop closed earlier for the aged material and it is only the lack of sensitivity in measuring r which does not show this.

Some of the natural oxyhydroxides were also investigated and the results are given in Table 3.4. It was not possible to collect sufficient precipitate from interstitial waters for a measurement to be made but both a naturally precipitated oxyhydroxide and oxyhydroxides precipitated from natural waters rich in dissolved iron were used.

The Cadover Bridge precipitate produced an isotherm very similar to that for the Fe(III) derived oxyhydroxide (Figure 3.1.8) but the surface area was slightly lower than for the amorphous synthetic precipitates. The pore size range was also closer to that for the more crystalline oxyhydroxide yet no evidence of crystallinity was observed by the other techniques used to characterise the precipitates. This apparent anomaly is probably due to organic



Table 3.3 The pore size range of Fe(III) and Fe(II) derived precipitates

Precipitate	Age (hours)	Hysteresis Closure P Po	Pore size range r Å
Fe(III) derived	2	0.45 - 0.80	20 - 50
Fe(III) derived	48	0.30 - 0.75	15 - 40
Fe(III) derived	288	0.40 - 0.95	15 - 200
Fe(II) derived	48	0.45 - 0.95	20 - 200
Fe(II) derived	168	0.50 - 0.95	20 - 200

÷...

:

Precipitate	S.A. m ² g ⁻¹	Isotherm type B.D.D.T.	Hysteresis type De Boers	Pore size range r Å
Cadover Bridge stream precipitate	141	IV	E	15-200
Lady Bertha Mine stream precipitate	6.4	II	D	15-200+
Mine stream sediment	164	II/IV	None	Non- porous

.

Table 3.4 The adsorption isotherm data for natural precipitates

matter precipitated on and with the iron oxyhydroxide and this has been shown to decrease the surface areas of natural iron oxyhydroxides (41). This precipitate is obtained from water containing a high concentration of Fe(II) which was oxidised by bubbling air through the solution increasing the pH, and as stated in the experimental section the Fe(III) produced by this action did not precipitate out until the ionic strength of the solution had been increased. It is felt that the stabilisation of the Fe(III) was due to dissolved organic matter, and this may have been precipitated out together with the iron when the ionic strength was adjusted. This behaviour suggests that if Fe(II) was to enter a natural water containing organic material an amorphous iron oxyhydroxide would be precipitated rather than the Lepidocrocite formed in the organic-free model solutions.

The two other natural precipitates examined both came from the Lady Bertha Mine stream and both gave surprising results. This stream water is also rich in Fe(II) (=1.5 mg 1⁻¹) and this readily precipitated from solution if air was bubbled through for a few minutes. When the surface area measurement was made hardly any uptake of N₂ occurred, and the surface area is very low at 6.4 m² g⁻¹. This suggests a very crystalline precipitate, and the adsorption isotherm and hysteresis loop (Figure 3.1.9) are similar to those found for the Fe(II) derived Lepidocrocite. However no crystalline structure is indicated by any of the



other techniques used, and there is no explanation for this unusual precipitate.

The isotherm for the Lady Bertha stream sediment is shown in Figure 3.1.10, and this is the only non-porous precipitate examined. Despite being non-porous it has a surface area of 164 $m^2 g^{-1}$ which is the largest of the areas found for the natural precipitates. The isotherm shape does not fit neatly into any of the B.D.D.T. classifications and it appears to be a hybrid of types II and IV. Evidence of crystallinity is given in the X-ray diffraction study as will be shown later, but it is felt that this sediment is a mixture containing a high percentage of iron but no single crystalline form. The high surface area suggests that the sediment may be important in the partitioning of dissolved constituents in the mine stream and indeed high arsenic levels were found in this sediment by X-ray fluorescence (Figure 3.1.11). Arsenic is one of the metals commercially extracted from Lady Bertha Mine and the stream drains some of the waste tips which are still barren because of their arsenic content. The oxyhydroxide precipitated from the stream water did not contain any arsenic measurable by X-ray fluorescence (Figure 3.1.12) and this may indicate the expected lack of activity due to its small surface area, or that the uptake onto the sediment is a slow process. The very large difference in surface areas may indicate that the precipitation that occurs naturally involves a different mechanism to that employed in the laboratory, showing how important the method of precipitate formation is to the









precipitate character.

This surface area study has shown some of the differences between the Fe(II) and Fe(III) derived precipitates, and this will be useful in the phosphate adsorption studies in explaining some of the behaviour found. The comparison between synthetic and natural precipitates indicated the complexity found in the natural environment, but also proved that naturally occurring iron precipitates can have large specific surface areas. These measurements were made on precipitates removed from solution and care must be taken not to use the surface areas found as absolute figures but to use them for comparative purposes only. These simple measurements have produced a considerable amount of detailed information on the iron oxyhydroxides but identification of the synthetic and natural precipitates cannot be made using this data In the following four sections a variety of alone. complementary techniques are used to identify the precipitates 3.1.2 Electron Microscopy

The electron microscope is a valuable tool used in the study of surface chemistry, and its single most remarkable attribute is its versatility (203). The variety of techniques that has been developed for the electron microscope such as electron diffraction, X-ray emission, extended electron loss fine structure (EXELFS), and Z-contrast images (atomic number maps), enable the elemental composition, bonding and crystal structure of a sample to be determined. In this study high resolution imaging using transmission

electron microscopy (T.E.M.), one of the simpler techniques, is used to examine the synthetic and natural iron oxyhydroxides. The electron micrographs show the morphology of each precipitate and enable comparisons to be made between precipitates of different origin. If an ordered precipitate was observed an electron diffractogram was taken to investigate the crystallinity but no clear patterns were obtained so these have not been included. Therefore scanning electron microscopy (S.E.M.) was used to investigate the Fe(II) derived precipitate in an attempt to elucidate the three dimensional and surface characteristics of the apparently crystalline precipitate observed by T.E.M. The S.E.M. has an added advantage that when investigating natural precipitates the elemental composition can be determined using an X-ray dispersive energy probe. This facility was not available on the transmission microscope. This probe is vital when studying such precipitates as it is one of the few ways of positively identifying an amorphous iron precipitate as viewed by the electron microscope. This extra information is required because of the large number of substances that can occur in natural precipitates which cannot be identified by observation alone. Care is also necessary when observing specific samples of a natural precipitate so that a representative section is chosen whereas for a synthetic sample only the substances mounted should be present, and these must be investigated rather than the unusual or scarce objects which are more probably due to

contamination.

Ξ.

The following electron micrographs show at least two views of each precipitate. The first is a general picture to show a characteristic sample for each precipitate followed by at least one, and where necessary, two or three, views at higher magnification to indicate the particle structure size and shape of each oxyhydroxide.

The precipitate derived from Fe(III) in seawater is shown in Plates 3.1 and 3.2. These Fe(III) derived oxyhydroxides have the same morphology whether they are precipitated in seawater or distilled water at high or low pH values and the ageing of the precipitate only yields a more compact oxyhydroxide with no additional structure visible. The masses of compacted precipitate can be large, 10-20 μ m in length, but when dispersed ultrasonically, or disrupted by the heat generated by the lamp evaporating off the solution from the grid, the fundamental particles are the same as for fresh precipitates, see Plate 3.2. The fundamental particles that make up the amorphous oxyhydroxide appear to be small spheres ranging from 5-30 nm in diameter. This type of oxyhydroxide is commonly found as the product of Fe(III) precipitation (11-13) and the size of the spheres will vary according to the concentrations of iron and concentration and type of base used (13). Generally the higher the initial concentration of iron the larger the particles. Whether the base is added to an Fe(III) solution, or Fe(III) is added to an alkaline solution



SCALE BAR = 200 nm

Plate 3.1



SCALE BAR= 100 nm

Plate 3.2

may also affect the particle size due to the possibility of localised concentration effects if the second method is used. No crystallinity was observed in these precipitates even after 6 month ageing periods, and this may be due to the low concentration of iron used, or, that storage at room temperature requires even longer ageing periods before crystallinity can be observed by the electron microscope. The precipitate is likely to be very active, and have a large specific surface area because of its amorphous nature and small particle size. A large surface area was found as discussed in Section 3.1.1 above and the adsorption activity will be investigated later.

The precipitate formed in seawater from FeCl, is shown in Plates 3.3 and 3.4 and it contrasts with the previous amorphous oxyhydroxide, as crystalline regions are dominant. The oxyhydroxide has an unusual morphology which is most clearly shown in Plate 3.4. The oxyhydroxide has filamentous particles which appear to be produced by a folded film randomly radiating from masses which are joined by the filaments. At very high magnification (200,000x) (Plate 3.5) the filaments stand out very clearly from what appears to be amorphous material which cannot be resolved even at this magnification, and there is no internal structure of layers visible in the crystalline areas. The degree of crystallinity did vary between precipitates but this appeared to be independent of the media or the pH. Age had little effect on the amount of crystalline material.



SCALE BAR = 20,um

Plate 3.3



SCALE BAR = 1,um

Plate 3.4



SCALE BAR = 50 nm

Plate 3.5



SCALE BAR=100 nm

Plate 3.6

and even very fresh precipitate contained a considerable amount of the structured oxyhydroxide. Some of the Fe(II) derived oxyhydroxides were precipitated in the presence of phosphate but this had no observable effect on the morphology of the oxyhydroxide (Plates 3.6, 3.7 and 3.8). The particle size has no real meaning for this precipitate, but the length of filaments is measurable at between 50 nm In an attempt to obtain additional information and 250 nm. on the morphology of these precipitates, and as a further comparison with the Fe(III) derived oxyhydroxides, scanning electron micrographs were taken, and these are shown in Plate 3.9 for the Fe(III) and Plate 3.10 for Fe(II) derived precipitates. Unfortunately, no detailed information could be extracted but there are visible differences between the masses derived from different sources. The larger masses shown in Plate 3.10 are approximately 50 μ m in length and some "grain" is apparent whereas the masses for Fe(III) derived material shown in Plate 3.9 are smaller at 10-20 um in length and have a much smoother appearance. Therefore it is likely that the particles massed together are smaller when derived from Fe(III) rather than Fe(II), but this is no more than has been shown by the T.E.M.

The crystalline nature of this oxyhydroxide plus the general larger size of the precipitate masses indicates a smaller surface area than that for the Fe(III)derived material and this was found to be so. The crystalline nature also



SCALE BAR = 50nm

Plate 3.7



SCALE BAR = 200 nm

Plate 3.8



Plate 3.9



Plate 3.10



SCALE BAR = 500nm

Plate 3.11



Plate 3.12

SCALE BAR = 100 nm



SCALE BAR=100nm

Plate 3.13



SCALE BAR = 5 Jum

Plate 3.14



SCALE BAR = 2 Jum

Plate 3.15



SCALE BAR = 400 nm

Plate 3.16

commonest species in the sediment. These precipitate particles are made up from spheres as is the Fe(III) derived material, but their size is much larger, and the spheres do not appear to be made up from further units.

The oxyhydroxides precipitated from stream waters are all very similar, and some of the clearest photomicrographs were obtained for the Carnon River precipitates, Plates 3.17-3.19. The precipitate again comprises of spherical particles but these do not appear to be as dense and are constructed of amorphous precipitate which could not be resolved. The spheres are between 50 and 100 nm in diameter and although no ageing study was carried out. these may form similar particles to those observed for the Lady Bertha Mine stream. The general appearance is very similar to that for the Fe(III) derived oxyhydroxide but with larger, less compact particles. These precipitates are expected to have large surface areas, and the possible presence of dissolved organic matter coprecipitating with the iron does not alter the form of the oxyhydroxide. For the oxyhydroxides precipitated from interstitial waters there does appear to be a change in the morphology of the iron oxyhydroxide due to organic coatings, and this is shown in Plates 3.20 and 3.22. The particles are again spherical but a film appears to join particles so that the particle masses are generally larger. This is the most direct evidence of organic material interacting with the iron oxyhydroxides, and this interaction is discussed with


SCALE BAR =1 Jum

Plate 3.17



SCALE BAR = 200 nm

Plate 3.18



SCALE BAR = 100 nm

Plate 3.19



SCALE BAR=200 nm

Plate 3.20



SCALE BAR=100 nm

Plate 3.21



Plate 3.22

SCALE BAR = 50 nm

respect to changes in the surface areas and degree of crystallinity.

As mentioned above, it is vital to identify the particles that are examined under the electron microscope and this has been done for the Cadover Bridge stream sediment. No electron micrographs of this precipitate have been shown as the other precipitates gave clearer electron micrographs of the typical particles found. Figure 3.1.13 shows the X-ray dispersive energy spectrum for one particle of the stream sediment. It clearly shows the predominance of iron in the sediment particle and with small amounts of aluminium, silicon, phosphorus and sulphur also present. These four elements are not unexpected in a natural sample but some of the aluminium peak may be due to back scattering from the stub that the sample was mounted on. Figure 3.1.14 shows the spectrum for the Fe(II) derived precipitate with the two peaks of the Fe K_{α} and Fe K_{β} lines with a small peak for the aluminium, and a very small peak for Cu, this latter element arising from the sample holder which is made of brass.

The results of the electron microscopy clearly show the differences in the two synthetic precipitates and enable predictions to be made about their expected behaviour. In conjunction with the X-ray analysis of the S.E.M. the natural precipitates are identified and again predictive behavioural information is possible.







Figure 3.1.14. X-ray dispersive energy microprobe analysis of Fe(II) derived iron oxyhydroxide (Lepidocrocite).

3.1.3 X-ray Diffraction

Powder X-ray diffraction is a non-destructive technique used to identify crystalline powders when milligramme quantities are available. The majority of X-ray diffractograms are measured using a Cu K_{α} source with a wavelength of 1.542 Å, but when studying iron oxyhydroxides a shorter wavelength radiation is required and in this study a Mo K_{α} source with a wavelength of 0.710 Å is used. The tables used to calculate d spacings from the θ° values are calibrated with respect to Cu K_{α}; therefore it is necessary to convert the values obtained from the tables for the Mo K_{α} wavelength radiation. The d spacings are calculated using the Bragg equation

$$d = \frac{\lambda}{2 \sin \theta} \qquad \dots Eq. (3.1)$$

Therefore the conversion must be:

d
$$(Cu K_{\alpha}) \cdot \frac{0.710}{1.542} = d (Mo K_{\alpha})$$

d $(Mo K_{\alpha}) = 0.46 d (Cu K_{\alpha})$

It is an easy matter then to look up the d (Cu K_{α}) value corresponding to the angle at which a peak occurs on the diffractogram and calculate the d spacing for Mo K_{α} . These are then compared to d spacings of various iron oxyhydroxides given in the A.S.T.M. card file until a good fit is found. The diffractograms for the synthetic and natural oxyhydroxides are shown in the figures following, and the data for each precipitate is tabulated

and compared with the data for the oxyhydroxide of "best fit" extracted from the A.S.T.M. card.

The first diffractogram (Figure 3.1.15) is for aged Fe(II) derived oxyhydroxide compared with Lepidocrocite and it has 6 distinct peaks which correspond to peaks in the spectrum for Lepidocrocite. The d spacings for these peaks have been calculated, and are listed in Table 3.5 alongside the d spacings for Lepidocrocite. There is very good agreement between the values but the most intense peak in the standard is missing from the sample. This is because the diffraction occurs at an angle less than 4^o and the diffractogram was started at 4^o to avoid straight through radiation effects.

The diffractogram for Fe(III) derived oxyhydroxide is shown in Figure 3.1.16 and this does not have any strong distinct peaks but has two very broad bands indicating amorphous material. There are peaks that appear above the background noise and these have been analysed and are shown in Table 3.6. There is moderate agreement, but some of the most intense d spacings are not present, and some of the peaks analysed give d spacings that do not correspond to those in the standard. This identification is not as definite as that for the Fe(II) derived oxyhydroxide and it is more realistic to use the lack of distinct peaks as an indication of amorphous iron oxyhydroxide rather than to use the very weak peaks as a clear indication of Goethite.



Figure 3.1.15. X-ray diffractograms for aged Fe(II) derived iron oxyhydroxide (lower trace) and a synthetic crystalline Lepidocrocite (upper trace).

θο	d (Cu K _a) A	d (Mo K _a) R	d A (a)	Intensity I/I ₀ %
			6.26	100
6.325	6.98	3.21	3.29	90
8.35	5.29	2.44	2.47	80
10.70	4.14	1.91	1.94	70
			1.73	40
13.625	3.63	1.50	1.52	40
14.40	2.99	1.37	1.37	30
17.35	2.58	1.19	1.19	20
			1.07	40

Table 3.5 Comparison of d spacings for Fe(II) derived precipitates with Lepidocrocite

(a) Taken from A.S.T.M. card file 8-98 for

Lepidocrocite





:

	θ	d (Cu K _a)	d (Μο Κ _α)	d A (a)	Intensity I/I ₀ %
				4.97	60
				4.18	100
	6.60	6.689	(3.080)	3.36	60
	7.00	6.308	(2.904)	2.69	. 70
	7.90	5.593	2.575	2.58	55
	8.10	5.456	2.51	2.48	40
÷			÷	2.44	80
i	9.20	4.808	2.214	2.25	60
	9.50	4.657	2.144	2.18	60
	9.8	4.516	2.079	2.01	20
:	10.0	4.427	2.04	1.92	40
	10.2	4.341	1.999	1.80	50
	11.7	3.797	1.748	1.77	30
	11.90	3.728	1.716	1.72	70
	12.00	3.697	1.702	1.69	50
				1.66	40
				1.60	50
ļ	13.10	3.392	1.562	1.56	65
	13.55	3.281	1.511	1.51	60
	13.80	3.223	(1.484)	1.46	40
				1.45	60
					l

Table 3.6 Comparison of d spacings for Fe(III) derived precipitate with Goethite

(a) Taken from A.S.T.M. card file 3.0249

for Goethite

The analysis for the Fe(III) derived oxyhydroxide highlights the difficulties in using X-ray diffraction on amorphous or poorly crystalline precipitates, and these problems are even worse when the natural precipitates are examined. Only the diffractogram for the Lady Bertha Mine stream sediment contains peaks of sufficient intensity to enable d spacings to be calculated (Figure 3.1.17). The other natural oxyhydroxides precipitated from the Cadover Bridge and Lady Bertha Mine stream waters give similar diffractograms to that for Fe(III) derived oxyhydroxide and are not analysed (Figures 3.1.18 and 3.1.19). The problem in the analysis for the sediment is shown in Table 3.7 which compares the d spacings for the natural precipitate with those for Goethite (α -FeOOH) and Lepidocrocite (γ -FeOOH). The diffractogram for γ -FeOOH is also shown in Figure 3.1.17 to show the similarity in the diffractograms that initially were thought to indicate Lepidocrocite. However agreement is found for d spacings of both α -FeOOH and γ -FeOOH and this obviously makes identification difficult. Traces of both these crystalline forms may be present, but Mössbauer spectroscopy does not indicate the presence of Goethite, and infra-red spectroscopy gives a spectrum indicating an amorphous precipitate. There is also the strong possibility that the sediment contains crystalline forms which do not contain iron and some of the d spacings obtained from the diffractogram do not correspond to d spacings for any iron phase.







Figure 3.1.18. X-ray diffractogram for Cadover Bridge stream precipitate.



Figure 3.1.19. X-ray diffractogram for Lady Bertha Mine stream precipitate.

Table 3.7 Comparison of d spacings for Lady Bertha Mine stream sediment with Lepidocrocite and Goethite

γ-FeOOH ^(a) I/I _o dÂ		Lady Bertha Mine Sediment d A ₀ d A			a-FeOO d A	a-FeOOH ^(b) d I/I _o		
					4.97	60		
100	6.26				4.18	100		
90	3.29	3.28	6.20	3.28	3.36	60		
		2.79	7.30	2.79	2.69	70		
80	2.47	2.55	8.0	2.55	2.58	55		
					2.48	40		
					2.44	80		
30	2.34	2.29	8.90	2.29	2.25	60		
		2.21	9.25	2.21	2.18	60		
		2.13	9.6	2.13	2.01	20		
		2.00	10.2	2.00	1.92	40		
70	1.94	1.96	10.4	1.96	1.80	50		
40	1.73	1.795	11.4	1.795	1.77	30		
					1.72	70		
		1.68	12.15	1.68	1.69	50		
		1.65	12.40	1.65	1.66	40		
					1.60	50		
					1.56	65		
40	1.52	1.515	13.65	1.515	· 1.51	60		
					1::46	40		
					1.45	60		
30	1.37	1.375	15.0	1.375	1.37			

(a) Taken from A.S.T.M. card file 8-98

(b) Taken from A.S.T.M. card file 3.-0249

Therefore from X-ray diffraction data this iron rich sediment consists of a small amount of Goethite and Lepidocrocite with amorphous iron oxyhydroxides predominant and possibly other unidentified crystalline substances.

The oxyhydroxides precipitated from the mine streams are amorphous to X-rays and it is not possible to identify the precipitates using X-ray diffraction. However, the diffractogramsshown in Figures 3.1.18 and 3.1.19 are very similar to the diffractogram for the Fe(III) derived precipitate showing that in natural waters containing Fe(II) an amorphous oxyhydroxide is precipitated initially in preference to Lepidocrocite which is formed in the chemically simpler model solutions.

X-ray diffraction is most useful when a well crystallised single component is present and then the identification is authoritative. However when amorphous and/or mixed phases are present the analysis is not as helpful and other techniques must be used either in conjunction with or instead of X-ray diffraction.

3.1.4 Mössbauer Spectroscopy

Only a few elements are Mössbauer active and this nuclear spectroscopic technique gives information on the oxidation state and chemical environment of the nucleus under examination (204). Iron was the first, and is the most common element to be studied using this method and it is hoped that the information obtained from this technique will aid the identification of the synthetic and natural iron oxyhydroxides formed in this study. One limitation encountered with this method arises from all the oxyhydroxides containing Fe(III). The symmetry of the d⁵ electron shell of Fe³⁺ can make separation of different compounds difficult (205), especially when the chemical environment of the iron nucleus is similar as is the case for oxyhydroxides. Consequently all the chemical or isomer shift (δ) values are very similar at approximately 0.4 mm s^{-1} and the errors on this measurement make any differences found meaningless. As there are only 3 or 4 oxyhydroxides that are likely to be formed given the experimental conditions used, this limitation is not serious. Both the quadropole splitting (Δ) and the behaviour in an applied magnetic field of amorphous iron oxyhydroxide, Goethite (α -FeOOH), Akaganite (β -FeOOH) and Lepidocrocite $(\gamma$ -FeOOH) are sufficiently different, as shown in Table 3.8 for positive identification to be made in most cases. Lepidocrocite is perhaps the most difficult to positively identify as liquid helium temperatures (4K) are required for magnetic hyperfine splitting to occur, and this facility was not available. The data extracted from the spectra of synthetic and natural precipitates is also given in Table 3.8 and each precipitate will be discussed in turn.

Figures 3.1.20 and 3.1.21 show the spectra for a freshly precipitated Fe(III) derived oxyhydroxide at 293K and 77K respectively. Both spectra consist of doublets

			Behaviour						
			293K						
Precipitate	Oxide	State	^δ s−1	[∆] s−1 mm s−1	Magnetic field T	State	^δ s−1	[∆] s-1	Magnetic field T
Goethite ^(a)	а −ГеООН	a.f.	0.53± 0.06	0±0,1	36.4± 3.7	a.f.	0.78± 0.06	_	51.5± 4.3
Akaganite ^(a)	β-FeOOH	Р	0.43± 0.06	0,62± 0.06	0	a.f.	-	-	46.6± 4.9
Lepido- crocite (a)	ү-ГеООН	р	0.48 <u>+</u> 0.06	0.54 <u>+</u> 0.06	0	р	0.62 <u>±</u> 0.06	0.62 <u>±</u> 0.06	0
Ferri- hydrite (a)	_δ −FeOOH	P	-	-	-	a.f?	0.45± 0.11	0 <u></u> ±0 . 11	53.3± 5.1
Amorphous gel (b)	Fe(OH)3	Р	0.50 <u>+</u> 0.01	0.72± 0.03	0	р	0.62± 0.01	0.81± 0.03	0
Fresh Fe(III) derived	Fe(OH) ₃	р	0.32± 0.1	0.68± 0.05	0	р	0.40 <u>+</u> 0.1	0.68± 0.05	0

Table 3.8 Summary of Mössbauer data between crystalline Fe(III) oxyhydroxides and natural and synthetic precipitates

.

