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THE CATALYTIC OXIDATION OF MANGANESE IN  
WATER TREATMENT CLARIFICATION PROCESSES

BY

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Abstract

The Catalytic Oxidation of Manganese in Water  
Treatment Clarification Processes.

by

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The removal of dissolved manganese in water treatment floc blanket clarifiers has been studied. The removal mechanisms may be broadly classed as adsorption and oxidation. Adsorption of manganese (II) occurs rapidly and is completed in less than five minutes under conditions prevailing in a floc blanket clarifier. The extent of adsorption is determined by pH, iron and manganese concentrations. Manganese adsorption is relatively insensitive to the concentration of other cations and anions present in natural water, although large increases in ionic strength increase the adsorption ratio. As pH and manganese concentrations increase, there appears to be a transition from non specific to specific adsorption of manganese. Indeed specific adsorption would appear to be the precursor of oxidation of adsorbed manganese. Specifically adsorbed manganese is oxidised at the iron (III) oxide surface when solution pH approaches 8.5. The initial reaction product is presumed to be a manganese (III) oxide. The extent to which these removal processes contribute to manganese removal at plant scale will depend on the retention time of both liquid and solid components of flow within the clarifier, as well as clarifier pH. The retention time of solids in the floc blanket is considered to be particularly critical. If adsorbed manganese is discharged from the floc blanket at a higher rate than it is oxidised, then the contribution of oxidation to manganese removal will be insignificant.

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1. INTRODUCTION

## 1.1 Objections to Manganese and Iron in Water Supply.

Manganese and iron frequently occur in underground water that is to be treated for public supply. Both metals must be reduced to low concentration in order to avoid discolouration, astringent taste and deposition of oxides in pipes. Manganese is not as readily oxidised as iron and frequently remains in solution. When dissolved manganese is exposed to oxidising conditions e.g. in washing machines, it precipitates as dark coloured oxides. World Health Organisation limits<sup>1</sup> for manganese and iron in drinking water state that the highest desirable levels for manganese and iron are  $0.05 \text{ mg l}^{-1}$  and  $0.1 \text{ mg l}^{-1}$  respectively. Experience in the U.K.<sup>2</sup> has shown that, in order to avoid the above problems, the mean manganese and iron levels must be approximately half the limits suggested by the World Health Organisation. Water treatment works are, therefore, designed to produce water with mean manganese and iron levels of  $0.03 \text{ mg l}^{-1}$  and  $0.05 \text{ mg l}^{-1}$  respectively.

## 1.2 Sources of Manganese and Iron

These elements are derived from underground rocks and minerals. Rainwater percolating through soil into an aquifer is saturated with dissolved oxygen. The oxygen level is progressively reduced by bacterial action on organic matter present in the strata. Despite this oxygen demand, aerobic conditions normally prevail in the groundwater, unless a relatively impermeable layer, such as clay, isolates the groundwater from percolating aerobic water. Under aerobic conditions the solubility of manganese and iron species is limited by the solubility of manganese (IV) and iron (III) oxides. These oxides<sup>3</sup> are practically insoluble at near neutral pH. Thus in an aerobic aquifer, concentrations of dissolved manganese and iron are usually extremely low. When an aquifer is overlaid by an impermeable strata, anaerobic conditions may develop, because the aquifer is isolated from percolating aerobic water. This situation occurs in the Ashdown Beds, which are overlaid throughout large areas of Kent and Sussex by Wadhurst Clay. Water in such aquifers is also characterised by high carbon dioxide levels, derived from intense

bacterial activity in the clay strata. Hydrogen sulphide, arising from the action of sulphate reducing bacteria, may also be present. Thus manganese and iron bearing rocks and minerals are exposed to a reducing environment. Under such conditions manganese (II) and iron (II) hydroxide, carbonate, hydrogen carbonate and sulphide species are appreciably soluble. Typical analyses of groundwater containing manganese and iron are given in Table 1. It is noteworthy that the reducing nature of the aquifer increases with the distance from the area of rainwater percolation. Thus the St. Leonards borehole, which is close to exposed Ashdown Beds where rainwater freely percolates, has lower manganese and iron levels than Goudhurst borehole, which is overlaid to a radius of five miles by Wadhurst Clay.

Table 1.

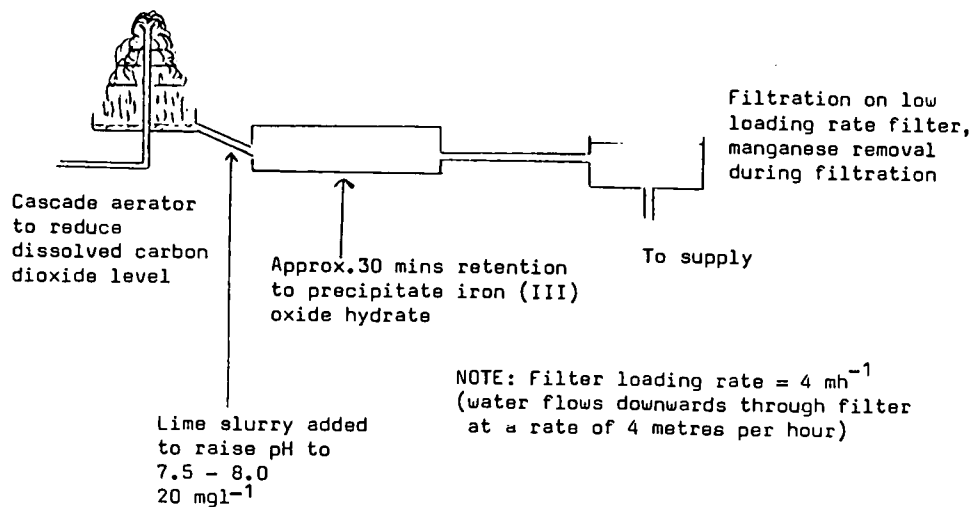
Site	pH	Hardness mg <sup>-1</sup> CaCO <sub>3</sub>	Alkalinity to methyl orange mg <sup>-1</sup> CaCO <sub>3</sub>	Conductivity μScm <sup>-1</sup>	Total Fe mg <sup>-1</sup>	Total Mn mg <sup>-1</sup>	Free CO <sub>2</sub> mg <sup>-1</sup>
St. Leonards, Sussex.	6.6	187	123	610	2.8	1.6	70
Goudhurst, Kent.	6.3	136	80	400	10.5	2.2	110

### 1.3 Water Treatment Works Design

Three typical water treatment plants are shown in the following block diagrams.

- (a) Site. Powdermill Pumping Station, Near Battle, East Sussex.

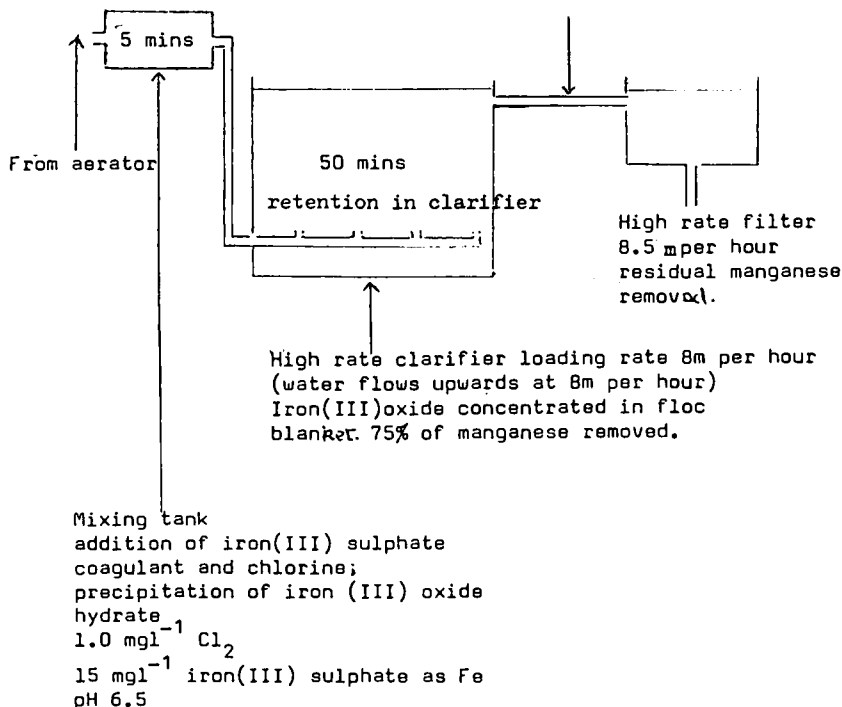
Description. Raw water from boreholes in Ashdown Beds, relatively low manganese and iron  
Treatment by aeration and filtration.  
Manganese 0.5 mg<sup>-1</sup> Iron 4.0 mg<sup>-1</sup>



In this works, manganese is removed during filtration, iron is oxidised and precipitated in the retention tank. Diagram 1 shows a typical sand filter.

(b) Site. Filsham Pumping Station, St. Leonards-on-Sea, East Sussex.

Description. Raw water from several boreholes in Ashdown Beds, relatively low manganese and iron. Treatment by aeration, sedimentation and filtration. Mean manganese  $0.9 \text{ mg l}^{-1}$ , mean iron  $3.0 \text{ mg l}^{-1}$ . Sodium Hydroxide added to raise pH to 8.0

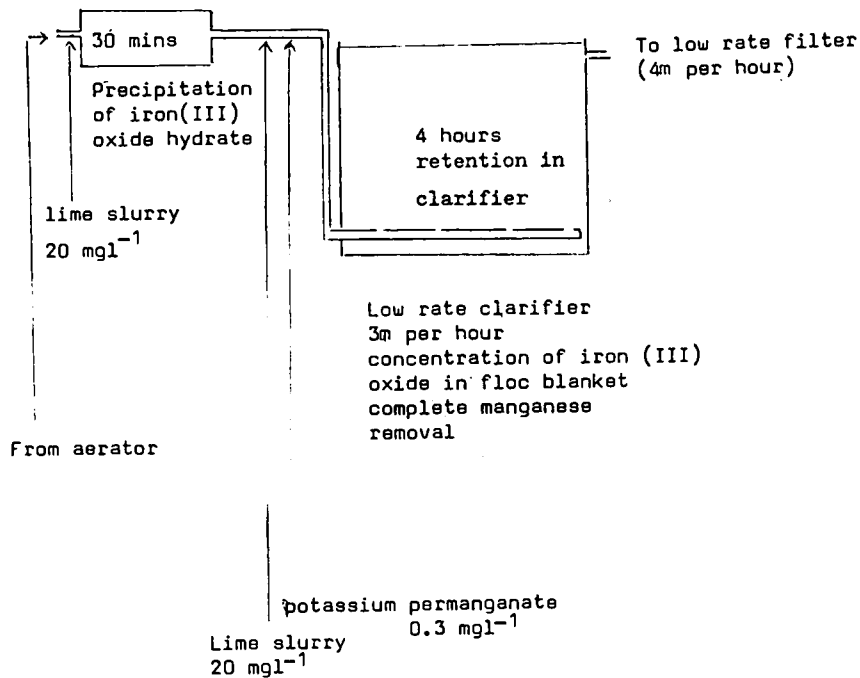




This is a modern plant with high loading rates in the clarifiers and filters. Manganese is oxidised by chlorine. In this works manganese removal is carried out wholly or partly in the floc blanket clarifier (sedimentation tank) and any residual manganese is removed during filtration. Diagram 2 shows a typical floc blanket clarifier.

(c) Site. Goudhurst Pumping Station, Kent.

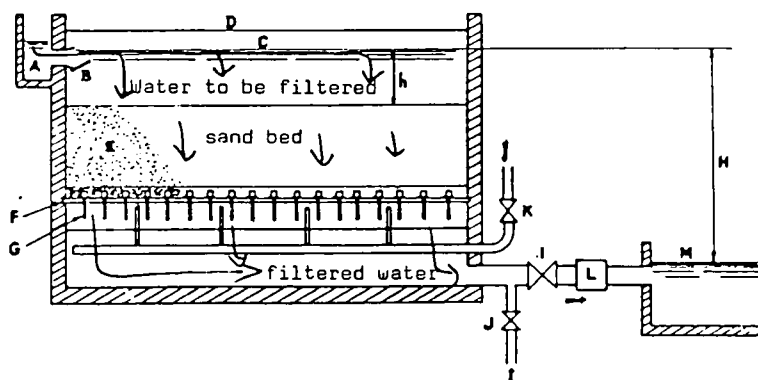
Description. Raw water from boreholes in Ashdown Beds, high manganese and iron. Treatment by aeration, sedimentation and filtration. Manganese  $2.5 \text{ mg l}^{-1}$  Iron  $11.0 \text{ mg l}^{-1}$



Lime slurry is added in two stages before and after pumping. This avoid scale formation in the pump. Manganese is completely removed in floc blanket.

Ion exchange has also been applied to the removal of manganese but this procedure has not been used in the U.K.

DIAGRAM 1  
**THE "AQUAZUR" FILTER**



CHARACTERISTICS OF AN AQUAZUR FILTER

- |  |  |
|--|--|
| <p>A - Raw water inlet channel<br/>         B - Raw water inlet clack-valve<br/>         C - Water level during filtration<br/>         D - Sludge weir<br/>         E - Filter bed<br/>         F - Filter floor<br/>         G - Nozzles</p> | <p>I - Filtered water outlet valve<br/>         J - Wash-water inlet valve<br/>         K - Scour air inlet valve<br/>         L - Regulator<br/>         M - Water level in the filtered water siphon discharge tank<br/>         N - Head, approx. 2 metres (about 7 ft)<br/>         h - Head of water height during filtration, 0.35 to 0.5 metre (14 to 20 in).</p> |
|--|--|

● General characteristics of the AQUAZUR filter.

The AQUAZUR filter consists of a rectangular concrete tank with a filter floor into which are screwed a large number of plastic nozzles provided with very fine slots; these are covered to a depth of 31 1/2" to 39 3/8" (0.80 m to 1 m) (30 to 40 in) with a mass of homogeneous sand having an effective grain size of 0.9 mm (0.035").

During filtration the height of the water above the sand is from 0.35 to 0.50 m (14 to 20 in).

On the outside of each lateral wall of the filter there is a discharge channel for carrying off the wash-water which overflows into it.

The raw water is admitted onto the filter through an automatic clack valve and the filtered water is discharged through a pipe system beneath the floor. This pipe system is connected to the wash-water supply and to the regulation device to which the clogging (head-loss) indicator is also connected.

The header pipe for the scour air is also located beneath the floor.

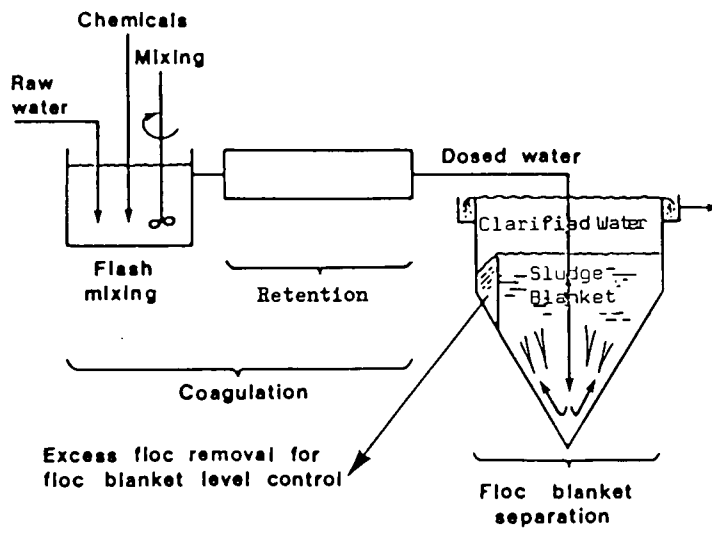
It will thus be seen that the filter has only three operating valves:

- A filtered water outlet valve,
- A wash-water inlet valve,
- A scour air inlet valve.

During washing, the water level on the filter rises as high as the sludge discharge channel and this rise in level results in the closing of the raw water inlet clack valve. At this moment the height of the water above the sand is low, some 0.50 to 0.70 m (about 20 to 28 in) only, and this enables the sludge to be evacuated very quickly with considerable saving in the consumption of wash-water.

Further, this shallow depth makes it possible to reduce the total height of the filter and thus the cost of building it.

DIAGRAM 2  
FLOC BLANKET CLARIFIER



## 1.4 Design Aspects

Waterworks construction is carried out on an extremely competitive basis. The area of greatest cost sensitivity lies in the civil engineering work where cost is proportional to size. Modern developments in waterworks technology seek to minimise cost by increasing the ratio of flow to unit size, i.e. increasing the loading rate of units. The loading rate in clarifiers is restricted by the need to maintain a stable floc blanket and research has been directed towards improving blanket stability. The loading rate in filters is limited by the concentration of suspended solids in raw water and the need to achieve a given specification for filtrate quality. Research has sought to increase the solids holding capacity of the filter by experimenting with different particle size sand and alternative filter media. The development of sand filters has almost certainly reached a plateau. Unless filtrate quality standards are relaxed, it is unlikely that filters will be designed with loading rates higher than those presently available. Recent developments have concentrated on optimising the combinations of air scour and backwash rate necessary to clean the filter. It should be noted that for a given raw water, filter loading rate does not much affect filtrate quality<sup>4</sup>. As loading rate increases from 5 - 10  $\text{mh}^{-1}$  the filtrate quality remains stable but the frequency of backwashing increases. Thus filter loading rate is largely a compromise between a high loading rate, small filter, needing frequent backwashing, and a low loading rate, large filter, needing less frequent backwashing. The above remarks apply only to removal of suspended matter from water. They do not apply to use of a filter as a chemical reactor in the removal of manganese. In this case, filtrate quality depends on retention time in the reactor and is affected by loading rate. Traditional filters<sup>5</sup> have been designed with loading rates of 4 - 5  $\text{mh}^{-1}$  through 0.8m of sand. Modern high rate filters<sup>4</sup> are available to treat water through 0.8m of sand at 9  $\text{mh}^{-1}$ .

In direct contrast to filter design, floc blanket clarifiers are being continuously developed to allow higher loading rates. Traditional designs have used an upward flow rate of 1.3 - 4.3  $\text{mh}^{-1}$  through tanks giving 1 - 3 hours retention<sup>6</sup>. Designers have identified that floc blanket stability is critical and two schools

of thought have emerged. One has concentrated on minimising the disturbance of the floc blanket by designing the raw water inlet to avoid eddy currents<sup>7</sup>. The other has concentrated on carefully controlled mixing of the blanket to prevent the development of weak areas which encourage eddy currents<sup>8</sup>. Modern high rate clarifiers are available with upward flow rates of  $9\text{mh}^{-1}$  in tanks giving 30-minutes retention. The settling velocity of the floc imposes a theoretical limitation on upward flow rate. Under certain circumstances, this velocity may exceed  $20\text{mh}^{-1}$ . It is, therefore, likely that clarifiers with higher loading rates will become available in the future.

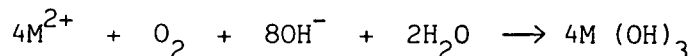
### 1.5 Restrictions imposed by need to remove Manganese and Iron

For iron removal, the restrictions are mainly physical. The kinetics of iron oxidation and flocculation are compatible with the highest rate plants available. The restriction during clarification is floc settling velocity. The restriction during filtration is the tendency for floc to block the filter or pass through under pressure. For manganese removal, the above remarks apply to low rate plants only. As loading rate increases, retention time in the unit may become less than the time required to achieve complete removal of manganese. A survey<sup>9</sup> of waterworks designed to remove manganese and iron, indicates that when manganese exceeds  $1\text{mgl}^{-1}$ , filtration at  $4\text{mh}^{-1}$  through 2m of sand has been used. This information suggests that removal of significant manganese levels may not be achieved on modern high rate filters.

If a waterworks is to secure the economic benefits of high rate filters, significant manganese oxidation must be achieved before filtration. Catalytic oxidation in clarifiers has been described by Bolas<sup>10</sup>. This work was carried out in a plant with a low loading rate of  $3\text{mh}^{-1}$  and only empirical conclusions were drawn concerning the kinetics of manganese removal. There is no quantitative information available concerning the removal of manganese in floc blanket clarifiers.

## 1.6 Chemical Reactions used in Manganese and Iron Removal

It is convenient to discuss manganese and iron removal together, as the same reactions are used. Both metals are removed from aqueous solution by oxidising the relatively soluble divalent species to high valency, insoluble hydrated oxides. The precipitates are separated by filtration or sedimentation. The most commonly used oxidising agent is dissolved oxygen. Oxygen is introduced into the anaerobic groundwater during the first stage of treatment, when the water is aerated to dispel carbon dioxide and reduce acidity. The reactions may be represented as:-



Where M = Fe or Mn

The rates of both reactions increase as the pH is raised. Iron oxidation proceeds rapidly above pH 7.5 while manganese oxidation is very slow below pH 9.0, unless a catalyst is present. It is desirable to supply water that is neither corrosive, nor possessing a tendency to deposit carbonate scale. For water derived from Ashdown Beds this condition exists at approximately pH 8.0, when the free carbon dioxide level is very low. It is, therefore, convenient to operate a water-works at pH 8.0, using a catalyst to ensure rapid oxidation of manganese. Oxidation of manganese at high pH values has been practised in the past and this has led to cementing of sand filter grains by calcite, precipitating from the unstable alkaline water. The physical characteristics of manganese and iron oxides are very important. After oxidation, oxides must rapidly precipitate and coagulate as heavy flocculant particles, which settle rapidly or are readily retained on sand filters. As the iron concentration normally greatly exceeds that of manganese, conditions favourable to iron flocculation must dominate the situation.

## 1.7 Optimum Conditions for Precipitation and Flocculation of Iron

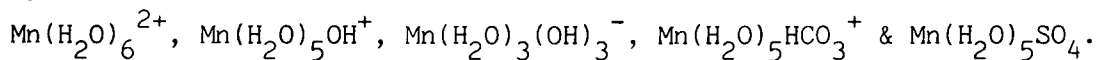
The oxidation of iron (II) in natural water has been studied by Stumm and Lee<sup>11</sup>. The results indicate that the rate is first order with respect to iron and oxygen and second order with respect to hydroxyl ions. Three different processes are involved in removal of dissolved iron from aqueous solution.

- (a) Oxidation of iron (II) to iron (III).
- (b) Change in degree of hydration of iron (III).
- (c) Precipitation and flocculation of the hydrated oxide.

The rate (a) increases 100 fold for each unit rise in pH and a pH of at least 7.5 is required to give a significant rate of oxidation in water treatment.<sup>11</sup> Empirical observations in water treatment and laboratory studies<sup>11,12</sup> have shown that (b) and (c) are fastest in the pH range 5 - 7. In water treatment practice, it is found that iron concentration, as well as pH, is a determining factor in (c). Below 5 mg l<sup>-1</sup> iron, the settling characteristics of flocs deteriorate. In this case it is normal practice to either dispense with the settling stage and filter the precipitate, or to add iron(III) salts as a coagulant to enhance flocculation. The choice between these alternatives is largely an economic consideration.

### 1.8 Oxidation of Manganese in Water

The inorganic chemistry of manganese and its oxides is well known; factors controlling occurrence and distribution in natural water are less clearly understood. Morgan<sup>13</sup> has published an informative paper summarising thermodynamic and solubility data and presenting results of laboratory experiments on the oxidation of manganese in water. Morgan considers that in natural water, solid phases controlling solubility include: Mn(OH)<sub>2</sub>, MnCO<sub>3</sub> and MnS. In the absence of oxidising agents, he presumes that the principle soluble species are:-



Thermodynamic data are summarised in Potential Diagrams, the most relevant to natural water being the Mn - O<sub>2</sub> - CO<sub>2</sub> - H<sub>2</sub>O system. This diagram shows that in oxygenated natural water, MnO<sub>2</sub> is the only stable oxide. It also indicates that various oxides may be metastable depending on solution pH.

Morgan describes investigations into the stoichiometry of manganese oxides. He confirms the findings of earlier workers, that oxidation by oxygen produces metastable, non-stoichiometric species. The measurement of oxygen uptake, using a Warburg manometer, shows a rapid uptake over 30-minutes, followed by a more gradual uptake over

ten hours. Experiments were carried out in the pH range 9 - 11 and results demonstrate that the final product depends on the hydroxide to manganese ratio. The product corresponds to hausmannite ( $Mn_3O_4$ ) for ratios close to unity. With 18 equivalents of hydroxide to 1 equivalent of manganese it corresponds to manganese (IV) oxide. These results appear to suggest that the degree of oxidation increases with increasing pH. Structures are confirmed by X-ray studies and show oxygen deficiency. Results of kinetics experiments are presented. Buffer solutions of varying pH were saturated with oxygen and manganese (II) perchlorate was added to give  $2 \times 10^{-4} M$  manganese (II). Portions of the solution were withdrawn at intervals for colorimetric analysis. No significant oxidation was observed below pH 8.6 but the rate rose rapidly with increasing pH. In carbonate media at pH 9, the reaction was found to be autocatalytic and heterogeneous, with pH, oxygen, temperature and alkalinity being the principle rate determinants. Morgan points out that in many experiments in carbonate ion containing media, the solution was supersaturated with respect to manganese (II) carbonate. He suggests that the manganese hydrogen carbonate ion pair solubility may be an important factor.

Morgan is co-author of a later paper<sup>14</sup> which presents results of further studies into the auto oxidation of manganese in aqueous solution. In the introduction, earlier work<sup>13,15</sup> is criticised for using experimental conditions involving supersaturation of manganese (II) carbonate or hydroxide. It is suggested that co-precipitation in these studies may have given rise to the wide range of reported stoichiometries for manganese oxides. In this study manganese (II) perchlorate is oxidised at pH 9 in oxygen saturated ammonia buffer solutions. The initial manganese concentration was  $5 \times 10^{-4} M$  and less than the theoretically predicted solubility. The stoichiometry of precipitated oxides was studied by determining the total manganese concentration and equivalent weight. It is concluded that the initial oxidation product is  $MnOOH$ . It is also demonstrated that if the oxide surface area is increased by abrasion, further oxidation takes place. From this observation it is concluded that the rate of oxide formation, relative to its rate of accretion, may be important. It is postulated that a mixture of oxides with manganese to oxygen ratio  $MnO_{1.5}$  arises when the oxide is precipitated and



removed from the oxygenated aqueous environment at the same rate. At low pH, when precipitation rate is low, the oxide is only slowly covered by further accretion and is exposed to oxygen for a longer period and oxidation to manganese (IV) oxide may occur. At high pH, the oxidation rate is so high that manganese (IV) oxide may be formed before precipitation occurs. It is suggested that compounds containing a manganese to oxygen ratio of less than  $MnO_{1.5}$  result from co-precipitation with manganese (II) hydroxide or carbonate. The literature cited so far refers to laboratory studies of batch experiments carried out at elevated pH in the absence of a catalyst. It should be noted, however, that Morgan identified the product of oxidation to be a catalytic species<sup>13</sup>.

