BET NITROGEN ADSORPTION STUDIES OF IRON OXIDES FROM NATURAL AND SYNTHETIC SOURCES.

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ABSTRACT

A vacuum microbalance technique has been used to obtain the surface areas and porosities of iron oxyhydroxides derived from $Fe(III)$ and $Fe(II)$ sources. The pore shape of the $Fe(III)$-derived material was of the wide-bodied, narrow-necked type, whereas the $Fe(II)$-derived precipitates were composed of parallel plates or slit-shaped pores. The surface area of the $Fe(II)$-derived material was found to be influenced by the temperature of the precipitate formation. These differences in surface character are discussed in relation to the adsorption of trace constituents at the iron oxyhydroxide-water interface.

INTRODUCTION

Many important chemical reactions in aquatic systems take place at the solid-solution interface. Thus there is an urgent need to determine the surface properties of solids as an aid to the interpretation of adsorption behaviour (ref.1). Naturally occurring iron oxyhydroxides (as precipitates or surface coatings) are known to control the partitioning of elements between the dissolved and solid phases (e.g. ref.2) and recent work has been directed toward the evaluation of their surface characteristics (refs.3-7). Of crucial importance in the partitioning process is the amount of surface available for adsorption and the pore shape/size, which can control the reversibility of the adsorption process (ref.8). Ideally the surface area studies of precipitates or particulates should be carried out *in situ*, using the adsorption of an appropriate constituent (refs.9-11). However, care must be taken when applying some of the *in situ* techniques, such as negative adsorption, since they apply only to non-porous surfaces (ref.12), which are not present in iron oxyhydroxides. The major advantage of the vacuum microbalance technique is that the nitrogen adsorption/desorption hysteresis loops for the dried solid yield valuable data on both pore shape and size. Comparable hysteresis experiments using a dissolved constituent are difficult to perform *in situ*.

In this study Fe(II)- and Fe(III)-derived materials were precipitated from

synthetic and natural solutions, under carefully controlled conditions of temperature and ph and at Fe concentrations comparable to those encountered in the environment. The solids were isolated in such a way as to retain the reticular structure of the original matrix (refs.13, 14). The data obtained here is relevant to the understanding of adsorption processes involving phosphate (refs.7, 15) and arsenate/arsenite (ref.20) at the iron oxyhydroxide-water interface.

EXPERIMENTAL

The detailed experimental procedures have been described elsewhere (ref.7). All synthetic precipitations were carried out with 30 litre samples of distilled water at pH = 7.0 ± 0.5 using a 2 mM $NaHCO_3$ buffer. The precipitations were at a controlled temperature of either 15 °C or 2 °C. The synthetic solutions contained either Fe(II) or Fe(III) salts with total iron concentrations of 1×10^{-4} M. The natural precipitates were obtained from 20 litres of natural water which was filtered through a 0.45 μm filter prior to precipitation. The relative amounts of dissolved Fe(II)/Fe(III) were measured spectrophotometrically at 5620 Å using the Ferrozine complex (ref.16). In all cases the precipitates were recovered by large volume centrifugation and washed with acetone to remove gel water from the surface and pores. This process also inhibits the ageing process and the subsequent slow drying at room temperature retains the integrity of the solid network (ref.14).

The surface areas of the precipitates were measured using about 0.1 g samples of the solid using a gravimetric BET nitrogen adsorption technique. A CI Mark 2B vacuum microbalance was used which gave μg to mg sensitivity for this amount of sample. The solids were outgassed on the vacuum microbalance at room temperature to constant weight. The nitrogen adsorption was measured in sequential steps at 77 K and the hysteresis effects were observed during desorption on reduction of the gas pressure, using equilibration times of up to one hour.

Infrared spectra of the samples were obtained using a Perkin-Elmer 257 double beam spectrophotometer, with 1-2 mg of the solid dispersed in a KBr disc. X-ray powder diffraction patterns of the precipitates were obtained from a Hilger-Watts X-ray diffractometer using MoKα radiation. The transmission electron microscopy (TEM) was carried out on a Philips 300 TEM.

