The Role of Adsorption in the Adsorbing Colloid Flotation of Anions

PhD Thesis
Swinburne University of Technology

Giulia Angerosa
ABSTRACT

Adsorbing colloid flotation of mercury(II), as a function of chloride concentration and pH, and sulphate and phosphate as a function of pH was carried out in the total carry-over mode (Sanciolo, 1993) and found to be highly successful. A mixed hydrous oxide containing equal portions of aluminium(III) and iron(III) was used in the case of mercury and a mixed hydrous oxide containing a 2:1:1 ration of aluminium(III):iron(III):iron(II) was used in the case of sulphate and phosphate. A dual surfactant mixture of sodium dodecyl sulphate (SDS) and dodecanoic acid (DA) was used in all three cases. Flotation was found to be effective both for model, simulated waste samples and for industrial effluents from a chloro-alkaline factory (high in mercury(II)) and a dye-making factory (high in sulphate).

Adsorption experiments were also carried out, for the simulated waste, under similar conditions to the flotation experiments, and were found to correlate remarkably well with each other. Precipitates of small size were found to occur at low to medium pH due to the relatively insolubility of dodecanoic acid at low pH. In the presence of mercury, these precipitate altered in appearance, particle size and number. Surfactant, specifically dodecanoic acid was then found to significantly change the adsorption profile of mercury, especially at high chloride concentrations.

Sulphate and phosphate were found to adsorb, and to float, in a fashion expected of anionic materials. Specifically, their removal decreased as pH increased. Mercury, in the presence of high concentrations of chloride, exists predominantly in an anionic form (eg. HgCl$_4^{2-}$) and might have been expected to mimic the behaviour of sulphate and phosphate. However, it did not. Mercury removal was enhanced at high pH values, similar to that observed with aqueous heavy metal cations (Crawford et al., 1993a), and chloride inhibited both adsorption and flotation.
ACKNOWLEDGEMENTS

I would like to express my heartfelt thanks to all the staff and postgraduate students within the chemistry department at Swinburne University with special mention to:

Dr Peter Sanciolo and Dr Russel Crawford for their friendship and support.

Dr David Mainwaring for his initial guidance and supervision.

Dr Ian H. Harding for his guidance, patience, advice, supervision and above all friendship.

To my parents and brother for their understanding faith and support.

To my husband Paul Jeffery I love you.

To my eldest son Joel Jeffery who in the face of adversity gave me the courage and strength to continue.

(To my child who will never see light, may your spirit continue to shine)
DECLARATION

This thesis is submitted in full completion of a PhD at Swinburne University of Technology. It contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge it contains no material previously published or written by another person except where due reference is made in the text of the thesis. Where assistance or help has been given in order to complete all or any portion of the research in this thesis, due recognition has been given.

Ms Giulia Angerosa

23/12/05
TABLE OF CONTENTS

Abstract ........................................................................................................................................ i
Acknowledgement ................................................................................................................... ii
Declaration ..................................................................................................................................... iii
Table of Contents ....................................................................................................................... iv
List of Figures ............................................................................................................................ ix
List of Tables .............................................................................................................................. xix

Chapter One: INTRODUCTION .............................................................................................. 1

Chapter Two: REMOVAL FROM SOLUTION OF MERCURY(II), SULPHATE AND PHOSPHATE ................................................................................................................................. 3
2.1 Aqueous Chemistry and Treatment Technologies ............................................................... 3
2.1.1 Mercury ............................................................................................................................... 3
2.1.1.1 Chemical Precipitation .................................................................................................... 6
2.1.1.2 Chemical Reduction ........................................................................................................ 6
2.1.1.3 Ion Exchange .................................................................................................................. 7
2.1.1.4 Solvent Extraction .......................................................................................................... 8
2.1.1.5 Filtration ........................................................................................................................ 9
2.1.1.6 Chemical Absorption/Adsorption ................................................................................... 9
2.1.1.7 Adsorbing Colloid Flotation ......................................................................................... 9
2.1.2 Phosphate .......................................................................................................................... 10
2.1.2.1 Electrodialysis .............................................................................................................. 12
2.1.2.2: Filtration Reverse Osmosis ......................................................................................... 13
2.1.2.3 Precipitation .................................................................................................................. 14
2.1.3 Sulphate ............................................................................................................................. 15
2.1.3.1 Treatment as a Sewage Waste ....................................................................................... 15
2.1.3.2 Screening and Sedimentation ....................................................................................... 18
2.1.3.3 Filtration ....................................................................................................................... 18
2.1.3.4 Precipitation ................................................................................................................ 18
2.1.3.5 Electrodialysis and Reverse Osmosis .......................................................................... 19
2.1.3.6 Ion Exchange .............................................................................................................. 19
2.2 Adsorption from Solution ...................................................................................................... 19
2.2.1 Site Binding and its Role in Adsorption Processes ............................................................ 20
2.2.2 Adsorption of Cations versus Anions ........................................... 21

2.3 Adsorbing Colloid Flotation ......................................................... 24
  2.3.1 History of Adsorbing Colloid Flotation (ACF) ......................... 25
  2.3.2 Definition of Adsorbing Colloid Flotation ............................ 25
  2.3.3 Apparatus and Techniques .................................................... 26
  2.3.4 Process Variables ............................................................... 29
    2.3.4.1 Surfactant concentration ............................................ 30
    2.3.4.2 Colloid Concentration .............................................. 30
    2.3.4.3 pH of the solution .................................................... 31
    2.3.4.4 Ionic strength ......................................................... 31
    2.3.4.5 Foam Stability ......................................................... 31
    2.3.4.6 Induction time ......................................................... 32
    2.3.4.7 Temperature ............................................................ 32
    2.3.4.8 Gas flow-rate ......................................................... 33
  2.3.5 Examples of Successful Adsorbing Colloid Flotation ............... 33

2.4 Summary .......................................................................................... 35

Chapter Three: EXPERIMENTAL METHODOLOGY .......................... 37

3.1 Reagents and Solutions ............................................................. 37
  3.1.1 Glassware ........................................................................... 37
  3.1.2 Stock Solutions ................................................................. 37
    3.1.2.1 Sulphate Experiments ............................................. 37
    3.1.2.2 Mercury Experiments ............................................. 38
    3.1.2.3 Phosphate Experiments ......................................... 38
    3.1.2.4 Nitrate Experiments .............................................. 38
  3.1.3 Surfactants ........................................................................... 38
  3.1.4 “Model” Waste Samples .................................................... 39
    3.1.4.1 Sulphate ................................................................. 39
    3.1.4.2 Mercury ................................................................. 39
    3.1.4.3 Phosphate ............................................................... 39
    3.1.4.4 Nitrate ................................................................. 39
  3.1.5 Industrial Waste Samples .................................................... 39
    3.1.5.1 Sulphate Industrial Waste Samples ............................ 39
    3.1.5.2 Mercury Industrial Waste Samples ............................ 40
    3.1.5.3 Phosphate and Nitrate Industrial Waste Samples .......... 41
3.2 Oxide Preparation .............................................................................. 41
3.3 Adsorption Experiments ................................................................. 42
3.4 Flotation Experiments ...................................................................... 44
  3.4.1 Adsorbing Colloid Flotation ......................................................... 44
  3.4.2 Foam Stability ........................................................................... 46
  3.4.3 Foam Type ................................................................................ 46
3.5 Surface Characterisation ................................................................... 47
  3.5.1 Particle Size ............................................................................. 47
  3.5.2 Surface Area ................................................................................ 47
  3.5.3 Electrophoretic Mobility ............................................................... 48
    3.5.3.1 Phosphate and Mercury Experiments ..................................... 48
    3.5.3.2 Sulphate Experiments ............................................................ 49
3.6 Analytical Procedures ....................................................................... 49
  3.6.1 Sulphate ................................................................................... 49
  3.6.2 Phosphate .................................................................................. 49
  3.6.3 Mercury ..................................................................................... 49
  3.6.4 Nitrate ....................................................................................... 50
  3.6.5 pH .............................................................................................. 51

Chapter Four: ADSORBING COLLOID FLOTATION OF SULPHATE ....... 52
4.1 Introduction ....................................................................................... 52
4.2 Preliminary Investigation .................................................................... 53
  4.2.1 Choice of Surfactant and Colloid Mixtures ................................. 53
  4.2.2 Concentration of Colloid ............................................................ 58
4.3 Sulphate Adsorption .......................................................................... 60
  4.3.1 Sulphate Adsorption - Percent Adsorption ............................... 61
  4.3.2 Sulphate Adsorption - Adsorption per Mass of Substrate .......... 64
  4.3.3 Sulphate Adsorption – Adsorption per Mole of Substrate ......... 66
  4.3.4 Sulphate Adsorption - pH Adjustment ....................................... 68
4.4 Electrophoretic Mobility ..................................................................... 73
  4.4.1 Electrophoretic Mobility of Hydrous Aluminium(III) Oxide ....... 74
  4.4.2 Electrophoretic Mobility of Hydrous Iron(III) Oxide ................. 77
  4.4.3 Electrophoretic Mobility of Hydrous Iron(II) Oxide .................. 78
  4.4.4 Electrophoretic Mobility of Hydrous Mixed Oxide .................... 81
4.5 Implications to Models of Sulphate Adsorption ............................... 83
LIST OF FIGURES

Figure 2.1: Mercury cycling in fresh water ........................................... 4

Figure 2.2: Key Processes that Affect the Speciation and Mobility
of Mercury(II) in Aquatic Systems ...................................................... 4

Figure 2.3: Phosphorus Cycle .......................................................... 11

Figure 2.4: Phosphorus Marine Cycle ............................................... 11

Figure 2.5: Sulphate Concrete Corrosion ......................................... 16

Figure 2.6: The Sulphur Cycle .......................................................... 17

Figure 2.7: Stylised Adsorption of Anions onto Hydrous Metal Oxides .... 23

Figure 2.8: Stylised Adsorption of (Hydrolysable) Cations onto Hydrous
Metal Oxides ...................................................................................... 24

Figure 2.9: Schematic Diagram of Adsorbing Colloid Flotation
(batch mode) ..................................................................................... 26

Figure 2.10: Schematic Diagram of Adsorbing Colloid Flotation
(continuous mode) ........................................................................... 27

Figure 3.1: Water Jacketed Reaction Vessel for Adsorption Studies ........ 43

Figure 3.2: Schematic Diagram of Adsorbing Colloid Flotation ............... 45

Figure 4.1: Foam Type as a function of the experimental conditions listed
in Table 4.1 ......................................................................................... 57
Figure 4.2: Adsorption of 2,000 ppm sulphate using a mixed hydrous oxide formed from a solution of Al(III):Fe(III):Fe(II) in the ratio of 2:1:1 ................................................................. 59

Figure 4.3: Percentage (%) adsorption of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 ppm (total) metal ion ................................................................. 61

Figure 4.4: Adsorption, by mass, of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 (total) metal ion ........................................................................... 65

Figure 4.5: Adsorption, by mole, of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 (total) metal ion ........................................................................... 67

Figure 4.6: Electrophoretic mobility of hydrous aluminium(III) oxide in the presence and absence of 1,000 ppm sulphate ......................... 75

Figure 4.7: Electrophoretic mobility of hydrous iron(III) oxide in the presence and absence of 1,000 ppm sulphate ......................... 77

Figure 4.8: Electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of 1,000 ppm sulphate ......................... 79

Figure 4.9: Electrophoretic mobility of mixed hydrous oxide in the presence and absence of 1,000 ppm sulphate. The mixed hydrous oxide was formed from a solution containing Al(III):Fe(III):Fe(II) at a ratio of 2:1:1 by mass ......................... 82

Figure 4.10: Schematic illustration of the difference between inner and outer sphere coordination of sulphate ions to a surface site ...... 84

Figure 4.11: Schematic illustration of inner and outer sphere adsorption at hydrous oxide surface .............................................. 85
Figure 4.12: Percentage (%) flotation of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 ppm (total) metal ion. Total surfactant concentration was 300 ppm and consisted of a 2:1 mixture of SDS to DA 89

Figure 4.13: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous aluminium(III) oxide formed from 1,000 ppm Al(III) 92

Figure 4.14: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous iron(III) oxide formed from 1,000 ppm Fe(III) 93

Figure 4.15: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous iron(II) oxide formed from 1,000 ppm Fe(II) 94

Figure 4.16: Comparison of adsorption and flotation of 1,000 ppm sulphate using a mixed hydrous oxide formed from a solution of 1,000 ppm (total) Al(III):Fe(III):Fe(II) in the ratio 2:1:1 95

Figure 4.17: Percentage (%) flotation of 25 ppm nitrate, using a mixed hydrous oxide, in the presence of 1,000 ppm sulphate using 300 ppm mixed surfactant consisting of SDS and DA in the ratio 2:1. The hydrous mixed oxide was formed from a solution of 1,000 (total) metal ion containing Al(III):Fe(III):Fe(II) in the ratio 2:1:1 98

Figure 4.18: Flotation of an industrial (PMA) waste sample containing 1,000 ppm sulphate. Flotation was effected with a mixed hydrous oxide formed from a 1,000 total metal ion solution of Al(III):Fe(III):Fe(II) in the ratio 2:1:1 and 300 ppm mixed surfactant consisting of SDS and DA in the ratio 2:1 100
Figure 5.1: Percentage (%) adsorption of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion ................................................................. 106

Figure 5.2: Adsorption, by mass, of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion ................................................................. 109

Figure 5.3: Adsorption, by mole, of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion ................................................................. 110

Figure 5.4: Electrophoretic mobility of hydrous aluminium(III) oxide in the presence and absence of 25 ppm phosphate ................. 112

Figure 5.5: Electrophoretic mobility of hydrous iron(III) oxide in the presence and absence of 25 ppm phosphate ......................... 114

Figure 5.6: Electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of 25 ppm phosphate ......................... 118

Figure 5.7: Electrophoretic mobility of mixed hydrous oxide in the presence and absence of 25 ppm phosphate. The mixed hydrous oxide was formed from a solution containing Al(III):Fe(III):Fe(II) at a ratio of 2:1:1 by mass ......................... 119

Figure 5.8: Percentage (%) flotation of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion. Total surfactant concentration was 300 ppm and consisted of a 2:1 mixture of SDS to DA ................................. 124

Figure 5.9: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous aluminium(III) oxide formed from 50 ppm Al(III) .... 127
Figure 5.10: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous iron(III) oxide formed from 50 ppm Fe(III) .......... 128

Figure 5.11: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous iron(II) oxide formed from 50 ppm Fe(II) .......... 129

Figure 5.12: Comparison of adsorption and flotation of 25 ppm phosphate using a mixed hydrous oxide formed from a solution of 50 ppm (total) Al(III):Fe(III):Fe(II) in the ratio 2:1:1 ......................... 130

Figure 6.1: Eh-pH Diagram for Mercury (adapted from Davis et al.(1997)) ...... 134

Figure 6.2: Speciation of 50 ppb Mercury(II) in 0.0001 M Cl⁻ solution ............... 136

Figure 6.3: Speciation of 50 ppb Mercury(II) in 0.001 M Cl⁻ solution ............... 137

Figure 6.4: Speciation of 50 ppb Mercury(II) in 0.01 M Cl⁻ solution ............... 137

Figure 6.5: Speciation of 50 ppb Mercury(II) in 0.1 M Cl⁻ solution ............... 138

Figure 6.6: Speciation of 50 ppb Mercury(II) in 1 M Cl⁻ solution ............... 138

Figure 6.7: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) ................................................................. 143

Figure 6.8: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA ................................................................. 145
Figure 6.9: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with no added chloride ........................................ 147

Figure 6.10: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with 0.01 M chloride ........................................ 149

Figure 6.11: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with 0.1 M chloride ........................................ 151

Figure 6.12: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with no added chloride ........................................ 153

Figure 6.13: Mercury remaining (ppb) following adsorption of “Hydrogen Effluent A” onto a mixed hydrous oxide of aluminium(III) and iron(III) in a mass ratio of 1:1 ......................................................... 154

Figure 6.14: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 4.0 .......... 156

Figure 6.15: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, in the presence of 400 ppb mercury, at pH 4.0 ................................................................. 157
**Figure 6.16:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added chloride and no added mercury, at pH 4.0 ......................................................... 157

**Figure 6.17:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 5.0 ................................................................. 158

**Figure 6.18:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 6.0 ................................................................. 158

**Figure 6.19:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 6.0 ................................................................. 159

**Figure 6.20:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 7.0 ................................................................. 159

**Figure 6.21:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 7.0 ................................................................. 160

**Figure 6.22:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 8.0 ................................................................. 160

**Figure 6.23:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 8.0 ................................................................. 161

**Figure 6.24:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 9.0 ................................................................. 161
Figure 6.25: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 9.0 ................................................................. 162

Figure 6.26: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 10.0 .......................................................................................... 162

Figure 6.27: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 10.0 .......................................................................................... 163

Figure 6.28: Adsorbing colloid flotation of Hydrogen Effluent A (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 and initial pH of 10.8) using 300 ppm SDS:DA at a ratio of 2:1 .................................................................................................. 166

Figure 6.29: Adsorbing colloid flotation of Hydrogen Effluent A (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 and initial pH of 10.8) using 200 ppm of mixed hydrous oxide formed from a 1:1 mixture of Al(III) and Fe(III) .......... 167

Figure 6.30: Percentage (%) floated of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III). The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 ................................................................. 169

Figure 6.31: Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at zero added chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1 .................................................................................................. 171
**Figure 6.32:** Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 0.01 M chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1 ...... 172

**Figure 6.33:** Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 0.1 M chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1 ...... 173

**Figure 6.34:** Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 1.0 M added chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1 ...... 174

**Figure 6.35:** Adsorbing colloid flotation of “Hydrogen Effluent A” (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 M and initial pH of 10.8) .............................................. 176

**Figure 6.36:** Adsorbing colloid flotation of “Cell Hosedown” (initial Hg concentration of 25,000 ppb, initial equivalent chloride concentration of 0.21 M and initial pH of 12.8) ......................... 176

**Figure 6.37:** Adsorbing colloid flotation of “Total Chlorine” (initial Hg concentration of 200 ppb, initial equivalent chloride concentration of 0.0024 M and initial pH of 10.8) ........................................ 177

**Figure 6.38:** Adsorbing colloid flotation of “14th Avenue” (initial Hg concentration of 56 ppb, initial equivalent chloride concentration of 0.063 M and initial pH of 9.5) ................................................................. 177
**Figure 6.39:** Adsorbing colloid flotation of “Chlorine Condensate” (initial Hg concentration of 300 ppb, initial equivalent chloride concentration too high to measure and initial pH of 4) .............................................. 178

**Figure 6.40:** Adsorbing colloid flotation of "Hydrogen Effluent B" (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 M and initial pH of 10.0) ....................................................... 178
LIST OF TABLES

Table 2.1: Typical Characteristics of Adsorption Processes .......................... 20

Table 3.1: Mercury Collected at ICI Chloro-Alkali Plant in Botany .................. 41

Table 3.2: Surface Area of Hydrous Metal Oxide Substrates .......................... 48

Table 4.1: Experimental Conditions used to Determine Foam Type during ACF of 1,000 pp, "Model" Sulphate Waste (concentations expressed in ppm) ................................................................. 56

Table 4.2: pH changes during the Adsorption of 1,000 ppm $\text{SO}_4^{2-}$ onto 1,000 ppm Hydrous Aluminium(III) Oxide ....................................................... 69

Table 4.3: pH changes during the Adsorption of 1,000 ppm $\text{SO}_4^{2-}$ onto 1,000 ppm Hydrous Iron(III) Oxide ......................................................... 70

Table 4.4: pH changes during the Adsorption of 1,000 ppm $\text{SO}_4^{2-}$ onto 1,000 ppm Hydrous Mixed Oxide (Al(III):Fe(III):Fe(II) = 2:1:1) .......... 71

Table 4.5: pH changes during the Adsorption of 1,000 ppm $\text{SO}_4^{2-}$ onto 1,000 ppm Hydrous Iron(II) Oxide ......................................................... 72
INTRODUCTION

Chemicals released into the environment are dispersed into air, water and soil/sediment at rates and in forms which are dependent on their physico-chemical properties. They can undergo chemical degradation by abiotic as well as biological processes, often resulting in degradation products which are more harmful than the original chemical. It is thus important to control the release of chemicals into the environment.

Industrial wastewaters contain organic and inorganic wastes, including heavy metals and anions. Numerous studies have been conducted on the treatment of heavy metals, but less so on the treatment of anionic waste. In this thesis anions will be the main focus of study.

Anions released into the aquatic environment are potentially hazardous to rural and urban waterways. Sulphate for example, causes acidification (sulphuric acid) of waterways which not only poses a threat to the environment through the deleterious effects of acidity, but also causes decay and degradation of materials used for channelling water (e.g. concrete storm water drains) (Binnie et al., 2002). Sulphate is also reduced to hydrogen sulphide under the anaerobic conditions of underground water systems and this results in subsequent problems to the air quality in such drains. Phosphate is another anion which causes considerable problems to the environment because of the eutrophication effect where ecology is disturbed by an abundant nutrient supply to micro-organisms and algae, causing them to undergo a population explosion (Jenkins and Ives, 1973).

Less obvious sources of anionic wastes include metal ions, such as mercury. Mercury can be discharged in a variety of chemical forms, one example of which results from the complexation of mercury(II) ions with anionic ligands, such as chloride and bromide, to form anionic complexes (e.g. \( \text{HgCl}_4^{2-} \)). These anions, together with the other common forms of discharged mercury; the metal and mercuric oxide, are all mildly toxic compounds (Hartung and Dinman, 1972). Their toxicity however is elevated by the conversion by microorganisms of inorganic mercury to monomethyl and dimethyl mercury (Jenson and Jernelov, 1969). Such organic forms of mercury have a greater residence time in the ecosystem, present greater physiological effects and are more concentrated through the biological food chain. Poisoning by methylmercury compounds results in neurological disorders. Damage is chiefly in the cerebellum and sensory pathways with lesions in the cerebral cortex of man (Holden, 1972).
With even the simplest of anions, such as sulphate and phosphate, causing environmental damage and well known toxic substances such as mercury being discharged in anionic form, it is not surprising that the requirements for clean water are becoming increasingly more stringent. Industry has been constantly searching for techniques to produce the cleanest possible effluent at minimum cost. The most common methods used to reduce anionic waste from entering waterways include precipitation, coagulation, ion exchange, chemical reduction, solvent extraction, chemical absorption, chemical adsorption, reverse osmosis and filtration; all of which will be discussed in the following chapter (Chapter 2), with specific reference to anionic mercury, sulphate and phosphate.

The purpose of this thesis is to investigate one such technology, that of adsorbing colloid flotation, for its effectiveness in treating anionic wastes such as sulphate, phosphate and mercury(II) chloride. A further goal will be to illustrate the importance (or lack thereof) of the adsorption step to the ultimate success of adsorbing colloid flotation.
REMOVAL FROM SOLUTION OF MERCURY(II), SULPHATE AND PHOSPHATE.

2.1 Aqueous Chemistry and Treatment Technologies

2.1.1 Mercury

Mercury can exist in the environment as the metal, as monovalent and divalent salts or as organomercurials (Holden, 1972; Ravichandran, 2004), and is toxic to most living organisms. Inorganic mercury compounds are rapidly accumulated in the kidney, the main target organ for these compounds. Methyl mercury rapidly appears in the blood where, in man, 80-90% is bound to red cells. The greater intrinsic toxicity of methyl mercury compared with inorganic mercury is due to its lipid solubility, which permits it to cross biological membranes more easily than inorganic mercury, especially into the brain, spinal cord, and peripheral nerves, and across the placenta (Hartung and Dinman, 1972). Mercury salts are excreted from the kidney, liver, intestinal mucosa, sweat glands, salivary glands and through milk, with the most important routes via the urine and faeces. The major effects of mercury poisoning take the form of neurological and renal disturbances, which are primarily associated with organic and inorganic mercury compounds respectively. (Forstner, 1979). The contamination of the environment by mercury laden industrial wastewater presents serious problems. As stated above, not only is inorganic mercury toxic but more importantly can readily convert to methyl mercury. Inorganic mercury discharged into deep water is acted upon by bacteria in bottom sediments to form methyl and dimethyl mercury. Fish and mammals absorb and retain methyl mercury thus accumulating it along the food chain (Holden, 1972).

The fate of mercury in the environment, and the major environmental process which affect speciation of mercury and mobility of mercury through the environment are illustrated in Figures 2.1 and 2.2 respectively.

The chemical and physical properties of mercury have resulted in many and varied applications ranging from the preparation of chlorine and caustic soda to its use in combination with other chemicals as a food seed fungicide. Of the many applications, chlorine and caustic soda preparation catalysts, agriculture, and paper manufacture probably result in the greatest direct discharge to the environment. In practice, a large portion of mercury and inorganic mercury compounds present in such industrial wastewater streams is removed prior to its disposal. Furthermore, mercury is, itself, a
Figure 2.1: Mercury cycling in fresh water

Figure 2.2: Key Processes that Affect the Speciation and Mobility of Mercury(II) in Aquatic Systems.
precious commodity and if in sufficient quantity may be economically recovered from that waste. However, although zero mercury discharge is the eventual goal, it is not economically achievable with current technology (Rajeshwar et al., 1994).

Safe disposal of mercury and mercury compounds along with ever more efficient waste minimisation schemes should be studied. In the USA, for example, approximately 100 metric tons of mercury per year (that is, for the years 1989 and 1990) is released into the environment from mining and mineral processing (Jasinski, 1995). In Australia, the major mercury consuming industry is the chloro-alkali industry. The chloro-alkali industry uses a continuous flow mercury cathode cell to produce chlorine and pure caustic soda, both being required to have a very low chloride content. A mercury cell is able to provide this because of mercury’s unusual propensity to form an amalgam with chloride. The ultra low chloride residual then results in a very pure grade of caustic soda (Hartung and Dinman, 1972).

Mercury in the chloro-alkali industry can be lost during several phases of the process including the formation of the caustic soda product, the overall cleaning of the mercury cell room, the brine solution saturate, and to air. The quantity of mercury that ultimately reaches the environment depends, to a large measure, on the overall operating efficiency of each phase involved. Mercury cell processes involve electrolysis of a sodium chloride solution. The mercury serves as the cathode, graphite as the anode. Sodium ion reacts with the mercury to form an amalgam, and chlorine gas is produced at the anode. The mercury flows through the cell, where the amalgam is mixed with water and forms one-half of an electrolytic cell, with iron serving as the other electrode. The regeneration cell removes sodium salt from the amalgam and produces caustic soda (approximately 50 % solution) and hydrogen gas. The regenerated mercury is then returned to the mercury cell, and the process is repeated. The brine solution leaves the mercury cell, is vacuum de-chlorinated and then purged with air to remove the last of the chlorine. The solution is then saturated with salt, and this is followed by a purification step, in which various impurities from the newly added salt are precipitated. The brine is passed through a filter and back to the mercury cell.

The major problem associated with the chloro-alkali plants at present is the safe disposal of the mercury containing brine sludges. The brine cannot be resaturated since the partly depleted brine (from electrolysis) requires solid salt by the mercury cell process. If only brine is available, this must be evaporated first to produce solid salt (EPA, 1985).
One irony in the above industrial process is that seawater is used to hose down all effluents into a holding tank. Thus, although the goal in terms of the chlorine and caustic soda is to have an ultra low level of chloride, the mercury waste ends up in the presence of very high concentrations of chloride.

There are various methods employed in the removal of mercury(II) from wastewater streams. They include chemical precipitation, chemical reduction, ion exchange, solvent extraction, filtration, chemical absorption and adsorption with activated carbon (EPA, 1972). All these methods will be discussed below. It is important to remember that although adequate, none of these methods are ideal and the search for a more efficient method is ever present.

2.1.1.1 Chemical Precipitation

Inorganic mercury can be removed from liquid solution by direct precipitation as an insoluble metal salt either with or without further processing. Raising the pH to the range of 10 to 12 with sodium hydroxide or sodium hypochlorite will result a hydrous mercuric oxide, which can then be removed by filtration. Mercury(II) ions can also be precipitated as mercuric sulphide by the addition of a soluble sulphide or hydrogen sulphide gas to the liquid solution. Sodium sulphide is generally used, and the colloidal mercuric sulphide formed can be separated from the liquid stream through flocculation with ferric chloride. Both these methods, however, suffer from incomplete precipitation (effluent contains approximately 1 ppm mercury) and the fine precipitate formed is difficult to remove (Logsdon and Symons, 1973).

2.1.1.2 Chemical Reduction

Mercuric ions can be chemically reduced by a variety of agents; alkali, metals, zinc, antimony, iron, aldehydes, hydrazine hydrate, and sodium borohydride among many others. Direct reduction of mercuric ions by passing the waste stream and an alkali metal amalgam through either an active bed of amalgamated steel turnings and pieces or an inert bed whereby additional amalgam is obtained along with metallic mercury appears to be a unique and clean way of removing mercury, but tests so far have indicated that a relatively high level of mercury ions remain in the treated effluent. Two commonly used chemical reduction schemes are the Ventron sodium borohydride process and the zinc reduction process both of which result in low ppb mercury limits (EPA, 1985).

In the Ventron process, sodium borohydride is used as a powerful reducing agent capable of reducing both mercuric and mercurous ions to the metal almost instantaneously. The
reaction has the advantage of taking place at low temperatures and is not critically pH dependent. Wastewater, containing inorganic mercury compounds, is fed with a 12 percent solution of sodium borohydride (in 40 percent caustic soda) into a static mixer. The pH is held between 9 and 11. The hydride reduces the mercury compounds yielding metallic mercury precipitate and hydrogen gas. Following separation of the gas, the sludge is passed to a cyclone containing polishing filters, where 80 to 90 percent of the mercury is recovered and purified by vacuum distillation (EPA, 1985).

In the zinc reduction process, mercury is treated as an aqueous solution, typically having a pH between 7 and 11 and containing 1 to 500 ppm of dissolved mercury. Treatment is effected by contact with a bed of reductor metal. Mercury is recovered as the metal with a typical removal efficiency of 90 %. The simplest method is to add an excess of zinc dust and to keep the dust suspended in the solution by constant stirring. The tanks and stirring blades should be baffled to avoid the formation of an air vortex, which would result in loss of the metallic zinc. The excess zinc settles quickly to the bottom of the bank when the agitation is stopped and the tank effluent will usually still contains a few ppm zinc. The metallic mercury obtained by reduction using zinc can be removed by filtration, although a method more applicable to the treatment of industrial wastewater is to pass the streams containing mercuric ions through a bed of coarser commercial zinc powders. The metallic mercury forms an alloy with zinc in the bed, which can be recovered later by heating the crude alloy, distilling off the mercury, and condensation of the vapours (USA EPA REPORT).

2.1.1.3 Ion Exchange

Ion exchange is another effective method for removing mercury (and other contaminants) from solution (Lloyd-Jones et al. 2004). By exchanging mercury onto a resin and then eluting it during regeneration, a harmful substance is removed from waste streams and transformed to a concentrated solution where it can be more easily precipitated by conventional techniques. A few cation exchangers have been successful in extracting ionic mercury, including Dowex 500w x-8, Dowex Al and Amberlite IRC-50 (Sanz et al., 2004; Kara, 2005; Kirzog et al., 2005). However cation exchange resins have little application in brine solutions where, because of the high chloride concentration, mercury exists as the anionic mercuric chloride ion. The most successful ion exchange processes for the removal of mercury from solution employs either anion exchangers or chelating resins. A number of patents exist describing the use of quaternary ammonium cross-linked resins and strongly basic anion exchange resin, having insoluble quaternary ammonium composition, are used to remove mercuric ions from liquid solution. Typical
effluent mercury concentrations of less than 0.01 ppm (100 ppb), are achieved with regeneration of the ion exchange resins using aqueous sulphide solution. Of the commercial ion-exchangers, Amberlite IRA-400 has been shown to adsorb significant quantities of mercury, regardless of pH, as long as the mercury is present as an anion (Becker and Eldridge, 1992). Two proven processes in commercial operations are the Osaka Soda Process (Daiso Co Ltd, 2005) and the Aktiebolaget Billingsfors-Langed Process, both of which are applicable to most mercury bearing streams and have the ability to reduce the mercury content in wastewater to less than 5 ppb.

In the Osaka Soda Process, wastewater is first collected in a storage tank, where any metallic mercury present is allowed to settle out. It is then chemically treated by adjustment of pH and free chlorine concentration, followed by ion exchange in a tower packed with Osaka's propriety ion exchange resin "IE". The mercury content of the wastewater is thus reduced to a range of 100-150 ppb. The stream then passes through a tower packed with another Osaka proprietary resin, designated "MR". Mercury content is reduced to an undetectable level in the MR tower when a fresh charge is used, however the effluent concentration gradually builds up to 5 ppb. Mercury is recovered from the ion exchange by periodic stripping. A sodium amalgam or other reducing agent is then added to the pregnant stripping liquid to reduce the mercury to metallic form (EPA, 1985).

In the Aktiebolaget Billingsfors-Langed process, the wastewater is first passed to a vessel where pH is adjusted to between 5 and 7 and mercury in colloidal form is oxidized by chlorination. Since the resins subsequently used are sensitive to oxidisers, excess chlorine is removed in a dechlorinator via activated carbon filtration. The water is then piped to a series of ion exchange towers filled with a stable resin, Q-13, which reduces the mercury level to approximately 100 ppb. The mercury level is reduced to a few parts per billion in an absorption tower containing another resin, Q-sorb. The Q-13 resin is regeneratable to an electrolytic circuit for recovery of the metal (EPA, 1985), the case is not the same for Q-sorb.

2.1.1.4 Solvent Extraction

Solvent extraction of mercury for waste minimisation was presented as a viable option by Chapman and Capan (EPA, 1985). The mercury content in the feed is first converted to mercuric chloride, and the pH of the solution is adjusted to less than 3.0 by the addition of excess hydrochloric acid. The liquid waste stream is brought into contact with a xylene phase that contains tri-iso-octylamine (TIOA), so that the mercuric chloride reacts with the amine, thus entering the xylene phase. The solubilities of both TIOA and TIOA salts in
water are negligible. In turn, the organic phase can be stripped of nearly all its mercury content with a small volume of brine at an equilibrium pH from 9 to 13. This can be accomplished by the addition of enough sodium hydroxide to neutralize the hydrochloric acid in amine and bring the equilibrium pH to the desired value. By using a high organic to aqueous phase volume ratio, a resulting aqueous phase up to 10,000 times more concentrated in mercury can thus be obtained. Such concentrated solutions can undergo further processing more easily, both from a technical and an economic viewpoint (EPA, 1985).