,

Table 3.8 - continued

			Behaviour							
			293К			77K				
Precipitate	Oxide	State	^گ	mm s-1	Magnetic field T	State	گ mm s ⁻¹		Magnetic field T	
Aged Fe(III) derived	Fe(OH) ₃ /α-FeOOH	р	0.40 <u>+</u> 0.1	0.60± 0.05	0	a.f.	0.48± 0.1	0.64± 0.05	48.6	
Fresh Fe(II) derived	ү-ГеООН	-	-	-	-	р	0.36± 0.1	0.54± 0.05	0	
Aged Fe(II) derived	ү-ГеООН	-	-	-	-	р	0.40± 0.1	0.56± 0.05	ο	
Lady Bertha Mine		-	-	-	-	q	0.44± 0.1	0.74± 0.05	ο	
Lady Bertha Mine sediment		-	-	-	_	р	0.46± 0.1	0.76± 0.05	ο	
Cadover stream		р	0.44 0.1	0.70 0.05	0	-	-	-	-	

•

113.

~

Table 3.8 - continued

		Behaviour								
		293K			77K					
Precipitate	Oxide	State	mm s-1	[∆] s−1	Magnetic field T	State	^گ - 1	^ل مس s ⁻¹	Magnetic field T	
Cadover stream sediment		p	0.44± 0.1	0.76± 0.05	0	q	0.32± 0.1	0.72± 0.05	0	

.

(a) Data taken from Rossiter and Hodgson (206)

(b) Data taken from Coey and Readman (207)

Abbreviations δ = Isomer Shift

.

- Δ = Quadropole Splitting
- p = Paramagnetic
- a.f. = Antiferromagnetic

114.





with an isomer shift of approximately 0.4 mm s⁻¹ which is expected for the Fe³⁺ nucleus. The absence of hyperfine splitting at 77K means that α -FeOOH, β -FeOOH and δ -FeOOH can be discounted and as this precipitate is known to be X-ray amorphous the identification can be taken no further.

Figures 3.1.22 and 3.1.23 are for a similarly derived precipitate which has been aged in solution, and although the spectrum at 293K is almost identical to Figures 3.1.20 and 3.1.21 when the temperature is decreased to 77K hyperfine splitting can be seen, and a magnetic field of 48.6T is measured. This spectrum has a complicated structure with the peaks collapsing towards the centre probably because of the small particle size. The variation in the peak heights is also due to the small particle size, and also because it is a mixed oxyhydroxide containing up to 30% Goethite with the remainder being amorphous Fe(III) gel. The baseline for the spectrum measured at 293K is much more scattered than those in Figures 3.1.20 and 3.1.21 and this is almost certainly due to the Goethite which is antiferromagnetic at room temperature and would therefore give hyperfine splitting.

The spectra for Fe(II) derived precipitates are very similar, and only those measured at 77K are shown. Figure 3.1.24 is for a fresh precipitate, and Figure 3.1.25 for an aged precipitate. Both are doublets with δ values at $\Re 0.4 \text{ mm s}^{-1}$ indicating that they are Fe(III) oxyhydroxides.









The spectra show no signs of hyperfine splitting, and therefore are either amorphous iron oxyhydroxides or Lepidocrocite. From infra-red and X-ray diffraction data, the latter is identified and so the Mössbauer data does not contradict this identification. The spectra for Fe(II) derived oxyhydroxides are different from those for Fe(III) derived oxyhydroxides as the quadropole splitting (Δ) values for Fe(II) derived precipitates are 0.54-0.56 mm s⁻¹ compared with 0.64-0.68 mm s⁻¹ for Fe(III) derived precipitates. These figures are lower than those for pure Goethite or Lepidocrocite because of the small particle size.

The natural iron rich precipitates all gave spectra indicating the presence of Fe(III) and only the spectrum for the Cadover Bridge stream sediment is unusual (Figure 3.1.26). This spectrum, taken at 77K, is not a doublet and is very difficult to interpret. When a spectrum was measured using less of the sediment a doublet was formed (Figure 3.1.27) and it is thought that organic compounds may be masking the iron oxyhydroxide spectrum in some way (208). This is an unusual result, and probably warrants further investigation, but this could not be done in this study. The Cadover Bridge stream precipitate gave the more normal spectrum (Figure 3.1.28) and this is almost certainly an amorphous sample with the Δ values at \gtrsim 0.7 mm s⁻¹ being closer to the synthetic Fe(III) derived precipitates rather than the Fe(II) derived. This again is supportive evidence for the findings of the infra-red and



Figure 3.1.26. Mössbauer spectrum for Cadover Bridge stream sediment at 77K.



Figure 3.1.27. Mössbauer spectrum for Cadover Bridge stream sediment at 77K.



Figure 3.1.28. Mössbauer spectrum for Cadover Bridge stream precipitate at 77K.

X-ray diffraction methods.

An identical picture is obtained for the Lady Bertha Mine stream sediment (Figure 3.1.29) and precipitate (Figure 3.1.30) with an amorphous Fe(III) oxyhydroxide indicated. The \triangle values are slightly higher at 0.76 and 0.74 mm s⁻¹ respectively and this probably indicates a larger particle size, but with no Goethite formation apparent in the sediment. One advantage the Mössbauer spectroscopy has over X-ray diffraction of the sediments is that Mössbauer will only give the spectrum for the iron compounds whereas the X-ray diffraction will respond to any crystalline phases, such as quartz, making the diffractogram much more difficult to interpret.

Although Mössbauer spectroscopy did not identify the natural precipitates all the information is supportive of that obtained by other methods. The most important fact to arise from the data on the synthetic precipitates is the quantitative value given for Goethite in the aged Fe(III) derived oxyhydroxide. This precipitate is X-ray amorphous, but in conjunction with the infra-red data the percentage content of Goethite can be given to within a few percent as will be seen in Section 3.1.5 below.

3.1.5 Infra-red Spectroscopy

Infra-red spectroscopy is a useful technique for identifying oxyhydroxides especially if only small quantities are available as a spectrum can be obtained from 1 or 2 mg of sample quite easily. The technique has









Figure 3.1.30. Mössbauer spectrum for Lady Bertha Mine stream precipitate at 77K.
advantages over X-ray diffraction when the oxyhydroxides are not particularly crystalline and X-ray diffractograms can be ambiguous and indistinct. The Fe-O bonds in an oxyhydroxide are I.R. sensitive and by comparing spectra of the unknown samples with well defined oxyhydroxides it is possible to obtain a positive identification (56). Further information can be extracted as to the degree of crystallinity from the intensity of certain peaks, and this has been used in the case of the aged Fe(III) derived oxyhydroxide. Infra-red spectra were measured for the synthetic precipitates and the Lady Bertha Mine stream sediment and precipitate as well as the Cadover stream precipitate. Spectra for α -FeOOH (Goethite) and γ -FeOOH (Lepidocrocite) were also measured, and used to compare with the synthetic precipitates. Only a section of the spectrum is shown as all the bands of interest fell between 1400 cm^{-1} and 400 cm^{-1} .

Figure 3.1.31 is a comparison between the spectra of α -FeOOH and the aged Fe(III) derived oxyhydroxide. The relevant bands for α -FeOOH are at 890 cm⁻¹, 795 cm⁻¹ and 650 cm⁻¹ and these 3 bands can quite clearly be seen on the lower trace. The Fe(III) derived precipitate is not as clear but there are 2 very weak bands at 890 cm⁻¹ and 795 cm⁻¹ and these can be used in the identification of this precipitate. The spectra for the aged and fresh Fe(III) derived precipitates are shown in Figure 3.1.32 and the bands at 890 cm⁻¹ and 795 cm⁻¹ only occur for the



aged precipitate. From this information an estimate of the percentage content of Goethite in the aged precipitate can be made if a comparison is made with the results shown in Figure 10 of Landa and Gast (20). By simple inspection of the variation in the band intensity in Figures 3.1.31 and 3.1.32 a value of 10-20% Goethite can be estimated. Therefore this precipitate is initially totally amorphous but as it ages Goethite is formed and the I.R. spectroscopy measures this in a semiquantitative way. The percentage given agrees with the results from the Mössbauer spectroscopy which indicated less than 30% crystalline Goethite in the aged precipitate.

Figure 3.1.33 compares well crystalline Lepidocrocite with the aged Fe(II) derived precipitate and the two bands at 1020 cm⁻¹ and 750 cm⁻¹ are obviously congruent and the synthetic precipitate is Lepidocrocite (γ -FeOOH). Considering the disordered nature of this precipitate when viewed under the electron microscope, the need for liquid helium temperature for Mössbauer spectroscopy, and the careful analysis required for X-ray diffraction because of the similarities in iron oxyhydroxide diffractograms the infra-red spectrum is the easiest and clearest method used in positively identifying Lepidocrocite.

When the spectra for the natural precipitates are examined no peaks are visible, and the spectra for Lady Bertha Mine stream sediment (Figure 3.1.34) Lady Bertha Mine stream precipitate (Figure 3.1.35) and Cadover Bridge



Figure 3.1.32. Infra-red spectra for aged Fe(III) derived (upper trace) and freshly precipitated Fe(III) derived (lower trace) iron oxyhydroxides.





Figure 3.1.34. Infra-red spectrum for Lady Bertha Mine stream sediment.



Figure 3.1.35. Infra-red spectrum for Lady Bertha Mine stream precipitate.

stream precipitate (Figure 3.1.36) all indicate amorphous iron oxyhydroxides. The spectra are almost featureless and no indication of organic molecules is visible although both humic acids and other organic molecules might have been expected to occur in the precipitates. There may be insufficient organic matter in the very small samples used to give a peak and the way in which the spectra of organic molecules is affected by iron oxyhydroxides is not known (208). All 3 natural spectra are different and do not coincide with that for the synthetic iron oxyhydroxide showing the variations that can occur in I.R. spectra of amorphous precipitates which make characterisation difficult.

Infra-red spectroscopy proved to be very useful in identifying the crystalline and partially crystalline oxyhydroxides but gave very little information on the amorphous synthetic and natural precipitates.

3.1.6 Summary of Characterisation of Precipitates

The characterisation of all the precipitates will be summarised by a simple listing for each precipitate examined.

(a) The fresh Fe(III) derived precipitate is an amorphous Fe(III) oxyhydroxide with a large specific surface area of $234 \text{ m}^2 \text{ g}^{-1}$. It is constructed of small 5-10 nm spheres which are massed together to give a porous precipitate. (b) The aged Fe(III) derived precipitate is a mixture of amorphous Fe(III) oxyhydroxide and Goethite (α -FeOOH). It contains between 10 and 20% Goethite and has a surface area



of 159 m² g⁻¹. The crystallinity cannot be observed by electron microscopy or X-ray diffraction, but is indicated by infra-red and Mössbauer spectroscopy and supported by the changes in pore size distribution from the surface area measurements.

(c) The fresh and aged Fe(II) derived precipitates are poorly crystalline Lepidocrocite (γ -FeOOH) with surface areas between 100 and 120 m² g⁻¹. The degree of crystallinity does not vary with age nor conditions of preparation but changes in the matrix could occur due to Lepidocrocite being an unstable phase relative to amorphous Fe(III) oxyhydroxide and Goethite. The porosity in the sample is due almost entirely to its crystallinity, and its appearance is of a folded film or bent laths with a small particle size.

(d) The Lady Bertha Mine stream sediment is an iron rich precipitate containing amorphous Fe(III) oxyhydroxide which may be as coatings on other components as there is no porosity despite a surface area of $164 \text{ m}^2 \text{ g}^{-1}$. The sediment contains a measurable amount of arsenic and may well consist of other mineral phases, but these were not investigated. The iron oxyhydroxide is derived from Fe(II) but no crystalline iron compounds are found and perhaps ageing of the amorphous oxyhydroxide is hindered by organic compounds.

(e) The Lady Bertha Mine stream precipitate is an amorphous Fe(III) oxyhydroxide which has a very low surface area of 6 m² g⁻¹. This is a more pure Fe(III) oxyhydroxide than the sediment and is also derived from Fe(II) but why it

has such a low surface area cannot be explained. Organic coatings may be present, and these have been found to reduce the surface area of iron oxyhydroxides but it is doubtful whether such a dramatic decrease could occur. (f) The Cadover Bridge stream sediment is an Fe(III) rich precipitate possibly containing substantial amounts of precipitated organic matter.

(g) The Cadover Bridge stream precipitate is similar to the sediment but has been more extensively studied. It has a surface area of 140 m² g⁻¹ and is an amorphous Fe(III) oxyhydroxide. No evidence of crystallinity was found although the pore size distribution is similar to that for aged Fe(III) derived oxyhydroxide. The slightly lower surface area than the synthetic oxyhydroxides may be due to organic coatings.

(h) Both the Carnon River precipitate and the interstitial water precipitates were only examined by electron microscopy. The precipitates from both sources appeared to be mixtures of amorphous iron oxyhydroxide and organic matter. The iron was in the Fe(III) state and no crystallinity was observed despite the fact that these were formed from waters containing Fe(II).

Using this comprehensive suite of techniques the synthetic iron oxyhydroxides have been carefully and thoroughly identified. No single technique can be used to identify these precipitates completely and there is no conflicting evidence between the techniques used. The pre-

cipitation from natural waters both in the laboratory and in sediment formation points to the possible involvement of organic matter which appears to restrict crystal formation. All natural waters chosen contained Fe(II) but no precipitates similar to the Lepidocrocite formed from the model solutions could be found.

The formation of oxyhydroxides from Fe(III) and Fe(II) under simulated natural conditions will be examined in the following section. These studies are made in solutions free from dissolved organic matter and this is a simplification of the system that may decrease the direct relevance to the natural system but is felt necessary for a reproducible model to be developed.

3.2 Precipitate Formation

3.2.1 Nephelometry

In Section 3.1 two different iron oxyhydroxides resulting from the precipitation of Fe(II) and Fe(III) were identified. Following on from this the formation of these precipitates under varying conditions of pH and ionic strength was investigated. A nephelometric technique was used to examine the changes in light scattering, at 90° to an incident beam, resulting from the formation of microscopic iron oxyhydroxide particles in various aqueous media. These results provided information on relative rates and mechanisms for the transformations from dissolved to solid phase. Problems in calibrating the nephelometer meant that only semiquantitative analysis and generalised mechanisms were extracted from the data. However, these were very useful in themselves and also proved to be a reasonable guide in evaluating the interactions of the freshly forming iron oxyhydroxides with phosphate, as will be shown later.

The raw nephelometric data consists of plots of relative intensity of scattered light (R.I.) and pH as a function of time, see Figure 3.2.1. The general form of an R.I. curve can be split into three parts:

- (a) the initial rise in R.I. due to colloid formation resulting from the hydrolysis and polymerisation of Fe(III);
- (b) a plateau region where the amount of colloid in



Figure 3.2.1. General form of nephelometry trace including pH variation for Fe(III) derived precipitates in distilled water.

suspension remains constant;

(c) a decrease in R.I. as the colloid is destabilised and flocculates. This causes an increase in size but decrease in number of particles, both factors producing a decrease in the amount of scattered light. Part (a) of the curve is thought to be due to Rayleigh scattering which produces a symmetrical angular scattering distribution. However, as the radius of the scattering particle becomes comparable with the wavelength of the radiation, i.e. approximately 360 nm, the scattering is no longer $\approx \lambda^{-4}$ Rayleigh scattering. When the particle is in the size range 0.1 $\lambda \leq r \leq 25\lambda$ the scattering is no longer symmetrical with respect to the perpendicular to the direction of the incident beam and the amount of forward scattering increases, which may account for part (c) of the curve. The light scattering produced by the suspensions used in this study may be further complicated by other factors such as particle shape (see Plate 3.4), size distribution, concentration and other physical and optical anisotropies.

The magnitude and exact shape for each of the three sections is dependent on pH, ionic strength and the initial oxidation state of the iron. The changes in R.I. arise from two reactions, one of colloid formation and the other of colloid flocculation which may occur concurrently or consecutively. Colloid formation and flocculation occur at the same time in seawater because

of the destabilising effect of anions on the iron colloid, especially doubly charged species such as sulphate (209). This gives an R.I. curve with no visible plateau, and because the colloidal particles are flocculated as they form the total increase in R.I. is less than for a comparable reaction in distilled water. In the distilled water case the iron first forms colloidal particles which are quasi-stable and which only slowly flocculate.

This descriptive analysis of the nephelometric data is of little value either for comparing the numerous model traces obtained, or for predicting the behaviour of natural systems. In the analysis of these curves the initial rise in R.I. is considered to be the most important section of the data because it represents the appearance of an active surface, and by using the concept of a rise time this can be expressed numerically. The rise time is defined as the time taken for 10% to 90% of the equilibrium value of the initial rise in R.I. to be attained and the method of calculation is shown in Figure 3.2.2. This gives a single numerical value for each curve which can be used in comparisons and it also removes any errors due to inaccuracies in measuring the total increase in R.I. where long plateaux occur. The variations found in rise times with pH^a and/or salinity are described in the following sections for Fe(III) and Fe(II) derived precipitates.

^aAll pH values quoted best represent the pH at which the reactions are occurring and unless otherwise stated are not more than 0.5 pH units below the initial pH.



Figure 3.2.2. Method of calculating rise time from relative intensity curves

3.2.2 Fe(III)Derived Precipitates

The precipitation of an iron oxyhydroxide derived from Fe(III) can be hypothesised as a sequence of reactions as shown in Equation (3.2):-Fe(III)(aq) $\xrightarrow{}$ Fe(OH)₃ $\xrightarrow{}$ Polymerisation Hydrolysis Fe(OH)₃ Polymerisation Fe_x(OH)_y(colloid) $\xrightarrow{}$ FeOOH (ppt)

... Eq. (3.2)

This is a simplified system as both the hydrolysis and polymerisation stages are complex reactions which have received detailed investigation as shown in Chapter 1. In this study the nephelometer is monitoring the colloid formation and flocculation and consequently only inferences on these reactions can be made directly from the data.

The rise times for Fe(III) derived precipitates formed in distilled water, NaCl solutions, brackish waters, seawater and natural fresh waters are displayed in Table 3.9. The data indicates the variations in rise time with pH and the duration of the plateau sections is also listed where they occur. This latter parameter is difficult to measure accurately and it is easier to define when a plateau is not present than to measure the short term stability of the colloid system. In distilled water the rise times are constant at approximately 2.2 seconds for pH values between 6.2 \leq pH \leq 8.1 and there is a slight increase in the duration of plateaux as the pH increases.

Table 3.9 Summary of nephelometric data for Fe(III) (5 x 10^{-5} M Fe³⁺) colloid formation and

|--|

.

<u></u>	<u>.</u>			r	<u> </u>
MEDIA	IONIC STRENGTH (M)	SALINITY	рН	RISE TIME (secs)	DURATION OF PLATEAU (secs)
Dis-					
water ^(a)	ο	ο	4.3	No pre- cipita- tion	-
	0	0	5.1	No pre- cipita- tion	-
-	0	0	5.9	No pre- cipita- tion	-
	0	0	5.9	8 ^(b)	-
	0	0	6.0	6.0	0
	0	0	6.2	2.0	10
	0	0	6.2	2.4	10
	0	0	6.4	2.6	10
	0	0	6.5	1.8	15
	0	0	6.7	2.6	10
	0	0	7.1	2.0	10
	0		7.8	2.0	40
	0	0	7.8	2.4	-
	0	0	8.1	2.2	35
NaC1					
Solu-	0.01	0	5.0	3.2	10
tions	0.01	0	9.6	3.0	0
	0.05	0	5.0	3.0	5
	0.05	0	9.6	4.6	о
	0.10	0	4.0	5.0	20
	0.10	0	4.9	2.8	100
	0.10	0	5.1	3.5	5
			l		

Table 3.9 - continued

•

MEDIA	IONIC STRENGTH (M)	SALINITY (%)	рН	RISE TIME (secs)	DURATION OF PLATEAU (secs)
NaC1					
Solu-	0.10	0	5.2	3.5	5
tions	0.10	о	· 5.8	3.0	о
	0.10	ο	6.0	3.2	о
	0.10	0	6.2	3.0	20
	0.10	0	8.0	3.0	0
	0.10	0	8.0	4.0	0
	0.10	0	8.2	3.0	5
	0.10	0	8.8	3.0	0
	0.10	0	9.0	2.8	10
	1.00	0	5.0	3.4	0
	1.00	0	5.2	3.9	10
	1.00	0	8.0	2.6	О
Sea-					
water					
Solu-	0.007	0.34	4.0	80.0	0
tions	0.007	0.34	7.8	2.5	0
	0.007	0.34	9.9	2.6	8
	0.007	0.34	9.9	2.8	8
	0.007	0.34	10.0	3.9	0
	0.017	0.85	6.9	3.2	15
	0.017	0.85	7.2	4.4	20
	0.017	0.85	7.5	2.8	20
	0.034	1.70	9.4	2.2	0
	0.034	1.70	10.0	2.2	0
	0.085	4.25	6.5	2.6	8
	0.085	4.25	6.6	2.8	10
	0.085	4.25	7.0	3.2	12
	0.085	4.25	7.2	3.0	15
	0.085	4.25	7.6	2.7	10
	0.34	17.0	7.2	2.3	5

. .•

Table 3.9 - continued

MEDIA	IONIC STRENGTH (M)	SALINITY	рН	RISE TIME (secs)	DURATION OF PLATEAU (secs)
Sea- water Solu tions	0.68 0.68 0.68 0.68 0.68 0.68 0.68 0.68	34.0 34.0 34.0 34.0 34.0 34.0 34.0 34.0	6.6 6.9 7.4 7.4 7.4 7.6 8.0 8.0	1.9 2.3 2.4 2.0 2.4 2.5 2.2 2.6	12 0 0 0 0 0 0 0
Natural Fresh waters with added Fe ^{3+(c)}	0 0	0 0	7.5 7.8	3.0 3.4	10 30
Iron- rich natural waters(0 0 d) 0.017	0 0 0 0.85	7.0 8.0 8.1 6.0	6.0 3.5 3.0 2.8	830 120 100 .0

(a) The distilled water contained a 2 mM NaHCO $_3$ buffer.

(b) Approximate rise time due to noisy output.

(c) Filtered River Plym water with 5 x 10^{-5} M Fe³⁺ added.

(d) Cadover Bridge mine stream water containing 4.5 x 10^{-5} M Fe (total iron), pH on collection 5.4.

The rise times at pH = 5.9 and pH = 6.0 have increased to approximately 6-8 seconds, with the rise time at pH = 5.9not as precise as the others because of air bubbles disturbing the trace towards the end of the initial rise in relative intensity. At pH \leq 5.1 there is no increase in the light scattering indicating the non-appearance of the colloid. With a total Fe concentration of 5×10^{-5} M and pH < 5 this is possible, since, while hydrolysis may occur the solubility of am-Fe(OH), is only just exceeded (31) and with only a very low ionic strength (2 mM $NaHCO_2$) it is possible that the $Fe_{x}(OH)_{v}$ colloid is not formed. The second result at pH = 5.9 is more difficult to explain as am-Fe(OH)₃ should be precipitated but this may be an unrepresentative result. The rise times are just starting to increase at pH \simeq 6.0 so the border between colloid formation and stability of dissolved phases has almost been reached and contamination of the system may have produced this odd result. The stability of the colloid before flocculation occurs appears to be slightly greater at the higher pH's. This shows that even in distilled water the colloid is a transient phase in the development of the precipitate, with the total time for the rise and plateau being in the range 12-40 s. Subsequently the particle size increases through polymerisation processes and the flocculated particles give less scattered light.

The rise times in NaCl solutions vary from 2.6 to 5.0

seconds and do not show a clear trend in the pH range 4.0 \leq pH \leq 9.0. These solutions did not contain a pH buffer, consequently pH control was poor with changes of more than 1 pH unit occurring during the course of some experiments. Rise times at 4.0 \leq pH \leq 5.2 do not appear to be greater than for the rest of the pH range, possibly indicating the effect of the NaCl in causing colloid formation by destabilising the hydrolysis products. Trends in the duration of the plateau may be obscured by the poor pH control although it appears that shorter plateaux are obtained at high pH and/or ionic strength and it is expected that high concentrations of Cl⁻ will destabilise the colloid.

