ARSENIC ADSORPTION FROM GEOTHERMAL WATER

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Abstract

previous studies of arsenic adrorption have often identified a discrepancy between observed ***and*** *theoretically predicted arsenic behaviour in fresh* ***and*** *marine waters;* ***a*** *discrepancy which* ***also*** *occurs in geothermal bore waters. On the basis of published experimental data and model predictions using MINTEQA2, complete arsenic adsorption onto hydrous Fe-oxide (HFO)* ***may*** *be expected under optimum pH and* ***HFO*** *concentrations. Experimental adrorption of both As^{III} and As^{V} from the bore water of Wairakei Flashplatit 10 showed that both As^{III} and As^{V} were rapidly adsorbed onto* ***HFO.*** *However, only As^{V} at pH <5 approached the 90% adrorption predicted by MINTEQA2. At pH <9, As^{III} adsorption was consistently $<50\%$ of the predicted value, while As^{V} adsorption ranged from 33-* ***95%*** *of the predicted value. It* **is** *tentatively concluded that theoretically calculated As adrorption fails to correctly account for either the changes in* ***HFO*** *surface potential and/or bonding site competition which* ***arises*** *through the adrorption of major* ***ions,*** *or for the effect of dissolved arsenic complex formation.*

1. INTRODUCTION

The Wairakei Geothermal field in New Zealand discharges a bore water which routinely carries arsenic concentrations of *ca.* **4** mg/kg. **This** bore water is discharged into the Waikato River and, at a time when international limits for arsenic concentrations in drinking water are being steadily lowered (eg., WHO, **1993),** arsenic removal prior to discharge is desirable. Arsenic removal by adsorption onto hydrous iron oxide (HFO) is an option which has previously been investigated **in** field trials by Buisson et **al (1979)** and Finlayson & Webster **(1989)** and is currently being re-examined. **As** part of this project, ESR was requested to undertake an experimental study of the oxidation and adsorption **rates** of arsenic in Wairakei bore effluent. **This** provided an opportunity to compare theoretically-predicted with observed arsenic adsorption behaviour in an arsenic-rich system.

In theory, many aspects of arsenic chemistry and adsorption characteristics are relatively straightforward. **In** most natural aqueous systems, arsenic occurs predominantly in either an As^{III} or As^{V} oxidation state and **as** negatively charged ion species ($H_2AsO_3^-$, $H_2AsO_4^-$, $HAsO_4^{-2}$), with the exception of an uncharged As^{III} species ($H_3AsO_3^0$). The oxidation of As^{III} to As^{V} is slow in near-neutral pH waters unless catalyzed by bacteria, but the adsorption chemistry of both oxidation states is similar (eg., Pierce & Moore, **1982).** Both As^{III} and As^{V} are readily adsorbed onto hydrous oxides in natural waters and, **as anions,** adsorb more readily at acid pH. Arsenic can therefore be preferentially removed from effluents by .adsorption under conditions which do not favour the adsorption of other metals, such **as** copper, lead and zinc, which occur **as** cationic species **in** natural waters.

The MINTEQA2 computer program (Allison et al., **1991)** is one of the few chemical speciation models to include adsorption processes, and can be **used** to theoretically predict the degree of metal adsorption in natural systems. However, recent studies of arsenic partitioning between sediments and solution in New Zealand freshwaters and *estuaries* by the authors have demonstrated significant discrepancies between observed and theoretically predicted arsenic adsorption. Analytical results indicate that arsenic is occurring predominantly in dissolved forms, while theoretical predictions using MINTEQA2 suggest that, at near-neutral pH, most of the arsenic should be bound in the HFO-bearing particulate phase.

This paper reports the results of the recent experiments designed to test As^{III} and As^{V} adsorption from bore water onto HFO. The results are compared with the degree of arsenic adsorption predicted using MINTEQA2, highlighting some of the problems which can occur when trying to reconcile observed and theoretically predicted arsenic behaviour.