The only quantitative study of manganese oxidation under conditions appropriate to waterworks operation, has been published by Graveland and Heertjes<sup>16</sup>. This paper presents results of the study of catalytic oxidation of manganese (II) species in a cylindrical tube packed with sand grains. The authors identify that the catalytic species in sand filters is a mixture of non-stoichiometric oxides of the hausmannite structure. They suggest that the oxygen deficiency in the crystal structure is the source of catalytic activity in promoting ionisation of oxygen adsorbed at the surface. It is demonstrated that hydrated iron (III) oxide also catalyses the reaction, but not as strongly as manganese oxides. Results of kinetics studies are presented which indicate that the reaction is first order with respect to manganese (II), hydroxide and hydrogen carbonate and zero order with respect to oxygen (above  $1 \text{ mg l}^{-1}$ ). The effect of other ions at concentrations normally encountered in natural water is reported to be insignificant. The authors also suggest that catalytic activity ceases if oxidation proceeds to manganese (IV) oxide and state that this occurs at oxygen concentrations larger than the equilibrium level in natural water. Data relevant to mass transfer are also presented and the influences of fluid velocity, sand grain diameter and transport velocities of ionic species are studied. The reaction is considered to occur at the surface of oxide precipitates, with manganese (II) in solution reacting with adsorbed oxygen. It is concluded that rate of oxidation is proportional to fluid velocity and inversely proportional to sand grain diameter. This paper provides a detailed explanation of the chemical and

physical factors affecting manganese oxidation. The chemical conditions relate closely to those prevalent in a sand filter treating natural water. Unfortunately, the physical conditions are not applicable to sand filter technology. The principal deviations being the use of recirculation conditions and flow rates much lower than those used in water treatment. The authors have carried out certain experiments in an apparatus which recirculates the water through the sand bed. This apparatus was preferred to the 'once through' flow system. The authors state that 'The main series of experiments have been performed with recirculation because in that case the concentration of some of the variables is more easily adjusted'. This approach tends to invalidate the application of data and derived equations to sand filters. For example, results in the recirculation apparatus indicate that the rate constant is proportional to the flow rate. In a waterworks sand filter, water passes once only through the filter and retention time in the reactor zone is inversely proportional to flow rate and rate constant. The low flow rates used also hinder the application of results to sand filters, e.g. experiments were carried out in the range  $0.05 - 0.4 \text{ cm sec}^{-1}$  ( $0.18 - 1.4 \text{ mh}^{-1}$ ) and the authors note that 'The bed has the characteristics of an ideal tube reactor and that the whole sand surface takes part in the process in the stationary state'. Sand filters are built to treat water at flow rates of  $4 - 9 \text{ mh}^{-1}$  and in this range of flows, matter carried in suspension affects reactions taking place at the sand surface. It is, therefore, incorrect to assume that the whole of the sand bed will function as an ideal reactor. When a filter is put into service all of the sand layer is available for reaction. As filtration proceeds, solids carried in suspension penetrate the bed, coating the sand and reducing the surface area available for reaction. This penetration of the bed eventually causes a reduction in flow rate and the filter is taken out of service and backwashed. The actual course of manganese removal is, therefore, considerably more complex than the simple model proposed by the authors.

Bolas<sup>10</sup> has described the use of potassium permanganate to catalyse manganese oxidation in floc blanket clarifiers. The paper describes the operational steps taken to maintain manganese removal in a plant receiving an increased concentration of manganese in raw water.

Very little scientific data is presented and the author's theories are based on supposition, rather than actual experiment. Nevertheless, the paper makes many useful empirical observations concerning the removal of manganese. A block diagram of Bolas' plant is shown in 1.3(c). Bolas describes the manganese removal regime before the manganese concentration in raw water is increased. With  $10 \text{ mg l}^{-1}$  iron and  $2 \text{ mg l}^{-1}$  manganese present,  $1.5 \text{ mg l}^{-1}$  manganese (II) were removed in the floc blanket and  $0.5 \text{ mg l}^{-1}$  manganese were removed in the sand filters. This situation was maintained at a flow of  $4250 \text{ m}^3/\text{day}$  corresponding to 3-hours retention in the clarifier. At the pH used (8.0) uncatalysed manganese oxidation by air is very slow and thus the oxidation must be catalysed in the floc blanket. He describes the result of using a new source with  $10 \text{ mg l}^{-1}$  iron and  $3 \text{ mg l}^{-1}$  manganese. Under these conditions,  $0.5 \text{ mg l}^{-1}$  manganese was still present after filtration. The author does not indicate the relative proportions now removed during clarification and filtration. He does, in fact, suggest that manganese is not being removed in the clarifier because the colour of the floc blanket changes from milk chocolate brown to ochre. The author then suggests that at low manganese levels, oxidation of manganese gives rise to an equilibrium level of manganese (IV) oxide (responsible for dark brown floc blanket). At high iron and manganese levels, he suggests that hydrated iron (III) oxide coats the manganese (IV) oxide preventing manganese oxidation and causing the colour change in the floc blanket. He then describes how manganese oxidation was re-established by adding potassium permanganate solution at  $0.3 \text{ mg l}^{-1}$  just before the clarifier. This point was chosen to ensure that all iron had been oxidised to the iron (III) state. Thus permanganate reacts with manganese (II) in alkaline solution. The author suggests that the reaction

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 4\text{OH}^- \longrightarrow 5\text{MnO}_2 + 2\text{H}_2\text{O}$$

produces manganese (IV) oxide which coats the outside of the iron(III) oxide hydrate and re-establishes manganese oxidation. Results are presented which indicate that manganese removal is now completed during clarification. The author also states that oxidation is maintained at  $5500 \text{ m}^3/\text{d}$  when retention time is reduced to  $2\frac{1}{2}$ -hours. In conclusion, very little scientific data is presented by Bolas and only the initial and final levels of iron and manganese are given. No data is presented to substantiate the author's suggestion of catalytic action, which are clearly at variance with other published information<sup>16</sup>.

Two particularly important points must be considered.

(i) Colour change of floc blanket

Bolas suggests that the change from dark brown to ochre indicates coating of manganese (IV) oxide catalyst by iron (III) oxide and suppression of catalytic action. Graveland and Heertjes<sup>16</sup> have demonstrated that iron (III) oxide acts as a catalyst. It is likely that the colour change, which implies a lower concentration of manganese(III) or (IV) oxide, was a result of reduction in the rate of oxidation. This may be due to a decreased residence time of catalytic species in the floc blanket. This arises from a higher rate of solids input from higher iron and manganese levels, with a consequent reduction in time of residence in the blanket.

(ii) Nature of catalytic oxides of Manganese

Graveland and Heertjes<sup>16</sup> assert that manganese (IV) oxide is not a catalyst and that permanganate acts purely as an oxidising agent. Bolas' results imply catalytic action with  $0.3 \text{ mg l}^{-1}$  permanganate apparently effecting removal of  $1.5 \text{ mg l}^{-1}$  manganese.

## 1.9 Summary

The oxygen oxidation of manganese in water at elevated pH has been widely studied. Little work has been carried out on the removal of manganese under conditions prevailing in water treatment plant. Certain features of reaction studies at elevated pH may be related to water treatment practice e.g. the heterogeneous, autocatalytic nature of the oxidation reaction is recognised in the use of conditions that conserve the reaction product. The use of sand filters and floc blanket clarifiers may be likened to fixed bed and slurry phase chemical reactors. It is suspected that the relatively simple concept of manganese removal by oxidation may not completely describe the complex environment of a floc blanket clarifier.

#### 1.10 Aims of Work

To study conditions prevailing in floc blanket clarifiers and the associated chemical dosing plant, with the intention of identifying features that may affect the removal of manganese.

To isolate and study at laboratory scale such features, while ensuring that experimental conditions do not deviate significantly from plant scale processes.

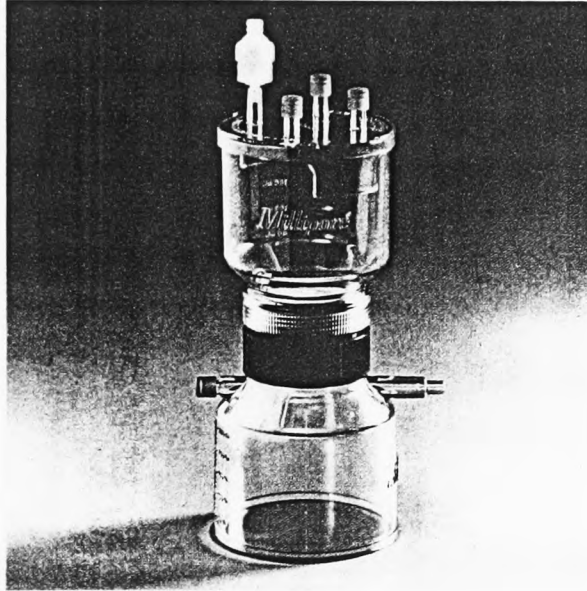
To attempt to apply experimental results to the design of clarifiers and determine the theoretical upper limit for manganese removal in modern high rate clarifiers.

### Separation of manganese (II),(III) and (IV) species

In the following experiments, soluble manganese (II) species are separated by filtration through a 0.45 micron cellulose acetate membrane filter. This procedure assumes that manganese (III) or (IV) species are insoluble under conditions prevailing in natural water and that only soluble manganese (II) species pass through the filter. Under aerobic conditions, at near neutral pH and in the absence of strong complexing agents, the only stable manganese (III) and (IV) species in natural water are oxides.<sup>13</sup> These oxides are known to have analytically undetectable solubility.<sup>3</sup> The validity of the latter assumption was tested by carrying out the o-tolidine test for manganese (III) and (IV)<sup>17</sup> on various filtrates. In all cases, the concentration of manganese (III) and (IV) species was less than the detection limit of  $0.001 \text{ mg l}^{-1}$ .

The filtration was carried out in a Millipore filtration assembly of polycarbonate construction (Diagram 3). The apparatus was cleaned before each experiment by soaking in 1M hydrochloric acid and rinsing with deionised water. 100 ml filtrates were stabilised immediately by adding 2 mls of 5M hydrochloric acid. In order to avoid repetition in description of experiments, the procedure referred to above is described as "filtration and stabilisation". Stabilised filtrates were stored in acid washed polythene bottles.

## 2. EXPERIMENTAL WORK



**Sterifil Aseptic System, 47mm**  
**Sterifil Holder, 47mm**

XX11 047 00  
 XX11 047 10

**Function** Vacuum filtering of liquids for analysis of particulate or biological contamination. The Sterifil Aseptic System is designed as a closed unit to protect the sample being filtered and the filtrate from environmental contamination. The Sterifil Holder base and funnel assembly are available separately (without the receiver flask and flask cover) for use with any standard 1-liter vacuum filtering flask. Autoclavable with filter in place.

**Materials** Polycarbonate funnel, funnel cover, receiver flask cover, polypropylene holder base and filter support screen, neoprene stopper, silicone O-ring.

**Filter size** 47 mm diameter.

**Filter Area** Approximately 13.8 cm<sup>2</sup>.

**Prefilter size** Type AP depth prefilter, 42 mm diameter; Type AW prefilter, 47 mm diameter

**Capacity** 250 ml (funnel and receiver flask).

**Pressures** Vacuum only.

**Connections** Perforated stopper on holder outlet mounts in standard 1-liter filtering flask or Millipore filtering manifolds (available separately). Two ports on receiver flask accept either 1/4" tubing or male Luer slip connection for vacuum and drain or vent. Four female Luer slip ports on funnel cover can be used for vent and aseptic inlet.

**Dimensions** Holder 76 mm (3") diameter x 127 mm (5") high; height 203 mm (8") with receiver flask.



## Experiment 1

### Preparation of manganese (II) carbonate solution. Determination of time to reach equilibrium solubility.

Apparatus: Grant cooled incubator  
Millipore membrane filtration assembly  
300 ml Winchester screw capped bottles  
E.I.L. Model 7030 pH meter and Bryans recorder

Reagents: Analar grade reagents and deionised water were used.  
Manganese (II) sulphate tetrahydrate 0.1M solution.  
2.231 g were dissolved in water and diluted to 100 mls in a graduated flask.  
Sodium carbonate anhydrous 1.0M solution. 10.6 g were dissolved in water and diluted to 100 mls in a graduated flask.

#### Procedure (i) preparation of manganese (II) carbonate

1.0M sodium carbonate solution (5.0 mls) was pipetted dropwise with stirring into 50 mls of 0.1M manganese sulphate solution in a 250 ml conical flask. The precipitate was allowed to settle and as much supernatant as possible was carefully decanted. The precipitate was washed by decantation with three 100 ml portions of deionised water. Three hours were allowed for settlement before each decantation. After decanting the final wash, the precipitate was transferred to a 10 ml graduated flask and diluted to the mark with deionised water. The flask was then stored at room temperature for three days.

#### (ii) determination of time to reach equilibrium solubility

The aged precipitate was mixed by inversion and 1 ml portions were pipetted into each of six 300 ml bottles. The bottles were completely filled with tap water, capped and immersed in an incubator at 25° C. After definite periods (1, 2, 18, 30, 48 and 72 hours) a bottle was removed and the pH of the suspension was determined. A 100 ml portion was filtered and stabilised, prior to analysis for soluble manganese. As each bottle was removed, it and the remaining bottles were mixed by inversion. It should be noted that during pH measurement, the solution,

was stirred gently with the pH probe, to minimise loss or gain of carbon dioxide. pH equilibrium was taken as <0.02 units drift per minute. A chart recorder was used to facilitate observation of equilibrium.

Manganese was determined in the filtrates by atomic absorption spectroscopy on a Perkin Elmer Model 360 instrument. Measurements were made at the 279.5 nm resonance line using standard manganese solutions in the linear range 0 - 3 mg l<sup>-1</sup>, using conditions prescribed in the Perkin Elmer analytical methods book<sup>18</sup>. The instrument was calibrated to allow direct readout in concentration. Blank determinations were found to be unnecessary for manganese and all other metals determined by atomic absorption spectroscopy in following experiments i.e. the level of metals in reagents and water used for dilution was less than the detection limit.

Results

See Figure 1.

Time (hours)	1	2	18	30	48	72
pH	7.59	7.70	7.78	7.67	7.67	7.60
Soluble Mn(II) mg l <sup>-1</sup>	4.43	4.73	5.13	4.90	5.00	4.85

Observations

Equilibrium solubility is reached after 24-hours. Measurement of pH does not appear to give a reliable indication of the attainment of equilibrium.

## Experiment 2

### Determination of the solubility of manganese (II) carbonate in tapwater at 25°C.

Apparatus: Reagents as in Experiment 1.

Procedure: A manganese (II) carbonate suspension was prepared by the procedure given in Experiment 1. A series of 400 ml portions of tapwater were placed in glass beakers and the pH was adjusted to cover the range 5 to 9 by addition of 0.1M sodium hydroxide or 0.1M hydrochloric acid. Each solution was used to fill a 300 ml bottle, containing 1 ml of the manganese (II) carbonate suspension.

The bottles were immersed in an incubator at 25°C and mixed by inversion after definite periods (14, 18, 24, 38, 44 and 48 hours). After forty-eight hours, the pH of the suspension was measured, adopting the precautions noted in Experiment 1. A 100 ml portion was filtered and stabilised prior to determination of soluble manganese using the procedure described in Experiment 1. Free carbon dioxide and alkalinity to methyl orange were also determined on some samples. Alkalinity was titrated with 0.025 M sulphuric acid<sup>19</sup>. (1 ml = 1 mg CaCO<sub>3</sub>). Free carbon dioxide was titrated to phenolphthalein using 0.022 M sodium carbonate<sup>19</sup>, freshly prepared in boiled deionised water (1 ml = 1 mg CO<sub>2</sub>).

### Results

Initial pH	Final pH	Soluble Manganese mg l <sup>-1</sup>	Alkalinity to Methyl Orange mg l <sup>-1</sup> CaCO <sub>3</sub>	Free Carbon Dioxide mg l <sup>-1</sup> CO <sub>2</sub>
5.00	6.72	31.31	57.5	-
6.00	7.00	17.85	61.6	-
6.90	7.40	9.84	40.0	14.5
7.00	7.59	5.17	63.6	-
7.20	7.60	5.20	51.0	6.5
8.00	8.08	0.99	66.7	-
8.00	8.05	2.04	56.0	2.0

Solubility vs pH has been plotted in Figure 2.

Observations

It should be noted that the composition of the tapwater changed during this experiment. This accounts for the apparent discrepancy in the relationship between alkalinity and pH.

Experiment 2 (Repeat)

Determination of the solubility of manganese (II) carbonate in tapwater at 25°C.

Experiment 2 was repeated with a freshly prepared suspension of manganese (II) carbonate, using initial pH of 8.00, 8.50 and 9.00

<u>Results</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>Dissolved manganese (II)</u> <u>mg l<sup>-1</sup></u>
	8.00	7.80	3.30
	8.50	8.20	1.65
	9.00	8.70	0.58

This data has been inserted in Figure 2.

### Experiment 3

#### Preparation and analysis of pure manganese (II) carbonate. Determination of solubility of the specimen in water.

Apparatus: As in Experiment 1.

Reagents: Analar grade reagents and deionised water were used.  
Manganese (II) sulphate tetrahydrate.  
Sodium hydrogen carbonate.  
Nitric acid 0.1 M solution. A CVS ampoule was opened and diluted to the mark in a 500 ml graduated flask (Grade A) at 20°C.  
B.D.H. "4.5" indicator.

Procedure: Manganese (II) sulphate tetrahydrate (11 g) was dissolved in 500 mls deionised water. Sodium hydrogen carbonate (8.49g) was dissolved in 100 mls deionised water and added to the former solution, dropwise with stirring. The precipitate was allowed to settle over night and then washed by decantation with three 500 ml portions of deionised water. The precipitate was then transferred to a 50 ml graduated flask and diluted to the mark with deionised water. The suspension prepared above (25 mls) was allowed to settle. The supernatant was decanted as completely as possible. The precipitate was then washed by decantation with three 50 ml portions of acetone. After the final decantation, the slurry was transferred to a watch glass and dried at 40°C for one hour in an oven. Accurately weighed portions of the dry carbonate were placed in a 250 ml conical flask and suspended in 50 mls of deionised water. The suspension was brought to incipient boiling on a Bunsen burner and 5 drops of indicator were added. A trial titration was carried out to determine the approximate end point by slowly adding acid to the boiling solution until the indicator changed from blue to grey. Accurate titrations were then performed by adding 95% of the trial volume and boiling gently for 5 minutes to expel carbon dioxide. The remaining acid was then added dropwise until a permanent grey colour was obtained. A blank titration was made on 50 mls deionised water plus 5 drops of indicator. As a comparison, a specimen of Hopkin & Williams manganese (II) carbonate was also analysed.

Results ( i ) analysis

	Weight (mg)	Titre (mls)	MnCO <sub>3</sub> %
Prepared manganese (II)carbonate	1 73.9	12.10	94.07
	2 69.0	11.45	95.33
Hopkin & Williams manganese(II) carbonate	1 100.9	11.55	65.76
	2 104.9	12.40	67.91

Blank 0.05 mls 1 ml 0.1M Nitric Acid = 5.475 mg MnCO<sub>3</sub>

Mean % MnCO<sub>3</sub> in prepared specimen = 94.70

Mean % MnCO<sub>3</sub> in commercial specimen = 66.84

(ii) solubility - determined as in Experiment 2.

<u>Initial pH</u>	<u>Final pH</u>	<u>Soluble manganese (II)</u>
7.00	7.30	7.74
5.00	6.62	25.83

These points have been inserted in Figure 2.

Observations

The prepared specimen was off white while the commercial specimen was dark brown. It was necessary to grind the latter in a mortar and pestle in order to achieve sufficiently rapid reaction with the acid. The preparation procedure, referred to by Partington<sup>20</sup> was altered by omitting the passage of carbon dioxide through the solution. It was found that passage of carbon dioxide prevented precipitation of the carbonate. Examination of Figure 2 indicates that the specimen prepared by the above procedure shows similar solubility to the specimens prepared in Experiment 2.

#### Experiment 4

#### Determination of stability of theoretically supersaturated manganese (II) solutions.

Apparatus: Millipore membrane filtration assembly  
100 ml clear glass peg stoppered bottles  
E.I.L. Model 7030 pH meter

#### Procedure:

Saturated manganese (II) carbonate solutions, prepared in Experiment 3 were filtered through an 0.45 micron membrane filter. The pH of these solutions was adjusted to 9.00 with 0.01 M sodium hydroxide. The solutions were used to completely fill 100 ml glass bottles, which were then stoppered so as to exclude air bubbles. The bottles were stored at ambient temperature in daylight and examined periodically for evidence of precipitation. The examination was carried out by holding the bottle to a beam of light in a darkened room and noting any turbidity. After precipitation, the pH of the sample was determined. A portion was filtered and stabilised, prior to determination of soluble manganese, using the procedure described in Experiment 1.

#### Results:

Approx. initial dissolved manganese(II) mg l <sup>-1</sup>	Period before onset of precipitation hours	pH after precipitation	Dissolved manganese (II) mg l <sup>-1</sup>
3.5	72	8.60	2.50
7.7	40	8.78	0.20
26	10	8.10	16.88

The theoretically predicted solubility at pH 9.0 has been calculated in Appendix 1 and found to be 0.142 mg l<sup>-1</sup> Mn. This data has been plotted as log(initial dissolved manganese(II) x theoretically predicted solubility<sup>-1</sup>) vs log period before onset of precipitation in Figure 3.



## Experiment 5

Sampling and analysis at Powdermill Reservoir, Sedlescombe with reference to the solubility of manganese (II) species.

Apparatus: Cassella sampler (see Diagram 4)  
Orion portable pH meter  
Millipore membrane filtration assembly  
Thermometer - mercury in glass 0 - 50°C  
100 ml glass bottles with peg stoppers  
200 ml acid cleaned polythene bottles

Reagents: Analar grade reagents and deionised water were used.  
Manganese (II) sulphate solution. 50 g  $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$  were dissolved in water and diluted to the mark in a 100 ml graduated flask.

Alkaline iodide solution. 400 g sodium hydroxide and 900 g sodium iodide were dissolved in 600 mls water. The solution was cooled and diluted to one litre in a graduated flask.

Sodium azide solution 2.5% solution of  $\text{NaN}_3$ .

Alkaline iodide-azide solution. A 1 litre volume of alkaline iodide was mixed with 300 mls sodium azide solution.

Hydrochloric acid 5M.

All solutions were carried in bottles filled with dropping pipettes.

Procedure: Samples were taken from a boat moored in the deepest part of the reservoir at TQ 8000,1935. Starting from 10 cm below the surface, samples were taken at approximately 1 m intervals until the bottom had been reached at 9 m. Depth was measured by reference to 1 m marks on the Cassella sampler's rope. The bottom sample corresponded to the inlet level of the sampler i.e. 30 cm above the reservoir bed. As soon as the sampler had been raised to the surface, the temperature of the sample was measured with a thermometer and the pH, if required, was measured using the portable pH meter. The inner glass bottle was then removed and 1 ml portions of manganese (II) sulphate solutions and alkaline iodide azide solutions were added, in

that order to the bottles. The stoppers were then inserted, taking care not to trap air bubbles. The bottles were mixed by inversion and after 15 minutes settling were mixed again. These bottles were later taken to the laboratory for Winkler determination<sup>19</sup> of dissolved oxygen. Portions of sample taken at the surface, mid-depth and bottom, were stabilised for determination of iron and manganese. The sample for total metals was stabilised by adding 2 mls of 5M hydrochloric acid to 100 mls of unfiltered sample in a plastic bottle. The sample for dissolved metals was stabilised after filtration. Samples for other analyses were transported to the laboratory in Winchester glass bottles, for analysis on the same day. Manganese was determined by the procedure described in Experiment 1. Iron was also determined by atomic absorption spectroscopy at the 248.5 nm resonance line. Iron standards were prepared in the linear calibration range 0 - 5 mg l<sup>-1</sup>, with the instrument scale calibrated to allow direct readout in concentration. Conditions prescribed in the Perkin Elmer analytical methods book<sup>18</sup> were used. Alkalinity was determined by the procedure described in Experiment 2. Total hardness was determined by titration with 0.01 M E.D.T.A.<sup>19</sup> (1 ml = 1 mg CaCO<sub>3</sub>) using Solochrome Black indicator. Dissolved oxygen was determined by titrating the iodine liberated when the fixed samples were acidified with 2 mls concentrated sulphuric acid<sup>19</sup>. The liberated iodine was titrated with 0.0125M sodium thiosulphate (1 ml = 1 mg O<sub>2</sub>)<sup>19</sup> using starch indicator. Conductivity was determined by using a Hach conductivity meter. Dissolved organic carbon was determined after filtration through a Whatman GF/C glass fibre circle, which had been previously ashed for one hour at 450°C. A Phase Separations Ltd. TOCSIN mark 2b analyser was used for this determination. In this instrument inorganic carbonates are decomposed

by acidification and the liberated carbon dioxide is expelled from solution by purging with nitrogen. Organic carbon is then converted to methane and determined with a flame ionisation detector.

Results: See also Diagram 6.

Depth of Sample (m from surface)	Dissolved* Oxygen mg <sup>-1</sup> O	Temperature °C	Total Manganese mg <sup>-1</sup> Mn	Dissolved Manganese mg <sup>-1</sup> Mn	pH
0.1	9.8	18.5	0.14	0.032	7.3
1	9.4	18.0			
2	9.4	17.8			
3	8.8	17.8			
4	7.5	17.5			
5	4.8	17.4	0.35	0.28	
6	0.3	16.5			
7	0.2	14.0			
8.5	0.1	13.0	10.75	9.85	6.9

\*NOTE - Saturation level of dissolved oxygen at 18.5°C = 9.4mg<sup>-1</sup>  
(This information was obtained from Table<sup>19</sup>)

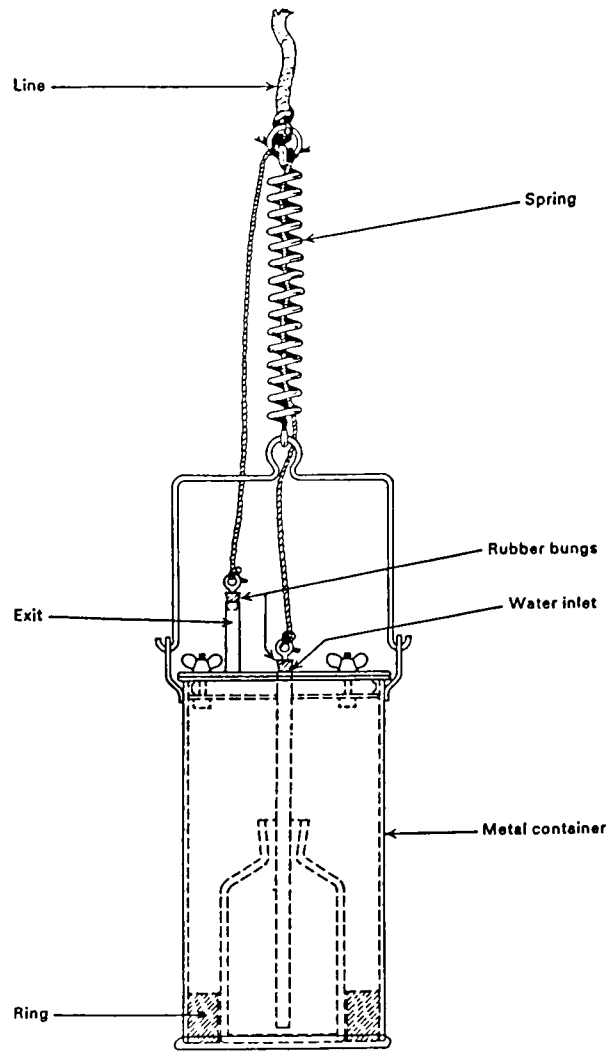
Depth of Sample (m from surface)	Total Iron mg <sup>-1</sup> Fe	Soluble Iron mg <sup>-1</sup> Fe	Total Hardness mg <sup>-1</sup> CaCO <sub>3</sub>	Alkalinity to Methyl Orange mg <sup>-1</sup> CaCO <sub>3</sub>	Conductivity S/cm	Dissolved organic carbon mg <sup>-1</sup> C
0.1	0.085	0.032	80	41	290	5.9
8.5	11.50	9.50	124	122	375	7.4

Observations:

The predicted soluble manganese level at pH 6.9 in the presence of 124 ml/l alkalinity as CaCO<sub>3</sub> (150 mg/l HCO<sub>3</sub><sup>-</sup>) was calculated by the procedure given in Appendix 1 and found to be 7.75 mg/l. This result and the observed solubility have been inserted in Figure 2.

Diagram 4.

Cassella Sampler



## Experiment 6

### Preparation of iron (III) and manganese (IV) oxides for adsorption experiments

Reagents: Analar grade reagents and deionised water were used.  
Potassium permanganate 0.1 M solution. 1.580 g were dissolved in water and diluted to 100 mls in graduated flask.  
Manganese (II) sulphate tetrahydrate 0.1 M solution (see Experiment 1)  
Iron (III) sulphate solution. E and A West's 'W' grade (Analysis is given below)

Apparatus: Magnetic stirrer  
15 l plastic bucket

#### Procedure: ( i) hydrated iron (III) oxide

Tap water (10 l) was placed in the bucket. (Analysis of tap water is given below). A stirrer was added and the water was stirred at low speed on a magnetic stirrer. Iron (III) sulphate solution ( 1 ml) was added by pipette and the solution was stirred for two hours. The stirrer was then turned off and the oxide suspension was allowed to settle overnight. At the end of this period, most of the supernatant was carefully decanted, leaving a concentrated suspension in approximately 100 mls. The suspension was transferred to a 250 ml graduated flask and diluted to the mark with tap water. A portion of 50 mls of the concentrated solution was reserved for determination of suspended solids, total iron and total manganese. Iron and manganese were determined by atomic absorption spectroscopy. Suspended solids were weighed after one hour's drying at 105°C following filtration through a tared Whatman GF/C glass fibre circle.<sup>19</sup>

#### (ii) hydrated manganese (IV) oxide

The procedure given above was followed with potassium permanganate (0.5 mls) and manganese (II) sulphate(0.75 mls) added to 10 l water instead of iron (III) sulphate.