RESULTS AND DISCUSSION
Synthetic precipitates

Fig. 1 shows the nitrogen adsorption/desorption isotherm for an Fe(III)-derived precipitate aged for 48 h at 15 °C. The X-ray diffraction pattern and infrared analyses of this sample showed it to be am-FeOOH. TEM of the amorphous
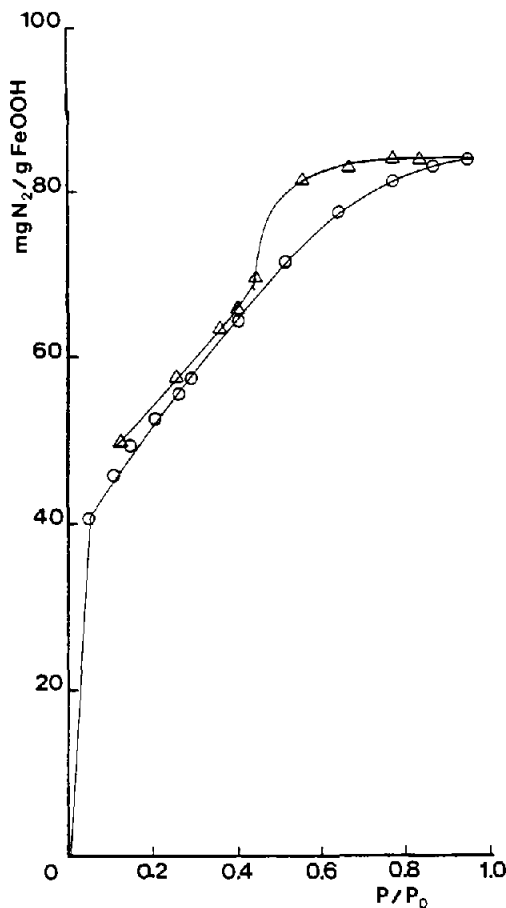
Fig. 1. Nitrogen adsorption/desorption isotherm for a synthetic Fe(III)-derived precipitate, aged 48 h at 15 °C (O- adsorption; △- desorption).

aggregates showed them to be small spheres, with diameters in the range 50 Å to 300 Å. The BET surface area was 234 m^2 g^{-1} and the pore sizes were in the range 15-40 Å, as estimated from the closure at either end of the hysteresis loop. The shape of the hysteresis loop suggests the pores are of the wide-bodied, narrow-necked type, so called 'ink-bottle' pores (ref.17). The hysteresis shows that the pressure has to be reduced by about 30 % before desorption of nitrogen from the matrix occurs. The diffusion of the nitrogen from the solid is restricted because evasion from the wide body is prohibited by the narrow neck.

In contrast to this behaviour the Fe(II)-derived material gave the isotherms shown in Fig. 2. At 15 °C the surface area was 121 m^2 g^{-1} with pore sizes in the range 20-200 Å and pores composed of parallel plates or slits. This general
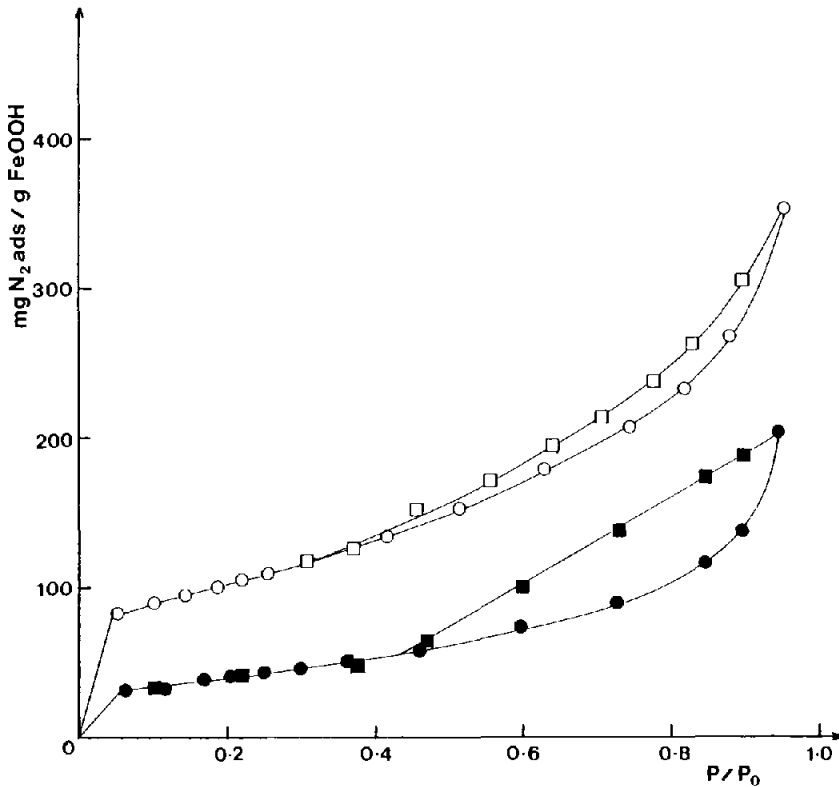
Fig. 2. Nitrogen adsorption/desorption isotherm for synthetic Fe(II)-derived precipitates, aged 48 h. (At 15 °C, ● - adsorption; ■ - desorption; at 2 °C, ○ - adsorption; □ - desorption).