2. METHODS

2.1 Sample collection and analytical method

Six litres of bore water were collected from Flashplant 10 in February 1994. Three litres were collected into normal polyethylene sampling bottles to be used for experiments requiring As^{V}. Three litres were collected into air tight glass sampling bottles, excluding air and minimising air contact with the sample, for use in experiments requiring As''. Major ion concentrations in the bore water were determined by High Pressure Ion Chromatography. Bore water contained in the glass bottles was analyzed immediately upon opening for both total arsenic and As'': total As concentrations ranged from' 3.5 - 4.5 mg/kg *As*, of which more than 90% was As^{III}. Bore water to be used in experiments requiring arsenic as As^{V} was oxidised by the addition of 2.5 ml 30% H_2O_2 per 500 mls bore water, 7 days before use. For experiments using As^{V}, samples were analyzed for total inorganic arsenic. Samples were pre-reduced using KI and HCl then analyzed by hydride-generation atomic adsorption spectrophotometry (HGAAS), using a reaction vessel and reagents similar to those used by Aggett and Aspell (1976) to generate arsine gas (AsH_3). The gas passed through an electrically heated quartz tube, instead of a flame, placed in the optical path of the lamp.

For As^{III} analysis, the sample was not pre-reduced but was instead analyzed in a citrate buffer (pH = 6), so that only *As'''* reacted to form arsine gas. As^{V} concentrations were determined by difference. In the latter stages of the study, total *As* and As^{III} concentrations were determined using a continuous flow hydride generation system, with a flame-heated quartz tube.

2.2 Experimental methods

In a 500 ml round bottomed flask, a solution containing 0.202g $Fe(NO_3)_3.9H_2O$ was acidified with HNO_3 to pH ca. 2. The pH was then slowly raised to 7, by the addition of 1m NaOH, to precipitate amorphous HFO at a concentration of 1×10^{-3}m. The precipitate was allowed to age and settle overnight, before removing the overlying solution from the flask and refilling the flask with the bore water.

Initially adsorption experiments were run for up to 60 minutes to determine the time taken to attain equilibrium between adsorbed and dissolved arsenic species. Separate runs were made *at* pH = 5 and pH = 8 (see Fig. 1).

In addition to the runs in which pH was controlled, two further experiments were undertaken to show the relationship between arsenic adsorption and pH (see Fig. 2). From a starting point of high pH (9.1 for **As''** and 11.9 for As^{III}), pH was gradually lowered **with** consecutive additions of HNO,. After each addition the solution was allowed 30 minutes to re-equilibrate with the oxide before the next aliquot **was** extracted for analysis.

In all experiments, the 10 ml aliquots extracted from the bulk solution were immediately filtered through a 0.45 μm Millipore filter to remove any particulate iron, and were analyzed for arsenic. The bore water **used** to test **As^{III}** adsorption was re-analyzed for total arsenic at the end of the experiment to confirm that oxidation to As^{V} had not occurred.

