VACUUM BALANCE AND RELATED STUDIES OF GREEN AND RED RUSTS

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ABSTRACT

   Green and red rusts are formed when iron is partially or completely oxidised.
Analogues of the rusts may be precipitated from iron(II) and iron(III) salt
solutions treated with alkali under reducing or oxidising conditions. Variations
in surface area and porosity have been investigated by gravimetric nitrogen gas
sorption, using vacuum microbalance techniques.
   Freshly-precipitated red rusts, hydrous iron(III) oxide, have surface areas
of about 200-400 m^2g^{-1}. When they are added to iron(II) hydroxide suspensions
kept at pH 7, the green Fe(II)-Fe(III) rusts formed have lower surface areas
of about 40-100 m^2g^{-1}, depending on the initial iron(II) sulphate concentrations.

INTRODUCTION

   The commonest type of rust seen on the surface of corroded iron is red to
reddish-brown in colour, when the iron is mainly in the Fe(III) state, as hydrous
iron(III) oxide. For iron to rust at room temperature, both water and oxygen
must be present. In air, rusting becomes appreciable above 50 % humidity and
the corrosion is severe at 80 % humidity (1). Rusting is initiated by the
electrochemical processes of iron, $2Fe \rightarrow 2Fe^{2+} + 4e$, and dissolved oxygen in the
water, $O_2 + 2H_2O + 4e \rightarrow 4OH^-$, leading to formation of iron(II) hydroxide,
$Fe(OH)_2$. The water acts catalytically as an electron carrier and further
oxidation of Fe^{2+} to Fe^{3+} and subsequent hydrolysis produces iron(III) hydroxide,
often formulated as $Fe(OH)_3$. Although this is empirically the same as Fe_2O_3,
$3H_2O$, the water of constitution does not normally exceed that of Fe_2O_3, H_2O.
Additional water is present as adsorbed water, often in gel form, so that no
characteristic trihydrate crystal lattice has been found, analogous to those of
the alumina trihydrates. The empirical Fe_2O_3,H_2O is really an iron(III)
oxyhydroxide, FeOOH, of which there are 5 crystal forms known, viz. α, β, γ, δ
and δ'. Thus the term hydrous iron(III) oxide covers both water of constitution
and adsorbed water and also defines red rust.

   Green rusts may be formed if there is insufficient oxygen for complete
oxidation of the iron. Thus in steel reinforcements in concrete piles, access
of air is insufficient to oxidise the iron fully to the Fe(III) state and
surface films are commonly black (Fe_3O_4) or sometimes white, green or yellow

(Fe(OH)$_2$ and basic salts containing some Fe(III) iron), changing rapidly to red on exposure to air. Similarly in soils coloured by iron oxides, anoxic regions contain green layers where red hydrous iron(III) oxides have been partially reduced to the iron(II) state.

The term "green rusts" is used in a general way to describe any green oxide material resulting from the corrosion of iron. However, iron(II) hydroxide, Fe(OH)$_2$, is white when pure and becomes green on partial oxidation or when it forms basic salts with acid radicals, e.g., sulphate formed from sulphur dioxide pollution in the atmosphere. Thus green rusts are essentially mixed hydrous Fe(II)-Fe(III) oxides. There is some chemical combination between the Fe(II) and Fe(III) oxides producing material with a characteristic crystal lattice and definite chemical formula within stoicheiometric limits (2, 3). This material is termed "Green Rust" with capitals G and R to distinguish it from the non-stoicheiometric green rusts. In the Green Rust crystal lattice, some of the OH$^-$ groups can be replaced by SO$_4{}^{2-}$ radicals (from basic Fe(II) salts) without extensive modification of the lattice structure; similarly, there may be replacement by carbonate CO$_3{}^{2-}$ radicals.

Analogues of the rusts may be precipitated from solutions of iron(II) and iron(III) salts treated with alkali under reducing or oxidising conditions. In the present research, the composition, surface activity and porosity of green and red rusts have been investigated using thermogravimetric, electro-chemical, Mössbauer and infra-red spectroscopic techniques in conjunction with X-ray diffractometry and vacuum microbalance techniques. Changes in surface area and porosity of the rusts during their production and ageing have been determined by gravimetric nitrogen gas sorption.