The saline media do contain a pH buffer at higher salinities such that pH variation in media of $S \ge 17\%_0^0$ are $\leqslant 0.5$ pH units whereas pH changes around LO pH units occurred at lower salinity. Throughout a pH range of pH = 6.5 to pH = 10.0 the rise times are almost constant between 1.9 and 3.9 seconds for all seawater solutions. The one exception is at very low pH in a very dilute saline medium where the rise time is 80 seconds at pH = 4.0. In distilled water at this pH there would be no colloid formation but in this case the low concentration of seawater ions may induce colloid formation over an extended period. This colloid is destabilised and flocculates as it forms so that there is little or no plateau region. The general trend is for either no plateau in high salinity

media or a short term plateau at lower pH values. Therefore, in brackish waters in the natural pH range colloid formation will be fast with the colloid being immediately destabilised by the anions to give a flocculent. In distilled water there is some short term colloid stability both at high and low pH's, with some decrease in the rate of colloid formation at low pH. In NaCl solutions the rate of colloid formation is fast throughout a wide pH range, and the colloid is destabilised at high ionic strengths.

The results above are for model systems, and the final section in Table 3.9 gives data for natural fresh waters that may contain high concentrations of dissolved organic matter. The colloidal forms of iron that are transported by rivers are thought to be stabilised by organic matter (104) and this hypothesis may be supported by the duration of the plateaux especially for the iron rich stream water. However, for runs involving the addition of Fe(III) to a filtered river water, the rise times and plateau duration are very similar to those parameters measured in buffered distilled water at the same pH. Therefore, there was either insufficient dissolved organic matter to stabilise the colloid, or the iron colloid is flocculated before an iron-organic interaction occurs to stabilise the colloidal form. The precipitation of iron from a filtered acid mine water appeared to give a colloid with enhanced stability compared to all the other solutions. At pH = 7.0 the colloid forms comparatively slowly and is stable for several

minutes. At higher pH the rise time is similar to those found in the distilled water solutions where the colloid is still stable for up to 100 seconds. In the final case some concentrated seawater was added to the acidic stream water to give a pH = 6.0 but despite this low pH colloid formation and precipitation were extremely rapid. Thus the organic matter does appear to stabilise the iron colloid that forms from the natural source of iron providing that the ionic strength is not increased. It is thought that dissolved organic matter is also precipitated on entering an estuary (118) and this may be the reason for the absence of a plateau and the fast rise time at pH = 6.0 when the seawater ions are added^a.

Only a few of the natural solutions investigated are listed here as the traces tended to be much noisier and difficult to analyse. The oxidation state of the iron was not determined and in some instances the iron-rich stream water produced complex R.I. traces which involved two stages in the initial rise. This could have resulted from two processes occurring simultaneously, i.e. the precipitation of the Fe(III) and the oxidation of the Fe(II) resulting in further precipitation. The acid iron rich stream was later found to contain predominantly Fe(II) but when these experiments were carried out this had not been investigated and did not constitute part of the study. With careful sample manipulation it might

^aOnly 210% of the D.O.M. is precipitated but this may be the most important fraction with respect to iron colloid stability.

have been possible to separate the two reactions so that rise times could be calculated for each. This would also require further model studies using solutions containing both Fe(III) and Fe(II), but rather than adding to the complexity of the model a series of experiments using Fe(II) were carried out.

3.2.3 Fe(II) Derived Precipitates

The sequence of reactions shown in Eq. (3.2) can be extended quite simply to include Fe(II) as the initial reactant thus:-

The rate of oxidation will control the rate of formation of Fe(III)(aq) which will obviously affect the rate of hydrolysis and all subsequent reactions. The rate of oxidation has been shown to be pH and ionic strength dependent (56) but there is a secondary factor introduced as the iron oxyhydroxide surface is thought to catalyse the oxidation, and there is the possibility of Fe(II) being adsorbed directly onto the oxyhydroxide surface (210).

The R.I. curves for Fe(II) derived precipitates are shown for seawater in Figure 3.2.3 and distilled water in Figure 3.2.4. There is a progression in both media such that the steeper the initial rise the greater the maximum R.I. value illustrating the effect of oxidation on the rate of particle formation. In seawater it might be expected that the slow formation of Fe(III)(aq) followed by the very fast flocculation as observed in Section 3.2.2 would give a very small increase in R.I. because of the small number of colloidal particles available at any one time. This is not observed however and the autocatalysis of the Fe(II) oxidation by the FeOOH surface may be called upon as an explanation (56). A cycle is set up where the more iron oxyhydroxide produced the faster Fe(II) can be oxidised which increases the amount of colloidal particles which flocculate to produce more iron oxyhydroxide. Thus the rate of colloid formation will increase initially and then decrease as the Fe(II) is depleted giving a curve of the form shown in Figure 3.2.4 at pH = 7.4. The curves in Figures 3.2.3 and 3.2.4 are on different scales, and as for the case of Fe(III) the trend is for lower total R.I. increases in seawater compared with distilled water.

The effect of phosphate on the precipitation was investigated as it has been shown to accelerate the rate of oxidation (54). The effect of $1 \times 10^{-6} M [(PO_4)]$ in



Figure 3.2.3. Relative intensity curves for Fe(II) derived precipitates in distilled water at various pH's



Figure 3.2.4. Relative intensity curves for Fe(II) derived precipitates in seawater at various pH's

distilled water is shown in Figure 3.2.5. The dotted line is the normal curve without phosphate whereas the lower solid curve is for a phosphate containing solution. In seawater there is no observable difference; consequently it is the destabilising effect on the colloidal particles of the negatively charged phosphate species that is being shown by the changes in R.I. curves rather than the catalysis of the oxidation.

Having illustrated the types of R.I. curve obtained for Fe(II) derived precipitates the data is summarised in Figure 3.2.6 for distilled water and Figure 3.2.7 for seawater. In each figure the rise time versus pH is plotted and although there is considerable scatter, the trends are quite clear. In distilled water the rise times vary from ≈ 15 seconds at pH = 8.3 to ≈ 400 seconds at pH = 7.0, while in seawater the variation is from $\simeq 100$ seconds at pH = 8.3 to $\simeq 1000$ seconds at pH = 7.4. Obviously the rise times are much slower for Fe(II) derived precipitates than for Fe(III) derived precipitates at the same pH indicating the rate determining role of the oxidation reaction prior to particle formation. This is also revealed by the inverse behaviour of the particle formation in seawater compared with distilled water between the Fe(II) and Fe(III) derived precipitate. The changes in rise time with changing salinity are shown in Figure 3.2.8 for Fe(II) at constant pH, and



Figure 3.2.5. Relative intensity curves showing effect of phosphate $(1 \times 10^{-6} M [PO_4])$ on precipitate formation in distilled water. Continuous trace for solution containing phosphate









derived precipitates. $\bigcirc -pH = 7.9; \triangle - pH = 7.4$

although the data set is not complete, it appears that rise times are most greatly affected by changes in salinity in the 0% to 10% range. This is complicated by the effects of pH such that at pH = 7.9 the change in rise time is from 70 seconds at S = 0% to 300 seconds at S = 32% compared with a change in rise time at pH = 7.4 from 100 seconds for S = 0% to 1000 seconds at S = 32% i.e. from a 4.5 fold increase to a 10 fold increase in rise time from pH = 7.9 to pH = 7.4.

The rise times for both the Fe(II) and the Fe(III) derived precipitates are shown in Figure 3.2.9 with the points for Fe(III) derived precipitates lying almost along the x-axis. This figure summarises almost all the data for precipitate formation in various media with the two possible starting materials. The general form of this diagram will occur in later discussion when examining the phosphate uptake onto freshly forming model and natural iron oxyhydroxides.

3.2.4 Kinetic Analysis of Nephelometry

Nephelometry measures the formation of colloidal particles and the reaction sequence hypothesised in Equation (3.2) and Equation (3.3) give the reactions for both colloid formation and colloid flocculation. If the removal by flocculation is ignored it may be possible to derive kinetic equations for the formation as measured by the nephelometer.



X-Fe(II) in seawater; O-Fe(II) in distilled water; Δ -Fe(III) in distilled water and seawater 164.
As a first assumption let the colloid formation from Fe(II) be a single stage process with the colloid forming directly from the Fe(II), as shown in Equation (3.4), which may occur for rapid oxidation cases.

$$Fe(II)(aq) + A \xleftarrow{k_1} Fe_x(OH)_y(colloid) + A$$
$$\overset{k_1'}{k_{-1}'} Fe_x(OH)_y(colloid) + A$$
... Eq. (3.4)

Where A = Unconsumed component such as OH^- as pH is held constant or O_2 because system is open and initial concentration of Fe(II) is small.

If
$$[Fe(II)(aq)] = x_0$$

 $[Fe_x(OH)_y(colloid)] = x_1$
and $[A] = x$
then $\frac{dx_1}{dt} = x(x_0 - x_1) k'_1 - x x_1 k'_{-1}$
... Eq. (3.5)

By replacing k_1' and k_{-1}' by concentration dependent terms Equation (3.6) is obtained thus:

$$\frac{dx_1}{dt} = x_0 k_1 - x_1 (k_1 + k_{-1}) \dots Eq. (3.6)$$

Where $k_1 = k'_1 \times k_{-1} = k'_{-1} \times k_{-1}$

At time t = 0 when $x_1 = 0$ Equation (3.6) integrates to

$$x_1 = \frac{k_1}{k_1 + k_{-1}} \quad x_0 [1 - \exp(-t(k_1 + k_{-1}))]$$

... Eq. (3.7)

At equilibrium $x_1 \rightarrow x_{1\infty}$, $t \rightarrow \infty$

$$x_{1\infty} = \left[\frac{k_1}{(k_1 + k_{-1})}\right] x_0$$

$$\therefore \frac{x_1}{x_{1\infty}} = \left[1 - \exp\left(-t\left(k_1 + k_{-1}\right)\right)\right]$$

and rearranging:

$$-\ln \left[1 - \frac{x_{1}}{x_{1\infty}}\right] = t (k_{1} + k_{-1})$$
... Eq. (3.8)

As $x_1 = [Fe_x OH_y(colloid)]$ this can be equated to the increase in R.I. at time t with $x_{1\infty}$ being the maximum value of the R.I. Thus plotting - $\ln \left[1 - \frac{R \cdot I \cdot}{R \cdot I \cdot max}\right]$ against time should give a straight line for this simple model.

This data is plotted in Figure 3.2.10 for distilled water and Figure 3.2.11 for seawater and in both cases curves are obtained except for pH values greater than pH = 8.0 in distilled water only. This is not a surprising result as the simplicity of the initial hypothesis requires the rate of oxidation to be of similar magnitude to that of the colloid formation from Fe(III). From the rise times obtained for the oxidation reactions and other work done on this system (56) this condition is only likely to be met at high pH values in distilled water. Therefore for the next calculation a two stage process is proposed as shown in Equation (3.9).



Figure 3.2.10. Plot for single stage kinetic analysis of relative intensity curves for Fe(II) in distilled water. $\times - pH = 7.0$; $\Delta - pH = 7.3$; O - pH = 7.8; $\Box - pH = 8.2$



Figure 3.2.11. Plot for single stage kinetic analysis of relative intensity curves for Fe(II) in seawater. $\Delta - pH = 7.4$; O - pH = 7.8; O - pH = 8.1; $\Box - pH = 8.3$

and it is assumed as a first approximation that $k_2 = 2k_1$ and $k_{-2} = 2k_{-1}$ (i.e. that colloid formation is twice as fast as the oxidation).

If [Fe(II)(aq)] = x₀
[Fe(III)(aq)] = x₁

and $[Fe_x(OH)_y(colloid)] = x_2$ the rate equations can be written down thus:

$$\frac{d x_0}{dt} = k_1 x_1 - k_{-1} x_0 \qquad \dots \quad Eq. \quad (3.10)$$

$$\frac{d x_1}{dt} = k_1 x_0 + k_{-2} x_2 - k_2 x_1 - k_{-1} x_1$$

$$\dots \quad Eq. \quad (3.11)$$

$$\frac{d x_2}{dt} = k_2 x_1 - k_{-2} x_2 \qquad \dots \quad Eq. \quad (3.12)$$

The full integration of these simultaneous equations is described elsewhere (211) and applying the limit that at t = 0, $x_2 = 0$ with the assumed relationships between the rate constants, then:

$$x_{2} = \frac{k_{1}^{2} x_{0}}{(k_{1}+k_{-1})} [1 - \exp(-t(k_{1}+k_{-1}))]^{2}$$

At equilibrium $x_2 \rightarrow x_{2_{\omega}}, t \rightarrow \infty$

$$x_{0} = \frac{x_{2\infty} (k_{1} + k_{-1})}{k_{1}^{2}}$$

$$\therefore \frac{x_{2}}{x_{2\infty}} = [1 - \exp(-t (k_{1} + k_{-1}))]^{2}$$

and rearranging:

$$- \ln \left[1 - \left(\frac{x_{2}}{x_{2}}\right)^{\frac{1}{2}}\right] = t \left[(k_{1} + k_{-1})\right]^{2}$$

... Eq. (3.13)

As $x_2 = [Fe_x(OH)_y(colloid)]$ the same assumption can be made as for the single stage process, and so by plotting - ln $\left[1 - \left(\frac{R.I.}{R.I.}\right)^{\frac{1}{2}}\right]$ against time a straight line will be obtained for a two stage process. The results of this analysis are plotted in Figure 3.2.12 for distilled water and Figure 3.2.13 for seawater. In seawater there is still little agreement with the proposed mechanism except at pH = 8.3. However in distilled water straight lines are obtained for the reactions at pH = 7.6, 7.8 and 8.2, but for pH \leq 7.5 no straight lines are obtained. This indicates that the oxidation step fits the assumption of its rate constant being half as large as that for the colloid formation for pH > 7.5 in distilled water. In seawater this only fits at $pH \ge 8.3$.

By using a simple mechanism, and assuming an arbitrary relationship between the rates for the two stages an improvement in the model is obtained. However this is as far as this simple mechanistic approach can be taken because if $k_2 \neq 2k_1$ and $k_{-2} \neq 2k_{-1}$ the integrated rate



relative intensity curves for Fe(II) in distilled water. X - pH = 7.1; △ - pH = 7.3; ∇ - pH = 7.6; O - pH = 7.8; □ - pH = 8.2



equation for x_2 is still cumbersome and cannot be simplified easily. Increasing the number of stages for the process would also involve large complex equations so that this simplified two stage process is the best mechanistic model that can be obtained.

The one and two stage models fit the reaction sequences originally hypothesised under certain conditions. For a one stage process the rate of oxidation must be as fast as the colloid formation which can only occur at high pH's in distilled water. For a two stage process assuming that the rate of colloid formation is twice as fast as the oxidation the mechanism works in distilled water at $pH's \ge 7.6$ and in seawater at $pH's \ge 8.3$. Below these respective pH's the mechanism is more complex and as stated above, additional reactions such as direct adsorption of Fe(II) may occur and add complexity to the reaction sequence. Furthermore in seawater and distilled water at pH < 7.5 the removal of the colloid by flocculation is almost certainly occurring simultaneously with the colloid formation. The data for kinetic analysis was extracted from the R.I. curves which were assumed to equate to the concentration of $Fe_{x}(OH)_{y}(colloid)$ alone, consequently the removal mechanism will obviously affect the measurements and hence the calculations.

3.2.5 Summary of Precipitate Formation

(a) Colloid formation from Fe(III) is extremely fast and pH independent in NaCl solutions and seawater. In

these higher ionic strength media the colloid is immediately destabilised by the anions.

(b) Colloid formation from Fe(III) is also very fast in distilled water and although pH dependent, no measurable change in the rate of formation is obtained other than at the low end of the natural pH range (pH \leq 6.0). The colloid has a limited stability in distilled water and flocculates slowly at high pH's.

(c) Colloid formation from Fe(II) is controlled by the rate of oxidation of Fe(II). At high pH in distilled water the formation of colloid appears to be a single stage process, at high pH in seawater and $pH \ge 7.6$ in distilled water the formation of colloid appears to be a two stage process. The destabilising of the colloid in seawater and at low pH in distilled water hinder any further mechanistic analysis.

(d) By examining the rise times of the R.I. curves a field diagram can be drawn indicating the comparative rates of precipitate formation from Fe(III) and Fe(II) in distilled water and seawater at various pH's.

3.3 Phosphate Adsorption

For this part of the study a variety of adsorption experiments were carried out in order to model the possible interactions of iron oxyhydroxides with dissolved phosphate in estuarine media. Reference is made to the results obtained in Sections 3.1 and 3.2 as many of the adsorption phenomena can be explained at least in part by differences in precipitate formation and/or character. The first section deals with the variables chosen and controlled in this study and discusses their relevance to the natural estuarine environment. The uptake is described qualitatively in the next two sections, each distinguished by the precipitate age. Quantitative analysis then follows, including analysis of natural samples, and this is also split into two sections involving aged and fresh precipitates. Finally the results are summarised so that the comparison between natural and model experiments can be clearly made.

3.3.1 Discussion of Chemical Modelling

The reactions were carried out in filtered seawater and distilled water containing a sodium bicarbonate buffer. These solutions represent the end members of an estuarine system and no solutions of intermediate salinity were used. Variation of the salinity in model solutions to cover the estuarine range would have required a considerable increase in the number of experiments. It was felt that the data obtained from the examination of

reactions at S = 0_{00}° and S = 34_{00}° would enable limits to be given to the extent and rates of adsorption, plus any mechanistic information on the interactions between iron oxyhydroxides and phosphate. Previous studies have shown that the low salinity region is important for estuarine iron/phosphate interactions (114). However, the nephelometric technique used in this study has shown that the rate of particle formation from Fe(II) is not altered dramatically by salinity changes above 10_{00}° (Figure 3.1.3) and rate of particle formation from Fe(III) is almost constant throughout the natural pH range and at any ionic strength up to 0.7M.

Seawater has a relatively constant composition when sampled away from freshwater and anthropogenic inputs, as was the case in this work, whereas river water can vary considerably in composition with season, weather and the geology of the catchment area, plus other factors, not least of which is human activity. Therefore seawater of low organic carbon content (<1.0 mg 1^{-1}) was used as the saline end-member for the model and buffered distilled water was used as the fresh water end-member, the latter being a comparatively poor analogue. However, this simplified solution removes some of the variation which makes field measurements so difficult to analyse and enabled repeat experiments to be done without the necessity of checking or adjusting the composition of the media.

The oxyhydroxides derived from both Fe(II) and Fe(III) salts were formed <u>in situ</u> as fresh precipitates, or aged for 20 h before phosphate addition. The experiments using fresh precipitates modelled inputs of dissolved iron from either streams, sediment pore waters or stirring across the oxic/anoxic boundary of stabilised lakes, while the aged oxyhydroxides modelled possible crystalline forms of iron oxyhydroxides derived from crustal weathering and other solid phases of iron found in natural waters.

The majority of experiments were carried out at 15° C but a few were repeated at 2° C to investigate the temperature dependence of the interactions. These two temperatures are approximate limits of normal estuarine temperature ranges. A temperature of 15° C was chosen not only because it is representative of natural water temperatures but also for comfort since experiments were carried out in temperature controlled rooms set at the appropriate values.

Thus the above parameters of initial concentration of reactants, precipitate source and age, solution composition and temperature were combined with pH to model the numerous possibilities of estuarine adsorption phenomena in a laboratory controlled environment.

3.3.2 General Discussion on Aged Precipitates in

Model Solutions

The adsorption of phosphate onto aged Fe(III) derived precipitates is shown in Figure 3.3.1 for seawater and



Figure 3.3.2 for distilled water in the pH range pH = 6.9 to pH = 8.3. Each of these curves is produced from data for at least 2 identical runs. Further single experiments at various intermediate pH's were also carried out but these are not shown for clarity, and also because the subsequent kinetic analysis was only done on those runs which had sufficient data for well defined curves to be drawn. The extent of adsorption is dependent on pH in both media with the equilibrium value^a decreasing with increasing pH. The trend is more pronounced in distilled water with the amount adsorbed at equilibrium at pH = 8.5 being less than 20% compared with 80% at pH = 6.9. In seawater the adsorption at equilibrium at pH = 8.1 is 60% compared with more than 90% at pH = 6.9and so the extent of adsorption is also enhanced in seawater compared with that in distilled water at the same The possible explanations for these adsorption pH. profiles involve either a chemical adsorption mechanism or a physical adsorption mechanism or perhaps more realistically, a mixture of both. Adsorption isotherms may indicate adsorption mechanisms and both the Langmuir and Freundlich equations were applied to data from uptake curves at fixed pH but varying phosphate concentration. Initial phosphate concentrations used were 0.5, 1.0, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0 and 10.0 μ mol 1⁻¹ and the pH in seawater was pH = 8.1 and in distilled water was pH = 7.4. The Langmuir equation produced no definitive trend and the ^aThis is taken as the concentration of PO_A adsorbed after 2 h.



water by aged Fe(III) derived oxyhydroxides. O- pH = 8.5; Δ - pH = 8.3; \Box - pH = 7.3; χ - pH = 6.9 data for both seawater and distilled water gave randomly scattered points. Previous work has stated that it is unlikely that the Langmuir isotherm would be appropriate for application to the adsorption of charged phosphate ions onto charged oxide surfaces (143) and therefore the Langmuir calculations are not shown. The Freundlich isotherms are shown in Figure 3.3.3 as some relationship is apparent although it is not simple in either seawater or distilled water. The more usual form for the Freundlich isotherm is a single straight line whose slope and intercept are equivalent to the empirical constants of the Freundlich equation as shown in Equation (1.5). In the distilled water case the data forms two straight lines of differing slope which could also be drawn as a smooth curve. Whichever way this isotherm is depicted it appears to represent two segments of adsorption behaviour depending on phosphate concentration. The Freundlich equation models adsorption in which the affinity for adsorption decreases exponentially as the amount adsorbed increases (140). It is expected that the affinity for adsorption will decrease in this case as the surface charge on the iron oxyhydroxide will increase in negative charge with increasing adsorbed phosphate. It is unlikely that a saturation of surface sites is occurring at the comparatively low levels of phosphate used in this study as considerably higher concentrations (3 mg $PO_{a}-P 1^{-1}$) have been used by other workers (131) without reaching the limits of the adsorption capacity. Consequently



increasing the phosphate adsorbed decreases the affinity for adsorption but not exponentially as the Freundlich model predicts. A similar argument can be proposed for the adsorption in seawater although the isotherm has a discontinuity at approximately 2.0 μ mol 1⁻¹ initial phosphate concentration. The change in slope of the two parts of the isotherm is less than that in the distilled water example which may indicate the lessening of the effect of phosphate adsorption on surface charge in the presence of high concentrations of other ions. There is no explanation of the discontinuity as experiments were not sufficiently precise to investigate this section in greater detail. The amount of phosphate adsorbed was calculated from equilibrium concentrations measured after 20 h. This time period was taken as the completion of phosphate uptake without additional uptake resulting from long term incorporation of phosphate into the iron oxyhydroxide matrix to produce an iron phosphate (134). The equilibrium values in distilled water were virtually identical after 2 h with those after 20 h whereas in seawater there was considerable additional uptake over the longer period. This phenomenon emphasises the differences in the uptake between the two media and it may be easier to explain these differences using a more physical type of adsorption mechanism rather than chemisorption involving ligand exchange which is as shown in Equation (3.14).

 $Fe - OH + H_2PO_4 \implies Fe - H_2PO_4 + OH$

... Eq. (3.14)

The extent of this reaction depends on the coordinating tendency of iron with phosphate species compared with the hydroxyl ion. This can be found semiquantitatively by examining the affinity of the aqueous Fe(III) ion towards OH⁻ and the phosphate species, e.g.