2.1.1.5 Filtration

Diatomite filtration is used to remove the insoluble mercury particulate matter that does not normally settle out during conventional treatment methods, and can reduce the mercury content of industrial waste from, for example, 5 ppm to less than 0.5 ppm. If the mercury is dissolved the waste stream is first chemically treated to convert the mercury to an insoluble form; elemental mercury, mercuric oxide or mercuric sulphide. A more direct approach, however, is the Ecotech process which employs a filter medium of inorganic mineral containing magnesium. Mercury, in any ionic form, is directly reduced to elemental mercury in the filter medium, so that removal from wastewater can be accomplished in a single step. According to the manufacturer of Ecotech, the process is best suited for removing trace elements of mercury from large volumes of wastewaters, such as those found in paper and Kraft mill effluents (USA EPA REPORT

2.1.1.6 Chemical Absorption/Adsorption

The application of chemical absorbents for removing mercury from wastewater has been widely studied. Laboratory and pilot plant data with a propriety absorbent have demonstrated that concentrations of mercury contaminants can be reduced from 2000 ppm to 50 ppb, and even lower levels may be possible (EPA, 1985). MacMillan (2001) proposed a mercury removal system comprising of a bed of activated carbon sandwiched between nickel mesh pads, and reported that the mercury content of a mercury cell caustic soda liquor was reduced from 0.8 ppm at the beginning to 0.1 ppm after passing through the carbon-nickel bed. In both cases, however, the mercury concentration in the treated effluent is still considerably above the recommended level (Thiem et al., 1976)

2.1.1.7 Adsorbing Colloid Flotation

Whist all of the above technology show promise, there is a need to continually seek different, potentially better, removal technologies. Adsorbing colloid flotation is another
technique which has shown considerable promise and will be discussed, in detail, later (Section 2.3)

2.1.2 Phosphate

Phosphate is a limiting reagent to the growth rate of plant material since phosphorus is vital to the operation of energy transfer systems of the cell. Phosphate is the prime source of that phosphorous in plants and is a critical factor in the maintenance of biogeochemical cycles as illustrated in Figures 2.3 and 2.4.

The “food chain” is a concept often misunderstood but generally meant to imply the predatory nature of ecology and its impact on chemicals in the environment. At the base of the food chain are simple, often mono-cellular bacteria and protozoa. Algae are close to the “bottom” of the food chain and, in common with all members of the plant kingdom, obtain energy for their growth from photosynthesis. Algae can be fast growing, needing only CO$_2$, O$_2$, sunlight and limited nutrients to proliferate. The often-toxic blue-green algae, by comparison, have a relatively slow rate of growth. Under optimum conditions, however, they are able to double their numbers in a matter of days. Optimum conditions, for “nasty” organisms such as blue-green algae usually involve high levels of nutrient and particularly high levels of phosphate. As far back as Sawyer (1944) it was known that high phosphate concentration increased plankton production in a lake, occurring at 20 $\mu$g/l in this particular case.

The excessive growth of algae and plankton, caused by excessive quantities of nutrients, causes numerous problems to the environment. Turbidity increases, oxygen exchange across the air/water interface decreases and the algae themselves may be toxic. The overall effect is referred to as eutrophication, prematurely ages a water body, causes damage to the ecology (fish and other organisms can’t breath because of the lack of oxygen) and can be a public health hazard.

The nutrients may originate from stormwater or sewage discharges into a catchment or stream, excessive use of fertilisers on agricultural land and general runoff. Some of the phosphate will precipitate and become bound up in the bottom sediments only to be released when the storage stratifies in summer and the bottom water becomes anaerobic. This phosphorus will continue to be available for further algal growth for some time after removal of the original nutrient source.
In Australia, the blue-green algal species of *Anacystis (Microcystis)*, *Anabaena* and *Nodularia* are commonly dominant in blooms. These blooms are highly toxic and have resulted in the death of fish, and other aquatic organisms, as well as herd cattle which drank from the eutrophic water (Wood, 1975; Francis, 1978).

**Figure 2.3:** Phosphorus Cycle

**Figure 2.4:** Phosphorus Marine Cycle
Phosphates arise from a variety of sources with agricultural run-off the largest single problem to the environment (Hart et al., 2004). Notwithstanding this, small amounts of condensed phosphates are added to some water supplies during treatment. Larger quantities are added when the water is used for laundering or other cleaning because phosphates are one of the major constituents of most commercial cleaning preparations. Orthophosphates are also utilized in agricultural or residential cultivated land as fertilizers and are carried into waters with storm runoff and to a lesser extent melting snow. In Australia, as yet, there is no legal requirement for the discharge to sewer of phosphates. Furthermore, bacterial action favours the conversion of polyphosphates into directly assimilable orthophosphates. While the composition of wastewater is commonly such that two thirds of the total phosphorous is present as polyphosphate and one third as orthophosphate, this ratio is reversed for biologically purified water.

The technique most commonly used to reduce the amount of phosphate in industrial wastewaters is co-precipitation (de Bashan and Bashan, 2005), in which aluminium and/or iron salt are added to activated sludge followed by separate precipitation. In some cases phosphates are removed in an activated sludge plant by adding precipitants to the supernatant from anaerobically-treated waste sludge. Biological removal of phosphate is commonly achieved by alternating anaerobic and aerobic processes. The resulting phosphate removal ranges from 90 to 100 % (Poon and Brueckner, 1975).

The following sections outlines, in more detail, the treatment technologies available for phosphate remediation.

2.1.2.1 Electrodialysis

Electrodialysis involves removing inorganic ions from water by applying an electrical potential across the water, resulting in the migration of cations and anions to the cathode and anode, respectively (Lee and Chou, 1994). By alternately placing anionic and cationic permeable membranes, a series of concentrating and diluting compartments result. The amount of electric current required for the stripping of anodes is proportional to the number of ions removed from the diluting compartments.

To minimize membrane fouling and maintain long runs it is essential that suspended solids, colloids, and trace organics be removed prior to the electrodialysis cell. Large organic ions and colloids are attracted to the membranes by electrical forces and result in fouling of the membranes. This results in an increase in electrical resistance which, at constant stack voltage, decreases the current and hence the effective capacity of the
equipment. Suspensions in the feed result in membrane fouling. Thus the conventional methods of coagulation, filtration, and adsorption are preferably employed. Brunner (1967) obtained removal of 40 percent of the total dissolved solids in a wastewater with a concentrate of 10 percent (by volume) of the influent water. Poon and Brueckner (1975) reported up 75 - 85 % removal of ortho-phosphate.

2.1.2.2: Filtration Reverse Osmosis

Membrane filtration includes a broad range of separation processes from filtration and ultra-filtration to reverse osmosis (Dietze, 2002). In the treatment of phosphate, reverse osmosis is the most common and most effective method. Generally, processes defined as filtration refer to systems in which discrete holes or pores exist in the filter media, generally of the order of $10^2$ to $10^4$ nm or larger. The reverse osmosis process employs a semipermeable membrane and a pressure differential to drive fresh water to one side of the cell, concentrating salts on the input or rejection side of the cell. In this process, fresh water is literally squeezed out of the feed water solution.

The reverse osmosis process can be best described by first considering the normal osmosis process. Here, a salt solution is separated from its pure solvent (or a solution of less concentration) by a semi-permeable membrane. The semi-permeable membrane is permeable to the solvent and impermeable to the salt. The chemical potential of the pure solvent is greater than that of the solvent in solution and, therefore, pure solvent will move through the membrane to dilute the solution. This flow of solvent increases the chemical potential of the solvent in solution, and therefore drives the system to equilibrium. If pressure is placed on the solution compartment, the solvent flow through the membrane will decrease. When sufficient pressure has been applied to bring about thermodynamic equilibrium with pure solvent, that pressure is equal to the osmotic pressure of the solution. If a pressure in excess of the osmotic pressure is applied to the more concentrated solution chamber, pure solvent is caused to flow from this chamber to the pure solvent side of the membrane, leaving a more concentrated solution behind. This phenomena is the basis of reverse osmosis.

Membrane life can be drastically shortened by undesired constituents in the feed water, such as phenols, bacteria and fungi as well as high temperatures and high or low pH values. Generally, membranes will last up to two years until the loss in flux efficiency becomes significant. Membranes consisting of cellulose acetate are subject to hydrolysis at high, and at low, pH values. The optimum pH is approximately 4.7 with operating
ranges between 4.5 to 5.5. The presence of scale-forming constituents, such as calcium carbonate, calcium sulphate, oxides and hydroxides of iron, manganese and silicon, barium and strontium sulphates, zinc sulphide and calcium phosphate, must be controlled by pH adjustment, chemical removal, precipitation, inhibition and/or filtration. Organic debris and bacteria can be controlled by filtration, carbon, pretreatment, and chlorination. Oil and grease must also be removed to prevent coating and fouling membranes.

2.1.2.3 Precipitation

Precipitation is one of the common methods used in the removal of phosphate. It usually involves chemical dosing with alum or ferric salts to form a precipitate and then action, such as filtration or flotation, to remove the precipitate. Municipal and industrial sewage is the area of primary interest for phosphate precipitation. Other applications include mineral separation processes and the restoration of eutrophic lakes and streams. Some examples of well established industrial use of precipitation techniques are:

- In a two stage process developed by Daniels and Parker (1970), phosphates are first precipitated by the addition of a soluble salt of aluminium, calcium or iron. Phosphates still remaining in solution are then precipitated by addition of a soluble lanthanide metal salt or other similar salt. Separation is facilitated by the use of a flocculating agent, usually a water-soluble organic anionic polyelectrolyte such as a partially hydrolyzed polyacrylamide. The process is applicable to any large scale aqueous system in which the dissolved phosphate concentration is to be reduced to the lowest possible value.

- The concentration of phosphate can be efficiently reduced by incorporating from about 10 to 30 ppm by weight of trivalent aluminium ion into the waste, followed by the application of an acrylamide acrylic copolymer under flocculating conditions. According to Wukasch (1970), the preferred copolymer is a compound from about 50 to 80 ppm weight percent acrylamide or methacrylamide interpolymerised with from about 20 to 50 % acrylic or methacrylic acid or the alkali and ammonium salts thereof, and is further characterized by a molecular weight of at least 2 million. The procedure involves dosing waste with aluminium ion to yield a 1.0% by weight of aluminium solution in water, agitation and addition 0.5ppm of 70% acrylamide / 30% sodium acrylate polymer. The polymer is introduced under conditions characterized as "flash mixing", i.e. agitation sufficient to promote solids agglomeration without simultaneous shearing of flocs. A removal efficiency of 80 to 90% is effected and activated sludge becomes heavier, thus the sludge Volume Index falls. Separate precipitation is usually applied, after the above coprecipitation, as a polishing technique. In this case, separation is carried out by filtration, and effluent phosphorus content drops to below
0.2 mg/l. Precipitation may be useful in very small storages to precipitate phosphate from the water stream and fix it in the sediments. However, the costs and uncertainty over long term effects preclude this method from use on a large scale.

2.1.3 Sulphate

The importance of sulphate treatment in industrial waste waters has only recently been recognised. The problem of concentrated sulphide in sewers arises essentially because bacteria that utilize the sulphate ion as a source of oxygen can flourish in warm anaerobic sewers (Aesoy et al., 1998). The ensuing corrosion, together with vile sulphide odours and the poisonous nature of hydrogen sulphide has provided the stimulus for its treatment as an industrial effluent.

Typical damage caused by sulphate corrosion is shown in Figure 2.5 and the mechanism with which sulphate enters the environment, and travels through it, can be illustrated by the sulphur cycle, as shown in Figure 2.6.

The corrosion of concrete pipes and steel fixtures by H₂S in sewers well known (Boon, 1985). Sulphate ions, together with suitable carbon sources (or their precursors) and other necessary nutrients, transfer from the flowing effluent into an anaerobic slime layer, which is attached to the sewer wall below the waterline. The exact form of attraction between sulphate and the negatively charged extracellular polymer material which forms this slime layer is not well understood, however nutrients are attracted. Sulphate reducing bacteria within the slime layer (biofilm) convert the sulphate ions to hydrogen sulphide which diffuses out of the slime layer into the liquid phase. This hydrogen sulphide is subsequently released into the vapour phase above the sewer water line. Biological oxidation of the hydrogen sulphide may then occur, resulting in sulphuric acid, which weakens and corrodes the concrete. Eventually, collapse of the sewer can occur.

2.1.3.1 Treatment as a Sewage Waste

Removal of sulphate from wastewaters is usually effected in sewage wastewater treatment plants. The choice of treatment processes for any particular application depends on the quality of the raw water, the required quality of the treated water, and the economic resources available. Treatment processes are selected by considering the
general physical form, as well as the chemical and biological nature, of the other impurities to be removed. The physical form of impurities may be either dissolved or suspended, and the suspended matter may be coarse, fine or colloidal in size. Coarse material and some of the fine matter generally settles quickly and may be conveniently removed by gravity sedimentation. Dissolved and colloidal matter and the remainder of the fine suspended matter, however, are not easily removed by conventional sedimentation. Physical processes are generally the simplest forms of treatment and comprise, principally, of screening, sedimentation and filtration. Other physical processes such as flotation, gas transfer and adsorption are also important to specific cases. Sulphate, like phosphate, is usually discharged to sewer where it undergoes primary treatment. It is desirable, and companies are becoming increasingly pressured, to ensure that sulphate, as well as other industrial wastes are treated at the source of discharge to the sewer, thus minimising the deleterious effects caused by the concentration of sulphate in sewers.

Figure 2.5: Sulphate Concrete Corrosion
Figure 2.6: The Sulphur Cycle
2.1.3.2 Screening and Sedimentation
Screening by racks, coarse or fine screens, and/or comminutors is carried out at the head of most treatment plants, where it constitutes a form of preliminary treatment for removing coarse material which could interfere with the treatment process or pumping equipment. Much sulphate is removed at this stage due to its adsorption, or occlusion, onto the fine particulate material which is being screened.

Sedimentation, on its own or together with further treatment, in both water and wastewater treatment plants, is used to remove the major part of the contaminants. Where impurities are present in solution, or in suspensions too fine for removal by sedimentation, other processes are used to convert them into a form which settles. In the case of some inorganic salts, chemical precipitation is used, while colloids and fine suspended matter are settled by chemical coagulation followed by flocculation. Sulphate can again be largely removed by adsorption onto, or occlusion with, these precipitates.

2.1.3.3 Filtration
Filtration through a bed of fine porous material is normally carried out after sedimentation in order to remove fine particles which have not settled in the sedimentation tank effluent.

2.1.3.4 Precipitation
Chemical precipitation is the most common method used in the treatment of sulphate waste prior to release into the sewerage system. One common procedure applicable in the case of high sulphate content involves the cold precipitation of gypsum CaSO₄·2H₂O by adding Ca²⁺ in the form of lime (usually done with acid water) or CaCl₂ (as in the case of brine):

\[
\text{SO}_4^{2-} + \text{Ca}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}
\]

The sulphate concentrations obtained depend on the salinity, the activity of the medium, and the amount of Ca²⁺ added, which in the case of lime, is limited by the acidity to be neutralized. The residual levels obtained are typically:

- 2 to 3 g/l SO₄ in brine purification using CaCl₂.
- 1.5 to 2 g/l SO₄ in neutralizing acidic water without using CaCl₂.
A second precipitation procedure involves the precipitation of barium sulphate by adding BaCl₂. The residual solubility obtained is less than 20 mg/l, but the reagent is very expensive and rarely used.

2.1.3.5 Electro dialysis and Reverse Osmosis
Electrodialysis and reverse osmosis can also be employed in the reduction/removal of sulphate from wastewater, although at present these techniques are mainly used for the treatment of drinking water. Electrodialysis has been discussed and detailed earlier for phosphate, are only suitable for fresh or slightly brackish water since the flow capacity falls as the salinity of water increases. The lower the salinity of the water the greater the current required because of increased resistivity. As a result, this method is of limited use for water with a salinity of less than 500 mg/l. Reverse osmosis, also described earlier for phosphate, is also used in the removal of sulphate.

2.1.3.6 Ion Exchange
Ion exchange is a common process used for sulphate treatment on an industrial scale. An example is the Azurion process where sulphate, as well as nitrate and carbonate, is removed from water. The anions are exchanged with chloride ions on the resin which is later regenerated by sodium chloride. The concentration of chloride in the treated water may consequently be excessive and it is thus essential that a discharge channel for the elutes be provided.

2.2 Adsorption from Solution
Adsorption can be described in many different ways resulting in terminology which is ambiguous, poorly defined and sometimes contradictory. It is thus of value to discuss the terminology used in this thesis. Adsorption refers to the concentration, at the interface between two phases, of a molecular or ionic species. If the ions are adsorbed only with simple electrostatic attraction or H-bonding (i.e. the absence of a direct chemical bond), the process should be termed physical adsorption, and adsorption is generally assumed to involve outer-sphere complexation. If however, adsorbed ions, result from the formation of a chemical bond then the process should be termed chemical adsorption, and adsorption is generally assumed to involve inner-sphere complexation.
Table 2.1: Typical Characteristics of Adsorption Processes

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding force</td>
<td>Due to physical force of attraction, thus this process is also called as Vanderwaal’s adsorption</td>
<td>Due to chemical forces or bonding, thus this process is also called as activated adsorption.</td>
</tr>
<tr>
<td>Saturation uptake</td>
<td>Multilayer phenomena</td>
<td>Single layer phenomena</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>No activation energy involved</td>
<td>May be involved</td>
</tr>
<tr>
<td>Temperature Range (over which adsorption occurs)</td>
<td>Adsorption is appreciable at lower temperature below boiling point of adsorbate</td>
<td>Adsorption can take place even at higher temperature</td>
</tr>
<tr>
<td>Nature of Adsorbant</td>
<td>Amount of adsorbant removed depends more on adsorbate than on adsorbent</td>
<td>Depends on both adsorbent and adsorbate</td>
</tr>
<tr>
<td>Crystallographic specificity</td>
<td>Virtually independent of surface atomic geometry</td>
<td>Marked variation between crystal planes</td>
</tr>
<tr>
<td>Heat of adsorption</td>
<td>1 Kcal/mole</td>
<td>50 - 100 Kcal/mole</td>
</tr>
</tbody>
</table>

Physical adsorption (physisorption) involves intermolecular forces (van der Waals forces, hydrogen bonds, etc.), whereas chemical adsorption (chemisorption) involves valency forces as a result of the sharing of electrons by the solid (adsorbent) and the adsorbed substance (adsorbate). The classification of chemisorption and physisorption is shown in Table 2.1.

Positive adsorption at the solid/liquid interface results in the removal of solutes from solution and their concentration at the surface of the solid, until there is a dynamic equilibrium between the solute remaining in solution and the surface. Thus adsorption onto a colloidal interface which usually has a large surface area can often be determined directly from the depletion of the adjoining liquid phase, especially if the adsorbate is present in fairly dilute solution. If there is no specific interaction between the species and the colloidal surface, hydration forces repel the species and it is said to be negatively adsorbed.
2.2.1 Site Binding and its Role in Adsorption Processes

When materials such as oxides, sulphides, insoluble salts, and activated carbons are immersed in aqueous solution, they acquire a surface charge the presence of which controls much of their interfacial behaviour. This charge arises from the dissociation of surface functional groups. For example, when a metal oxide surface is exposed to water, adsorption of water molecules produces a hydroxylated surface:

\[ \text{MO (surf)} + \text{H}_2\text{O} \rightleftharpoons \text{MO.H}_2\text{O (surf)} \rightleftharpoons \text{MOH.OH (surf)} \]  \hspace{1cm} \text{Equation 2.1} \\

Subsequent protonation and dissociation (i.e., deprotonation) of the surface hydroxyls produce a charged oxide surface:

\[ \text{MOH (surf)} + \text{H}^+ \rightleftharpoons \text{MOH}^{2+} \text{(surf)} \]  \hspace{1cm} \text{Equation 2.2} \\
\[ \text{MOH (surf)} \rightleftharpoons \text{MO}^- \text{(surf)} + \text{H}^+ \]  \hspace{1cm} \text{Equation 2.3} \\

That is, the surface hydroxyl can act both as a basic site (Equation 2.2) or an acidic site (Equation 2.3). When the hydroxyl group acts as a basic group, adsorption of H\(^+\) yields a positively charged site. On the other hand, when the hydroxyl group behaves as an acidic group, it can deprotonate to give a negatively charge site.

A number of excellent papers exist which detail the development of surface charge in terms of acid/base site dissociation (Breeuwsma and Lyklema, 1973; Davis et al., 1978; Healy and White, 1978; James and Parks, 1982; Boland and Barrow, 1984; Harding and Healy, 1985c; Koopal and van Riemsdijk, 1989; Sprycha, 1989; Dzombak and Morel, 1990; Kleijn, 1990; Shubin and Kekicheff, 1993; Usui and Healy, 2001; Duc et al., 2005) and reference to these will be made during the results and discussion chapters of this thesis. Similarly, a number of authors have used surface complexation and/or surface precipitation (Barrow and Cox, 1992a,b; Gunneriusson and Sjoberg, 1993; Ali and Dzombak, 1996; Persson and Lovgren, 1996; Zelazny et al., 1997; Bargar et al., 1997; Geelhoed et al., 1997; Dzombak and Morel, 1990; Peak et al., 1999; Blesa et al., 2000; Daughney, 2002; Burns et al., 2004; Lefevre, 2004) of cations and anions to model their adsorption onto colloidal substrates and these will also be referred to, as required.
2.2.2 Adsorption of Cations versus Anions

It is quite clear from the literature that there is a fundamental difference between the adsorption, from solution, of cations and anions and this will have a profound affect on decision making in processes such as adsorbing colloid flotation. The difference is most apparent when plotting adsorption as a function of pH and is shown Figures 2.7 and 2.8. Hydrous metal oxides are chosen as the substrate to base generalisations on, however it should be noted that these generalisations hold true for a number of other substrates including clay (e.g. Rodda, 1993; Harris, 2001), coal (e.g. Burns, 2004), chitosan beads (e.g. Gotoh et al., 2004), bacteria (e.g. Daughney et al., 2002) and sawdust (Marin and Azel, 2003).

The pH dependent adsorption of anions onto hydrous metal oxides typically has the shape seen in Figure 2.7, characterised by pH dependent maximum which appears to correlate with the pKa of the conjugate acid to the anion involved, although for many anions, such as sulphate, the pKa is too low for this to be obvious. Above the pKa, the anion is predominantly in the negative charged form and favourably interacts with the positively charged surface. As the pH is increased, the surface becomes increasingly more negatively charged, or increasingly less positively charged, depending on the pH of the isoelectric point (iep), thus adsorption becomes increasingly less favourable. Below the pKa, the anion is predominantly in the protonated (hydrogen) form and this form is not as attracted to the positively charged surface as the negatively charged anionic form is. The net result is a decrease in adsorption at either end of the pH scale.
Figure 2.7: Stylised Adsorption of Anions onto Hydrous Metal Oxides.

The situation is quite different in the case of cations, as shown in Figure 2.8. Generally, if cations are not hydrolysable (e.g. Na\(^+\), K\(^+\), Cs\(^+\) etc.) they do not significantly adsorb. If weakly hydrolysable (e.g. Ca\(^{2+}\), Mg\(^{2+}\)) they only significantly adsorb at very high pH values. For the majority of aqueous heavy metals (e.g. Cd\(^{2+}\), Cu\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\), Zn\(^{2+}\), Ni\(^{2+}\)), adsorption follows the pattern shown in Figure 2.8 where adsorption is negligible at low pH and rises quite sharply to complete removal (assuming there is enough surface area to remove all the metal ion with a single monolayer) at high pH. There is a strong correlation between the pH at which this rise occurs and the first hydrolysis product of the aqueous heavy metal such that hydrolysis must occur, albeit to a very limited extent (< 1%) before any appreciable adsorption can take place.
2.3 Adsorbing Colloid Flotation

The technique of Adsorbing Colloid Flotation (ACF) has evolved from, and is very similar to, microflotation and precipitate flotation (Lemlich, 1972) and it is sometimes difficult to distinguish between them. ACF is based on the adsorption of material, in this case the waste to be treated, onto colloidal sized particles which then collect at the gas liquid interface. It typically involves the formation of a hydrous metal oxide (e.g. hydrous oxides of Fe (III) and Al(III)) and the adsorption or coprecipitation of waste species onto this hydrous metal oxide. If not hydrophobic, the colloid is made so by the addition of a surfactant. Flotation of the hydrophobic colloid is then effected by passing it through a stream of gas (usually compressed air) where the surfactant coated colloid is collected into a foam. The foam is sometimes stabilised by a second surfactant termed a stabiliser. The foam, when separated from the mother liquid, contains the waste in a concentrated form suitable for land disposal or, less commonly, re-use and/or re-cycle. Note that land disposal of waste products is generally prohibitive unless that waste is immobilised or otherwise treated for toxic heavy metals. The foam produced here gives rise the possibility of a stabilised land disposal form. In traditional studies the foam is physically removed from the mother liquid by, for example, skimming. An alternative used in this

Figure 2.8: Stylised Adsorption of (Hydrolysable) Cations onto Hydrous Metal Oxides.
study is to allow all of the original solution to be collected in the foam (total carry-over mode), and design the process such that the foam drains cleanly (i.e. the waste remains in the foam following drainage). The key steps in ACF can be summarised as follows:

1. Formation of a colloidal phase
2. Removal of waste from solution
3. Hydrophobisation of the colloid
4. Flotation
5. Drainage

Much of the significance and control of these steps can be traced through the history and origin of ACF, and particularly its similarity to microflotation and precipitate flotation.

2.3.1 History of Adsorbing Colloid Flotation (ACF)
The technique was first used in the late 1960s and early 1970s (Karger et al, 1967; Grieves, 1969; Pinfold, 1970, Kim and Zeritlin, 1972; Lemlich, 1972; and Clarke and Wilson, 1978) and today has many industrial applications including the separation of toxic substances, suspended solids, micro-organisms etc. from residual, industrial, sea and potable waters (Clarke and Wilson, 1983; Alexandrova, 1994; Lin and Huang, 1994; Choi and Choi (1996); Zouboulis and Matis, 1997; Lu and Chen, 2003; Jurkiewicz, 2005; Matis et al., 2005). The book edited by Lemlich (Lemlich, 1972) presents a general treatment of all flotation techniques, including their development up to 1972, and is still widely referred to. More recently, Clarke and Wilson (1983) and Hiraide and Mizuike(1982a, 1982b), discuss the theory and applications of foam separation, with considerable reference to ACF and Zouboulis and Matis (1997) have written a review on ACF of anions.

Much of the early development was centred in the USA, USSR, Japan and China due to their major mining industries. It is unfortunate that the Russian work in particular is largely ignored, however the literature is difficult to obtain.

2.3.2 Definition of Adsorbing Colloid Flotation
There are a number of separation techniques, all of which rely to some extent on control of hydrophobicity, and all of which involve dispersed solids, precipitates, colloids and/or dissolved substances adsorbing onto an ascending gas stream, thus being removed from the liquid mass in which they were initially suspended. Flotation is often classified simply
according to phenomenology with Karger et al. (1967) proposing main types of flotation depending on whether or not the technique involves foaming. Later, Pinfold (1970) suggested flotation should be classified according to the adsorption mechanism, depending on the flotation of particles, ions and molecules. This latter option is more logical, however the classification by Karger et al. (1973) continues to be the more widely accepted due to its simplicity and historical precedence. Karger et al. (1973) divided the techniques into foaming and nonfoaming separations of which ACF forms part of the foaming technique.

2.3.3 Apparatus and Techniques

A simple flotation apparatus for use in adsorbing colloid flotation is shown schematically in Figure 2.9. This was, in fact, the apparatus used in this thesis and the diagram and description is repeated in the Experimental Methodology Chapter (Section 3.4.1).

Figure 2.9: Schematic Diagram of Adsorbing Colloid Flotation (batch mode).
1. Humidified air inlet
2. Rotameter
3. 20 cm³ flotation cell (ID 2.5 cm, height 10 cm)
4. Porous glass frit (porosity 4)
5. Foam Collection Vessel

The apparatus described in Figure 2.9 is suitable for small scale laboratory operations but not for medium to large scale industrial clean-up. Figure 2.10 illustrates an adsorbing colloid flotation set-up which has been used for continuous operation and has been used for small scale industrial pilot plant operations (Sanciolo et al., 1993).
Figure 2.10: Schematic Diagram of Adsorbing Colloid Flotation (continuous mode).

1. Humidified air inlet
2. Rotameter
3. 20 cm$^3$ flotation cell (ID 2.5 cm, height 10 cm)
4. Porous glass frit (porosity 4)
5. Foam collection trays
6. Final foam collection tray
7. Holding cell for generation of adsorbant
8. pH measurement and control
9. Surfactant storage reservoir
10. Pump
11. Pump
12. Sampling port
13. “Clean” liquid drainage

(1) Humidified Air Inlet which can include the following devices:
- Gas generating source. This can be a small air compressor or gas cylinder. Air is the gas most commonly used, however nitrogen, helium or argon have also been used.
- Gas washing flask. Its main purpose is to presaturate the gas to prevent uncontrolled evaporation in the system. In some cases particularly in research studies, it is used to eliminate carbon dioxide from the system and avoid undesirable reactions in the column and control pH. Gas washing flasks are not always used, as in most cases the rotameter is sufficient.

(2) Rotameter which can include the following devices:
- Regulator system for controlling pressure and gas flow (needle valves, etc)
- Flow meter for measuring the gas flow rate through the column; normally a soap bubble flow meter is used.
(3) Flotation Cell. The flotation cell used is usually a glass column although sometimes plastic is used.

(4) Sintered glass frit, used to generate bubbles of uniform (i.e. monodisperse) and hopefully relatively small particle size. By changing the porosity of the frit, different sized bubbles can be generated.

(6) Foam collection apparatus, which may for laboratory scale processes be as simple as a watch glass. For large scale operations large laboratory trays may suffice, or a stack arrangement may be used (Sanciolo et al., 1993) as shown in this figure. The purpose of the stack arrangement is to maximise the surface area of the foam thereby allowing it to drain faster.

(7) Holding Cell. Allows the colloid to be formed external to the flotation cell and thus the colloid can be equilibrated at the appropriate pH for a given induction time before entering the flotation cell. This is essential for continuous mode operation where the colloid should be formed before flotation takes effect.

(8) pH measurement and control. Although not essential, this allows experimentation to be carried out, allows trouble shooting when things go wrong and provides for better quality control during operation.

(9) Surfactant Reservoir. Allows a mixture of surfactants to be gradually fed into the flotation cell during continuous operation.

(10) Pumps. Peristaltic pumps are normally the choice for continuous operation, delivering reagents with controlled flow rate to the column. Pumps are also used to deliver air supply in some processes

(11) as in (10).

(12) Sampling port. Used for trouble shooting, quality control and laboratory experimentation.

(13) “Clean liquid drainage”. A vessel, or pipe, needs to be attached here to collect the clean water as it drains from the foam.

Adsorbing colloid flotation is assumed to occur in the following key steps (which are repeated in the Experimental Methodology Chapter (Section 3.4.1):

1. The colloid pre-cursors (usually Al(III), Fe(III), Fe(II) or a mixture thereof) must first be formed into a colloid, usually by an increase in pH. Under industrial conditions it might be possible to form the colloid simply by adding the precursors directly to the waste and using the pH of the waste to form the colloid.
2. The waste material adsorbs onto the formed colloid, removing the waste from solution. Under the conditions of adsorbing colloid flotation used in this study, the waste adsorbs onto the colloid at the same time as the colloid forms, thus it is possible that co-precipitation rather than adsorption is the removal mechanism. Crawford et al. (1993a,b, 2002) have shown that coprecipitation can be far more efficient than adsorption as a removal mechanism so should be encouraged.

3. Surfactant is added for two purposes. Firstly, it renders the colloid hydrophobic and allows attachment to air bubbles. Secondly, it serves to stabilize the foam. The foams from adsorbing colloid flotation are believed to be solids stabilised (Sanciolo et al., 1993) and for this to happen there needs to be a delicate balance between adsorbing enough surfactant to render the surface hydrophobic enough to attach to bubbles, but not enough to cause desorption and/or destabilisation (Dickinson et al., 2004). Desorption and/or destabilisation will occur if the surfactant causes the surface to become too highly (negatively) charged.

4. Flotation is effected, in this case, by a very high air flow rate. This causes all the liquid in the flotation tube to be floated. Sanciolo et al. (1992, 1993) have described this form of flotation, referred to as “total carry-over mode” (TLC) and have described the properties of foam formed from such a mode. The conditions of flotation used in the current work reflect that of Sanciolo et al. (1993).

5. The foam is collected in a second container (Figure 2.9) or a drainage tray (Figure 2.10) where it is allowed to drain. The goal is for the foam to drain “cleanly”, i.e. for the waste analyte to be trapped in the foam and not to desorb back into solution.

6. Once drainage is complete, the foam is removed for reuse, recycle, destruction and/or landfill.

2.3.4 Process Variables

Several factors influence the flotation process, including solution and operational factors. Most of the former are of basic importance to all flotation techniques and include coprecipitate and collector concentrations, pH and ionic strength. The latter (operational parameters) are usually specific to a particular technique and include induction time, gas flow rate, porosity of the sintered-glass plate, average bubble size, and the column geometry. For example, in an ACF system you need enough adsorbing colloid to adsorb the waste and then enough collector to facilitate flotation. The pH is important as it effects the surface characteristics and the chemistry of the system. The ionic strength needs to be monitored as too high an ionic strength often means ineffective ACF (Lin and Huang,
The gas flow rate needs to be established for each process and the column geometry needs to be taken into consideration to provide the optimum efficiency. It is important to have uniform bubble size and this is provided by a glass frit. These parameters are discussed below, but it is important to note that all of the parameters, although similar in some processes are interdependent and specific to each process.

### 2.3.4.1 Surfactant concentration

If the surfactant concentration is too low, there will not be enough surfactant coating on the colloid to render it sufficiently hydrophobic to be floated. Furthermore, insufficient surfactant will result in a non-stable foam making handling of the foam difficult, if not impossible. Alternatively, if too high a concentration of surfactant is present, there is a decrease in flotation efficiency. Sheim and Pinfold (1968) describe two mechanisms by which this occurs:

- As the surfactant concentration is increased, it becomes possible for a second layer of surfactant ions to adsorb on the coprecipitate. These surfactant ions are orientated with their ionic heads pointing away from the coprecipitate and toward the water, thus making the coprecipitate hydrophilic. This observation was also reported by Wilson and Kennedy (1979).
- As the surfactant concentration is increased, its surface concentration at the air-water interface becomes sufficiently large that hydrophilic bubbles are formed due to a decrease in the air-water surface free energy.