EXPERIMENTAL

Preparation of samples

Iron(III) oxyhydroxides (red rust analogues) are precipitated from Fe(III) salt solutions by addition of alkali mainly at pH levels of about 3. Iron(II) hydroxides precipitate from Fe(II) salt solutions mainly at pH 6-7. Thus green rusts are prepared best by keeping the pH just above 7 to avoid dissolution of iron(II) hydroxide. These principles are illustrated in the following preparations.

(a) Samples of iron(III) oxyhydroxide red rusts were precipitated from solutions of 0.1M.FeCl$_3$ by addition of M.KOH. The pH was taken to about 11, so that virtually all of the iron would have come out of solution. One sample was then left to age in solution for approximately 8 months. Subsequently, the precipitate was removed, washed twice with distilled water and acetone to arrest ageing (4), before being dried in air at room temperature. As shown by the X-ray, Mössbauer and infra-red spectra, the end-product was a sample of well-crystalline

goethite (α-FeOOH).

(b) Two samples of hydrous iron(II) oxides were precipitated from solutions of $0.1M.FeSO_4$ and $0.1M.FeCl_2$ with $M.KOH$ and $0.1M.NaOH$, respectively, under anoxic conditions (nitrogen bubbling of solutions in an enclosed vessel). The green precipitates were washed with nitrogen-saturated acetone in a nitrogen-filled glove-box and then vacuum dried. The precipitates were so unstable to oxidation that even these procedures resulted in some oxidation of the material, so that they were lime-green to yellow after vacuum drying. The dried materials were stored in sealed test-tubes under nitrogen until required. The X-ray diffraction traces showed both samples to be amorphous, but in accordance with earlier electro-chemical evidence (from pH changes during precipitation (5)), they consisted mainly of $Fe(OH)_2$ with some basic Fe(II) salts and Fe(III) impurities. The instability of the basic salts to form $Fe(OH)_2$ as more alkali is added during preparation probably accounts for the low crystallinity of the final products.

(c) Samples of green rusts, mixed Fe(II)-Fe(III) hydrous oxides, were made by the addition of hydrous iron(III) oxide suspension to solutions of iron(II) sulphate under anoxic conditions. The hydrous iron(III) oxide suspensions were made by the addition of $0.1M.NaOH$ to 50 cm^3 $0.1M.FeCl_3$ or $Fe(NO_3)_3$ until the pH was approximately 7.0–7.5. Iron(II) sulphate solutions of 0.1M, 0.05M, 0.025M and 0.01M concentrations were taken to just above pH 7 by addition of M.KOH in the presence of flowing nitrogen. Thus the initial ratios of Fe(II):Fe(III) ions were 5:1, 2:1, 1:1 and 0.4:1 respectively. The resulting Fe(II) and Fe(III) hydrous oxide suspensions were mixed by magnetic stirring and also by the nitrogen bubbling. The pH was maintained at just above 7 by adding more alkali as required. Depending on the initial ratio of Fe(II):Fe(III), the original greenish-brown mixed suspensions acquired colours ranging from dark-green to murky-green after 2–3 hours. The precipitates were removed by means of separating funnels and centrifuging in stoppered test-tubes, before being washed with nitrogen-saturated acetone and finally vacuum dried. X-ray diffraction traces of the two samples with initial Fe(II):Fe(III) ratios of 5:1 and 2:1 identified them as true Green Rust compounds with some contamination of goethite.