 $Fe^{3+} + PO_4^{3-} \rightleftharpoons FePO_4 \log_{10} K = 22$... Eq. (3.15) $Fe^{3+} + 2(OH^-) \rightrightarrows Fe(OH) \log_{10} K = 36$

$$Fe^{3} + 3(OH) = Fe(OH)_3 + 109_{10} K = 30$$

... Eq. (3.16)

Therefore the OH⁻ has a stronger affinity for Fe³⁺ than PO_{a}^{3-} and the same applies to other phosphate species (31). However, this reaction will depend on the concentrations of OH⁻ and PO_4^{3-} according to the ratio of $[PO_4^{3-}]/[OH_]^3$. and so as pH decreases the PO_4^{3-} will tend to enter the coordination sheath of the Fe³⁺. This simple mechanism is not the complete picture since both the phosphate speciation and the surface charge on the iron oxyhydroxide will vary with pH. Thus, in distilled water the trends can be represented in Table 3.10, where the pH of zero point charge (pHZ.P.C.) of am-FeOOH is 7.9 (49). Even from this simplified picture the favourable electrostatic interaction at pH < 7.9 contrasts with the electrostatic repulsion at pH > 7.9. Therefore electrostatic interactions follow the same trend as predicted for chemical interactions with regard to changes in pH, i.e. uptake is

Table 3.10. Changes in speciation and surface charge due to pH for iron oxyhydroxide and phosphate in distilled water.

рН	Dominant surface group on iron oxyhydroxide	Dominant phosphate species
<7.9	$Fe - OH_2^+$	H ₂ PO ₄
≃7.9	Fe - OH	н ро <mark>2-</mark>
>7.9	Fe - 0	н ро ₄ 2-

more favourable at lower pH. However, there is no information on which of these mechanisms predominates and although both fit the uptake curves as shown in Figures 3.3.1 and 3.3.2 the chemisorption model does not predict the enhanced equilibrium adsorption found in seawater nor the differences between the two Freundlich isotherms. The adsorption of phosphate from seawater is complicated by adsorption of seawater ions onto the iron oxyhydroxide surface (73, 74). The normal pH_{Z.P.C.} for Goethite is depressed to $pH_{2.P.C.} = 7.1$ in seawater by adsorption of SO_4^{2-} (50). Consequently the electrostatic interactions appear to be less favourable in seawater at natural pH's than in distilled water yet the observed behaviour is for adsorption to be enhanced. This can be explained in terms of a model recently developed to examine the surface chemistry of α -FeOOH in seawater (73, 90). By examining the adsorption of major seawater ions the model proposed that at pH = 7.040% of the surface sites would be neutrally charged, 27% positively charged mainly by Mg^{2+} and Ca^{2+} adsorption and 33% negatively charged predominantly by SO_4^{2-} and CI^{-} anions. At pH = 8.0 37% are neutrally charged, 36% positively charged with Mg OH⁺ becoming important as well as Mg²⁺ and Ca^{2+} and 27% negatively charged by the same anions as above. Consequently although the $pH_{Z.P.C.} = 7.1$ predicts an overall negative charge at pH's above this value, the adsorption of Ca^{2+} and Mg^{2+} may well increase the number

of available sites for phosphate adsorption. Furthermore, the dominant form of phosphate in seawater is HPO_4^{2-} (159) but complexation with Mg^{2+} and Ca^{2+} is likely and this complexation may occur either with the surface adsorbed cations or in solution so that cation-phosphate complexes could be adsorbed. To obtain further information on these reactions the temperature dependence of the adsorption was investigated in an attempt to elucidate the dominant mechanism of adsorption. Temperature changes may affect the reaction in two ways. Firstly physical adsorption has no appreciable activation energy whereas an activation energy may be involved in chemisorption (212); thus the rate of uptake for physical adsorption will not be affected by temperature changes. Secondly, physical adsorption is an exothermic process so that from Le Chatelier's Principle a decrease in temperature will give an increase in the amount of phosphate adsorbed at equilibrium. The adsorption of phosphate at 2°C and 15°C is shown for seawater in Figure 3.3.4 and for distilled water in Figure 3.3.5. If rate constants are available for the reactions at the different temperatures the Arhenius equation can be used to calculate the activation energy for adsorption thus:

$$\log_{10}\left(\frac{k_{2}}{k_{1}}\right) = \frac{E}{2.303 \text{ R}} \left(\frac{T_{2} - T_{1}}{T_{2}T_{1}}\right) \dots \text{ Eq. (3.17)}$$







Where $k_1 & k_2 = Rate$ constants for the reactions at 275K and 288K respectively

 $T_1 \& T_2 = Temperature in {}^{O}K$

and

 $R = Gas constant [kJ K^{-1} mol^{-1}]$

E = Activation Energy [kJ mol⁻¹]Equation (3.17) will be used in the complete kinetic analysis in Section 3.3.4 to calculate an activation energy for the adsorption in distilled water. In this medium the rate of uptake is dependent on temperature, and the equilibrium value is equal at both temperatures. This further confirms that the reaction in distilled water is predominantly a ligand exchange process but in seawater as shown in Figure 3.3.4 the rate of uptake and equilibrium adsorption is independent of temperature; consequently electrostatic and co-adsorption phenomena play a more important part in the process. Thus the mechanism for the association between phosphate and aged Fe(III) derived oxyhydroxide will depend on in which media the reactions occur. Yates and Healy (84) have carried out calculations for the seawater ion adsorption using a site binding model which combines specific and electrostatic interactions and which does not separate the mechanisms. The results presented here support this type of model and the degree of physical or chemical nature of the reaction mechanisms will alter depending on various parameters, and a better predictive quality to the models should be obtained if the mechanisms are not kept mutually exclusive.

In dramatic contrast to the complex adsorption behaviour of aged Fe(III) derived precipitates Figure 3.3.6 shows that aged Fe(II) derived precipitates do not adsorb phosphate either in distilled water or seawater in the natural pH range even when the experiments were extended for a period of 50 h. This is a surprising result as there should be little difference in the , surface groups of am-FeOOH and the Fe(II) derived precipitate which has been identified as Lepidocrocite (γ -FeOOH) in Section 3.1. The ligand exchange mechanism appears only to be valid for aged Fe(III) precipitates; it cannot explain why adsorption does not occur in this case. Although the $pH_{Z_2}P_2C_2$ for γ -FeOOH is not as well documented as that for am-FeOOH (7.9) and α -FeOOH (8.1) values of $pH_{Z,P,C} = 6.2$ (192) and 6.9 (213) have been found. These are certainly lower than the pHZ.P.C's of Fe(III) derived oxyhydroxides and they may well be decreased in seawater by the same mechanism of SO_4^{2-} adsorption that has already been proposed. Consequently this oxyhydroxide will have a stronger electrostatic repulsive force than the others examined and this may be sufficient to prevent adsorption under the conditions examined. The pH was lowered to pH = 5.3 in the distilled water and some $(\chi 20\%)$ adsorption was found. Difficulties in maintaining this pH prevented complete investigation of conditions that are outside the natural range and when the pH drifted upwards, as the buffer regained its equilibrium, desorption



of phosphate occurred. Thus this adsorption phenomena appears to be predominantly physical but may not occur in the natural pH range. The surface area for γ -FeOOH is smaller than the extremely large values obtained for amorphous precipitates, with surface areas of about 100-170 $m^2 g^{-1}$ previously quoted (192) and areas up to $120 \text{ m}^2 \text{ a}^{-1}$ found in this study. Thus there is still a substantial area available for adsorption. The occurrence of Lepidocrocite in the natural environment has been recorded predominantly in ground waters (41). Its occurrence in acid mine streams may mean that the composition of these streams will be different from other natural waters as they may not contain an efficient adsorbant to affect the partitioning of various constituents between the solid and dissolved phases. Lepidocrocite has not yet been identified as a component of estuarine sediments and it is thought that the more common forms of Goethite and amorphous FeOOH are predominant. Consequently the importance of Lepidocrocite to estuarine adsorption processes remains unknown. 3.3.3 General Discussion on Fresh Precipitates in

Model Solutions

Freshly forming iron oxyhydroxides produced by adding dissolved Fe(III) to solutions containing phosphate were found to be very efficient removers of phosphate from solution as shown in Figure 3.3.7 for seawater and Figure 3.3.8 for distilled water. In distilled water experiments





were carried out at pH = 6.5. 7.0 and 7.8 at 15° C and pH = 7.2 at 2^oC and in seawater the pH Values used were 6.7, 8.0 and 8.2 at 15° C and pH = 7.4 and 8.1 at 2° C. In all these experiments approximately 90% of the phosphate was removed from solution within 30 seconds and equilibrium was reached within 5 minutes. Under the experimental conditions used any differences in the rate of adsorption could not be discerned and it can be concluded that the adsorption behaviour is independent of pH, and ionic strength. The change in temperature could slow the rate of uptake by an order of magnitude, but the results show no obvious decrease in rate at the lower temperature and this suggests that the rate of uptake is still extremely fast at 2°C. The nephelometric study showed that over a wide pH range in distilled water and seawater the appearance of the colloid occurred in <10 seconds. This rapid development of a very active surface in the presence of phosphate would tend to mask the effect of the two variables. Unfortunately no nephelometric experiments were carried out at 2°C and no conclusions can be drawn as to the effects of temperature on the particle formation; however hydrolysis of Fe(III) has been shown to be temperature dependent by other workers (6).

The rate of these reactions makes kinetic analysis impossible from the methods used and there is little evidence on which to hypothesise mechanisms for the

reactions. As Fe(III) was added to a solution containing phosphate it is possible that Fe PO_A was precipitated depending on pH and initial phosphate concentration. Consideration of the solubility of Fe PO_A (31) indicates that this phase is stable if precipitated at pH < 5 but the concentration used in this study is low enough to prevent precipitation of Fe PO, especially in the pH range used. Furthermore the low concentrations of phosphate used compared with the Fe(III) concentration would mean that more $Fe(OH)_3$ than Fe PO₄ would be precipitated and identifying the latter solid would be almost impossible. Whether $Fe(OH)_3$, Fe PO₄ or mixed oxide/phosphates were formed under the varying conditions did not affect the rate of removal of the phosphate from solution. This can be explained by the general trend in rates of complex formation of an aquo ion with a ligand and such reactions are thought to proceed in two stages (205). Initially an aquo ion-ligand outer sphere complex is formed and this is followed by the elimination of H₂O. If a similar mechanism occurs for the iron oxyhydroxide/phosphate system the rate of formation will show little or no dependence on the identity of the ligand i.e. phosphate or OH and so the rate of adsorption will not indicate whether $Fe(OH)_3$ or $Fe PO_4$ is formed. The uptake is so rapid and independent of all variables tried that no information as to the mechanism for adsorption is available other than to say uptake is dependent on the rate of particle formation.

Freshly forming Fe(II) derived precipitates have a more complex adsorption behaviour although the rate of phosphate adsorption is also dependent on rate of particle

formation. However, in this case the rate determining step was found to be the rate of oxidation of Fe(II) which was dependent on pH, ionic strength and temperature. Figure 3.3.9 shows the relatively slow removal of phosphate in seawater at various pH's. The adsorption at pH = 8.1was complete within 30 minutes and the equilibrium concentration was approximately $0.15_{\rm u}$ mol 1⁻¹. At pH = 7.4 the removal was much slower and was not complete until approximately 150 minutes with a similar equilibrium concentration to that at pH = 8.1. The pH changes during the course of an experiment were usually < 0.2 pH units and occurred as the acidic Fe(II) was added to the solution. The buffer capacity of the seawater then returned the pH to its original value over a period of approximately 10 minutes and during this pH rise no desorption of the phosphate was observed. A few experiments were carried out at 2⁰C and the results of one of these experiments is shown in Figure 3.3.10 in which the adsorption under identical conditions except a temperature of 15°C is included as a comparison. It was expected that this reaction would be temperature dependent as the rate of oxidation of Fe(II) is known to be dependent on this parameter. This temperature dependence will be used to calculate an apparent activation energy for this uptake in the section on kinetic





Figure 3.3.10. Adsorption profiles showing effect of temperature upon uptake of phosphate from seawater by Fe(II) derived oxyhydroxides at pH = 8.1. O - $15^{\circ}C$; X - $2^{\circ}C$
analysis. The results from the few experiments carried out on temperature dependence will be plotted on diagrams in the kinetic analysis to show possible effects of temperature for comparison with natural adsorption phenomena.

The adsorption onto freshly forming Fe(II) derived oxyhydroxides from distilled water is shown in Figure 3.3.11 and in this medium the changes in pH during the course of an experiment did result in desorption. In Figure 3.3.11 only one curve is shown for clarity and this is for two runs where pH changes were identical. The curves were very sensitive to the changes in pH such that desorption would be retarded for a few minutes if the minimum in pH persisted for a short time. The concentration of phosphate remaining in solution at maximum adsorption was dependent on pH although the desorption made this difficult to measure. The maximum change in pH was 0.4 pH units and the carbonate buffer returned the pH to equilibrium after about 15 minutes. Additional desorption occurred after the pH stabilised and this occurred over 24 h and may have been linked with morphological changes in the γ -FeOOH precipitated. The equilibrium concentrations after 24 h were pH dependent as shown in Table 3.11.

The initial rate of uptake appears to be $[PO_4]_0$ independent as shown in Figure 3.3.12 when adsorption at pH = 8.1 reaches a maximum with approximately 0.2 µmol 1⁻¹

Table 3.11 pH dependence of equilibrium concentration of PO_4 in distilled water

рН	^{[PO} 4] INITIAL	[PO4]EQM
6.5	0.88	0.60
7.9	0,95	0.50
8.1	0,95	0.40
8.3	0.75	0.37
8.1	1.73	0.50
8.1	1.96	0.85
8.4	4.20	2.05



Figure 3.3.11. Adsorption profile for the removal of dissolved phosphate from distilled water by freshly precipitating Fe(II) derived oxyhydroxide pH = 8.0.



Figure 3.3.12. Adsorption profiles for uptake onto precipitating Fe(II) derived oxyhydroxides in distilled water at pH = 8.1 showing dependence on $[PO_4]_0$ $\times -1.0 \mu mol 1^{-1}; O - 2.0 \mu mol 1^{-1}$

remaining in solution for initial concentrations of 1.0 μ mol 1⁻¹ and 2.0 μ mol 1⁻¹. The long term uptake to equilibrium is [PO₄] dependent as shown in Figure 3.3.12 and Table 3.11. Figure 3.3.13 shows the desorption is also reversible over medium length time periods if the pH changes. By decreasing the pH from pH = 8.0 to pH = 5.7 readsorption occurs to a similar level to that at initial maximum adsorption where pH fell to pH = 7.0. Furthermore increasing the pH produces desorption again showing the labile nature of the phosphate on this oxyhydroxide surface. This behaviour was not observed for a similarly derived precipitate in seawater even when pH changes were purposely increased. Consequently, as was the case for aged Fe(III) derived precipitates the mechanism for phosphate binding to the respective oxyhydroxides appears to be different between seawater and distilled water. The adsorption behaviour of Fe(II) derived precipitates in seawater is amenable to quantitative analysis but quantitative studies of the reaction in distilled water would require an even tighter control over pH. This could be obtained by using premixed CO2/air gas mixtures of varying concentration bubbled continuously through the solutions during the course of an experiment. Although this may make analysis easier, it would push the model further away from the reactions occurring in natural waters which will not have such an elaborate pH buffer.



dissolved phosphate and Fe(II) derived oxyhydroxide in distilled water

3.3.4 Kinetic Analysis of the Uptake onto Aged Precipitates

The qualitative description of the previous sections is of little use in predicting natural adsorption phenomena and the numerous adsorption profiles must be analysed to give quantitative information. In this way it was possible to summarise the important aspects of the data. Furthermore, mechanistic and kinetic information extracted from this data may indicate which of the two possible processes proposed, i.e. physical adsorption or chemical adsorption, is predominant. If, for example, rate constants for the various reactions can be calculated as a function of temperature this would enable activation energies to be obtained. This would also assist in the prediction of phosphate removal under varying conditions in the natural aquatic environment.

However, in this study only two data sets can be quantitatively analysed. Firstly, the adsorption onto aged Fe(III) derived precipitates in both distilled water and seawater and secondly, the adsorption onto freshly precipitating Fe(II) derived oxyhydroxides in seawater. This is because aged Fe(II) derived oxyhydroxides do not adsorb in the pH range examined, freshly precipitating Fe(III) derived oxyhydroxides adsorb the phosphate too rapidly for analysis to be carried out and the desorption observed in freshly forming Fe(II) precipitates in distilled water makes analysis difficult.

Attempts were made to fit the integrated rate equations for lst and 2nd order reactions to the adsorption curves of aged Fe(III) derived precipitates in distilled water and seawater. This analysis did not produce meaningful results and therefore the order of the reactions in each medium was calculated using the initial rate method at varying initial phosphate concentrations, $[PO_4]_0$. Thus, by measuring the slope of the tangent drawn to the adsorption curve at t=0 for two initial phosphate concentrations the order can be calculated using equation (3.18):-

$$m_{x} = \frac{\log_{10} \left(\frac{dx}{dt}\right)_{1} - \log_{10} \left(\frac{dx}{dt}\right)_{2}}{\log_{10} [x]_{1} - \log_{10} [x]_{2}}$$

... Eq. (3.18)

where
$$\left(\frac{dx}{dt}\right)_{1}$$
 & $\left(\frac{dx}{dt}\right)_{2}$ = Slope of the tangent to curves
1 and 2 respectively.
[x]₁ & [x]₂ = Initial concentration of
phosphate, [PO₄]₀.
n_x = Order of reaction with respect
to component x.

The order in distilled water was found to be approximately 1.4 with values varying from 1.1 to 1.5, using 4 runs with the initial concentrations in the range 0.5 μ mol 1⁻¹ to 10 μ mol 1⁻¹. For seawater $n_{\chi} \simeq 0.7$ with a range of values from 0.5 to 0.9. In both cases a wide spread of values was found which was due to the steepness of the curves at the start of the adsorption for each media. The four values

of the order showed that $n_v < 1.0$ for seawater and $1.0 < n_v$ < 2.0 for distilled water. These values indicate some difference in the uptake in seawater and distilled water. However, since the order in both cases is not a whole number the reaction is thought to be complex and it is unlikely that simple kinetics will fit the data (214). Rather than attempting to formulate exact rate laws, a working predictive model was required, so that the uptake in the model systems could be compared to that in natural systems. In order to accomplish this a set of standard integrated rate equations for several reversible reactions (215) were chosen and applied to the data in order to find the "best fit". From the calculations of the order of reaction it is unlikely that even these simple mechanisms (shown in Table 3.12) represent the complete system. However, as will be seen the chosen system does enable the required comparisons between the model and natural systems to be made.

The tests of the 5 reversible reactions in Table 3.12 for the seawater data are shown in Figure 3.3.14 and for distilled water in Figure 3.3.15. The y-axes for these plots are given as $\ln(f)$ where the function, f, is given in Table 3.12. In both cases the reversible 2nd order reaction involving either equal concentrations of two components (reaction 5) or two components of the same type (reaction 4) give a straight line fit to the data using with $[PO_4]_0 = 2.0 \ \mu mol \ 1^{-1}$. Reaction 5 is not favoured

Rea Mec	ction hanism		ln(f)
1.	× =	A	$\frac{[x]_0 - [x]_{\infty}}{[x] - [x]_{\infty}}$
2.	x ≓	A+B	$\frac{[x]_{0}^{2} - [x]_{\infty}[x]}{([x] - [x]_{\infty}) [x]_{0}}$
3.	2x ≓	A	$\frac{([x]_{0}^{0} - [x]_{\infty})([x][x]_{0} + [x]_{0}^{\infty})}{([x]_{\infty}^{0} - [x]_{\infty})([x][x]_{0} + [x]_{0}([x]_{\infty} - [x][x]_{\infty})}$
4.	2 X ‡ oi X+V =	A+B c A+B ^a	$\frac{[x]_{0}[x]_{\infty} - 2[x][x]_{\infty} + [x][x]_{0}}{[x]_{0}([x] - [x]_{\infty})}$
-•	AT . C		

Table 3.12 ln(f) functions for reaction mechanism examined

 $[x]_0 = \text{Initial concentration of } x.$ $[x]_{\infty} = \text{Equilibrium concentration of } x.$ [x] = Concentration of x at time t. $\stackrel{a}{\text{ for equal concentrations of } x \text{ and } y.$



Figure 3.3.14. Mechanism test for aged Fe(III) derived precipitates in distilled water at 15^oC using ln(f) vs t where ln(f) is derived from the integrated rate equations of the following mechanisms tested:

$$\begin{array}{c} x - 2X \rightleftharpoons A+B \\ 0 - 2X \rightleftharpoons A \\ \Box - X \rightleftharpoons A \\ \Delta - X \rightleftharpoons A+B \\ 211. \end{array}$$



$$\begin{array}{c} x-2X \rightleftharpoons A+B \\ 0-2X \rightleftharpoons A \\ \Box - X \rightleftharpoons A \\ \Delta - X \rightleftharpoons A+B \end{array}$$
212.

as it would appear to involve the consumption not only of phosphate but also of the active sites on the iron oxyhydroxide surface. Even if it is assumed that one phosphate ion binds to a single reactive site on the oxyhydroxide surface, or possibly as a binuclear complexation as suggested by Lijklema (131), the concentrations of phosphate adsorbed are small when compared to the number of active sites on the solid. Consequently the concentration of sites effectively remains constant and hence the reaction should follow pseudo-first order kinetics. A similar argument would apply to other possible reactants such as OH because the pH is held constant. Therefore, the mechanism involving the two reactants is discounted. This leaves reaction 4 involving two phosphate ions which combine in some unspecified way on the oxyhydroxide surface. This mechanism is difficult to envisage and as will be seen later it cannot be designated as the actual mechanism, despite the fact that the data fits it reasonably well. This method of manipulating the data was adopted and the data was processed to show the dependence of the rate of adsorption on pH, ionic strength, phosphate concentration and temperature. Figure 3.3.16 shows the ln(f) versus time plots for reaction 4, Table 3.12 (2X \rightleftharpoons A+B) in distilled water at varying $[PO_4]_0$ and constant pH. From the slopes of these lines \log_{10} k values can be calculated ^a, and these \log_{10} k values are then plotted against the square root of the initial concentration of phosphate as shown in

^aThis was done using standard kinetic formulae as found in Laidler (214).



gure 3.3.16. Plot of ln(f) versus t for $2X \rightleftharpoons A+B$ in distilled water with varying initial concentration of phosphate at pH = 7.4. $\blacktriangle = 1.0 \ \mu mol$ $1^{-1}; \ \nabla = 4.0 \ \mu mol \ 1^{-1}; \ O = 5.0 \ \mu mol \ 1^{-1};$ $\times = 10.0 \ \mu mol \ 1^{-1}; \ \Box = 2.0 \ \mu mol \ 1^{-1}.$ Figure 3.3.17. This diagram includes \log_{10} k values calculated for seawater from the $\ln(f)$ plots shown in Figure 3.3.18. A single line has been drawn through the points, but least squares regression on the data for each medium give the following relationships; in seawater \log_{10} k = 5.49 - 0.85 \sqrt{c} with a correlation coefficient of r = 0.97 and in distilled water \log_{10} k = 5.67 - 0.92 \sqrt{c} with r = 0.98. The adsorption of phosphate onto iron oxyhydroxides has previously been found to be proportional to the square root of the phosphate concentration (131) and this is said to result from the following reaction (Equation (3.19)), reaching equilibrium. This represents a chemical

Fe - OH
+
$$H_2PO_4^ \rightleftharpoons$$
 Fe-O
Fe - OH
Fe - OH
Fe - OH
Fe - O

... Eq. (3.19)

sorption process and although this is possible for the reaction in distilled water from the results of this study, it does not explain why the dependence of $\log_{10} k$ is very similar in seawater to that in distilled water as shown in Figure 3.3.17. In a sense the \sqrt{c} dependence is quite arbitrary and further investigations into the concentration effects are required.