#### Results: ( i) iron (III) oxide hydrate

Suspended solids dried at 105°C	=	1140 mg l <sup>-1</sup>
Total Iron	=	574 mg l <sup>-1</sup>
Total Manganese	=	< 0.30 mg l <sup>-1</sup>

(ii) manganese (IV) oxide hydrate

Suspended solids dried at 105°C	=	52 mg l <sup>-1</sup>
Total Iron	=	<0.50 mg l <sup>-1</sup>
Total Manganese	=	17.4 mg l <sup>-1</sup>

E. & A. West 62.5% W/V "Ferric Sulphate Solution"

Iron (III) Sulphate 62.5% W/V, Sulphuric Acid (free) 0.5% W/V

Nickel	410	mg l <sup>-1</sup>
Copper	0.2	mg l <sup>-1</sup>
Lead	0.4	mg l <sup>-1</sup>
Manganese	917	mg l <sup>-1</sup>
Zinc	430	mg l <sup>-1</sup>
Cadmium	41	mg l <sup>-1</sup>
Chromium	1.9	mg l <sup>-1</sup>
Cobalt	1.9	mg l <sup>-1</sup>
Titanium	620	mg l <sup>-1</sup>

Tap water used for adsorption and solubility experiments

Total Hardness	120	mg l <sup>-1</sup> CaCO <sub>3</sub>
Alkalinity to methyl orange	55	mg l <sup>-1</sup> CaCO <sub>3</sub> (0.001M as HCO <sub>3</sub> <sup>-</sup> )
Conductivity at 25°C	350	µScm <sup>-1</sup>
Calcium	65	mg l <sup>-1</sup> Ca (0.0016M)
Magnesium	5.5	mg l <sup>-1</sup> Mg (0.00023M)
Sodium	23	mg l <sup>-1</sup> Na (0.001M)
Potassium	3.4	mg l <sup>-1</sup> K (0.000087M)
Sulphate	56	mg l <sup>-1</sup> SO <sub>4</sub> <sup>2-</sup> (0.0058M)
Dissolved organic carbon	3.5	mg l <sup>-1</sup> C
Chloride	37	mg l <sup>-1</sup> Cl (0.001M)
Free carbon dioxide	10	mg l <sup>-1</sup> CO <sub>2</sub>
pH	7.20	
Dissolved solids dried @ 180°C	256	mg l <sup>-1</sup>

Approximate ionic strength 0.0064M (calculated using procedure proposed by Stumm and Morgan<sup>15</sup>)

## Experiment 7

### Determination of time to reach adsorption equilibrium

Apparatus: Grant cooled incubator.  
Millipore membrane filtration assembly.  
Top drive variable speed stirrer.  
E.I.L. Model 7030 pH meter.  
Fish Tank Aerator.  
E.I.L. Dissolved Oxygen Meter.

Reagents: Manganese (II) sulphate tetrahydrate 0.1M  
(See Experiment 1).

Procedure: ( i )  
Portions of the iron (III) and of manganese (IV) oxide suspensions (200 mls) prepared in Experiment 6 were cooled to 10°C and placed in 250 ml beakers, immersed in the incubator at 10°C. The oxides were maintained in suspension by gentle stirring and the pH was raised to 8.0 by dropwise addition of molar sodium hydroxide solution. Aliquots of 0.1M manganese (II) sulphate (1 ml) were added and the suspensions were stirred continuously for 30 minutes. During this period, the pH was readjusted as necessary to pH  $8.0 \pm 0.05$ . After definite periods (5, 15 and 30 minutes), 20 ml portions were filtered and stabilised. Manganese was determined by atomic absorption spectroscopy.

(ii)

This experiment was repeated using a sample of borehole water containing dissolved iron and manganese (analysis of water is given below). The water was first aerated until saturated with dissolved oxygen. Two 400 ml portions were placed in 500 ml beakers in the incubator and cooled to 10°C. The solutions were stirred continuously and their pH's were raised to 8.00 and 9.00 respectively with molar sodium hydroxide solution. Immediately and after definite periods (5, 15, 30, 60 and 120 minutes), samples were filtered and stabilised. The pH was not controlled during this experiment.

Results:

(i) iron (III) oxide hydrate		(i) manganese(IV) oxide hydrate	
Time (mins)	Dissolved manganese $\text{mgl}^{-1}$	Time (mins)	Dissolved manganese $\text{mgl}^{-1}$
5	5.02	5	10.56
15	5.08	15	10.71
30	5.00	30	10.71

(ii) borehole water			
Time (mins)	Total iron $\text{mg l}^{-1}$	Dissolved manganese $\text{mg l}^{-1}$	
		pH8.00	pH9.00
0	8.80	1.30	1.30
5		1.15	0.75
15		1.05	0.70
30		1.10	0.70
60		1.10	0.65
120		1.05	0.60

These results are displayed in Figure 4.

Observations:

In procedure (i) it was noted that approach to equilibrium was accompanied by a decrease in the amount of sodium hydroxide solution needed to maintain pH 8.00.

Borehole water used for adsorption equilibrium experiments

Total Hardness	90 $\text{mg l}^{-1}$	$\text{CaCO}_3$
Alkalinity to Methyl Orange	130 $\text{mg l}^{-1}$	$\text{CaCO}_3$
Conductivity at 25°C	480 $\mu\text{Scm}^{-1}$	
Calcium	35 $\text{mg l}^{-1}$	Ca
Magnesium	5.0 $\text{mg l}^{-1}$	Mg
Sodium	70 $\text{mg l}^{-1}$	Na
Potassium	2.0 $\text{mg l}^{-1}$	K
Sulphate	45 $\text{mg l}^{-1}$	$\text{SO}_4$
Chloride	45 $\text{mg l}^{-1}$	Cl
Free Carbon Dioxide	30 $\text{mg l}^{-1}$	$\text{CO}_2$
pH	6.90	



## Experiment 8

### Determination of adsorption isotherms for manganese (II) on iron(III) oxide hydrate and manganese (IV) oxide hydrate at 10°C

Reagents: Manganese (II) sulphate tetrahydrate 0.1M  
(See Experiment 1)

Apparatus: Grant cooled incubator.  
Millipore membrane filtration assembly.  
Top drive variable speed stirrer.  
E.I.L. Model 7030 pH meter.  
All glassware was washed in 0.1M HCL and deionised water.

Procedure: ( i ) Preparation of oxide suspensions

These were prepared using the procedure described in Experiment 6 , except that the concentrated suspensions were diluted in this case to 500 mls in graduated flasks and an aliquot (100 mls) was reserved for iron, manganese and suspended solids analyses. In order to investigate the significance of adsorption onto iron (III) oxide of other cations present in tap water, samples were filtered and stabilised (1) prior to addition of iron (III) sulphate and (2) after overnight settlement.

(ii) General procedure for adsorption experiments

The oxide suspensions (400 mls) were placed in 500 ml beakers and cooled to 10°C in the incubator. The suspensions were stirred continuously at slow speed and the pH was raised to the selected level by dropwise addition of molar sodium hydroxide solution. Appropriate incremental aliquots of 0.1M manganese (II) sulphate solution were added by pipette. After each increment the pH was readjusted as necessary to the selected pH level. Adsorption equilibrium was considered to have been reached when the solution pH had remained constant for five minutes ( $\pm 0.02$  pH). At this point 20 mls of solution were withdrawn in 5 ml and 15 ml pipettes. The 5 ml portions were used to flush the filtration assembly. The 15 ml portion was filtered and 10 mls were withdrawn by pipette and stabilised, by adding 0.2 mls of five molar hydrochloric acid.

The following specific variations were used at the selected pH levels:

pH 8.00 iron (III) oxide and manganese (IV) oxide.

Aliquots of 0.1M manganese (II) solution (0.20,0.40,0.60,1.00 and 2.00 mls) were added by pipette.

pH 8.50 iron (III) oxide.

Aliquots of 0.1M manganese (II) solution (0.50, 1.00, 1.50, 2.00 and 2.50 mls) were added by pipette. Suspensions were allowed to settle for 5 minutes after equilibrium pH had been reached. The 20 ml sample was withdrawn from the clear supernatant.

pH 8.50 manganese (IV) oxide.

Aliquots of 0.1M manganese (II) solution (0.25, 0.50, 0.75, 1.00 and 1.25 mls) were added by pipette.

pH 9.00 iron (III) oxide.

Aliquots of 0.1M manganese (II) solution ( 1.00, 2.00, 3.00, 4.00 and 5.00 mls) were added by pipette. The suspensions were settled prior to sampling, as described above. The suspension was reserved for use in Experiment 10, procedure (3).

pH 9.0 manganese (IV) oxide.

Aliquots of 0.1M manganese (II) solution (0.50, 1.00, 1.50, 2.00 and 2.50 mls) were added by pipette.

A blank determination was carried out on 400 mls of tap water at pH 9.00. This solution was placed in the apparatus and 5 mls of 0.1M manganese (II) were added. Samples were filtered and stabilised (1) immediately after mixing and (2) after stirring for 30 minutes. Iron and manganese were determined by previously described AAS procedures. Calcium, magnesium, sodium and potassium were all determined by atomic absorption spectroscopy using the following conditions:-

	<u>Resonance Line</u>	<u>Calibration range(linear)</u>
Calcium*	422.5 nm	0 - 5 mg $l^{-1}$
Magnesium*	285.4 nm	0 - 0.5 mg $l^{-1}$
Sodium	589.0 nm	0 - 2 mg $l^{-1}$
Potassium	765.5 nm	0 - 1 mg $l^{-1}$

\* In order to eliminate interference from sulphates, standards and samples were diluted with lanthanum chloride solution to give 0.25% La in the final dilution.

<u>Results:</u>	<u>pH 8.00 iron (III) oxide suspension</u>	
	Suspended solids dried at 105°C	= 620 mg $l^{-1}$
	Total Iron	= 344 mg $l^{-1}$
	Total Manganese	= 0.19 mg $l^{-1}$
	<u>manganese (IV) oxide suspension</u>	
	Suspended solids dried at 105°C	= 10 mg $l^{-1}$
	Total Manganese	= 6.0 mg $l^{-1}$

Oxide	Manganese II added	Manganese II in solution at equilibrium	Total Volume
	mls 0.1M Mn(II)	mg l <sup>-1</sup> Mn	mls
iron (III) oxide	0.20	0.31	400.2
"	0.40	0.76	380.4
"	0.60	1.41	360.6
"	1.00	2.81	341.0
"	2.00	10.71	322.0
manganese(IV)oxide	0.20	1.43	400.2
"	0.40	3.57	380.4
"	0.60	6.12	360.6
"	1.00	12.24	341.0
"	2.00	28.57	322.0

	Suspended Solids dried at 105°C mg l <sup>-1</sup>	Total Iron mg l <sup>-1</sup>	Total Manganese mg l <sup>-1</sup>
pH 8.50			
iron(III)oxide suspension	572	313	-
manganese(IV)oxide suspension	-	-	17.1

Oxide	Manganese II added	Manganese (II) in solution at equilibrium	Total Volume
	mls 0.1M Mn (II)	mg l <sup>-1</sup>	mls
iron (III) oxide	0.50	0.92	400.5
"	1.00	2.41	381.0
"	1.50	4.25	361.5
"	2.00	6.23	342.0
"	2.50	9.63	322.5
manganese(IV)oxide	0.25	0.40	400.25
"	0.50	1.59	380.5
"	0.75	3.67	360.75
"	1.00	6.12	341.0
"	1.25	8.87	321.25

	Suspended Solids dried at 105°C	Total Iron	Total Manganese
<u>pH 9.00</u>	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l <sup>-1</sup>
iron(III)oxide suspension	522	285	-
manganese(IV) oxide suspension	15	-	5.81

Oxide	Manganese II added mls 0.1M Mn (II)	Manganese II in solution at equilibrium mg l <sup>-1</sup>	Total Volume mls
iron (III) oxide	1.00	0.86	401
"	2.00	2.33	382
"	3.00	3.98	363
"	4.00*	5.20	344
"	5.00*	6.12	325
manganese(IV)oxide	0.50*	1.01	400.5
"	1.00*	2.66	381
"	1.50*	3.98	361.5

\* After adding each increment, it was not possible to maintain a constant pH of 9.00. A downward drift in pH was observed. This was attributed to oxidation of manganese (II) and hydrolysis of the oxidised species with release of protons. Samples were filtered and stabilised exactly 15 minutes after adding the increment of manganese (II) solution. The pH was continuously readjusted to  $9.0 \pm 0.02$  during this period.

<u>Blank</u>	<u>Sample</u>	<u>Dissolved Manganese(II)</u> mg l <sup>-1</sup>
	(1) 5 mls 0.1M manganese(II) in 400 mls 0.1M hydrochloric acid	68.0
	(2) 5 mls 0.1M manganese(II) in 400 mls tap water, immediately after mixing.	70.0
	(3) As (2) but 30 minutes later.	68.4

Adsorption of other cations

	Dissolved				
	pH	Ca <sub>-1</sub> mg l <sup>-1</sup>	Mg <sub>-1</sub> mg l <sup>-1</sup>	Na <sub>-1</sub> mg l <sup>-1</sup>	K <sub>-1</sub> mg l <sup>-1</sup>
Water before addition of iron (III) sulphate	7.20	36.0	5.2	18.0	2.9
Water after precipitation of iron (III) oxide	5.50	38.0	5.4	18.0	2.9

Calculations - iron (III) oxide

pH	Weight of oxide* mg Fe	Total Mn(II)* mg Mn	Soluble Mn(II) mg Mn	Adsorbed Mn(II) mg Mn
8.0	137.5	1.10	0.12	0.98
8.0	130.6	2.15	0.29	1.86
8.0	123.8	3.14	0.51	2.63
8.0	116.9	5.17	0.96	4.21
8.0	110.0	10.37	3.43	6.94
8.5	125	2.75	0.37	2.38
8.5	125	5.48	0.92	4.56
8.5	125	8.18	1.54	6.64
8.5	125	10.85	2.13	8.72
8.5	125	13.48	3.11	10.37
9.0	114	5.50	0.34	5.16
9.0	114	10.98	0.89	10.09
9.0	114	16.43	1.44	14.99
9.0	114	21.85	1.79	20.06
9.0	114	27.25	1.99	25.26

Calculations - manganese (IV) oxide

pH	Weight of oxide* mg Mn	Total Mn(II)* mg Mn	Soluble Mn(II) mg Mn	Adsorbed Mn(II) mg Mn
8.0	2.40	1.10	0.57	0.53
8.0	2.28	2.15	1.36	0.79
8.0	2.16	3.13	2.20	0.93
8.0	2.04	5.16	4.16	1.00
8.0	1.92	10.36	9.14	1.22
8.5	6.84	1.38	0.16	1.22
8.5	6.51	2.69	0.61	2.08
8.5	6.17	3.92	1.32	2.60
8.5	5.83	5.08	2.09	2.99
8.5	5.49	6.16	2.85	3.31
9.0	6.85	2.75	0.40	2.35
9.0	6.52	5.36	1.01	4.35
9.0	6.18	7.83	1.44	6.39

\* corrected for loss in sampling.

This data for adsorption on iron (III) oxide has been plotted as the Langmuir<sup>21</sup> equation at constant pH:-

$$\bar{\Gamma}_A = \Gamma_{A_{Max}} / (K_1 + C_{equil}) \quad \text{- Equation (1)}$$

where  $\bar{\Gamma}_A$  = Adsorption per unit mass of oxide (adsorption ratio)

$\Gamma_{A_{Max}}$  = maximum " " " " " "

$C_{equil}$  = equilibrium concentration of dissolved manganese(II)

$K_1$  = adsorption coefficient

This equation has been rearranged to give:

$$\bar{\Gamma}_A^{-1} = K_1 \Gamma_{A_{Max}}^{-1} + C_{equil} \Gamma_{A_{Max}}^{-1} \quad \text{- Equation (2)}$$

See Figure 5.

iron (III) oxide

pH	C equil mg Mn	$\Gamma_A$		C equil mg Mn	$\Gamma_A^{-1}$
		mg Mn	Mg Fe <sup>-1</sup>		
8.0	0.12	0.0071		16.9	
8.0	0.29	0.014		20.7	
8.0	0.51	0.021		24.3	
8.0	0.96	0.036		26.7	
8.0	3.43	0.063		54.4	
8.5	0.37	0.019		19.5	
8.5	0.92	0.036		25.5	
8.5	1.54	0.053		29.1	
8.5	2.13	0.070		30.4	
8.5	3.11	0.083		37.5	
9.0	0.34	0.045		7.6	
9.0	0.89	0.088		10.1	
9.0	1.44	0.13		11.1	
9.0	1.79	0.18		9.9	
9.0	1.99	0.22		9.0	

This data has been plotted in Figure 5.

The results have also been plotted according to the following trial equations at constant pH:

$$\Gamma_A = K_1 C_{\text{equil}} \quad \text{- Equation (3)}$$

and  $\Gamma_A = K_2 \text{Mn}_{\text{tot}} \quad \text{- Equation (4)}$

where  $\text{Mn}_{\text{tot}} = \text{total manganese (adsorbed + dissolved)}$

$K_1, K_2$  constants

iron (III) oxide

pH	$\int A$ mg Mn mg Fe <sup>-1</sup>	C equil mg Mn	Mn <sub>tot</sub> mg Mn
8.0	0.0071	0.12	1.10
8.0	0.014	0.29	2.15
8.0	0.021	0.51	3.13
8.0	0.036	0.96	5.16
8.0	0.063	3.43	10.36
8.5	0.019	0.37	2.75
8.5	0.036	0.92	5.48
8.5	0.053	1.54	8.18
8.5	0.070	2.13	10.85
8.5	0.083	3.11	13.48
9.0	0.045	0.34	5.50
9.0	0.088	0.89	10.98
9.0	0.130	1.44	16.43
9.0	0.180	1.79	21.85
9.0	0.220	1.99	27.25

This data is plotted in Figures 6 and 7.

manganese (IV) oxide

pH	$\int A$ mg Mn mg Mn <sup>-1</sup>	Mn <sub>tot</sub> mg Mn	C equil mg Mn	C equil $\int A^{-1}$ mg Mn
8.0	0.22	1.10	0.57	2.59
8.0	0.35	2.15	1.36	3.89
8.0	0.43	3.13	2.20	5.12
8.0	0.49	5.16	4.16	8.49
8.0	0.64	10.36	9.14	14.28
8.5	0.18	1.38	0.16	0.89
8.5	0.32	2.69	0.61	1.85
8.5	0.42	3.92	1.32	3.14
8.5	0.51	5.08	2.09	4.09
8.5	0.60	6.16	2.85	4.75
9.0	0.34	2.75	0.40	1.18
9.0	0.67	5.36	1.01	1.51
9.0	1.03	7.83	1.44	1.39

This data is plotted according to equations (2), (3) and (4) in Figures 8, 9 and 10.



The data has also been plotted according to the trial equation:

$$\Gamma A = K_3 \text{Mn}_{\text{tot}} + K_4 \text{Mn}_{\text{tot}} \Gamma A \quad - \text{Equation (5)}$$

where  $K_3$  and  $K_4$  are constants

This equation may be rearranged to give:

$$\frac{1}{\text{Mn}_{\text{tot}}} = \frac{K_1}{\Gamma A} + K_2 \quad - \text{Equation (6)}$$

manganese (IV) oxide

pH	$\frac{1}{\text{Mn}_{\text{tot}}}$ mg Mn <sup>-1</sup>	$\frac{1}{\Gamma A}$ mg Mn mg Mn <sup>-1</sup>
8.0	0.91	4.55
8.0	0.47	2.86
8.0	0.32	2.32
8.0	0.19	2.04
8.0	0.096	1.56
8.5	0.72	5.56
8.5	0.37	3.13
8.5	0.26	2.38
8.5	0.20	1.96
8.5	0.16	1.67
9.0	0.36	2.94
9.0	0.19	1.49
9.0	0.13	0.97

This data is plotted in Figure 11.

Observations:

During measurement of isotherms on iron (III) oxide at pH 8.50 and 9.00 it was noted that the colour of the oxide changed from dark orange to brown. This is attributed to oxidation of adsorbed manganese (II) at the oxide surface. The iron (III) oxide colour remained dark orange during measurement of the isotherm at pH 8.00.

Experiment 8 Repeat

This experiment was repeated using different batches of oxides, prepared according to experiment 6. The following variation was made in the procedure for manganese (IV) oxide in certain experiments carried out at pH 8.50:

Incremental volumes of 0.1M manganese (II) sulphate were not added to the same oxide suspensions but five identical 11 suspensions were prepared from a stock suspension and the 5 different volumes of manganese (II) solution were added to separate 11 portions of oxide suspensions.

Results:                      Iron (III) oxide suspensions

Total iron = 574 mg l<sup>-1</sup> Fe

200 mls were diluted to 400 mls for all experiments, excepting \* when 100 mls were used.

pH	Manganese (II) added mls 0.1M Mn (II)	Manganese (II) dissolved at equilibrium mg l <sup>-1</sup> Mn
8.0	1.0	3.52
8.0	2.0	8.72
8.5	1.0	3.83
8.5	2.0	6.89
9.0 *	0.5	0.58
9.0	2.5	2.14
9.0	5.0	4.13

Calculations - Iron (III) oxide suspensions

pH	Wt. of oxide mg Fe	Total manganese mg Mn	Dissolved manganese mg Mn	Adsorbed manganese mg Mn	Adsorption ratio $\frac{\Gamma_R}{R}$ mg Mn mg Fe <sup>-1</sup>
8.0	114.8	5.50	1.41	4.09	0.036
8.0	109.1	10.73	3.31	7.42	0.068
8.5	114.8	5.50	1.53	3.97	0.035
8.5	109.1	10.73	2.62	8.11	0.074
9.0	114.8	13.75	0.86	12.89	0.11
9.0	109.1	26.81	1.57	25.24	0.23
9.0	57.4	2.75	0.23	2.52	0.04

Because of variable losses of oxides via decantation, during preparation, it was not possible to reproduce exactly the oxide : sorbate ratios used in experiment 9. Therefore to facilitate comparison between different batches of oxides, equation 4 was rearranged to correct for different ratios of adsorbent to sorbate viz:

$$\Gamma_A = K_2 \text{ Mn tot x Fe oxide}^{-1} \quad - \text{Equation (7)}$$

where Fe oxide = total iron in iron (III) oxide

All data for iron (III) oxide is tabulated below and has been plotted in Figure 12.

pH	Mntot Fe oxide <sup>-1</sup> x 100	$\Gamma_A$	
8.0	0.8	0.0071	
8.0	1.7	0.014	
8.0	2.5	0.021	
8.0	4.4	0.036	
8.0	9.4	0.063	
8.0	4.8	0.036	Repeat Batch
8.0	9.8	0.068	
8.5	2.2	0.019	
8.5	4.4	0.036	
8.5	6.5	0.053	
8.5	8.7	0.070	
8.5	10.8	0.083	
8.5	4.8	0.035	Repeat Batch
8.5	9.8	0.074	
9.0	4.8	0.045	
9.0	9.6	0.088	
9.0	14.5	0.13	
9.0	19.2	0.18	
9.0	23.0	0.22	
9.0	11.9	0.11	Repeat Batch
9.0	24.4	0.23	
9.0	4.8	0.044	

Results - Manganese (IV) oxide suspensions

pH	Manganese(IV)oxide suspension total Mn mg l <sup>-1</sup> Mn	Manganese(II)added mg l <sup>-1</sup> Mn	Manganese(II)dissolved at equilibrium mg l <sup>-1</sup> Mn	Total Volume mls
8.0	4.13	19.77	17.10	10,000
8.0	4.34	14.10	11.73	380
8.5	4.34	14.10	10.20	380
8.5	6.90	1.38	0.31	1,000
8.5	6.90	2.75	0.92	1,000
8.5	6.90	4.13	1.68	1,000
8.5	6.90	5.50	2.57	1,000
8.5	6.90	6.90	3.52	1,000

Calculations - Manganese (IV) oxide suspensions

For reasons given, equation 5 has been adjusted to allow for variation in the adsorbent : sorbate ratio :

$$\Gamma_A = K_3 \text{Mn}_{\text{oxide}} \text{Mn}_{\text{tot}}^{-1} + K_4 \text{Mn}_{\text{oxide}} \text{Mn}_{\text{tot}}^{-1} \Gamma_A \quad \text{- Equation (8)}$$

which may be rearranged to give:

$$\text{Mn}_{\text{oxide}} \text{Mn}_{\text{tot}}^{-1} = K_3 \Gamma_A^{-1} + K_4 \quad \text{- Equation (9)}$$

All data for adsorption on manganese (IV) oxide is tabulated below and has been plotted in Figure 13.

pH	$\text{Mn}_{\text{oxide}} \text{Mn}_{\text{tot}}^{-1}$ mg Mn mg Mn <sup>-1</sup>	$\Gamma_A^{-1}$ mg Mn mg Mn <sup>-1</sup>
8.0	2.20	4.55
8.0	1.10	2.86
8.0	0.69	2.32
8.0	0.40	2.04
8.0	0.19	1.56
8.0	0.31	1.82
8.0	0.21	1.54
8.5	4.96	5.56
8.5	2.42	3.13
8.5	1.57	2.38
8.5	1.15	1.96
8.5	0.89	1.67
8.5	0.31	1.12
8.5	5.00	5.88
8.5	2.51	3.45
8.5	1.67	2.56
8.5	1.25	2.13
8.5	1.00	1.85

Repeat Batch

Repeat Batch

## Experiment 9

Adsorption of manganese (II) on iron (III) oxide hydrate, precipitated in situ at pH 8.50 and 10°C.

Apparatus: As in Experiment 8.

Reagents: Manganese (II) sulphate tetrahydrate 0.1M  
(see Experiment 1)  
Iron (II) sulphate heptahydrate solution. 0.745 g of the Analar salt were dissolved in 50 mls deionised water containing 2 mls 5M hydrochloric acid. The solution was diluted to the mark in a 100 ml graduated flask. (1 ml = 1.50 mg Fe).

### Procedure:

Five 1l portions of tap water were placed into five 1.25l plastic beakers with magnetic stirrer bars. The beakers were placed on magnetic stirrers and stirred continuously at slow speed. Portions of the iron (II) solution (10ml) were added by pipette to each beaker. Aliquots of 0.1M manganese (II) solution (0.1, 0.2, 0.3, 0.4 and 0.5 mls) were added to separate beakers by pipette. The pH of each solution was raised by dropwise addition of 0.1M sodium hydroxide to  $8.5 \pm 0.02$ . The solutions were stirred for fifteen minutes and the pH was continuously readjusted to  $8.5 \pm 0.02$  during this period. Samples from each beaker were then filtered and stabilised. This experiment was repeated with two different batches of tap water containing 0.10, 0.15, 0.2, 0.3 and 0.5 mls of 0.1M manganese (II) solution.

The experiment was repeated with a fourth batch of water in which iron (III) oxide was precipitated before the manganese (II) solution was added. Aliquots of iron (II) solution (8.2 mls) were added to 4 beakers containing 1l tap water. The pH was raised to  $8.5 \pm 0.02$  by dropwise addition of 0.1M sodium hydroxide and the precipitated iron (III) oxide was stirred continuously during 24-hours. At the end of this period aliquots of 0.1M manganese (II) solution (0.1, 0.2, 0.3 and 0.4 mls) were added and the solutions were stirred for 30-minutes. The pH was continuously readjusted to  $8.5 \pm 0.02$  during this period. Samples from each beaker were then filtered and stabilised. Dissolved manganese (II) was determined in each sample by atomic absorption spectroscopy, using the procedure described in Experiment 1.