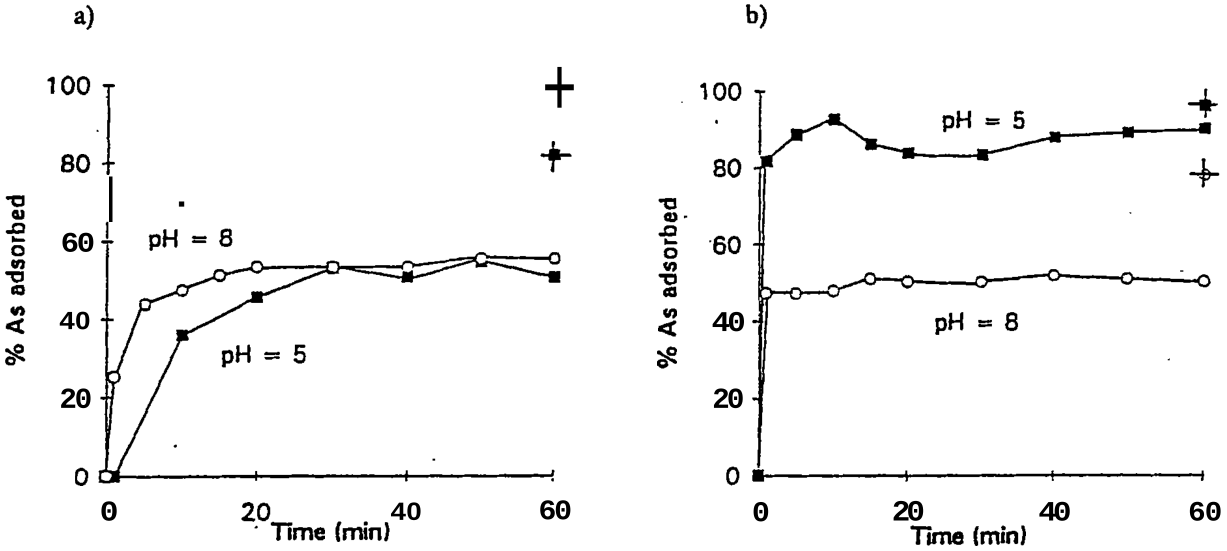

Fig. 1. Experimental **As^{III}** (a) and As^{V} (b) adsorption onto amorphous HFO at pH = 5 and 8. Initial As concentrations were As"': 3.74 mg/kg at pH = **5, 3.57mg/kg** at pH = 8, and As^{V}: 3.88 mg/kg at pH = 5 and 3.11mg/kg at pH = 8. The concentration of HFO = 1 X 10^{-3}m. Arsenic adsorption predicted by MINTEQA2 is also shown **as** -○- & -■-.

3. RESULTS

3.1 As^{III} and As" adsorption rates

The results of the As^{III} adsorption rate experiments are shown in Fig. la. At both pH = 5 and 8, As"' was adsorbed quickly but incompletely. At pH = 5, As'" adsorption increased to 36% in the first 10 minutes, settling at 50% after 30 minutes. There appeared to be no further adsorption as the solution still contained 1.85 mg/kg arsenic after 1 hour in contact with amorphous Fe oxide. At pH = 8, As^{III} adsorption increased to **44%** in 5 minutes and to 53% after 20 minutes. Again there appeared to be a no further adsorption, with 1.59 mg/kg arsenic remaining in solution after 1 hour.

The results of the As^{V} adsorption rate experiments are shown in Fig. lb. At pH = 5 and 8 As^{V} was, like **As^{III},** adsorbed very quickly. A sample taken after only one minute of contact with the oxide showed that 47% of As^{V} at pH = 8 and 89% of As^{V} at pH = 5 had been adsorbed. At both pH = **5** and 8, As^{V} concentrations in solution remained mainly unchanged after the first minute, although small fluctuations were observed with time for As^{V} adsorption at pH = 5. As^{V} concentrations vary between 0.23 mgkg and 0.57 mgkg over the period 1 minute to 1 hour, perhaps oscillating as equilibrium between the dissolved and adsorbed As" is established.