Similar equations showing the dependence of $\log_{10} k$ upon pH are found with Figure 3.3.19 showing the ln(f) v time plots for the pH values for distilled water (pH = 6.9 and





Figure 3.3.18. Plot of ln(f) versus t for seawater with varying initial concentration of phosphate at pH = 8.1. $O = 2.0 \ \mu mol \ 1^{-1}$; $X = 4.0 \ \mu mol \ 1^{-1}$; $\Box = 5.0 \ \mu mol \ 1^{-1}$; $\Delta = 6.0 \ \mu mol \ 1^{-1}$; $\nabla = 10 \ \mu mol \ 1^{-1}$



pH = 8.3) and seawater (pH = 6.9 and pH = 8.2). The plots at other pH values were omitted for clarity, but all the data is shown on Figure 3.3.20. This gives the following relationships between $\log_{10} k$ and pH, in seawater $\log_{10} k = 7.52 - 0.33$ pH with r = 0.98 and in distilled water $\log_{10} k = 9.19 - 0.64$ pH with r = 0.97. From these equations it can be seen that the rate of uptake is more dependent on pH in distilled water than in seawater. This supports the hypothesis that seawater ions affect the surface charge and/or type of available binding site thus decreasing the effect of pH, these factors being controlled by pH alone in the distilled water.

Two sets of equations have been produced relating \log_{10} k to pH and $[PO_4]_0$; unfortunately insufficient experiments were carried out to enable the equations to be combined as was done by Lijklema (131). The rate constants calculated in this study are dependent on the concentration of phosphate, consequently care must be exercised in the use of these values as they are not true rate constants. No conclusions as to the mechanism should be drawn from the plots and the mechanism proposed (2X \rightleftharpoons A+B) does not necessarily represent the mechanism for the reaction. The diagrams produced indicate that the rate of uptake has a similar dependence on the concentration of phosphate whether in seawater or distilled. However, the pH dependence is larger in distilled water than in seawater. Further evidence of the differences in the processes in the two media was



Figure 3.3.20. Plot of \log_{10} k against pH for aged Fe(III) derived precipitates at 15° C. 0 - distilled water; X- seawater. $[PO_4]_0 = 1.0 \mu mol 1^{-1}$

obtained by studying the uptake at $2^{\circ}C$ and $15^{\circ}C$ (see Figure 3.3.21, which shows plots of $\ln(f)$ against time for the temperature dependence of the reactions). In seawater there is no temperature dependence (see adsorption profiles Figure 3.3.4) and the rate constant at pH = 8.2, $PO_{4,O}$ = 1.0 mol 1⁻¹, T = $2^{\circ}C/15^{\circ}C$ is $\log_{10} k = 4.85$. In contrast the uptake is temperature dependent in distilled water with $\log_{10} k = 4.37$ at $2^{\circ}C$ and $\log_{10} k = 4.64$ at $15^{\circ}C$. Use of these data in equation (3.17) yields an activation energy, E = 31.9 kJ mol⁻¹. This should be regarded as an apparent activation energy (214) since:-

 $E_{(True)} = E_{(Apparent)}$ + Heat of adsorption If, in the case of distilled water, the uptake is chemisorption then the lower limit to the heat of adsorption is approximately 80 kJ mol⁻¹ (212) and so total activation energy may be as high as 110 kJ mol⁻¹. In seawater no activation energy was measured and if the process is dominated by a physical adsorption mechanism, already proposed, the heat of adsorption would be less than 40 kJ mol⁻¹ (212). The reason that the activation energy could not be measured may possibly be due to the near equivalence of the true activation energy and heat of adsorption although this would be rather fortuitous. Overall, the adsorption has thus been found to be more physical in nature when occurring in seawater, and more chemical in nature when



Figure 3.3.21. Graph showing temperature dependence of ln(f) for $2X \rightleftharpoons A+B$. X = aged Fe(III) in distilled water at 2°C and pH = 7.3; O = aged Fe(III) in distilled water at 15°C and pH = 7.3; Δ = aged Fe(III) in seawater at 2°C and pH = 8.2; \Box = aged Fe(III) in seawater at 15°C and pH = 8.2; \Box = aged Fe(III)

The next stage was to examine the adsorption onto naturally occurring precipitates using estimates of log10 k as the summary of the model experiments. Only a few adsorption experiments were carried out on aged natural precipitates. The natural iron rich waters chosen contained predominantly Fe(II) so that the major investigation concentrated on freshly forming precipitates from these sources. Figure 3.3.22 shows the behaviour of aged precipitates derived from the Lady Bertha mine stream. When aged in fresh water the precipitate does not adsorb phosphate as can be seen for the traces at pH = 8.1 and pH = 7.2. However, when aged in a saline medium (S $\simeq 15^{\circ}_{00}$) adsorption did occur as shown in the trace at pH = 7.4 and a \log_{10} k value was calculated for the profile and is plotted on Figure 3.3.23. This diagram contains the values calculated from the models, and the values calculated from the aged natural precipitates. In the case of the Lady Bertha Mine precipitate the $\log_{10} k$ value is not comparable with any of the model predictions. This precipitate is not expected to adsorb phosphate because it was found to have a very low surface area and it does not adsorb in distilled water. However, it does adsorb in saline media but the equilibrium concentration is high, and the $\log_{10} k = 4.19$ which is smaller than expected under the experimental conditions. As it is of intermediate salinity the \log_{10} k value may be expected to be lower than \log_{10} k = 5.05 but it appears that this is an anomalous adsorption perhaps occurring because of some interaction in the more



 $[Fe]_{TOT} = 2.4 \text{ mg } 1-1; [Fe(II)] \approx 68\%$



complex natural media. A much better fit to the model is found for aged precipitate derived from the River Carnon. The adsorption curves for this system are shown in Figure 3.3.24 and the log₁₀ k values plotted on Figure 3.3.23. Figure 3.3.24 also contains plots for the uptake by freshly forming Carnon River precipitates and this supports the findings that this Fe(II) rich water produces adsorption behaviour much closer to that found for model Fe(III) systems. Even at the comparatively low pH values investigated removal is almost instantaneous and there is only a very small amount of desorption. No reasons can be given for this behaviour as a limited number of experiments were carried out using this water. Excellent agreement is found for the uptake by two aged precipitates, and it is unfortunate that further results could not be obtained for this natural water. The reason for this was a problem with. the analytical method for measuring phosphate which appeared to be susceptible to considerable interference from this Absorption values did not remain natural water. constant after 10 minutes as was usual but continued to increase for over an hour making the determination of phosphate almost impossible. This interference was suspected as being due to high arsenic concentrations, this element is known to interfere with this method for measuring phosphate (183) and high arsenic levels have been recorded for the waters and sediments of this river (216). Consequently the absorbance measured at 10 minutes was assumed



to be proportional to the concentration of phosphate, the colour development due to arsenic taking longer as the molybdenum arsenic complex formation was not catalysed. The fourth point on Figure 3.3.23 is for an aged interstitial derived precipitate formed in seawater. The rate of adsorption onto this precipitate has a $\log_{10} k = 4.53$ at pH = 8.05 which is lower than that predicted by the model. If this result is compared to that for the Lady Bertha Mine stream precipitate both are lower than expected but the interstitial water derived precipitate does fall between the boundaries for seawater and distilled water whereas the other result lies below these limits. For these very limited examples the model predicts the behaviour in natural freshwaters when adsorption occurs, but the adsorption onto natural precipitates in saline media has lower rate constants than those predicted by the model. This may mean that organic matter, or some other component of the natural precipitates reduces the effect of the seawater ions. These natural precipitates have been identified as am-FeOOH with surface areas somewhat smaller than synthetic oxyhydroxides and it was suggested that the reduction in surface area was due to organic coatings. Even the anomalous Lady Bertha Mine stream precipitate appears to obey the adsorption behaviour expected by consideration of surface areas by its nonadsorptive behaviour. Thus the model is a good analogue for the fresh waters, but organics may complicate the

behaviour to such an extent as to produce overestimates for the rate of uptake from seawater.

3.3.5 Kinetic Analysis for Uptake onto Fresh Precipitates

As mentioned above, only data for the formation of precipitates derived from Fe(II) in seawater can be kinetically analysed and this is then used as the model for the precipitates forming from iron rich natural waters. The rate of adsorption was thought to be limited by the rate of oxidation of Fe(II) and so for the first approximation the rate of uptake of phosphate was analysed by adapting the equations used by Sung and Morgan (56). The general rate law for homogeneous oxidation was found to be:

$$\frac{d [Fe(II)]}{dt} = k [OH^{-}]^{2} P_{0_{2}} [Fe(II)]$$

where k = Homogeneous rate constant (M⁻² atm⁻¹ min⁻¹)[OH⁻] = Concentration of hydroxyl ions[Fe(II)] = Concentration of total Fe(II)

At constant pH and P_0 equation (3.20) reduces to a first order equation:

$$-\frac{d [Fe(II)]}{dt} = k_1 [Fe(II)] \dots Eq. (3.21)$$

where $k_1 = k[OH^-]^2 P_{O_2} (mins^{-1})$
... Eq. (3.22)

Equation (3.21) integrates to

$$[Fe(II)] = [Fe(II)]_0 \exp(-k_1 t)$$

... Eq. (3.23)

By assuming that the rate of oxidation of Fe(II) is

equivalent to the rate of removal of $[PO_4]$ i.e.

 $\frac{-d [Fe(II)]}{dt} = \frac{-d [PO_4]}{dt}$

Then the Fe(II) terms in Equation (3.23) can be replaced by PO_4 thus

 $[PO_{4}] = [PO_{4}]_{0} \exp(-k, t) \dots Eq. (3.24)$ If the assumptions are correct and the oxidation is pseudofirst order, values of k_1 can be calculated from plots of $\log_{10} ([PO_4]/[PO_4]_0)$ against time. The slopes of the straight lines are used in the modified Equation (3.20) with P_{O2} assumed to be 0.21 atm and [OH⁻] calculated from the pH and a value for K_w of 13.58 (56). For the profiles at pH = 7.1 and pH = 7.3 (T = 15° C) shown in Figure 3.3.25 the values obtained were $k = 1.3 \times 10^{11} M^{-2} atm^{-1} min^{-1}$ and $k = 3.7 \times 10^{12} M^{-2} atm^{-1} min^{-1}$, respectively. These estimates are in good agreement with values of k obtained by other workers for the homogeneous oxidation of ferrous iron, which lie in the range 5 x 10^{11} to 2 x 10^{13} M⁻² atm⁻¹ min⁻¹ (56). At pH \ge 7.4 straight lines were not obtained for those experiments at 15°C and under these conditions heterogeneous oxidation is occurring with autocatalysis of the oxidation of Fe(II) by the iron oxyhydroxide surface. Thus, the rate of phosphate uptake is determined by the rate of oxidation of Fe(II) in seawater; at 15°C and at pH < 7.4. Therefore, the homogeneous oxidation of the Fe(II) and the uptake of the phosphate are very strongly coupled. Before examining the adsorption at pH > 7.4, the



profiles obtained at 2°C were analysed. These profiles give a straight line when analysed by the first order Equation (3.24). The K_w and P_{O_2} are as above for this approximation because the pH control is not tight enough to warrant rigorous calculation and at pH = 7.9 and temperature = 2° C a value of k = 5.4 x 10^{10} M⁻² atm⁻¹ min⁻¹ was obtained. Thus there is a considerable reduction in rate at the lower temperature despite the higher pH but more importantly the reaction in seawater appears to be reduced to a first order process at this lower temperature. The data for an experiment carried out at $2^{\circ}C$ and pH = 8.1 are also shown in Figure 3.3.25 and it is apparent that there is no fit to the straight line drawn, and the heterogeneous oxidation occurs under these conditions. The integrated rate equation for the heterogeneous oxidation is $[Fe(II)] = \frac{[Fe(II)]_0 (k_1 + k_2 [Fe(II)]_0)}{(k_1 + k_2 [Fe(II)]_0)}$

$$k_{2} [Fe(II)]_{0} + k_{1} \exp[(k_{1} + k_{2} [Fe(II)]_{0}) t]$$

... Eq. (3.25)

This equation was used to analyse the adsorption data at higher pH as before with k_1 being calculated from Equation (3.22) and assigning various values to k_2 in an attempt to fit the data. No value of k_2 gave a plot which matched the data and the rate of uptake of phosphate cannot be determined using the equation for heterogeneous oxidation. The rate of oxidation is increased at higher pH, consequently it is no longer the rate determining step for the adsorption process. At low pH values and/or low temperatures the rate of

oxidation of Fe(II) is slower than precipitate formation and/or phosphate adsorption and the rate of uptake of phosphate is limited by the oxidation and so can be analysed using the equations derived for the oxidation. At pH \ge 7.4 at 15^oC the rate of oxidation is similar to or greater than the rate of adsorption and/or precipitate formation and the equations derived for this heterogeneous oxidation cannot be used to analyse the rate of uptake of phosphate.

In an attempt to model the adsorption from seawater for the whole pH range under examination a similar approach was adopted to that used in analysing the adsorption onto aged precipitates. Figure 3.3.26 shows the mechanism tests with the ln(f) values shown in Table 3.12. Two mechanisms gave straight lines for the data at pH = 7.9 $[PO_A]_{O} = 1.0 \ \mu mol \ l^{-1}$ depending on the temperature. The first order equation for reaction 1. Table 3.12 gave a straight line for the data at 2°C as was expected following the analysis derived above and the equation for reaction 4, Table 3.12 gave a straight line for the data at 15°C. Consequently, by plotting ln(f) against time at pH \ge 7.4 as shown in Figure 3.3.27 values for \log_{10} k can be calculated as shown before in Section 3.3.4. Figure 3.3.27 includes results for an experiment in which the initial concentration of Fe(II) was 0.7 mg 1^{-1} compared with 2.8 mg l^{-1} as in all other experiments. This illustrates the effect of reducing the concentration of Fe(II) and the



Figure 3.3.26. Mechanism test for fresh Fe(II) derived precipitates in seawater using ln(f) against time where ln(f) is derived from the integrated rate $O 2X \neq A+B 15^{\circ}C$ equation for the following $O 2X \neq A+B 2^{\circ}C$ mechanisms tested:

	X≒A	15° C
K	X ≒ A	2°C



igure 3.3.27. Plot of ln(f) against time for fresh Fe(II) precipitates in seawater at 15°C. \Box - pH = 7.9, [Fe(II)] TOT = 0.7 mg 1⁻¹; X - pH = 7.4; \bigcirc - pH = 7.5; \triangle - pH = 7.7; \bigcirc - pH = 7.9; [Fe(II)] TOT = 2.8 mg 1⁻¹

adsorption profile is shown in Figure 3.3.28 and the reaction still follows the second order mechanism. The log₁₀ k values are plotted against pH in Figure 3.3.29 and this gives the relationship as $\log_{10} k = -16.8 + 2.86$ pH with r = 0.99. This is the function used as the model for comparison with the uptake onto natural precipitates. Figure 3.3.30 shows the variation in log₁₀ k when temperature and initial concentrations of Fe(II) and phosphate were altered. The rate constants at pH = 7.9 and at the two temperatures can be used to calculate an activation energy as before with $\log_{10} k = 4.75$ at 2^oC and $\log_{10} k =$ 5.73 at 15°C. The value of the apparent activation energy is 115 kJ mol⁻¹ which is considerably higher than that calculated for the adsorption onto aged Fe(III) derived oxyhydroxide probably showing the influence of oxidation on the adsorption process. This is thought to be the first time an activation energy has been reported for the adsorption of phosphate onto freshly forming Fe(II) derived iron oxyhydroxide.

These trends in \log_{10} k may be helpful when examining the natural samples as levels of phosphate and Fe(II) may not be identical to those used in the model. The natural samples did not always give clean adsorption curves which reduced the amount of analysable data while others produced very good fits to the ln(f) v time plots as shown in Figure 3.3.31 for the precipitates derived from interstitial water. The results are plotted in Figure 3.3.32 and this includes




Figure 3.3.29. Plot of \log_{10} k against pH for uptake onto fresh Fe(II) derived oxyhydroxides [PO₄]₀ = 1.0 µmoll⁻¹;S = 34%





Figure 3.3.31. The ln(f) against time plots for uptake of phosphate from seawater by iron precipitates derived from interstitial waters. $\triangle - pH =$ 7.5 [Fe(II)] = 1.8 mg 1⁻¹; $\square - pH =$ 7.9 [Fe(II)] = 1.3 mg 1⁻¹; $\bigcirc - pH =$ 8.1 [Fe(II)] = 2.4 mg 1⁻¹



experiments carried out in natural fresh waters as well as saline media. The uptake onto precipitates forming from iron rich interstitial waters produces log₁₀ k values that follow the model line throughout the pH range. The iron rich mine stream results at S = 15°_{00} and S = 30°_{00} are also in good agreement making this the best analogue out of those systems examined. From these results it should be possible to predict the relative rates of removal of phosphate from solution if a source of Fe(II) enters a phosphate containing saline water. These results only apply to the conditions of temperature, $[PO_4]_0$ and $[Fe(II)]_{O}$ given and changes in any of these parameters will alter the rate as shown in Figure 3.3.31. It is interesting to note the \log_{10} k values for the uptake onto natural precipitates in fresh water as these are the only results analysed for this system. This was possible due to the low pH of the solution, and the absence of desorption resulting from small pH changes and the formation of am-FeOOH rather than γ -FeOOH. In fresh water the rate of uptake is faster than in seawater as is expected from the uptake curves although the model fresh waters could not be analysed. It is only because the pH for these natural waters was low that enabled analysis to be done and at pH > 7.2 the adsorption curves were similar to those obtained from freshly precipitating Fe(III) derived model systems, including the absence of desorption, emphasising the fact that a different iron oxyhydroxide is formed. Finally, experiments

involving uptake from interstitial samples at 2°C are also reported in Figure 3.3.32. The rate constant in seawater at pH = 7.6 for an interstitial water containing 63% of total iron as Fe(II) was $\log_{10} k = 3.75$ at 2^oC and \log_{10} k = 4.38 at 15^oC (the latter value estimated from Figure 3.3.32). The apparent activation energy was found to be 74.2 kJ mol⁻¹ which is lower than that for the model reaction of $E_{(app.)} = 115 \text{ kJ mol}^{-1}$ at pH = 7.9. This reduction in E may arise from the presence of Fe(III) in the natural water. This will be precipitated almost immediately when added to the seawater thus creating a fresh oxyhydroxide surface on which both adsorption of phosphate and also autocatalysis of the oxidation can occur. The rate constant in fresh water for a similar interstitial sample at pH = 7.1 and $2^{\circ}C$ is $\log_{10} k = 3.18$ and this value is too low to be plotted on Figure 3.3.32. The rate constant at 15°C is plotted and using this value of $\log_{10} k = 4.38$ and the \log_{10} k value at 2[°]C an activation energy of 141.2 kJ mol⁻¹ was calculated. This is the highest value for E found and this is due to the slow oxidation of Fe(II) at the low pH and temperature used. Although this solution also contains Fe(III) this may be stabilised by dissolved organic matter and would not precipitate in the absence of destabilising ions such as Cl^{-} and SO_{A}^{2-} . Consequently neither the rate of adsorption or rate of oxidation are enhanced and a high apparent activation energy ensues.

3.3.6 Summary of Phosphate Adsorption

For this part of the study chemical models were produced to examine the removal of phosphate from solution under the extremes of estuarine conditions. The relevance and possible improvements to these models will be discussed in Chapter 4 but even in the comparatively simple systems chosen considerable differences in behaviour were found. Possible reasons for these differences and the kinetic analysis for each system can be summarised as follows:-(a) The adsorption of phosphate onto aged Fe(III) derived precipitates appears to be a chemisorption process in distilled water with a strong pH dependence for both rate of uptake and equilibrium concentration.

(b) The adsorption onto aged Fe(III) derived precipitate in seawater appears to be a physical adsorption with the adsorption at equilibrium enhanced when compared with adsorption in distilled water by a mechanism thought to involve the seawater cations Ca^{2+} and Mg^{2+} .

(c) The reactions were found not to have simple kinetic orders.

(d) Apparent rate constants have been calculated for the adsorption phenomena in (a) and (b) using the mechanism 2X A+B. These are not true rate constants as a dependence on initial phosphate concentration was found such that $\log_{10} k \approx 5.58 \pm 0.88 \sqrt{c}$. The dependence of $\log_{10} k$ on pH for both media was also determined.

(e) Experiments were carried out at 2°C and 15°C to examine

the effect of temperature on the uptake. The apparent activation energy in seawater was found to be zero and in distilled water was found to be 31.9 kJ mol^{-1} .

(f) Natural aged precipitates showed good agreement with models for distilled water system, but considerable variation was found for the natural precipitates in saline media possibly suggesting an inhibition of the role of the seawater ions.

(g) Adsorption onto aged Fe(II) derived precipitates did not occur in the natural pH range in seawater or distilled water and this may indicate a physical adsorption process inhibited by the nature of the Y-FeOOH surface formed. (h) Adsorption by freshly forming Fe(III) precipitate is extremely efficient and rapid under the conditions used. It is thought that the rate of removal is determined by the rate of particle formation. No information on the mechanism of adsorption could be extracted from the data. (i) The adsorption onto freshly forming Fe(II) derived precipitate is also dependent on the rate of particle forma-In distilled water the adsorption appears to be tion. physical with the phosphate exchanging with hydroxyl ions during small changes in pH. The rate of this reaction and the desorption due to pH and morphological changes prevent kinetic analysis being carried out. The adsorption in seawater can be analysed to give \log_{10} k values with two possible mechanisms depending on pH and temperature. At low pH and/or temperature the rate of phosphate uptake is

described by first order process dependent on the homogeneous oxidation of Fe(II). At higher pH and temperature the oxidation is heterogeneous and is no longer the rate determining step. The uptake at pH > 7.4 can be defined by the second order mechanism as obtained in (d) above and $\log_{10} k = -16.8 + 2.86$ pH with an apparent activation energy of 115 kJ mol⁻¹.

(j) The uptake onto iron oxyhydroxides forming from Fe(II) rich natural waters in saline media has rate constants in good agreement with those of the model system. The activation energies for these iron oxyhydroxides are 74.2 kJ mol⁻¹ in seawater and 141.2 kK mol⁻¹ in distilled water. This may indicate that the natural iron rich waters containing both Fe(II), Fe(III) and other dissolved constituents have different mechanisms for their adsorption processes in distilled water and seawater.

(k) By calculating the rate constants using the arbitrarily chosen standard mechanism the variation in rate of adsorption for changes in pH, ionic strength and temperature can be compared for both model and natural systems.

4. SUMMARY AND CONCLUSIONS

In this final chapter the three areas of the study will be drawn together to present the overall picture obtained and show the inter-relationships found between the separate investigations. The methods used will be discussed and the suggestions for further work listed. The findings of the work will be put into perspective with respect to natural water chemistry and water quality control and the possible use of the results in fieldwork presented.

4.1 Surface Characteristics and Phosphate Uptake

The studies on the synthetic iron oxyhydroxides have shown significant differences in adsorption behaviour arising from precipitate age and precipitates derived from Fe(II) or Fe(III) sources. These differences can be linked to the changes in surface character found and examined using various techniques in this study. This suggests that careful control of experimental conditions is required when modelling adsorption processes in natural waters particularly precipitate age which is of considerable importance for the surface area and the porosity of the oxyhydroxides. Consideration of the specific type of natural iron precipitate that is being modelled is important and it appears that the freshly precipitated and those precipitating chemically in the presence of other dissolved phases are the more relevant systems, rather than weathered crystalline forms, when considering the chemical and physical timescales

involved in natural waters. Thus when modelling natural adsorption processes the use of aged iron oxyhydroxides should be limited to those aged for no more than a few Furthermore, the use of iron oxyhydroxides preciphours. itated directly from iron-rich natural waters in adsorption studies should be treated with extreme caution as the nature of the solid is very variable. In this study it has been shown that precipitates obtained from acid mine stream waters have a variety of characteristics which appear to depend on the composition of the original media. This probably highlights the omission of dissolved organic matter from the models used for adsorption studies so that attempted correlations between adsorption processes involving synthetic and natural iron oxyhydroxides may bear little comparison. Investigations on the effect of humic acids upon the surface of α -FeOOH have been made (91), but whether similar interactions could occur in an estuarine environment where D.O.C. and dissolved iron are precipitated under similar conditions (112, 116) is not known. When studying the interaction between phosphate and iron oxyhydroxide with reference to nutrient availability in soils adsorption processes lasting for days and weeks may be relevant but for the more dynamic natural water systems the short term processes lasting only a few hours are more significant.