Results:

	Volume of 0.1Mn(II) mls	Dissolved Mn(II) mg l <sup>-1</sup>
Batch 1	0.10	0.28
	0.20	0.73
	0.30	1.13
	0.40	1.59
	0.50	2.02
Batch 2	0.10	0.28
	0.15	0.40
	0.20	0.61
	0.30	0.77
	0.50	1.81
Batch 3	0.10	0.24
	0.20	0.66
	0.50	1.87
Batch 4	0.10	0.46
	0.20	0.83
	0.30	1.16
	0.40	1.53

Calculations:

	Mass of Iron (III) oxide mg Fe	Total manganese mg	Dissolved manganese mg	Adsorbed manganese mg	Adsorption ratio mgMn mgFe <sup>-1</sup>
B1	15.0	0.55	0.28	0.27	0.018
	15.0	1.10	0.74	0.36	0.024
	15.0	1.65	1.14	0.51	0.034
	15.0	2.20	1.61	0.59	0.039
	15.0	2.75	2.04	0.71	0.047
B2	15.0	0.55	0.28	0.27	0.018
	15.0	0.83	0.40	0.43	0.029
	15.0	1.10	0.63	0.47	0.031
	15.0	1.65	0.78	0.87	0.058
	15.0	2.75	1.84	0.91	0.061
B3	15.0	0.55	0.25	0.30	0.020
	15.0	1.10	0.67	0.43	0.029
	15.0	2.75	1.91	0.84	0.056
B4	12.3	0.55	0.46	0.09	0.0073
	12.3	1.10	0.83	0.27	0.022
	12.3	1.65	1.16	0.49	0.040
	12.3	2.20	1.53	0.66	0.054

B = Batch

These results are displayed in Figure 14. A straight line has been fitted to Batch 1 - 3 using regression analysis.<sup>22</sup>

For an equation of the form  $Y = a + bX$ , the Y on X regression line is described:

$$\sum Y = na + b \sum X \quad (i)$$

$$\sum XY = a \sum X + b \sum X^2 \quad (ii)$$

and the X on Y regression line is described by:

$$\sum X = na + b \sum Y \quad (i)$$

$$\sum XY = a \sum Y + b \sum Y^2 \quad (ii)$$

where a = intercept on X or Y axis

Y = adsorption ratio

b = slope of graph

X = manganese added

n = number of pairs X, Y

Y	X	XY	X <sup>2</sup>	Y <sup>2</sup>
0.018	0.55	0.0099	0.30	0.00032
0.024	1.10	0.026	1.21	0.00058
0.034	1.65	0.056	2.72	0.0012
0.039	2.20	0.086	4.84	0.0015
0.047	2.75	0.129	7.56	0.0022
0.018	0.55	0.0099	0.30	0.00032
0.029	0.83	0.024	0.69	0.00084
0.031	1.10	0.034	1.21	0.00096
0.058	1.65	0.096	2.72	0.0034
0.061	2.75	0.168	7.56	0.0037
0.020	0.55	0.011	0.30	0.00040
0.029	1.10	0.032	1.21	0.00084
0.056	2.75	0.154	7.56	0.0031

$$\Sigma Y = 0.464 \quad \Sigma X = 19.53 \quad \Sigma XY = 0.836 \quad \Sigma X^2 = 38.18 \quad \Sigma Y^2 = 0.0194$$

substitution in equations for regression of Y on X gives:

$$0.464 = 13a + 19.53b \quad (i) \quad \text{multiply } \times \frac{19.53}{13}$$

$$0.836 = 19.53a + 38.18b \quad (ii)$$

$$0.70 = 19.53a + 29.34b \quad (i)$$

subtract (i) from (ii)

$$0.136 = 8.84b$$

$$b = 0.0154$$

$$a = 0.013$$

substitution in equations for regression of X on Y gives:

$$19.53 = 13a + 0.464b \quad (i) \quad \text{multiply } \frac{0.464}{13}$$

$$0.836 = 9.464a + 0.0194b \quad (ii)$$

$$0.70 = 0.464a + 0.0166b \quad (i) \quad \text{subtract (i) from (ii)}$$

$$0.136 = 0.0028b$$

$$b = 48.6$$

$$a = -0.23$$

Correlation coefficient =  $\sqrt{b_{X \text{ on } Y} \times b_{Y \text{ on } X}} = 0.87$  i.e. good correlation

The straight line described by  $Y = 0.0154X + 0.013$  has been inserted in Figure 14.



The data from Batch 4 has also been plotted as

$\Gamma_A$  vs total manganese x iron in oxide<sup>-1</sup> in Figure 12.

<u>Mn tot oxide Fe<sup>-1</sup></u> <u>mgMn mgFe<sup>-1</sup></u>	<u><math>\Gamma_A</math></u> <u>mgMn Fe<sup>-1</sup></u>
0.045	0.0073
0.089	0.022
0.134	0.040
0.179	0.054

\*Assuming both variables to be normally distributed, the 95 per cent critical point for a sample size 13 is approximately 0.5.

## Experiment 10

Determination of the desorption of manganese (II) from iron (III) and manganese (IV) oxide hydrates on lowering pH. Determination of the effect of temperature on adsorption equilibrium.

Apparatus and Reagents: As in Experiment 8.

### Procedure:

#### ( i) Iron (III) oxide, qualitative test, initial pH 8.00

An hydrated iron (III) oxide suspension was prepared, using the procedure described in Experiment 6. The suspension (200 mls) was placed in a 500 ml glass beaker and diluted to 400 mls with tap water. Manganese (II) sulphate (0.5 ml of 0.1M) was added and the pH of the suspension was raised to  $8.00 \pm 0.02$  by dropwise addition of M sodium hydroxide. The solution was stirred slowly and maintained at pH 8.00 for thirty minutes. At the end of this period, the stirrer was turned off and the suspension was allowed to settle until a clear supernatant was obtained. 10 mls of supernatant were then withdrawn, placed in a plastic bottle and stabilised by addition of 0.2 mls of 5M hydrochloric acid. The pH was then lowered in successive 1.00 decrements to approximately 7.00, 6.00, 5.00, 4.00 and 3.00 by dropwise addition of either 0.1M or 5M hydrochloric acid. After each decrement the suspension was stirred for thirty minutes and the pH was maintained at a constant level. At the end of each thirty minute period, the suspension was settled and sampled as described above.

#### (ii) Iron (III) oxide quantitative test, initial pH 8.00

The procedure described in (i) was carried out in the cooled incubator at 10°C with the following variations: Manganese (II) solution (2 mls) was added initially. After each 30 minute period of stirring, the suspension was not settled but instead aliquots (5 mls and 15 mls) were withdrawn by pipette. The membrane filtration assembly was rinsed with 5 mls solution and 15 mls were then filtered. An aliquot of the filtrate (10 mls) was stabilised by adding 0.2 mls of 5 M hydrochloric acid.

After the last pH decrement, the pH was raised to 7.00 and the suspension was stirred for 30 minutes. At the end of this period, a sample was filtered and stabilised. The temperature of the incubator was then raised in successive 5°C increments to 15°, 20° and 24°C. After each increment, the suspension was stirred for 30 minutes and then sampled as above.

(iii) Ircn (III) oxide quantitative test, initial pH 9.00

The suspension reserved in Experiment 8 was acidified to pH 4.00 by dropwise addition of 5M hydrochloric acid. After stirring for thirty minutes, a portion was filtered and stabilised.

(iv) Manganese (IV) oxide quantitative test, initial pH 8.00

Potassium permanganate (0.5 mls of 0.1M) and manganese (II) sulphate (0.75 mls of 0.1M) were pipetted into 1 l tap water contained in a plastic beaker. The solution was stirred for 30 minutes and then allowed to stand overnight. Manganese (II) sulphate (1.00 mls of 0.1M) were added and the solution was stirred continuously. The pH was raised to 8.00 by dropwise addition of M sodium hydroxide solution. The suspension was maintained at this pH for 30 minutes and at the end of this period aliquots(5 + 15 mls)were filtered and stabilised. The pH was then lowered in successive 1.00 decrements by dropwise addition of 5 or 1 M hydrochloric acid to approximately pH 7.00, 6.00, 5.00, 4.00, 3.00 and 2.00. After each decrement, the pH was maintained constant during thirty minutes. At the end of this period, a portion was filtered and stabilised. The experiment was repeated but allowing one hour for desorption after each pH decrement. Iron and manganese were determined by the procedures described in Experiments 1 and 5.

Results: Procedure (i)

Suspended solids in iron (III) oxide floc = 1250 mg<sup>l</sup><sup>-1</sup>

Total Iron " " " " " = 662 mg<sup>l</sup><sup>-1</sup>

<u>pH</u>	<u>Dissolved manganese (II)</u> <u>mg<sup>l</sup><sup>-1</sup></u>
8.00	1.95
7.00	4.47
6.00	7.83
5.10	8.16
4.20	8.06
3.00	8.16

Procedure (ii)

Suspended solids in iron (III) oxide floc = 1100 mg $l^{-1}$

Total iron " " " " " = 520 mg $l^{-1}$

Initial mass of dissolved manganese(II) = 1.10 mg

pH	Dissolved manganese (II)
	mg $l^{-1}$
7.00	0.44
6.80	1.86
5.90	2.38
5.10	2.49
4.10	2.68

Temperature °C	Dissolved manganese (II)
	mg $l^{-1}$
10	2.06
15	2.04
20	1.95
25	1.86

Procedure (iii)

Suspended solids in iron (III) oxide floc = 522 mg $l^{-1}$

Total iron " " " " " = 285 mg $l^{-1}$

pH	Dissolved manganese (II)
	mg $l^{-1}$
9.00	6.12
4.00	60.44

Sample volume 325 mls.

Procedure (iv)

Initial concentration of manganese (IV) oxide =

6.90 mg $l^{-1}$  Mn (obtained by calculation)

Initial concentration of dissolved manganese (II) =

5.50 mg $l^{-1}$  Mn

pH		Total Volume mls		Dissolved Manganese mg $l^{-1}$	
1	2	1	2	1	2
8.00	8.00	1000	1000	3.60	3.67
7.00	6.70	980	980	4.05	4.05
6.20	6.10	960	960	4.28	4.28
5.10	5.00	940	940	4.36	4.28
3.80	4.00	920	920	4.82	4.82
3.00	3.00	900	900	4.74	4.97
2.10	2.10	880	880	5.36	5.89

1 = 30 minutes equilibration 2 = 60 minutes equilibration

Calculations:

Procedure (i)

The results of Procedure (1) indicate no further desorption below pH 4.00.

Procedure (ii)

Initial total manganese = 1.10 mg Mn

pH	Volume mls	Adsorbed Mn(II)** mg Mn	Dissolved Mn(II) mg Mn	Adsorbed Mn(II) as % of *
7.80	400	0.924 *	0.176	100
6.80	380	0.338	0.707	36.5
5.90	360	0.133	0.857	14.4
5.10	340	0.088	0.847	9.5
4.10	320	0.022	0.858	2.4

\*\* corrected for loss in sampling. \* Adsorbed manganese(II) at pH 7.80  
See Figure 15.

Procedure (iii)

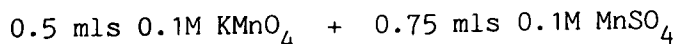
See also calculations Experiment 8 , iron (III) oxide pH 9.00

Mass of manganese (II) desorbed at pH 4.00 = (60.44 - 6.12)0.325  
= 17.65 mg

Therefore, % mass of manganese II adsorbed pH 4.00  
mass of manganese (II) adsorbed pH 9.00  
=  $\frac{(25.26 - 17.65)}{25.26} \times 100$   
= 30.1%

Procedure (iv)

The mass of manganese in precipitated manganese (IV) oxide that was derived from the initial dissolved manganese (II) is calculated from the stoichiometry of the reaction:



pH		Total Manganese(II)		Dissolved Manganese(II)		Adsorbed Manganese(II)		Manganese adsorbed as % of *	
1	2	1	2	1	1	1	2	1	2
8.0	8.0	5.50	5.50	3.60	3.67	1.90*	1.83*	100	100
7.0	6.7	5.39	5.39	3.97	3.97	1.42	1.42	74.7	77.6
6.2	6.1	5.28	5.28	4.11	4.11	1.17	1.17	61.5	63.9
5.1	5.0	5.17	5.17	4.19	4.02	0.98	1.15	51.5	62.8
3.8	4.0	5.06	5.06	4.43	4.43	0.63	0.63	33.2	34.4
3.0	3.0	4.95	4.95	4.27	4.47	0.68	0.48	35.8	26.2
2.1	2.1	4.84	4.84	4.72	5.18	0.12	-0.34	6.3	-18.6

1 = 30 minutes equilibration 2 = 60 minutes equilibration

\* Adsorbed manganese (II) at pH 8.00.

This data is displayed in Figure 15.

#### Effect of Temperature

Volume mls.	Temp. °C	Total Mn(II) mg Mn	Dissolved Mn(II) mg Mn	Adsorbed Mn(II) mg Mn
320	10	0.0880	0.659	0.221
300	15	0.825	0.612	0.213
280	20	0.770	0.546	0.224
260	25	0.715	0.484	0.231

## Experiment 11

### Effect of calcium and magnesium concentration and variation in ionic strength on the adsorption of manganese (II) on iron (III) oxide hydrate.

Apparatus: As in Experiment 8.

Reagents: Manganese (II) sulphate tetrahydrate 0.1M

(See Experiment 1)

0.63% solutions of iron (III) sulphate were prepared by diluting 1 ml of E. & A. West W grade "ferric sulphate" (See Experiment 6) (i) to 100 mls with deionised water in a graduated flask, (ii) to 100 mls with 10 mls concentrated sulphuric acid and deionised water in a graduated flask.

Procedure: Samples of tap water were obtained having low, medium and high hardness. The following determinations were made on each sample: hardness, conductivity, calcium, magnesium and dissolved solids. The first four determinants were measured, using procedures described in Experiments 1, 5 and 8. Dissolved solids were determined by evaporating a 100 ml portion in a tared silica crucible on a steam bath<sup>19</sup>. The residue was then dried to constant weight at 180°C. An aliquot of each sample (1 l) was placed into one of three 1.2 l plastic beakers containing a magnetic stirrer bar. The beakers were placed on magnetic stirrers and stirred continuously at slow speed throughout the experiment. Manganese (II) solution (0.4 mls of 0.1M) were added to each beaker and the pH was raised to  $8.00 \pm 0.02$  by dropwise addition of 1M or 0.1M sodium hydroxide. Portions of 10 mls were withdrawn by pipette and stabilised in plastic bottles by adding 0.2 mls of 5M hydrochloric acid. Dilute iron (III) sulphate solutions (10 mls of (i) and (ii) were added by pipette and the pH was adjusted as necessary to  $pH 8.00 \pm 0.02$  and maintained at this level during 30 minutes. The total volume of sodium hydroxide added to each solution was recorded. At the end of

this period, portions were filtered and stabilised, prior to determination of dissolved manganese (II) by atomic absorption spectroscopy. Further portions were stabilised, without filtration, for determination of total iron. This experiment was repeated using different batches of tap water having similar hardness levels.

Results:

Temperature of water samples = 25°C

Volume of M sodium hydroxide (i) 0.8 mls (ii) 19.0 mls

Using iron (III) sulphate solution (i) low ionic strength

	Low Hardness		Medium Hardness		High Hardness	
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2
	Calcium $\text{mg l}^{-1}$ Ca	26	20	40	38	58
Magnesium $\text{mg l}^{-1}$ Mg	3.5	2.8	5.2	5.2	6.0	6.4
Total Hardness $\text{mg l}^{-1}$ $\text{CaCO}_3$	64	63	129	120	213	183
Conductivity $\mu\text{Scm}^{-1}$	220	220	400	380	460	530
Dissolved solids $\text{mg l}^{-1}$	165	160	310	285	340	400
Initial dissolved Mn(II) $\text{mg l}^{-1}$	2.36	2.11	2.30	2.17	2.36	2.20
Final dissolved Mn(II) $\text{mg l}^{-1}$	1.68	1.59	1.84	1.56	1.90	1.62
Total Iron $\text{mg l}^{-1}$ Fe	17.9	17.8	15.6	17.9	15.9	18.0

Using iron (III) sulphate solution (i) high ionic strength

	Low Hardness		Medium Hardness		High Hardness	
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2
	Initial dissolved Mn(II) $\text{mg l}^{-1}$	2.30	2.14	2.33	2.20	2.30
Final dissolved Mn(II) $\text{mg l}^{-1}$	1.39	1.16	1.38	1.19	1.29	1.47
Total Iron $\text{mg l}^{-1}$ Fe	17.5	17.7	17.9	18.1	18.4	17.9

Calcium, Magnesium and Hardness as in (i)



Calculations: The following assumptions have been made:-

- (1) That the apparent variation in total iron within each batch arises from analytical error. An average has been calculated for each batch.
- (2) The water sample ionic strength  $\sim$  dissolved solids  $\times 2.5 \times 10^{-5}$  as proposed by Stumm and Morgan<sup>15</sup>.
- (3) That in the experimental procedures, the ionic strength calculated above is increased by formation of sodium sulphate arising from neutralisation of (i) 0.8 mls M sodium hydroxide and (ii) 19.0 mls M sodium hydroxide.

Therefore, ( i ) = 0.057 g sodium sulphate(0.0004 M)  
(ii) = 1.35 g sodium sulphate(0.0095 M)

Thus the contributions to ionic strengths are:-

- ( i )  $\frac{1}{2}(0.0008)1^2 + \frac{1}{2}(0.0004)2^2 = 0.0012 \text{ M}$
- (ii)  $\frac{1}{2}(0.019)1^2 + \frac{1}{2}(0.0095)2^2 = 0.0285 \text{ M}$

Total Ionic Strength

	Low Hardness	Med. Hardness	High Hardness
Low I Batch 1	0.005 M	0.009 M	0.010 M
High I Batch1	0.033 M	0.036 M	0.037 M
Low I Batch 2	0.005 M	0.008 M	0.011 M
High I Batch 2	0.033 M	0.036 M	0.039 M

Adsorption ratios - Low Ionic Strength

	Low Hardness		Medium Hardness		High Hardness	
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2
Adsorbed manganese(II)mgMn	0.68	0.52	0.46	0.61	0.46	0.58
Iron (II)oxide mgFe	16.4	17.9	16.4	17.9	16.4	17.9
Adsorption ratio $\bar{\Gamma}_A \text{ mgMnmgFe}^{-1}$	0.041	0.029	0.028	0.034	0.028	0.032
$\bar{\Gamma}_A$ mean of Batch 1 + 2	0.035		0.031		0.030	

Adsorption ratios - High Ionic Strength

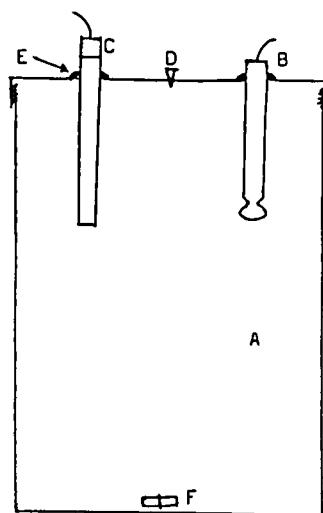
	Low Hardness		Medium Hardness		High Hardness	
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2
Adsorbed manganese(II)mgMn	0.98	0.71	0.95	1.01	1.01	0.83
Iron(II)oxide mgFe	17.9	17.9	17.9	17.9	17.9	17.9
Adsorption ratio $\Gamma_A$ mgMnmgFe <sup>-1</sup>	0.055	0.040	0.053	0.056	0.056	0.046
$\Gamma_A$ mean of Batch 1 + 2	0.048		0.055		0.051	

## Experiment 12

### Determination of oxygen uptake during oxidation of manganese (II) on iron (III) oxide.

Reagents: Analar grade reagents and deionised water were used.  
Manganese (II) sulphate tetrahydrate 0.1M  
(See Experiment 1)  
Iron (III) sulphate solution. E. and A. West 'W' grade  
(See Experiment 6)  
Magnesium sulphate solution. (5000 mg l<sup>-1</sup> Mg).  
5.070 g of MgSO<sub>4</sub> · 7H<sub>2</sub>O were dissolved in water and diluted to the mark in an 100 ml graduated flask.  
Sodium sulphite. 5% m/V solution of Na<sub>2</sub>Na<sub>2</sub>SO<sub>3</sub> · 7H<sub>2</sub>O.

Apparatus: Top drive electric stirrer.  
E.I.L. Model 7015 dissolved oxygen meter and recorder.  
E.I.L. Model 7030 pH meter.  
Magnetic stirrer.  
1.35 l plastic screw top jar (see diagram)



- A 1.35 L plastic jar with screw top.
- B pH probe.
- C Dissolved oxygen probe.
- D Plus for addition of alkali via burette.
- E Plasticine seal.
- F Magnetic stirrer bar.

TECHNICAL

The apparatus was filled to exclude air with various oxide suspensions. Dissolved oxygen and pH were measured on the two sensors, sealed into the screw top. Solution pH was controlled by removing the plug and inserting a burette tip to add reagents. Excess solution leaked through the screw thread and was soaked up by adsorbent paper under the apparatus. The apparatus was placed on a magnetic stirrer and the contents were stirred continuously during all experiments.

Calibration of dissolved oxygen sensor and determination of oxygen consumption characteristics.

The probe was calibrated, according to the manufacturers instructions. The zero point was set in 5% m/V sodium sulphite solution. The upper calibration point was set by allowing the wet probe to reach equilibrium in air, saturated with water vapour. The dissolved oxygen content of the oxygen saturated water film was obtained by reference to a Table<sup>19</sup>. The probe was calibrated before starting each procedure. The apparatus was filled with oxygen saturated tap water and the dissolved oxygen level was recorded for 2.5 hours. The change in dissolved oxygen level was noted and used to calculate the oxygen consumption of the dissolved oxygen sensor.

Procedure 1      (a) Oxygen consumption of iron (III) oxide suspension  
                         (b) pH at which oxidation becomes significant

4 mls of Iron (III) sulphate solution (4 mls) was added to 40 l of tap water in a plastic dustbin. The water was stirred slowly for 30 minutes. The precipitated iron (III) oxide was then allowed to settle overnight. The supernatant was decanted and a 500 ml portion was reserved for 'topping up' operations. The concentrated oxide suspension was transferred to the apparatus and filled with reserved supernatant. The pH was raised to 7.50 with M sodium hydroxide and the dissolved oxygen level was recorded for 30 minutes. The pH was then raised to 8.00 and 8.50 and the dissolved oxygen level was recorded for 30 minutes at each level.

The pH was then lowered to 7.50 with M hydrochloric acid and an aliquot of 0.1M manganese (II) solution (10 mls) was added. The pH was maintained at 7.50 and the dissolved oxygen level was recorded for 30 minutes. The pH was then raised to 8.00 and the pH was maintained at this level for 30 minutes while the dissolved oxygen level was recorded. The pH was then raised to 8.50 and maintained at this level while the dissolved oxygen was recorded for 120 minutes. At the end of this period a portion of the suspension was filtered and stabilised. A further portion was reserved for determination of total iron and suspended solids.

### Procedure 2

A concentrated iron (III) oxide suspension was prepared as in Procedure 1 and used to almost fill the apparatus. The pH was raised to 7.50 and an aliquot of 0.1M manganese (II) solution (20 mls) was added and the apparatus was topped up with supernatant. The pH was raised to 8.5 and the pH probe was removed and after 10 minutes a 20 ml portion was removed by pipette and filtered and stabilised. The apparatus was topped up with supernatant, the pH probe was replaced and the stirrer was restarted and the dissolved oxygen level was recorded for 120 minutes. At the end of this period a portion of the suspension was filtered and stabilised. A further portion was reserved for determination of total iron and suspended solids.

### Procedure 3

As in Procedure 2, except that the magnesium solution (10 mls) was added before the Manganese (II) solution (10 mls of 0.1M) was added.

### Procedure 4

As in Procedure 2, except that the iron (III) oxide suspension was prepared from 8 mls of iron (III) sulphate solution in 80 l of tap water. Manganese (II) (10 mls of 0.1M) solution was added.

### Procedure 5

As in Procedure 2, except that manganese (II) solution (15 mls of 0.1M) was added.

### Procedure 6

As in Procedure 2, except that the iron (III) oxide suspension was prepared using 2 mls iron (III) sulphate solution. Manganese (II) solution (3 mls of 0.1M) was added. Sampling after 10 minutes and 120 minutes was omitted.

### Procedure 7

As in Procedure 2, except that manganese (II) solution (10 mls of 0.1M) was added. Five minutes after raising the pH to 8.50, the top of the container was unscrewed and the pH was immediately lowered to 4.00, by dropwise addition of 5M and 0.1M hydrochloric acid. The acidified suspension was stirred for 30 minutes and the pH was readjusted as

necessary to 4.00. At the end of this period, a portion was filtered and stabilised. The initial concentration of manganese (II) in the apparatus was determined after placing manganese (II) solution (10 mls of 0.1M) in the apparatus and filling with tap water.

Procedure 7 was carried out in duplicate.

Iron, manganese and suspended solids were determined using the methods described in Experiments 1, 5 and 6. The temperature of the suspensions was measured at the start and finish of each experiment with a mercury in glass thermometer.

Results:

Oxygen consumption of dissolved oxygen sensor

Initial dissolved oxygen = 7.50 mg l<sup>-1</sup> O<sub>2</sub>

Dissolved oxygen after 2.5 hours 7.30 mg l<sup>-1</sup> O<sub>2</sub>

Volume of water = 1.35 l . Therefore oxygen consumption =

$$\frac{7.50 - 7.30}{2.5} \times 1.35$$

(This agrees exactly with the manufacturer's claim) - 0.11 mg/hour

Temperature of solutions 20 ± 1°C in all procedures

Dissolved oxygen concentration records - These are displayed in

Figure 16.

Procedure	Total Iron in Suspension mg l <sup>-1</sup> Fe	Suspended Solids mg l <sup>-1</sup>	Volume of 0.1M Mn(II) cm <sup>3</sup>	Dissolved Manganese after 10 mins. mg l <sup>-1</sup>	Dissolved Manganese after 120 mins. mg l <sup>-1</sup>
1	431	880	10	5.16	2.03
2	376	904	20	25.56	4.92
3	406	926	10	4.39	1.56
4	850	1676	10	1.32	0.37
5	494	1050	15	7.04	1.16
6	247	490	3	-	-
7	385,445		10,10	-	-

Procedure	Drop in Dissolved Oxygen $\Delta$ raising pH to 8.5 $\text{mg l}^{-1} \text{O}_2$	Subsequent rate of fall in dissolved oxygen $\text{mg l}^{-1} \text{O}_2 \text{ hr.}^{-1}$
1	*	0.8
2	2.5	2.2
3	1.9	0.6
4	1.4	0.7
5	2.3	1.3
6	-	0.2
7	(1) 1.50 (2) 1.40	-

\*not comparable with dissolved oxygen drop in other procedures as manganese (II) solution was added 90 minutes before raising pH to 8.50

Procedure 7 Initial dissolved manganese (II) =  $40.55 \text{ mg l}^{-1} \text{Mn}$   
(This is in excellent agreement with the calculated result obtained by diluting 10 mls 0.1M manganese(II) to 1.35 l i.e.  $40.74 \text{ mg l}^{-1}$ )

Dissolved manganese (II) at pH 4 (1) -  $31.37 \text{ mg l}^{-1} \text{Mn}$

(2) =  $32.13 \text{ mg l}^{-1} \text{Mn}$

Manganese associated with iron (III) oxide at pH 4  
(Initial dissolved manganese (II) - dissolved manganese (II) at pH 4)

(1) =  $9.18 \text{ mg l}^{-1} \text{Mn}$

(2) =  $8.42 \text{ mg l}^{-1} \text{Mn}$

### Calculations

Procedure	Initial* dissolved manganese(II) $\text{mg l}^{-1} \text{Mn}$	Manganese(II) adsorbed after 10 mins $\text{mg l}^{-1} \text{Mn}$	Ratio adsorbed manganese at 10 mins to total iron $\text{MnFe}^{-1}$	Manganese removed from solution during 120 mins % of initial dissolved Mn(II)
1	40.7	35.5	0.082	95
2	81.5	55.9	0.15	94
3	40.7	36.3	0.089	96
4	40.7	39.4	0.046	99
5	61.1	54.1	0.11	98
6	12.1			-

\*Calculated from volume of 0.1M manganese(II) after dilution to 1.35 l.