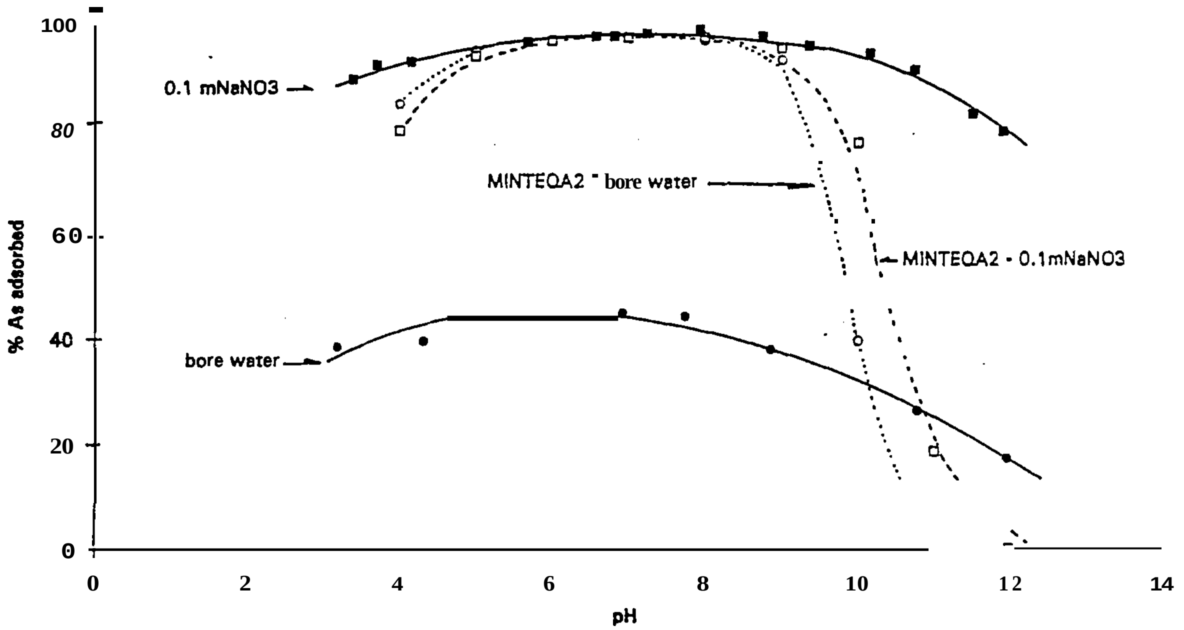

Fig. 2. As^{III} adsorption on HFO as function of pH in bore waters, as determined experimentally and as predicted by MINTEQA2. The adsorption of As^{III} from 0.1m $NaNO_3$ as determined by experiment and as predicted by MINTEQA2 is also shown. Initial As^{V} concentrations = 2.40 mg/kg and HFO concentrations = 1 x 10^{-3}m.