The surface area investigation revealed that the adsorption of N_2 involved a narrow-necked, wide-bodied pore structure, commonly called "ink bottle pores", for the

Fe(III) derived precipitates. The desorption of N₂ from the body of these pores was delayed by the slower evaporation from the constricted necks (217). The adsorption/desorption of phosphate from am-FeOOH has been shown to exhibit hysteresis when subject to pH changes (131). This phenomenon could be explained by the "ink bottle" shape of the pores, assuming that the am-FeOOH has a similar structure when in solution as when dried for surface area measurements, which may contain a gel of water molecules which restrict the diffusion of phosphate through the narrow necked pores. This may apply to other dissolved constituents and has important implications for buffering mechanisms as adsorption responds to pH changes comparatively rapidly whereas desorption is retarded and may not occur at all.

The uptake onto iron oxyhydroxides forming in the presence of phosphate is extremely rapid as the precipitates formed are very active and have large surface areas which could not be measured using the techniques described here. Although iron and phosphate concentrations were maintained at typical environmental levels, the competition between phosphate and other dissolved constituents may reduce the activity of the iron phases with respect to phosphate adsorption. The uptake onto freshly precipitated Fe(II) derived oxyhydroxides in distilled water appears to be controlled by changes in the surface charge of the precipitate although why it adsorbs when freshly formed and not when aged for 20 h is not known. The absence of uptake

onto the aged Fe(II) derived oxyhydroxide is thought to arise from an electrostatic repulsion related to surface charge with $pH_{Z.P.C.} \approx 6.2$ and phosphate speciation. In the case of other trace constituents which have a more favourable electrostatic interaction through their speciation uptake may take place.

4.2 A Method for Predicting the Behaviour of Phosphate

in the Presence of Iron in Estuarine Media

As stated above, the rate of uptake of phosphate onto freshly forming precipitates appears to be dependent upon the rate of particle formation. A simple guide is required to enable estimates for the time scales of the removal of phosphate from solution to be made. Figure 4.2.1 demonstrates the simple method chosen. The y-axis is the time taken for maximum adsorption and this was selected since it removes the problem arising from the desorption that occurs for Fe(II) derived precipitates in distilled water. It is the short term (2 h) uptake data that are examined here as these represent the time scales that are important for estuarine processes and also, in most cases, the adsorption was almost complete. The purpose of such a diagram is that it can be used in an applied way for the prediction of phosphate behaviour in the presence of precipitating iron, bearing in mind that the concentration of phosphate is 1.0 μ mol 1⁻¹ and iron is 0.05 m mol 1^{-1} . It should also be noted that the curve for uptake onto Fe(II) derived precipitates in distilled water conceals the form of the adsorption profiles at low pH's. There tends to be a delay of a few minutes without any removal of phosphate followed by rapid removal so that the time for maximum adsorption is ≈10 minutes at pH = 6.5. There is no explanation for this behaviour as no delay in the onset of precipitation was found in the nephelometric study although the pH range used only went as



low as pH = 7.0. However, from this nomograph the approximate time for phosphate to be removed from solution by an input of iron can be estimated. For example in seawater at pH = 8.0 removal will take ~15 minutes if the source of iron is predominantly Fe(II) or 1 minute if the source contains predominantly Fe(III). Figure 4.2.2 shows the results of the uptake onto precipitate derived from natural sources of dissolved iron, and the agreement is very good. For each natural water the points lie close to the model predictions. The iron precipitating from Carnon River water adsorbs phosphate at an equivalent rate to that for the Fe(III) model system, again indicating the strange behaviour of this iron-rich acidic stream. The analysis revealed predominantly Fe(II) while precipitate behaviour and character indicate high Fe(III) content. These are interesting results and warrant further investigation although this source of iron rich natural water was abandoned after 2 sampling trips because of its complexity and confusing behaviour which perturbed the experiments which were done to investigate certain parts of the adsorption. The time taken for precipitates forming from other mine stream waters to adsorb the phosphate were usually slower than the model at the same pH although at higher pH values (pH = 7.5 - 8.0) good agreement was found. The presence of dissolved organic matter could be the cause of this behaviour as it has been shown to retard the rate of oxidation of Fe(II) in some cases (53). It may also affect





Summary of precipitate formation from nephelometric study. Δ - Fe(III) derived precipitate in seawater and distilled water, O - Fe(II) derived precipitate in distilled water; X - Fe(II) derived precipitate in seawater

the surface charge; previous investigations on Goethite have shown that adsorption of humic acids produce a negatively charged particle even at high pH values (91). In seawater and brackish waters ($S = 15^{\circ}_{O}$) the possible effect of organic matter would not be as great, as this would be flocculated in the high ionic strength media, so that it may have less effect on the oxidation and also upon the surface character.Consequently, natural precipitates forming in saline media generally follow the model profile. The consequences of an acidic Fe(II) rich water or Fe(II) inputs from sediment pore waters entering the seawater end of an estuary could be the existence of dissolved Fe(II) in the water column for up to 2 h resulting in the very slow removal of phosphate and other dissolved constituents from solution.

Finally, the two predictive diagrams should be compared to the results of the nephelometric study (Figure 4.2.3) which is a repeat of Figure 3.2.9. In Figure 4.2.3 the relative rates of particle formation of fresh precipitates are shown for the two sources of iron examined. Comparison of Figure 4.2.3 with Figure 4.2.1 shows a direct correlation between the removal of phosphate from solution and the appearance of the colloid. Thus the adsorption is strongly linked to processes affecting the hydrolysis and oxidation of Fe(II) and the hydrolysis of Fe(III) in solution. To a large extent then, phosphate chemistry in estuarine media will follow the behaviour of iron.

4.3 Conclusions from Complete Study

The examination of three different aspects of the behaviour of two iron oxyhydroxides has yielded the following information.

(a) Amorphous FeOOH is formed by the addition of Fe(III) to distilled or seawater and γ -FeOOH is formed by the addition of Fe(II). Both these oxyhydroxides have large surface areas (in the range 97-234 m² g⁻¹) but their porous structure and surface characteristics are very different. The rate of precipitate formation from Fe(III) is extremely rapid at natural pH's in both distilled and saline waters, whereas the rate of precipitate formation of Fe(II) which is comparatively slow at the lower end of the natural pH range and in high ionic strength media.

(b) The adsorption of phosphate onto aged Fe(III) derived oxyhydroxides appears to be dominated by a physical mechanism in seawater and is a chemisorption process in distilled water. This is proposed from the adsorption at equilibrium and the calculations of activation energies. The adsorption processes studied are the relatively short term reactions with equilibrium reached within 20 h in seawater, and 2-3 h in distilled water. The rate and extent of adsorption is enhanced in seawater possibly via a mechanism involving the seawater cations, especially Mg^{2+} and Ca^{2+} . There is no adsorption onto the aged γ -FeOOH derived from Fe(II) in seawater or distilled water in the

range 6.0 \leq pH \leq 8.5. This is because the γ -FeOOH surface may have a strong negative charge in this pH range and consequently repels the negative phosphate species. (c) The adsorption onto freshly forming iron oxyhydroxides is controlled by the rate of particle formation. For Fe(III) this adsorption is extremely rapid and no mechanistic or kinetic information can be extracted. For Fe(II) the process differs between seawater and distilled water although in both cases the rate of oxidation plays an important part in the adsorption process. In seawater uptake is relatively slow and dependent on pH and temperature, but there is no desorption. In distilled water the adsorption is rapid, and complicated by a desorption resulting initially from pH changes over a period of minutes and subsequently from morphological changes over a period of hours. The desorption is reversible and at least some part of the adsorbed phosphate is labile and capable of responding to changes in pH within a few minutes.

(d) The adsorption reactions onto aged Fe(III) precipitates in seawater and distilled water and fresh Fe(II) precipitates in seawater have been quantitatively analysed using a second order reversible reaction to give the following relationships for the rate constants:

For Fe(III) $\log_{10} k = 5.49 - 0.85 \sqrt{c}$ in seawater $\log_{10} k = 5.67 - 0.92 \sqrt{c}$ in distilled water $\log_{10} k = 7.52 - 0.33$ pH in seawater $\log_{10} k = 9.19 - 0.64$ pH in distilled water

For Fe(II) log₁₀ k = -16.8 + 2.86 pH in seawater Numerous attempts to calculate true rate constants that were independent of the concentration of phosphate were made but the equations and mechanisms used did not produce the desired results. However the equations above clearly indicate the relative dependence of each reaction upon pH, and this could be important when examining rates of adsorption both in estuarine systems and for water quality control.

(e) Activation energies were calculated from experiments carried out at 2° C and 15° C for both synthetic and natural systems. For aged Fe(III) derived oxyhydroxides the activation energy for uptake from seawater was zero but was 31.9 kJ mol⁻¹ in distilled water.

For fresh Fe(II) derived oxyhydroxides the activation energy for uptake from seawater was 115 kJ mol^{-1} .

For fresh precipitates derived from interstitial water activation energy was 74.2 kJ mol⁻¹ in seawater and 141.2 kJ mol⁻¹ in distilled waters.

These values indicate possible changes in mechanism for the model systems and show to what extent the uptake onto natural precipitates compares with that of synthetic oxyhydroxides.

(f) It was possible to analyse the adsorption of phosphate onto fresh Fe(II) derived precipitates in seawater using kinetic equations set up to examine the oxidation of Fe(II). The equations were only found to fit at pH < 7.4 at 15° C and pH < 7.9 at 2° C in seawater and this was a result of the

oxidation being a comparatively slow first order reaction which limited the rate of uptake. Rate constants were calculated from this data such that at pH = 7.1 and 15° C \log_{10} k = 1.3 x 10^{11} M⁻² atm⁻¹ min⁻¹, at pH = 7.3 and 15° C \log_{10} k = 3.7 x 10^{12} M⁻² atm⁻¹ min⁻¹ and at pH = 7.9 and 2° C \log_{10} k = 5.4 x 10^{10} M⁻² atm⁻¹ min⁻¹.

(g) The nephelometric study indicated the relative rates of precipitate formation for the various systems examined. In the case of Fe(II) the precipitation follows a two stage reaction at $pH \ge 7.6$ in distilled water and at $pH \ge 8.3$ in seawater. This appears to be the case when the rate of hydrolysis and colloid formation is approximately twice the rate of oxidation and this can only be so under conditions favouring faster rates of oxidation. Apart from this limited analysis the complexity of the particle formation from Fe(II) and Fe(III) sources meant that comparative studies only could be done.

4.4 Recommendations for Future Work

(a) The chemical model developed was kept as simple and as reproducible as possible, the most important omission was excluding organic matter from the fresh water analogue. Further model studies with a well defined organic material such as humic or fulvic acid should be done as a comparison to the results of this work and perhaps as a better model of the natural system.

(b) The characterisation studies concentrated on precipitates formed in distilled water and a similar suite of experiments could be done in seawater for both model and natural precipitates.

(c) The characterisation of precipitates derived from interstitial waters was limited by the very small quantities of solid available. It may be possible to extract larger volumes of interstitial waters by using box cores and extraction by centrifugation or compression, and thus have sufficient precipitate for surface area determination to be carried out as well as the other characterisation techniques. (d) The Carnon River samples gave contradictory data between their measured adsorption behaviour and that expected from analysis of iron content. The phosphate analysis was also found to be difficult and this natural water probably warrants a separate investigation in its own right. The measurement of Fe(II) may have to be done using a polarographic technique as well as the colorimetric as this has been found to be the definitive method for measuring Fe(II)

in the presence of Fe(III) (190).

(e) The original stimulus for this work arose from the buffering mechanism hypothesised for results of a survey of the Tamar Estuary (160). No desorption processes were investigated in this study and the occurrence of this phenomenon could be investigated for changes in phosphate concentration, salinity and pH.

REFERENCES

- EMSLEY, J. Phosphate Cycles. Chem. in Br. <u>13</u> 459-463 (1977).
- 2. MASON, B. Principles of Geochemistry, 3rd edition Wiley and Sons, New York pp 379 (1966).
- 3. BOWEN, H.J.M. Trace Elements in Biochemistry. Academic Press, New York pp 241 (1966).
- 4. SAXBY, J.D. Metal-Organic Chemistry of the Geochemical Cycle. Rev. Pure Appl. Chem. <u>19</u> 131-150 (1969).
- 5. BIEDERMANN, G. & CHOW, J.T. Studies on the Hydrolysis of Metal Ions (57). The Hydrolysis of Fe III and the Solubility Product of Fe(OH) Cl_{0.3} in O.5M Na⁺ Cl⁻ Media. Acta Chem.^{2.7} Scand. <u>20</u> 1376-1388 (1966).
- 6. SYLVA, R.N. The Hydrolysis of Iron III. Rev. Pure Appl. Chem. <u>22</u> 115-132 (1972).
- 7. DOUSMA, J. & DE BRUYN, P.L. Hydrolysis-Precipitation Studies of Iron Solutions. (1) Model for Hydrolysis and Precipitation from Fe III Nitrate Solutions. J. Colloid Interface Sci. <u>56</u> 527-539 (1976).
- MESMER, R.E. Hydrolysis of Fe II in Dilute Chloride at 25°C. Inorg. Chem. <u>10</u> 857-858 (1971).
- 9. MILBURN, R.M. & VOSBURGH, W.C. A Spectrophotometric Study of the Hydrolysis of Fe III.
 2) Polynuclear Species. J. Am. Chem. Soc. <u>77</u> 1352-1355 (1955).
- 10. MULAY, L.N. & SELWOOD, P.W. Hydrolysis of Fe³⁺. Magnetic and Spectrophotometric Studies of Ferric Perchlorate Solutions. J. Am. Chem. Soc. <u>77</u> 2693-2701 (1955).
- 11. MURPHY, P.J., POSNER, A.M. & QUIRK, J.P. Characterisation of Partially Neutralised Ferric Ion Solutions. J. Colloid Interface Sci. <u>56</u> 270-319 (1976).
- 12. SODERQUIST, R. & JANSSON, S. X-ray and Electron Microscope Studies of Precipitates Formed by the Hydrolysis of Fe III in O.5M Na Cl. Acta Chem. Scand. <u>20</u> 1417-1418 (1966).

- 13. MATIJEVIC, E. & SCHEINER, P. Ferric Hydrous Oxide Sols. III) Preparation of Uniform Particles by Hydrolysis of Fe Cl₃, Fe (NO_3)₃ and Fe (ClO₄)₃ Solutions. J. Colloid Interface Sci. <u>63</u> 504-524 (1978).
- HSU, P.H. & RAGONE, S.E. Ageing of Hydrolysed Fe III Solutions. J. Soil Sci. <u>23</u> 17-31 (1972).
- 15. RYDEN, J.C., McLAUGHLIN, J.R. & SYERS, J.K. Mechanisms of Phosphate Sorption by Soils and Hydrous Ferric Oxide Gel. J. Soil Sci. <u>28</u> 72-92 (1977).
- 16. HSU, P.H. Appearance and Stability of Hydrolysed Fe(ClO₄) Solutions. Clay Clay Miner. <u>21</u> 267-277 (1973).
- 17. VAN DER GEISSEN, A.A. The Structure of Fe III Oxide Hydrate Gels. J. Inorg. Nucl. Chem. <u>28</u> 2155-2159 (1966)
- BREEUSMA, A. & LYKLEMA, J. Interfacial Electrochemistry of Haematite (α-Fe₂ O₃). Disc. Faraday Soc. <u>52</u> 324-333 (1971).
- 19. LAHANN, R.W. Surface Charge Variation in Ageing Fe (OH)₂. Clay Clay Miner. <u>24</u> 320-326 (1976)
- 20. LANDA, E.R. & GAST. R.G. Evaluation of Crystallinity in Hydrated Fe III Oxides. Clay Clay Miner. <u>21</u> 121-130 (1973).
- 21. TOWE, K.M. & BRADLEY, W.F. Mineralogical Constitution of Colloidal Hydrous Ferric Oxides. J. Colloid. Interface Sci. <u>24</u> 384-392 (1967).
- 22. HARVEY, H.W. Note on the Colloidal Ferric Hydroxide in Sea Water. J. Mar. Biol. Assoc. <u>22</u> 221-225 (1937).
- 23. JONES, B.F., KENNEDY, V.C. & ZELLWEGER, G.W. Comparison of Observed and Calculated Concentrations of Dissolved A1 and Fe in Stream Water. Water Resources Res. <u>10</u> 791-793 (1974).
- LAEVASTU, T. & THOMPSON, T.G. Soluble Iron in Coastal Waters. J. Mar. Res. <u>16</u> 192-198 (1958).
- 25. BYRNE, R.H. & KESTER, D.R. Solubility of Hydrous Ferric Oxide and Iron Speciation in Seawater. Mar. Chem. <u>4</u> 255-274 (1976).

- 26. MILL, A.J.B. Colloidal and Macromolecular Forms of Iron in Natural Waters. 1: A Review. Environ. Tech. Letts. <u>1</u> 97-108 (1980).
- KOENINGS, J.P. <u>In situ</u> Experiments on the Dissolved and Colloidal State of Iron in an Acid Bog Lake. Limnol. Oceanogr. <u>21</u> 674-683 (1976).
- 28. THEBAULT. P., CASES, J.M. & FIESSINGER, F. Mechanism Underlying the Removal of Organic Micropollutants During Flocculation by an Al or Fe Salt. Water Res. <u>15</u> 183-189 (1981).
- 29. HSU, P.H. Comparison of Iron (III) and Aluminium in Precipitation of Phosphate From Solution. Water Res. <u>10</u> 903-907 (1976).
- 30. LECKIE, J. & STUMM, W. Phosphate Precipitation In "Water Quality Improvement by Physical and Chemical Processes". Water Resources Symp. No. 3 (Eds. Gloyna, E.F. & Eckenfelder, W.W.) 237-249. Univ. Texas Press (1970).
- 31. STUMM, W. & MORGAN, J.J. Aquatic Chemistry. Wiley Interscience, New York. 2nd Ed. pp 780 (1981).
- 32. ATKINSON, R.J., POSNER, A.M. & QUIRK, J.P. Crystal Nucleation in Fe (III) Solutions and Hydroxide Gels. J. Inorg. Nucl. Chem. <u>30</u> 2371-2381 (1968).
- 33. HEMMES, P., RICH, L.D., COLE, D.L. & EYRING, E.M. Kinetics of Hydrolysis of Ferric Ion in Dilute Aqueous Solution. J. Phys. Chem. <u>75</u> 929-932 (1971).
- 34. SPIRO, T.G., ALLERTON, S.E., RENNER, J., TERZIS, A., BILS, R. & SALTMAN, P. The Hydrolytic Polymerization of Iron III. J. Am. Chem. Soc. <u>88</u> 2721-2726 (1966).
- 35. ASTON, S.R. & CHESTER, R. The Influence of Suspended Particles on the Precipitation of Iron in Natural Waters. Estuarine Coastal Mar. Sci. <u>1</u> 225-231 (1973).
- 36. GLASSON, D.R. Personal Communication. Plymouth Polytechnic. (1980).
- 37. MACKAY, A.L. Some Aspects of the Topochemistry of the Iron Oxides and Hydroxides. In "Reactivity of Solids". 571-583 Proceedings of the 4th International Symp. on the Reactivity of Solids (Ed. De Boer, J.H.) 762 pp. Elsevier, London (1960).
- 38. MURRAY, J.W. Iron Oxides. Min. Soc. America Short Course Notes <u>6</u> 47-98 (1979). Marine Minerals (Ed. Burns, R.G.) <u>380</u> pp. Min. Soc. America, Washington.

- 39. GOLDBERG, E.D. Chemical Scavengers of the Sea. J. Geol. <u>62</u> 241-265 (1954).
- 40. LANGMUIR, D. & WHITTEMORE, D.O. Variations in the Stability of Precipitated Ferric Oxyhydroxides. In "Nonequilibrium Systems in Natural Water Chemistry" 209-234 Chap. 8. A.C.S.Symposium Series No. 106 (Ed. Hem, J.D.). Washington (1971).
- 41. SCHWERTMANN, U. & TAYLOR, R.M. Natural and Synthetic Poorly Crystallised Lepidocrocite. Clay Miner. <u>14</u> 285-293 (1979).
- 42. CARLSON, L. & SCHWERTMANN, U. Natural Occurrence of Ferroxyhite (δ '-FeOOH). Clays Clay Miner. <u>28</u> 272-280 (1980).
- 43. SCHWERTMANN, U. & FISCHER, W.R. Natural "Amorphous" Ferric Hydroxide. Geoderma <u>10</u> 237-247 (1973).
- 44. CARLSON, L. & SCHWERTMANN, U. Natural Ferrihydrites in Surface Deposits from Finland and their Association with Silica. Geochim. Cosmochim. Acta <u>45</u> 421-429 (1981).
- 45. SINGER, P.C. & STUMM, W. Acidic Mine Drainage: The Rate Determining Step. Science <u>167</u> 1121-1123 (1970).
- 46. BROCK, T.D., COOK, S., PETERSEN, S. & MOSSER, J.L. Biogeochemistry and Bacteriology of Ferrous Iron Oxidation in Geothermal Habitats. Geochim. Cosmochim. Acta. <u>40</u> 493-500 (1976).
- 47. SCHWERTMANN, U. The Inhibiting Effect of Soil Organic Matter on the Crystallization of Amorphous Ferric Hydroxide to Goethite. Nature <u>212</u> 645-646 (1966).
- 48. SCHWERTMANN, U., FISCHER, W.R. & PAPENDORF, H. The Influence of Organic Compounds on the Formation of Iron Oxides. Trans. 9th Congr. Soil Sci. <u>1</u> 645-655 (1968).
- 49. PARKS, G.A. Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals; Isoelectric Point and Zero Point of Charge. In "Equilibrium Concepts in Natural Water Systems 121-160. A.C.S. Symp. Ser No. 67 Washington, D.C. (1967)
- 50. PARKS, G.A. Adsorption in the Marine Environment. In "Chemical Oceanography" <u>1</u> 241-308 (Ed. Riley, J.P. & Skirrow, G.). Academic Press, New York (1975)

- 51. HEM, J.D. Chemical Factors that Influence the Availability of Iron and Manganese in Aqueous Systems. Geol. Soc. Am. Bull. <u>83</u> 443-450 (1972).
- 52. THEIS, T.L. & SINGER, P.C. The Stabilization of Ferrous Iron by Organic Compounds in Natural Waters. In "Trace Metals and Metal-Organic Interactions in Natural Waters" 303-320. (Ed. Singer, P.C.). Ann. Arbor Sci. Michigan (1973).
- 53. THEIS, T.L. & SINGER, P.C. Complexation of Iron II by Organic Matter and its Effect on Iron II Oxygenation. Environ. Sci. Tech. <u>8</u> 569-573 (1974).
- 54. TAMURA, H., GOTO, K. & NAGAYAMA, M. Effect of Anions on the Oxygenation of Ferrous Ion in Neutral Solutions. J. Inorg. Nucl. Chem. <u>38</u> 113-117 (1976).
- 55. FOSTER, P., HUNT, D.T.E. & MORRIS, A.W. Metals in an Acid Mine Stream and Estuary. Sci. Tot. Environ. <u>9</u> 75-86 (1978).
- 56. SUNG, W. & MORGAN, J.J. Kinetics and Product of Ferrous Iron Oxygenation in Aqueous Systems. Environ. Sci. Tech. <u>14</u> 561-568 (1980).
- 57. STUMM, W. & LEE, G.F. Oxygenation of Ferrous Iron. Ind. Eng. Chem. <u>53</u> 143-146 (1961).
- 58. GHOSH, M.M. Oxygenation of Ferrous Iron (II) in Highly Buffered Waters. In "Aqueous Environmental Chemistry of Metals". 193-218. (Ed. Rubin, A.J.) Ann. Arbor Sci. Michigan (1974).
- 59. DAVISON, W. & HEANEY, S.I. Ferrous Iron-Sulphide Interactions in Anoxic Hypolimnetic Waters. Limnol. Oceanogr. <u>23</u> 1194-2000 (1978).
- RICHARDS, F.A. Anoxic Basins and Fjords. In
 "Chemical Oceanography"<u>1</u> 611-645. (Eds. Riley, J.P. & Skirrow, G.). Academic, London (1965).
- 61. THORNTON, I., WATLING, H. & DARRACOTT, A. Geochemical Studies in Several Rivers and Estuaries used for Oyster Rearing. Sci. Tot. Environ. <u>4</u> 325-345 (1975).
- 62. BOYDEN, C.R., ASTON, S.R. & THORNTON, I. Tidal and Seasonal Variations of Trace Elements in Two Cornish Estuaries. Estuarine Coastal Mar. Sci. <u>9</u> 303-317 (1979).