Procedure 7 - calculation of the ratio manganese to oxygen in  
reaction at iron (III) surface

In Experiment 9 it was demonstrated that 97.6% of the manganese (II) adsorbed onto iron (III) oxide may be desorbed by acidifying the solution to pH 4.00. It is, therefore, assumed that the manganese associated with the iron (III) oxide at pH 4.00 in this experiment, is combined as a manganese oxide. It is also assumed that the observed rapid decrease in dissolved oxygen, which accompanies manganese adsorption, results from oxidation of the manganese (II). The manganese associated with iron (III) oxide at pH 4.00 is obtained by subtracting dissolved manganese (II) at pH 4.00 from the initial dissolved manganese.

	(1)	(2)
∴ Manganese associated with iron(III) oxide at pH 4.00	= 9.18 mg l <sup>-1</sup>	8.42 mg l <sup>-1</sup>
Dissolved oxygen decrease	= 1.50 mg l <sup>-1</sup>	1.40 mg l <sup>-1</sup>
Ratio manganese : oxygen	= 6.12	6.01

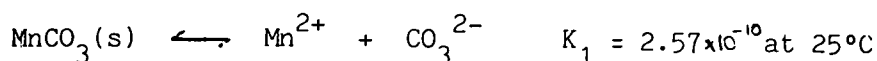
The drop in dissolved oxygen on raising the pH to 8.50 is plotted against the ratio of adsorbed manganese (II) to total iron in Figure 17. The subsequent rate of fall in dissolved oxygen is plotted against total manganese in Figure 18. Oxygen consumption of the dissolved oxygen sensor was considered to be negligible during the period of this experiment.

### 3. DISCUSSION

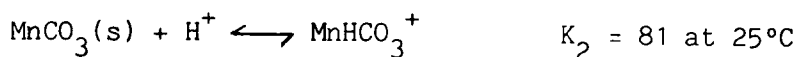
### 3.1 Solubility and stability of dissolved manganese (II) solutions.

Morgan<sup>13</sup> has suggested that the pertinent equilibria which control the solubility of manganese (II) in water containing dissolved carbonic species are:-

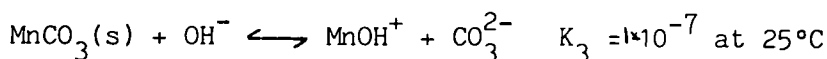
( i ) solubility of manganese (II) carbonate:



( ii ) formation of manganese (II) hydrogen carbonate ion pair:



(iii) hydrolysis of manganese (II) carbonate:



( iv ) hydrogen carbonate acidity:



( v ) Ionic product of water:  $K_w = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$

Then:

$$\text{Dissolved manganese(II)} = \frac{H^+ K_1}{C_t K_4} + \frac{K_w K_3}{H^+} + K_2 H^+ \quad \text{Equation (10)}$$

where  $H^+$  = hydrogen ion concentration

$C_t$  = total dissolved carbonic species (approximately equal to  $\text{HCO}_3^-$  in pH range 7 - 8)

This data is represented graphically in Figure 2 for water with  $C_t = 76 \text{ mg l}^{-1}$  in the pH range 6 - 9. The thermodynamic constants have been converted to stoichiometric constants by use of the Davies Equation<sup>23</sup>.

$$pk_{so} = p^c K_{so} + (nZ_m^2 + mZ_n^2) \left( \frac{0.5 \sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

Where  $pK_{so}$  = Stoichiometric constant  
 $p^c K_{so}$  = Thermodynamic constant  
 $Z$  = charge on reacting species  
 $m, n$  = number of atoms reacting  
 $I$  = ionic strength

A specimen calculation is shown in Appendix 1. Davies' equation corrects for the ionic strength arising from a mixture of strong electrolytes. It has been assumed that water sample was equivalent to a solution of ionic strength,  $I = 0.0064$  M.

Various authors<sup>13,14</sup> have commented on the inadvisability of carrying out experiments involving supersaturated manganese (II) solutions. They have cited specifically the problem of distinguishing between oxidation of manganese (II) to insoluble oxides and coprecipitation of manganese (II) with other precipitating species. Water Treatment Plants, however, are operated under conditions of theoretical manganese (II) supersaturation. Thus the bulk of experimental work reported in this study has been carried out under similar conditions.

There is equivocal evidence<sup>24</sup> of the stability of theoretically supersaturated manganese solutions in natural water. The work cited was apparently not carried out under conditions that ensure representative sampling and analysis of dissolved manganese species. However, in view of the known ability of trace organic matter in natural water to stabilise theoretically supersaturated solutions<sup>25</sup>, it was considered that a brief study of the solubility and stability of manganese (II) species was warranted. It was considered that the dissolution of commercially available specimens of manganese (II) carbonate did not represent conditions prevailing in natural water. In Experiments 1 and 2, manganese (II) carbonate suspensions were prepared and after ageing for three days, their solubility was determined in tap water samples of varying pH. Thus the carbonate specimens were kept under water at all times. The variation in manganese (II) solubility with pH is shown in Figure 2 and the rate of dissolution is plotted in Figure 1. As the procedure used to prepare the carbonate in Experiment 1 is known to introduce manganese (II) hydroxide as impurity<sup>20</sup>, Experiment 3 was carried out using a procedure capable of producing the pure carbonate<sup>20</sup>. The manganese (II) carbonate specimen was separated from water and dried before determining its purity. Problems were encountered when an attempt was made to back titrate with standard alkali to the end point of BDH 4.5 indicator after dissolution in excess standard acid. It was noted that as the orange to grey end point was approached, a brown colour developed which masked the end point. This was attributed to precipitation of manganese (II) hydroxide, following by oxygen

Figure 1

Time to reach solution equilibrium  
Manganese (II) carbonate in tap water at 25°C

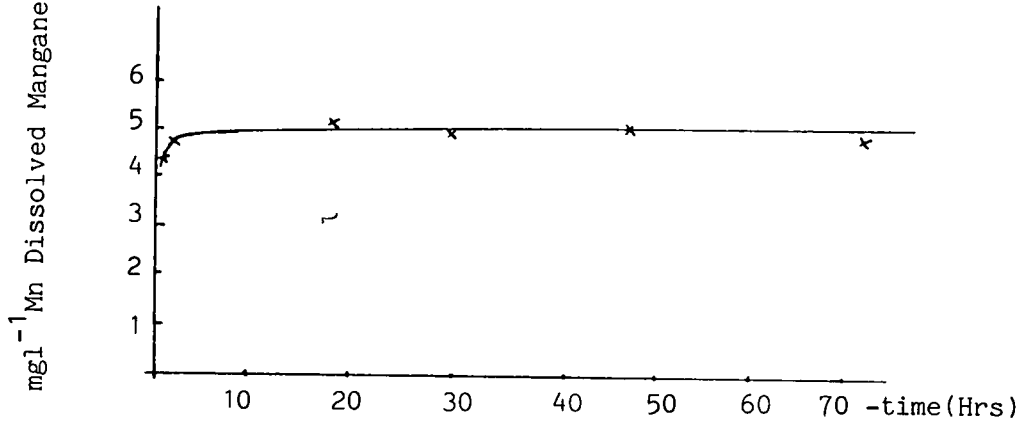
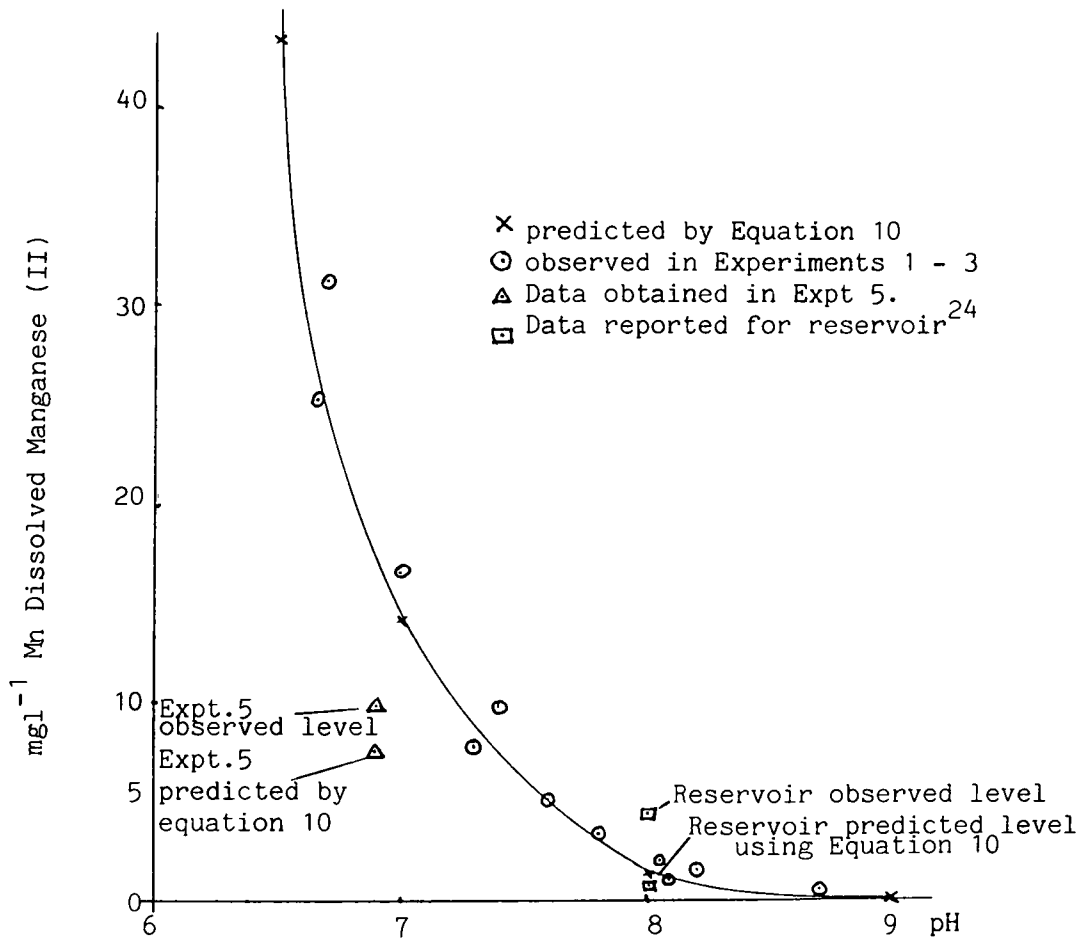


Figure 2

Observed and predicted solubility of manganese(II) species in water containing dissolved carbonic species



oxidation to manganese (III) & (IV) oxide. The effect was diminished but not removed by boiling the solution or purging with nitrogen during titration. The carbonate was successfully analysed by direct titration in boiling solution with decimolar acid. This procedure gave an extremely sharp end point with BDH 4.5 indicator. The result indicated an average manganese (II) carbonate content of 94.70%. The analysis of a commercially available specimen indicated only 66% purity. Discussions with the manufacturers revealed that their precipitated salt was dried at 110°C and that superficial oxidation to higher oxides occurred during this stage. Analysis was made via the total manganese content and the manufacturers agreed that the stated 96% purity arose from a fortuitous combination of oxide and carbonate with similar proportions of manganese.

The stability of theoretically supersaturated solutions containing manganese (II) species was determined by raising the pH of solutions containing various initial manganese levels to 9. The solutions were then stored and examined periodically for precipitation. Precipitation occurred between 10 and 72 hours. The data has been plotted in Figure 3 as log induction period vs log initial concentration + theoretically predicted solubility. A linear relationship has been observed over a limited range of several studies into the kinetics of homogeneous nucleation<sup>26</sup>. The variation in dissolved manganese remaining after precipitation is attributed to uncertainty in measuring the induction period. Thus there was a variation of up to one hour between observation of precipitation and filtration of the sample. A limited study only of the stability of theoretically predicted supersaturated solutions was carried out. The initial results confirmed prolonged stability of highly supersaturated solutions and, therefore, no further work was carried out into this subject. In Experiment 5, dissolved manganese levels were determined in the anaerobic layer of water near the bed of a stratified reservoir. Stratification is a phenomenon whereby a body of water is isolated into two layers by a temperature gradient. (See Diagram 5). The bottom layer is isolated from the surface layer and aeration by oxygen diffusion from the surface ceases. Thus the dissolved oxygen level in the bottom water decreases because of the oxygen consumption processes operating on organic detritus. Under conditions of prolonged stratification, water near the bed may become anaerobic. Under

Diagram 5

A Stratified Reservoir

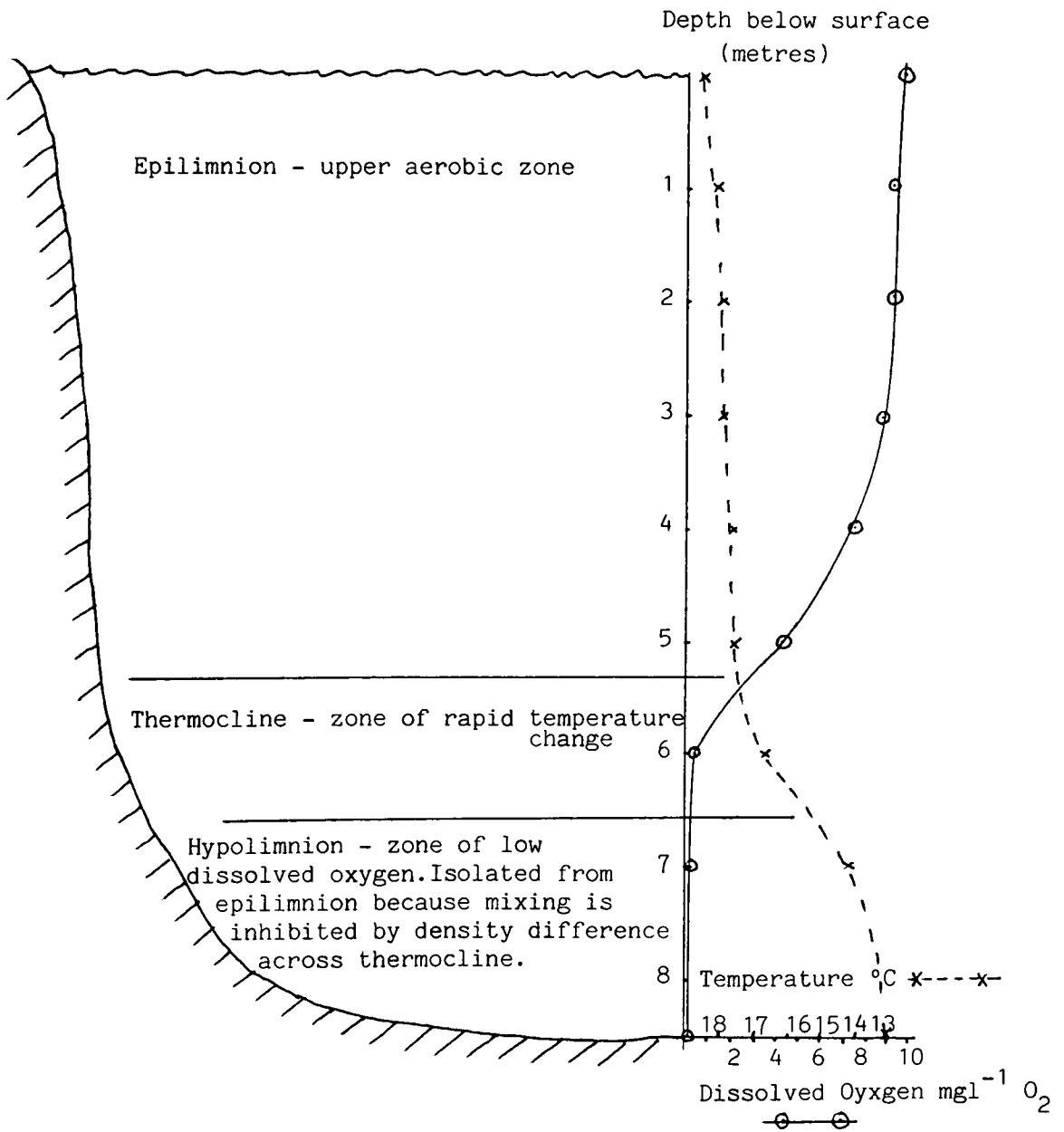
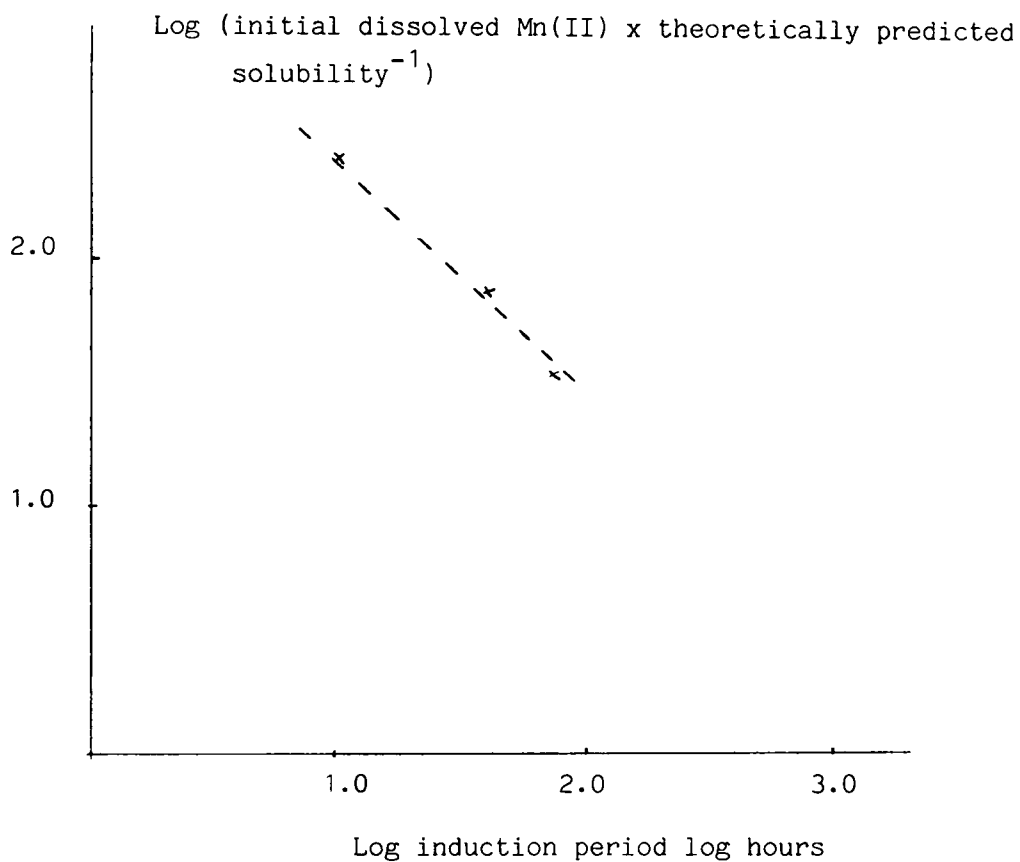


Figure 3

Log. Supersaturation ratio vs Log. Induction Period





reducing conditions, the concentration of dissolved manganese rises as insoluble oxides are reduced by organic matter in biochemically mediated reactions. Precautions were taken to ensure that the sample composition was not disturbed prior to analysis. These precautions included:

- ( i ) Use of a displacement type sampler to avoid aeration of the sample.
  - ( ii ) Measurement of pH on site.
  - ( iii ) Filtration and stabilisation of manganese (II) species on site.
- The dissolved manganese concentration is shown on Figure 2 and significantly exceeds theoretically predicted solubility.

The results of Experiments 1 to 5 lead to the conclusion that Equation 10 slightly underestimates the solubility of manganese (II) species in natural water. Somewhat higher solubilities have been obtained both in tap water and reservoir water. It is considered that in both cases the observed solubility probably arises from stabilisation of supersaturated solutions by dissolved organic matter and/or failure to exceed the critical supersaturation ratio necessary for precipitation. Manganese oxides are precipitated in aerobic layers of water and settle with organic detritus to form the bottom sediment. The reduction of manganese (III) and (IV) species is accompanied by fermentation of organic matter with liberation of methane and carbon dioxide. It is, therefore, possible that the acid environment in the sediment yields a manganese (II) solution of a higher concentration than is theoretically possible in the overlaying water. The dissolved organic carbon analyses in Experiment 5 suggest the possibility of stabilisation of supersaturated manganese (II) solution. The low supersaturation ratio of approximately 2, indicated in Figure 2, would again enhance stability of the manganese (II) solution. It is well known that compounds, freshly precipitated from strongly oversaturated solutions may persist in metastable active state that has higher solubility than the aged precipitate. The ageing period for precipitated manganese (II) carbonate is unknown but it is conceivable that the three day period used in Experiments 1 - 3 was insufficient to deactivate the precipitate. It may be considered that under conditions of precipitation of manganese (II) species in natural water, there is no ageing period before dissolution commences. The limited data used to plot Figure 3 suggests that a supersaturation ratio of at

at least 500 may be required to ensure immediate precipitation of manganese (II) carbonate. For this reason, it is concluded that the use of typical supersaturation ratios of 10 - 100 in the adsorption studies, does not invalidate any of the results presented. The stability of supersaturated manganese (II) in iron (III) and manganese (IV) oxide suspensions indicates that the hydrous oxides do not provide suitable adsorption sites for initiation of crystallisation.



### 3.2 Adsorption properties of hydrous iron (III) and manganese(IV)oxides.

In view of the known affinity of hydrous iron (III) and manganese (IV) oxides for cations,<sup>13</sup> adsorption studies were carried out under conditions appropriate to water treatment. In Experiment 6, hydrous oxides were prepared under conditions known to produce amorphous precipitates.<sup>27</sup> The instability in surface properties of freshly prepared hydrous oxides has been reported<sup>27</sup>. Therefore, all oxide suspensions were aged for approximately 24-hours before use. In Experiment 7, attainment of adsorption equilibrium was taken to be indicated by the plateau of the graph relating dissolved manganese to contact time. This relationship is displayed in Figure 4. In the concentrated iron (III) and manganese (IV) oxide suspensions, equilibrium has been reached after five minutes. This time increased to fifteen minutes at the low iron (III) oxide concentration in natural water. Raising the pH of natural water from 8.0 to 9.0 did not affect the rate of attainment of equilibrium although the quantity of manganese adsorbed was significantly higher. Approach to equilibrium was accompanied by a decrease in the volume of alkali necessary to maintain pH 8.0 i.e. little alkali was required after five minutes to maintain pH 8.0. Adsorption isotherms were determined in Experiment 8 at pH 8.0, 8.5 and 9.0 at 10°C, these levels being of particular relevance in water treatment. The insignificant loss of dissolved manganese on the glass beaker is of note as it provides additional confirmation of the findings in Experiment 4. The blank determination was carried out on the highest concentration of dissolved manganese, used at pH 9.0. The results indicated no loss of dissolved manganese in thirty minutes from a solution containing  $68 \text{ mg l}^{-1}$  manganese (II) i.e. almost five hundred times higher than the predicted solubility. The analyses of dissolved group 1 and 2 metals before and after precipitating iron (III) oxide, showed insignificant differences. Thus adsorption of these cations during preparation of the oxide is insignificant.

The results of adsorption experiments have been fitted to various equations in attempts to explain the nature of the interaction between adsorbent and sorbate. In Figures 5 and 8, the data has been plotted as the Langmuir Adsorption Isotherm<sup>21</sup>. Similar trends are exhibited on both iron (III) and manganese (III) oxides. The fit is near linear at pH 8.0 and shows increasing deviation as the pH rises. Morgan and Stumm<sup>28</sup> have reported a linear fit to the Langmuir equation for

Figure 4

Time taken to reach adsorption equilibrium

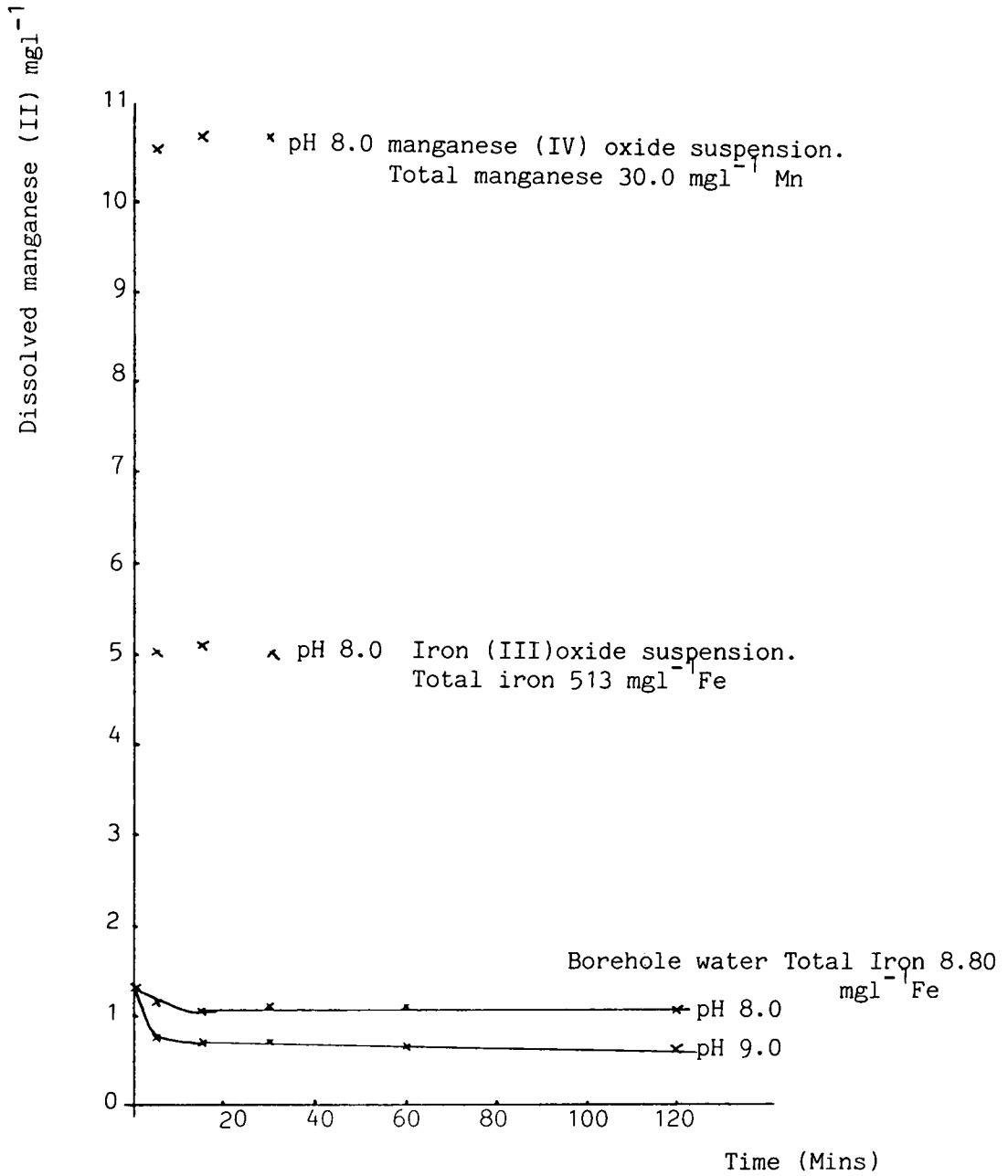


Figure 5

Adsorption of manganese (II) on iron (III) oxide  
Data plotted as Langmuir Equation at constant pH  
and 10°C

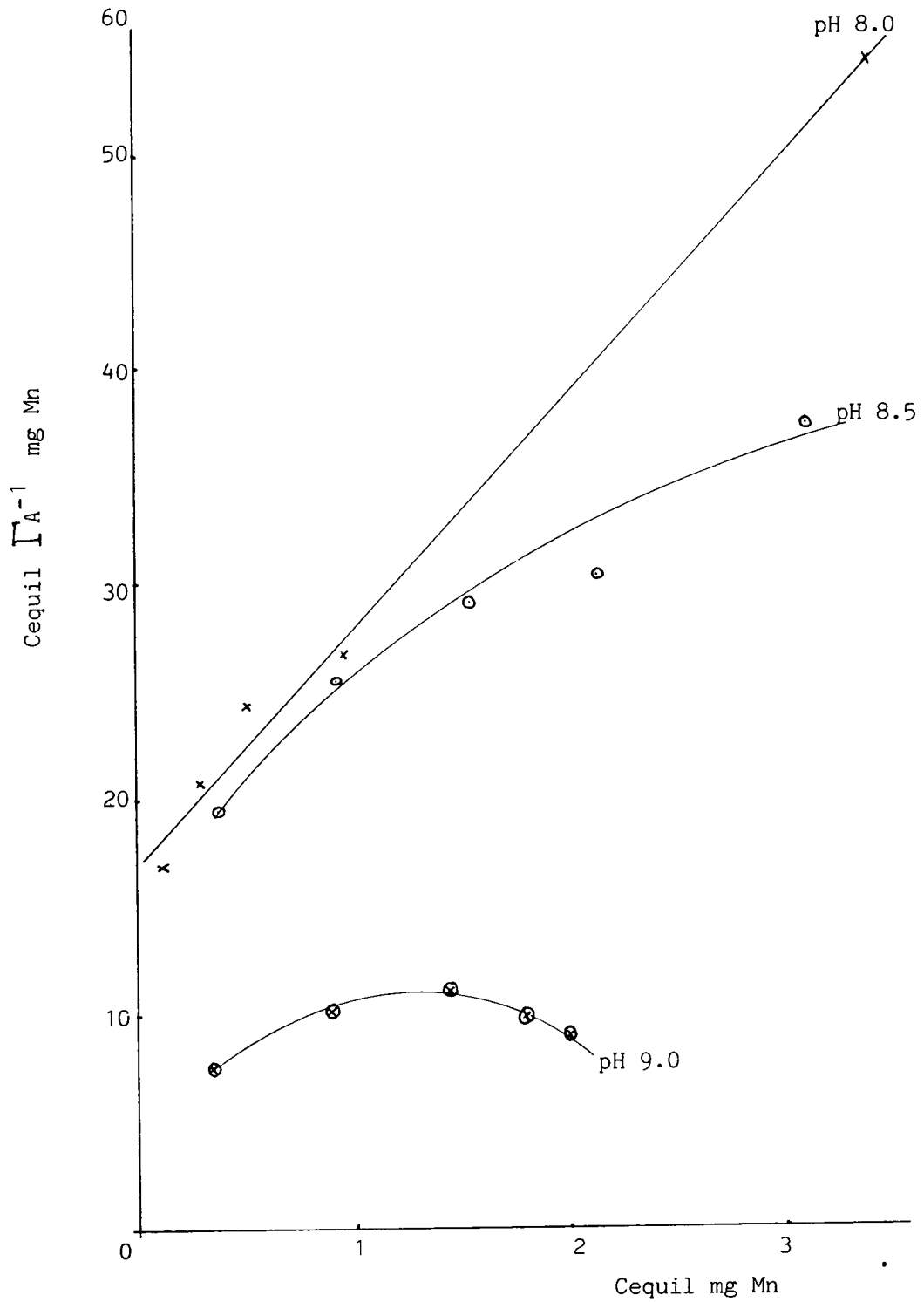


Figure 6

Adsorption ratio  $\Gamma_A$  v dissolved manganese  
Cequil at constant pH and 10°C. Manganese (II)  
on iron (III) oxide.