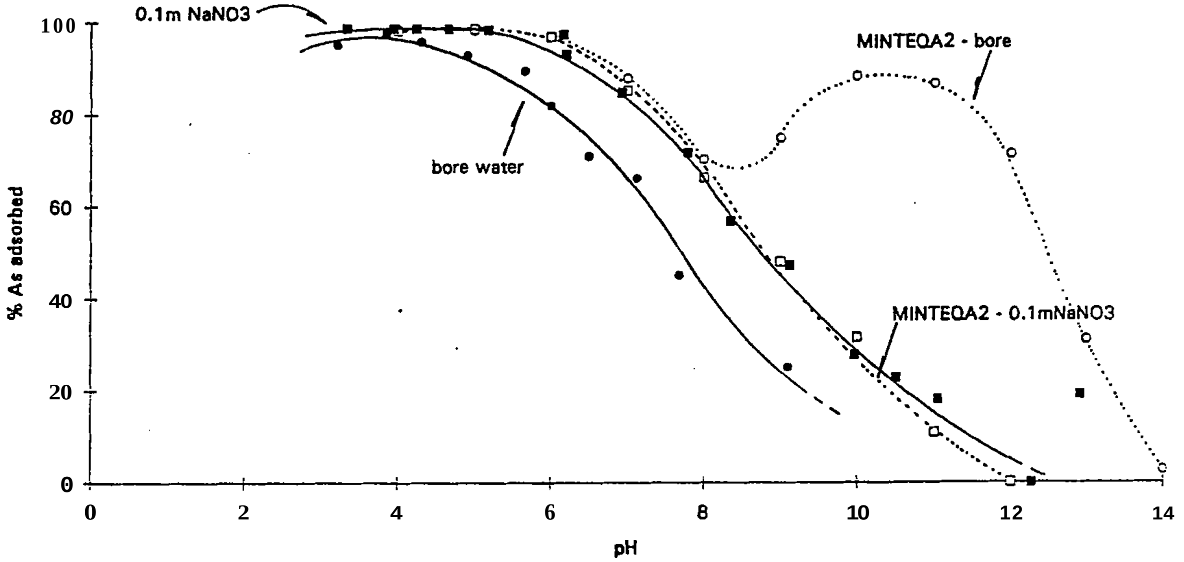

Fig. 3. As^{V} adsorption on HFO as function of pH in bore waters, as determined experimentally and as predicted by MINTEQA2. The adsorption of As^{V} from 0.1m NaNO, as determined by experiment and as predicted by MINTEQA2 is also shown. Initial As^{V} concentrations = 3.73 mg/kg and HFO concentrations = 1 x 10^{-3}m.

3.2 As''' and As^V adsorption as a function of pH

The results of As^{III} adsorption from bore water onto HFO, as a function of pH, are shown in Fig. 2, identifying optimum conditions for adsorption between pH = 4 and 8. At pH >8, A B adsorption decreases from *ca.* 45% to 17% at pH = 12 and, by extrapolation, to 0% at or near pH = 14.

The results of As^V adsorption as a function of pH are shown in Fig. 3, demonstrating a similar but more exaggerated trend. Optimum conditions for As^V adsorption are between pH = 3 and 5.5, limited at low pH by the stability of **HFO** which dissolves at pH < 3. As^V adsorption shows a linear decrease from >90% at pH = 5.5, to 25% at pH = 9. If the trend continues above pH = 9, 0 % adsorption might be expected at pH = 11.

These results confirm those of the previous adsorption rate experiments in which a high degree of arsenic adsorption was observed only for As^V at pH = **5.** Although As^V adsorption occurs more rapidly and to a greater degree **than As^{III}** under optimum pH conditions, these pH conditions evidently occur over a narrow range. Therefore, for arsenic removal from bore water, to maintain any advantage gained by oxidising arsenic to As^V, prior to removal by adsorption onto HFO, the pH of adsorption would need to be maintained at pH < 7.

4. DISCUSSION

In Figs. 1 - 3 reporting experimentally determined arsenic adsorption, the degree of arsenic adsorption predicted using MINTEQAZ is also shown. With the exception of As^V adsorption at low pH, MINTEQAZ predicts higher arsenic adsorption from bore water than observed. However, for As adsorption from 0.1m $NaNO_3$, MINTEQA2 predictions are consistent with experimental results for As^V, and for As^{III} at pH <9. Because neither Na or NO_3 ions affect arsenic adsorption, this *can* be considered to represent arsenic adsorption in the absence of interfering ions.

Neither previous experimental studies (eg., Leckie et al., 1980) nor MINTEQA2 calculations support the possible argument that the incomplete adsorption of arsenic is due to a shortage of available binding sites on the HFO, i.e., that the adsorption capacity of HFO has been exceeded. Furthermore, this difference has been repeatedly noted during the authors' previous attempts to model arsenic behaviour in freshwater and estuarine systems, where HFO is often readily available in excess of the amount required to adsorb the low levels of metals present.

To begin to solve this problem, the way in which MINTEQA2 calculates arsenic adsorption must be more closely examined.

4.1 Modelling arsenic adsorption

As previously discussed, As'' and As^V exist predominantly as uncharged or negatively charged ions in solution. As'' occurs as H_3AsO_3 (arsenious acid) which dissociates at pH = 9.3 to form $H_2AsO_3^-$. As^V occurs as $H_2AsO_4^-$ which dissociates at pH = 6.9 to form $HAsO_4^{-2}$, which further dissociates to form AsO_4^{-3} at pH = 11.5. Each of the negatively charged arsenic species can potentially bind to the HFO surface if the surface maintains a positive charge. In most freshwaters, the surface of HFO has a positive charge at pH C 7.