As a general rule, then, it is necessary to have a surfactant concentration which is high enough to form a stable and persistent foam and high enough to ensure that the colloid is hydrophobic, but not so high as to enable bilayers to form. Furthermore it is important to note that surfactants are expensive and may actually be responsible for pollution if used in excess.

### 2.3.4.2 Colloid Concentration

The colloid concentration is related to the surfactant concentration in that there has to be enough surfactant left, after adsorption onto the colloid, to effect an efficient flotation. Thus it may be necessary to use different colloid concentrations with different surfactant concentrations (or vice-versa). Too little adsorbing colloid results in incomplete adsorption
and therefore poor removal of the species of interest (in the case of this thesis SO$_4^{2-}$, HgCl$_4^{2-}$ and PO$_4^{3-}$). Considerable evidence is available in the literature showing a correlation between colloid concentration and waste treatment efficiency. Aoyama, Hobo and Suzuki (1982) and Jorgensen et al. (1973), showed that an increase in the adsorbing colloid hydrous aluminium oxide results in more phosphate being removed from waste water.

2.3.4.3 pH of the solution
Arguably the most critical variable of Adsorbing Colloid Flotation is the pH of the solution, since it will determine the sign and magnitude of the charges on the colloidal surface, the bubble, and some of the ionic species in solution. Clarke and Wilson (1975), were able to effect an adsorbing colloid flotation of fluoride using colloidal aluminium hydroxide and SDS over a range of pH values, however the pH range of 7.3 - 7.8 seemed to produce the best results. Currin et al. (1979), also studied the effect of pH and affected the best separation in the pH range 6 - 7 for their system. In both these cases the pH has to be alkaline enough to produce the hydrous metal colloid but not too alkaline, as the surfactant sodium dodecyl sulphate loses its flotation effectiveness at high pH where the surface charge of the colloid is too negative. Sanciolo et al. (1993), however, have shown that food ACF results can be obtained at high pH if a mixture of surfactants is used.

2.3.4.4 Ionic strength
A number of competing and sometimes contradictory phenomena occur when studying the effect of ionic strength, and these generally have their origin in the adsorption process. Usually an increase in ionic strength will decrease the effectiveness of ACF (Lin and Huang, 1994; Huang, et al., 1995; Huang and Liu, 1999) and this is probably due to competition between ions for adsorption sites. Surfactant adsorption at the gas-liquid interface, however, can increase with increasing ionic strength, and thus flotation can be enhanced when the ionic strength is increased. This is particularly true when a dual surfactant mixture (Lin and Huang, 1994; Huang et al., 1995) or a polyelectrolye (Huang et al., 2000) is used.

2.3.4.5: Foam Stability
Foam stability can also be affected by ionic strength (and is the probably mechanism for its affect on adsorbing colloid flotation). There is also an increase in drainage from the foam. An example was shown by Sheiham and Pinfold (1968), where an increase of
anions in the film reduces their stabilising repulsion and allows them to become thinner, the bubbles are thus more susceptible to rupture and drainage from them is more rapid. Clarke and Wilson (1978) showed that an increase in the ionic strength of the system results in a smaller zeta potential due to compression of the electrical double layer.

Far from being a terminal problem, the instability of foam in high ionic strength can be turned to an advantage in terms of ACF selectivity. Robertson, Wilson and Wilson (1976), for example, demonstrated that increasing ionic strength interferes with the adsorbing colloid flotation of heavy metal cations. Specifically, as the ionic strength was increased from 0 to 0.100 NaNO₃ M the residual level of lead increased, but not that of other heavy metals. Thus the technique could be used for the selective flotation of some metals over others.

2.3.4.6  Induction time
Induction time, or equilibration time, refers to the duration of agitation of the sample before it is transferred to the flotation cell and its effect is dependent on the chemical nature of the system. For example, if the coprecipitate is subject to oxidation then induction time is usually kept to a minimum. Usually however, the longer the induction time, the more complete are precipitation, adsorption and coprecipitation processes, and therefore the more effective the overall process. This is illustrated by the results of Sheiham and Pinfold (1968), for the flotation of strontium carbonate precipitates, where they showed that an increase in induction time increased from 10 to 30 minutes resulted in an increase from 50% to almost 100% flotation effectiveness.

2.3.4.7  Temperature
In general, temperature has been found to have only a minor affect, provided that foam structure is not thermally destroyed. However since laboratory temperature is generally kept constant and is rarely varied, it is possible that there might be as yet undetected temperature affects. Furthermore, adsorption is known to be affected by temperature, and an increase in temperature will increase solubility and foam instability.

Spargo and Pinfold (1970) found, when floating hexacyanoferrate(II) with dodecyl pyridinium chloride, that a temperature rise from 5 to 35°C resulted in a 50% reduction in flotation effectiveness. In this case adsorption is shown to be an exothermic process, such that an increase in temperature leads to a decrease in adsorption, and thus flotation.
effectiveness. By contrast, Ghazy et al. (2001, 2004) found a slight increase in adsorbing colloid efficiency with temperature when floating Cu(II) with powdered carbon and marble.

2.3.4.8 Gas flow-rate

The best gas flow rate is dependent on the sample size, the column size and the porosity of the sintered-glass plate fitted to the column. A steady uniform stream is required in order to maintain a consistent foam which supports the colloid, without allowing its re-entry into solution. In general it is better to use small uniform bubbles due to their large gas-liquid interface.

The removal of a particle is partly governed by the stability of the particle and any aggregate it might form. If the flocs are easily broken up, an increased gas flow rate will enhance that break up, leading to ineffective flotation. A stable floc which can attach to an ascending bubble without breakdown, however, can be enhanced by an increase in gas flow rate leading to effective, rapid flotation. It is important to note that the total removal of flocs also depend on stoichiometric relationships which occur at the gas interface (i.e. is the ratio of bubble surface area to floc sufficient to effect flotation?).

2.3.5 Examples of Successful Adsorbing Colloid Flotation

The literature for ACF, although not extensive, is very well established. Lemlich (1968) detailed the relationship of precipitate flotation to other forms of flotation. Kargar et al. (1967) compared and contrasted precipitate, colloid, and ion flotation by studying the flotation of cyanide, dichromate, and the ferric iron. Pinfold (1970) discussed precipitate flotation and its relationship to other foaming methods. Several comprehensive reviews have been written from the early years of ACF (Pinfold, 969) to more recent times (Zouboulis and Matis, 1997).

Adsorbing colloid flotation has been successfully applied to a number of waste samples including cations (Choi et al., 1999; Huang et al., 2000; Sabti et al., 2002; Pacheco and Torem, 2002; Marcu and Turtureanu, 2003; Lu and Chen (2003), Jurkiewicz, 2005) and anions (Zhao et al., 1996a; Zhao et al., 1996b; Zhou et al., 1996; Zouboulis and Matis, 1997; Huang and Liu, 1999).

In one of the earliest successful applications, Zeitlin et al. (1971) used adsorbing colloid flotation as a preconcentration technique for trace elemental analysis of sea water. The
cations eventually studied included zinc and copper (Zeitlin et al., 1972), silver (Zeitlin et al., 1976) and mercury (Zeitlin et al., 1974). The anions eventually studied were phosphate and arsenate (Zeitlin et al., 1974), molybdenate (Zeitlin et al., 1971), vandate (Zeitlin et al., 1976), and selenite (Zeitlin et al., 1978). Matsuzaki and Zeitlin (1973) also undertook an extensive and systematic study in the use of different collectors and coprecipitates.

Although this early work involved both cations and anions, cations dominate both theoretical and practical aspects of ACF. The separation of copper from other metals using ACF, for example, has been studied by many authors. Zeitlin et al. (1972), found they could separate zinc and copper from sea water at a pH of 7.6, using ferric hydroxide as the floc and dodecylamine as the collecting surfactant. At this pH dodecylamine is protonated and acts as a cationic surfactant. Thus, as the pH increases the floatability of the negatively charged ferric hydroxide floc decreases. Wilson et al. (1977) carried out a similar study and found that greater removal of copper was achieved when the copper (II) and the iron (III) adsorbing colloid are mixed prior to pH adjustment and the cationic surfactant dodecylamine used. Similar cationic surfactants such as hexadecylammonium chloride and dodecylpyridinium chloride were unsuccessful in facilitating a good separation.

In later studies, Wilson et al. (1979), affected the removal of copper(II), lead(II), and zinc(II) with ferric hydroxide and the anion collector sodium dodecyl sulphate (SDS). The method was found to be effective in the pH range of 6 to 7 at an ionic strength below 0.1 M. Luo and Huang (1993) successfully removed copper from aqueous ammine copper solutions using hydrous iron(III) oxide and SDS and Lin and Huang (1994) successfully removed copper from high ionic strength using hydrous iron(III) oxide and a mixture of SDS and oleic acid (but not using SDS alone). Alexandrova et al. (1994) used the traditional activator, xanthate, to form a precipitate with copper to effect removal, Ghazy et al. (2001) used activated carbon as the absorbent for copper removal, Sabti et al. (2000) and Matis et al. (2005) used hydrous iron(III) oxide, Marcu and Turtureanu (2003) used expanded pearlite, Ghazy et al. (2004) used powdered marble waste.

Chatman et al. (1977) developed an adsorbing colloid flotation procedure using SDS and ferric hydroxide at pH 6.5 and questioned in this paper whether separation is affected by coprecipitation or adsorption. Crawford et al. (1993a,b, 2002) later showed that
coprecipitation was far more effective at removing metal ions than adsorption suggesting that if adsorbing colloid flotation is performed under coprecipitating conditions the results would be at an optimum.

Various surfactants have been tried to effect adsorbing colloid flotation, including sodium dodecyl sulphate (Grieves and Bhattacharyya, 1968; Robertson et al., 1976; Chatman et al., 1977; Sanciolo et al., 1992; Sanciolo et al., 1993; Luo and Huang, 1993; Lin and Huang, 1994; Zhou et al., 1996; Huang and Liu, 1999; Choi et al., 1999, Choi et al., 2000; Pacheco and Torem, 2002), Tween 80 (Jurkiewica, 2005), dodecanoic acid (Sanciolo et al., 1992; Sanciolo et al., 1993; Jurkiewicz, 2005), dodecylamine (Zhou et al., 1996, Zhao et al., 1996a,b), oleic acid (Alexandrova, 1994; Lin and Huang, 1994; Marcu and Turtureanu, 2003; Ghazy et al., 2004), sodium stearate (Jurkiewicz, 2005) and the cationic surfactant ethylhexadecyl dimethyl ammonium bromide (Grieves and Bhattacharyya, 1968).

Although there are many instances of successful flotation using a single surfactant, surfactant mixtures appear to work best (Sanciolo et al., 1992, Sanciolo et al., 1993; Lin and Huang, 1994; Huang et al., 1995; Sabti et al., 2002).

2.4 Summary

Adsorbing colloid flotation has enjoyed widespread use in both laboratory and industrial situations, successfully treating almost all types of aqueous waste. Unlike many procedures which tend to suffer considerably from interference, the more complex adsorbing colloid flotation is made, the more likely it is to be successful. Such complex systems are sometimes difficult to predict, but their complexity acts to buffer interference and also increases the likelihood of a suitable adsorbing colloid being formed (Sanciolo et al., 1992, Sanciolo et al., 1993). Thus a mixture of surfactant, rather than a single surfactant, is recommended and a mixture of substrates, rather than a single substrate is recommended.

Adsorption of anions and adsorption of (hydrolysable) cations were shown to be quite dissimilar. The role of this dissimilarity in flotation is not, however, clear. That is, the role of adsorption in the flotation of cations is quite clear. The more a cation adsorbs, the more likely it is to be removed by flotation. The higher the pH, the more a
(hydrolysable) cation adsorbs, and the more it is removed by flotation. For anions, the role of pH is more complex and adsorption does not simply increase with an increase in pH. Will, then, flotation of anions also be more complex and reflect the influence of pH over adsorption, or will flotation simply increase with pH as do metal ions. Sulphate, phosphate and nitrate are chosen largely because they are highly representative of nutrients which create eutrophic conditions in natural water ways. Mercury complexes are chosen because of access to “real” industrial samples of considerable concern to local industries within Australia.

The following chapters will investigate the role of adsorption in the adsorbing colloid flotation of aqueous sulphate, phosphate and mercury chloride, using a mixed surfactant and a mixed hydrous oxide.
EXPERIMENTAL METHODOLOGY

3.1 Reagents and Solutions
All reagents used to prepare solutions were of analytical grade (AR) unless otherwise specified. All solutions were prepared in 10^{-3} \text{KNO}_3 background electrolyte. All solutions were prepared using conductivity water. Conductivity water was prepared by distillation of water, followed by passing the water through a mixed bed ion exchange resin (to remove inorganic impurities) then followed by activated charcoal (to remove any organic impurities), and finally distilling the water a second time using a Teflon coated electrode in pyrex distillation apparatus. The resultant conductivity water was stored in pyrex containers and had a conductivity of approximately 1.0 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}, a pH of 5.7 \pm 0.2 and a surface tension of 72.8 \pm 0.2 \text{mN m}^{-1} at 20^\circ\text{C}. The pH 5.7 \pm 0.2 of the conductivity water is acidic and is indicative of dissolved carbonate. During adsorption experiments, dissolved carbonate was kept to a minimum by bubbling nitrogen through the solution prior to pH adjustment.

3.1.1 Glassware
All glassware and storage bottles were soaked in dilute nitric acid for at least 24 hrs, after which they were washed with copious amounts of conductivity water.

3.1.2 Stock Solutions
All stock solutions were prepared using conductivity water as outlined above and in a background electrolyte of 10^{-3} \text{M KNO}_3. Stock solutions were diluted as required.

3.1.2.1 Sulphate Experiments

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Description</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>40,000 ppm Fe(III)</td>
<td>AR grade Fe(NO_3)_3.9H_2O</td>
<td>Ajax chemicals</td>
</tr>
<tr>
<td>40,000 ppm Fe(II)</td>
<td>AR grade FeCl_2.4H_2O</td>
<td>BDH chemicals</td>
</tr>
<tr>
<td>40,000 ppm Al(III)</td>
<td>AR grade Al(NO_3)_3.9H_2O</td>
<td>BDH chemicals</td>
</tr>
<tr>
<td>5,000 ppm SDS</td>
<td>LR grade sodium dodecyl sulphate</td>
<td>BDH chemicals</td>
</tr>
<tr>
<td>5,000 ppm DA</td>
<td>LR grade dodecanoic acid</td>
<td>BDH chemicals</td>
</tr>
</tbody>
</table>

Dissolved in 45°C – 50°C warm alkaline solution.
3.1.2.2 Mercury Experiments

20 000 ppm Fe(III) AR grade FeCl$_3$.6H$_2$O   Ajax chemicals
20 000 ppm Al(III) AR grade AlCl$_3$.6H$_2$O   BDH chemicals
20 000 ppm Fe(II) AR grade FeSO$_4$.7H$_2$O   BDH chemicals
acidified and made daily to avoid oxidation.
5 000 ppm SDS LR grade sodium dodecyl sulphate BDH chemicals
5 000 ppm DA LR grade dodecanoic acid   BDH chemicals
dissolved in 45°C - 50°C warm alkaline solution

3.1.2.3 Phosphate Experiments

20 000 ppm Fe(III) AR grade Fe(NO$_3$)$_3$.9H$_2$O   BDH chemicals
20 000 ppm Fe(II) AR grade FeCl$_2$.4H$_2$O   Ajax chemicals
20 000 ppm Al(III) AR grade Al(NO$_3$)$_3$.9H$_2$O   BDH chemicals
5 000 ppm SDS LR grade sodium dodecyl sulphate BDH chemicals
5 000 ppm DA LR grade dodecanoic acid   BDH chemicals
dissolved in 45°C - 50°C warm alkaline solution

3.1.2.4 Nitrate Experiments

20 000 ppm Fe(III) AR grade Fe(NO$_3$)$_3$.9H$_2$O   BDH chemicals
20 000 ppm Fe(II) AR grade FeCl$_2$.4H$_2$O   Ajax chemicals
20 000 ppm Al(III) AR grade Al(NO$_3$)$_3$.9H$_2$O   BDH chemicals
5 000 ppm SDS LR grade sodium dodecyl sulphate BDH chemicals
5 000 ppm DA LR grade dodecanoic acid   BDH chemicals
dissolved in 45°C - 50°C warm alkaline solution

3.1.3 Surfactants

The choice of surfactant was determined by considering the chemistry, availability, cost and possible toxicity of surfactant. The types of surfactants used in wastewater treatment include the anionic surfactants dodecanoic acid (DA) and sodium dodecylsulphate (SDS) (Sanciolo et al., 1992), and the cationic surfactant cetyl triethylammonium bromide (CTAB). In this thesis, a dual surfactant mixture of DA and SDS was predominantly the surfactant of choice.

The dual surfactant mixture of DA and SDS was used as it has been shown to be effective even under conditions of high ionic strength or competing anions (Sanciolo, et
The two surfactants together extend the pH at which either surfactant will work efficiently on their own (Kulkarni and Somasundaran, 1975; Wilson, 1982; Gannon and Wilson, 1987, Sarker et al., 1987; Huang et al., 1995). When the dual surfactant mixture was used, it was generally prepared to give a 100 mg/L dodecanoic acid and 200 mg/L sodium dodecylsulphate final concentration (Sanciolo et al., 1992). The choice of total concentration, and ratio, is somewhat arbitrary but was informed by experiments to be presented in Chapter 4 (Figure 4.10 and Chapter 6 (Figure 6.1). CTAB, when used, was prepared as a 5% (w/w) stock.

3.1.4 “Model” Waste Samples

Model wastes samples, in contrast to industrial samples, have a “known chemistry” which is known and reproducible. The model samples used in this study were designed to mimic industrial samples in both their nature and concentration. All model waste samples were prepared immediately prior to use. All anions of interest, with the exception of mercury chlorides, were prepared from potassium salts of the anion.

3.1.4.1 Sulphate

The sulphate used in these experiments was K₂SO₄ with a molecular weight of 174.3

3.1.4.2 Mercury

The mercury used in these experiments was HgCl₂, with a molecular weight of 271.5

3.1.4.3 Phosphate

The phosphate used in these experiments was K₃PO₄ with a molecular weight of 134.1

3.1.4.4 Nitrate

The nitrate used was KNO₃ with a molecular weight of 101.1

3.1.5 Industrial Waste Samples

All industrial samples collected were analysed immediately on collection and again analysed for the ion of interest at the time of use.

3.1.5.1 Sulphate Industrial Waste Samples

There were two industrial samples collected. The first sample was collected from Hawker-Dehaviland (Melbourne, Australia) and was expected to contain a high level of
sulphate. The sample was collected from a “high sulphate” waste stream but analysis showed a low sulphate concentration (< 100 ppm). A visual inspection confirmed that that a sediment formed, and that the sediment increased with time indicating the presence of a precipitating agent within the industrial waste. Whilst this negated the use of the Hawker-Dehaviland waste in the current studies, it does indicate that precipitates often form in “real” industrial waste and that technologies which rely on the formation of a precipitate (such as adsorbing colloid flotation) are sometimes more efficient than predicted from theory because of the presence of precipitating agents within the waste itself (see Sanciolo, 1992).

The second sample was collected from Pigment Manufacturers of Australia (PMA). This plant has since closed due to economical factors where it was decided that the cost involved in upgrading the plant to comply with environmental and safety issues was too great. The samples collected here were analysed and found to have 1,000 ppm SO$_4^{2-}$. Analysis was originally carried out using the quantitative method of nephelometry and confirmed using ion chromatography (with thanks to Ms M. Mitri from Monash University Caulfield Campus). Sulphate was expected to be the major contaminant in this sample and a full chemical analysis of other components was not carried out. This is common practice in industry, where the removal of a problematic contaminant must be demonstrated in the presence of otherwise unknown chemical composition.

### 3.1.5.2 Mercury Industrial Waste Samples

Industrial samples of mercury containing waste were collected from the ICI chloro-alkali plant in Botany. The plant was sampled at different stages of processing and the samples were analysed using flow injection cold vapour atomic absorption spectroscopy (Tao and Fang, 1993). All samples were measured, on collection, for mercury content, pH and chloride content as shown in Table 3.1. Values were re-measured immediately prior to use and were found not to change significantly.
Table 3.1: Mercury Collected at ICI Chloro-Alkali Plant in Botany

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Hg(ppb)</th>
<th>INITIAL pH</th>
<th>EQUIVALENT CHLORIDE(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Effluent (A)</td>
<td>2000</td>
<td>10.8</td>
<td>0.0025</td>
</tr>
<tr>
<td>Hydrogen Effluent (B)</td>
<td>2000</td>
<td>10.0</td>
<td>0.0025</td>
</tr>
<tr>
<td>14th Avenue</td>
<td>56</td>
<td>9.5</td>
<td>0.063</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>200</td>
<td>10.5</td>
<td>0.33</td>
</tr>
<tr>
<td>Cell Hosedown</td>
<td>25000</td>
<td>12.8</td>
<td>0.21</td>
</tr>
<tr>
<td>Chlorine Condensate</td>
<td>300</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>Brine</td>
<td>20000</td>
<td>-</td>
<td>1.8</td>
</tr>
</tbody>
</table>

3.1.5.3 Phosphate and Nitrate Industrial Waste Samples

No industrial sample of phosphate or nitrate were obtained, however industrial evidence (Melbourne Water, 2000) indicated that industrial effluent being released to sewer was typically 30 – 100 ppm in phosphate. A value of 50 ppm was chosen as a realistic discharge concentration. Analysis of phosphate was carried out using the Molybdenum blue method (Cotton et al., 1980; Vogel, 1983).

Nitrate experiments were based on the concentrations added during adsorbing colloid flotation and not on their typical industrial waste concentrations. Nitrate was analysed using the method of APHA (1998).

3.2 Oxide Preparation

Many studies have been carried out using various substrates as models for soil, environmental or waste colloids. Many of these "model" colloids are chosen for their chemical simplicity, monodispersity and ease of preparation. Matijevic and coworkers (McFadyen and Matijevic, 1973; Catone and Matijevic, 1974, Matijevic et al., 1975; Matijevic and Scheiner, 1978), for example, have prepared a series of ideal, model, spherical, monodisperse, insoluble colloids. Harding and Healy (1985 a, b) have used polystyrene latex particles, and Burns et al. (2004) have used brown coal. For studies which mimic industrial waste treatment, however, Crawford et al. (1993a, 1993b, 2002) and Sanciolo et al (1992, 1993) have argued that the amorphous, hydrous metal oxides...
formed from hydrolysis of aqueous heavy metal solutions are the most appropriate models, despite their significant detractors in that their surface is poorly characterised, irregular and non-crystalline.

A further discussion of why hydrous metal oxides are a good choice for studies which are designed to mimic industrial waste treatment is given in Section 4.2, where it is also argued that a 2:1:1 mixture of Al(III):Fe(III):Fe(II) may serve the best “model”.

When such oxides are formed, it is common to purify them and obtain a dispersion which is at low ionic strength, relatively free of the anions which have been used to balance the heavy metal cation of interest and free of any coagulum or small, improperly formed particles (e.g. James et al. (1985)). A counter argument, however, is that such model colloids do not represent the colloidal dispersions likely to be used during industrial waste clean-up. During industrial waste clean-up, it is likely that hydrous metal oxides would be formed and then used without further treatment since any further treatment would add to cost and would probably not enhance effectiveness anyway.

The decision in this thesis was to prepare hydrous metal oxides using the stock solutions discussed in Section 3.1.2, simply by raising the pH and waiting for an appropriate induction period for the colloid to form. The minimum time for colloid formation was 30 minutes, but longer times were used as specified throughout the thesis. No further treatment (e.g. dialysis to purify the colloid) was carried out.

3.3 Adsorption Experiments

Adsorption of sulphate, phosphate and mercury onto the various hydrous oxides were carried out in 400 cm³ jacketed flange flask reaction cells, as shown in Figure 3.1. The cells were kept at a constant temperature of 25°C by use of a Haake constant temperature water bath. Exposure to air was kept to a minimum by use of high purity nitrogen. The nitrogen was passed firstly through a silica suspension followed by acid and base (not shown in Figure 3.1) prior to entering the reaction cell. This process ensures the purity of nitrogen and avoids evaporation of the solution and subsequent volume loss. pH measurements, addition of reagents and sample removal were carried out through glass quickfit connections in the flange top (port of sampling). The solutions were constantly stirred using a Teflon coated magnetic stirrer bead and
degassed for at least two hours prior to pH adjustment, thus ensuring a carbonate free atmosphere and constant pH. An equilibration time of 60 minutes was selected. Preliminary adsorption experiments with an equilibration of 24 hours yielded no difference in adsorption for either the adsorption of mercury or the adsorption of sulphate (data not presented here).

![Figure 3.1: Water Jacketed Reaction Vessel for Adsorption Studies](image)

The metal ion salts used to prepare the colloidal dispersions were added to the reaction vessel, along with an appropriate volume of $10^{-3}$ M KNO$_3$ solution. Note that although $10^{-3}$ M KNO$_3$ was used as a background electrolyte, for all experiments, this was more a matter of consistency than necessity. In almost all cases, the background electrolyte remaining through unreacted components of the metal salts was sufficient to generate a background electrolyte concentration well in excess of $10^{-3}$ M and it is an unfortunate, but unavoidable, consequence of the methodology that experiments carried out with differing colloid concentrations have differing ionic strengths.

The pH was raised to the starting pH of the experiment (usually pH 4) and the analyte of choice (sulphate, phosphate, mercury) was added. A further 30 minutes equilibration time was allowed before sampling through the “port of sampling”. The sample was then filtered through a 0.2 μ Millipore filter to separate the colloid from its serum and the analyte concentration in the supernatant was measured. Adsorption was calculated from the difference between the initial concentration and the concentration in the supernatant.
Following sampling, the pH was raised by an increment of no more than 0.5 pH unit. An equilibration period of 15 minutes was allowed before readjusting the pH back to the desired value. pH drift was common, and the direction was measured in all cases. In some cases, notably the sulphate adsorption experiments, the extent of pH drift was measured and recorded. Acid (HNO₃) and/or base (KOH) was used to maintain the pH at the desired level until there was no further pH drift (defined by < 0.1 pH unit per minute).

Following equilibrium, a further sample was taken and analysed as above, and the pH again rose by no more than 0.5 pH units. The above process was then repeated until the conclusion of the experiment (usually around pH 10).

3.4 Flotation Experiments
3.4.1 Adsorbing Colloid Flotation
Industrial wastewater and synthetic wastewater were treated using the same flotation methodology. A 20 cm³ aliquot of sample wastewater was dosed with the required amount of metal ion (usually Al(III), Fe(III), Fe(II), or a mixture thereof) and placed into a modified Hollimond cell (see Figure 3.2). The natural pH of the dosed waste sample was generally low (less than a pH of 4), particularly in the case of Fe(II). If the pH was not less than 4, acid was added to lower the pH to below 4 prior to mixing the waste with the colloid precursor. No attempt was made to purge the system of air since compressed air was to be used to effect flotation.

Colloid was formed by raising the pH using NaOH to the required value (pH 4 – 10) and was allowed to equilibrate for 15 minutes prior to addition of surfactant. Surfactant was added and a further 15 minute equilibration period was allowed before flotation took place. Instrument grade air was passed through a glass frit and bubbled through the modified Hollimond tube creating a foam. The foam, in turn, was allowed to migrate out of the Hollimond tube and was collected in a second vessel. The foam was then allowed to drain for 30 minutes and the drainage was removed for analysis. The percentage floated was determined by knowing the initial concentration, and volume, of analyte and the concentration, and volume, of analyte which drained from the foam.
The entire process, known as adsorbing colloid flotation in the total carry-over mode (Sanciolo 1992), can be further understood through the use of a schematic diagram, as shown in Figure 3.2.

**Figure 3.2**: Schematic Diagram of Adsorbing Colloid Flotation.

6  Humidified air inlet  
7  Rotameter  
8  20 cm³ flotation cell (ID 2.5 cm, height 10 cm)  
9  Porous glass frit (porosity 4)  
10 Foam Collection Vessel

Adsorbing colloid flotation is assumed to occur in the following key steps:

7. The colloid pre-cursors (usually Al(III), Fe(III), Fe(II) or a mixture thereof) must first be formed into a colloid, usually by an increase in pH. Under industrial conditions it might be possible to form the colloid simply by adding the precursors directly to the waste and using the pH of the waste to form the colloid.

8. The waste material (e.g. sulphate, phosphate or mercury) adsorbs onto the formed colloid, removing the waste from solution. Under the conditions of adsorbing colloid flotation used in this study, the waste adsorbs onto to the colloid at the same time as the colloid forms, thus it is possible that co-precipitation rather than adsorption is the removal mechanism. Crawford *et al.* (1993a, 1993b, 2002) have shown that coprecipitation can be far more efficient than adsorption as a removal mechanism so should be encouraged.
9. Surfactant is added for two purposes. Firstly, it renders the colloid hydrophobic and allows attachment to air bubbles. Secondly, it serves to stabilize the foam. The foams from adsorbing colloid flotation are believed to be solids stabilised (Sanciolo et al., 1992, 1993) and for this to happen there needs to be a delicate balance between adsorbing enough surfactant to render the surface hydrophobic enough to attach to bubbles, but not enough to cause desorption and/or destabilisation. Desorption and/or destabilisation will occur if the surfactant causes the surface to become too highly (negatively) charged.

10. Flotation is effected, in this case, by a very high air flow rate. This causes all the liquid in the flotation tube to be floated. Sanciolo et al. (1993) have described this form of flotation, referred to as “total carry-over mode” (TLC) and have described the properties of foam formed from such a mode. The conditions of flotation used in the current work reflect that of Sanciolo et al. (1993).

11. The foam is collected in a second container where it is allowed to drain for 30 minutes. The goal is for the foam to drain “cleanly”, i.e. for the waste analyte to be trapped in the foam and not to desorb back into solution. Any increase in analyte concentration in the drainage after 30 minutes is considered to reflect instability of the foam rather than inefficiency of the flotation step. Stability of the foam is an obvious next step for studies in this area and was studied in the current work on a limited, “need to know” basis, i.e. when it was important to know the stability of the foam it was measured.

3.4.2 Foam Stability
When required, foam stability was measured using peak heights as a function of time beginning immediately after the air was turned off. Peak heights were measured using a simple ruler and the height of the foam was determined from the highest clearly visible liquid component.

3.4.3 Foam Type
Foam type was determined, when required, by visual observation and is described, in detail, in Section 4.2.1.
3.5 Surface Characterisation

Techniques used to characterise the colloid substrate surface, in the absence and in the presence of absorbing analytes, are described below:

3.5.1 Particle Size

Particle size and number was measured using a Coulter N4 particle size instrument. The technique uses dynamic light scattering and is restricted to particles under 5 μ. Where required, particle size distribution is reported, otherwise a weight average particle number is used. The bulk of particles formed during the preparation of hydrous metal oxides where well under 5 μ.

3.5.2 Surface Area

Measurement of the surface area of colloidal substrates is problematic with several techniques available, each with their own advantages and disadvantages. There is probably no unambiguously appropriate surface area to use as a representation of the available surface area for adsorption of anions from solution. The BET surface area from nitrogen adsorption is the most common technique used and has been used here. Although surface area is a key parameter to determining the extent of adsorption at any given pH, it should be noted that a number of authors, e.g. Crawford et al. (1996), have found (by modelling of the data) that even a substantial increase in surface area tends to shift the graph, relative to the pH axis, by only a slight amount. The main affect is, in fact, a slight change to the gradient of typical curves measured. Thus even substantial errors in the assumption of BET surface area are likely to be overshadowed by the intrinsic pH-dependent nature of adsorption and the absorbent’s intrinsic potential for adsorption (Davis et al., 1978).

The BET surface of the amorphous metal hydrous oxides formed using 1,000 ppm total metal ion was measured and the results are given in Table 3.2.

As can be seen from Table 3.2, the surface areas are relatively high reflective of the amorphous nature of hydrous metal oxides (Crawford et al., 2003a, 2003b).
Table 3.2: Surface Area of Hydrous Metal Oxide Substrates

<table>
<thead>
<tr>
<th>HYDROUS OXIDE</th>
<th>B.E.T. SURFACE AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>240 m² g⁻¹</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>235 m² g⁻¹</td>
</tr>
<tr>
<td>Al(III)</td>
<td>187 m² g⁻¹</td>
</tr>
<tr>
<td>Al(III), Fe(III), Fe(II): 2:1:1</td>
<td>83 m² g⁻¹</td>
</tr>
</tbody>
</table>

3.5.3 Electrophoretic Mobility

As will be explained in detail in Section 4.4, surface charge can be measured as zeta potential which can, in turn, be determined from measurements of electrophoretic mobility. Data trends in electrophoretic mobility are reflective of changes to the surface charge and electrophoretic mobility is commonly used to describe such phenomenology without conversion to zeta potential.

Electrophoretic mobility was measured using a Coulter, DELSA 440 (Doppler Electrophoretic Light Scattering Analyzer). The electrophoretic mobility of suspensions with particles ranging from 0.02 μm to 30 μm was measured by the Doppler shift of the laser light scattering spectrum. The colloidal or macromolecular particles are subjected to an electric field and the drift velocity is measured using laser Doppler measurements at four different angles simultaneously. The resulting composition of spectra allows the electrophoretic mobility to be measured.

3.5.3.1 Phosphate and Mercury Experiments

Electrophoretic mobility was measured simultaneously with adsorption experiments (see Section 3.3). Samples were placed directly into the DELSA electrophoresis cell at 25°C ensuring no air bubbles were present. The sample was ultrasonified for approximately 20 sec to ensure dispersion of colloidal particles. The stationary positions of the cell both upper and lower were detected using the digital to analog converter test as described by Coulter Electronics. The electrophoretic measurement value is the average of both the stationary values.
3.5.3.2 Sulphate Experiments
The sulphate adsorption experiments were conducted under very high colloidal concentrations, and these concentrations were above the threshold of the DELSA instrument (all light scattering techniques require low turbidity). In this instance, a sample was collected by syringe and centrifuged at 10,000 r.p.m. for 10 minutes. A small amount of colloidal substrate was resuspended in the mother liquor giving a low concentration sample which could be (and was) analysed as described in Section 3.5.3.1.