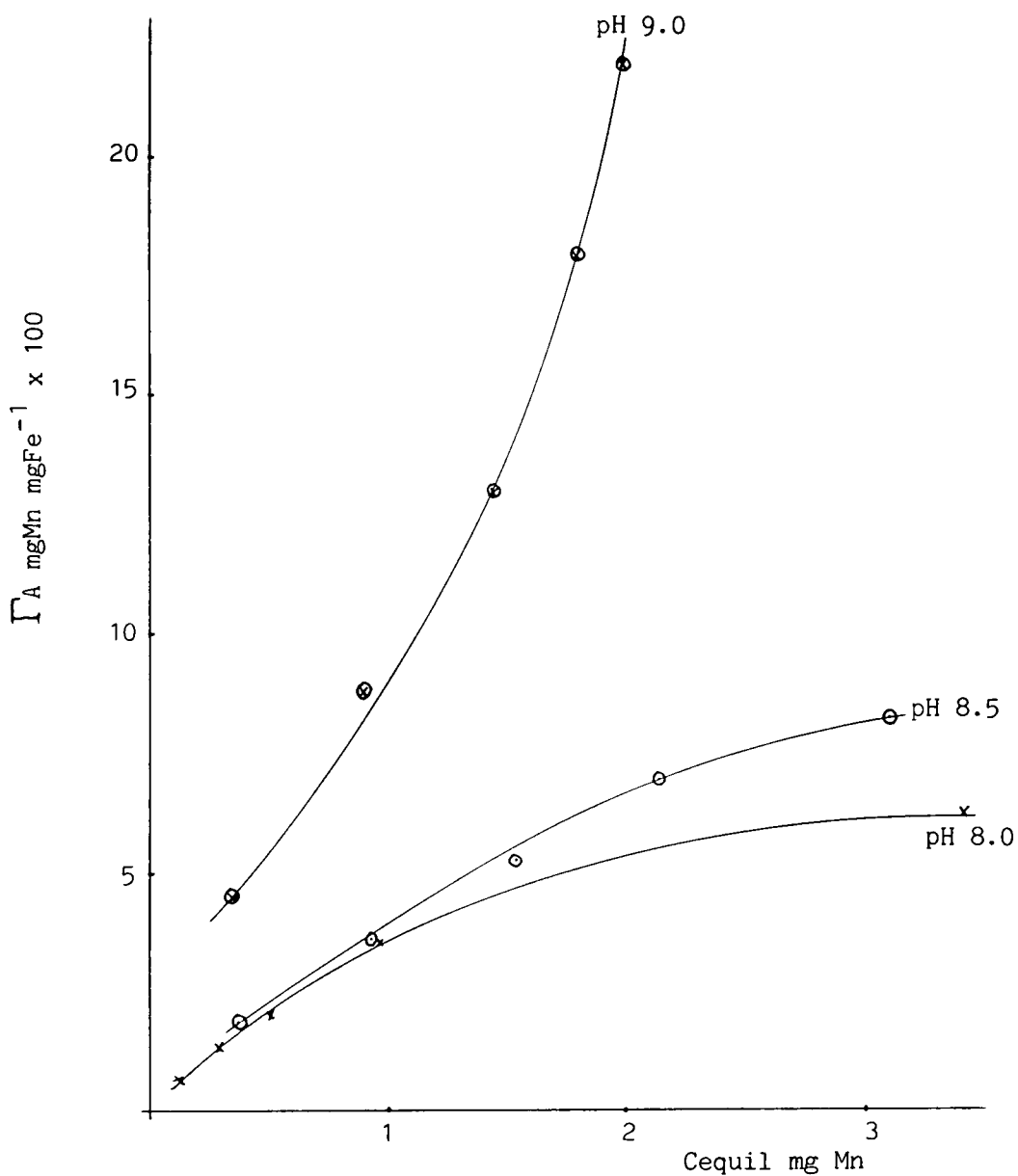


Figure 7

Adsorption Ratio  $\Gamma_A$  vs total manganese at constant pH and 10°C. Manganese (II) on iron (III) oxide.

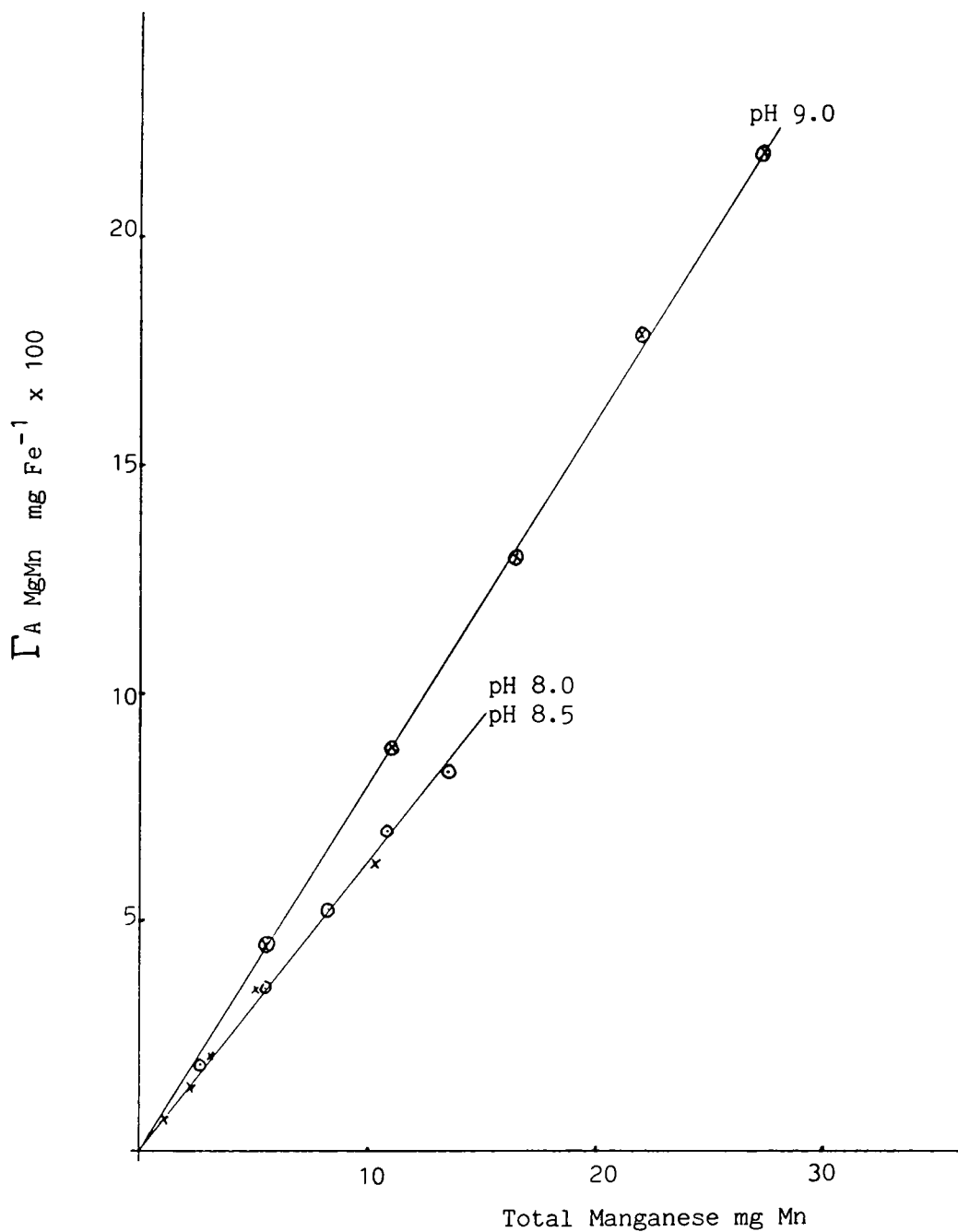


Figure 8

Adsorption of manganese (II) on manganese (IV) oxide  
Data plotted as Langmuir Equation at constant pH & 10°C

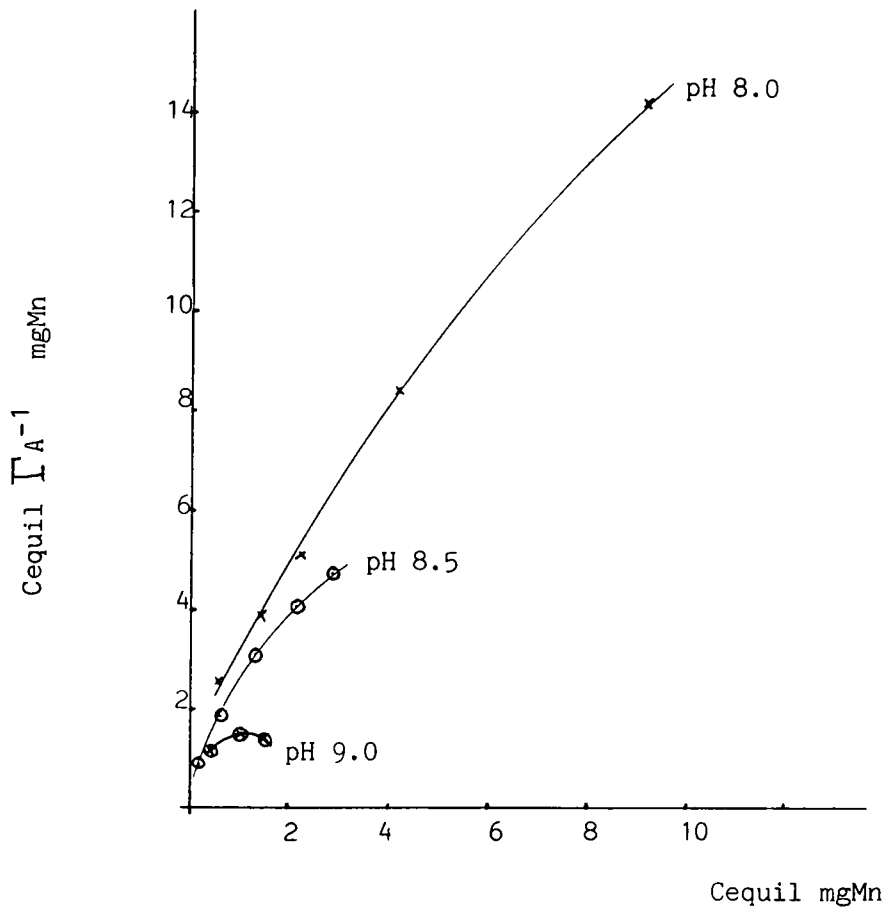




Figure 9

Adsorption Ratio  $\Gamma_A$  vs dissolved manganese  
Cequil at constant pH and 10°C. Adsorption of  
Manganese (II) on Manganese (IV) oxide.

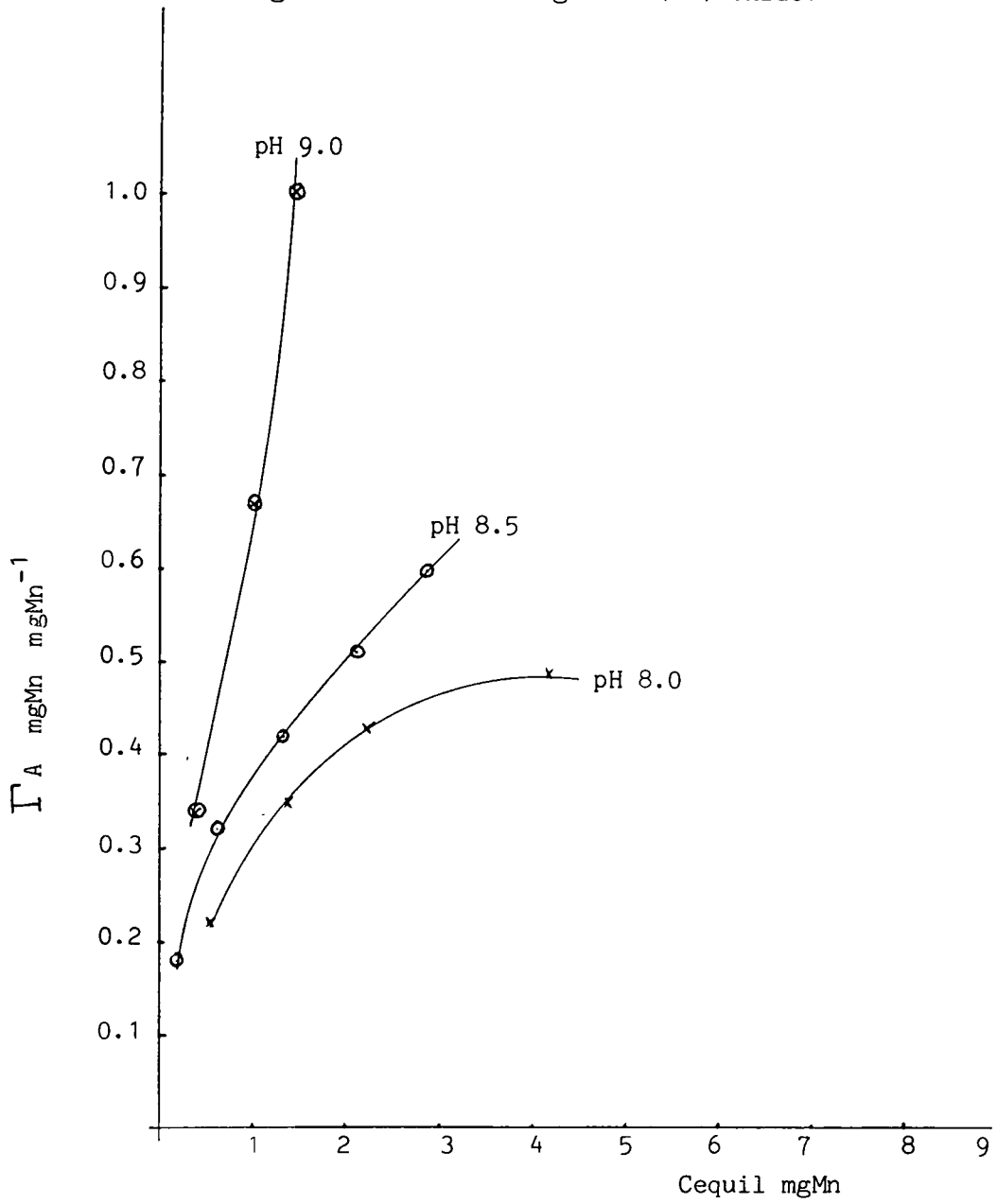


Figure 10

Total manganese vs Adsorption Ratio  $\Gamma_A$  at constant pH and 10°C. Adsorption of manganese (II) on manganese (IV) oxide.

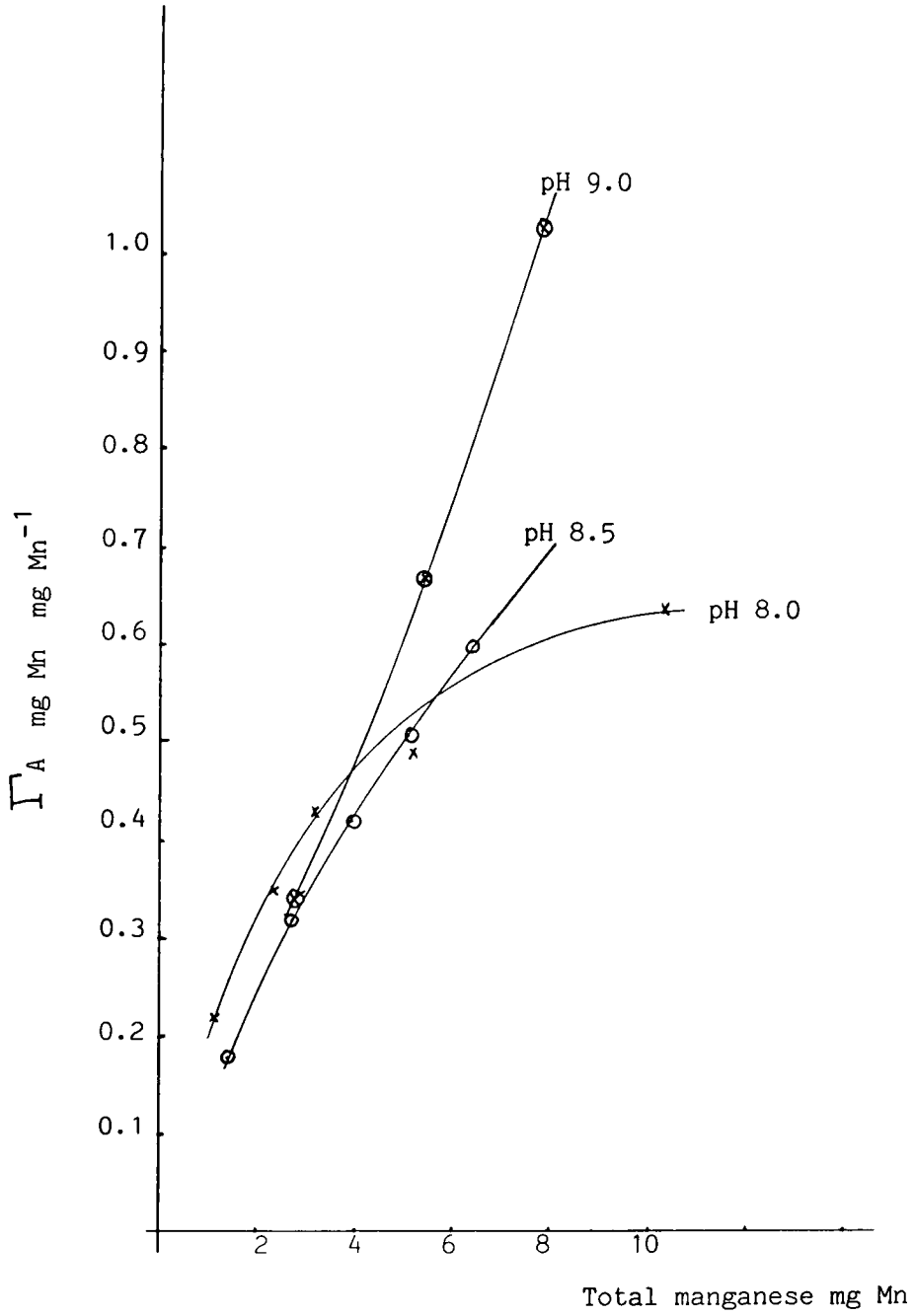
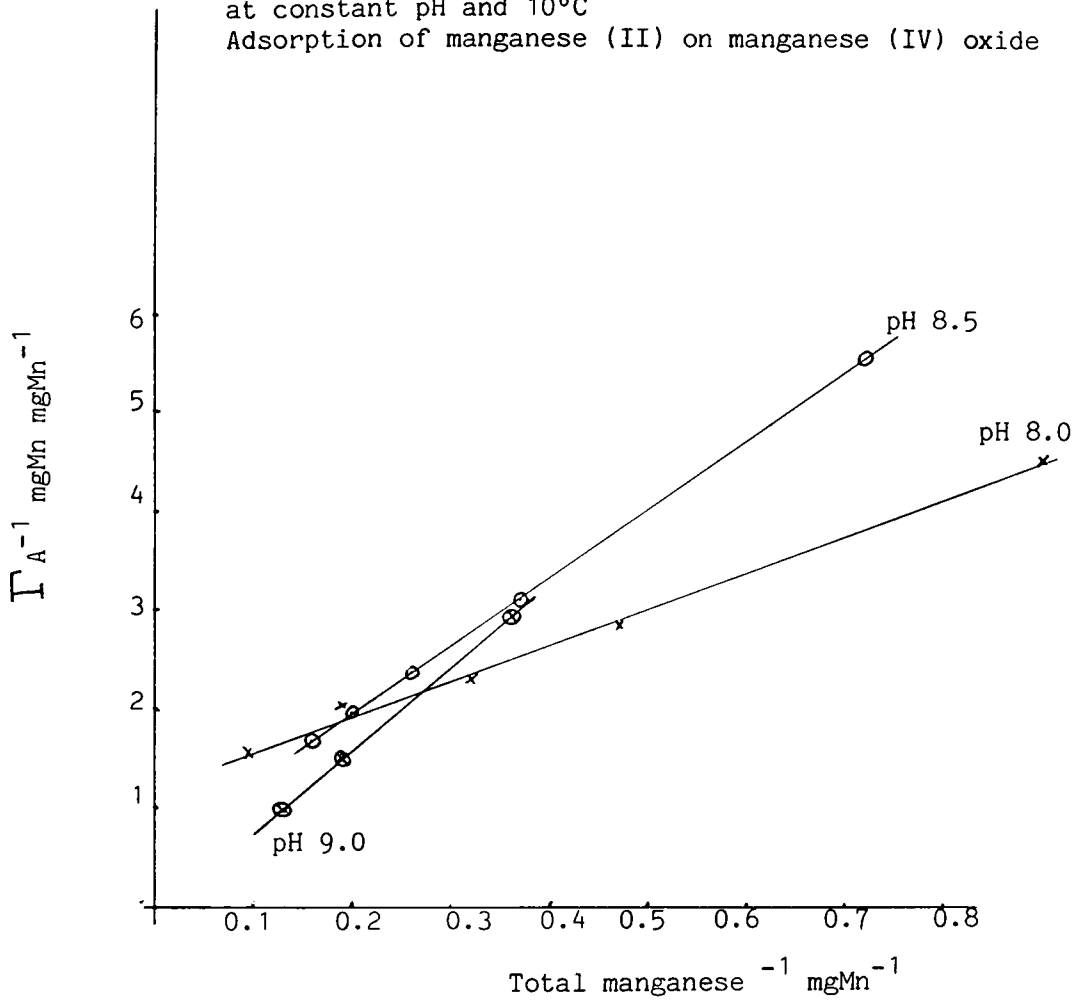


Figure 11

Reciprocal total manganese vs  
reciprocal adsorption ratio  $\Gamma_A$   
at constant pH and 10°C

Adsorption of manganese (II) on manganese (IV) oxide



adsorption of manganese (II) on manganese (IV) oxide at pH 7.5.

The Langmuir Equation assumes:-

1. A fixed number of adsorption sites.
2. One molecule can be held on each adsorption site.
3. Heat of adsorption is constant.
4. No interaction between adsorbed molecules.

Examination of the graphs shows that the rate of change of dissolved manganese per unit change in adsorption ratio, decreases with increase in dissolved manganese. This indicates that the adsorption ratio does not tend towards a constant level, as predicted by the Langmuir Equation. At pH 9.0 the plot for both adsorbents passes through a maximum. This indicates that the adsorption ratio is increasing as the dissolved manganese level increases. This may be interpreted in terms of reaction at the surface of the adsorbent to give a product with greater sorption capacity than the adsorbent. This hypothesis is supported by the observation that it was not possible to maintain a constant pH at 9.0 for adsorption of manganese (II) on either oxide. The downward drift in pH is explained by release of protons in the oxidation of manganese (II) and subsequent hydrolysis of the reaction product. Further support is provided in the observation that at pH 8.5 to 9.0 the iron (III) oxide colour changes from orange to brown. This is presumed to arise from the oxidation of manganese (II) to manganese (III) or (IV) oxides. In Figures 6 and 9 the data has been plotted according to the equation.

$$\Gamma_A = K_1 C_{\text{equil}} \quad \text{- Equation (3)}$$

This equation is equivalent to the Langmuir isotherm for weak adsorption. The graphs show that at pH 8.0 and 8.5, the rate of increase in adsorption ratio falls with increase in equilibrium level of dissolved manganese(II). At pH 9.0 the rate of increase in adsorption ratio rises with increase in equilibrium level of dissolved manganese. This confirms the observation of a maximum in the Langmuir plot at pH 9.0 For adsorption of iron (III) oxide, a linear fit is obtained for the equation:-

$$\Gamma_A = K_2 \text{Mn}_{\text{tot}} \quad \text{- Equation (4)}$$

Where  $\text{Mn}_{\text{tot}}$  = Total manganese

This equation is plotted in Figure 7.

The equation assumes that the adsorbed manganese is effective in the adsorption process. Within experimental error, the slope of the graph is the same for adsorption at pH 8.0 and 8.5, while a slightly higher slope is obtained at pH 9.0. Adsorption on manganese (IV) oxide does not give a linear fit to Equation (4) (Figure 10). A linear fit is obtained, however, by adding an additional term to Equation (4).

$$\Gamma_A = K_3 \text{Mn}_{\text{tot}} + k_4 \text{Mn}_{\text{tot}} \Gamma_A \quad - \text{Equation (5)}$$

See Figure 11.

This equation assumes that two manganese adsorption processes are operative, with different affinities for dissolved manganese (II). The second term attributes a specific affinity to the adsorbed fraction.

The overall conclusion drawn from Experiment 8 is that the adsorption process is followed by oxidation of the sorbate to give a manganese oxide that has a higher affinity for the sorbate. It is noted that manganese (IV) oxide has a much higher affinity for manganese (II) than iron (III) oxide at the given pH. This difference in affinity probably accounts for the apparent anomaly that two constants must be introduced to describe adsorption on manganese (IV) oxide. Adsorption on iron (III) oxide satisfies Equations (4) and (5), while adsorption on manganese (IV) oxide fits only Equation (5). It is noted, however, that Equation (5) reduced to Equation (4) at low adsorption ratio and thus equally describes the relatively weak adsorption on iron (III) oxide and strong adsorption on manganese (IV) oxide. When Experiment 8 was repeated, the procedure was varied so as to determine whether the apparent difference in the adsorption properties between the two oxides arose, in fact, from a defect in experimental procedure. In the original procedure, increments of manganese (II) were added to the same oxide suspension. As the experiment lasted some 45 minutes, it was considered that the earlier increments might have been oxidised before later increments were added. This would alter the surface properties of the original oxide. In the repeat experiment on manganese (IV) oxide, five separate mixtures of adsorbent and sorbate were studied. The results are displayed in Figure 13 and suggest that the two procedures give concordant results. The results of repeating Experiment 8 confirm that after ageing for 24 hours, both oxides show reproducible surface properties. In Figures 12 and 13, Equations (4) and (5) have been plotted after weighting the total manganese with the

Figure 12

Adsorption ratio  $\Gamma_A$  vs total manganese x  
oxide iron<sup>-1</sup> at constant pH and 10°C.  
Manganese (II) on iron (III) oxide.