morphology was evident from the TEM studies and both X-ray diffraction and infrared spectroscopy data suggested the presence of poorly crystallised lepidocrocite (γ-FeOOH).

The difference between the precipitates shown in Figs. 1 and 2 arises mainly from the rate of precipitate nucleation. Nephelometric studies (ref.7) at 15 °C and pH = 7.0 have shown that the appearance of a colloid from Fe(III) salts occurs in less than 10 s and changes of temperature have little effect on the colloid formation processes. In the case of Fe(II) salts there is an initial oxidation step which is dependent on both temperature and pH and the appearance of the colloid can take several minutes. For example, it has been shown (ref.18) that the half-life of the homogeneous oxidation of Fe(II) at pH ~ 6.9 and at 15 °C is about 63 minutes, whereas at the same pH and at 5 °C it is 315 minutes. The slower oxidation rate at the lower temperature could give a more finely-divided material with a larger surface area. This mechanism may explain why in

this study the precipitate formed at 2 °C had a surface area more than twice that of a similar material formed at 15 °C.
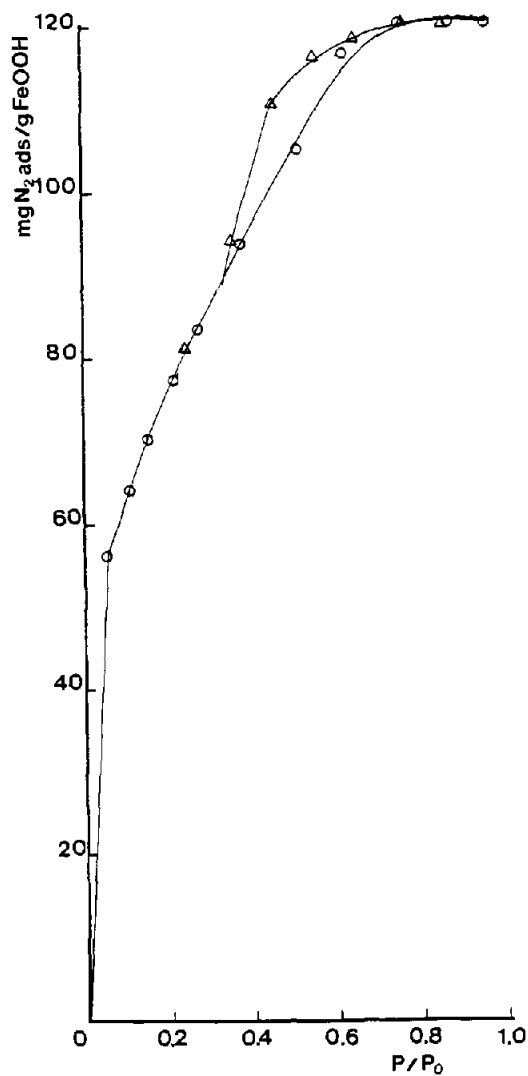
Natural precipitates

Fig. 3. Nitrogen adsorption/desorption isotherm for a natural precipitate from an acid mine stream originally containing 63 % dissolved Fe(II), aged 48 h at 15 °C. (O - adsorption; Δ - desorption).