3.6 Analytical Procedures
All samples collected were filtered with 0.23 μm Millipore nitrocellulose filters into glass vials and analysed for the analyte of interest.

3.6.1 Sulphate
Sulphate was determined by nephelometry using a Corning-Eel nephelometer. Nephelometry is based on the intensity of scattering of light under defined conditions and sulphate standards were used to compare with light scattering by the sample. For the analysis of sulphate, an excess of barium chloride was added to the sulphate mixture in order to produce the turbid suspension which was measured to give a quantitative analysis of sulphate.

3.6.2 Phosphate
Phosphate was determined using the molybdenum blue method. Molybdophosphoric acid is formed and reduced by the reducing agents stannous chloride, ascorbic acid or hyrazinium sulphate to an intensely coloured molybdenum blue. Colour intensity (which is directly proportional to concentration of analyte) was measured using a Cary 1E UV-VIS spectrophotometer with the determining wavelenth at 880 nm. The claimed detection limit is 5μg P/L (APHA, 1998).

3.6.3 Mercury
Mercury was analysed using flow injection hydride generation cold vapour atomic absorption spectroscopy, using a Perkin Elmer 1100 FIAS 200. The system uses a gas/liquid separator rather than a membrane separator and is characterized by low
sample consumption, high efficiency and high sensitivity with a detection limit of 0.06 μg/L (analysis was performed, with thanks, by Mr Max Amos of Monash University).

All mercury samples were acidified at the point of sampling and filtered through a 0.23 μm Millipore nitrocellulose filter. The hydride was formed using sodium or potassium borohydride as the reductant in acid medium and swept into the atomizer with the inert carrier gas Argon. The determination was swift with 1-2 minutes required for a measurement, thus suppressing any slower possibly interfering reactions. The use of a large mixing chamber eliminates the chances of interference by surfactants being introduced into the atomizer (i.e. not bubbling up into the atomizer). Surfactant blanks were used to ensure there were no instrumental artifacts of measurement.

3.6.4 Nitrate
The true ionic strength of the mixture used is difficult to ascertain because of the large quantities of ionic species, for e.g. NO₃⁻, remaining in solution in which the background colloidal material is prepared.

The electrolyte concentration used in adsorption and coprecipitation experiments was dominated by the high concentration of nitrate required to prepare the colloidal substrates (precipitated from a solution of the appropriate metal nitrate, 1000 ppm with respect to the metal in the case of sulphate), the concentration of the adsorbing /coprecipitating metal anion solutions (mercury chlorides, potassium phosphate, potassium sulphates or potassium nitrates) and the acid or base required for adjustment of the pH. It is difficult to estimate the resultant electrolyte concentration since an unknown amount of the electrolyte is occluded and/or adsorption by the colloidal phase and thus lost to the solution.

The total background concentration used was determined to be the equivalent of 0.0175 M KNO₃ by calibration of the colloidal suspension’s conductivity with standard KNO₃ solutions. The colloid chosen was the 2:1:1 mix of Al(III), Fe(III) and Fe(II) respectively. It was found that the conductance of these solutions did not change over the pH range 3 to 11, and was only marginally dependent on the type of colloid chosen.

In one experiment, the concentration of nitrate was directly measured using a Cary 1E UV-VIS visible spectrometry. The absorbance was measured at 220 nm and a second
reading was taken at 275 nm. The difference between the two absorbance measurements was calculated using $\text{Abs}_{220} - 2^{\text{Abs}_{275}}$.

**3.6.5 pH**

pH measurements were made using an Activon model 209 pH/mV meter which was calibrated using 0.05 M AR grade potassium hydrogen phthalate (BDH chemicals), and LR grade 0.01 M sodium tetraborate (Ajax chemicals).
4.1 Introduction

Sulphate, as stated earlier, is a problematic contaminant in wastewater. Microbial action on sulphate leads to the production of toxic gas H₂S and under acidic conditions, sulphate can attack cement drains leading to their collapse. New remediation techniques are constantly being sought and the process of adsorbing colloid flotation (ACF) is one such means by which sulphate contaminated wastewater can be treated.

Adsorption of sulphate onto colloidal substrates has been studied by a number of authors (see for example; Chao et al., 1964; Aylmore et al., 1967; Barrow, 1969; Breeusma and Lyklema, 1973; Parfitt and Smart, 1978; Rajan, 1978; Rajan, 1979; Fuller et al., 1985; Hue et al., 1985; Hodges and Johnson, 1986, MacDonald and Hart, 1990; Curtin and Syers, 1990a,b,c; Zhang and Sparks, 1990; Autry and Fitzgerald, 1993; MacDonald et al., 1994; Ali and Dzomback, 1996; Persson and Lovgren, 1996; Geehoed et al., 1997; He et al., 1997; Hug 1997, Gobran et al., 1998; Eggleston et al., 1998; Peak et al., 1999, Rietra, 1999; Rietra et al., 2001b, Gustaffson, 2001; Juang and Wu, 2002; Moret and Rubio, 2003; Kimsey et al., 2004; Paul et al., 2005).

Fewer authors have specifically studied the adsorbing colloid flotation of sulphate (see for example; Rubin and Haverkost, 1973; Currin et al., 1979; Pluta, 2001).

The following chapter will investigate the adsorption and flotation of sulphate using hydrous metal oxides of aluminium(III), iron(III), iron(II), and a mixture thereof. It will also investigate the affect of adsorption on surface characteristics of those hydrous oxides.
4.2 Preliminary Investigation

Adsorbing Colloid Flotation is presented, in this thesis, as a viable alternative to a number of other wastewater treatment technologies, specifically for the removal of dissolved aqueous contaminants such as mercury, sulphate and phosphate. In choosing an appropriate substrate, cost, practicality, effectiveness, efficiency and environmental sustainability are amongst the many parameters which will influence the final choice in an industrial environment. A pragmatic approach can be adopted whereby the starting materials are those substrates which have been commonly used as adsorbents in wastewater treatment, particularly in adsorbing colloid flotation. Popularity of study is an indicator of the likely success of the adsorbent and will be used here to make an initial choice. Validation studies, to determine the effectiveness and efficiency of those substrates, will then be carried out, in particular to determine an appropriate concentration and mixture of substrates to use.

4.2.1 Choice of Surfactant and Colloid Mixtures

Metal hydrous oxides have been widely used in adsorbing colloid flotation and have been successfully applied to the removal of various ions from aqueous media. Zeitlin and Chaine (1974), for example, were successful in the removal of phosphate and arsenate using ferric hydroxide. Mukai et al. (1979) used ferric oxide in the removal of mercury. Barnes et al. (1979) used ferric hydroxide and aluminium oxide in the removal of nickel and manganese. Sanciolo et al. (1992), were successful in the removal of electroplating waste using ferric and aluminium hydrous oxides. Thus hydrous oxides of aluminium and iron are adsorbents of choice in adsorbing colloid flotation and will be used in this thesis.

Notwithstanding the use of hydrous aluminium and iron oxides in adsorbing colloid flotation, they have also been extensively studied as simple adsorbents, particularly in the soil literature where it is recognised that they are major constituents in soil. Rajan (1978), Parfitt and Smart (1978), Curtain and Syers (1990a,b,c) and Boland and Barrow (1984), for example, all use these oxides as model for soil, to effect adsorption.

Most importantly for the work to be presented in this thesis is the use of hydrous iron and aluminium oxides by Sanciolo et al. (1992, 1993) and Crawford et al. (1993a, 1993b, 1996, 1997, 1999, 2002). Sanciolo et al. (1993) pioneered the use of dual surfactant systems and the use of total carry over mode which enables adsorbing colloid flotation to work more effectively than previously reported. Crawford et al (1993a, 1993b, 1996,
1997, 1999, 2002) then carried out a fundamental characterisation of the oxides involved (predominantly hydrous iron oxide) and their ability to act as adsorbents for aqueous heavy metals (specifically Zn(II), Ni(II) and Cr(III)). The work presented in this thesis follows on from these studies, applying a similar removal technique to anions (e.g. sulphate) rather than heavy metal cations.

Sanciolo et al. (1992, 1993) used a mixture of dodecanoic acid (DA) and sodium dodecyl sulphate (SDS) to effect flotation and these will also be tried here. In their case, however, the species to be floated were cationic heavy metals. Given that the species of interest in this thesis are anionic, it is logical to assume that a cationic surfactant would be appropriate. Cetyl triethylammonium bromide (CTAB) was chosen because it is ubiquitous, inexpensive and widely used.

Preliminary investigation appeared to indicate that the choice of surfactant and colloid mix was crucial in determining foam type. Foam type is of crucial importance to the success of adsorbing colloid flotation as either an industrial waste treatment or an environmental scrubbing treatment technology. Full analysis of the foam, and particularly its treatment following adsorbing colloid flotation, was considered outside the scope of this thesis. However, it can be assumed that the technology will only be useful if the foam is “spadeable”, meaning that it can be mechanically scooped in large quantities without destabilisation. The goal, then, is to remove the foam to an area for further treatment, which could involve:

- destruction to a small volume by, for example, treatment with concentrated acid,
- landfill,
- reuse in areas such as agriculture where a foam containing soil wetting properties (from the surfactant), nutrient (from the sulphate and/or phosphate) and soil conditioners (from the hydrous metal oxide) may be marketable, and/or
- recovery of analytes such as gold, silver and possible mercury which may be of intrinsic value.

Preliminary experiments of sulphate treatment using ACF were used to determine the foam type obtained from various concentrations and types of surfactant, and various concentrations of mixed oxide precursors. The results are given in Figure 4.1 and correspond to the conditions given in Table 4.1.
The stability of the foam is dependent upon type and concentration of adsorbing colloid and surfactant. To illustrate the characteristics of the foams formed in these preliminary experiments, the following categories were used:

1. No foam formed, or its persistence time was less than 30 seconds.
2. A foam which persisted for more than 30 seconds in the column but did not contain any adsorbing colloid and collapsed during the experiment (10 to 20 minutes).
3. A foam which persisted in the column but collapsed in collection was formed; i.e. there was foam but no uptake of the adsorbing colloid and flotation was not successful.
4. A foam which persisted both in the column and collection was formed but there was no uptake of the adsorbing colloid, i.e. a foam was formed but flotation was unsuccessful.
5. A foam which persisted in the column for more than 30 seconds did contain adsorbing colloid but collapsed and released the colloid during the time scale (10 to 20 minutes) of the experiment.
6. A foam which persisted in the column for the full duration of the experiments (10 to 20 minutes) was formed but collapsed instantly on collection (or when the air flow was stopped).
7. A foam persisted both in the column and following collection was formed, and it contained colloid. This type of foam however was gelatinous and sometimes started releasing colloid shortly after collection, i.e. flotation was successful but to use this configuration in a continuous mode would be unsuccessful.
8. A foam which persisted both in the column and following collection was formed. The colloid containing foam was stable for up to 2 minutes.
9. A foam which contained the adsorbing colloid both in the column and upon collection was formed. The colloid containing foam was stable for up to 20 minutes.

The foam type we sought for successful adsorbing colloid flotation was foam type 9, although foam types 7 and 8 would show promise and were not dismissed out of hand.
The data shown in Figure 4.1 illustrate that a “good” foam is not always formed and requires judicious choice of both the colloid precursor and surfactant.

Best foams were formed from colloids involving a mixture of aluminium(III), iron(III) and iron(II). Not shown in these results is a number of trial and error experiments which were performed in a rigorous fashion but which indicated that the iron(II) was particularly helpful in obtaining a good foam and that aluminium(III) on its own was never found to form a good foam.

A mixture of DA and SDS was found to result in the best choice of surfactant and CTAB was found to interfere with foam stability even when present in small amounts. At first sight this may appear counter-intuitive since the waste analyte (SO₄²⁻ in this case) was, like DA and SDS, negatively charged and, particularly at high pH the colloid also carries a negative charge. It might have been reasonable to expect that adsorption of the cationic surfactant (CTAB) could enhance the adsorption of the

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Mg²⁺</th>
<th>Fe²⁺</th>
<th>Fe³⁺</th>
<th>Al³⁺</th>
<th>DA</th>
<th>SDS</th>
<th>CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td></td>
<td>100</td>
<td>200</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td></td>
<td>100</td>
<td>200</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td></td>
<td>50</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td></td>
<td>50</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td></td>
<td>100</td>
<td>200</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>100</td>
<td></td>
<td>50</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mg²⁺ was added as MgCl₂, Fe²⁺ was added as FeCl₂
Fe³⁺ was added as Fe(NO₃)₂ DA is dodecanoic acid
SDS is sodium dodecyl sulphate CATB is cetyl triethylammonium bromide
Figure 4.1: Foam Type as a function of the experimental conditions listed in Table 4.1.

anionic waste (SO4$^{2-}$), help to keep the overall surface charge near neutral and thus
promote foam stability. Sanciolo et al. (1992), however, have shown this surfactant
mixture to work very well (with heavy metal cations) at high pH where the surface
charge on the substrates was negative. They attribute the ability of the system to
remain stable even under conditions where the surface charge might be near zero to
the enhanced stabilising properties of using a mixed surfactant (DA plus SDS). Even
so, at very high pH where the colloid is significantly negative, flotation was inefficient according to both the studies of Sanciolo et al. (1992) and those found here (see Figure 4.11).

Further evidence that CTAB is a poor choice of surfactant for adsorbing colloid flotation is presented in the mercury chapter (Chapter 6).

4.2.2 Concentration of Colloid

Having selected the hydrous oxides of aluminium and iron (both ferric and ferrous) as model adsorbents, preliminary investigation (not shown here) indicated that a mixture of Al(III):Fe(III):Fe(II) with a ratio of 2:1:1 (by mass of metal ion used to form the colloid) provided a very effective substrate in terms of floatability. Such a mixed colloid is also indicated by the “real” situation likely to be encountered in industry. Both Fe(III) and Al(III) are common in industrial wastes and sometimes form a colloid during simple pH control, obviating the necessity to deliberately add a colloid to initiate adsorbing colloid flotation (Sanciolo, 1992). This process probably also occurs in nature where it is believed that adsorption onto oxide and clay components of soil is a major control feature for aqueous contaminants (Jenne, 1968; Suzuki, 1997). Ferrous sulphate is often used as a flotation aid (Sanciolo 1992) without necessarily a good understanding of why. Consequently, all three oxides are often present as a mixed hydrous oxide in “real world” situations. Full investigation of an optimum ratio (i.e. was 2:1:1 the best ratio?) was considered outside the scope of this thesis.

To determine an appropriate colloid concentration for use in later studies, the mixed oxide system (Al(III):Fe(III):Fe(II) = 2:1:1) was chosen as the most representative and used to adsorb sulphate. The foam stability data in Figure 4.1 shows this to be also a fortuitous choice in terms of foam type and stability. The results are presented in Figure 4.2, where the percent removal of sulphate from a 2,000 ppm sulphate solution is plotted as a function of total colloid concentration. Colloid concentration is defined as the mass of metal ion used to form the hydrous metal oxide, i.e. a 1000 ppm total colloid would be formed from 500 ppm Al(III) present as Al(NO₃)₃, 250 ppm Fe(II) present as Fe(Cl₂), and 250 ppm Fe(III) present as Fe(NO₃)₃. In each case, hydrolysis results in the formation of a hydrous, amorphous metal oxide (a mixed metal hydroxide in this case).
Figure 4.2 illustrates that as the concentration of the colloid increases so to does the % of sulphate adsorbed, in an almost linear fashion up to a concentration of about 3,000 ppm., an observation also supported by the results of Chao et al. (1964). The pattern is not so clear above 3,000 ppm, where the % removal at pH 8.5 actually falls. The three pH values chosen, pH 6.5, pH 7.0 and pH 8.5, were chosen to represent typical pH values found in the environment and under industrial situations. pH 7.0 is, of course, neutral, pH 6.5 represent slightly acidic values and pH 8.5 represents slightly alkaline values. At high colloid loadings (above 2,000 ppm) there is a marked

![Graph showing the adsorption of sulphate as a function of colloid concentration for different pH values.](image)

**Figure 4.2:** Adsorption of 2,000 ppm sulphate using a mixed hydrous oxide formed from a solution of Al(III):Fe(III):Fe(II) in the ratio of 2:1:1.

difference between the results for different pH values, with the lower pH values resulting in higher percent adsorption of sulphate. This is to be expected, since sulphate is likely to be more attracted to the positive nature of surfaces at lower pH values and such electrostatics will form a major theme in further discussion in this chapter. The apparent lack of pH dependence at low solids loadings (below 1,000 ppm) is more interesting but may simply reflect the generally low % adsorption observed.
It is tempting to take the data in Figure 4.2 as a clear observation that “more is better” and that a high solids concentration is desirable because it is more effective at removing sulphate. But is it more efficient? Efficiency in this case must take into account the added cost of additional substrate both in terms of the cost of material and the cost in terms of the additional waste generated by excessive use of the colloid. It should be remembered, in this case, that the colloid is formed by hydrolysing a solution of metal nitrate (or metal chloride) and that this inevitably leads to some contamination from nitrates and chlorides. The extent of contamination is not clear since the colloid formed will also adsorb (or entrap) some of the anion used to make it. It is likely that this process will be more efficient at low colloid concentrations than at high concentrations where the concentration of nitrate (or chloride) which needs to be removed is proportionally higher.

From Figure 4.2, it would appear that doubling the colloid concentration from 1,000 ppm to 2,000 ppm roughly doubles the percent removal and that increasing it further results in a lesser gain. A doubling of concentration results in a near doubling of operational costs and possibly a greater than doubling of environmental costs. Thus there would appear to be little benefit to using a higher colloid concentration. The decision made for sulphate removal, is to use the same concentration of colloid as that of the material being removed. The majority of experiments will be carried out using 1,000 ppm sulphate, so the decision was made to use 1,000 ppm colloid. This choice is fortuitous given the favourable foam type data presented in Figure 4.1.

4.3 Sulphate Adsorption

Adsorption is almost certainly the first step involved in the adsorbing colloid flotation technique and is also worthy of study in its own right due to the importance of adsorption as a control of concentration of contaminants in the environment (Jenne, 1968; Suzuki, 1977). The role of the adsorptions step in adsorbing colloid flotation is a major theme in this thesis.
4.3.1 Sulphate Adsorption - Percent Adsorption

The effectiveness with which the various hydrous metal oxides remove sulphate, through adsorption, was measured and the data given in Figure 4.3.

There are several trends immediately apparent from this graph and these are:

Hydrous aluminium(III) oxide is the most effective under the conditions studied.
Hydrous ferrous oxide was the least effective under the conditions studied. The mixed oxide, not surprisingly, falls between its pure components, i.e. it is more effective than the hydrous iron oxides but less effective than the hydrous aluminium(III) oxide.

![Graph showing sulphate adsorption percentages]

**Figure 4.3:** Percentage (%) adsorption of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 ppm (total) metal ion.
reason for the low effectiveness of hydrous ferrous oxide is not immediately apparent, especially given that this material had the highest surface area (see Table 3.2).

- Clearly, hydrous aluminium(III) oxides form an intrinsically more effective adsorbent for sulphate than does hydrous ferric oxide which, in turn, is more effective than hydrous ferrous oxide.

- At moderate to high pH values, percent adsorption decreases as pH increases. This is almost certainly due to electrostatic forces. As the pH is increased, colloidal surfaces become increasingly more negatively charged (or decreasingly positively charged depending on the isoelectric point of the colloid). Sulphate, being negatively charged, will be increasingly less favourably attracted to the surface as pH is increased.

- At low pH, percent adsorption decreases as pH decreases. This result is unexpected on the basis of electrostatic interactions but may be explained by incomplete formation of the colloid at low pH, particularly in the case of hydrous aluminium(III) oxide, which forms at a higher pH than the hydrous iron oxides. Hydrous aluminium(III) oxide, for example, requires a pH above 5 to fully form (see, for example, Parks (1965)). Until it has fully formed, it cannot act as a good adsorbent.

- Adsorption at low pH values may be greater than predicted on the basis of simple hydrous oxide formation. Crawford et al. (2003a) has clearly shown that hydrous metal oxides can precipitate at pH values below their adsorption curves if the formation of the colloid occurs in the presence of a contaminant. In this case, a coprecipitate forms and is a more effective adsorbent than if the colloid was allowed to fully form prior to the introduction of the contaminant. A similar mechanism may be occurring in Figure 4.3. The solid formed was visible as a white gelatinous material and may be partly jurbanite (AlOHSO₄) as suggested by Hue et al. (1985). This observation can be supported by solubility data (Curtain and Syers, 1990c).

- Notwithstanding any of the above points, it is pleasing to note that adsorption of sulphate was significant at a one to one (by mass) ratio. Sulphate is considered an intractable waste and is very difficult to treat. Although the percent adsorption only fleetingly reaches above 90% removal (value of which are quite common for metal ion removal (Harding and Healy, 1985a, Harding and Healy, 1985b, Crawford et al, 1992), the removals reached are considered more than adequate for industrial control of sulphate, particularly if the process can be repeated as a polishing stage,
and specifically if the percent removal by adsorption can be matched by adsorbing colloid flotation.

The removal of sulphate, by adsorption, with hydrous aluminium and/or iron oxide has been previously reported and the findings are consistent with the data in Figure 4.3. Rajan (1978), for example, effected adsorption of sulphate in a nitrogen atmosphere with a 3 hour reaction time using alumina with a maximum adsorption of 817 μeq/g at pH 5. Parfitt and Smart (1977) obtained a maximum adsorption of 600 μeq/g at pH 4.5 using ferric oxide. No data is known to this author for sulphate adsorption by hydrous ferrous oxide. Although the reported data is not fully consistent with the absolute value of pH at maximum adsorption, it is consistent with the phenomenon of a maximum, and slight differences in experimental conditions (e.g. substrate to contaminant ratio) can easily account for the slight differences of pH maximum. Rajan (1978) also studied the kinetics of sulphate adsorption and demonstrated that approximately 90% of the reaction was over in ten minutes. The equilibration time of 1 hour used in obtaining the results of Figure 4.2 is, then, justified.

Although the results of Figure 4.3 would immediately suggest hydrous aluminium(III) oxide as the substrate of choice, there are ameliorating factors which make the use of aluminium less attractive. Not the least of these is the (probably unwarranted) attention aluminium has gained due to its supposed link to Alzheimers Disease. Aluminium is also more expensive than iron giving a sound economic reason for using iron(III) oxide.

A mixed hydrous metal oxides may be the most appropriate model for both environmental and industrial situations because of its greater complexity. The results presented in Figure 4.3 are, overall, consistent with the general trends seen in sulphate adsorption by complex materials such as soil (MacDonald et al., 1990; Autry et al., 1993; MacDonald et al., 1994 and Fuller et al., 1985), particularly the often cited dependence on the amount and ratio of Fe(III) and Al(III) in soil (Gobran et al., 1998; Aylmore et al., 1967; Hue et al., 1985; Curtain and Syers 1990a; Curtain and Syers, 1990b; Curtain and Syers, 1990c; Hodges et al. 1986; Barrow, 1969; Gobran et al., 1997 and Johnson, 1998). Further analysis of all four substrates is thus still warranted.
4.3.2 Sulphate Adsorption - Adsorption per Mass of Substrate

As stated earlier, the results presented in Figure 4.3 are contrary to that expected from surface area (Table 3.2) alone. However, this may be an artifact of the way the data is presented. It is instructive, therefore, to present the data in a number of different ways. Substrate concentration, in Figure 4.3, is determined by the mass of each metal ion within the hydrous metal oxide. Since the different hydrous metal oxides have differing stoichiometries, the overall mass of colloid is not constant. Hydrous ferrous oxide (Fe(OH)$_2$, for example, will contain less mass than hydrous ferric oxide (Fe(OH)$_3$), although both have the same mass of iron (Fe). The data in Figure 4.3 can be transformed (on the assumption that the stoichiometries of the hydrous metal oxides formed are Al(OH)$_3$, Fe(OH)$_3$ and Fe(OH)$_2$), by dividing the mass of sulphate adsorbed (g) by the mass of colloidal substrate formed (g) (assuming total conversion of the metal ion salt into the hydrous metal oxide, and assuming no chloride or nitrate is occluded along with the oxide). The so-transformed data, as a function of pH, is shown in Figure 4.4.

Consistent with the data trends shown in Figure 4.3, the data in Figure 4.4 shows a maximum in sulphate adsorption (for hydrous aluminium(III) oxide), a decrease in adsorption as a function of pH for most of the pH range studied, and significant adsorption capacity. These trends, of course, are expected to remain since the data has only been transformed and not otherwise altered.
Figure 4.4: Adsorption, by mass, of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 (total) metal ion.

The transformed data (Figure 4.4) would be expected to, and does, favour hydrous ferrous oxide (Fe(OH)$_2$) as an adsorbent because it has the lightest mass, however the extent of transformation is dramatic and well worth reporting. Fe(OH)$_2$, as presented in Figure 4.3 is the least effective of the adsorbents, but as presented in Figure 4.4 is the most effective. This type of transformation illustrates the care with which one needs to examine data, particularly when making qualitative judgments. Moreover, it demonstrates the difference between “effective” and “efficient”. Hydrous aluminium(III) oxide remains the most effective of the adsorbents trialled because, as shown in Figure 4.3 it adsorbed the greatest quantity of sulphate. This is not apparent in Figure 4.4 only because the Y-axis does not represent a total quantity, rather it represents a
relative quantity (relative to the mass of adsorbent). Hydrous ferrous oxide is the most efficient substrate because, as shown in Figure 4.4, it removed significant quantities of sulphate using the least overall mass of substrate. As shown in Figure 4.3, however, it remains relatively less effective because the total amount of sulphate removed was still lower than for hydrous aluminium(III) oxide.

The implications, in terms of industrial practice as well as adsorption theory, behind the transformation of data from Figure 4.3 and Figure 4.4 should not be overlooked. From Figure 4.3 we would dismiss hydrous ferrous oxide as a suitable adsorbent yet from the same data as presented in Figure 4.4 we would promote it. Moreover, the data as presented in Figure 4.4 is now consistent with the surface area data in Table 3.2, leading to the normally accepted conclusion (Harding and Healy, 1979) that substrates with higher surface areas are more effective adsorbents.

### 4.3.3 Sulphate Adsorption - Adsorption per Mole of Substrate

Sulphate data as presented in Figure 4.3 indicates that hydrous aluminium(III) oxide is the better adsorbent whilst data presented in Figure 4.4 indicates that hydrous ferrous oxide is the better adsorbent. As a largely esoteric exercise, it would be interesting to see if there were a transformation which would result in hydrous ferric oxide as apparently the better adsorbent. This can, in fact, be achieved by plotting adsorption as amount adsorbed on a mole per mole basis, as shown in Figure 4.5. The data is transformed, again assuming the stoichiometries are Al(OH)₃, Fe(OH)₃ and Fe(OH)₂ and that no nitrate or chloride is included in the colloidal material. By definition, the number of mole of Fe(OH)₃ and Fe(OH)₂ must be the same since the experiment is based on equal masses of Fe. The lower molar mass of Al yields more mole of hydrous aluminium(III) oxide than hydrous ferric oxide, and thus hydrous aluminium(III) oxide would need to adsorb more sulphate to record the same removal efficiency. Whilst hydrous aluminium(III) oxide did adsorb more mole of sulphate, it was not enough to make it clearly more efficient, especially at low pH values where the hydrous aluminum oxide had not fully formed.
It should be noted that this particular method of displaying data is considered esoteric since it assumes a mole ratio is an appropriate parameter to base comparison of adsorption efficiencies on. Most moles of substance, however, lie within the colloid and not on the surface where interaction with solution occurs. Thus the number of moles has no true relevance to adsorption phenomena.

Figure 4.5: Adsorption, by mole, of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 (total) metal ion.
4.3.4 Sulphate Adsorption - pH Adjustment

In most cases, adsorption of sulphate was accompanied by an expected increase in pH, presumably due to reactions similar to the exchange reaction:

\[-\text{Al-OH}_2^- + \text{SO}_4^{2-} \rightleftharpoons \text{Al-OH-SO}_4^- + \text{OH}^-\]  

Equation 4.1

where the Al open bond is meant to indicate a surface and the reaction represents sulphate binding to an oxide functional surface site.

The increase in pH, and the volume of acid required to negate that increase, is of interest and is presented in Tables 4.2 to 4.5. In these tables, the initial pH represents the starting pH of the entire experiment. A given volume of base was added to give rise to the required, final pH. Very shortly thereafter, however, the pH drifted, presumably as a result of a reaction similar to Equation 4.1. After a 30 minute time period (which was generally more than enough for the pH drift to stabilise, < 0.1 pH unit / min) the resultant pH was recorded as “Sulphate pH”. Acid was then slowly added to return the pH to the “final” pH, this process taking a further 30 minutes and resulting in a now stable “final” pH. Whilst the final pH is the only value of import in terms of adsorption isotherms such as those in Figure 4.23, the extent of pH change is worthy of noting and is characterised, here, by \(\Delta \text{pH}\). To facilitate comparison with the adsorption isotherms (Figure 4.3), data which corresponds to the highest percent adsorption are bolded.

For three of the four substrates studied (hydrous aluminium(III) oxide, hydrous iron(III) oxide and hydrous mixed oxide) the expected trend is seen, i.e. the pH drift is greatest where adsorption is greatest providing good indication that the release of hydroxide ions (or the thermodynamically indistinguishable uptake of protons) accompanies adsorption of sulphate ions.

Hydrous ferrous oxide, however, provides anomalous data, with almost no drift in pH seen, including around pH 4 where a maximum in percent adsorption was noted. This indicates that there is no release or uptake of hydroxide (or protons) during the
adsorption step, contrary to the pattern observed for nearly all adsorption behaviour recorded, including those of Tables 4.2, 4.3 and 4.4 in this study. It is difficult to unambiguously propose an adsorption mechanism which can predict this result, however one possible reason could be that oxidation of Fe(II) to Fe(III) occurs during or shortly after adsorption onto the surface. Without attempting to provide a balanced set

**Table 4.2: pH changes during the Adsorption of 1,000 ppm SO$_4^{2-}$ onto 1,000 ppm Hydrous Aluminium(III) Oxide**

<table>
<thead>
<tr>
<th>Initial pH (1)</th>
<th>Final pH (2)</th>
<th>Sulphate pH (3)</th>
<th>Δ pH pH(3) –pH(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.20</td>
<td>4.0</td>
<td>3.8</td>
<td>-0.2*</td>
</tr>
<tr>
<td>3.15</td>
<td>4.5</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td>3.20</td>
<td>5.0</td>
<td>6.3</td>
<td>1.3</td>
</tr>
<tr>
<td>3.20</td>
<td>5.5</td>
<td>6.85</td>
<td>1.35</td>
</tr>
<tr>
<td>3.20</td>
<td>6.0</td>
<td>7.25</td>
<td>1.25</td>
</tr>
<tr>
<td>3.22</td>
<td>6.5</td>
<td>7.65</td>
<td>1.15</td>
</tr>
<tr>
<td>3.35</td>
<td>7.0</td>
<td>7.85</td>
<td>0.85</td>
</tr>
<tr>
<td>3.20</td>
<td>7.5</td>
<td>8.28</td>
<td>0.75</td>
</tr>
<tr>
<td>3.25</td>
<td>8.0</td>
<td>8.7</td>
<td>0.70</td>
</tr>
<tr>
<td>3.25</td>
<td>8.5</td>
<td>9.1</td>
<td>0.60</td>
</tr>
<tr>
<td>3.20</td>
<td>9.0</td>
<td>9.54</td>
<td>0.25</td>
</tr>
<tr>
<td>3.25</td>
<td>9.5</td>
<td>9.95</td>
<td>0.40</td>
</tr>
<tr>
<td>3.25</td>
<td>10.0</td>
<td>10.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* At pH 4.0 Al(III) is still soluble
Table 4.3: pH changes during the Adsorption of 1,000 ppm SO$_4^{2-}$ onto 1,000 ppm Hydrous Iron(III) Oxide

<table>
<thead>
<tr>
<th>Initial pH (1)</th>
<th>Final pH (2)</th>
<th>Sulphate pH (3)</th>
<th>$\Delta$ pH pH(3) –pH(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.15</td>
<td>4.0</td>
<td>5.53</td>
<td>1.53</td>
</tr>
<tr>
<td>2.15</td>
<td>4.5</td>
<td>6.22</td>
<td>1.72</td>
</tr>
<tr>
<td>2.15</td>
<td>5.0</td>
<td>6.42</td>
<td>1.42</td>
</tr>
<tr>
<td>2.15</td>
<td>5.5</td>
<td>7.05</td>
<td>1.40</td>
</tr>
<tr>
<td>2.15</td>
<td>6.0</td>
<td>7.45</td>
<td>1.45</td>
</tr>
<tr>
<td>2.15</td>
<td>6.5</td>
<td>7.55</td>
<td>1.00</td>
</tr>
<tr>
<td>2.15</td>
<td>7.0</td>
<td>7.95</td>
<td>0.95</td>
</tr>
<tr>
<td>2.15</td>
<td>7.5</td>
<td>8.30</td>
<td>0.75</td>
</tr>
<tr>
<td>2.15</td>
<td>8.0</td>
<td>8.52</td>
<td>0.52</td>
</tr>
<tr>
<td>2.15</td>
<td>8.5</td>
<td>9.02</td>
<td>0.5</td>
</tr>
<tr>
<td>2.15</td>
<td>9.0</td>
<td>9.40</td>
<td>0.4</td>
</tr>
<tr>
<td>2.15</td>
<td>9.5</td>
<td>9.80</td>
<td>0.3</td>
</tr>
<tr>
<td>2.15</td>
<td>10.0</td>
<td>10.20</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 4.4: pH changes during the Adsorption of 1,000 ppm SO$_4^{2-}$ onto 1,000 ppm Hydrous Mixed Oxide (Al(III):Fe(III):Fe(II) = 2:1:1)

<table>
<thead>
<tr>
<th>Initial pH (1)</th>
<th>Final pH (2)</th>
<th>Sulphate pH (3)</th>
<th>Δ pH pH(3) –pH(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.25</td>
<td>4.0</td>
<td>3.95</td>
<td>0.05</td>
</tr>
<tr>
<td>2.25</td>
<td>4.5</td>
<td>5.20</td>
<td>0.70</td>
</tr>
<tr>
<td>2.25</td>
<td>5.0</td>
<td>6.25</td>
<td>1.25</td>
</tr>
<tr>
<td>2.25</td>
<td>5.5</td>
<td>6.85</td>
<td>1.35</td>
</tr>
<tr>
<td>2.25</td>
<td>6.0</td>
<td>7.40</td>
<td>1.40</td>
</tr>
<tr>
<td>2.25</td>
<td>6.5</td>
<td>7.80</td>
<td>1.30</td>
</tr>
<tr>
<td>2.25</td>
<td>7.0</td>
<td>8.25</td>
<td>1.20</td>
</tr>
<tr>
<td>2.25</td>
<td>7.5</td>
<td>8.54</td>
<td>1.04</td>
</tr>
<tr>
<td>2.25</td>
<td>8.0</td>
<td>8.75</td>
<td>0.75</td>
</tr>
<tr>
<td>2.25</td>
<td>8.5</td>
<td>9.00</td>
<td>0.50</td>
</tr>
<tr>
<td>2.25</td>
<td>9.0</td>
<td>9.30</td>
<td>0.30</td>
</tr>
<tr>
<td>2.25</td>
<td>9.5</td>
<td>9.65</td>
<td>0.15</td>
</tr>
<tr>
<td>2.25</td>
<td>10.0</td>
<td>10.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table 4.5: pH changes during the Adsorption of 1,000 ppm SO₄²⁻ onto 1,000 ppm Hydrous Iron(II) Oxide

<table>
<thead>
<tr>
<th>Initial pH (1)</th>
<th>Final pH (2)</th>
<th>Sulphate pH (3)</th>
<th>Δ pH (pH(3) – pH(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>4.0</td>
<td>4.0</td>
<td>0.00</td>
</tr>
<tr>
<td>1.65</td>
<td>4.5</td>
<td>4.76</td>
<td>0.26</td>
</tr>
<tr>
<td>1.65</td>
<td>5.0</td>
<td>5.18</td>
<td>0.18</td>
</tr>
<tr>
<td>1.65</td>
<td>5.5</td>
<td>5.7</td>
<td>0.20</td>
</tr>
<tr>
<td>1.65</td>
<td>6.0</td>
<td>6.06</td>
<td>0.06</td>
</tr>
<tr>
<td>1.65</td>
<td>6.5</td>
<td>6.45</td>
<td>-0.04</td>
</tr>
<tr>
<td>1.65</td>
<td>7.0</td>
<td>6.90</td>
<td>-0.11</td>
</tr>
<tr>
<td>1.65</td>
<td>7.5</td>
<td>7.50</td>
<td>-0.02</td>
</tr>
<tr>
<td>1.65</td>
<td>8.0</td>
<td>7.95</td>
<td>-0.04</td>
</tr>
<tr>
<td>1.65</td>
<td>8.5</td>
<td>8.45</td>
<td>-0.05</td>
</tr>
<tr>
<td>1.65</td>
<td>9.0</td>
<td>8.95</td>
<td>-0.05</td>
</tr>
<tr>
<td>1.65</td>
<td>9.5</td>
<td>9.45</td>
<td>0</td>
</tr>
<tr>
<td>1.65</td>
<td>10.0</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

of equations, the process could be illustrated by a two-step process involving adsorption and oxidation as follows:

\[-\text{Fe-OH} + \text{SO}_4^{2-} \rightleftharpoons -\text{Fe-SO}_4^{-} + \text{OH}^{-}\]  \hspace{1cm} \text{Equation 4.2}

\[-\text{Fe-SO}_4^{-} + \text{H}_2\text{O} \rightleftharpoons -\text{Fe-OH-SO}_4^{-} + \text{H}^{+}\]  \hspace{1cm} \text{Equation 4.3}

Thus sulphate has adsorbed to the ferrous surface, which has oxidised to ferric releasing a proton, and there has been no net change in solution hydroxide (or hydrogen) concentration.
4.4 Electrophoretic Mobility

As previously discussed, sulphate adsorption onto hydrous metal oxides is likely to be at least partly driven by electrostatic forces, specifically the attraction between negatively charged sulphate ions and positively charged sites on the surface of the oxide. The importance of electrostatic interactions can be seen in Figures 4.2 and 4.3 where it is apparent that adsorption decreases, at high pH values and for all substrates studied, as pH is increased. This decrease is assumed to be due to the lessening of electrostatic interaction between the negatively charged sulphate ion and the increasingly negatively charged (or decreasingly less positively charged) surface.