Experimental **studies** of arsenic adsorption from 0.01 and *0.*1m NaNO, onto HFO by Pierce & Moore (1982) and Leckie et al. (1980) have **been** used by Dzombak & Morell (1990) to derive the data which is used **as** the database for MINTEQA2. Dzombak and Morell (1990) list, and give surface complexation **constants** for, the following reactions which govern arsenic adsorption at the HFO surface (represented here **as** $\equiv \mathbf{FeOH^{o}}$**):**

For As^{III} ...

$$\equiv FeOH^{o} + H_3AsO_3^{o} = \equiv \mathbf{FeH_2AsO_3^{o}} + H_2O \tag{1}$$

For As^{V} ...

$$\equiv FeOH^{o} + H_3AsO_4^{o} = \equiv \mathbf{FeH_2AsO_4^{o}} + H_2O \tag{2}$$

$$\equiv FeOH^{o} + \mathbf{H_2AsO_4^{-}} = \equiv \mathbf{FeHAsO_4^{-}} + H_2O \tag{3}$$

$$\equiv FeOH^{o} + \mathbf{HAsO_4^{-2}} = \equiv \mathbf{FeAsO_4^{-2}} + H_2O \tag{4}$$

$$\mathbf{\equiv FeOH^{o} + AsO_4^{-3} = \equiv FeOHAsO_4^{-3}} \tag{5}$$

MINTEQAZ partitions arsenic between these HFO-bound and dissolved arsenic species on the basis of surfacecomplex and complex equilibrium constants, using the HFO-bound species to derive the total proportion of adsorbed arsenic. The activity of individual HFO-bound arsenic species in 0.1m **NaNO,** is shown in Fig. **4 as** a function of pH, in the absence of interfering ions. The presence of other ions ***can*** adversely affect arsenic adsorption in at least three ways: by complexing arsenic in solution, by competing for binding sites on HFO, and by altering the surface charge of the HFO. In bore waters of the Wairakei geothermal field, Ca appears **to** be the only ion which **can** affect arsenic adsorption in **this** way. Comparing the predicted curves for arsenic adsorption from a typical bore water and 0.1m $NaNO_3$ shown in Fig. 2 & 3, suggests that:

> - Although **SO,** adsorption appears to adversely affect As'' adsorption at low pH **(see** Fig. **2), SO,** concentrations are too low in the bore water for this **to** be a major affect.
>
> - Ca adsorption should increase As^{V} adsorption at pH > 8. As shown in Fig. **4,** the predominant surface As^{V} species at pH > 6 is $\equiv FeOHAsO_4^{-3}$, and it is the formation of this species which is enhanced by the co-adsorption of Ca. Ca adsorpt'ion alters HFO surface potential, creating a more positively charged surface to bind arsenic ions. As''' adsorption, on the other hand, does not appear to increase in the presence of Ca adsorbed onto the HFO surface.

4.2 Theory and practice

Evidently, although MINTEQAZ does allow for the effect of co-adsorption of **SO,** and Ca on As^{III} and As^{V} adsorption respectively, the difference between observed and predicted adsorption shown in Fig.s 1 - 3, remains a problem. Either **this** difference is due to co-adsorption of Ca and **SO,,** but is incorrectly modelled, or is due to some other factors inherent in natural systems which are not correctly taken into account by MINTEQA2. For example, are the data used in the arsenic database of MINTEQAZ appropriate for application to natural systems? Are there strong complexes of arsenic which are not considered? Arsenic can form covalent bonds with carbon, creating a variety of stable organic **compounds** and complexes, such **as** dimethyl arsenic. **These** species are not included in the MINTEQA2 database, but **are** also unlikely to be of importance in bore waters. Thiocomplexes of As^{III} *can* occur in sulphide-bearing **fluids** such **as** the bore waters, although relative **high** sulphide concentrations would be **required** before $H_3AsO_3°$ would cease to be the predominant arsenic species for the pH conditions of interest (Webster, 1990).