- 63. LYONS, W.B., GAUDETTE, H.E. & ARMSTRONG, P.B. Evidence for Organically Associated Iron in Nearshore Pore Fluids. Nature <u>282</u> 202-203 (1979).
- 64. TROUP, B.N., BRICKER, O.P. & BRAY, J.T. Oxidation Effect on the Analysis of Iron in the Interstitial Water of Recent Anoxic Sediments. Nature <u>249</u> 237-245 (1974).
- 65. PRESLEY, B.J., KOLODNY, Y., NISSENBAUM, A. & KAPLAN, I.R. Early Diagenesis in a Reducing Fjord. Saanich Inlet, British Colombia. II. Trace Metal Distribution in Interstitial Water and Sediment. Geochim. Cosmochim. Acta <u>36</u> 1073-1090 (1972).
- 66. FANNING, K.A. & MAYNARD-HENSLEY, V.I. Oxidative Changes to Nitrate and Boron in Marine Pore Waters. Nature <u>287</u> 38-41 (1980).
- 67. OSCARSON, D.W., HUANG, P.M., DEFOSSE, C. & HERBILLON, A. Oxidative Power of Mn (IV) and Fe (III) Oxides with respect to As (III) in Terrestrial and Aquatic Environments. Nature <u>291</u> 50-51 (1981).
- 68. PRESLEY, B.J. & TREFRY, J.H. Sediment-Water Interactions and the Geochemistry of Interstitial Waters. In "Chemistry and Biogeochemistry of Estuaries" 187-232. (Eds. Olausson, E. & Cato, I.) Wiley Interscience, Chichester, U.K. (1980).
- 69. MORRIS, J.C. & STUMM, W. Redox Equilibria and Measurements of Potentials in the Aquatic Environment. In "Equilibrium Concepts in Natural Water Systems" 270-285. A.C.S. Ser. No. 67 Washington, D.C. (1967).
- 70. BOWDEN, J.W., POSNER, A.M. & QUIRK, J.P. Generalised Model for Anion and Cation Adsorption at Oxide Surfaces. Nature <u>245</u> 81-84 (1974).
- 71. DAVIS, J.A., JAMES, R.O. & LECKIE, J.D. Surface Ionisation and Complexation at the Oxide/Water Interface. 1. Computation of Electrical Double Layer Properties in Simple Electrolytes. J. Colloid Interface Sci. <u>63</u> 480-499 (1978).
- 72. BREEUWSMA, A. & LYKLEMA, J. Physical and Chemical Adsorption of Ions in the Electrical Double Layer on Hematite $(\alpha - Fe_2O_3)$. J. Colloid Interface Sci. 43 437-448 (1973).

- 73. BALISTRIERI, L.S. & MURRAY, J.W. Surface of Goethite (α-FeOOH) in Seawater. In "Chemical Modelling in Aqueous Systems - Speciation, Sorption, Solubility and Kinetics". 275-298 (Ed. Jenne, E.A.) A.C.S. Symp. Ser. No. 93 (1979).
- 74. BALISTRIERI, L.S. & MURRAY, J.W. The Surface Chemistry of Goethite (α -FeOOH) in Major Ion Seawater. Am. J. Sci. 281 788-806 (1981).
- 75. HEM, J.D. Reactions of Metal Ions at Surfaces of Hydrous Iron Oxide. Geochim. Cosmochim. Acta <u>41</u> 527-538. (1977).
- 76. TAKEMATSU, N. Sorption of Transition Metals on Manganese and Iron Oxides, and Silicate Minerals. J. Oceanogr. Soc. Japan <u>35</u> 36-42 (1979).
- 77. VENKATARAMANI, B., VENKATESWARLU, K.S. & SHANKA, J. Sorption Properties of Oxides. III. Iron Oxides. J. Colloid Interface Sci. <u>67</u> 187-194 (1978).
- 78. JAMES, R.O. & HEALY, T.W. Adsorption of Hydrolysable Metal Ions at the Oxide-Water Interface. III. A Thermodynamic Model of Adsorption. J. Colloid Interface Sci. <u>40</u> 65-81 (1972).
- 79. JAMES, R.O., STIGLICH, R.J. & HEALY, T.W. Analysis of Models of Adsorption of Metal Ions at Oxide/Water Interfaces. Faraday Discus. Chem. Soc. <u>59</u> 142-156 (1975).
- 80. DAVIS, J.A. & LECKIE, J.O. Effect of Adsorbed Complexing Ligands on Trace Metal Uptake by Hydrous Oxides. Environ. Sci. Tech. <u>12</u> 1304-1315 (1978).
- 81. DAVIS, J.A. & LECKIE, J.O. Surface Ionisation and Complexation at the Oxide/Water Interface. II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions. J. Colloid Interface Sci. 67 90-107 (1978).
- B2. DAVIS, J.A. & LECKIE, J.O. Surface Ionisation and Complexation at the Oxide/Water Interface.
 3. Adsorption of Anions. J. Colloid Interface Sci. <u>74</u> 32-43 (1980).
- PARFITT, R.L. & RUSSEL, J.D. Adsorption on Hydrous Oxides. IV. Mechanisms of Adsorption of Various Ions on Goethite. J. Soil Sci. <u>28</u> 297-305 (1977).

- 84. YATES, D.E. & HEALY, T.W. Mechanisms of Anion Adsorption at the Ferric and Chromic Oxide/Water Interfaces. J. Colloid Interface Sci. <u>52</u> 222-228 (1975).
- 85. STUMM, W., HUANG, C.P. & JENKINS, S.R. Specific Chemical Interaction Affecting the Stability of Dispersed Systems. Croat. Chemica. Acta. <u>42</u> 223-245 (1970).
- 86. DAVIS, J.A. & LECKIE, J.O. Speciation of Adsorbed Ions at the Oxide/Water Interface. In "Chemical Modelling in Aqueous Systems - Speciation, Sorption, Solubility and Kinetics" 299-317 (Ed. Jenne, E.A.) A.C.S. Symp. Ser. No. 93 (1979).
- 87. HOHL, H. & WESTALL, J. A Comparison of Electrostatic Models for the Oxide/Solution Interface. Adv. Colloid Interface Sci. <u>12</u> 265-294 (1980).
- 88. YATES, D.E. The Structure of the Oxide/Aqueous Electrolyte Interface. Ph.D. Thesis. Melbourne University, Australia (1975).
- 89. EGASHIRA, K. & AOMINE, S. Effects of Drying and Heating on the Surface Area of Allophane and Imogolite. Clay Sci. <u>4</u> 231-242 (1974).
- 90. BALISTRIERI, L.S. & MURRAY, J.W. The Adsorption of Cu, Pb, Zn and Cd on Goethite from Major Ion Seawater. Geochim. Cosmochim. Acta. Submitted for publication.
- 91. TIPPING, E. The Adsorption of Aquatic Humic Substances by Iron Oxides. Geochim. Cosmochim. Acta. <u>45</u> 191-194 (1981).
- 92. THOMPSON, T.G. & BREMNER, R.W. The Occurrence of Iron in the Waters of the North East Pacific Ocean. J. Cons. Int. Explor. Mer. <u>10</u> 39-47 (1935).
- 93. COOPER, L.H.N. Some Chemical Considerations on the Distribution of Iron in the Sea. J. Mar. Biol. Assoc. <u>27</u> 314-321 (1948).
- 94. COOPER, L.H.N. The Distribution of Iron in the Waters of the Western English Channel. J. Mar. Biol. Assoc. <u>27</u> 274-313 (1948).
- 95. DUINKER, J.C. & NOLTING, R.F. Distribution Model for Particulate Trace Metals in the Rhine Estuary and Dutch Wadden Sea. Neth. J. Sea Res. <u>10</u> 71-102 (1976).

- 96. HEAD. P.C. Observations on the Concentration of Fe in Seawater with Particular Reference to Southampton Water. J. Mar. Biol. Assoc. <u>51</u> 891-903 (1971).
- 97. JOYNER, T. The Determination and Distribution of Particulate Aluminium and Iron in the Coastal Waters of the Pacific North West. J. Mar. Res. <u>22</u> 254-268 (1964).
- 98. KREMLING, K. & PETERSEN, H. The Distribution of Mn, Fe, Zn, Cd and Cu in Baltic Seawater. A Study on the Basis of One Anchor Station. Mar. Chem. <u>6</u> 155-170 (1978).
- 99. ATKINSON, L.P. & STEFANSSON, U. Particulate Aluminium and Iron in Seawater off the S.E. Coast of the United States. Geochim. Cosmochim. Acta 33 1449-1453 (1969).
- 100. WILLIAMS, P.M. & CHAN, K.S. Distribution and Speciation of Iron in Natural Waters: Transition from River Water to a Marine Environment, British Colombia, Canada. J. Fish. Res. Bd. Can. <u>23</u> 575-593 (1966).
- 101. KESTER, D.R. & BYRNE, R.H. Chemical Forms of Iron in Seawater. In "Ferromanganese Deposits on the Ocean Floor" 107-116 (Ed. Horn, D.R.) Colombia University, Palisades, New York (1972).
- 102. RILEY, J.P. & CHESTER, R. Introduction to Marine Chemistry. Academic Press, London and New York, pp 465 (1971).
- 103. BEWERS, J.M., SUNDBY, B. & YEATS, P.A. Distribution of Trace Metals in the Western North Atlantic off Nova Scotia. Geochim. Cosmochim. Acta. <u>40</u> 687-696 (1976).
- 104. BOYLE, E.A., EDMOND, J.M. & SHOLKOVITZ, E.R. The Mechanism of Iron Removal in Estuaries. Geochim. Cosmochim. Acta. <u>41</u> 1313-1324 (1977).
- 105. BEWERS, J.M. & YEATS, P.A. Oceanic Residence Times of Trace Metals. Nature <u>268</u> 595-598 (1977).
- 106. GIBBS, R.J. Mechanisms of Trace Metal Transport in Rivers. Science <u>180</u> 71-73 (1973),
- 107. EDZWALD, J.K., UPCHURCH, J.B. & O'MELIA, C.R. Coagulation in Estuaries. Environ. Sci. Tech. <u>8</u> 58-63 (1974).

- 108. HUNTER, K.A. & LISS, P.S. The Surface Charge of Suspended Particles in Estuarine and Coastal Waters. Nature <u>282</u> 823-825 (1979).
- 109. GIBBS, R.J. Transport Phases of Transition Metals in the Amazon and Yukon Rivers. Bull. Geol. Soc. Am. <u>88</u> 829-843 (1977).
- 110. SHOLKOVITZ, E.R. Chemical and Physical Processes Controlling the Chemical Composition of Suspended Material in the River Tay Estuary. Estuarine Coastal Mar. Sci. <u>8</u> 523-545 (1979).
- 111. SHOLKOVITZ, E.R. & PRICE, N.B. The Major Element Chemistry of Suspended Matter in the Amazon Estuary. Geochim. Cosmochim. Acta <u>44</u> 163-171 (1980).
- 112. SHOLKOVITZ, E.R., BOYLE, E.A. & PRICE, N.B. The Removal of Dissolved Humic Acids and Iron During Estuarine Mixing. Earth Plan. Sci. Letts. <u>40</u> 130-136 (1978).
- 113. SHOLKOVITZ, E.R. The Flocculation of Dissolved Fe, Mn, Al, Cu, Ni, Co and Cd During Estuarine Mixing. Earth Plan. Sci. Letts <u>41</u> 77-86 (1978).
- 114. BALE, A.J. & MORRIS, A.W. Laboratory Simulation of Chemical Processes Induced by Estuarine Mixing: The Behaviour of Iron and Phosphate in Estuaries. Estuarine Coastal Shelf Sci. <u>13</u> 1-10 (1981).
- 115. EATON, A. Removal of "Soluble" Iron in the Potomac River Estuary. Estuarine Coastal Mar. Sci. <u>9</u> 41-49 (1979).
- 116. MOORE, R.M., BURTON, J.D., WILLIAMS, P.J. Le B. & YOUNG, M.L. The Behaviour of Dissolved Organic Material, Iron and Manganese in Estuarine Mixing. Geochim. Cosmochim. Acta. <u>43</u> 919-926 (1979).
- 117. HOLLIDAY, L.M. & LISS, P.S. The Behaviour of Dissolved Iron, Manganese and Zinc in the Beaulieu Estuary, S.E. England. Estuarine Coastal Mar. Sci. <u>4</u> 349-353 (1976).
- 118. SHOLKOVITZ, E.R. Flocculation of Dissolved Organic and Inorganic Matter During the Mixing of River Water and Seawater. Geochim. Cosmochim. Acta. <u>40</u> 831-845 (1976).
- 119. WINDOM, H.L., BECK, K.C. & SMITH, R. Transport of Trace Metals to the Atlantic Ocean by Three South-eastern Rivers. S. East. Geol. <u>12</u> 169-181 (1971).
- 120. EVANS, D.W., CUTSHALL, N.H., CROSS, F.A. & WOLFE, D.A. Manganese Cycling in the Newport River Estuary, North Carolina. Estuarine Coastal Mar. Sci. <u>5</u> 71-80 (1977).
- 121. EATON, A. Observations on the Geochemistry of Soluble Copper, Iron, Nickel and Zinc in the San Francisco Bay Estuary. Environ. Sci. Tech. <u>13</u> 425-432 (1979).
- 122. LANGFORD, C.H., WONG, S.M. & UNDERDOWN, A.W. The Interaction of a Soil Fulvic Acid with Precipitating Hydrous Ferric Oxide at pH = 6. Can. J. Chem. <u>59</u> 181-186 (1981).
- 123. SENESI, N., GRIFFITH, S.M., SCHNITZER, M. & TOWNSEND, M.G. Binding of Fe⁻ by Marine Materials. Geochim. Cosmochim. Acta. <u>41</u> 969-976 (1977).
- 124. PARFITT, R.L., FRASER, A.R. & FARMER, V.C. Adsorption on Hydrous Oxides. III Fulvic Acid and Humic Acid on Goethite, Gibbsite and Imogolite. J. Soil Sci. <u>28</u> 289-296 (1977).
- 125. KROM, M.D. & SHOLKOVITZ, E.R. On the Association of Iron and Manganese with Organic Matter in Anoxic Marine Pore Waters. Geochim. Cosmochim. Acta. <u>42</u> 607-611 (1978).
- 126. SHOLKOVITZ, E.R. & COPLAND. D. The Coagulation, Solubility and Adsorption Properties of Fe, Mn, Cu, Ni, Cd, Co and Humic Acids in a River Water. Geochim. Cosmochim. Acta. <u>45</u> 181-189 (1981).
- 127. PICARD, G.L. & FELBECK, Jr. G.T. The Complexation of Iron by Marine Humic Acid. Geochim. Cosmochim. Acta. 40 1347-1350 (1976).
- 128. MANTOURA, R.F.C., DICKSON, A. & RILEY, J.P. The Complexation of Metals with Humic Materials in Natural Waters. Estuarine Coastal Mar. Sci. <u>6</u> 387-408 (1978).
- 129. STUMM, W. & MORGAN, J.J. Case Studies: Phosphorus, Iron and Manganese 514-563. In "Aquatic Chemistry" 1st Edition. Wiley Interscience, New York, pp 583 (1970).

- 130. HSU, P.H. Complementary role of Iron (III), Sulfate and Calcium in Precipitation of Phosphate from Solution. Environ. Letts. <u>5</u> 115-136 (1973).
- 131. LIJKLEMA, L. Interaction of Orthophosphate with Iron III and Aluminium Hydroxides. Environ. Sci. Tech. <u>14</u> 537-541 (1980).
- 132. BERKHEISER, V.E., STREET, J.J., ROA, P.S.C. & YUAN, T.L. Partitioning of Inorganic Orthophosphate in Soil-Water Systems. C.R.C. Critical Reviews In Environmental Controls <u>10</u> 174-224 (1980).
- 133. McLAUGHLIN, J.R., RYDEN, J.C. & SYERS, J.K. Development and Evaluation of a Kinetic Model to Describe Phosphate Sorption by Hydrous Ferric Oxide Gel. Geoderma <u>18</u> 295-307 (1977).
- 134. RYDEN, J.C., McLAUGHLIN, J.R. & SYERS, J.K. Time Dependent Sorption of Phosphate by Soils and Hydrous Ferric Oxides. J. Soil Sci. <u>28</u> 585-595 (1977).
- 135. RYDEN, J.C. & SYERS, J.K. Desorption and Isotopic Exchange Relationships of Phosphate Sorbed by Soils and Hydrous Ferric Oxide Gels. J. Soil Sci. <u>28</u> 596-609 (1977).
- 136. KUO, S. & LOTSE. E.G. Kinetics of Phosphate Adsorption and Desorption by Hematite and Gibbsite. Soil Sci. <u>116</u> 400-406 (1974).
- 137. FITTER, A.H. & SUTTON, C.D. The Use of the Freundlich Isotherm for Soil Phosphate Sorption Data. J. Soil Sci. <u>26</u> 241-246 (1975).
- 138. BACHE, B.W. & WILLIAMS, E.G. A Phosphate Sorption Index for Soils. J. Soil Sci. <u>22</u> 289-301 (1971).
- 139. BARROW, N.J. & SHAW. T.C. The Slow Reactions Between Soil and Anions: 2. Effect of Time and Temperature on the Decrease in Phosphate Concentration in the Soil Solution. Soil Sci. <u>119</u> 167-177 (1975).
- 140. BARROW, N.J. The Description of Phosphate Adsorption Curves. J. Soil Sci. <u>29</u> 447-462 (1978).
- 141. OLSEN, S.R. & WATANABE, F.S. A Method to Determine a Phosphorus Adsorption Maximum of Soils as Measured by the Langmuir Isotherm. Proc. Soil Sci. Soc. Am. <u>21</u> 144-149 (1957).

274.

- 142. VEITH, J.A. & SPOSITO, G. On the Use of the Langmuir Equation in the Interpretation of "Adsorption" Phenomena. Soil Sci. Soc. Am. J. <u>41</u> 697-702 (1977).
- 143. POSNER, A.M. & BOWDEN, J.W. Adsorption Isotherms: Should they be Split? J. Soil Sci. <u>31</u> 1-10 (1980).
- 144. GUNARY, D. A new Adsorption Isotherm for Phosphate in Soil. J. Soil Sci. <u>21</u> 72-77 (1970).
- 145. CHEN, Y.S.R., BUTLER, J.N. & STUMM, W. Adsorption of Phosphate on Aluminium and Kaolinite from Dilute Aqueous Solutions. J. Colloid Interface Sci. <u>43</u> 421-436 (1973).
- 146. GUPTA, S.K. Phosphate Removal in Systems H_3PO_4 - γ -FeOOH and H_3PO_4 -Fe Cl₃ and Characteristics of Sludge Phosphate. Ph.D. Thesis. University of Bern, Switzerland. 138 pp (1977).
- 147. STEFANNSON, U. & RICHARDS. F. Processes Contributing to the Nutrient Distributions of the Colombia River and Strait of Juan de Fuca. Limnol. Oceanogr. <u>8</u> 394-410 (1963).
- 148. POMEROY, L.R., GRANT, E.E. & SMITH, C. The Exchange of Phosphate Between Estuarine Water and Sediments. Limnol. Oceanogr. <u>10</u> 167-172 (1965).
- 149. NELSON, B.W. Sedimentary Phosphate Method for Estimating Paleosalinities. Science <u>158</u> 917-920 (1967).
- 150. CARRITT, D.E. & GOODGAL, S. Sorption Reactions and Some Ecological Implications. Deep Sea Res. <u>1</u> 224-243 (1954).
- 151. CHEN, Y.S.R., BUTLER, J.N. & STUMM, W. Kinetic Study of Phosphate Reaction with Aluminium Oxide and Kaolinite. Environ. Sci. Tech. <u>7</u> 327-332 (1973).
- 152. MORTIMER, C.H. Chemical Exchanges Between Sediments and Water in the Great Lakes - Speculations on Probable Regulatory Mechanisms. Limnol. Oceanogr. <u>16</u> 387-406 (1971).
- 153. WILLIAMS, J.D.H., SYERS, J.K., SHUKLA, S.S., HARRIS, R.F. & ARMSTRONG, D.E. Levels of Inorganic and Total Phosphorus in Lake Sediments as Related to Other Sediment Parameters. Environ. Sci. Tech. <u>5</u> 1113-1120 (1971).

- 154. LI, W.C., ARMSTRONG, D.E., WILLIAMS, J.D.H., HARRIS, R.F. & SYERS. J.K. Rate and Extent of Inorganic Phosphate Exchange in Lake Sediments. Proc. Soil Sci. Soc. Am. <u>36</u> 279-285 (1972).
- 155. EMERSON, S. & WIDMER, G. Early Diagenesis in Anaerobic Lake Sediments. II. Thermodynamic and Kinetic Factors Controlling the Formation of Iron Phosphate. Geochim. Cosmochim. Acta. <u>42</u> 1307-1316 (1978).
- 156. LIJKLEMA. L. The Role of Iron in the Exchange of Phosphate Between Water and Sediments. In "Interactions Between Sediments and Fresh Water" 313-317. S.I.L.-UNESCO Symp. Amsterdam; Junk, The Hague (1976).
- 157. BANOUB, M.W. Experimental Investigation on the Release of Phosphorus in Relation to Iron in Freshwater/Mud System. In "Interactions Between Sediments and Fresh Water" 324-330. S.I.L.-UNESCO Symp. Amsterdam; Junk, The Hague (1976).
- 158. MAYER, L.M. & GLOSS, S.P. Buffering of Silica and Phosphate in a Turbid River. Limnol. Oceanogr. 25 12-22 (1980).
- 159. KESTER, D.R. & PYTKOWICZ, R.M. Determination of the Apparent Dissociation Constants of Phosphoric Acid in Seawater. Limnol. Oceanogr. <u>12</u> 243-252 (1967).
- 160. BUTLER, E.I. & TIBBETS, S. Chemical Survey of the Tamar Estuary. 1) Properties of the Waters. J. Mar. Biol. Assoc. <u>52</u> 681-699 (1972).
- 161. BLANCHARD, J.R. Kinetic Studies on Adsorption and Desorption of Phosphate by Sediments. M.Sc. Thesis, Univ. Southampton, 77 pp (1976).
- 162. SALOMONS, W. & GERRITSE, R.G. Some Observations on the Occurrence of Phosphorus in Recent Sediments from Western Europe. Sci. Tot. Environ. <u>17</u> 37-49 (1981).
- 163. KROM, M.D. & BERNER, R.A. Adsorption of Phosphate in Anoxic Marine Sediments. Limnol. Oceanogr. <u>25</u> 797-806 (1980).
- 164. MORRIS, A.W., BALE, A.J. & HOWLAND, R.J.M. Nutrient Distributions in an Estuary: Evidence of Chemical Precipitation of Dissolved Silicate and Phosphate. Estuarine Coastal Shelf Sci. <u>12</u> 205-217 (1981).