The Green Rusts have been defined as mixed Fe(II)-Fe(III) hydroxy compounds with basic formula $Fe_x^{2+} - Fe_y^{3+}$ (O^{2-}_y, OH^-_{2x+y}), where $x = 1.95$–3.6 and $y = 0.9$–2.55 and some of the OH^- groups can be replaced by anions such as Cl^-, Br^-, SO_4^{2-} or CO_3^{2-} etc. Thus the ratios of Fe(II):Fe(III) are in fixed ranges, viz., 4:1 to 2:1 to 0.75:1. Accordingly, the remaining two samples prepared with low initial Fe(II):Fe(III) ratios of 1:1 and 0.4:1 were shown by X-ray diffraction and infra-red spectroscopy to be mainly goethite. Nevertheless, all four of the precipitates showed an infra-red absorption band for sulphate at 1100–1250 cm^{-1}. The Mössbauer spectra of the samples show the presence of

both Fe^{2+} and Fe^{3+} ions along with a magnetic hyperfine field due to goethite. The decrease in Fe(II):Fe(III) ratios in the precipitates as the initial Fe(II): Fe(III) ratios decrease is very evident in the Mössbauer spectra.

Gravimetric nitrogen gas sorption

The surface areas of the samples were determined by a gravimetric gas sorption technique (6), using nitrogen adsorption at $-196\ ^{\circ}C$ recorded on a CI Electronics Microforce Mark 2B balance. The samples were outgassed in vacuo at room temperature beforehand and their dry weights were between 100-250 mg. Balance sensitivity ranges used were 0-2.5 mg, 10 mg and 100 mg for measuring the nitrogen uptake. The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges.

Thermogravimetric and titrimetric analysis

The total iron content of the hydrous Fe(II)-Fe(III) oxide samples was determined by TG, calcining portions at 1000 $^{\circ}C$ for 1-2 h to give a residue of $\alpha-Fe_2O_3$. The % Fe^{2+} was determined by dissolving a portion of the sample in 6M.HCl and titrating the solution with 0.005M.Ce$(SO_4)_2$. The ferroin indicator was sufficiently sensitive at this low concentration, but required a blank determination correction of about 0.2-0.3 cm^3.

The % SO_4^{2-} was determined by dissolving a portion of the sample in 6M.HCl and adding barium chloride to precipitate the sulphate as $BaSO_4$ for gravimetric determination.

RESULTS AND DISCUSSION

The adsorption isotherms for the hydrous iron oxide samples are shown in Fig. 1-4. The isotherms give linear B.E.T. plots from which the calculated specific surface areas are shown in Table 1. The chemical compositions of the hydrous Fe(II)-Fe(III) oxides are given in Table 2.

In Fig. 1, the adsorption isotherms are shown for (i) hydrous Fe(II) oxide precipitated from $FeSO_4$, (ii) hydrous Fe(II) oxide precipitated from $FeCl_2$, and (iii) well-crystalline goethite precipitated from $FeCl_3$. They are all type IV.