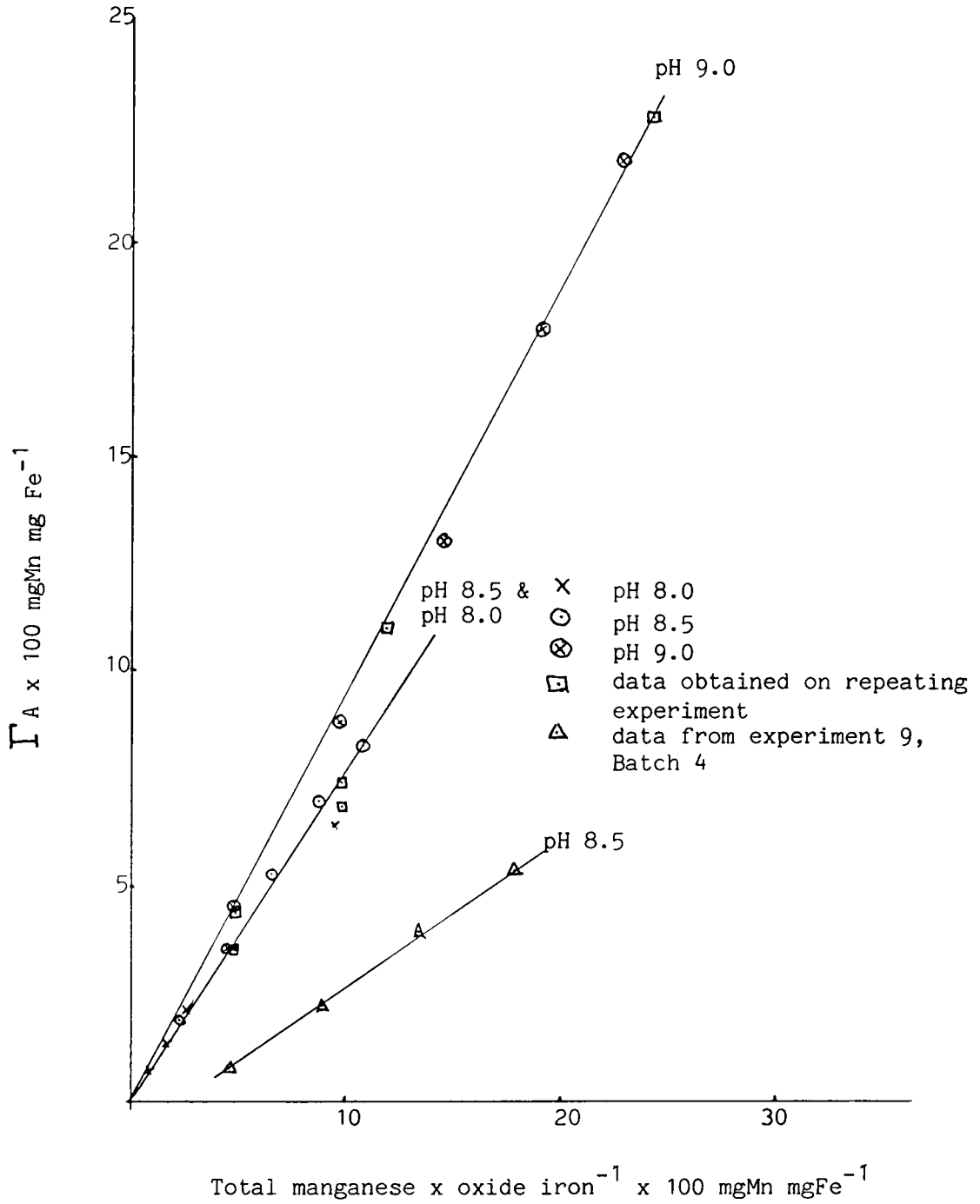
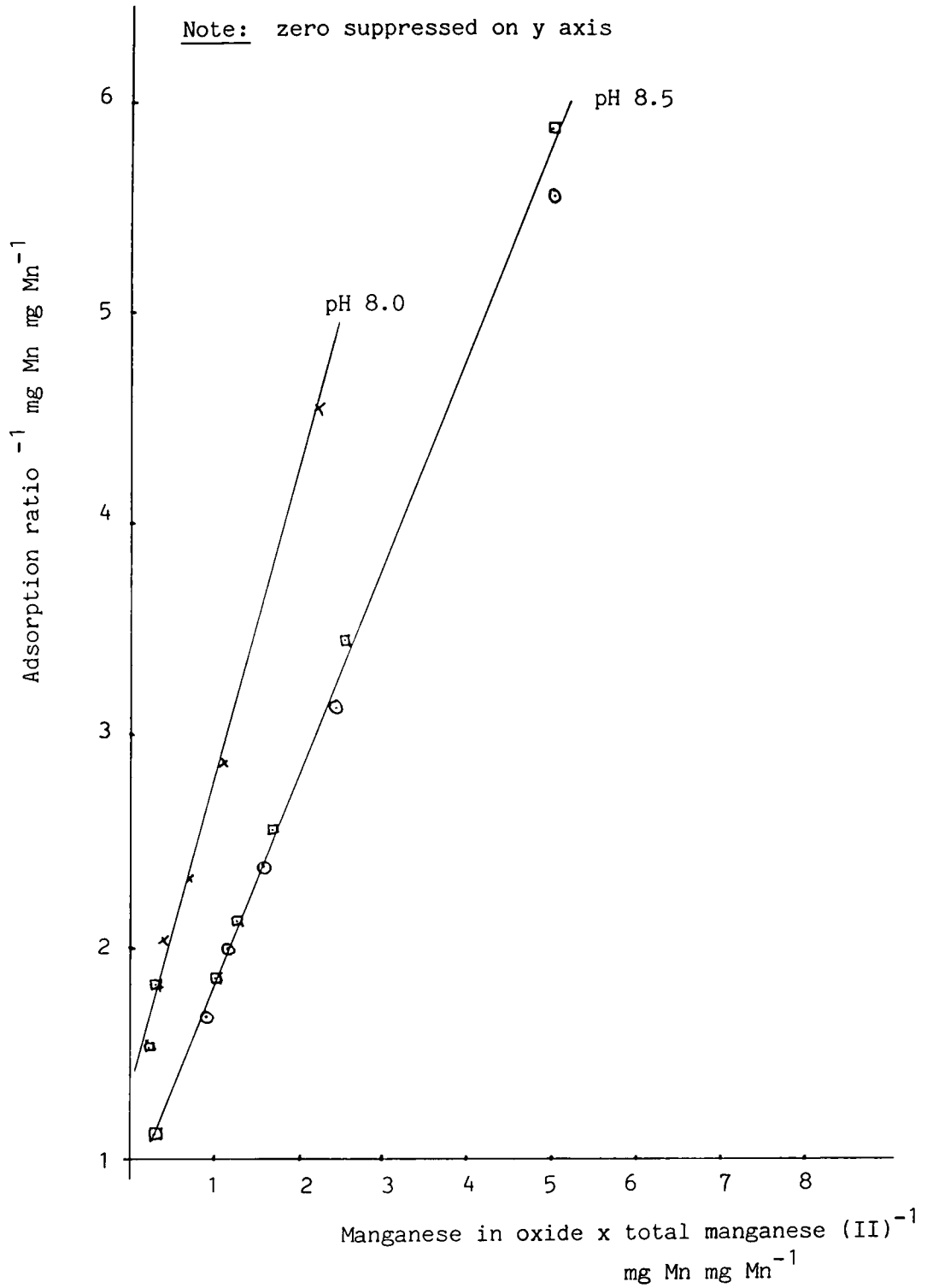


Figure 13

Manganese in oxide x total manganese (II)<sup>-1</sup>  
vs adsorption ratio<sup>-1</sup>

Note: zero suppressed on y axis



mass of adsorbent. This reduces (4.) and (5) to : adsorbed manganese =  $K_2(\text{total manganese})$  and adsorbed manganese =  $K_3(\text{total manganese}) + K_4(\text{adsorbed manganese})$  respectively.

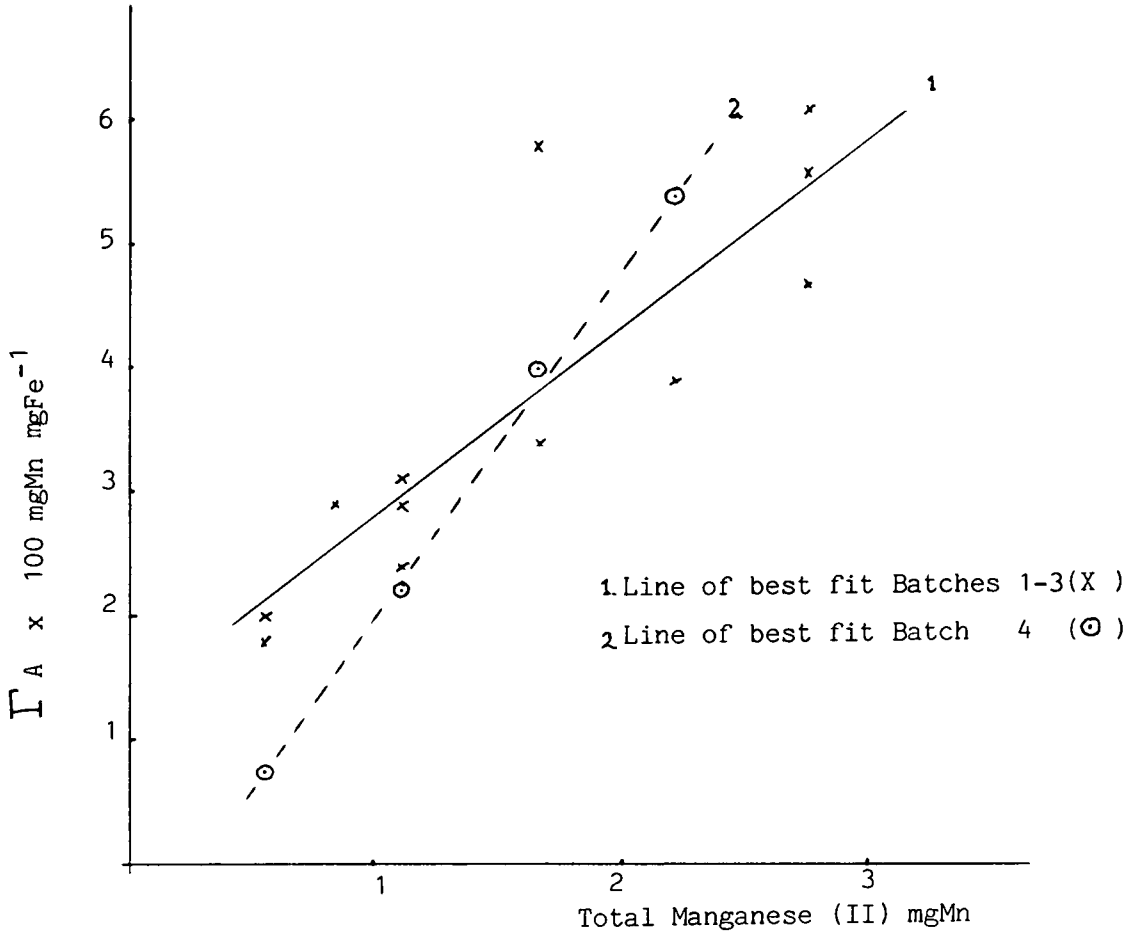
The independence of adsorbed manganese from the oxide concentration appears to apply only to the limited range of concentrations used in Experiment 8. The control data obtained in Batch 4 of Experiment 9, which used a much lower oxide concentration, is displayed in Figure 12 and exhibits a significantly lower slope than data from Experiment 9. This difference in slope is discussed later.

Experiment 9 was carried out in order to determine whether precipitation of iron (III) oxide in the presence of dissolved manganese (II) gave different manganese removal to that observed in Experiment 8. Experiment 9 more closely resembles the conditions in water treatment plant. In view of the known unstable surface properties of freshly precipitated iron (III) oxide<sup>27</sup>, the experiment was repeated three times. In a fourth batch a control experiment was carried out using similar iron(III) oxide concentrations, precipitated prior to addition of manganese (II). In Figure 14, the plot of adsorption ratio against total manganese confirms highly erratic removal of manganese for the same levels of adsorbent and sorbate. A possible cause of the erratic results became apparent while carrying out the experiment. It was extremely difficult to add the alkali in a reproducible manner that achieved a gradual rise in pH and precipitation of the iron (III) oxide. After pH 6 - 7 had been reached, even dropwise addition of alkali tended to cause transient peaks in pH of 9 or 10. It is assumed that below pH 6, the alkali is mainly used to neutralise the acid present in the solution. This neutralisation is practically instantaneous. Above pH 6, oxidation becomes more significant and acidity is produced by the relatively slow release of protons in oxidation and hydrolysis. Thus addition of alkali caused pH peaks, which are reduced by slow release of protons. Adsorption is obviously enhanced by pH peaks and this also causes a relatively slow release of protons. A variable degree of co-precipitation or occlusion of manganese (II) carbonate may also occur at high pH. The transient peaks in pH are considered to be of potential relevance in water treatment plant operation. It has been observed that in a simple batch experiment, it is difficult to ensure a steady rise in pH to the chosen level of pH 8. It is, therefore, assumed that in a flow system, with an outlet pH of 8.0 there must be



Figure 14

Adsorption ratio  $\Gamma_A$  vs Total Manganese (II)  
at pH 8.5 and 10°C

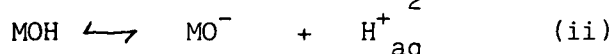


transient zones of high pH arising from the slow release of protons in iron oxidation. Additional peaks in pH will be superimposed by (i) relatively slow release of protons arising from adsorption of manganese (II) and (ii) localised high concentration of alkali in the region of the dosing point.

It is difficult to deduce from Figure 14 whether manganese removal is altered when iron (III) oxide is precipitated in situ. The difference in slope of lines 1 and 2 almost certainly lies within the experimental error of batches 1 - 3 in Experiment 9. The slope of the plot for batch 4, relative to the slope observed at pH 8.5 in Figure 12, has already been noted and is discussed later.

In Experiment 10, the effect of pH and temperature on adsorption were studied. Figure 15 indicates that manganese (II) adsorbed at pH 8.0 is almost completely desorbed at pH 4.0 from iron (III) oxide and at pH 2.0 from manganese (IV) oxide. There is some uncertainty in the data for manganese (IV) oxide, which is attributed to partial dissolution of the oxide at low pH. These observations lend qualitative support to the approximate fit to the Langmuir Equation for adsorption at pH 8.0, as displayed in Figures 5 and 8. At pH 8.0 the adsorbed manganese (II) is not oxidised and adsorption is reversible. The results for procedure (3) of Experiment 10 confirm that after adsorption at pH 9.0, a fraction of the manganese is not desorbed at pH 4.0. This supports the hypothesis that oxidation of manganese (II) has taken place. The limited study of the effect of temperature shows that adsorption increases by only 4% as the temperature rises from 10° to 25°C. For this reason, later experiments were made without stringent temperature control.

The relationship between manganese (II) adsorption and pH is most easily explained in terms of the relationship of solution pH to the pH of zero point of charge (ZPC). The ZPC of a system is the pH at which there is no net charge on the species of interest<sup>29</sup>. In an aqueous suspension of hydrated oxides, it may be considered that electrical charge at the oxide surface is derived from the following interactions between solid and solute.



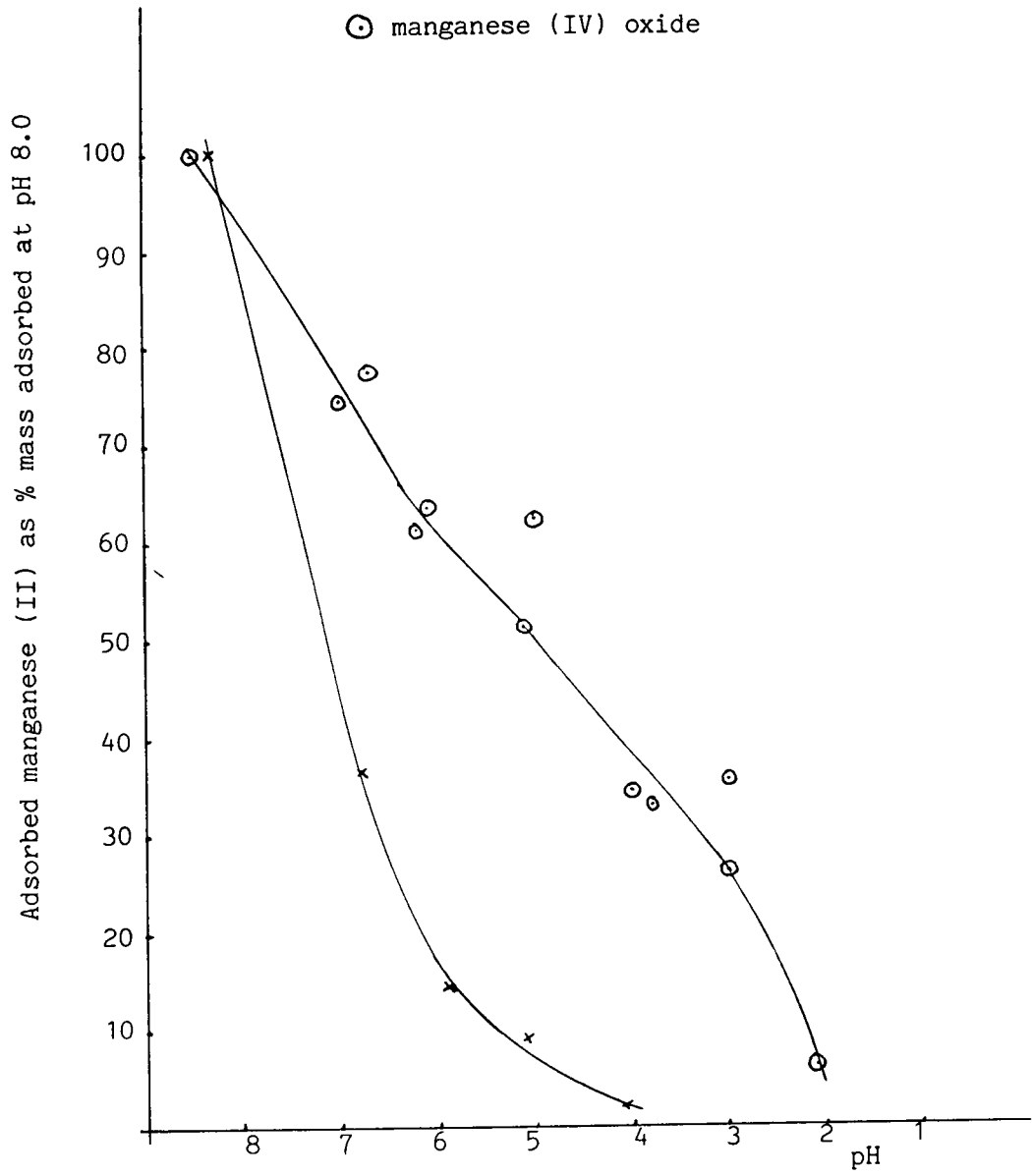
Thus, (i) represents protonation of surface hydroxide groups giving a positively charged surface. (ii) represents dissociation of surface hydroxide groups, giving a negatively charged surface. pH, therefore, determines the surface potential. At ZPC the net surface charge is zero and

Figure 15

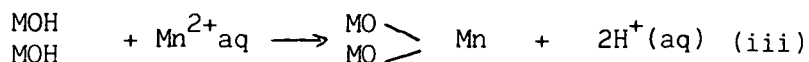
Adsorbed manganese (II) v.s. pH

× iron (III) oxide

⊙ manganese (IV) oxide



above ZPC, the surface charge becomes increasingly negative. The Gouy-Chapman<sup>30</sup> theory of the electrical double layer assumes that a negative surface charge is balanced by an accumulation of positive ions in a diffuse layer adjacent to the surface. Non specific adsorption of cations is treated as concentration of cations in this diffuse layer. Thus adsorption capacity for cations increases as pH increases above ZPC. Parks<sup>29</sup> has pointed out that adsorption of cations below ZPC i.e. adsorption against coulombic attraction, can only arise from a specific adsorption interaction between adsorbent and sorbate. Reaction (iii) represents specific adsorption via a surface reaction.



Parks<sup>29</sup> has also shown that in the presence of a high concentration of a specifically adsorbed cation, the pH dependence of adsorption is reduced. The ZPC for hydrated manganese (IV) and iron (III) oxides have been cited as 2.8 and 8.5 respectively<sup>29</sup>. In procedures (i) and (ii) of Experiment 10, it is noted that manganese (II) is adsorbed below pH 8.5 on iron (III) oxide i.e. specific adsorption has occurred. This observation raises the possibility that both specific and non-specific adsorption may contribute to the interaction between manganese (II) and iron (III) oxide.

The preceding observations are considered to explain the trends displayed in Figure 12. The data from Experiment 8 indicates that manganese (II) adsorption does not increase significantly as pH rises from 8.0 to 8.5 and increases by only 20% as the pH rises from 8.0 to 9.0. Kinniburgh et al<sup>31</sup> have reported that non-specific adsorption of strontium (II) and magnesium (II) on iron (III) oxide hydrate increases by 40% over the pH range 8.0 to 9.0. The contribution of specific adsorption may therefore explain the reduced sensitivity of adsorption to pH change, observed in Experiment 8. The data obtained in Batch 4, in Experiment 9, when compared with data obtained in Experiment 8 shows almost 70% less adsorption of manganese (II) at pH 8.5. Furthermore, zero adsorption is indicated for a positive concentration of manganese (II). Experiment 9 was carried out using manganese (II) concentrations approximately ten times lower than those employed in Experiment 8. It is, therefore, assumed that at lower manganese (II) concentrations, there is a transition from specific adsorption to non specific incorporation into the diffuse double layer. As non specific adsorption is zero at ZPC, the data from Experiment 9, which was obtained at the approximate ZPC of iron (II) oxide, shows zero adsorption, below a certain concentration of sorbate.

Experiment 11 was carried out to determine whether changes in composition of manganese (II) bearing water affect the adsorption ratio. It was assumed that calcium and magnesium ions, typically present in combined excess of twenty fold, might compete with manganese (II) for adsorption sites. Within experimental error, it is not possible to distinguish any effect of variation in calcium and magnesium levels on manganese (II) adsorption. The experimental error is significant, with between 10% and 25% difference in duplicate tests. This error is ascribed to factors discussed in Experiment 9. Increase in ionic strength does, however, significantly affect the adsorption ratio. The adsorption ratio approximately doubles for a fourfold increase in ionic strength. The range of ionic strengths used in this experiment greatly exceeds the variation in natural manganese bearing water. In such waters, the ionic strength lies in the range 0.05 to 0.10 M. It is, therefore, concluded that, in natural water, only the concentrations of iron and manganese species will significantly affect the adsorption of manganese (II) on iron (III) oxide. The results of Experiment 11 suggest that manganese (II) is specifically adsorbed, even in the presence of high concentrations of alkaline earth metals. Morgan and Stumm<sup>28</sup> have suggested that metal ions with strong tendencies to form hydroxo complexes are preferentially incorporated into a hydrous oxide structure. Thus the adsorption ratio of the less hydrolysable ions, calcium and magnesium is lower. The observed effect of ionic strength is in accordance with the Gouy-Chapman<sup>30</sup> theory of the electrical double layer. This theory predicts that at high ionic strength, the thickness of the double layer decreases and at a given pH, the surface charge rises. Thus cations are adsorbed more strongly at high ionic strength.

### 3.3. Oxidation of manganese (II) adsorbed on iron (III) oxide hydrate

The apparatus used in Experiment 12 was designed so as to simulate a section of a floc blanket. It was considered that a particularly important feature was to maintain constant pH throughout the experiment. This feature was selected after studying pH conditions within a floc blanket clarifier. It was noted that, except in the region of chemical dosing points, pH changes were gradual, with only an 0.2 pH change throughout the floc blanket. It was therefore assumed that the flow into the floc blanket has sufficient alkalinity and buffer capacity to neutralise protons released during adsorption and oxidation. Preliminary trial experiments established that unless constant pH was maintained, the rate of oxidation declined rapidly. In order to monitor the dissolved oxygen consumption, it was necessary to carry out the experiment in apparatus completely filled, so as to exclude air.

After establishing the oxygen consumption characteristics of the sensor, the rate of consumption by the iron (III) oxide floc was determined. It was noted that 0.2 mg of oxygen per hour were consumed and that this rate was substantially constant over the pH range 7.5 to 8.5. This consumption was initially attributed to oxidation of manganese (II), adsorbed from the trace quantity present in tap water. However, as later findings indicated that this consumption should be pH dependent, it was assumed that the consumption arose from weak adsorption of oxygen on iron (III) oxide. The pH at which manganese oxidation became significant was then determined. The onset of oxidation was clearly indicated by a sudden drop in dissolved oxygen level. This occurred when the pH was raised from 8.0 to 8.5. This finding supports the observation of a colour change at pH 8.5 during adsorption of manganese (II) on iron (III) oxide, as noted in Experiment 8. The dissolved oxygen consumption characteristics for several concentrations of iron (III) oxide and manganese (II) are displayed in Figure 16. An initial rapid decrease in dissolved oxygen concentration is observed in all procedures. In procedure (3) a mass of magnesium (II), equivalent to the manganese (II) mass, was added in an attempt to influence the adsorption ratio, and thus obtain information about the reaction mechanism. In the calculations of Experiment 12, various possibly relevant parameters have been tabulated and examined to facilitate comparison of the results of different procedures.