Fig. 3 shows the isotherm for a precipitate obtained for mine stream waters where only 63 % of the iron was in the Fe(II) form. This isotherm is similar to

that of the synthetic Fe(III)-derived precipitate, shown in Fig. 1, with the 'ink-bottle' pores. However, the surface area of 141 $m^2 g^{-1}$ is lower than that of the synthetic material and the pore size is greater. In this case the precipitate characteristics appear to be determined by the presence of 37 % 'dissolved' Fe(III) in the original water. The formation of the Fe(III) colloid would be almost instantaneous and it would provide active sites for the rapid heterogeneous oxidation of Fe(II) (ref.18). This would tend to confer Fe(III)-type character onto the amorphous precipitate. This result contrasts with an am-FeOOH precipitate derived from an acid mine stream water containing 100 % Fe(II), see Fig. 4. The surface area of this material is 211 $m^2 g^{-1}$ and the pore shape is of the parallel plate or slit type.
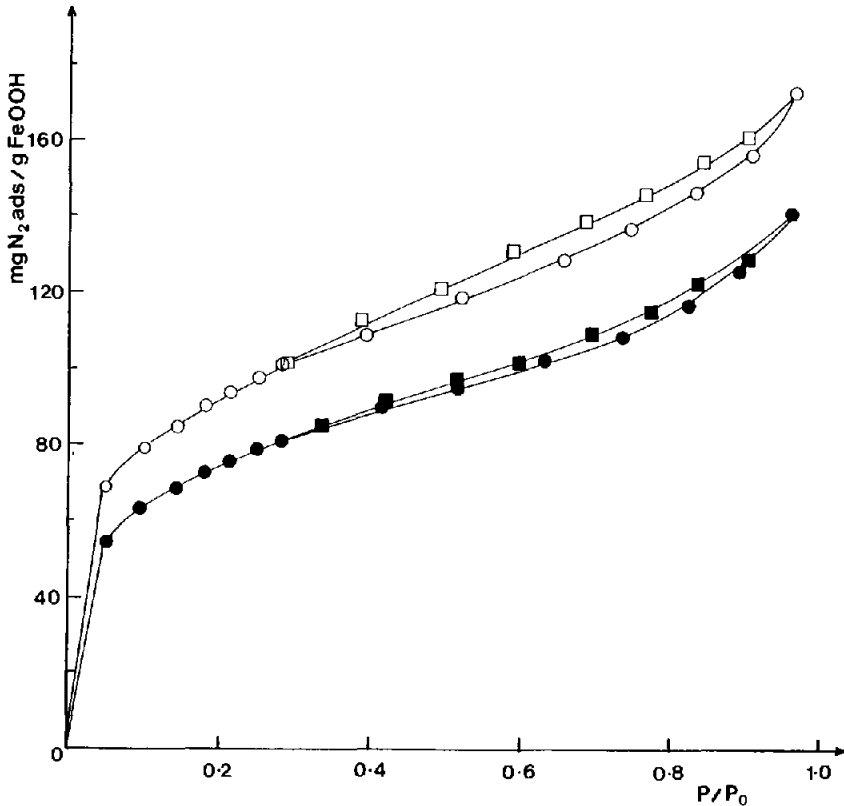

Fig. 4. Nitrogen adsorption/desorption isotherms for natural solids from an acid mine stream. (● - adsorption; ■ - desorption, precipitate aged 48 h at 15 °C, original water 100 % Fe(II); ○- adsorption;□ - desorption, suspended flocculant in the same mine stream at 7 °C, pH ~ 5.5).

Natural particulates

Fig. 4 also shows the isotherm for suspended iron flocculants collected in the same acid mine stream from which the precipitate was obtained. This has pore characteristics similar to that of the precipitate (see Table 1) but the surface area is increased by about 20 %. This could be due to the effect of temperature on the precipitation process mentioned earlier, since the temperature of the mine stream water was approximately 7 °C whereas the precipitations were carried out at 15 °C.

TABLE 1

Surface areas and porosities of Fe(III)- and Fe(11)-derived iron oxyhydroxides.

Precipitate source	Precipitation temperature, °C	Surface area, $m^2 g^{-1}$	Pore size, Å
Synthetic precipitates			
Fe(III)[a]	15	234	15–40
Fe(II)[b]	15	121	20–200
Fe(II)[b]	2	299	20–200+
Natural precipitates			
Fe(II)/Fe(III); 63 % Fe(II)[a]	15	141	15–200+
Fe(II); 100 % Fe(II)[a]	15	211	20–200+
Natural particulates			
Suspended iron flocculant[a]	7	260	20–200+
Suspended particulates[c]	9	41	20–200+

[a] am-FeOOH.
[b] Poorly crystallised γ-FeOOH.
[c] Lithogenous material with an iron coating of 0.6 % of the total iron.