Isotherm (iii) shows adsorption hysteresis above a relative pressure of 0.5, indicating an almost full range of mesopores (3 to 50 nm diameter). The surface area of this 8-months aged goethite is 149 m^2g^{-1}. Samples of freshly-produced material have higher specific surfaces of 200-400 m^2g^{-1}. Thus it is apparent that ageing in solution has improved the crystallinity of the goethite. The freshly-prepared samples with the highest surface areas (ca. 400 m^2g^{-1}) give type I isotherms (Fig. 2), indicating some microporosity (pores below 2 nm diameter). The micropores evidently disappear on ageing leaving only meso and macropores, so that the isotherms change to type IV. When iron (III)
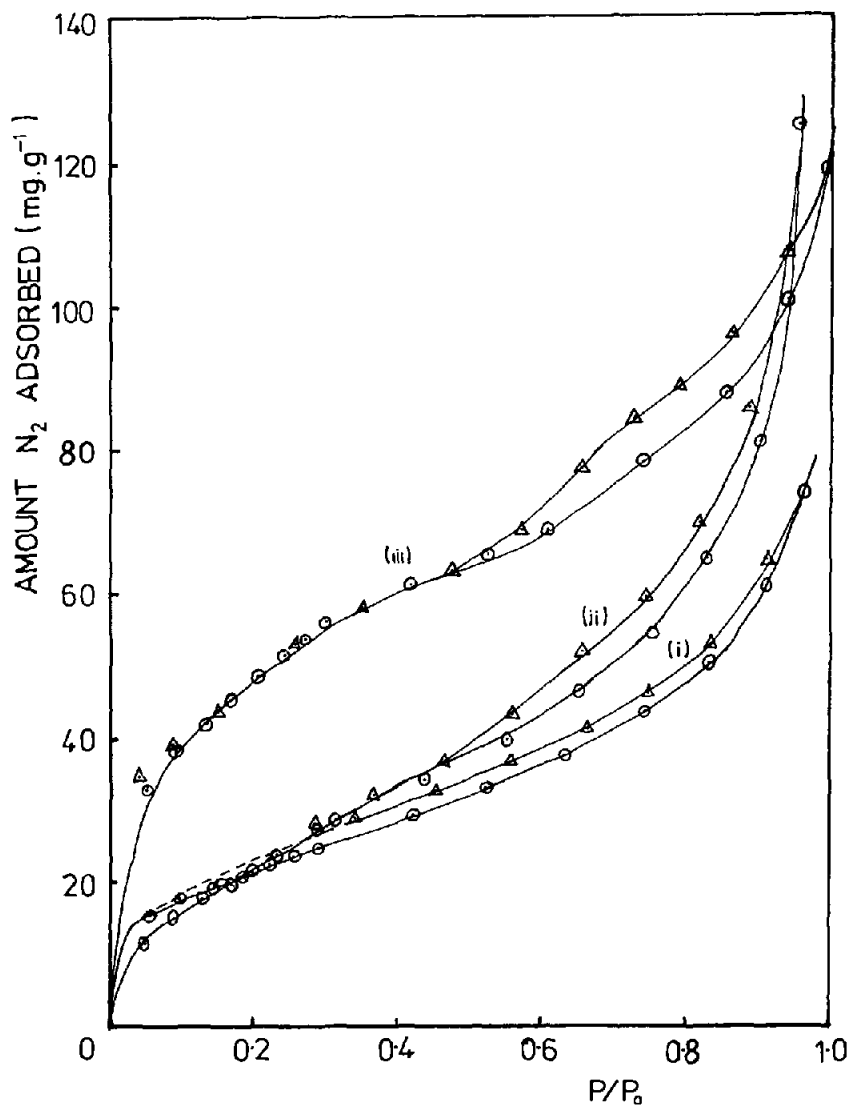
Key: (i)   hydrous Fe(II) oxide precipitated from FeSO₄
     (ii)   hydrous Fe(II) oxide precipitated from FeCl₂
     (iii) hydrous Fe(III) oxide precipitated from FeCl₃
   and aged 8 months to well-crystalline goethite

     ⊙ adsorption points   △ desorption points

Fig. 1.   Comparison of nitrogen adsorption isotherms at -196 °C
   between Fe(II)-derived and Fe(III)-derived hydrous oxides

TABLE 1

Surface areas of hydrous iron oxides

Sample No.	Description	Derivation	Initial Fe(II): Fe(III) ratio	Specific surface,
1	Hydrous Fe(II) oxide	0.1M.FeSO$_4$	——	64
2	Hydrous Fe(II) oxide	0.1M.FeCl$_2$	——	76
3	Hydrous Fe(III) oxide	0.1M.FeCl$_3$	——	149
4	Hydrous Fe(II)-Fe(III) oxide (Green Rust A)	0.1M.FeSO$_4$	5:1	44
5	Hydrous Fe(II)-Fe(III) oxide (Green Rust B)	0.05M.FeSO$_4$	2:1	55
6	Hydrous Fe(II)-Fe(III) oxide (green rust A)	0.025M.FeSO$_4$	1:1	98
7	Hydrous Fe(II)-Fe(III) oxide (green rust B)	0.01M.FeSO$_4$	0.4:1	93
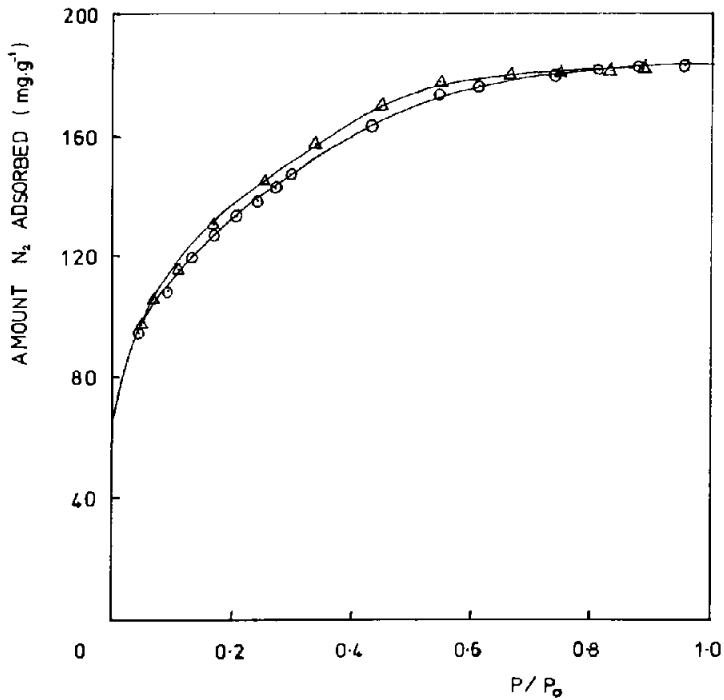
⊙ adsorption points   △ desorption points