Electrostatic interaction can be quantified by measurement of the surface potential which arises from surface charge. The approach relies on an electrokinetic model to transform the measured potential into a potential (usually the so-called zeta potential) and an electrical double layer (EDL) model to transform the zeta potential into a surface potential and thus a surface charge. Many authors (James et al., 1992, Crawford et al., 1996) model adsorption behaviour using a complex mathematical algorithm based on measurement of surface charge (by acid/base titration), zeta potential (by particle electrophoresis) and assuming a model of the EDL such as the triple layer model (Davis and Leckie, 1976; Zhang and Sparks, 1990; He et al., 1997). Other authors (e.g. James and Healy, 1985), Harding and Healy, 1985c) have used a more simple Gouy-Chapman EDL model with equal success in terms of modelling ability. The equal success of both the more complex, and the more simple, models are indicative that the number of unmeasurable parameters (e.g. inner layer capacitance) and the uncertainty in the parameters which are measurable (e.g. surface site density) leads to a large number of parameters which act as “fitting parameters”. Furthermore, few authors have been able to study systems in which the experimental conditions of adsorption experiments and zeta potential experiments are the same (Crawford et al., 1992, 1993 is one notable exception). Not surprising, then, that most models can predict the data from which the parameters are determined reasonably well.

EDL, site binding and adsorption models are very valuable, and give considerable insight into the adsorption process, however, the above arguments suggest that they are a more esoteric exercise than is justified in this thesis.
Notwithstanding the above, much qualitative information can be obtained from measurement and understanding of electrostatic interactions, with the standard approach being to measure the electrophoretic mobility of particles in the absence, and in the presence, of the adsorbing ion. Electrophoretic mobility is often then converted into zeta potential using, for example, the equations of O’Brien and White (1978, 1985). For qualitative purposes, however, this is not entirely necessary and, moreover, can result in trends which are dependent on the transformation model used. For this reason, electrophoretic mobility of particles has been measured and presented without further transformation or modelling of data.

4.4.1 Electrophoretic Mobility of Hydrous Aluminium(III) Oxide

The electrophoretic mobility data obtained for the hydrous oxide of Al(III) is given in Fig. 4.6. In the absence of sulphate, the data is consistent with that expected from literature, i.e. a relatively flat region of positive electrophoretic mobility (around 2.8 m² V⁻¹ s⁻¹) followed by a relatively sharp decrease in electrophoretic mobility from pH 8.5 to pH 10. The electrophoretic mobility undergoes a charge reversal (positive to negative) around pH 9.8. This point is referred to as the isoelectric point (iep) and is consistent with the literature for hydrous aluminium(III) oxide. Parks (1965), for example, sites literature values between 9.1 and 10, depending on the exact preparation protocol for the oxide.

The slight decrease in electrophoretic mobility at low pH (below pH 4) is less well documented in the literature and may well be an artifact of the incomplete formation of the hydrous aluminium(III) oxide substrate. Decreases in electrophoretic mobility at very low, or very high pH, values may be an artifact of ionic strength but this is very unlikely here, where the ionic strength is in excess of 10⁻³ M (KNO₃) and the decrease is seen at pH 4.

In the presence of sulphate, the electrophoretic mobility data is considerably changed indicating that sulphate not only adsorbs in response to surface electrical properties but also alters them greatly upon adsorption. The electrophoretic curve, in the presence of sulphate, shows a number of features which are illustrative of the nature of sulphate adsorption.
Figure 4.6: Electrophoretic mobility of hydrous aluminium(III) oxide in the presence and absence of 1,000 ppm sulphate.

Firstly, the electrophoretic mobility, in the presence of sulphate, is considerably lower, for all pH values, than that in the absence of sulphate. The extent of change may, however, be misleading due to the experimental conditions used. The concentration of colloid was too high to allow direct measurement of electrophoretic mobility on samples. For each measurement, a small sample was centrifuged and the supernatent used to dilute a very small second volume of sample. The principle is that the diluted material should see the same solution conditions as the concentrated material and therefore have the same electrophoretic mobility. It is possible, however, that the dilution results in further adsorption of sulphate and the electrophoretic mobility may be more representative of greater adsorption. Nevertheless, sulphate adsorption has been shown, here, to have a significant affect on the oxide’s electrophoretic mobility and thus changes the electrical double layer properties of the oxide onto which it has adsorbed.
Secondly, there has been a slight shift in the isoelectric point from 9.8 to 8.5, indicative of specific adsorption (Rajan, 1978), which is also consistent with continued adsorption past the isoelectric point (see Figure 4.3). The extent of this specific adsorption is, however, not clear since experimentation was only designed to continue until a pH of 10.

More striking, however, is the lack of charge reversal at lower pH values. The drop in electrophoretic mobility across the pH range from 4 to 10 is significant and supports the data presented in Figure 4.3 that sulphate can adsorb to large extents on the surface of hydrous aluminium(III) oxide. Why, then, was a negative electrophoretic mobility not reached? For most of the pH range, sulphate adsorption appears to be strong and results in a near-neutral surface, but does not appear to adsorb past that point. Charge reversal of strongly specific adsorbing ions, such as ionic surfactants or hydrous metal ion is well known (Osseo Asare, 1985; Crawford, 1997) but from the data in Figure 4.5 does not occur with sulphate, despite sulphate being a strongly adsorbing species. Harding and Healy (1985) have observed a similar inhibition of strongly adsorbing ions due to unfavourable overall electrostatics. In their case, amphoteric polystyrene latices of variable iep’s were prepared. Cadmium(II), which adsorbs strongly to the latex surface above its iep, was not adsorbed to any significant extent below it. Apparently, if the overall surface is electrostatically unfavourable to adsorption, ions cannot approach close enough to the surface to interact even though some surface sites may have the "right" electrostatic sign. A similar occurrence seems to happen with sulphate. Sulphate, being negatively charged, adsorbs strongly to the positively charged oxide surface, neutralising the charge. Once neutralised, the surface is still expected to contain some positively charged surface sites, these are simply neutralised by other negatively charged surface sites to give an overall neutral surface. Once the surface is neutral, or slightly negative, sulphate ions appear unable to approach the surface close enough to interact with those surface sites which are still positively charged.

Finally, adsorption (according to Figure 4.3) is at a maximum at pH values close to 7. From Figure 4.6, there is also a maximum drop in electrophoretic mobility of 2.6 x 10^{-8} m^2 V^{-1} s^{-1} at pH 7. Whilst this may simply be due to serendipitous choice of substrate...
and adsorbing ion, the correlation between maximum adsorption and maximum change in electrophoretic mobility is worth noting.

4.4.2 Electrophoretic Mobility of Hydrous Iron(III) Oxide

The electrophoretic mobility of hydrous iron(III) oxide, in the presence and absence of sulphate, is shown in Figure 4.7, and follows a similar pattern to that observed for hydrous aluminium(III) oxide.

![Graph of electrophoretic mobility](image)

**Figure 4.7:** Electrophoretic mobility of hydrous iron(III) oxide in the presence and absence of 1,000 ppm sulphate.

At first sight, the electrophoretic mobility curve for hydrous iron(III) oxide appears significantly different in that a flat region at low pH is not so apparent. Closer inspection, however, reveals that this trend is due to a single experimental point (at pH 4.0) and is not supported by similar results in the literature (e.g. Sanciolo et al., 1992). Furthermore, the nature of electrophoretic mobility measurements is such that a deviation of $0.8 \times 10^{-8} \, \text{m}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ (which is all that is required, here, to bring the point back to a value similar to the
ones proceeding it) is not unreasonable. It was not considered of sufficient impact on the observations in this thesis to repeat this experiment and it is assumed that the experimental point at pH 4.0 is misleading and that results follow the normal trend of a near flat curve at low pH values.

The data for electrophoretic mobility in the presence and absence of sulphate adsorption using hydrous iron(III) oxide (Figure 4.7) shows a similar pattern to the data using hydrous aluminium(III) oxide (Figure 4.6).

Again, the electrophoretic mobility data changes from positive to negative over a relatively short pH span, is considerably higher in the presence of sulphate than in its absence, the electrophoretic mobility data in the presence of sulphate approaches zero for a wide range of pH values, and charge reversal only occurs at relatively high pH values. Again, the isoelectric point in the presence of sulphate is lower than in its absence, indicative of specific adsorption (Parfit, 1978), but the lowering is not as great as with other specifically adsorbing ions. The isoelectric point for hydrous iron(III) oxide, in the absence of sulphate adsorption, was found to be 7.8 and in the presence of sulphate adsorption lowered to a value of 6.5. The maximum drop in mobility, following sulphate adsorption, was $2.4 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ and occurred at a pH of approximately 4. Again, this pH also corresponds to the maximum percent adsorption of sulphate on hydrous iron(III) oxide (Figure 4.3).

Most importantly, the electrophoretic data for sulphate adsorption onto hydrous iron(III) oxide again demonstrates the inability for sulphate to adsorb onto surfaces which have become overall positively charged.

### 4.4.3 Electrophoretic Mobility of Hydrous Iron(II) Oxide

The electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of sulphate adsorption is shown in Figure 4.8. Whilst there are a number of similarities to the data presented for hydrous aluminium(III) oxide (Figure 4.6) and hydrous iron(III) oxide (Figure 4.7) there are also a number of striking differences.
Figure 4.8: Electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of 1,000 ppm sulphate.

The first of these differences in the apparent peak in electrophoretic mobility (no sulphate present) at pH 7.5. Such a peak in electrophoretic mobility has not been reported before, which may not be surprising since the electrophoretic behaviour of iron(II) oxides are rarely studied. The experiment was repeated a number of times and the peak was reproducible. It could be speculated that the peak is influenced by the oxidation/reduction behaviour of iron(II) and iron(III) oxide. The iep of iron(III) oxide measured earlier was 7.6, consistent with literature values. The iep of iron(II) oxide measured here was approximately 10.3, slightly less than the values of 12.0 to 12.5 quoted in Parks (1965). It is probable that the slightly lower iep (for hydrous iron(II) oxide) found in this study is due to some contamination from hydrous iron(III) oxide, presumably caused by oxidation. If so, then oxidation may be occurring to a limited extent for the entire pH range, but does not necessarily occur to a consistent extent across all pH values. Given that the iep of hydrous iron(II) oxide is higher than the iep of hydrous iron(III) oxide, it would be expected that any surface oxidation (resulting in a...
higher level of iron(III)) would also result in a lowering of electrophoretic mobility. The peak in electrophoretic mobility at pH 7.5 may simply represent a minimum in the amount of oxidation, or at least greater oxidation at lower pH values than at higher pH values (the drop in mobility after pH 7.5 may represent the normal lowering of electrophoretic mobility with increasing pH).

The extent of any oxidation cannot, however, be very large. It is well known that the $\text{iep}$ of a colloidal substrate can be altered by just a small coating of a second substance, such that the electrokinetic behaviour of the sample now resembles that of the coating. Such is not the case here, as can be seen by comparison of Figures 4.7 (hydrous iron(III) oxide) and 4.8 (hydrous iron(II) oxide). The electrophoretic mobility for hydrous iron(II) oxide remains considerably more positive than that for hydrous iron(III) oxides across the entire pH range.

Notwithstanding this, a small amount of oxidation of iron(II) to iron(III) may result in both the abnormal peak seen at pH 7.5 and the slightly lower $\text{iep}$ obtained here compared to literature (Parks, 1965). There is, however, no other evidence to support surface oxidation of iron(II) oxide to iron(III) oxide and the argument remains highly speculative.

The electrophoretic data for hydrous iron(II) oxide in the presence of sulphate also shows an anomalous peak, albeit a very small one, around pH 5. Moreover, the shift in $\text{iep}$ on sulphate adsorption is considerably greater than for the other two substrates earlier studied. The $\text{iep}$ of hydrous iron(II) oxide, in the presence of sulphate, was 7.2 compared to 10.3 in its absence. Both phenomena (the peak at pH 5 and the large shift in $\text{iep}$) may not be overly significant given the overall trend for the influence of sulphate on electrophoretic mobility (i.e. a lowering of values almost to zero, but not becoming significantly negative). Nevertheless, it is interesting to speculate on the origins of these two phenomena. Again, oxidation is an obvious suggestion and may well be catalysed by the presence of sulphate adsorption, as indicated in the proposed mechanism shown in Equation 4.3. Zhang et al. (1991) has demonstrated that lepidocrocite ($\Delta$-FeOOH) can be formed at near neutral pH by fast oxidation of hydrous iron(II) oxide. At pH greater than 7, autocatalysis of the oxidation takes place.
According to Gupta (1976), lepidocrocite has an iep of 7.45 consistent with the iep found, here, for hydrous iron(II) oxide in the presence of sulphate.

The maximum shift in electrophoretic mobility, in the case of hydrous iron(II) oxide occurs at a pH of approximately 7.5 and results in a drop of approximately $3.6 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. In this case, the pH does not correspond to the maximum adsorption pH value which was at the lowest pH value tested, pH 4.0. Nevertheless, the drop in electrophoretic mobility, at pH 4.0 was also quite substantial at approximately $3.6 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Irrespective of any oxidation/reduction reactions which may be occurring, the presence of sulphate adsorption lowers the electrophoretic mobility to near zero, but does not result in a significantly negatively charged surface. Thus, whilst sulphate adsorption is strong and shows some tendency to specific adsorption, repulsive electrostatic interaction still prevents further sulphate adsorption from occurring.

### 4.4.4 Electrophoretic Mobility of Hydrous Mixed Oxide

Finally, the electrophoretic mobility of a mixed (Al(III):Fe(III):Fe(II) = 2:1:1) hydrous oxide was measured, as a function of pH and in the presence and absence of sulphate. The results are shown in Figure 4.9.

The electrophoretic mobility behaviour for the mixed hydrous oxide, in the presence and absence of sulphate, is consistent with a simple mixture of the behaviour for the three oxides which form it:

- The iep (in the absence of sulphate), 9.2, lies between the iep of hydrous aluminium(III) oxide (9.8), hydrous iron(III) oxide (7.8) and hydrous iron(II) oxide (10.3) and is, in fact, close to a weighted average of the three (which is 9.4).
- There is a significant drop in iep (from pH 9.2 to pH 6.5) upon sulphate adsorption. This iep (6.5) is lower than the iep of any of the individual oxides (in the presence of sulphate) which make up the mixed hydrous oxide. Whilst this might appear
contrary to common sense, it probably just reflects that there can be too much emphasis placed on the iep at the expense of the overall trend in data. Whilst the iep is 6.5, and values above the iep are negative, they are only barely negative and do not become significantly negative even when the final pH of 10 has been reached.

![Graph showing electrophoretic mobility of mixed hydrous oxide](image)

**Figure 4.9:** Electrophoretic mobility of mixed hydrous oxide in the presence and absence of 1,000 ppm sulphate. The mixed hydrous oxide was formed from a solution containing Al(III):Fe(III):Fe(II) at a ratio of 2:1:1 by mass.

- There is a significant drop in electrophoretic mobility over the entire pH range.
- The electrophoretic mobility, in the presence of sulphate and at pH values higher than the iep (in the presence of sulphate), remains close to neutral and does not become significantly negative until the original iep (in the absence of sulphate) is reached.
The electrophoretic mobility, in the presence of sulphate and at pH values lower than the (sulphate) iep approaches neutral, but does not become negative.

An unexplained peak in electrophoretic mobility, in the absence of sulphate, is again observed at a pH of approximately 6.5. Although unexplained, the peak was also observed in the hydrous iron(II) oxide case and was previously speculated upon.

4.5 Implications to Models of Sulphate Adsorption

It was not the intention of this thesis to delve deeply into the various models for adsorption of anions such as sulphate to colloidal surfaces, however the adsorption results, and particularly the electrophoretic mobility results presented in Sections 4.3 and 4.4, have implications within the current schools of thought on this topic.

Firstly, the drift in pH observed for most of the adsorbents when sulphate was added is consistent with the release of hydroxyl ions upon adsorption. This is consistent with a large number of authors who have attributed the release of hydroxyls to either a simple ligand exchange mechanism (Hingston et al., 1972; Rajan, 1978; Parfitt and Smart, 1978; Rao and Shridharan, 1984) as shown in Equation 4.2, or a more complex two-step mechanism involving surface site protonation following by simple electrostatic binding (Balistrieri and Murray, 1979; Davis and Leckie, 1980; Marsh et al., 1987, He et al., 1997) as shown in Equations 4.4 and 4.5.

\[
\text{Equation 4.4} \\
\text{Equation 4.5}
\]

where \( = \) represents bonding to the substrate.

Although these two mechanisms (ligand exchange and electrostatic site binding) are thermodynamically indistinguishable, it is common to assign ligand exchange to inner sphere coordination of sulphate to the surface site (Geelboed et al., 1997; Rietra et al.).
Figure 4.10: Schematic illustration of the difference between inner and outer sphere coordination of sulphate ions to a surface site.

1999), and electrostatic site binding to outer sphere coordination of sulphate to the surface site (Chalet et al., 1993; He et al., 1996). The difference between the two (inner and outer sphere coordination) is illustrated in Figures 4.10 and 4.11.
Figure 4.11: Schematic illustration of inner and outer sphere adsorption at hydrous oxide surface

Figure 4.10 shows the specific chemical nature of inner sphere complexation and the physical nature of outer sphere complexation. Figure 4.11 shows the orientation of specifically adsorbed ions (in this case anions) which are assumed to form inner
sphere complexes, and non-specifically adsorbed ions (in this case cations) which are assumed for form outer sphere complexes, as well as the orientation and structuring of water molecules in, and around, the electrical double layer.

Evidence that sulphate binds through an outer sphere coordination mechanism includes the observation that there is a decrease in adsorption of sulphate with increasing ionic strength, and that adsorption is considerably stronger on the acid side of the iep where the substrate is positively charged (Charlet et al., 1993). The latter observation was also seen in the current study (Figure 4.3), indicative of outer sphere complexation.

Evidence that sulphate binds through an inner sphere coordination mechanism includes the shift in iep, an observation also seen in the current study (Figure 4.3) particularly for the hydrous iron(II) oxide. He et al. (1997) have argued, however, that the two step mechanism shown in Equations 4.3 and 4.4. can also account for slight changes in the iep upon adsorption whilst still involving outer sphere complexation.

Complex surface equilibria modelling often requires inner sphere complexation to obtain a suitable “fit”. Ali and Dzombak (1996), for example, successfully modelled the adsorption of sulphate onto goethite, but using three different inner sphere surface complexes of sulphate. The best evidence for inner sphere complexation, however, probably lies in spectroscopic studies using, for example, transmission infrared (Parfitt and Smart, 1978; Turner and Kramer, 1991) and XPS (Martin and Smart, 1987). Both techniques indicate a bi-dentate inner sphere complexation. Mono-dentate inner sphere complexes have been indicated by in situ scanning tunnelling microscopy (Eggleston et al., 1998) and ATR-FTIR spectroscopy (Eggleston, et al., 1998; Hug, 1997).

Most spectroscopic techniques rely on drying, or other preparative procedures which may, or may not, alter the surface properties being measured. Furthermore, surface spectroscopic techniques do not always indicate inner sphere complexation. Persson and Lovgren (1996), for example, have used DRIFT infrared to indicate outer sphere complexation and Degenhardt and McQuillan (1999) have used ATR-FTIR to indicate
the same. Peak et al. (1999) have argued that ATR-FTIR gives an outer sphere complexation result for pH values above the iep of their substrate (which was 6.0) and inner sphere complexation at pH values below it.

The explicit observation (Figures 4.4 to 4.9) that electrophoretic mobility approaches zero (neutral) following sulphate adsorption, but does not become significantly negative has not been reported before and is further indication that surface complexation of sulphate is probably outer sphere in nature. Were surface complexation to be inner sphere, significant chemical adsorption would be expected and adsorption would continue even though the surface overall had obtained a negative surface charge. This would generate significant negative electrophoretic mobility.

Several authors (e.g. Sposito, 1989) have suggested that sulphate adsorption may be intermediate between inner and outer sphere complexation, sometimes adsorbing one way and sometimes the other. This proposal is supported by data such as that obtained by Yates and Healy (1975) using $\alpha$-FeOOH and $\alpha$-Cr$_2$O$_3$ as substrates. These two substrates have very different hydroxyl exchange rates, yet the rate of sulphate adsorption is very similar implying that adsorption cannot be due to inner sphere complexation. Yet sulphate adsorption caused a shift in the iep indicating chemical adsorption indicative of inner sphere complexation. It can even be argued that the one type of surface, such as the hydrous oxide surface used in this thesis, may exhibit inner sphere complexation for some batches and outer sphere complexation for other batches because of the inherent difficulties in maintaining constant morphology and crystallinity from one batch to another (Sujimoto and Wang, 1998).

The observations in this thesis that the iep shifts, but adsorption does not result in a significantly negative charge, and that adsorption is strong on the acid side of the substrate’s iep, indicates that sulphate adsorption to hydrous metal oxides probably involves an outer sphere complex.
4.6 Flotation of Sulphate

Whilst adsorption is the first step in removal by adsorbing colloid flotation, and whilst the adsorption data given here proves useful in the fundamental understanding of the adsorption step, it is the percentage removal by flotation which is of prime importance to the success of adsorbing colloid flotation as a waste remediation tool.

Adsorbing colloid flotation was carried out, as detailed in the Experimental Methodology section of this thesis. Briefly, this involved adding 1,000 ppm of a colloid precursor (e.g. aluminium nitrate) to a solution containing 1,000 ppm of the analyte of choice, in this case sulphate ions (from sodium sulphate). The pH was then increased to the desired value where it was kept constant for an induction period of 15 minutes. Following the induction period, a mixed surfactant solution containing a 2:1 ratio (by weight) of dodenacoic acid (DA) to sodium dodecyl sulphate (SDS) was added to give a total surfactant concentration of 300 ppm. Flotation was effected by air and carried out in the “total liquid carry-over” (TLC) mode such that the entire liquid volume was floated and allowed to drain from the foam. The concentration of sulphate in the drainage liquid was measured to give the data in Figure 4.12.

The results for the adsorbing colloid flotation of sulphate using the four substrates (hydrous metal oxides of aluminium(III), iron(III), iron(II) and a mixture thereof) are given in Figure 4.12.

A number of trends are immediately apparent from the data in Figure 4.12:

- Flotation behaviour, as a function of pH and as a function of the particular oxide chosen, shows a remarkably strong correlation with adsorption data (see Figure 4.3). This will be discussed in detail shortly.
- In most cases, removal by flotation decreased with increasing pH, consistent with the trend seen for adsorption in Figure 4.3.
- In the case of hydrous aluminium(III) oxide, flotation at very low pH values was poor, consistent with the incomplete formation of the oxide at this pH, as discussed earlier.
- The most effective substrate for flotation was hydrous aluminium(III) oxide, again consistent with the adsorption data as shown in Figure 4.3.
Figure 4.12: Percentage (%) flotation of 1,000 ppm sulphate using various hydrous oxides formed from solutions containing 1,000 ppm (total) metal ion. Total surfactant concentration was 300 ppm and consisted of a 2:1 mixture of SDS to DA.

- The least effective substrate for flotation was hydrous ferrous oxide, again consistent with the adsorption data as shown in Figure 4.3.
- The hydrous mixed oxide resulted in flotation which was intermediate between that of its components, again consistent with the adsorption data as shown in Figure 4.3.

A key feature of the flotation results is that removal occurs across a wide range of pH values, even though it becomes less effective as the pH increases. This has
considerable significance for the industrial (or environmental) use of adsorbing colloid flotation since pH control can be an expensive component in wastewater treatment. The data in Figure 4.12 shows that removal may be acceptable, although not optimal, over a wide pH range.

For adsorbing colloid flotation to be of use as a removal technique, it must be shown to be cost effective and technically effective. The colloids chosen, hydrous iron(III), iron(II) and Aluminium(III) oxides, were chosen because of their wide use in industrial waste treatment which indicates that they are already believed to be cost effective. A full cost analysis was outside the scope of this thesis. It should also be remembered that the results obtained here are without the commonly used practice of adding a small amount of frothing agent (e.g. ethanol).

The data in Figure 4.12 shows adsorbing colloid flotation to be technically effective in terms of reducing the concentration of sulphate in solution. As previously discussed, the technology does not need to obtain removals in excess of 90%, as would be common for heavy metal remediation (Sanciolo et al., 1992) since sulphate is considered an intractable waste for which even a moderate reduction in concentration would be of benefit. Furthermore, adsorbing colloid flotation lends itself to a second, or even a third, treatment, often referred to as a polishing stage (Sanciolo et al., 1993) such that higher percentage removals are possible.

A further requirement is not, however, apparent from data such as that given in Figure 4.12. This requirement is for the foam produced from adsorbing colloid flotation to be easily manageable (Sanciolo et al., 1992, 1993). Generally, adsorbing colloid flotation results in a foam which is light weight, relatively stable and easily removed from the treatment plant and taken to a separate area for disposal or reuse. The nature of the foam is not apparent from percent flotation data, but is apparent by observation during the experiment.

The foam produced using hydrous aluminium(III) oxide was gelatinous in nature, adhered to the modified Hollimand cell used for flotation and remained stable for only a short time after the experiment was concluded (i.e. Foam Type 7). Such foams are not
the most suitable for treatment following adsorbing colloid flotation and render hydrous aluminium(III) oxide a poor choice of colloid despite its apparent effectiveness. The other three oxides, including the mixed oxide, all gave suitable foams (at least Foam Type 8, usually Foam Type 9). The hydrous iron(II) oxide appeared the best foam and the presence of iron(II) in the hydrous mixed oxide gave it good stability despite the presence of aluminium(III). Although qualitative and subjective in nature, these observations are sufficient to again recommend against the use of hydrous aluminium(III) oxide, despite its better effectiveness.

4.7 Comparison of Adsorption and Flotation

As noted in Section 4.4, there is a strong correlation between the trends seen in adsorption (Figure 4.3) and flotation (Figure 4.4). This correlation is worth closer examination and can be achieved by plotting adsorption and flotation on the same graphs, as shown in Figure 4.13 to 4.16.
Figure 4.13: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous aluminium(III) oxide formed from 1,000 ppm Al(III).
Figure 4.14: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous iron(III) oxide formed from 1,000 ppm Fe(III).
Figure 4.15: Comparison of adsorption and flotation of 1,000 ppm sulphate using hydrous iron(II) oxide formed from 1,000 ppm Fe(II).
For much of the pH range studied, adsorption appears more effective than flotation. It is reasonable to believe, and the data here would support this, that adsorption must occur in order for the sulphate to be removed by flotation. A small loss, caused for example by any instability in the foam, would then lower the percentage removal of flotation compared to adsorption.
Another reason for the slight inefficiency of flotation compared to adsorption may lie in the presence of surfactant. Surfactant is present during the flotation experiments, but not the adsorption experiments, and is added (in the flotation experiments) after sulphate adsorption has occurred. Since the surfactants chosen are anionic they would be expected to compete with sulphate and potentially cause some desorption of the sulphate. This is an obvious source of diminished efficiency with flotation compared to adsorption. The effect, however, is minor given the closeness of flotation data to adsorption data.

Notwithstanding the above, adsorption correlates with flotation in all cases, usually involving a gradual decrease in adsorption/flotation with an increase in pH. The effectiveness of flotation, then, can be predicted by the effectiveness of adsorption.

The main exception to the general trends above is the adsorption and flotation behaviour using hydrous iron(II) oxide (Figure 4.15). Here, flotation is seen to be more effective than adsorption, although the two still correlate reasonably strongly. It was earlier stated that oxidation of Fe(II) to Fe(III) was a possible explanation for a number of anomalous adsorption behaviour using hydrous iron(II) oxide, and could again be the explanation here. Flotation involves the passage of high pressure air through the waste product in order to generate bubbles which effect the flotation. This is almost certain to lead to considerably more oxidising conditions in the case of flotation than adsorption. If oxidation is occurring, then the “true” oxide in the flotation case is more likely to contain high levels of iron(III) rather than the initial iron(II), and flotation is more likely to correlate with the adsorption behaviour of hydrous iron(III) oxide than hydrous iron(II) oxide. Since iron(III) oxide was shown to be a better adsorbant (Figure 4.8) than iron(II) oxide (Figure 4.9), this would explain the better efficiency of flotation than adsorption for the iron(II) oxide case.

Whilst not shown in data such as those shown in Figures 4.13 to 4.16, the nature of the foam produced using hydrous iron(II) oxide was also more desirable than the other oxides, and as stated earlier the nature of the foam produced from hydrous aluminium(III) oxide was the least desirable. There appears, then, good reason to use a mixture of oxides in order to gain desirable foam characteristics from the iron(II) component, good effectiveness from the aluminium(III) component and less expensive materials from the iron(III) component.
4.8 Adsorbing Colloid Flotation of Nitrate.

A major concern with the use of adsorbing colloid flotation, as described in the preceding sections, is that nitrate is used as the supporting anion to the metal ions which form the hydrous oxide. What is the fate of this nitrate? Although nitrate may be a more preferrable contaminant than sulphate, the concern remains that adsorbing colloid flotation may be successful at the removal of sulphate, but only at the expense of adding nitrate.

Nitrate is less problematic than sulphate given that it is ubiquitous and present at relatively high concentrations (compared to sulphate and the phosphate and mercury ions which will be of interest in later chapters). Nevertheless, nitrate is a nutrient and can cause eutrification if allowed to accumulate to high levels in the environment. Moreover, nitrate can be reduced to nitrite and ammonia, both of which are highly toxic and can be responsible for widespread death and destruction of aquatic wildlife. Nitrate is particularly important to study, in terms of treatment technologies such as adsorbing colloid flotation, since it is likely that nitrate contamination will be increased by the use of adsorbing colloid flotation. Whilst some of the nitrate will be occluded into the colloid formed, much of it will remain in solution and poses a potential hazard in its own right. Very few studies have been made of the fate of nitrates introduced as a result of wastewater treatment, and nitrate is considered one of the most difficult contaminants to treat in an industrial setting (for large scale, secondary (biological) treatment plants it is relatively straight forward).

To test the level of removal of nitrate under flotation conditions likely to be encountered, the level of nitrate remaining in solution after the flotation of sulphate by a mixed hydrous oxide (Figure 4.16) was measured. As per all other experimentation, this was then used to calculate a percent flotation by subtraction from the amount initially added. In this case, however, the nitrate may have been genuinely floated, or may have been occluded into the hydrous mixed oxide structure as the hydrous oxide was formed. In either case, however, the nitrate was removed from solution.