To compare with the above precipitates, iron-rich suspended particulates were collected from the River Carnon in Cornwall, S.W. England, which has a considerable metal input from active mine workings (ref.19). Suspended particulates were collected by large volume filtration in a part of the river where the pH $\approx$ 5.0 and the temperature was about 9 °C. The surface iron content of the particulates was 0.6 %, as determined by a 25 % acetic acid extraction. The nitrogen adsorption isotherm (Fig. 5) shows that even for a complex particulate coating, the iron appears to dominate the character of the surface. The similarity of the nitrogen adsorption isotherm to the above materials, along with the low surface area, is difficult to explain but clearly some of the activity of the iron must be accounted for in its binding with the clay surface. It is also possible that the coagulation of individual clay particles with each other could further reduce the available iron surface area. This

remains an unsolved problem but its importance cannot be underrated since there
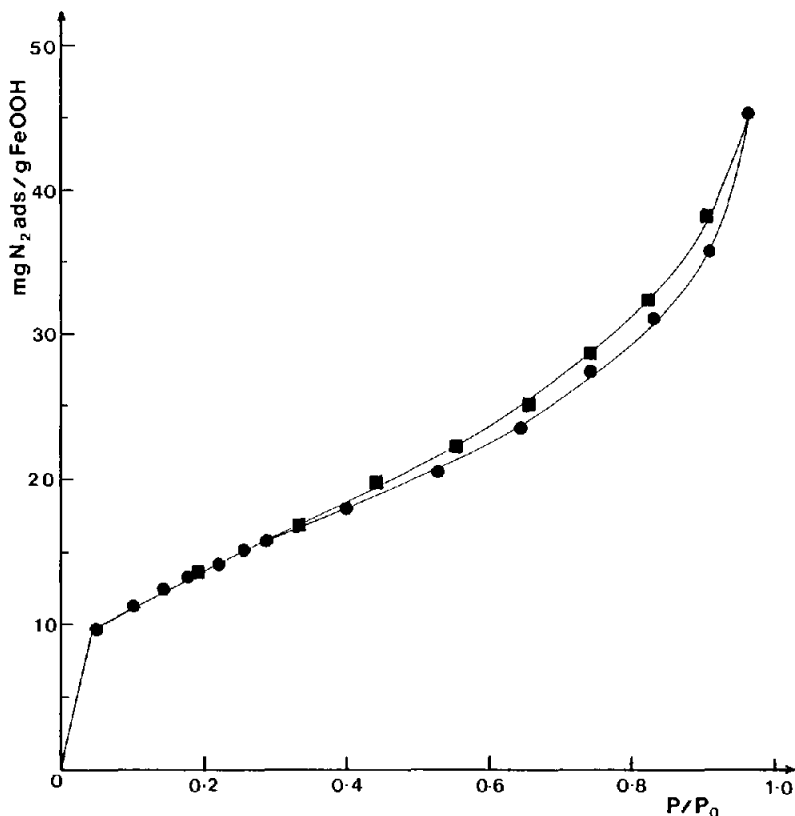are many sites where iron-coated particles control the composition of the
dissolved phase.

Fig. 5. N_2 adsorption isotherm and hysteresis loop for natural suspended
particulates from an acid mine stream. (● - adsorption; ■ - desorption).

SUMMARY AND CONCLUSIONS

The conclusions of this study are that the nature and activity of precipitated
iron oxyhydroxides depend on the starting conditions, particularly with respect
to the initial oxidation state of the iron. Fe(III)-derived oxyhydroxides have
been found to remove As(V) and P from both seawater and distilled water more
rapidly and efficiently than those derived from Fe(II) sources. In addition the
often observed irreversibility of phosphate adsorption onto am-FeOOH (ref.15)
can now be explained in terms of the 'ink bottle' pores, where the diffusion

of phosphate from the wide body of the pores is restricted by the narrow neck.

In the case of the Fe(II)-derived material a previously observed anomaly, namely the enhanced adsorption of As(V) by the Fe(II)-derived oxyhydroxides precipitated at 2 °C (compared with 15 °C), has been resolved now by the finding that there is an increased surface activity associated with precipitates formed at low temperatures. The significance of this result is that there could be seasonal differences in the surface areas available for adsorption processes. Thus, in the winter, lower water temperature would lead to a more finely-divided precipitate of larger surface area. In summer the converse would be true. While these studies relate to Fe(II) precipitates derived from acid mine streams, the hypotheses may be extended to other instances of Fe(II) precipitation, such as those occurring during mixing across the oxic/anoxic boundary in stabilised lakes and fjords and at the surface of anoxic sediments.

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