Fig. 2. Nitrogen adsorption isotherm at -196 °C on a freshly-prepared hydrous Fe(III) oxide. (S = 370 m^{2}g^{-1})
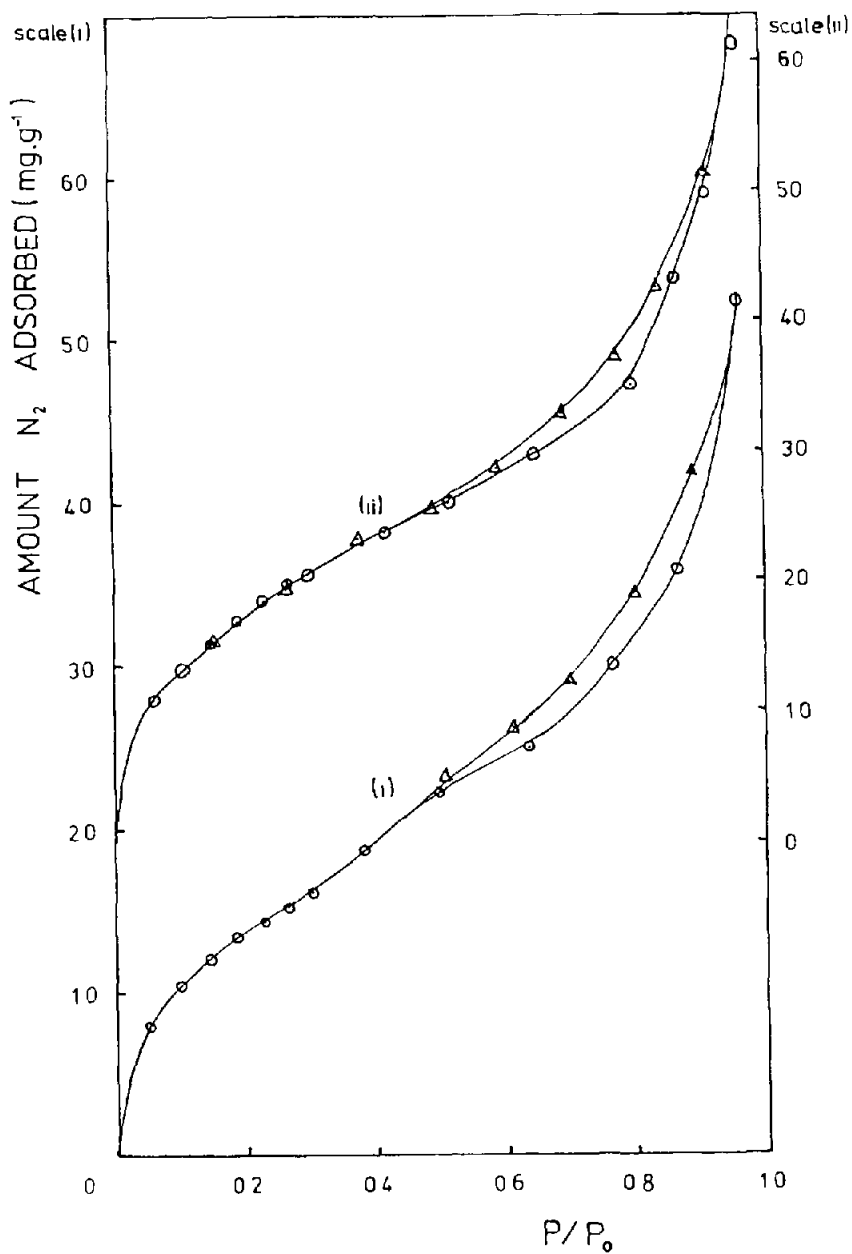
Key:-
(i) Green Rust A from 0.1M.FeSO₄ with an initial Fe(II):Fe(III) ratio of 5:1.
(ii) Green Rust B from 0.05M.FeSO₄ with an initial Fe(II):Fe(III) ratio of 2:1.