The results shown in Figure 4.17 show that the majority of the nitrate was removed from solution during the adsorbing colloid flotation process. This not only indicates that
contamination of the water sample by the technique used to clean it is at a minimum, it also indicates that adsorbing colloid flotation could be a successful treatment technology for nitrate. Continued experimentation with nitrate was considered outside the scope of this thesis.

Figure 4.17: Percentage (%) flotation of 25 ppm nitrate, using a mixed hydrous oxide, in the presence of 1,000 ppm sulphate using 300 ppm mixed surfactant consisting of SDS and DA in the ratio 2:1. The hydrous mixed oxide was formed from a solution of 1,000 (total) metal ion containing Al(III):Fe(III):Fe(II) in the ratio 2:1:1.

4.9 Adsorbing Colloid Flotation of an Industrial Sample
The true test of any remediation process is in its success, or otherwise, when applied to genuine industrial waste samples rather than the model sulphate samples used to date. Such samples are considerably more complex than model waste and may contain chemicals of unknown and variable composition.
A “real” industrial waste was obtained from Pigment Manufacturer of Australia (PMA) and was analysed to contain 1,000 ppm sulphate. Details of the sample, and sample collection, are given in the Experimental Methodology section (Chapter 3) of this thesis. Flotation experiments were initially carried out with oxides prepared from variable quantities of aluminium(III), iron(III) and iron(II) as well as different surfactant types (e.g. CTAB – see the Experimental Methodology section (Chapter 3)). These experiments were not quantified as their main purpose was to determine the conditions under which a good foam could be formed, specifically in the presence of the industrial sample. The results of these initial trials are subjective and are not further detailed, here, except that the end result was that a good foam, and possibly the best foam, could be produced using the same conditions as for the “mixed” oxide used throughout this chapter.

Specifically, then, the conditions of flotation were to use a colloid formed from 1,000 ppm (total) solution of a 2:1:1 mixture of Al(III):Fe(III):Fe(II). The surfactant chosen was a 2:1 mixture of sodium dodecyl sulphate (SDS) and dodecanoic acid (DA) of total concentration 300 ppm. The waste contained 1,000 ppm sulphate making the entire experiment directly comparable with the model experiments carried out earlier in this chapter.

The flotation of the PMA sample, under these conditions, as a function of pH, is shown in Figure 4.18.

The above graph illustrates that an industrial sample laden with sulphate can be successfully floated. The curve obtained is directly analogous to that obtained for a model sample (Figure 4.12) and is, if anything, even more efficient. The industrial sample contains a number of ingredients which could potentially interfere with flotation, but have not. In particular, the sample has a high ionic strength which is known to diminish electrostatic interactions and could, therefore, lead to less adsorption. Sanciolo et al. (1993) have argued that flotation systems must be in a state of “insipient flocculation” to obtain maximum flotation and maximum stability of the resultant foam. Thus any loss of adsorption caused, here, by the high ionic strength is more than compensated by the enhanced flotation conditions which a high ionic strength engenders.
At pH 4 the amount of sulphate removed by flotation is 750 ppm (75% of the initial quantity) and by pH 10 this has fallen to 400 ppm sulphate (40% of the initial quantity). Across the entire pH range, then, a reduction of between 40 and 75% from a highly contaminated (1,000 ppm sulphate) complex waste sample has been achieved.

**Figure 4.18:** Flotation of an industrial (PMA) waste sample containing 1,000 ppm sulphate. Flotation was effected with a mixed hydrous oxide formed from a 1,000 total metal ion solution of Al(III):Fe(III):Fe(II) in the ratio 2:1:1 and 300 ppm mixed surfactant consisting of SDS and DA in the ratio 2:1.
4.10 Summary

A number of important findings concerning the adsorption and flotation of sulphate using hydrous metal oxides have been found and can be summarised as follows:

- Sulphate was found to be removed by both adsorption and flotation from both a model and a “real” industrial waste. Adsorbing colloid flotation, then, has considerable potential for the treatment of intractable aqueous wastes containing high levels of sulphate.
- Nitrate levels remaining in solution after adsorbing colloid flotation were found to be low indicating that the technique was not simply replacing one contaminant (sulphate) with another (nitrate). It also indicated that future experimentation involving nitrate as the contaminant to be removed is warranted.
- Hydrous aluminium(III) oxide was found to be the most effective, on a weight for weight basis based on the metal ion, substrate for sulphate removal by adsorption. However, it was found to be the least effective on a weight for weight basis based on the total mass of colloid.
- Hydrous iron(II) oxide was found to result in a good quality foam and its incorporation into a mixed oxide gave that oxide a better quality foam.
- The most appropriate foam type was formed from a 2:1 mixture of SDS and DA. Interestingly, CTAB had a negative affect on foam type (and stability) even in small quantities.
- The high effectiveness of aluminium(III) oxide, the relative inexpense of iron(III) oxide (which can be used as a “filler”) and the foam stabilisation of iron(II) oxide indicate that a mixed oxide would provide the best choice for a substrate in adsorbing colloid flotation of sulphate.
- Removal of sulphate, by adsorption, was shown to increase in a near-linear fashion with increased amount of colloid used. For this reason, there was no advantage seen in using excessive quantities of colloid and a general “rule of thumb” was adopted to use a colloid concentration similar to the concentration of whatever contaminant was to be removed.
- Sulphate adsorption, and consequently flotation, was found to be dependent on pH such that removal decreased as pH increased. This is almost certainly due to the increasingly less favourable electrostatics as pH is increased.
The isoelectric point of all colloids were lowered in the presence of sulphate adsorption indicative of chemical adsorption. However, once the electrophoretic mobility was reduced to near zero (by sulphate adsorption), no further adsorption was indicated. This is consistent with physical adsorption.

Notwithstanding the above, the adsorption and electrokinetic data presented here is more consistent with an outer sphere complexation of sulphate with hydrous metal oxide surfaces than with inner sphere complexation.

In all cases, except hydrous iron(II) oxide, hydroxyls were released to solution during the adsorption of sulphate. In the case of iron(II) oxide there appeared no net uptake or release of protons or hydroxyls. This result was surprising and probably indicates that surface processes using iron(II) oxide are complicated by oxidation/reduction processes where iron(II) oxide is oxidised to iron(III) oxide during the adsorption and/or flotation process.

In all cases, adsorption and flotation appeared to correlate strongly with each other. This enables us to predict the future success of adsorbing colloid flotation, as a waste treatment or environmental scrubbing technique, on the basis of adsorption experiments. Adsorption experiments are commonly reported in literature whereas adsorbing colloid flotation is less well studied.

Most importantly, a complex industrial waste sample containing high levels of sulphate was successfully treated using the technique of adsorbing colloid flotation.
5.1 Introduction

In Chapter 4 it was demonstrated that adsorbing colloid flotation of a problematic anion, sulphate, could be effected by a mixed hydrous oxide. It was further demonstrated that flotation was strongly correlated to adsorption and that both phenomena were pH dependent, being influenced by the electrostatic interaction between the negative sulphate ion and the generally positive substrate surface charge. Sulphate is, of course, not the only anion of industrial or environmental interest and in this chapter we investigate the adsorption and flotation of phosphate ($\text{PO}_4^{2-}$).

Phosphate is problematic mostly to the environment rather than being corrosive to urban infrastructure as sulphate is. Nevertheless, the negative impact of phosphate on the environment means that phosphate waste is heavily proscribed and industry must treat phosphate prior to allowing it to enter our sewerage systems and/or our waterways. Phosphate is present in the agricultural industry and is commonly used in fertilisers. It is also a common ingredient in dishwashing powder and other soap products and is therefore common in household waste. When allowed to enter the environment, phosphate promotes the growth of bacterial and algae causing eutrification and potential outbreaks of harmful blue-green algae blooms. Again, the desire to find a clean-up technology for phosphate relates both to industrial wastewater treatment and to environmental remediation.

Adsorption of phosphate onto colloidal substrates has been studied by a number of authors (see for example; Syers et al., 1973; Parfitt and Atkinson, 1976; Barrow, 1984; Boland et al., 1984; Goldberg and Sposito, 1985; Nanzyo, 1986; Bolan et al., 1986; Tejedor-Tejedor and Anderson, 1990; Helmy et al., 1991; Nilsson et al., 1992; He et al., 1997; Geelhoed et al., 1997; 2001a; Rietra et al., 2001a; Gustafsson, 2001; Horanyi and Joo, 2002, Gao and Mucci, 2003; Lin et al., 2004; Genz et al., 2004; Tribe and Barja, 2004; Wang and Xing, 2004).
Fewer authors have specifically studied the adsorbing colloid flotation of sulphate (see for example; Chaine and Zeitlin, 1974; Currin et al., 1979; Aoyama et al., 1982, Aoyama et al., 1983, Tanaka et al., 1994; Zhao et al., 1996a)

The following chapter will investigate the adsorption and flotation of phosphate using hydrous metal oxides of aluminium(III), iron(III), iron(II), and a mixture thereof. It will also investigate the affect of adsorption on surface characteristics of those hydrous oxides.

5.2 Phosphate Adsorption

The adsorption of phosphate might be expected to mirror that of sulphate (Chapter 4) in that both are anions and both have similar electrostatic attraction to positively charged surfaces. The electrostatic interactions of phosphate, however, are considerably more complex than sulphate due to the aqueous chemistry involved. Sulphate protonates only at very low pH and it is reasonable to assume that the ion is a divalent negatively charged ion at all pH values of interest (e.g. those in Figure 4.3). This is not the case with phosphate. Phosphate exists mostly in the + 5 valence, i.e. P(V), and interacts with water over a wide pH range, as shown in Equations 4.1 to 4.3:

\[
\begin{align*}
H_3PO_4 + H_2O & \rightleftharpoons H_2PO_4^- + H_3O^+ \\
\text{K}_1 & \text{ Equation 5.1} \\
H_2PO_4^- + H_2O & \rightleftharpoons HPO_4^{2-} + H_3O^+ \\
\text{K}_2 & \text{ Equation 5.2} \\
HPO_4^{2-} + H_2O & \rightleftharpoons PO_4^{3-} + H_3O^+ \\
\text{K}_2 & \text{ Equation 5.3}
\end{align*}
\]

where pK_1 = 2.20, pK_2 = 7.20 and pK_3 = 12.3 (Jenkins et al., 1980)

Equations 5.1 to 5.3 show that phosphate does not have constant charge as a function of pH for values of interest. At neutral, or near neutral pH conditions, phosphate is
approximately equally present as \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \). \( \text{H}_2\text{PO}_4^- \) increasingly dominates at low pH until \( \text{H}_3\text{PO}_4 \) forms, but only at pH values too low to be of general interest. \( \text{HPO}_4^{2-} \) increasingly dominates at high pH until \( \text{PO}_4^{3-} \) forms, but only at pH values too high to be of general interest. The phosphate charge varies, over the pH range of general interest to waste water treatment, from a single negative charge to a double negative charge.

5.2.1 Phosphate Adsorption - Percent Adsorption

Adsorption of a model phosphate waste by various hydrous metal oxides was performed and the data presented in Figure 5.1. A value of 25 ppm was chosen as the "model" waste (compare 1,000 ppm sulphate) as it is representative of the much smaller concentrations typically found for phosphate in problematic wastes. An industrial sample, in this case, was not used as the template for determining experimental conditions, but rather a general knowledge of waste concentrations typically of interest to industry (Melbourne Water, 2003). Similarly, a colloid concentration of 1,000 ppm was not used as this would represent an unacceptable excess. 50 ppm metal ion was chosen to ensure good phosphate removal whilst remaining commensurate with the concentration of that phosphate.
Figure 5.1: Percentage (%) adsorption of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion.

The data in Figure 5.1 shows that phosphate adsorption shares a number of phenomenological features with sulphate adsorption. Specifically:

- The overall extent of adsorption (i.e. absolute amount removed), and the pattern of adsorption (i.e. which oxide is the most effective and what shape does the graph have?), are remarkably similar. This is reasonably good evidence that sulphate and phosphate, both being acidic anions, behave in similar fashions with respect to their adsorption onto hydrous oxides.
- Hydrous aluminium(III) oxide was again the most effective under the conditions studied. Hydrous ferrous oxide was the least effective under the conditions studied. The mixed oxide, not surprisingly, again fell between its pure
components. The reason for the low effectiveness of amorphous ferrous oxide is again not immediately apparent, remembering that this material had the highest surface area (see Table 3.2). Clearly, hydrous aluminium(III) oxides form an intrinsically more effective adsorbent for phosphate, as well as for sulphate, than does hydrous ferric oxide, which, in turn, is more effective than hydrous ferrous oxide.

- At moderate to high pH values, percent adsorption decreases as pH increases. This is again almost certainly due to electrostatic forces. As the pH is increased, colloidal surfaces become increasingly more negatively charged (or decreasingly positively charged depending on the isoelectric point of the colloid). Phosphate, being negatively charged, will be increasingly less favourably attracted to the surface as pH is increased. The situation is slightly more complex than the case with sulphate, however, since the average charge of the phosphate ion also increases with pH. Thus, although the colloid becomes less positive and therefore there is less attractive force, the phosphate becomes more negative and therefore there is slightly greater attractive force whilst the surface remains positive. Notwithstanding this, the data in Figure 5.1 still shows a relatively sharp decline in percent adsorption as pH is increased, indicating that the lowering of the hydrous oxide surface charge remains the dominant controlling feature.

- At very high pH values, there is almost no adsorption in any of the cases. This is good evidence that once the surface has become significantly negatively charged, phosphate is electrostatically repulsed from the surface and cannot adsorb.

- At low pH, percent adsorption decreases as pH decreases for the case of hydrous aluminium(III) oxide. As stated in Section 4.3.1, this is almost certainly due to the incomplete formation of the oxide below pH 5.

- Notwithstanding any of the above, it is again pleasing to note that adsorption of phosphate was significant at a one to two (by mass) ratio. Although not as difficult to treat as sulphate, phosphate can still be difficult to treat. Although the percent adsorption only fleetingly reaches above 90% removal, the removals reached are considered more than adequate to attract industrial interest in adsorbing colloid flotation.
The pattern of adsorption onto hydrous aluminium(III) oxide is the most interesting, showing a decline in adsorption at low pH, an almost flat “plateau” at intermediate pH values, and a large decline at high pH value. This pattern has also been reported by, for example, Bolan et al. (1986) and He et al. (1997).

5.2.2 Phosphate Adsorption - Adsorption per Mass of Substrate

In Section 4.3.2 it was shown that hydrous iron(II) was the most efficient substrate if data was plotted as a mass ratio rather than a percent adsorption. A similar exercise was performed for phosphate adsorption and the data plotted in Figure 5.2.

The reversal of apparent substrate efficiency is almost identical to that found for sulphate (Figure 4.4). Hydrous iron(II) oxide is the most efficient substrate when data is treated in this fashion, and hydrous aluminium(III) oxide the worst. Again, this illustrates the danger of too quickly dismissing an absorbent on the basis of effectiveness rather than also considering efficiency. Hydrous iron (II) oxide is a less effective adsorbent for phosphate as indicated by the data treatment displayed in Figure 5.1 but is a more efficient adsorbent on a mass basis as indicated by the data treatment displayed in Figure 5.2.

5.2.3 Phosphate Adsorption - Adsorption per Mole of Substrate

In section 4.2.3 it was shown that hydrous iron(III) oxide was the most efficient substrate (for sulphate adsorption) on a mole for mole basis. A similar exercise was performed for phosphate adsorption and the data plotted in Figure 5.3.
**Figure 5.2:** Adsorption, by mass, of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion.
**Figure 5.3:** Adsorption, by mole, of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion.
The reversal of apparent substrate efficiency is nearly identical to that found for sulphate (Figure 4.4), but not quite. Hydrous iron(III) oxide is the most efficient substrate (for phosphate) when data is treated in this fashion, but hydrous aluminium(III) oxide was not the worst. Most importantly, the data as presented in Figures 5.1, 5.2 and 5.3 illustrate that all three oxides (aluminium(III), iron(III) and iron(II)) can be shown to be the most efficient depending on the way in which data is presented. Nevertheless, hydrous aluminium(III) oxide remains the most effective under the conditions studied (it removed the most amount of sulphate) and the data transformation which gives hydrous iron(III) oxide an apparent high efficiency remains of limited value since colloidal substrates are controlled by their surface area and not by the total number of mole of substance within the colloid.

5.3 Electrophoretic Mobility

The role of electrostatics in the adsorption of phosphate to hydrous oxides is likely to be similar to, and reflect that of, the role of electrostatics in the adsorption of sulphate to hydrous oxides (Section 4.4). Again, it is likely that the interaction is predominantly attraction between negatively charged phosphate ions and positively charged hydroxide sites on the surface of the oxide. The importance of electrostatic interactions can be seen in Figure 5.1 where it is apparent that adsorption decreases, at high pH values and for all substrates studied, as pH is increased. This decrease is assumed to be due to the lessening of electrostatic interaction between the negatively charged sulphate ion and the increasingly negatively charged (or decreasingly positively charged) surface.

For reasons already discussed in Section 4.4, the electrophoretic mobility was measured, for the various hydrous oxides in the presence and absence of phosphate, and the data was not converted to zeta potential, but rather left in its raw form.

5.3.1 Electrophoretic Mobility of Hydrous Aluminium(III) Oxide

The electrophoretic mobility data obtained for the hydrous oxide of Aluminium(III) is given in Fig. 5.4. In the absence of sulphate, the data is consistent with that expected from literature, i.e. a relatively flat region of positive electrophoretic mobility (around 3.0 x 10⁻
\(8 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\) followed by a moderate decrease in electrophoretic mobility from pH 7.0 to pH 10. The electrophoretic mobility undergoes a charge reversal (iep) around pH 9.8.

The iep is consistent with the data in Figure 4.6 and also with literature such as the values quoted by Parks (1965). The shape of the graph is, however, not fully consistent with that in Figure 4.6. In Figure 5.4, the data (hydrous aluminium(III) oxide, no phosphate) is higher at the pH extremes that the equivalent data in Figure 4.6. These differences can be attributed to ionic strength effects. In the case of Figure 4.6 the ionic strength was much higher than in the case of Figure 5.4 since the colloid was formed from a 1,000 ppm total metal ion solution rather than a 50 ppm total metal ion solution. The increased values at pH extremes and sharper gradient through the iep observed in Figure 5.4 are consistent with a lower ionic strength.

**Figure 5.4:** Electrophoretic mobility of hydrous aluminium(III) oxide in the presence and absence of 25 ppm phosphate.
In the presence of phosphate, the electrophoretic mobility data is again considerably changed indicating that phosphate not only adsorbs in response to surface electrical properties but also alters them greatly upon adsorption. The electrophoretic curve, in the presence of phosphate, shows a number of features which are similar, but not as clearly indicated, to the case of sulphate (Section 4.4).

Firstly, the electrophoretic mobility, in the presence of phosphate, is considerably lower, for all pH values, than that in the absence of phosphate. This is a clear indication of the adsorption of a negatively charged ion.

Secondly, there has been a significant shift in the isoelectric point from 9.8 to 7.5, and more importantly quite negative electrophoretic mobilities between pH 7.5 (the iep in the presence of phosphate) and 9.8 (the iep in the absence of phosphate). These results are a clear indication of chemical specific adsorption occurring between pH 7.5 and pH 9.8. The apparent controlling affect of phosphate over electrophoretic mobility is consistent with the observations of Breeuwsma et al. (1973) who argue, in fact, that phosphate ions can be considered potential determining ions for hydrous metal oxides.

Notwithstanding this, however, at pH values less than 7.5 the electrophoretic mobility was significantly lowered but did not become negative. This is consistent with the results from sulphate adsorption and still indicates that for a wide pH range, the adsorbing potential is not sufficient to overcome repulsive electrostatics of any magnitude.

5.3.2 Electrophoretic Mobility of Hydrous Iron(III) Oxide

The electrophoretic mobility of hydrous iron(III) oxide, in the presence and absence of phosphate, is shown in Figure 5.5, and follows a similar pattern to that observed for hydrous aluminium(III) oxide at low pH values but quite a different pattern at high pH values.
The electrophoretic mobility for hydrous iron(III) oxide, in the absence of phosphate, shows a clear flat region at low pH and suggests that the decision to believe the lack of a flat region in the equivalent curve presented in the sulphate chapter (Figure 4.7) was a correct decision. Again, the electrophoretic mobility curve in the absence of phosphate (Figure 5.5) and the electrophoretic mobility curve in the absence of sulphate (Figure 4.7) are quite dissimilar, but their differences are easily accounted for by the differences in ionic strength. The data in Figure 5.5 (50 ppm metal ion colloid) is again more “compressed” than the data of Figure 4.7 (1,000 ppm metal ion colloid). That is, the absolute values at either pH extreme are higher, and the gradient through the iep is sharper. As with the hydrous aluminium(III) case (compare Figure 5.4 with Figure 4.6), these differences are attributed to the difference in ionic strength and are consistent with the expected pattern.
At low pH values (less than pH 7.5), the electrophoretic mobility data in the presence of phosphate is consistent with the data in the presence of sulphate, and also consistent with both sets of data using hydrous aluminium(III) oxide. In all cases, adsorption of the anion (phosphate in this case) leads to a dramatic lowering of the electrophoretic mobility (and thus surface charge) but does not lead to significantly negative values. This is indicative of an outer sphere complexation where electrostatics play a significant role in providing the attractive force driving adsorption. In the case of phosphate (Figure 5.5) this should, if anything, be more important that for the case of sulphate (Figure 4.7) since the ionic strength is lower and therefore electrostatic forces should be more dominant. Once the surface has become neutral, or near neutral, the electrostatic interaction becomes repulsive and this appears sufficient to prevent phosphate molecules from approaching the surface close enough to bond with the few positive surface sites which are still expected to exist even when the overall surface charge is negative.

At high pH values (above pH 8) the influence of phosphate adsorption on electrokinetic data is very different to that expected, and not consistent with the influence seen by phosphate adsorption onto hydrous aluminium(III) oxide (Figure 5.4), or the influence of sulphate adsorption (Figure 4.7). In the case of phosphate adsorption onto hydrous iron(III) oxide (Figure 5.5), the electrophoretic mobility in the presence of adsorbed anion actually increases the electrophoretic mobility to a less negative value. Exactly how the adsorption of a negatively charged ion onto a negatively charged surface can decrease that negative charge is not clear, however there are two possibilities.

The first is an experimental artifact again caused by changes in ionic strength. The ionic strength of the “phosphate” and “no phosphate” case in Figure 5.5 are not the same. In the “phosphate” case, 25 ppm phosphate (with associated potassium ions) and an unknown amount of acid and/or base (required to maintain the pH during adsorption) has been added, increasing the ionic strength. It is difficult to quantity the extra ionic strength of the “phosphate” case, but it will lower the electrophoretic mobility a little. It is interesting to note that the electrophoretic mobility curve in “with phosphate, 50 ppm metal ion” case is similar to the electrophoretic curve in the “no phosphate, 1,000 ppm metal ion” case. The increase in ionic strength may partly explain the unexpected results, however it is difficult to believe that it is a full explanation.
A more interesting, but highly speculative, possibility arises from the observation (unfortunately not quantified) that base was sometimes required (rather than acid) to maintain the pH during phosphate adsorption onto the hydrous oxides of iron(II) and iron(III). This generally occurred only in the middle pH range and was not observed for hydrous aluminium(III) oxide or for any of the sulphate adsorption experiments. A possible reason could be counter-ion binding as suggested by Nanyo (1994). The mechanisms can be illustrated using Equations 5.4 to 5.7

\[
\begin{align*}
\text{MOH} + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{MH}_2\text{PO}_4 + \text{OH}^- & \text{Equation 5.4} \\
\text{MOH} + \text{HPO}_4^{2-} & \rightleftharpoons \text{MHPO}_4^- + \text{OH}^- & \text{Equation 5.5} \\
\text{MH}_2\text{PO}_4 + \text{K}^+ & \rightleftharpoons \text{MHPO}_4\text{K} + \text{H}^+ & \text{Equation 5.6} \\
\text{MHPO}_4^- + \text{K}^+ & \rightleftharpoons \text{MHPO}_4\text{K} & \text{Equation 5.7} \\
\text{MOH} + \text{H}_2\text{O} & \rightleftharpoons \text{MO}^- + \text{OH}^- & \text{Equation 5.8}
\end{align*}
\]

Equations 5.4 and 5.5 represent two of the many surface site reactions which could be envisaged for phosphate adsorption onto a hydrous metal oxide surface (see also Equation 5.9 to 5.12). At high pH values, HPO\(^{4-}\) is likely to be the dominant solution species, with significant amounts of H\(_2\)PO\(_4^-\) also being present and either could easily bind to a neutral surface (at this pH value, positive surface sites are relatively few), resulting in a release of hydroxide. In both cases, however, the removal of that species from solution will disturb the equilibrium described in Equations 5.1 to 5.3 and this could easily result in more H\(^+\) being released to solution. Thus the amount of base released (and therefore the amount of acid required to neutralise that base and maintain the pH) may well be considerably less than in the equivalent sulphate case.

Potassium ions (K\(^+\)) were introduced as the counter ion to the added phosphate and also as the counter ion to the base required to generate the adsorption pH. Could counter-ion binding of K\(^+\) to the phosphate bound surface sites result in release of H\(^+\)? If K\(^+\) binds to the surface via a direct ligand exchange with protons, as suggested in Equation 5.7, then H\(^+\) is certainly released. If K\(^+\) binds to the surface via simple electrostatic attraction, as suggested in Equation 5.8 then there is no immediate, obvious release of H\(^+\). However, the potassium binding suggested in Equation 5.7 effectively neutralises a negative surface site. This may allow another negative surface site to form, as shown in Equation 5.8, and would indirectly result in the release of H\(^+\).
The overall affect on H⁺ or OH⁻ release given by the interplay of equations 5.4 to 5.8 is too difficult to predict, however it is quite possible that H⁺ release could dominate, resulting in the observed decrease in pH upon adsorption of phosphate. This assumes that phosphate adsorption is required before potassium can bind to the surface. Moreover, the interplay of Equations 5.4 to 5.8 could easily result in a less negative surface, particularly if the simplistic electrostatically driven potassium binding represented in Equation 5.7 is dominant.

A combination of potassium site binding and an increase in ionic strength resulting in compression of the electrical double layer could, combined, be an explanation of the lowering of the negative electrophoretic mobility of hydrous iron(III) oxide following phosphate adsorption. Considerably more work will need to be done, however, to fully conclude this since it remains difficult to believe that adsorption of a negatively charged species (phosphate) can decrease the negative charge on a surface.

5.3.3 Electrophoretic Mobility of Hydrous Iron(II) Oxide
The electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of phosphate adsorption is shown in Figure 5.6. Whilst there are a number of similarities to the data presented for hydrous aluminium(III) oxide (Figure 5.4) and hydrous iron(II) oxide (Figure 5.5) there are also a number of striking differences. These differences were similar to those shown with sulphate adsorption (Figure 4.8).

The electrokinetic data for hydrous iron(II) oxide, in the absence of phosphate, should reflect that of Figure 4.8. As seen in Figure 5.6 this is the case as far as the peak is observed, although the pH of this peak is slightly lower in Figure 5.6 than was observed with Figure 4.8. Again, this peak is attributed to oxidation of iron(II) to iron(III).

The pH of the iep shown in Figure 5.6 (about 7.8), however, was considerably lower than that found in Figure 4.8 (about 10.3) and is more consistent with hydrous iron(III) oxide rather than hydrous iron(II) oxide. Clearly, the batch prepared for the phosphate experiments was subject to considerably more oxidation that the batch prepared for the sulphate experiments suggesting that concentration and/or ionic strength play a vital
role in determining the extent of iron(II) oxidation at the surface. Further characterisation of this phenomenon was considered outside the scope of this thesis.

The electrophoretic mobility of hydrous iron(II) oxide in the presence of phosphate shows a pattern which is relatively easy to predict given the trends seen, to date, in this thesis. At relatively low pH value (less than 7) adsorption of phosphate lowers the electrophoretic mobility by a small amount, but not enough to render a negative surface charge. Again this is fully consistent with outer sphere, electrostatic driven, complexation of negatively charged phosphate with positively charged surface sites. At high pH values, phosphate has little to no influence on the electrophoretic mobility, except possibly at pH 8 where the electrophoretic mobility decreased to a less negative value. This phenomenon was also observed for hydrous iron(III) oxide, is difficult to explain and may again be a combination of increased ionic strength and potassium binding (see Section 5.3.2). It is also possible that the phenomenon only occurs in this experiment because the iron(II) has partly oxidised to iron(III) and it is the hydrous

**Figure 5.6:** Electrophoretic mobility of hydrous iron(II) oxide in the presence and absence of 25 ppm phosphate.
iron(III) oxide component of the subsequent colloid which is responsible for the phenomenon here.

For most of the pH range at high pH, however, the presence of phosphate has had little affect on the electrophoretic mobility. This is perfectly consistent with the very low, to non-existent, adsorption which occurs at very high pH values (see Figure 5.1).

5.3.4 Electrophoretic Mobility of Mixed Hydrous Oxide

The electrophoretic mobility of a mixed (Al(III):Fe(III):Fe(II) = 2:1:1) hydrous oxide was measured, as a function of pH and in the presence and absence of phosphate. The results are shown in Figure 5.7.
Figure 5.7: Electrophoretic mobility of mixed hydrous oxide in the presence and absence of 25 ppm phosphate. The mixed hydrous oxide was formed from a solution containing Al(III):Fe(III):Fe(II) at a ratio of 2:1:1 by mass.

The electrophoretic mobility behaviour for the mixed hydrous oxide, in the presence and absence of phosphate, is consistent with a simple mixture of the behaviour for the three oxides which form it, but not necessarily fully consistent with the pattern seen for electrophoretic mobility in the presence and absence of sulphate:

- The iep (in the absence of phosphate), 7.9, lies between the iep of hydrous aluminium(III) oxide (9.8), hydrous iron(III) oxide (7.8) and hydrous iron(II) oxide (7.6) but is not particularly close to a weighted average of the three (8.7). It is highly likely that oxidation of Fe(II) to Fe(III) is taking place in the mixed oxide (as well as the hydrous iron(II) oxide as discussed earlier). If so, then it is likely that the surface properties, at least with respect to the iep, could be dominated by iron(III).
- There is a significant drop in iep (from pH 7.9 to pH 7.0) upon phosphate adsorption, consistent with a rough averaging of the iep's of the individual oxides each in the presence of phosphate.
- There is a significant drop in electrophoretic mobility over the entire pH range indicating strong adsorption at all pH values. This indicates that adsorption onto the mixed hydrous oxide is specific and involves chemical interaction, probably inner sphere complexation, with the hydrous mixed oxide. Since the aluminium component also displayed chemical specificity, but the iron components did not, it is probable that the lowering of electrophoretic mobility at high pH values is due to the aluminium component.
- The unexplained peak observed in the electrophoretic mobility for the hydrous iron(II) oxide was barely perceptible in the mixed hydroxide case, possibly indicating that oxidation had occurred to a much greater extent than was observed earlier. The greater extent of oxidation would result in a surface which resembled hydrous iron(III) oxide with only a vestibule of iron(II) surface content. The unexplained peak was not observed at all in the presence of phosphate. This may be partly due to the above-mentioned oxidation effect, but is also likely to be due to the dominance of the aluminium component on adsorption.
• The apparent increased role in the aluminium component for the phosphate case as opposed to the sulphate case also explains the higher prominence of the mixed hydrous oxide curve in phosphate adsorption (Figure 5.1) compared to sulphate adsorption (Figure 4.3).

5.4 Implications to Models of Phosphate Adsorption

It is highly unlikely that adsorption would involve the triple valent phosphate ion \((\text{PO}_4^{3-})\) or the fully protonated species \((\text{H}_3\text{PO}_4)\) since these only exist at the pH extremes. The decline in adsorption at high pH, and the decline in adsorption at least for the hydrous aluminium(III) oxide case, would support this. Adsorption, then, probably involves the neutral \((\text{MOH})\) and/or positive \((\text{MOH}_2^+)\) surface sites of the oxide and the mono- \((\text{H}_2\text{PO}_4^-)\) or di- \((\text{HPO}_4^{2-})\) valent phosphate species. It is also unlikely that the negatively charged surface sites \((\text{MO}^-)\) would be involved greatly, and the decline in adsorption at high pH values (where the surface is negative) supports this. The data in Figure 5.4 shows, however, that at least in the hydrous aluminium(III) case, adsorption continues onto a negatively charged surface and thus many authors retain site binding to negative surface sites as a possibility. Inner sphere counter-ion binding by \(K^+\) may also occur, particularly onto hydrous iron(III) surfaces, and may be significant in controlling electrophoretic mobility.

Site binding of phosphate to surface sites on hydrous oxides can, then, be described by a series of chemical equations as shown in Equations 5.4, 5.5 and 5.9 to 5.12.

\[
\begin{align*}
\text{MOH}_2^+ + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{MOH}_2\text{H}_2\text{PO}_4 \quad \text{Equation 5.9} \\
\text{MOH}_2^+ + \text{HPO}_4^{2-} & \rightleftharpoons \text{MOH}_2\text{HPO}_4^- \quad \text{Equation 5.10} \\
\text{MOH} + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{MH}_2\text{PO}_4 + \text{OH}^- \quad \text{Equation 5.4} \\
\text{MOH} + \text{HPO}_4^{2-} & \rightleftharpoons \text{MHPO}_4^- + \text{OH}^- \quad \text{Equation 5.5} \\
\text{MO}^- + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{MHPO}_4^- + \text{OH}^- \quad \text{Equation 5.11} \\
\text{MO}^- + \text{HPO}_4^{2-} & \rightleftharpoons \text{MPO}_4^{2-} + \text{OH}^- \quad \text{Equation 5.12}
\end{align*}
\]
where M represents a metal ion bonded to the surface.