- 165. SMITH, J.D. & LONGMORE, A.R. Behaviour of Phosphate in Estuarine Water. Nature <u>287</u> 532-534 (1980).
- 166. STIRLING, H.P. & WORMALD, A.P. Phosphate/Sediment Interaction in Tolo and Long Harbours, Hong Kong and its Role in Estuarine Phosphorus Availability. Estuarine Coastal Mar. Sci. <u>5</u> 631-642 (1977).
- 167. UPCHURCH, J.B., EDZWALD, J.K. & O'MELIA, C.R. Phosphates in Sediments of Pamlico Estuary. Environ. Sci. Tech. <u>8</u> 56-58 (1974).
- 168. VANOUS, R.D. Understanding Nephelometric Instrumentation. Internat. Lab. Jan/Feb. 97-108 (1979).
- 169. FUREDI-MILHOFER, H., BRECEVIC, L.J., OLJICA, E., PURGARIC, B., GASS, Z. & PEROVIC, G. The Influence of Precipitation Conditions on the Formation and Transformation of Calcium Phosphate Precipitates. In "Particle Growth in Suspension" 109-129 (Ed. Smith, A.L.) Academic Press, London (1973).
- 170. HAYDEN. P.L. & RUBIN, A.J. Systematic Investigation of the Hydrolysis and Precipitation of Aluminium III. In "Aqueous-Environmental Chemistry of Metals" 317-381 (Ed. Rubin, A.J.) Ann. Arbor. Sci. Michigan (1974).
- 171. BALE, A.J.. MORRIS, A.W. & HOWLAND, R.J.M. Measuring the Size Characteristics of Suspended Particles in an Estuary by Laser Fraunhofer Diffraction. Paper presented to conference on Transfer Processes in Cohesive Sediment Systems at the Freshwater Biological Assoc. Ambleside, U.K. 14-17 September (1981).
- 172. COONLEY, Jr. L.S., BAKER, E.B. & HOLLAND, H.D. Iron in the Mullica River and in Great Bay, New Jersey. Chem. Geol. <u>7</u> 51-63 (1971).
- 173. KESTER, D.R., DUEDALL, I.W., CONNORS, D.N. & PYTKOWICZ, R.M. Preparation of Artificial Seawater. Limnol. Oceanogr. <u>12</u> 176-179 (1967).
- 174. GREG, S.J. & SING, K.S.W. "Adsorption, Surface Area and Porosity" pp 371, Academic Press, London (1967).
- 175. PADDAY, J.F. Measurement of Surface Area by the Adsorption of Dyes from Solution. In "Surface Area Determination" 331-340 (Ed. Everett, D.M. & Ottewill, R.H.) Proc. Int. Symp. Surface Area Determination. Butterworths, London (1969).

- 176. KIPLING. J.T. & WILSON, R.B. Adsorption of Methylene Blue in the Determination of Surface Areas. J. Appl. Chem. <u>10</u> 104-113 (1960).
- 177. GAST, R.G., LANDA, E.R. & MEYER, G.W. The Interaction of Water with Goethite (α -Fe OOH) and Amorphous Hydrated Ferric Oxide Surfaces. Clays Clay Miner. <u>22</u> 31-39 (1974).
- 178. BRUNAUER. S., EMMETT, P.H. & TELLER, E.J. Adsorption of Gases in Multimolecular Layers. J. Am. Chem. Soc. <u>60</u> 309-319 (1938).
- 179. TAYLOR, R.M. & SCHWERTMANN, U. The Influence of Aluminium on Iron Oxides. VII. Substitution of Al for Fe in Synthetic Lepidocrocite. Clays Clay Miner. <u>28</u> 267-271 (1980).
- 180. CLARKE. P.E., NICHOL, A.W. & CARLOW, J.S. A Precision Velocity Generator Suitable for Mössbauer Experiments. J. Sci. Insts. <u>44</u> 1001-1004 (1967).
- 181. BURTON, J.D. Problems in the Analysis of Phosphorus Compounds. Water Res. <u>7</u> 291-307 (1973).
- 182. MURPHY, J. & RILEY, J.P. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. Anal. Chim. Acta. <u>27</u> 31-36 (1962).
- 183. STRICKLAND, J.D.H. & PARSONS, T.R. A Practical Handbook of Seawater Analysis. Bull. Fish. Res. Bd. Canada, pp 310 (No. 167) (1968).
- 184. HAMILTON-JENKIN, A.K. Mines of Devon, Vol. 1. The Southern Area. David & Charles, Newton Abbot, England. pp 154 (1974).
- 185. KNOX, S., TURNER, D.R., DICKSON, A.G., LIDDICOAT, M.I., WHITFIELD, M. & BUTLER, E.I. Statistical Analysis of Estuarine Profiles. Application to Manganese and Ammonium in the Tamar Estuary. Estuarine Coastal Shelf Sci. <u>13</u> 357-371 (1981).
- 186. BENES, P. & STEINNES, E. <u>In situ</u> Dialysis for the Determination of the States of Trace Elements in Natural Waters. Water Res. <u>8</u> 947-953 (1974).
- 187. GIBBS, M.M. A Simple Method for the Rapid Determination of Iron in Natural Waters. Water Res. 13 295-297 (1979).

- 188. HUTCHINSON, G.E. Limnological Studies in Connecticut. 4. The Mechanism of Intermediary Metabolism in Stratified Lakes. Ecol. Monogr. <u>11</u> 21-60 (1941).
- 189. KENNEDY, V.C., ZELLWEGER, G.W. & JONES, B.F. Filter Pore Size Effects on the Analysis of Al, Fe, Mn and Ti in Water. Water Resources Res. <u>10</u> 785-790 (1974).
- 190. HEANEY, S.I. & DAVISON, W. The Determination of Ferrous Iron in Natural Waters with 2,2' Bipyridyl. Limnol. Oceanogr. <u>22</u> 753-760 (1977).
- 191. EVANS, T.D., LEAL, J.R. & ARNOLD, P.W. The Interfacial Electrochemistry of Goethite (α -FeOOH) Especially the Effect of CO₂ Contamination. J. Electroanal. Chem. <u>105</u> 161-167 (1979).
- 192. CABRERA, F., MADRID, L. & DE ARAMBARRI, P. Adsorption of Phosphate by Various Oxides. Theoretical Treatment of the Adsorption Envelope. J. Soil Sci. <u>28</u> 306-313 (1977).
- 193. FORBES, E.A., POSNER, A.M. & QUIRK, J.P. Specific Adsorption of Inorganic Mercury (II) Species and Cobalt (III) Complex Ions on Goethite. J. Colloid Interface Sci. <u>49</u> 403-409 (1974).
- 194. ATKINSON, R.J., POSNER, A.M. & QUIRK, J.P. Adsorption of Potential-Determining Ions at the Ferric Oxide-Aqueous Electrolyte Interface. J. Phys. Chem. <u>71</u> 550-558 (1967).
- 195. KANEKO, K., SERIZAWA, M., ISHIKAWA, T. & INOUYE, K. Dielectric Behaviour of Water Molecules Adsorbed on Iron (III) Oxide Hydroxides. Bull. Chem. Soc. Japan <u>48</u> 1764-1769 (1975).
- 196. SUNG, W. Catalytic Effects of the γ-FeOOH (Lepidocrocite) Surface on the Oxygenation Removal Kinetics of Fe (II) and Mn (II). Report No. AC-12-80. California Institute of Technology, Pasadena, California. pp 107 (1980).
- 197. ANDERSON, M.A. & MALOTKY, D.T. The Adsorption of Protolysable Anions on Hydrous Oxides at the Isoelectric pH. J. Colloid Interface Sci. <u>72</u> 413-427 (1979).

279.

198. DAVIS, J.A. Adsorption of Trace Metals and Complexing Ligands at the Oxide/Water Interface. Ph.D. Thesis, Stanford University, California 305 pp (1977).

- 199. AVOTINS. P.V. Adsorption and Coprecipitation Studies of Mercury on Hydrous Iron Oxides. Ph.D. Thesis, Stanford University, California 134 pp (1975).
- 200. VAN DEN HUL, H.J. & LYKLEMA, J. Determination of Specific Surface Areas of Dispersed Materials. Comparison of the Negative Adsorption Method with some Other Methods. J. Am. Chem. Soc. <u>90</u> 3010-3030 (1968).
- 201. BRUNAUER, S., DEMING. L.S., DEMING, W.S. & TELLER, E. Theory of the Van Der Waal's Adsorption of Gases. J. Am. Chem. Soc. <u>62</u> 1723 (1940).
- 202. DE BOER, J.H. The Structure and Properties of Porous Materials. p. 68. Butterworths, London (1958).
- 203. JEFFERSON, D.A., THOMAS. J.M. & EGERTON, R.F. Heterogeneous Catalysis and Electron Microscopy. Chem. in Br. <u>17</u> 514-521 (1981).
- 204. BANWELL, C.N. Fundamentals of Molecular Spectroscopy. Chap. 8 322-333. McGraw Hill, London (1972).
- 205. COTTON & WILKINSON. Advanced Inorganic Chemistry. Wiley Interscience, New York. 3rd Ed. pp 1145 (1972).
- 206. ROSSITER, M.J. & HODGSON, A.E.M. A Mössbauer Study of Ferricoxyhydroxides. J. Inorg. Nuclear Chem. 27 63-71 (1965).
- 207. COEY, J.M.D. & READMAN, P.W. Characterisation and Magnetic Properties of Natural Ferric Gel. Earth Planet. Sci. Letts. <u>21</u> 45-51 (1973).
- 208. DICKSON, D.P.E., HELLER-KELLAI, L. & ROZENSON, I. Mössbauer Spectroscopic Studies of Iron in Organic Material from Natural Sedimentary Environments. Geochim. Cosmochim. Acta <u>43</u> 1449-1453 (1979).
- 209. SHAW, D.J. Introduction to Colloid and Surface Chemistry. 2nd Ed. pp 236. Butterworths, London. (1970).

- 210. TAMURA, H., GOTO, K. & NAGAYAMA, M. The Effect of Ferric Hydroxide on the Oxygenation of Ferrous ions in Neutral Solutions. Corrosion Sci. <u>16</u> 197-207 (1976).
- 211. RODIGUIN, N.M. & RODIGUINA, E.N. Consecutive Chemical Reactions. D. Van Nostrand Co. Inc., New Jersey, pp 251 (1964).
- 212. BARROW, G.M. Physical Chemistry. 3rd Ed. McGraw Hill, Tokyo, pp 798 (1973).
- 213. SUNG, W., MORGAN, J.J. Oxidative Removal of Mn(II) from Solution Catalysed by the Y-FeOOH (Lepidocrocite) Surface. Geochim. Cosmochim. Acta 2377-2384 (1981).
- 214. LAIDLER, K.J. Chemical Kinetics. 2nd Ed. McGraw Hill, New York, pp 566 (1965).
- 215. SWINBOURNE, E.S. Analysis of Kinetic Data. Nelson, London pp 126 (1971).
- 216. ASTON, S.R., THORNTON, L., WEBB, J.S. MILFORD. B.L. & PURVES, J.B. Arsenic in Stream Sediments and Waters of South West England. Sci. Tot. Env. <u>4</u> 347-358 (1975).
- 217. LOWELL, S. Introduction to Powder Surface Area. Wiley Interscience, Chichester pp 199 (1979).

APPENDIX 1 Published Work

.

• •

.

.

.

.

Environmental Technology Letters, Vol. 2, pp. 371-378 © Science and Technology Letters, 1981

PHOSPHATE ADSORPTION ONTO IRON OXYHYDROXIDES AT NATURAL CONCENTRATIONS

S.A. Crosby, E.I. Butler +, D.R. Turner +, M. Whitfield +, D.R. Glasson + + and G.E. Millward*

Department of Marine Science, Plymouth Polytechnic, Plymouth PL4 8AA, Devon, U.K.

(Received 15 May 1981; in final form 22 July 1981)

ABSTRACT

The adsorption of phosphate onto iron oxyhydroxide precipitates derived from ferric and ferrous iron is reported using conditions very similar to those encountered in natural waters. The freshly precipitated material derived from ferric iron is very active and the adsorption is independent of pH, temperature and ionic strength, whereas for precipitated ferrous iron the adsorption is strongly dependent on all three factors. The aged (20 h) precipitates derived from ferric iron show an adsorption behaviour which is independent of temperature but which is dependent on pH and ionic strength. In contrast the aged precipitates derived from ferrous iron showed no phosphate uptake.

To whom correspondence should be addressed.

- [†] Marine Biological Association, The Laboratory, The Hoe, Plymouth, Devon.
- ^{††} Department of Environmental Sciences, Plymouth Polytechnic, Plymouth PL4 8AA, Devon.

INTRODUCTION

The relative importance of freshly precipitated or aged iron oxyhydroxides in controlling the composition of ratural waters is not fully understood despite extensive laboratory studies of the sorption of both anions 1-5 and cations 6-10. Iron-phosphate interactions in various media have been investigated in some detail¹¹⁻¹⁵. Most workers. however, have used synthetic precipitates prepared from ferric salts and experimental conditions more representative of the high P and/or Fe levels encountered in sewage and water treatment plants¹⁶ than of the natural environment. Furthermore, most studies involve the precipitation of iron oxyhydroxide by the hydrolysis of ferric salts whereas under natural conditions it is more commonly precipitated chemically by the hydrolysis and oxidation of ferrous compounds. In the environment ferrous compounds are present at the oxic/anoxic boundary in stabilised lakes and fjords, at the surface of anoxic sediments and in acid mine streams. Consideration of the solubility products of ferrous and ferric hydroxides¹⁷ indicates that the rate of nucleation of ferrous hydroxide is much slower than ferric hydroxide. This suggests that the precipitates derived from these two sources will have different morphologies and possibly different surface characteristics.

EXPERIMENTAL

The iron oxyhydroxides were formed by the addition of 0.05M FeCl₃ or FeCl₂ to either filtered seawater or distilled water. The latter contained a carbonate buffer of approximately 2m equivalents to stabilise the pH at values within the range 6.5 to 8.3. The pH was adjusted by the addition of 0.1M NaOH or HCl and the maximum variation of pH during the course of an adsorption experiment was ± 0.2 pH unit in seawater and ± 0.4 in distilled water. The experiments were carried out in temperature controlled rooms set at 15° C and 2° C. The iron concentration was 5×10^{-5} M. 1 litre batches of solution were used to reduce losses of iron to the walls of the vessel to <10%. The precipitates were either freshly prepared in situ or aged for 20 h in situ and in the case of Fe²⁺ derived precipitates the samples were stirred open to the air. The phosphate was then added in the form of NaH_2PO_4 , to give a total phosphate concentration of 1 μ M, which is typical of levels in natural waters. The uptake of phosphate was monitored over 2 h by removing 25 ml aliquots in a syringe and filtering the sample through 0.45 µm Millipore filters. The dissolved phosphate was measured using the molybdenum blue complex, single reagent method¹⁸, using 10 cm cells at 885 nm on a Pye Unicam SP500 spectrophotometer. A coefficient of variation of $\pm 5\%$ was obtained during calibration runs at a phosphate concentration of 1 μ M. FAA analyses of the filtrates for iron showed that, except for ferrous iron in seawater, all the iron was retained by the filter. The surface areas of the two aged iron oxyhydroxides prepared in distilled water were measured using the B.E.T. nitrogen adsorption technique after washing the precipitate with acetone and outgassing for 24 h at room temperature. The powder X-ray diffraction patterns of the precipitates were obtained from a Hilger-Watts Y90 X-ray diffractometer using a molybdenum source.

RESULTS AND DISCUSSION

The ferric derived precipitate had a surface area of $232 \text{ m}^2 \text{ g}^{-1}$ which is in agreement with values found for amorphous iron oxyhydroxides 19,20, but which is relatively large compared to the value of $48 \text{ m}^2 \text{ g}^{-1}$ reported for synthetic goethite (α -FeOOH)¹. The form of the B.E.T. isotherm and hysteresis was consistent with narrow-necked pores of size 2 to 20 nm. The X-ray diffraction patterns suggested a mixture of poorly crystallised goethite and amorphous ferric gel. The ferrous derived precipitates had a surface area of $121 \text{ m}^2 \text{ g}^{-1}$ with a more open pore structure and pore sizes in the range 5 to 50 nm. The surface area obtained for the ferrous derived material is consistent with that of lepidocrocite (γ -FeOOH)²¹ formed under similar conditions and the precipitates with lepidocrocite.

The adsorption studies were mainly carried out at 15⁰C with some experiments at 2⁰C and the pH range studied was 6.5 to 8.3. However, only a proportion of the results are shown here. Figure 1 shows the adsorption of phosphate onto fresh ferric and ferrous derived precipitates in seawater (pHs 7.4 and 7.9) and distilled water (pHs 7.9 and 8.0) at 15°C. The ferric derived material is very active and the equilibrium concentration which is reached within 5 minutes, is independent of pH, temperature and ionic strength. In contrast the adsorption onto the ferrous derived material is apparently linked to the rate of hydrolysis and oxidation of Fe^{2+} . The results reported here show that the rate of phosphate removal from solution decreases with increasing pH and increasing ionic strength. Additional experiments at 2°C showed that the removal is temperature dependent. The behaviour of the phosphate removal is similar to the known oxidation kinetics of Fe²⁺ in solution²² and the adsorption follows the appearance of the solid phase. The uptake of phosphate in distilled water at pH = 8.0 was initially rapid and



<u>Figure 1:</u> Phosphate adsorption onto freshly precipitated iron oxyhydroxides at 15° C. The graph shows the concentration of dissolved phosphate in the filtrate as a function of time. \triangle - ferric iron in distilled water and seawater; \bigcirc - ferrous iron in seawater; \bigcirc - ferrous iron in distilled water.

comparable with adsorption onto freshly precipitated ferric derived material. However, this uptake was followed by desorption with an equilibrium value of 0.42 µmole l^{-1} being achieved after about 20 h. Initially the desorption is due to the pH changes as equilibrium is regained (i.e. 10 minutes) after the addition of the acidic FeCl₂ but in the longer term (20 h) it is thought to be physically induced by a reduction in surface area accompanying the relatively rapid formation of a more crystalline material. Similar trends were observed at other pHs. In seawater the rate of removal by the ferrous derived precipitate was strongly pH dependent and was generally much slower than that observed for the ferric derived material.

Figure 2 shows the adsorption of phosphate onto aged ferric and ferrous derived precipitates in seawater and distilled water over the pH range 6.9 to 8.3, at 15° C. For the ferric derived precipitates the approach to equilibrium did not follow 1st or 2nd order kinetics. Equilibrium was achieved in about 60 minutes and the approach to equilibrium was temperature independent. The equilibrium value is inversely dependent on pH which suggests that the adsorption may be linked to the speciation of the anion and the charge on the surface.



Figure 2: Phosphate adsorption onto aged iron oxyhydroxides at 15° C. The graph shows the concentration of dissolved phosphate in the filtrate as a function of time. \triangle - ferrous iron in distilled water and seawater; \bigcirc - ferric iron in seawater; \bigotimes - ferric iron in distilled water.

In seawater at pH = 7.5 the major form is HPO_4^{2-} while at pH = 8.2 there is 70% of HPO_4^{2-} species and 30% of PO_4^{3-} species²³. A $PH_{ZPC} = 7.9$ has been obtained for iron oxyhydroxides in 0.111 NaNO₃¹ but in seawater the surface charge characteristics may be conditioned by the co-adsorption of Mg^{2+} and/or Ca²⁺ ions²⁴. If electrostatic interactions are important then increases in the proportion of PO_4^{3-} species would lead to an increase in electrostatic repulsion and a decrease in adsorption. A similar hypothesis can be invoked for the results in distilled water where below pH = 7.3, $H_2PO_4^{-}$ is the major form whilst above this value HPO_4^{2-} species become important²³. Again the adsorption could be explained by a change in phosphate speciation.

In contrast the aged ferrous derived precipitate is inactive in both seawater and distilled water. Phosphate was not adsorbed at any pH in the range 7.3 to 8.2, even when the experiments were extended for a period of 60 h. The product of the hydrolysis and oxidation of Fe^{2+} has been identified, in this work and elsewhere²², as lepidocrocite which has a pH_{ZPC} = 6.2^{21} . Thus, these experiments are carried out over a pH range where the surface was probably negatively chargeo so that electrostatic repulsion could be an important controlling factor on

phosphate uptake. This hypothesis may also be extended to explain the adsorption of phosphate onto synthetic goethite $(\alpha$ -FeOOH)¹, which has a pH_{ZPC} = 8.5²¹.

Field studies of phosphate behaviour in natural waters tend to suggest that a buffer mechanism maintains a constant inorganic phosphate concentration²⁵. However, phosphate removal has been observed in the low salinity region of estuaries²⁶ and in laboratory simulation experiments in which iron has been implicated in the removal mechanism^{27,28}. The results reported here suggest that there are important differences in the behaviour of ferric oxyhydroxide obtained from ferrous and ferric sources that must also be taken into consideration. This applies particularly to those iron compounds which are freshly precipitated and are highly active. The precipitation of Fe^{3+} removes about 90% of the phosphate independently of pH, temperature and ionic strength. Ferrous iron, remobilised from anoxic environments, also produces an active fresh precipitate but in this case the adsorption, particularly in saline waters, is less rapid and is dependent on pH, temperature and ionic strength. Furthermore, the initial rapid uptake onto fresh ferrous derived precipitates is followed by a slow desorption. The uptake of phosphate by the aged ferric derived precipitates is dependent on pH and ionic strength, whilst the aged ferrous derived precipitates. are inactive. This indicates that caution should be exercised in making generalisations about the role of iron oxyhydroxides in controlling the concentration of phosphate (and other trace components) in natural waters. In particular much more attention should be focussed on the behaviour of material derived from the hydrolysis and oxidation of ferrous iron.

ACKNOWLEDGEMENTS

The project is supported by an NERC (CASE) research studentship to S.A. Crosby.

REFERENCES

1.	Yates, D.E. & Healy, T.W. J. Colloid Interface Sci. <u>52</u> , 222-228 (1975)
2.	Parfitt, R.L. & Russell, J.D. J. Soil Sci. <u>28</u> , 297-305
	(1977)
3.	Anderson, M.A. & Malotky, D.T. J. Colloid Interface Sci.
	<u>72</u> , 413-427 (1979)
4.	Hsu, P.H. Water Res. <u>10</u> , 903-907 (1976)
5.	Lijklema, L. Env. Sci. Tech. <u>14</u> , 537-541 (1980)
6.	Vuceta, J. & Morgan, J.J. Env. Sci. Tech. <u>12</u> , 1302-1309
	(1978)
7.	Gadde, R.R. & Laitinen, H.A. Anal. Chem. <u>46</u> , 2022-2026 (1974)
8.	Davis, J.A. & Leckie, J.O. Env. Sci. Tech. <u>12</u> , 1309-1315
	(1978)
9.	Millward, G.E. Env. Tech. Letts. <u>1</u> , 394-399 (1980)
10.	Swallow, K.C., Hume, D.N. & Morel, F.M.M. Env. Sci. Tech.
	<u>14</u> , 1326-1331 (1980)
11.	Pomeroy, L.R., Grant, E.E. & Smith, C. Limnol. Oceanogr. 10,
	167-172 (1965)
12.	Mortimer, C.H. Limnol. Oceanogr. <u>16</u> , 387-404 (1971)
13.	Butler, E.I. & Tibbets, S. J. Mar. Biol. Ass. U.K. <u>52</u> ,
	681-699 (1972)
14.	Lijklema, L. in SIL-UNESCO Symposium, Amsterdam (Junk, Ine
	Hague, 1976)
15.	Upchurch, J.B., Edzwald, J.K. & O'Mella, C.R. Env. Sci. Tech.
	8, 55-58 (1974)
16.	Leckie, J.U. & Sturm, W. In water Quartey improvement by
	Folgestalden (L. H.) Hotor Posource Symposium 237-249
	(University of Toyac Press Austin 1970)
17	(university of fexas fress, Austin, 1970)
17.	Wurphy 1 & Piley 1 P Anal Chim Acta 27, 31-36 (1962)
10. 10	Takomatsu N $(1000 \text{ gr}, 500 \text{ gr})$ (1000 gr)
13.	Takella (50, 11. 0. occurregt : 000. 00p. <u></u> , 00. 0 (19.0)

rs =

.

- 20. Byden, J.C., McLaughlin, J.R. & Syers, J.K. J. Soil Sci. 28, 79-92 (1977)
- Cabrera, F., Madrid, L. & De Arambarra, P. J. Soil Sci.
 28, 305-313 (1977)
- 22. Sung, W. & Morgan, J.J. Env. Sci. Tech. 14, 561-568 (1980)
- Kester, D.R. & Pyktowitcz, R.M. Limnol. Oceanogr. <u>12</u>, 243-252 (1967)
- 24. Tipping, E. Geochim. Cosmochim. Acta 45, 191-199 (1981)
- 25. Liss, P.S. in 'Estuarine Chemistry' (Eds. Burton, J.D. & Liss, P.S.) 93-130 (Academic Press, London, 1976)
- 26. Morris, A.W., Bale, A.J. & Howland, R.J.M. Estuarine Coastal Shelf Sci. <u>12</u>, 205-216 (1981)
- 27. Sholkovitz, E.R. Geochim. Cosmochim. Acta 40, 831-845 (1976)
- 28. Bale, A.J. & Morris, A.W. Unpublished data.