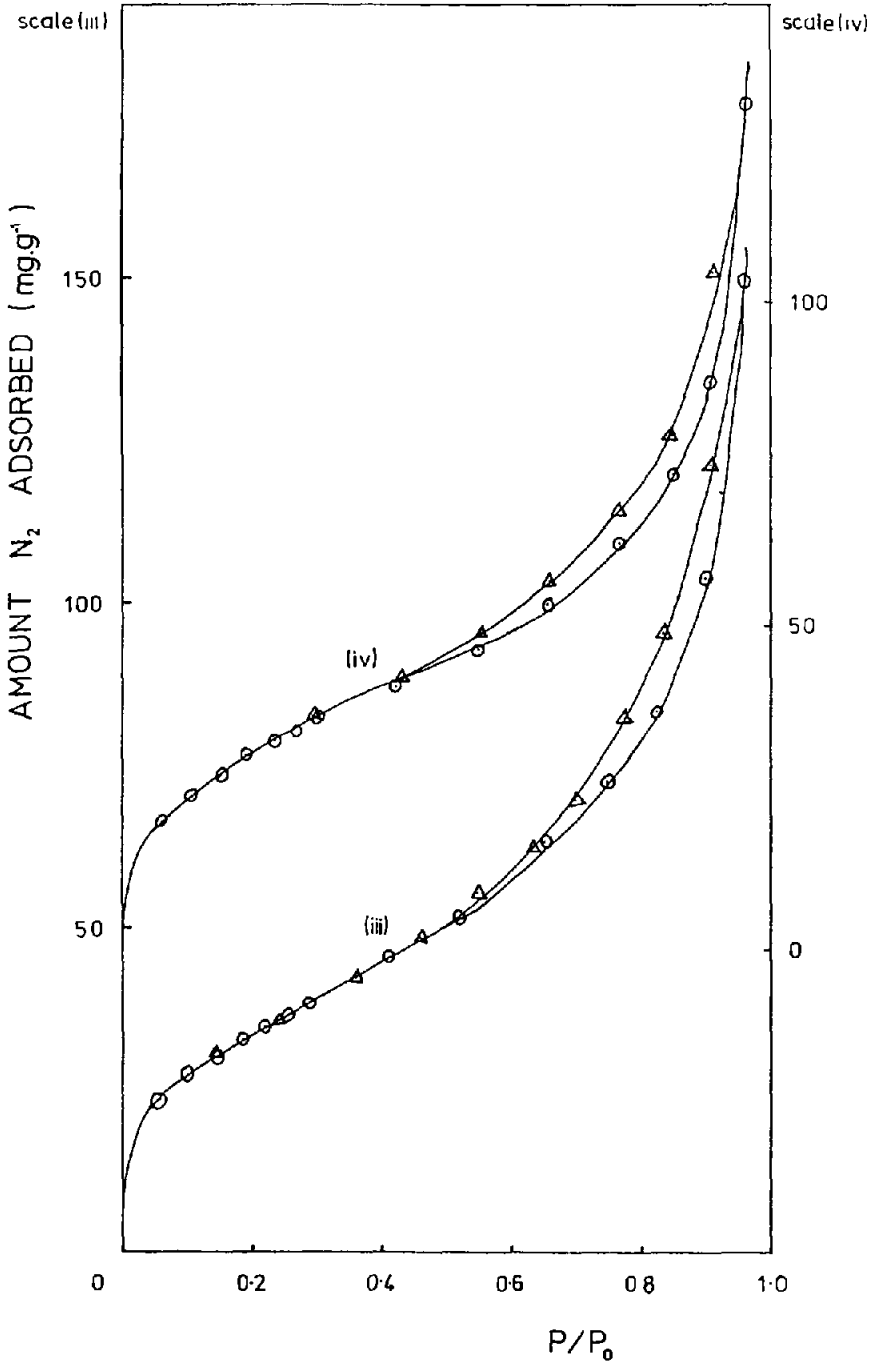Fig. 3. Nitrogen adsorption isotherms at -196 °C for Green Rusts.