The equations show a mixture of simple electrostatic reactions (Equations 5.9 and 5.10) which probably (but not necessarily) involve outer sphere complexation, reactions which are electrostatically unfavourable (Equations 5.11 and 5.12) and almost certainly would involve inner sphere, chemical specific, complexation and reactions which could easily be envisaged as hydrogen bonding driven (Lee et al., 1989) (Equations 5.4 and 5.5) and could be either inner or outer sphere in nature. Ligand exchange (Parfitt et al., 1978; Sposito, 1989; McBride, 1994) is again traditionally associated with inner sphere complexation, however could still be considered outer sphere complexation if the interaction occurs through a hydrogen bonded link with at least one water molecule remaining between the adsorbed ion and the surface site. The simple electrostatic reactions (Equations 5.9 and 5.10) can also be written on the assumption of an inner sphere complexation as shown in Equations 5.13 and 5.14.

\[
\begin{align*}
\text{MOH}_2^+ + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{MH}_2\text{PO}_4 + \text{H}_2\text{O} & \text{Equation 5.13} \\
\text{MOH}_2^+ + \text{HPO}_4^{2-} & \rightleftharpoons \text{MHPO}_4 + \text{H}_2\text{O} & \text{Equation 5.14}
\end{align*}
\]

In Chapter 4 it was argued that sulphate adsorption onto the various hydrous oxides was prominently electrostatic in nature with only weak evidence for chemical specific interaction. As such, adsorption patterns, solution chemistry (release of hydroxides to solution) and electrokinetic data were all consistent with outer sphere surface complexation of sulphate to the hydrous oxides. The case for phosphate is only partly similar. For the hydrous iron oxides, evidence would also indicate an outer sphere, non-chemically specific, adsorption of phosphate. The evidence is:

- Very little adsorption at high pH. The loss of adsorption at high pH for phosphate was more dramatic than the case with sulphate (Chapter 4) probably because phosphate exists predominantly as a divalent anion ($\text{HPO}_4^{2-}$) at relatively high pH. Thus the repulsion from surfaces which are now becoming negatively charged is greater than in the case of sulphate, and any chemical specificity would need to be that much higher to overcome the electrostatic repulsion.
As with case for sulphate, phosphate adsorption rarely produced a significantly negative electrophoretic mobility for the hydrous iron oxides.

There was little, if any, shift in the iep of the hydrous iron oxides on phosphate adsorption.

There is, however, some evidence for inner sphere, chemical specific, adsorption for the case of the hydrous aluminium(III) oxide. This can be seen in Figure 5.4 where it is clearly shown that phosphate continued to adsorb against a negative electrophoretic mobility. Again, however, the evidence is not compelling since adsorption declined at high pH where the surface was again negatively charged. At high pH, phosphate is now predominantly in the form HPO$_4^{2-}$, as opposed to H$_2$PO$_4^-$. This may indicate that HPO$_4^{2-}$ (as per Equation 5.5, 5.12 and 5.14) specifically adsorbs, but H$_2$PO$_4^-$ (as per Equations 5.4, 5.11 and 5.13) does not, presumably because the electrostatic repulsion from HPO$_4^{2-}$, being double that of HPO$_4^-$ is too strong to overcome.

Additionally, some of the adsorption of phosphate may be due to surface precipitation through the respective formation of AlPO$_4$ and FePO$_4$.

Although outside the scope of this thesis, the distinction between inner and outer sphere phosphate complexation can be made from experiments involving the variation of ionic strength (Hayes et al., 1988), and that variation can even be used to enhance adsorption (Nanzyo, 1986). It can also be inferred from any shift in iep (Hunter, 1981).

5.5 Flotation of Phosphate

It was shown in Chapter 4 (for sulphate) that adsorption was a good indicator to the ultimate success of adsorbing colloid flotation. To show this, sulphate flotation was carried out under similar conditions to adsorption and the two (flotation and adsorption) were shown to strongly correlate. A similar exercise is shown, here, for the flotation of phosphate. The conditions for flotation of phosphate were essentially the same as for sulphate, i.e. 1,000 ppm of a colloid precursor (e.g. aluminium nitrate) was added to a solution containing 1,000 ppm of the analyte of choice, in this case phosphate ions (from potassium phosphate). The pH was then increased to the desired value where it was kept constant for an induction period of 15 minutes. Following the induction period, a mixed surfactant solution containing a 2:1 ratio (by weight) of sodium dodecyl sulphate (SDS) to dodecanoic acid (DA) was added to give a total surfactant
concentration of 300 ppm. Flotation was effected by air and carried out in the “total liquid carry-over” (TLC) mode such that the entire liquid volume was floated and allowed to drain from the foam. The concentration of phosphate in the drainage liquid was measured to give the data in Figure 5.8.

![Graph showing pH vs % Phosphate Floated for different oxides](image)

**Figure 5.8:** Percentage (%) flotation of 25 ppm phosphate using various hydrous oxides formed from solutions containing 50 ppm (total) metal ion. Total surfactant concentration was 300 ppm and consisted of a 2:1 mixture of SDS to DA.

A number of trends are immediately apparent from the data in Figure 5.8 and most of these trends were also observed in the case of sulphate (Figure 4.12):
• Flotation behaviour, as a function of pH and as a function of the particular oxide chosen, shows a remarkably strong correlation with adsorption data (see Figure 5.1). This will be discussed in detail shortly.
• In most cases, removal by flotation decreased with increasing pH, consistent with the trend seen for adsorption in Figure 5.1 and falling almost to zero at very high pH.
• In the case of hydrous aluminium(III) oxide, flotation at very low pH values was poor, consistent with the incomplete formation of the oxide at this pH, as discussed earlier.
• The most effective substrate for flotation was hydrous aluminium(III) oxide, again consistent with the adsorption data as shown in Figure 5.1 and consistent with the adsorption and flotation of sulphate (Figures 4.2 and 4.11).
• The least effective substrate for flotation was again hydrous ferrous oxide, also consistent with the adsorption data as shown in Figure 5.1 and the adsorption and flotation of sulphate (Figures 4.2 and 4.11).
• The hydrous mixed oxide resulted in flotation which was slightly prejudiced towards the hydrous aluminium(III) oxide, again consistent with the adsorption data as shown in Figure 5.1, but not fully consistent with the adsorption and flotation of sulphate (Figures 4.2 and 4.11). This result illustrates the importance of the aluminium component in the mixed hydrous oxide for the removal of phosphate.

A key feature of the flotation results for phosphate is again that removal occurs across a wide range of pH values, even though it becomes less effective as the pH increases. The data is Figure 5.8 shows that removal may be acceptable, although not optimal, over a wide pH range, only “failing” above pH 9.

As discussed in Chapter 4 (for sulphate), the foam requirements for adsorbing colloid flotation are not apparent from data such as that given in Figure 5.8. The foam produced using hydrous aluminium(III) oxide was again gelatinous in nature, adhering to the modified Hollimand cell used for flotation and was not stable for any length of time following flotation (Foam Type 7). This renders the foam unsuitable for treatment following adsorbing colloid flotation and means that hydrous aluminium(III) oxide is again a poor choice of colloid despite its apparent effectiveness. The other three oxides, including the mixed oxide, all gave suitable foams with phosphate. The
hydrous iron(II) oxide again appeared the best foam, and the presence of iron(II) in the hydrous mixed oxide gave it good stability despite the presence of aluminium(III). Although qualitative and subjective in nature, these observations are sufficient to again recommend against the use of hydrous aluminium(III) oxide on its own, despite its better effectiveness.

Unlike the sulphate case, the hydrous mixed oxide and hydrous iron(III) oxide were only marginally poorer in effectiveness than the hydrous aluminium(III) oxide case (Figure 5.8). In both cases, however, the nature of the foam is greatly improved.

5.6 Comparison of Adsorption and Flotation

As noted in Section 5.5 (for phosphate) and Sections 4.4 and 4.7 (for sulphate) there is a strong correlation between the trends seen in adsorption (Figure 5.1) and flotation (Figure 5.8). This correlation is worth closer examination and can be achieved by plotting adsorption and flotation on the same graphs, as was done in Section 4.7 for sulphate. The results, for phosphate, are given in Figures 5.9 to 5.12.
Figure 5.9: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous aluminium(III) oxide formed from 50 ppm Al(III).
Figure 5.10: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous iron(III) oxide formed from 50 ppm Fe(III).
Figure 5.11: Comparison of adsorption and flotation of 25 ppm phosphate using hydrous iron(II) oxide formed from 50 ppm Fe(II).
In section 4.7 (Figures 4.12 to 4.15) it was shown that there was a strong correlation between adsorption and flotation for the removal of sulphate by all hydrous oxides studied. Here, in Figures 5.9 to 5.12 the correlation is shown, if anything, to be even stronger in the case of phosphate removal. In all cases except hydrous aluminium(III) oxide, flotation effectively parallels adsorption with an average of approximately 5% less efficiency. In the case of hydrous aluminium(III) oxide, flotation was slightly more efficient at high pH values.
5.7 Summary

A number of important findings concerning the adsorption and flotation of phosphate using hydrous metal oxides have been found and can be summarised as follows:

- Phosphate was found to be removed effectively and efficiently by both adsorption and flotation, from a model industrial waste. The same was earlier (Chapter 4) shown to be true for sulphate and further demonstrates that adsorbing colloid flotation has considerable potential for the treatment of intractable anionic aqueous wastes.

- Hydrous aluminium(III) oxide was found to be the most effective, on a weight for weight basis based on the metal ion, substrate for phosphate removal by adsorption. However, it was not found to be the most effective on a weight for weight basis based on the total mass of colloid.

- Hydrous iron(II) oxide was again found to result in a good quality foam (when used for phosphate removal) and its incorporation into a mixed oxide gave that oxide a better quality foam.

- The high effectiveness of aluminium(III) oxide, the relative inexpense of iron(III) oxide (which can be used as a “filler”) and the foam stabilisation of iron(II) oxide indicate that a mixed oxide would provide the best choice for a substrate in adsorbing colloid flotation of phosphate – an identical conclusion to that made for sulphate.

- Phosphate adsorption, and consequently flotation, was found to be dependent on pH such that removal decreased as pH increased. This is almost certainly due to the increasingly less favourable electrostatics as pH is increased, and particularly due to the formation of a doubly charged species ($\text{HPO}_4^{2-}$) which carries too much charge for chemically specific adsorption to overcome.

- Continued adsorption onto negatively charged hydrous aluminium(III) oxide at pH values around 5 to 9 indicated chemically specific, probably inner sphere complexation of phosphate with surface sites. The evidence was less compelling, but also present, for hydrous iron(III) oxide.

- The isoelectric point of all colloids were lowered in the presence of phosphate adsorption indicative of chemical adsorption.

- Notwithstanding the above, the adsorption and electrokinetic data presented here is more consistent with an outer sphere complexation of phosphate with hydrous...
iron oxide surfaces than with inner sphere complexation. The reverse is true for the hydrous aluminum oxide surface.

- In all cases, adsorption and flotation appeared to correlate very strongly with each other. Again, this enables us to predict the future success of adsorbing colloid flotation, as a waste treatment or environmental scrubbing technique, on the basis of adsorption experiments. Phosphate adsorption experiments are commonly reported in literature whereas adsorbing colloid flotation has been rarely reported.
6.1 Introduction

In Chapters 4 (Sulphate) and 5 (phosphate) it was demonstrated that adsorbing colloid flotation of anionic waste could be successfully achieved using a hydrous mixed oxide as the adsorbant and a mixture of sodium dodecyl sulphate (SDS) and dodecanoic acid (DA) as the collecting and foam stabilising agents. It was also demonstrated that there was a strong correlation between adsorption and flotation such that flotation effectiveness diminished when adsorption effectiveness diminished. Specifically, both adsorption and flotation decrease in efficiency as pH increases (particularly above pH 8) and, for hydrous aluminium oxide both decrease in efficiency as pH decreases below pH 5 (due to incomplete formation of the oxide). Mercury(II) wastes are often in the presence of very high concentrations of chloride (see Table 3.1) and under these conditions mercury is predominantly in the form of anionic species such as $\text{HgCl}_4^{2-}$ (see Figures 6.1 to 6.5). Thus it might be expected that mercury(II) adsorption and flotation would reflect the patterns seen in sulphate and phosphate (note that the data presented in this chapter will show this assumption to be in error).

Adsorption of mercury(II) onto colloidal substrates has been studied by a number of authors (see for example; MacNaughton and James, 1974; Newton et al., 1976; Thiem et al., 1976; Farrah and Pickering, 1978; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a; Barrow and Cox, 1992b, Gunneriusson and Sjoberg, 1993; Tiffreau et al., 1995; Yin et al., 1996; Mishra and Singh, 1999; Kelly et al., 2003; Kima et al., 2003; Mishra et al., 2004; Nagorny et al., 2004; Lloyd-Jones et al., 2004).

Fewer authors have specifically studied the adsorbing colloid flotation of mercury(II) (see for example; Voyce and Zeitlin, 1974; Huang and Wilson, 1976; Volke et al., 1984; Para et al., 1986; Kidokoro et al., 1988; Kabil, 1994; Ghazy et al., 2000; Chen et al., 2003)
6.1.1 Mercury Speciation in Chloride Solutions

The species form of mercury(II) in the environment depends on a number of factors including temperature, concentration, aqueous environment (sea water or natural water) and redox conditions. The role of redox conditions is particularly illuminating for typical environmental conditions, and is shown in Figure 6.1.

![Eh-pH Diagram for Mercury](adapted from Davis et al. (1997)).

*Figure 6.1:* Eh-pH Diagram for Mercury (adapted from Davis et al. (1997)).

It can be seen from Figure 1 that mercury can be present as the chloride (HgCl₂) (low pH) or hydroxide (Hg(OH)₂) (high pH) under aerobic conditions or as the sulphide (HgS) under anaerobic conditions (Reimers et al., 1974). There is only a small window where metallic mercury is the stable form. Mercurous compounds (Hg⁺) are not common in the environment as they are rapidly oxidised to mercuric forms (Hg²⁺) through hydrolysis with water.
What is not clear from diagrams such as Figure 6.1 is the full aqueous speciation likely to result from different concentration of chloride and pH. These are crucial to environmental concerns where sea water, estuarine conditions and bore water would all result in high chloride levels. They are also crucial to the industrial conditions of interest in this thesis where mercury(II) waste is hosed down by seawater resulting in a high chloride concentration in the final mercury(II) waste.

The speciation of mercury(II), as a function of pH, can be determined from the following suite of equations (where the equilibrium constants can be found in, for example, Ciavatta and Grimaldi, 1968):

\[
\begin{align*}
\text{Hg}^{2+} + \text{Cl}^- & \rightleftharpoons \text{HgCl}^+ \quad K_1 \quad \text{Equation 6.1} \\
\text{HgCl}^+ + \text{Cl}^- & \rightleftharpoons \text{HgCl}_2 \quad K_2 \quad \text{Equation 6.2} \\
\text{HgCl}_2(aq) & \rightleftharpoons \text{HgCl}_2(s) \quad K_{s0} \quad \text{Equation 6.3} \\
\text{HgCl}_2 + \text{Cl}^- & \rightleftharpoons \text{HgCl}_3^- \quad K_3 \quad \text{Equation 6.4} \\
\text{HgCl}_3^- + \text{Cl}^- & \rightleftharpoons \text{HgCl}_4^{2-} \quad K_4 \quad \text{Equation 6.5} \\
\text{Hg}^{2+} + \text{OH}^- & \rightleftharpoons \text{Hg(OH)}^+ \quad K_1 \quad \text{Equation 6.6} \\
\text{Hg(OH)}^+ + \text{OH}^- & \rightleftharpoons \text{Hg(OH)}_2 \quad K_2 \quad \text{Equation 6.7} \\
\text{Hg(OH)}_2(aq) & \rightleftharpoons \text{Hg(OH)}_2(s) \quad K_{s0} \quad \text{Equation 6.8}
\end{align*}
\]
\[ \text{Hg(OH)}_2 + \text{OH}^- \rightleftharpoons \text{Hg(OH)}_3^- \quad \text{K}_3 \quad \text{Equation 6.9} \]

\[ \text{Hg(OH)}_3^- + \text{OH}^- \rightleftharpoons \text{Hg(OH)}_4^{2-} \quad \text{K}_4 \quad \text{Equation 6.10} \]

Figures 6.2 to 6.7 show the resultant speciation of 50 ppb mercury(II) under various concentrations of chloride.

**Figure 6.2:** Speciation of 50 ppb Mercury(II) in 0.0001 M Cl\(^-\) solution.
**Figure 6.3:** Speciation of 50 ppb Mercury(II) in 0.001 M Cl⁻ solution.

**Figure 6.4:** Speciation of 50 ppb Mercury(II) in 0.01 M Cl⁻ solution.
**Figure 6.5:** Speciation of 50 ppb Mercury(II) in 0.1 M Cl\(^-\) solution.

**Figure 6.6:** Speciation of 50 ppb Mercury(II) in 1 M Cl\(^-\) solution.
The data illustrated in Figures 6.2 to 6.6 will be invaluable during explanation of both adsorption and flotation of mercury(II) under high, and variable, chloride conditions. They show a clear competition between the anionic chloride species, which dominate at low pH and high chloride concentrations, and the anionic hydroxide species, which dominate at high pH and low chloride concentrations. Neither of the precipitating species, HgCl₂(s) or Hg(OH)₂(s) play a significant role until very high pH (> pH 10 depending on mercury(II) concentration) when Hg(OH)₂ precipitates out of solution. The data in Figures 6.2 to 6.6 do not show precipitation, but experimentally it is obvious when it occurs as a highly visible white precipitate.

Hydrolysis of mercury(II) is clearly shown, from Figures 6.2 to 6.6 to be inhibited by the presence of chloride. At 0.0001 M Cl⁻, the inhibition is not particularly noticeable and the hydrolysis curve is almost the same as that in the total absence of Cl⁻. Even at 0.001 M Cl⁻, however, the hydrolysis of mercury(II) has been shifted to a higher pH as a result of ligand competition. Similar effects to these are rare in any other metal system and reflect the very high stability of aqueous anionic mercury complexes such as the mercury chlorides. In a 1.0 M Cl⁻ solution, hydrolysis has been effectively stopped and the system consists entirely of mercury(II) chlorides over the full pH range of interest. Many of the industrial waste mercury samples (see Table 3.1) had chloride concentrations between 0.1 and 1.0 M, indicating that hydrolysis is very much suppressed (by chloride) in systems of interest.

A further point of interest from the data in Figures 6.2 to 6.6 is the evolution of the mixed hydroxy-chloride Hg(OH)(Cl⁻). Although this species predominantly exists only in a relatively narrow pH range, it is often the range of interest and gradually increases in pH as the chloride concentration is increased. Moreover, it is the first hydroxy species to form as pH is increased.
6.2 Mercury Adsorption

The adsorption of mercury(II) chloride species (and mercury(II) hydroxide species) might be expected to mirror that of sulphate (Chapter 4) and phosphate (Chapter 5) in that all three analytes are anions and have similar electrostatic attraction to positively charged surfaces. Gunneriusson and Sjoberg (1993), Tiffreau et al. (1995), and Bargar et al. (1997), to name a few, have also proposed evidence for inner sphere ternary oxide – chloride – mercury complexation which would result in entrapped adsorption. The electrostatic interactions of mercury(II), however, are considerably more complex than sulphate or phosphate due to the aqueous chemistry involved, as illustrated in Equations 6.1 to 6.10. Furthermore, there is literature evidence which suggests that chloride binding of species such as mercury(II) inhibits the adsorption of those species (McNaughton and James, 1974; Forbes et al., 1974; Jackson et al., 1978; Kidokoro et al., 1988; Schuster, 1991). Nevertheless, flotation of mercury(II) in the presence of seawater has been observed (Voyce and Zeitlin, 1974; Walkowiak, W., 1976) as has the specific adsorption of chlorides (Kliejn and Lyklema, 1987) and the specific adsorption of Hg(OH)Cl (Kinnibugh and Jackson, 1978; Walcarius et al., 1999; Herrero et al., 2005). Thus the adsorption and flotation of mercury chloride complexes is well worth investigating.

6.2.1 Mercury Adsorption - Percent Adsorption

Adsorption of a model mercury waste by various hydrous metal oxides was performed and the data presented in Figure 5.1. The conditions of Figure 5.1 are quite different to the conditions of similar adsorption experiments involving sulphate (Figure 4.3) and phosphate (Figure 5.1) and these represent a number of decisions made following preliminary flotation trials involving mercury. Specifically:

- 400 ppb Hg was chosen as the initial analyte concentration to reflect a mid-range of the industrial samples to be studied (Table 3.1).
- 200 ppm total metal ion concentration was used for the colloid pre-cursor. This represents a considerable excess over the analyte (400 ppb) and is contrary to the philosophy used in earlier experiments where the analyte concentration was much higher, and the expense of using an excess of colloid was not justified. The higher colloid concentration (200 ppm) used here is justified on the grounds that low level
contamination of mercury is problematic and well worth the added expense of a higher colloid concentration.

- The excess of colloid used here also enables the concentration of colloid to be kept constant during later experiments (involving real industrial samples) where the concentration of analyte (mercury) varies, and can approach 25,000 ppb (25 ppm) (Table 3.1).

- Having established that foam stability is a major determinant in the choice of colloid precursor, a number of preliminary studies were undertaken to test the stability of foams formed during the adsorbing colloid flotation of mercury(II). These tests resulted in a number of conclusions, specifically:
  - Stable foams could not be formed from iron(III) on its own (the best foam formed was of type 5 (see Table 4.1). Adsorbing colloid flotation using iron(III) on its own has been successfully reported in the literature (see for example Luo and Huang, 1993; Lin and Huang, 1994; Zhao et al., 1996; Choi et al., 1999; Choi et al., 2000; Sabti et al., 2002; Lu and Chen, 2003; Matis et al., 2005), however did not necessarily involve the same surfactant mix and more importantly did not necessarily involve flotation in the total carry-over mode.
  - Stable foams could not be formed from aluminium(III) on its own (the best foam formed was of type 6 (see Table 4.1). Again, literature evidence suggests that aluminium(III) can be successfully floated on it own (Pacheo and Torem, 2002) however these studies again do not correspond to the total carry-over mode.
  - Iron(II) was not extensively trialled since it should only be used to give foam stability and is problematic in terms of oxidation, more toxic that the other metal ions and too expensive to use as the sole collector.
  - Very stable foams (Foam Type 9) were readily obtained from mixed foams of iron(III) and aluminium(III) (without Fe(II)). These foams were stable with both the model and industrial waste mercury samples. The results of Sanciolo et al., (1992, 1993) and Jurdiewics (2005) support this result.
  - The addition of iron(II) to the iron(III)/aluminium(III) mixture did not improve foam stability and sometimes caused excessive precipitation with the mercury/surfactant/metal ion system. This precipitation was often present in the absence of iron(II) (see Section 6.3) but was more prevalent when iron(II) was present.
Extensive studies to determine the best ratio of iron(III) to aluminium(III) to obtain the best foam were not carried out, however a 50:50 mix of equal mass appeared to work well and was therefore chosen.

- For the above reasons, a hydrous oxide formed from equal masses (1:1 ratio) of aluminium(III) and iron(III) was used.
- Adsorption onto the hydrous oxides formed from aluminium(III), iron(III) or iron(II) on their own were not performed since it was known that a stable foam with these oxides could not be readily formed.
- The role of surfactant choice was also investigated and will be discussed in Section 6.4.
- The overall, “S”-shape of the adsorption curves, particularly in the case of 0.001 M, also represents typical behaviour for the adsorption of aqueous heavy metal cations rather than anions.
- In the case of sulphate and phosphate adsorption, an inflection point was noted at approximately pH 5 due to the incomplete formation of the aluminium(III) component of the mixed oxide. No such infection point is seen here, presumably because there was insignificant adsorption at this pH.
- Notwithstanding any of the above, it is again pleasing to note that adsorption of mercury was significant. Unlike sulphate and phosphate, mercury adsorption appears to readily reach values above 90% (and approach 100%), but only at the higher pH values. pH values of the order of 8 to 9 result in significant mercury removal and are typical of many waste treatment pH values. pH values in excess of pH 9 show greater promise but would probably involve the expense of adding an alkalising agent.
The role of chloride shown in Figure 6.7 is to clearly inhibit adsorption and push the adsorption curve to higher pH values. This result, although contrary to the expectation that HgCl$_4^{2-}$ might be a good adsorbing species, is consistent with the role of chloride in a number of adsorption studies involving mercury(II) (Newton et al, 1976; Kinniburgh and Jackson, 1978; Farrah and Pickering, 1978; Thanabalasingam and Pickering, 1985; Barrow and Cox, 1992a; Barrow and Cox 1992b; Yin et al. 1996)
The role of pH in the adsorption of mercury is contrary to that expected of an anionic species and worth further scrutiny. In the absence of chloride, mercury would be expected to behave in a similar fashion to any other aqueous heavy metal cation. The expected pattern of adsorption for aqueous heavy metal cations is for adsorption to begin when trace quantities of hydrolysis (Hg(OH)$^+$) products form, i.e. one or two pH units below the pK1 for hydrolysis. As hydrolysis products become increasingly more important, adsorption increases. This observation is consistent with the adsorption of mercury in the absence of added chloride.

At 0.01 M Cl$^-$, the analysis given in Figure 6.4 indicates that hydrolysis has already been significantly inhibited. At pH 6, for example, the dominant species is HgCl$_2$ with a small amount of HgCl$_3^-$ and no trace of Hg(OH)$^+$. It is interesting to note that at pH 6, and for 0.01 M Cl$^-$, there is no adsorption. For the higher concentration chloride cases (0.1 M Cl$^-$ and 1.0 M Cl$^-$ respectively) HgCl$_3^-$ and HgCl$_4^{2-}$ become increasingly more important and HgCl$_4^{2-}$ dominates at 1 M Cl$^-$. On the basis of the adsorption results presented in Chapter 4 (sulphate) and Chapter 5 (phosphate), formation of these negatively charged ions might have been expected to result in significant adsorption at low to middle pH values (such as pH 6) where the surface is electrostatically attractive to anions. The opposite, however, is seen to be true and adsorption, in all cases, increases as the concentration of hydrolysis products increases. The lack of adsorption of anionic species in the case of mercury is even more surprising when it is realised that the ratio of colloid concentration to analyte is much higher in the mercury case (25:2) compared to the sulphate (1:1) or phosphate (2:1) cases.

There are, thus, two very strong pieces of information which suggest that mercury adsorption occurs through the hydrolysis products of mercury and not through the anionic chloride complexes:

1. Adsorption increases with increasing pH.
2. Adsorption decreases with increasing chloride concentration.
6.2.2 Mercury Adsorption - Percent Adsorption in the Presence of Surfactant

In Chapter 4 (sulphate) and Chapter 5 (phosphate) adsorption and flotation were found to have a close parallel and it was assumed that the presence of surfactant in the flotation case had minimal affect on this relationship. During the adsorbing colloid flotation of mercury, however, a precipitate was observed to form (see Section 6.3.2) and this was postulated to be a complex involving mercury and surfactant. The role of surfactant on the adsorption of mercury onto the mixed hydrous oxide is therefore worth presenting prior to full discussion of flotation.

The adsorption of 400 ppb mercury onto a mixed hydrous oxide formed from a 1:1 (by mass) mixture of aluminium(III) and iron(III) was studied in the presence of a 300 ppm mixture of dodecanoic acid (DA) and sodium dodecyl sulphate (SDS) and the results are given in Figure 6.8.

![Figure 6.8: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA.](image-url)
The pattern of adsorption for mercury, in the presence of surfactant (Figure 6.8), is very different to that in its absence (Figure 6.7). Adsorption is enhanced over a wide pH range such that adsorption can occur even at low pH values. This enhanced adsorption, in the presence of surfactant, has been reported before (Beveridge and Pickering, 1983). Curiously, the adsorption pattern now resembles that of the other anions studied (sulphate and phosphate) in that adsorption is strong at middle range pH values, decreases at high pH values and also decreases at low pH values where the aluminium component is not fully formed.

The influence of surfactant is difficult to conclusively prove, however it is postulated here that surfactant forms a complex with mercury which is able to exhibit strong adsorption onto the hydrous metal oxide colloid (Huang et al., 1976; Voyce et al., 1974; Feng et al., 1984; Yamaoto et al., 1975). The nature of this complex must be quite complicated and will be discussed in detail in the following sections:

### 6.2.3 Mercury Adsorption - Comparison of Adsorption in the Absence and the Presence of Surfactant

In order to understand better the role of surfactant on the adsorption of mercury onto the hydrous mixed metal oxide, a direct comparison is made, for each chloride concentration, of the adsorption data in Figure 6.7 (without surfactant) with the adsorption data in Figure 6.8 (with surfactant).

#### 6.2.3.1 Mercury Adsorption - Comparison of Adsorption in the Absence and the Presence of Surfactant – no added chloride

The adsorption of 400 ppb mercury onto 200 ppm total metal ion mixed hydrous oxide colloid (Al(III):Fe(III) = 1:1) in the presence of 300 ppm total surfactant (2:1 SDS:DA) with no added chloride is shown in Figure 6.9.

The affect of surfactant on mercury adsorption under these conditions is slight compared to the following sections, however, the trends are similar and the results are significant:
Figure 6.9: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with no added chloride.

- At very low pH (below pH 5) both curves decrease as pH is decreased. In the case of “without surfactant” this probably reflects the expected trend assuming mercury adsorbs in a similar fashion to other aqueous heavy metal cations. In the case of “with surfactant”, the decrease is probably due to the incomplete formation of the aluminium component of the mixed hydrous oxide.
- For mid-range pH values (5 to 8), adsorption is considerably enhanced in the presence of surfactant, possibly due to the formation of a mercury-surfactant
complex which is able to adsorb, or be coprecipitated into, the mixed hydrous oxide substrate. Given that dodecanoic acid (DA) is known to be only sparingly soluble at these pH values, it is logical to assume that the complex involves DA and Hg.

- At high pH (above pH 8) the “without surfactant” curve continues to high adsorption removals consistent with other aqueous heavy metal cations and the “with surfactant” curve starts to decrease consistent with anionic species such as sulphate and phosphate. It is unlikely, however that the mercury-surfactant complex (if it exists) would be anionic, so this is more likely due to a change in the nature of the precipitate which makes it less likely to be occluded into the oxide at high pH.

Metal ions are well known to bind to surfactants, and the species which may form through the interaction of DA and Hg probably has the simple stoichiometry Hg(DA)\textsubscript{2}. Since there was visual evidence of a precipitate it is presumed that the species formed must be neutral. It is not clear whether or not it would adsorb onto the surface of the hydrous mixed oxide, coprecipitate with the mixed hydrous oxide or form a colloidal sized precipitate in its own right. In all three cases, the mercury would be analysed as “adsorbed” since it had been removed from solution.

If the species remains soluble, or forms a nano sized precipitate, and does not adsorb or coprecipitate with the hydrous mixed oxide, then it will inhibit adsorption. Any Hg-DA complexation could, therefore, either enhance or inhibit adsorption depending on the precipitate’s nature.

6.2.3.2 Mercury Adsorption - Comparison of Adsorption in the Absence and the Presence of Surfactant – 0.01 M added chloride

The adsorption of 400 ppb mercury onto 200 ppm total metal ion mixed hydrous oxide colloid (Al(III):Fe(III) = 1:1) in the presence of 300 ppm total surfactant (2:1 SDS:DA) with 0.01 M added chloride is shown in Figure 6.10.
Figure 6.10: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with 0.01 M chloride.

The affect of surfactant on the apparent adsorption of mercury onto mixed hydrous oxides is particularly noticeable when performed in the presence of 0.01 M chloride (Figure 6.10). The trends are similar to, but more apparent, than in the “no added chloride” case (Figure 6.9):
At very low pH (below pH 5) the “with surfactant” curve is seen to decrease, probably due to the incomplete formation of the aluminium component of the mixed hydrous oxide. The “without surfactant” curve did not show significant enough adsorption to see any decrease below pH 5.

For mid-range pH values (5 to 8), adsorption is again considerably enhanced, probably due to the formation of a mercury-surfactant complex. Since adsorption in the “without surfactant” case is inhibited compared to Figure 6.9, the difference here (Figure 6.10) is more striking.

At high pH (above pH 8) the “no surfactant” curve again continues to high adsorption removals consistent with other aqueous heavy metal cations and the “with surfactant” curve again starts to decrease, this time at an earlier pH value. The decrease in adsorption at high pH values in the presence of surfactant is puzzling but may relate to the particle size of the complex formed. If the complex formed is soluble, or has a very low particle size, and is not adsorbed or coprecipitated into the hydrous oxide substrate, then the species will effectively remain in solution and be detected as non-adsorbed.

6.2.3.3 Mercury Adsorption - Comparison of Adsorption in the Absence and the Presence of Surfactant – 0.1 M added chloride

The adsorption of 400 ppb mercury onto 200 ppm total metal ion mixed hydrous oxide colloid (Al(III):Fe(III) = 1:1) in the presence of 300 ppm total surfactant (2:1 SDS:DA) with 0.1 M chloride is shown in Figure 6.10.
Figure 6.11: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with 0.1 M chloride.

The affect of surfactant on the apparent adsorption of mercury onto mixed hydrous oxides is again very noticeable when performed in the presence of 0.1 M chloride (Figure 6.11). The trends are similar to, but more apparent, than in the “without added chloride” case (Figure 6.9) and the 0.01 M Cl⁻ case:

- At very low pH (below pH 5) the “with surfactant” curve is seen to decrease, again probably due to the incomplete formation of the aluminium component of the mixed
hydrous oxide. The “without surfactant” curve again did not show significant enough adsorption to see any decrease below pH 5.

- For mid-range pH values (5 to 8), adsorption is again considerably enhanced, probably due to the formation of a mercury-surfactant complex. Since adsorption in the “no surfactant” case is inhibited compared to Figures 6.8 and 6.9, the difference here (Figure 6.11) is even more striking.

- At high pH (above pH 8) the “without surfactant” curve again continues to high adsorption removals consistent with other aqueous heavy metal cations, and the “with surfactant” curve again starts to decrease, but this time at a later pH value. The reason for this is not clear, but is consistent with adsorption behaviour in the absence of surfactant as displayed in Figure 6.7. The 0.1 M Cl⁻ curve in Figure 6.7 showed more adsorption than the general pattern of decreasing adsorption with increasing chloride would suggest. Again, in Figure 6.11, the 0.1 M Cl⁻ curve shows more adsorption than the general pattern would suggest. Speculation of the reason behind this, which might involve the role of mixed hydroxy surfactant metal complexes, is considered beyond the scope of this thesis.

6.2.3.4 Mercury Adsorption - Comparison of Adsorption in the Absence and the Presence of Surfactant – 1.0 M added chloride

The adsorption of 400 ppb mercury onto 200 ppm total metal ion mixed hydrous oxide colloid (Al(III):Fe(III) = 1:1) in the presence of 300 ppm total surfactant (2:1 SDS:DA) with 1.0 M added chloride is shown in Figure 6.12.