Figure 16

Dissolved oxygen v time

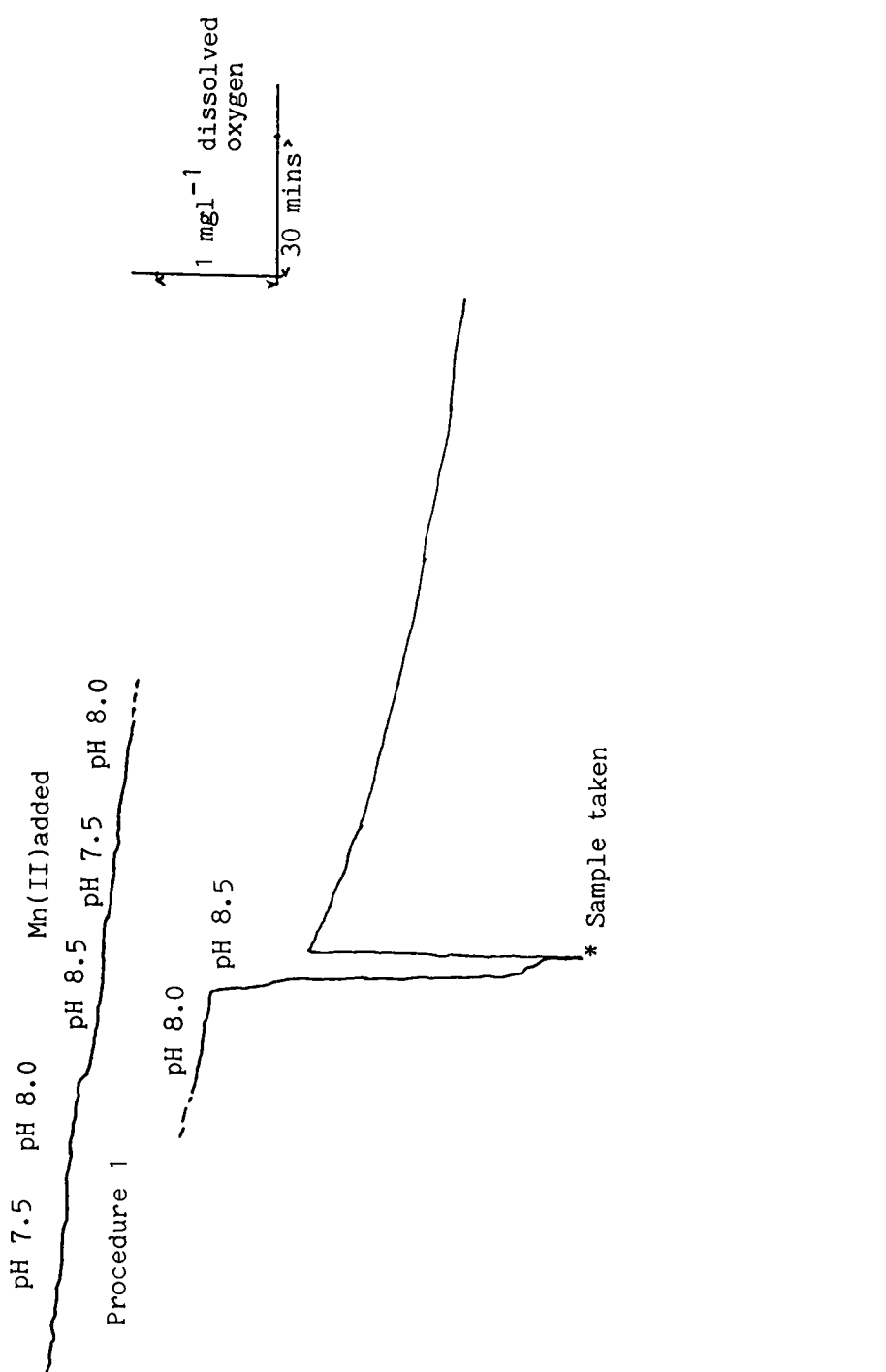


Figure 16 (continued)

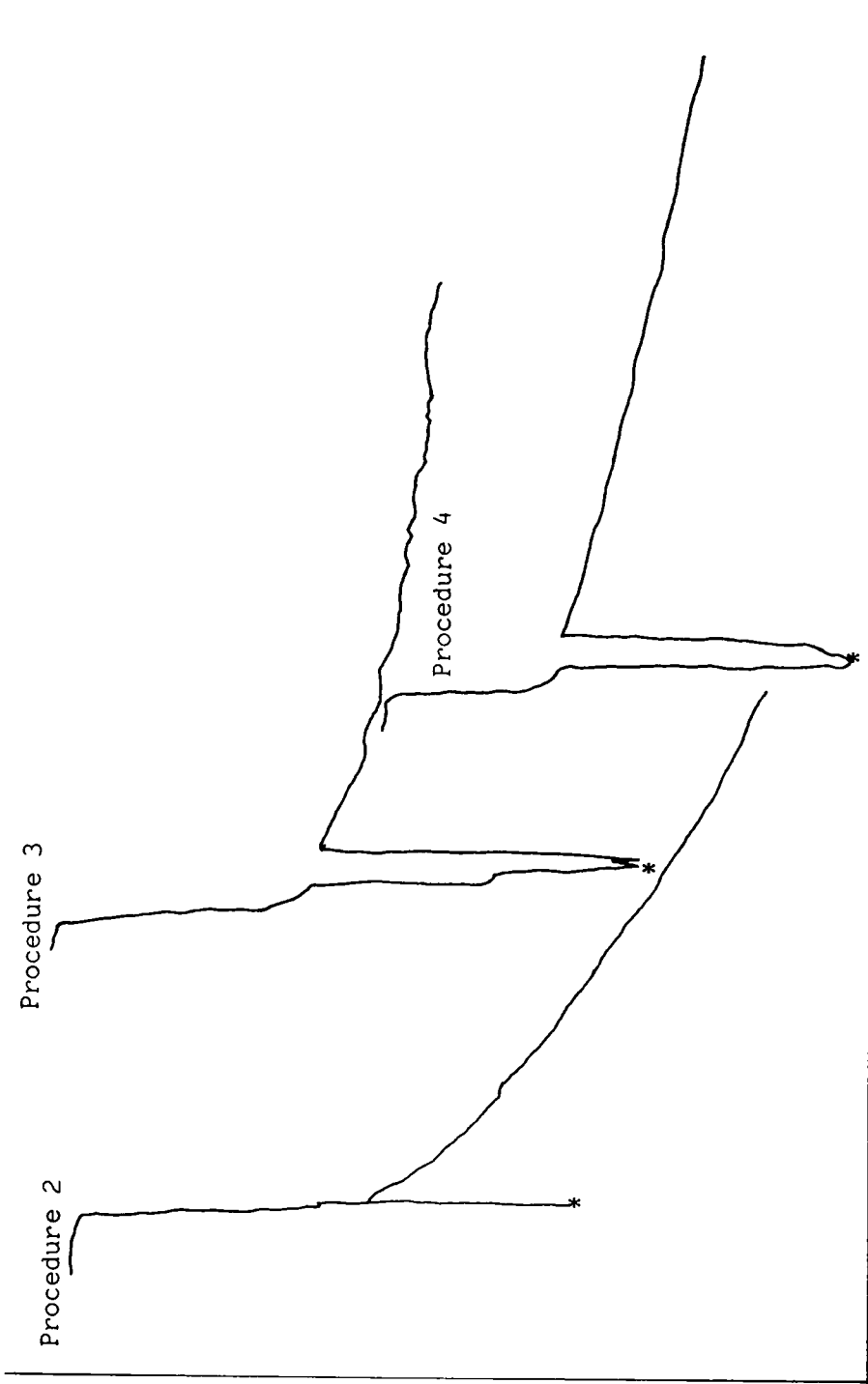
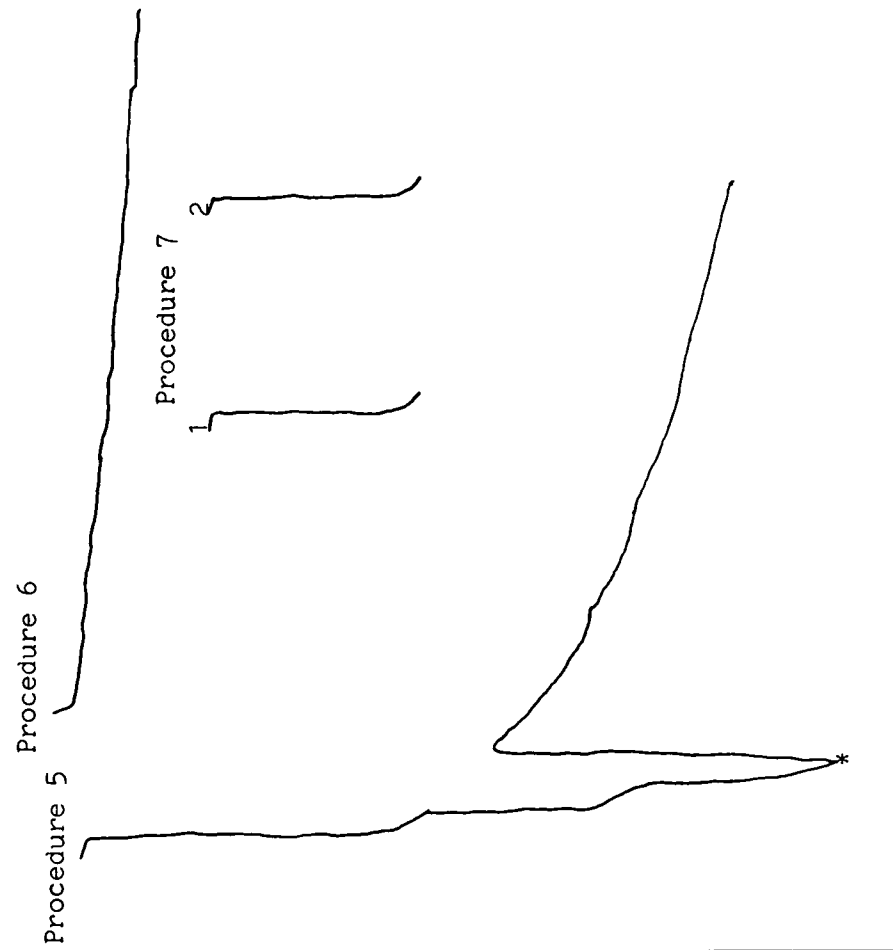




Figure 16 (continued)



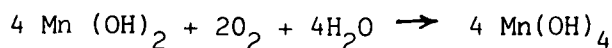
The initial rapid drop in dissolved oxygen, observed for all procedures, is of particular interest. The drop was not observed on iron (III) oxide alone and the initial interpretation was that the oxygen was selectively adsorbed onto manganese (II). Even if this were the case, it does not explain the pH dependency of the drop in dissolved oxygen. Oxygen molecules are uncharged and are presumably not affected by the variation in surface charge with solution pH. Furthermore, if adsorption were the explanation, it would be reasonable to expect a correlation between the total manganese, the initial adsorbed manganese and the drop in dissolved oxygen. This correlation is not observed. An attempt was then made to incorporate a surface concentration factor into the relationship and in Figure 17, the dissolved oxygen drop is plotted against the ratio of initial adsorbed manganese to total iron. This graph shows good correlation. It is therefore proposed that the drop in dissolved oxygen, which initiates the oxidation of manganese (II), arises from the chemical reaction with manganese (II) hydroxide, precipitated at the surface of the iron (III) oxide. This precipitation would be strongly dependent on the hydroxyl and manganese (II) ion concentrations at the oxide surface, which are dependent on the surface area of adsorbent. The oxygenation kinetics of pure manganese (II) hydroxide do not appear to have been studied. However, empirical observations in the Winkler<sup>19</sup> Test for dissolved oxygen, which may be represented:-



$$220\text{g Mn} + 32\text{g O} \quad \text{ratio Mn:O} = 6.9$$

indicate that the reaction is practically instantaneous in water.

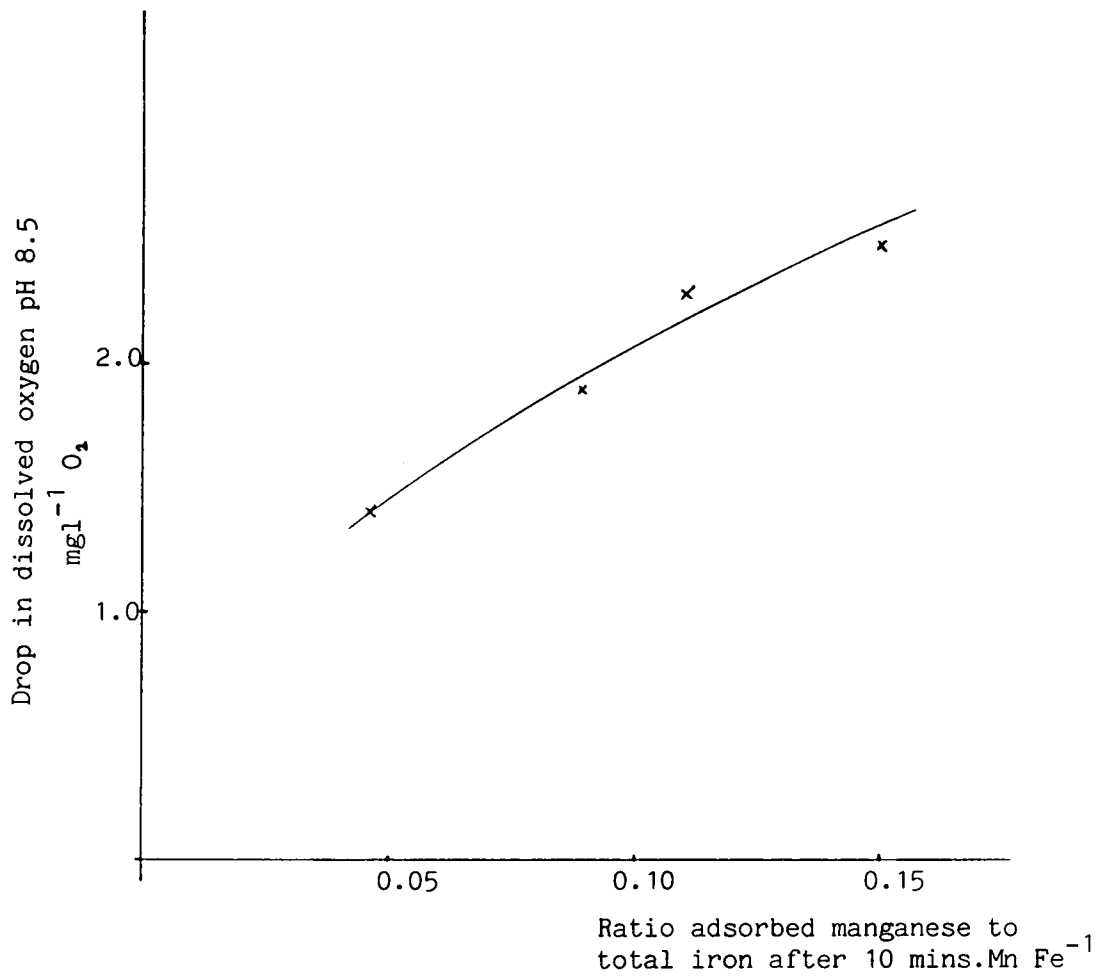
In procedure (7), the ratio of manganese to oxygen, combined in the initial product of manganese (II) oxidation, was determined. The ratio was calculated to be approximately 6.1. This ratio may be compared with 6.9 for oxidation to manganese (III) and 3.4 for oxidation to manganese (IV). These results provide strong evidence that the initial reaction product of manganese (II) oxidation is a manganese (III) oxide. The slightly higher proportion of oxygen, as found in procedure (7), is presumed to arise from continued oxidation to manganese (IV) oxide, or from adsorption of oxygen onto the manganese (III) oxide.



The formation of a manganese (III) or (IV) hydroxide is purely hypothetical and Kessick and Morgan<sup>14</sup> have suggested that  $\text{Mn(OH)}_3$  loses water to give  $\text{Mn OOH}$ .

Figure 17

Dissolved oxygen drop at pH 8.5 vs Ratio of adsorbed manganese to total iron after 10 mins.



Inspection of the percentage removal of manganese from solution tabulated in Experiment 12, indicates that the removal process is a first order reaction. It is observed that the % removal is sensibly independent of the initial manganese concentration. It is not possible to draw any firm conclusions about the reaction mechanism from the data presented. There appears to be a positive correlation between manganese in solution after ten minutes and the subsequent rate of removal of dissolved oxygen. However, as manganese in solution is directly proportional to adsorbed manganese, a positive correlation is also observed between adsorbed manganese after ten minutes and the subsequent rate of removal of dissolved oxygen. The effect of adding the magnesium salt in procedure 3 has altered the manganese adsorption ratio, although not to decrease it, as was intended. The manganese adsorption ratio has increased and this is presumed to arise from the effect of increased ionic strength, as noted in Experiment 11. If procedures 1 and 3 are compared in dissolved manganese after 10 minutes and subsequent rate of removal of dissolved oxygen, it appears that a decrease in dissolved manganese is accompanied by a decrease in oxygen consumption. However, as the ionic strengths of the two procedures were different, it is not possible to accept this observation as definite evidence that dissolved manganese(II) is the reacting species. Graveland and Heertjes<sup>16</sup> have suggested that manganese reacts in the dissolved state. Their conclusion was based on the increased rate of reaction when manganese (II) is displaced from adsorption sites by sodium in sodium hydrogen carbonate solution. However, as they have also shown that rate of reaction increases with bicarbonate alkalinity, their conclusion may not be justified. Any attempts to extrapolate laboratory data to plant scale performance must take account of three manganese removal mechanisms:-

- i) Adsorption of manganese (II) onto iron (III) oxide.
- ii) Oxidation of adsorbed manganese (II) to a manganese (III) oxide at the iron (III) oxide surface.
- iii) Adsorption of manganese (II) onto the manganese (III) oxide and subsequent oxidation.

The overall effect of (i) to (iii) is that the longer adsorbed manganese is retained in the floc blanket, the greater the manganese removal characteristics of the blanket will become. An equilibrium will eventually be established by the need to maintain a constant mass of floc by periodically discharging solids from the floc blanket.

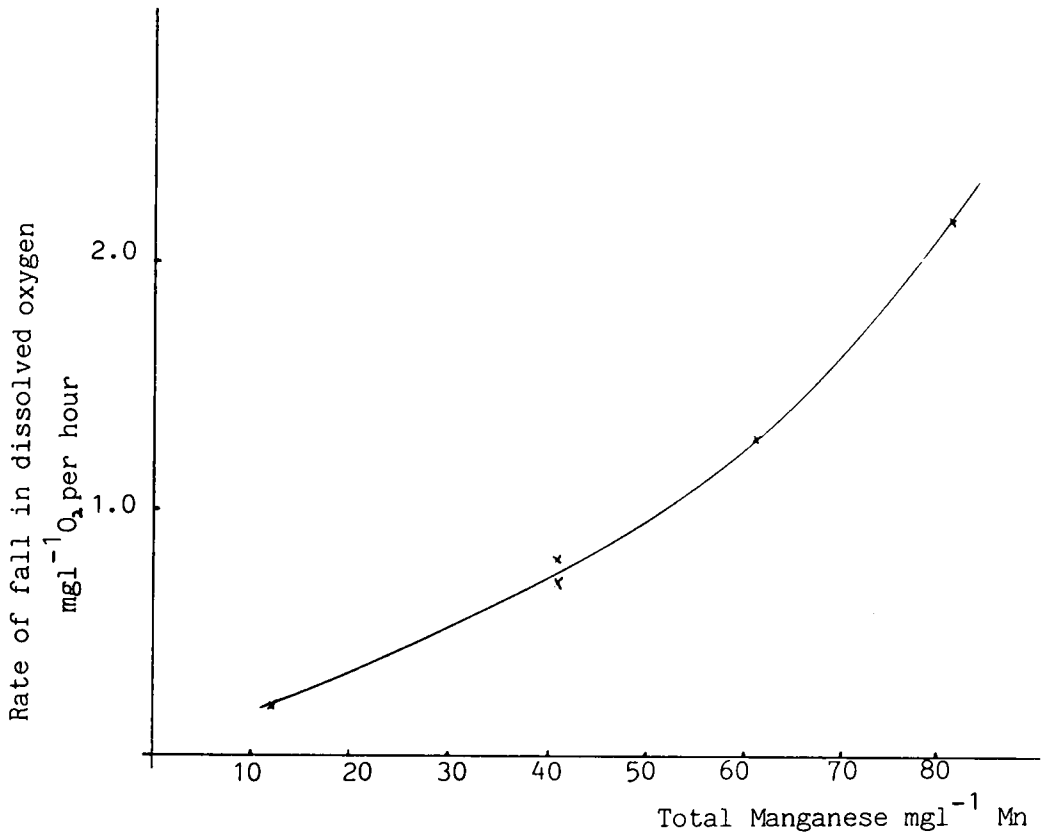
It would now appear unwise to extrapolate the results of a laboratory batch experiment in an attempt to predict the kinetics of a plant scale flow system. Thus, without resorting to at least pilot plant scale tests, it will not be possible to achieve the objective of determining an upper limit for manganese removal in high rate clarifiers. It is reasonable, however, to establish a criterion for manganese removal by oxidation to proceed i.e.

- Rate of oxidation of adsorbed manganese must exceed the rate of loss of adsorbed manganese in solids discharged from the floc blanket.

If this condition is achieved then the concentration of manganese oxides in the floc blanket will increase. The rate of oxidation of adsorbed manganese may be estimated from a plot of total manganese against rate of consumption of dissolved oxygen. This is plotted in Figure 18, although it should be noted that this data was obtained at 20°C and not at a typical plant operating temperature of 15°C. The rate of loss of adsorbed manganese requires the concentration of adsorbed manganese on iron (III) oxide and the rate of discharge of suspended solids from the floc blanket. The former information may be estimated from Figure 12 and the latter would be provided by the plant supplier.

Figure 18

Total Manganese (Initial dissolved Manganese) vs rate of fall in dissolved oxygen.



CONCLUSIONS

AND

RECOMMENDATIONS FOR FURTHER WORK

4. Conclusions and suggestions for further work.

The removal of dissolved manganese in water treatment floc blanket clarifiers has been studied. The removal mechanisms may be broadly classed as adsorption and oxidation. Adsorption of manganese (II) occurs rapidly and is completed in less than five minutes under conditions prevailing in a floc blanket clarifier. The extent of adsorption is determined by pH, iron and manganese concentrations. Manganese adsorption is relatively insensitive to the concentration of other cations and anions present in natural water, although large increases in ionic strength increase the adsorption ratio. As pH and manganese concentrations increase, there appears to be a transition from non specific to specific adsorption of manganese. Indeed specific adsorption would appear to be the precursor of oxidation of adsorbed manganese. Specifically adsorbed manganese is oxidised at the iron(III) oxide surface when solution pH approaches 8.5. The initial reaction product is presumed to be a manganese (III) oxide. The extent to which these removal processes contribute to manganese removal at plant scale will depend on the retention time of both liquid and solid components of flow within the clarifier, as well as clarifier pH. The retention time of solids in the floc blanket is considered to be particularly critical. If adsorbed manganese is discharged from the floc blanket at a higher rate than it is oxidised, then the contribution of oxidation to manganese removal will be insignificant.

The following areas would appear to warrant further study:

- (1) The effect of temperature on removal of manganese (II) from solution.

This would obviously have some direct relevance to the operation of manganese removal plants, following seasonal changes in



temperature. It is also possible that repeating Experiment 12 at 10°C would provide further information about the reaction mechanism . A weak dependence of manganese (II) removal and oxygen consumption on temperature would point to a diffusion controlled reaction. Strong dependence of these parameters on temperature would point to a reaction controlled purely by rate of chemical reaction.

(2) Pilot Plant Studies.

The use of batch conditions inhibits quantitative extrapolation of laboratory data to plant scale performance. By carrying out Experiment 12 under flow conditions at pilot plant scale, it might be possible to test quantitatively the criterion for manganese removal that has been suggested above.

## APPENDIX

### Effect of ionic strength on equilibrium constants relating to manganese (II) solubility.

#### Summary

Davies' Equation<sup>23</sup> is used to correct thermodynamic constants for the effect of ionic strength arising from a dilute mixture of strong electrolytes. The stoichiometric constants so calculated are then used to plot the variation in manganese (II) solubility with pH for a fixed concentration of dissolved carbonic species.

#### Davies' Equation

$$pK_{so} = p^c K_{so} + (nz_m^2 + mz_n^2) \left( \frac{0.5 \sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

where  $pK_{so}$  = Stoichiometric constant.

$p^c K_{so}$  = Thermodynamic constant.

$z$  = Charge on reacting species.

$m, n$  = Number of reacting atoms.

$I$  = Ionic strength.

Then using the notation given for Equation 10 and assuming an ionic strength of 0.0064M:

$$\begin{aligned} \text{for } \text{MnCO}_3(\text{s}) \rightleftharpoons \text{Mn}^{2+} + \text{CO}_3^{2-} \quad pK_{so} &= 10.41 + 8 \left( \frac{0.5 \sqrt{0.0064}}{1 + \sqrt{0.0064}} - 0.3 \times 0.0064 \right) \\ &= 10.69 \end{aligned}$$

$$K_{so} = 4.9 \times 10^{-10}$$

$$\begin{aligned} \text{for } \text{MnCO}_3(\text{s}) + \text{H}^+ \rightleftharpoons \text{MnHCO}_3^+ \quad pK_{so} &= 7.91 + 0.035 \\ &= 7.95 \end{aligned}$$

$$K_{so} = 89$$

For  $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$ , the equilibrium constant has been corrected for ionic strength, using the procedure recommended by Larson and Buswell<sup>33</sup>.

$$pK_{so} = p^c K_{so} - \frac{2 \sqrt{I}}{1 + 1.4 \sqrt{I}}$$

hence

$$pK_{so} = 10.32 - 0.14 = 10.18$$

$$K_{so} = 1.51 \times 10^{-10}$$

Substitution in Equation 1 for  $C_t = 0.0013$  M at the following pH values gives:

$$\text{pH 9 Mn(II)dissolved} = \frac{10^{-9} \times 4.9 \times 10^{-10}}{0.0013 \times 1.51} - 10 + 89 \times 10^{-9}$$

(The second term of Equation 1 is insignificant and has been ignored.)

$$= (2.496 \times 10^{-6}) + (0.089 \times 10^{-6}) \text{ M}$$

$$= 2.585 \times 10^{-6} \text{ M}$$

$$= 0.142 \text{ mg l}^{-1}$$

and by similar calculation:-

pH 8.0	Mn(II) dissolved	=	1.42 mg l <sup>-1</sup>
pH 7.5	Mn(II) dissolved	=	4.34 mg l <sup>-1</sup>
pH 7.0	Mn(II) dissolved	=	14.2 mg l <sup>-1</sup>
pH 6.5	Mn(II) dissolved	=	43.4 mg l <sup>-1</sup>

This data has been plotted in Figure 2.

## REFERENCES

1. "International Standards for Drinking Water". 3rd Edn. World Health Organisation, Geneva 1971, p 40.
2. Ridgway R., Ainsworth R.E., Gwilliam R. "Water Distribution Systems. Maintenance of Pipeline Integrity". Water Research Centre. Medmenham 1978, p 5.
3. "Handbook of Chemistry and Physics". 55th Edn. C.R.C. Press, Cleveland, U.S.A. 1974.
4. "The Aquazur Filter". Degremont Laing, London 1975.
5. Twort A.C., Hoather R.C., Law F.M. "Water Supply". 2nd Edn. Edward Arnold. London 1974, p 238.
6. Idem Ibid p 228.
7. Gregory R. "Technical Report III, Floc Blanket Clarification." Water Research Centre. Medmenham 1979, p 18.
8. "The Super Pulsator". Degremont Laing, London 1975.
9. Green L.A. "The Problems of Iron and Manganese in Water Supply." British Waterworks Association. London 1970.
10. Bolas P. J. Inst. Water Engrs. 1965, 9, 531.
11. Stumm W., Lee G.F. Indust. Eng. Chem. 1961, 53, 143.
12. Camp T.R., Root D.A., Bhoota B.V. J. Am. Water Works Ass. 1940, 32, 1913
13. Morgan J.J. in Faust S.D., Hunter J.V. Editors "Principles and Applications in Water Chemistry". Wiley, New York 1967.
14. Kessick M.A., Morgan J.J. Envr. Sci. Tech. 1975, 9, 157.
15. Stumm W., Morgan J.J. "Aquatic Chemistry". Wiley, New York 1970, p 534
16. Graveland A., Heertjes P.M. Trans. Inst. Chem. Engrs. 1975, 53, 154.
17. Morgan J.J. and Stumm W. J. Am. Water Works Ass. 1965, 57, 107.
18. "Analytical Methods of Atomic Absorption Spectroscopy". Perkin Elmer. Norwalk, Connecticut, U.S.A. 1973.
19. "Analysis of Raw Potable and Wastewater". HMSO, London 1972.
20. Partington J.R. "Textbook of Inorganic Chemistry". 6th Edn. McMillan, London 1953, p 902.
21. Langmuir J. J. Am. Chem. Soc. 1918, 40, 1361.

22. Gregory D, Ward H. "Statistics for Business". McCraw-Hill(UK)1974,  
p 105.
23. Stumm W, Morgan J.J. "Aquatic Chemistry". Wiley, New York 1970,p 83.
24. Davison A, Swales G.M. in "Effects of Storage on Water Quality".  
Water Research Centre. Medmenham 1975, p 39.
25. Campbell H.S., Turner E.D. presented at Institution of Water  
Engineers and Scientists Annual General Meeting,London, March 1980.
26. Nielsen A.E. "Kinetics of Precipitation". Pergammon,London 1964,  
p 97.
27. Swallow K.C., Hume D.N. Morel F.M.M. Envir.Sci.Tech. 1980,14,1327.
28. Morgan J.J., Stumm W. J.Colloid Sci. 1964, 19, 347.
29. Parks G.A. in "Equilibrium Concepts in Natural Water Systems.  
Advances in Chemistry Series No. 67". American Chemical Society,  
Washington D.C. 1967, p 121.
30. Moore W.J. "Physical Chemistry". 5th Edn. Longman, London 1974,  
p 510.
31. Kinneburgh D.G., Jackson M.L. Sayers J.K. Soil. Sci. Soc. Am.J.  
1976, 40, 796.
32. Moore W.J. "Physical Chemistry". 5th Edn. Longman,London 1974
33. Larson T.E., Buswell A.M. J.Am. Water Works Ass. 1942,34, 1667.