Further study will be required to identify the reason for the high degree of arsenic adsorption predicted by MINTEQA2, so that the model *can* be modified to more accurately predict arsenic behaviour. Particular attention should be paid to the effects of Ca co-adsorption **on** arsenic **adsorption** and **to** reanalysing the database used by MINTEQA2 **to** calculate arsenic speciation.

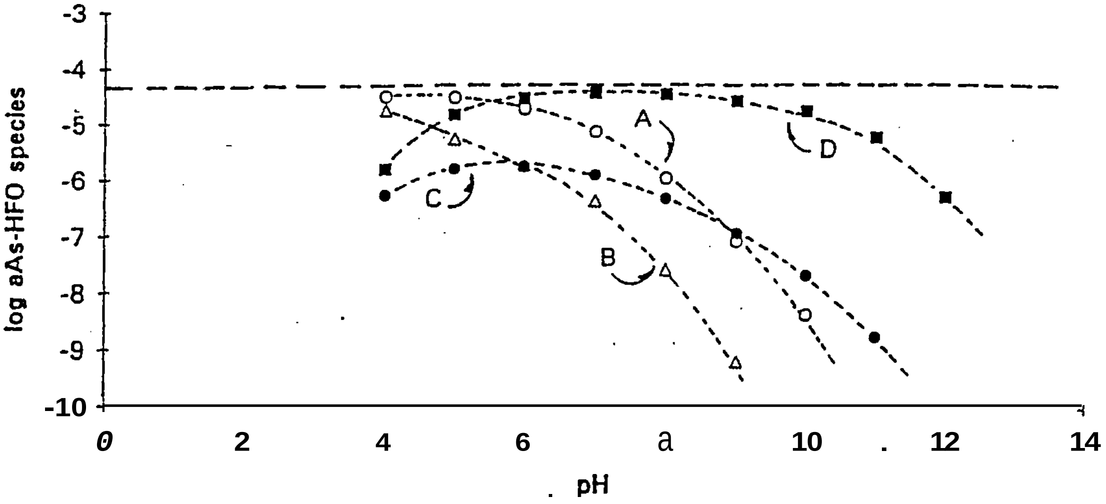

Fig. **4.** The log activity of As^V species bound at the HFO surface, **as** a function of pH in 0.1m NaNO,. $A \equiv FeHAsO_4^-$, $B = \equiv FeH_2AsO_4°$, $C = \equiv FeAsO_4^{-2}$ and $D = \equiv FeOHAsO_4^{-3}$. The horizontal dashed line represents log activity of total arsenic.

5. CONCLUSIONS

(a) Both As'' and As^V are rapidly adsorbed onto HFO at pH = **5** and pH = 8, and equilibrium conditions appear to be established in less than 30 minutes. Adsorption is, however, incomplete at *ca.* 50% of the initial arsenic concentration for all except As^V adsorption at pH = 5.

(b) The degree of **As''** and As^V adsorption onto HFO decreases with increasing pH **as** expected for anion adsorption. Optimum conditions for As^{III} adsorption are at a pH of between 3 and *9* (40 - 50% adsorption) and for As^V are pH between 3 and 6 (80 - 100%adsorption).

(c) Theoretical predictions made using MINTEQA2 significantly overestimate the degree of arsenic adsorption, particularly for As^{III}, and for As^V at pH > 8. This discrepancy has **also** been noted when modelling arsenic adsorption in freshwater and estuarine systems. It appears to be due to an error in the model predictions rather than in the analytical techniques used to determine, and to distinguish between, dissolved and particulate arsenic.

(d) It is tentatively concluded that the MINTEQA2 model is incorrectly assessing the effect of other ions on arsenic adsorption. Further study is required to identify the exact nature of this problem so that, if necessary, MINTEQA2 can be modified to more accurately predict particulate/ solution equilibria for arsenic in natural aquatic systems.

6. ACKNOWLEDGEMENTS

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