In the presence of extreme chloride concentrations (1 M), the adsorption behaviour of 400 ppm mercury onto hydrous oxides (Figure 6.12) is very different to previous cases (Figures 6.8 to 6.11). Here, adsorption is totally inhibited for all pH values above 5.5, but very high at the very low pH of 5. The high percent removal at low pH is probably due to the formation of a surfactant-mercury complex such as \text{Hg(DA)}_2 which either adsorbs, occludes or coprecipitates with the oxide, or is sufficiently large to be removed prior to analysis of remaining mercury. Beveridge and Pickering (1983) have also proposed a surfactant-mercury complex which must be sparingly soluble to affect the (mercury(II))adsorption phenomena seen in the presence of surfactant. High chloride concentrations inhibit the adsorption of mercury in the presence of surfactant and this is presumably due to some affect of chloride on the nature of the precipitate. The
precipitate formed was, however, quite large and significant. It can only be assumed that this precipitate does not adsorb at high chloride concentrations and is not large enough to be removed along with the colloid when analysing for remaining mercury.

Figure 6.12: Percentage (%) adsorption of 400 ppb mercury using a mixed hydrous oxide formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) and in the presence of 200 ppm SDS and 100 ppm DA, and with no added chloride.

6.2.3.5 Mercury Adsorption - Adsorption from an Industrial Sample

The lack of adsorption for some pH values for the “model” mercury wastes gives rise to some concern about the ultimate success of industrial samples. A brief experiment was
therefore carried out to test if mercury could be readily adsorbed from an industrial sample. The sample chosen was “Hydrogen Effluent A’ and it can be seen from Table 3.1 that this effluent had a relatively high initial mercury concentration of 2,000 ppb, a relatively low equivalent chloride concentration of 0.0025 M and an initial pH of 10.8. The pH was controlled and measured and adsorption carried out as described in the Experimental Methodology (Chapter 3). The results are given in Figure 6.13.

**Figure 6.13:** Mercury remaining (ppb) following adsorption of “Hydrogen Effluent A” onto a mixed hydrous oxide of aluminium(III) and iron(III) in a mass ratio of 1:1.

The results in Figure 6.13 are displayed as “remaining mercury” rather than percent adsorption since the percent adsorption is very close to 100% and any small variations in efficiency would be hidden by this high value. A value of 30 ppb, here, reflects a 98.5 % removal.

As can be seen from Figure 6.13, the adsorption of a “real” industrial waste is very high and lends hope to the success of adsorbing colloid flotation.
6.3 Precipitate Characterisation

In the preceding section, it was noted that dodecanoic acid was only partly soluble at low pH and that a precipitate was generally formed at low pH. The nature and extent of that precipitate altered when mercury was present and this could result in altered adsorption and flotation characterisation of the mercury. It should be noted that no such change to the nature of the precipitate was observed in the presence of phosphate or sulphate during the flotation of those anions. This is consistent with the belief that the precipitate formed in the presence of mercury was probably a simple salt of dodecanoic acid and mercury. Evidence in the literature suggests that mercury – surfactant complexes may occur, and may result in enhanced flotation (Huang et al., 1976; Voyce et al., 1974; Feng et al., 1984; Yamaoto et al., 1975), however the evidence is not fully conclusive.

An attempt was made to further characterise the nature of the precipitate in the presence and absence of mercury, and as a function of pH. Experiments were performed in an analogous fashion to that of the adsorption experiments, and samples taken for analysis by dynamic light scattering, using a Coulter N4 particle sizer. This instrument can measure particle count as well as particle size distribution, making the technique particularly useful for these studies. The philosophy was to measure the particle count, and size, as a function of pH and chloride content, and in the presence and absence of (400 ppb) mercury. Changes to the size and/or amount of precipitate could thus be determined and used to help explain the enhanced adsorption of mercury in the presence of surfactant.

When analysing this data, a number of restrictions need to be born in mind. Specifically:

- Particle count gives an idea of the number of particles but is misleading if the size of the particles change since large particle contain large mass but still count as one particle.
• Particles above 10 μm are not detected by the instrument and are treated as macroscopic particles which should be visible by eye. Such precipitates were sometimes observed and have been discussed when analysing the adsorption data. Further experimentation would need to be carried out to account for very large particles.

• Dodecanoic acid was in considerable excess over mercury. Thus even a very small change in the amount or nature of the precipitate could involve all of the mercury but only a fraction of the dodecanoic acid.

• Similar experiments were performed, for completeness, using sodium dodecyl sulphate alone in the presence and absence of mercury. No precipitates were detected (by the N4) for any of the samples whether in the presence or absence of mercury. Experiments using dodecanoic acid alone in the presence and absence of mercury gave similar results to those shown here.

Figure 6.14: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 4.0.
Figure 6.15: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, in the presence of 400 ppb mercury, at pH 4.0.

Figure 6.16: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added chloride and no added mercury, at pH 4.0.
Figure 6.17: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 5.0.

Figure 6.18: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 6.0.
Figure 6.19: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 6.0.

Figure 6.20: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 7.0.
Figure 6.21: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 7.0.

Figure 6.22: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 8.0.
**Figure 6.23:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 8.0.

**Figure 6.24:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 9.0.
Figure 6.25: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 9.0.

Figure 6.26: Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA, with no added mercury, at pH 10.0.
It was hoped that there might be a pattern to either the concentration or the size (or both) of particles formed and some clear trends were seen. At very high chloride concentrations, the particle count was high for all cases involving the presence of mercury, but not for those which didn't, indicating that chloride does have a significant affect on any mercury-surfactant complex. The most likely affect, from all the data shown, is that chloride inhibits the adsorption of the Hg-DA precipitate and also prevents it from growing to a macroscopic scale. This is not fully consistent with the particle size measured, and further experimentation needs to be carried out to truly understand the phenomenon.

Particle count was also high at low pH, both in the presence and absence of mercury, consistent with the insolubility of dodecanoic acid at low pH. The remaining trends, were, however hard to define and more work will need to done in this area.

**Figure 6.27:** Particle analysis of precipitates formed from a mixture of 200 ppm SDS and 100 ppm DA in the presence of 400 ppb mercury, at pH 10.0.
6.4 Flotation of Mercury

It was shown in Chapter 4 (for sulphate) and Chapter 5 (for phosphate) that adsorption was a good indicator to the ultimate success of adsorbing colloid flotation. To show this, flotation was carried out under similar conditions to adsorption and the two were shown to strongly correlate. It is less clear, in the case of mercury, whether a similar pattern will occur since surfactant was shown to have a significant affect on mercury adsorption. The experimental conditions of adsorption are, however, quite different to the experiment conditions of flotation in that a much longer induction (equilibrium) period is used for adsorption and adsorption is carried out under an inert (N₂) atmosphere. Furthermore, the foam itself provides competition for surfactants lowering the amount available to act as a complexing agent for mercury. It is likely that the influence of surfactant on mercury adsorption during adsorbing colloid flotation is less than during the simple adsorption experiments, and it may be that adsorption in the absence of flotation remains a better indicator of the nature of adsorption during adsorbing colloid flotation.

6.4.1 Flotation of Mercury – Preliminary Studies

It was earlier stated (Section 6.2.1) that a number of preliminary tests were performed to determine the stability of foams in the presence of mercury and various surfactant and hydrous oxides. A number of conclusions were drawn from these tests and they are repeated here:

- Stable foams could not be formed from aluminium(III) on its own (the best foam formed was of type 6 (see Table 4.1).
- Stable foams could not be formed from iron(III) on its own (the best foam formed was of type 5 (see Table 4.1).
- Iron(II) was not extensively trialled since it should only be used to give foam stability and is problematic in terms of oxidation, more toxic that the other metal ions and too expensive to be economically viable as the sole collector.
- Very stable foams (Foam Type 9) were readily obtained from mixed hydrous oxides of iron(III) and aluminium(III). These foams were stable with both the model and industrial waste mercury samples.
• The addition of iron(II) to the iron(III)/aluminium(III) mixture did not improve foam stability and sometimes caused excessive precipitation with the mercury/surfactant/ metal ion system. This precipitation was often present in the absence of iron(II) (see Section 6.3) but was more prevalent when iron(II) was present.

• Extensive studies to determine the best ratio of iron(III) to aluminium(III) to obtain the best foam were not carried out, however a 50:50 mix of equal mass appeared to work well and was therefore chosen.

Two further experiments were carried out to determine the optimum aqueous conditions for flotation. The first involved preliminary tests using one of the industrial samples, "Hydrogen Effluent A". It can be seen from Table 3.1 that this effluent had a relatively high initial mercury concentration of 2,000 ppb, a relatively low equivalent chloride concentration of 0.0025 M and an initial pH of 10.8. Adsorbing colloid flotation was carried out using this sample. The surfactant was a mixed surfactant of SDS and DA in the mass ratio of 2:1 and total concentration of 300 ppm and the adsorbing colloid was a mixed hydrous oxide of variable composition. The results are shown in Figure 6.28.

It should be noted that although the initial pH was 10.8, the other ingredients would have considerably lowered this. Since these were preliminary experiments, and also since they reflect the reality of an industrial clean-up, no attempt was made to control the pH during flotation.
Figure 6.28: Adsorbing colloid flotation of Hydrogen Effluent A (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 and initial pH of 10.8) using 300 ppm SDS:DA at a ratio of 2:1.

The X-axis in Figure 6.28 gives the concentration of Fe(III) and the Y-axis gives the concentration of Al(III) used to prepare the mixed hydrous oxide. Thus, for example, a series of oxides were formed using 50 ppm Al(III) and variable Fe(III) and this is reflected by a series of horizontal data points at Al(III) = 50 ppm. A similar exercise gave a series of vertical data points at Fe(III) = 50 ppm. The data points in Figure 6.28 are then coded to indicate the approximate concentration of mercury remaining in the foam drainage after adsorbing colloid flotation.

Even the “worst case” value of 30 – 40 ppb, which involved using only a small quantity of Fe(III), represents better than 98% removal, a very promising start. “Best” values were obtained with samples which were heavily biased towards one or other of the metal ion precursors, i.e. a 50:50 mix did not give the best removal. However, given that all
removals were above 98% this is not seen as justification for choosing any particular stoichiometry of mixed hydrous metal oxide. We return, then, to the foam type which was observed to be best for the 50:50 mixture.

A second experiment was performed in order to gain an approximation of the optimum surfactant concentration to use. Again, “Hydrogen Effluent A” was used and no attempt was made at pH control. The SDS to DA ratio of 2:1 has already been shown to be optimal for the removal of heavy metal cations (Sanciolo et al., 1993) and it was felt too time consuming to experiment with variations of this. The total concentration, however, was varied and the results shown in Figure 6.29.

![Figure 6.29: Adsorbing colloid flotation of Hydrogen Effluent A (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 and initial pH of 10.8) using 200 ppm of mixed hydrous oxide formed from a 1:1 mixture of Al(III) and Fe(III).]
Although there are only three data points, it is reasonably clear that flotation efficiency is already very high at the lowest surfactant concentration used and that the benefit of using higher concentrations diminishes rapidly. There is little perceived benefit to using a higher surfactant concentration that the highest value used here (300 ppm), and probably some benefit, in future, to lowering it. A full cost benefit of minimising reagents was beyond the scope of this thesis, but clearly less surfactant would be one possible economic gain.

6.4.2 Flotation of Mercury – Flotation of Model Waste

Adsorbing colloid flotation of model 400 ppb mercury waste was carried out to determine the success, or otherwise, of flotation of model wastes. 400 ppb mercury and a 1:1 mixture of Al(III) to Fe(III) of total concentration 200 ppm were chosen to reflect the adsorption experiments shown in Figures 6.7 and 6.8. A surfactant mixture of SDS and DA in a 2:1 ratio and total concentration 300 ppm was chosen to reflect the adsorption experiment shown in Figure 6.8. The results are given in Figure 6.30.

The results shown in Figure 6.30 share considerably commonality with the adsorption data in the absence of surfactant (Figure 6.7) rather than the adsorption data in the presence of surfactant (Figure 6.8). Specifically, adsorption follows the traditional “S” shaped adsorption isotherm common to the adsorption of aqueous heavy metals and does not show the high level plateau shown with adsorption in the presence of surfactant (Figure 6.9). This is good evidence that any mercury-surfactant complexation which might have occurred under the conditions of Figure 6.9 are less operative under the conditions of Figure 6.30, probably because of the shorter induction period and competition for surfactant by the foam.

Flotation again appears to mimic that of adsorption (in the absence of surfactant) and this can be more clearly demonstrated by a direct comparison of the two.
Comparison of Flotation with Adsorption

As noted in Section 5.6 (for phosphate) and Section 4.7 (for sulphate) there is a very strong correlation between the trends seen in adsorption and flotation for anions. Mercury in the presence of high concentrations of chloride, it has been argued, does not act like an anion, rather it acts like a heavy metal cation. Furthermore, mercury appears to complex with the surfactant used in adsorption colloid flotation. It is not known how these factors will influence the general correlation between adsorption and
flotation, although a first approximation on the basis of Figures 6.7 and 6.30 would indicate a correlation still exists.

The strength of the correlation was tested by plotting adsorption (in the absence of surfactant) and flotation on the same graph. Adsorption (in the presence of surfactant) is included as a comparator. The results are given in Figures 6.31 to 6.34.

The data in Figure 6.31 clearly shows that flotation is more closely correlated to adsorption in the absence of surfactant than to adsorption in the presence of surfactant. As has been previously discussed, this is probably partly because the foam formed during flotation competes for the surfactant, inhibiting mercury-surfactant complexes and because the induction time is not sufficiently long to allow extensive complexation to form.

The correlation between adsorption (in the absence of surfactant) and flotation is not as good as was seen with sulphate (Figures 4.13 to 4.16) or phosphate (Figures 5.9 to 5.12), but was nevertheless quite a reasonable correlation and suggests, again, that flotation effectiveness can be predicted from adsorption effectiveness. Flotation, as was the case with sulphate and phosphate, was slight less effective than adsorption, particularly at low pH where neither was particularly effective.

The data in Figure 6.32 show that with the addition of a small amount of chloride, the correlation between adsorption (no surfactant) and flotation remains reasonable, but the correlation between adsorption (with surfactant) and flotation becomes very poor. This is consistent with the results in the absence of chloride (Figure 6.31) and the reasoning behind a correlation of flotation to adsorption (no surfactant) rather than adsorption (with surfactant) remain the same.
Figure 6.31: Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at zero added chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1.
Figure 6.32: Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 0.01 M chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1.

Flotation is again slightly less effective than adsorption at low pH but is in fact noticeably more efficient at high pH values. The reason for the increase in flotation over adsorption at high pH values (circa pH 9) is not clear but may have to do with the formation of mixed hydroxy chloride complexes and/or mercury-surfactant complexes. Although these complexes may not strongly adsorb, they may be floated.
Figure 6.33: Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 0.1 M chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1.

The data in Figure 6.33 show that with the addition of a large amount of chloride, the correlation between adsorption (no surfactant) and flotation deteriorates, as does the correlation between adsorption (with surfactant) and flotation. This is consistent with the slight deterioration in correlation caused by the addition of a small amount of chloride (Figure 6.32). Nevertheless, there remains a correlation between flotation and adsorption (no surfactant) and again, the reasoning behind the correlation with adsorption in the absence of surfactant remains the small induction period of flotation and the competition for surfactant by the foam.

Flotation is again less effective than adsorption at low pH and is again more efficient at high pH values. Again, it is outside the scope of this thesis to postulate why flotation is
better than adsorption at high pH, however it is noted here that the increase is enhanced by the presence of high levels of chloride.

**Figure 6.34:** Comparison of adsorption (in the presence of surfactant), adsorption (in the absence of surfactant) and flotation data at 1.0 M added chloride. The surfactant used was a 300 ppm mixture of SDS and DA at a ratio of 2:1 and the colloid was formed from a solution containing 200 ppm of aluminium(III) and iron(III) at a mass ratio of 1:1.

The data in Figure 6.34 show that with the addition of an even larger amount of chloride, the correlation between adsorption (no surfactant) and flotation now improves whilst the correlation between adsorption (with surfactant) and flotation deteriorates to becoming nonexistent. Flotation is again slightly less effective than adsorption (no surfactant) at low pH and they approach similar effectiveness at high pH. In both cases removal appears inhibited by the excessive amount of chloride present, presumably because this level of chloride results in HgCl$_4^{2-}$, an apparently non-adsorbing ion, dominating even at relatively high pH values.
6.6 Adsorbing Colloid Flotation of Industrial Mercury Wastes

The results in this chapter, to date, have indicated that mercury adsorption and flotation is likely to be successful at high pH values and to reflect the behaviour expected of aqueous heavy metal cations rather than that of anions such as sulphate and phosphate. Thus a high pH would favour flotation of industrial waste. This is quite fortunate since the majority of mercury waste of interest (see Table 3.1) exists under quite alkaline conditions. Preliminary studies (Figure 6.28) have indicated that very high levels of removal might be achievable for industrial mercury wastes which have a high native pH.

Adsorbing colloid flotation was carried out as described in Section 3.4 using a series of industrial mercury waste samples. In each case, a surfactant mix of 200 ppm SDS and 100 ppm DA and a colloid formed from a solution of 100 ppm aluminium(III) and 100 ppm iron(III) was used. Flotation was effected in the “total carry-over” mode and foam was allowed to drain outside the flotation cell. The concentration of mercury in the drained liquid was measured as the criteria of flotation effectiveness. If 100% of the floated water were to drain from the foam, then this concentration would be a direct measure of the % floated, however, since only a portion (although usually a significant portion, well in excess of 80%) of the liquid drains from the foam, the percentage floated is not simply calculated from the ratio of mercury concentration remaining to initial concentration. This ratio is, in fact, an underestimate of the percent floated since the mass of mercury is dependent on the concentration and the volume and the volume of the drainage is less than the initial volume.

The results of the various industrial samples floated are given in Figures 6.35 to 6.40 and details of the industrial samples can be found in Table 3.1.
Figure 6.35: Adsorbing colloid flotation of “Hydrogen Effluent A” (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 M and initial pH of 10.8).

Figure 6.36: Adsorbing colloid flotation of “Cell Hosedown” (initial Hg concentration of 25,000 ppb, initial equivalent chloride concentration of 0.21 M and initial pH of 12.8).
**Figure 6.37:** Adsorbing colloid flotation of “Total Chlorine” (initial Hg concentration of 200 ppb, initial equivalent chloride concentration of 0.0024 M and initial pH of 10.8).

**Figure 6.38:** Adsorbing colloid flotation of “14th Avenue” (initial Hg concentration of 56 ppb, initial equivalent chloride concentration of 0.063 M and initial pH of 9.5).
Figure 6.39: Adsorbing colloid flotation of “Chlorine Condensate” (initial Hg concentration of 300 ppb, initial equivalent chloride concentration too high to measure and initial pH of 4).

Figure 6.40: Adsorbing colloid flotation of “Hydrogen Effluent B” (initial Hg concentration of 2,000 ppb, initial equivalent chloride concentration of 0.0025 M and initial pH of 10.0).
The data presented in Figures 6.35 to 6.40 show a number of important features with respect to adsorbing colloid flotation of industrial wastes. Specifically:

- Good removal was observed for most, but not all, of the samples.
- Better than 99% flotation was obtained for Hydrogen Effluent A, Hydrogen Effluent B and 14th Avenue samples.
- Flotation was found to be effective across the full pH range for the above samples.
- Very little flotation was observed for the Cell Hosedown and Chlorinated Condensate samples at any pH.
- The Cell Hosedown had by far the highest initial mercury concentration and it is possible that the conditions used simply did not produce enough colloid to remove significant amounts of mercury.
- The Chlorine Condensate sample had by far the lowest pH (pH = 4) and the flotation of model samples indicates that flotation would not be successful at that pH.
- It appears, for the Cell Hosedown and Chlorine Condensate samples that there was no removal at all, however this is misleading. As stated earlier, the volume of the drainage was not as large as the initial volume, thus some mercury must have remained in the foam. It is interesting to note, however, that a simple mass balance would indicate that the concentration of mercury in the foam was identical to the concentration in the drainage and that this was identical to that at the initial solution. This is consistent with mercury simply remaining in the liquid which remains in the foam.
- The Total Chlorine sample was the only sample which exhibited pH dependence in its flotation behaviour. This behaviour is consistent with the expected behaviour from the pH dependence of the model samples. At high pH (> 8) flotation removal was better than 99%.

6.7 Summary

A number of important findings concerning the adsorption and flotation of mercury in the presence of high concentrations of chloride have been found and can be summarised as follows:
• Stable foams could not be formed from aluminium(III) or iron(III) on their own.
• Iron(II) was not extensively trialled since it should only be used to give foam stability and is problematic in terms of oxidation, more toxic that the other metal ions, and too expensive to be economically viable to use as the sole collector.
• Very stable foams were readily obtained from mixed hydrous oxides of iron(III) and aluminium(III). These foams were stable with both the model and industrial waste mercury samples and iron(II) was not necessary to produce a good foam.
• A white precipitate was observed to form at low pH and assumed to be due to the insolubility of dodecanoic acid. The colour of this precipitate, its particle count and its particle size changed in the presence of mercury(II) and it was assumed that mercury – surfactant complexes can form under the conditions of adsorption experiments.
• Flotation experiments correlated to adsorption experiments in the absence of surfactant and not to adsorption experiments in the presence of surfactant. This appears to indicate that mercury-surfactant complexes are less important in flotation experiments, probably because (a) the induction time is shorter, so the precipitate has less time in which to form, and (b) the foam competes for surfactant lessening the interaction with mercury.
• The addition of iron(II) sometimes caused excessive precipitation with the mercury/surfactant system. Since it was also established that iron(II) was not needed for foam stability, iron(II) was not used for the flotation of mercury(II).
• Extensive studies to determine the best ratio of iron(III) to aluminium(III) to obtain the best foam were not carried out, however a 50:50 mix of equal mass appeared to work well and was therefore chosen.
• Adsorption of mercury(II), in the absence of surfactant, appeared to mimic that of typical aqueous heavy metal cations and not that of anionic species such as \( \text{SO}_4^{2-} \) or \( \text{PO}_4^{3-} \).
• Flotation of mercury(II) correlated to its adsorption in the absence of surfactant.
• Both adsorption (no surfactant) and flotation were pH dependent, showing less removal at low pH values and high strong removal at high pH values.
• The affect of chloride, on both adsorption (no surfactant) and flotation appeared to simply inhibit removal, presumably because chloride complexes with mercury stopping the mercury from hydrolysing. It is fairly well established that hydrolysis and heavy metal adsorption are linked.
• No advantage could be seen, under the conditions of flotation in this chapter, to increasing the total surfactant concentration beyond 300 ppm, except perhaps for the “Cell Hosedown” industrial effluent which contained very high levels of mercury.

• A number of industrial effluents containing variable quantities of mercury(II), chloride content and pH were successfully floated using adsorbing colloid flotation in the total carry-over mode.

• The industrial effluents which were not successfully floated where characterised by either a very high chloride content, a very low pH, or a very high mercury(II) content. The very high chloride content could easily be accounted for by mile dilution, and the technique was seen to work under conditions of high, just not very high, chloride content.

• These results lead to the recommendation of adsorbing colloid flotation for the treatment of low concentration mercury waste (i.e. scrubbing technology) provided that waste is not at a very low pH.

• The final waste product from industries such as the chloro-alkali Hg plant is highly suited to adsorbing colloid flotation.
CONCLUSIONS

Detailed summaries of each of the results and discussions section have already been given and these serve well the purpose of a conclusion to the thesis. For the purpose of completeness, the summaries are repeated here along with a brief overview.

7.1 Sulphate

A number of important findings concerning the adsorption and flotation of sulphate using hydrous metal oxides have been found and can be summarised as follows:

- Sulphate was found to be removed by both adsorption and flotation from both a model and a “real” industrial waste. Adsorbing colloid flotation, then, has considerable potential for the treatment of intractable aqueous wastes containing high levels of sulphate.
- Nitrate levels remaining in solution after adsorbing colloid flotation were found to be low indicating that the technique was not simply replacing one contaminant (sulphate) with another (nitrate). It also indicated that future experimentation involving nitrate as the contaminant to be removed is warranted.
- Hydrous aluminium(III) oxide was found to be the most effective, on a weight for weight basis based on the metal ion, substrate for sulphate removal by adsorption. However, it was found to be the least effective on a weight for weight basis based on the total mass of colloid.
- Hydrous iron(II) oxide was found to result in a good quality foam and its incorporation into a mixed oxide gave that oxide a better quality foam.
- The most appropriate foam type was formed from a 2:1 mixture of SDS and DA. Interestingly, CTAB had a negative affect on foam type (and stability) even in small quantities.
- The high effectiveness of aluminium(III) oxide, the relative inexpense of iron(III) oxide (which can be used as a “filler”) and the foam stabilisation of iron(II) oxide indicate that a mixed oxide would provide the best choice for a substrate in adsorbing colloid flotation of sulphate.
- Removal of sulphate, by adsorption, was shown to increase in a near-linear fashion with increased amount of colloid used. For this reason, there was no advantage seen in using excessive quantities of colloid and a general “rule of
thumb" was adopted to use a colloid concentration similar to the concentration of whatever contaminant was to be removed.

- Sulphate adsorption, and consequently flotation, was found to be dependent on pH such that removal decreased as pH increased. This is almost certainly due to the increasingly less favourable electrostatics as pH is increased.

- The isoelectric point of all colloids were lowered in the presence of sulphate adsorption indicative of chemical adsorption. However, once the electrophoretic mobility was reduced to near zero (by sulphate adsorption), no further adsorption was indicated. This is consistent with physical adsorption.

- Notwithstanding the above, the adsorption and electrokinetic data presented here is more consistent with an outer sphere complexation of sulphate with hydrous metal oxide surfaces than with inner sphere complexation.

- In all cases, except hydrous iron(II) oxide, hydroxyls were released to solution during the adsorption of sulphate. In the case of iron(II) oxide there appeared no net uptake or release of protons or hydroxyls. This result was surprising and probably indicates that surface processes using iron(II) oxide are complicated by oxidation/reduction processes where iron(II) oxide is oxidised to iron(III) oxide during the adsorption and/or flotation process.

- In all cases, adsorption and flotation appeared to correlate strongly with each other. This enables us to predict the future success of adsorbing colloid flotation, as a waste treatment or environmental scrubbing technique, on the basis of adsorption experiments. Adsorption experiments are commonly reported in literature whereas adsorbing colloid flotation is less well studied.

- Most importantly, a complex industrial waste sample containing high levels of sulphate was successfully treated using the technique of adsorbing colloid flotation.

### 7.2 Phosphate

A number of important findings concerning the adsorption and flotation of phosphate using hydrous metal oxides have been found and can be summarised as follows:

- Phosphate was found to be removed effectively and efficiently by both adsorption and flotation, from a model industrial waste. The same was earlier (Chapter 4) shown to be true for sulphate and further demonstrates that adsorbing colloid
flotation has considerable potential for the treatment of intractable anionic aqueous wastes.

- Hydrous aluminium(III) oxide was found to be the most effective, on a weight for weight basis based on the metal ion, substrate for phosphate removal by adsorption. However, it was not found to be the most effective on a weight for weight basis based on the total mass of colloid.

- Hydrous iron(II) oxide was again found to result in a good quality foam (when used for phosphate removal) and its incorporation into a mixed oxide gave that oxide a better quality foam.

- The high effectiveness of aluminium(III) oxide, the relative inexpense of iron(III) oxide (which can be used as a “filler”) and the foam stabilisation of iron(II) oxide indicate that a mixed oxide would provide the best choice for a substrate in adsorbing colloid flotation of phosphate – an identical conclusion to that made for sulphate.

- Phosphate adsorption, and consequently flotation, was found to be dependent on pH such that removal decreased as pH increased. This is almost certainly due to the increasingly less favourable electrostatics as pH is increased, and particularly due to the formation of a doubly charged species (HPO$_4^{2-}$) which carries too much charge for chemically specific adsorption to overcome.

- Continued adsorption onto negatively charged hydrous aluminium(III) oxide at pH values around 5 to 9 indicated chemically specific, probably inner sphere complexation of phosphate with surface sites. The evidence was less compelling, but also present, for hydrous iron(III) oxide.

- The isoelectric point of all colloids were lowered in the presence of phosphate adsorption indicative of chemical adsorption.

- Notwithstanding the above, the adsorption and electrokinetic data presented here is more consistent with an outer sphere complexation of phosphate with hydrous iron oxide surfaces than with inner sphere complexation. The reverse is true for the hydrous aluminum oxide surface.

- In all cases, adsorption and flotation appeared to correlate very strongly with each other. Again, this enables us to predict the future success of adsorbing colloid flotation, as a waste treatment or environmental scrubbing technique, on the basis of adsorption experiments. Phosphate adsorption experiments are commonly reported in literature whereas adsorbing colloid flotation has been rarely, if ever, reported.
7.3 Mercury

A number of important findings concerning the adsorption and flotation of mercury in the presence of high concentrations of chloride have been found and can be summarised as follows:

- Stable foams could not be formed from aluminium(III) or iron(III) on their own.
- Iron(II) was not extensively trialled since it should only be used to give foam stability and is problematic in terms of oxidation, more toxic that the other metal ions, and too expensive to be economically viable to use as the sole collector.
- Very stable foams were readily obtained from mixed hydrous oxides of iron(III) and aluminium(III). These foams were stable with both the model and industrial waste mercury samples and iron(II) was not necessary to produce a good foam.
- A white precipitate was observed to form at low pH and assumed to be due to the insolubility of dodecanoic acid. The colour of this precipitate, its particle count and its particle size changed in the presence of mercury(II) and it was assumed that mercury – surfactant complexes can form under the conditions of adsorption experiments.
- Flotation experiments correlated to adsorption experiments in the absence of surfactant and not to adsorption experiments in the presence of surfactant. This appears to indicate that mercury-surfactant complexes are less important in flotation experiments, probably because (a) the induction time is shorter, so the precipitate has less time in which to form, and (b) the foam competes for surfactant lessening the interaction with mercury.
- The addition of iron(II) sometimes caused excessive precipitation with the mercury/surfactant system. Since it was also established that iron(II) was not needed for foam stability, iron(II) was not used for the flotation of mercury(II).
- Extensive studies to determine the best ratio of iron(III) to aluminium(III) to obtain the best foam were not carried out, however a 50:50 mix of equal mass appeared to work well and was therefore chosen.
- Adsorption of mercury(II), in the absence of surfactant, appeared to mimic that of typical aqueous heavy metal cations and not that of anionic species such as SO$_4^{2-}$ or PO$_4^{3-}$.
- Flotation of mercury(II) correlated to its adsorption in the absence of surfactant.
• Both adsorption (no surfactant) and flotation were pH dependent, showing less removal at low pH values and high strong removal at high pH values.

• The affect of chloride, on both adsorption (no surfactant) and flotation appeared to simply inhibit removal, presumably because chloride complexes with mercury stopping the mercury from hydrolysing. It is fairly well established that hydrolysis and heavy metal adsorption are linked.

• No advantage could be seen, under the conditions of flotation in this chapter, to increasing the total surfactant concentration beyond 300 ppm, except perhaps for the “Cell Hosedown” industrial effluent which contained very high levels of mercury.

• A number of industrial effluents containing variable quantities of mercury(II), chloride content and pH were successfully floated using adsorbing colloid flotation in the total carry-over mode.

• The industrial effluents which were not successfully floated where characterised by either a very high chloride content, a very low pH, or a very high mercury(II) content. The very high chloride content could easily be accounted for by mile dilution, and the technique was seen to work under conditions of high, just not very high, chloride content.

• These results lead to the recommendation of adsorbing colloid flotation for the treatment of low concentration mercury waste (i.e. scrubbing technology) provided that waste is not at a very low pH.

• The final waste product from industries such as the chloro-alkali Hg plant is highly suited to adsorbing colloid flotation.

7.4 Overall Conclusions

Notwithstanding the above conclusions, the following generalised, brief, conclusions can be made from the basis of all the data presented in this thesis.

• Adsorbing colloid flotation was found to be very suitable as a remediation tool for the anionic wastes sulphate and phosphate. Both were found to be removed at pH values between approximately 5 and 9 and these are commonly found pH values for these wastes in industry and in the environment.
• Adsorbing colloid flotation of mercuric chloride (HgCl$_4^{2-}$) was not successful, however Hg(II) could still be satisfactorily removed at relatively high pH values, due to its hydrolysis properties. Mercury(II) wastes in very high chloride concentrations, or at low pH could not be satisfactorily treated however it was argued that these problems are easily overcome. A simple wash could lower the chloride concentration to a suitable value for mercury removal and most mercury wastes were already present at high pH.

• One of the surfactants of choice, dodecanoic acid, was only sparingly soluble at low pH and was observed to form a white precipitate. This dissolved readily at higher pH values and did not interfere with flotation of the sulphate or the phosphate at any pH. In the presence of mercury(II), however this precipitate became discoloured, changed particles size and inhibited flotation of the mercury. The origin and nature of the precipitate under these conditions was assumed to be a mercury surfactant salt, however further experimentation is needed to characterise it fully.

• Adsorption of mercury onto hydrous metal oxides in the presence of surfactant did not correlate well with adsorbing colloid flotation, however this was attributed to the different conditions in the two processes. During flotation, the system does not have as much time to come to equilibrium and slow forming species (such as the mercury surfactant complex?) would not have time to form. Furthermore, surfactant is attracted to, and forms, the foam and so less surfactant is available to interact directly with the mercury. For these reasons, adsorption of mercury in the absence of surfactant might be a more appropriate parameter to attempt to correlate with flotation.

• When adsorption experiments were carried out in the absence of surfactant, adsorption effectiveness and flotation effectiveness correlated very well for all three wastes. Mercury showed the poorest correlation, however it was still very good. Phosphate showed the best correlation and was remarkably good.

• The final conclusion is that adsorption profiles can lead to very good predictions of flotation efficiency. This is fortunate since there is voluminous literature data concerning adsorption, but not such copious data concerning flotation.
REFERENCES


Lazaridis, N.K., Jekel, M. and Zouboulis, A.I. (2003), “Removal of Cr(VI), Mo(VI), and V(V) Ions from Single Metal Aqueous Solutions by Sorption or Nanofiltration”, Separation Sci. and Technology, 38(10), 2201-2219 Suppl. S.