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Fig. 4. Nitrogen adsorption isotherms at -196 $^{\circ}$C for green rusts from 0.025 and 0.01M.FeSO$_4$ with lower initial Fe(II):Fe(III) ratios of 1:1 and 0.4:1.

TABLE 2

Chemical analysis of the hydrous Fe(II)-Fe(III) oxides

Sample	Initial Fe^{2+}:Fe^{3+} ratio	SO$_4^{2-}$	Fe^{2+}	Fe^{3+}	total Fe
Green Rust A	5:1	18.5	12.7	42.5	55.2
Green Rust B	2:1	15.2	8.3	41.5	49.8
green rust A	1:1	10.0	2.4	51.4	53.8
green rust B	0.4:1	-	0.7	55.8	56.5

oxyhydroxide is precipitated from very dilute FeCl$_3$ solutions (ca. 10^{-5}M), the rate of nucleation is slower and less active samples are produced (nearer 200 m^{2}g^{-1}). Thus Crosby et al (7, 8) have shown that these iron(III) oxyhydroxides on ageing increase their surface areas to a maximum before decreasing in the normal way. This has been ascribed to the conversion of the initially-precipitated δ-FeOOH to the more stable goethite, α-FeOOH, which subsequently ages.

The two hydrous iron oxides derived from the Fe(II) salts have adsorption isotherms which also show practically the full range of mesopores. Some of the desorption points at the low relative pressures on isotherm (1) have long equilibrium times and hence the hysteresis loop does not completely close experimentally. The initial material precipitated from the Fe(II) solutions was dark green in colour and very unstable to oxidation. Thus the nitrogen sorption measurements were therefore of the almost completely oxidised material, cf. Table 2. However, these Fe(II)-derived hydrous oxides have much lower surface areas (60-80 m^{2}g^{-1}) than the aged goethite which was Fe(III)-derived. So even though the final state of the iron in both types of materials is mainly or completely III, the initial iron state must be important to the microstructure of the end-product and hence to its surface area and porosity.

In Fig. 3 and 4, the adsorption isotherms are shown for the four hydrous Fe(II)-Fe(III) oxides with initial Fe^{2+}:Fe^{3+} ratios ranging from 5:1 to 0.4:1. The surface areas (Table 1) of the Green Rusts (samples 4 and 5) are considerably lower than what would be expected from corresponding mixtures of Fe(II)- and Fe(III)-derived oxides (cf. samples 1 and 3). This indicates that the Green Rust structures are markedly different from those of the materials from which they have been produced, as confirmed by X-ray diffraction. The two remaining green rust samples (6 and 7), prepared with low initial Fe(II):Fe(III) ratios of 1:1 and 0.4:1 were shown by X-ray diffraction to be mainly goethite; accordingly their surface areas are much higher than those of the Green Rusts, viz., 98 and 93 m^{2}g^{-1} compared with 44 and 55 m^{2}g^{-1}. Nevertheless, the surface areas in the 90-100 m^{2}g^{-1} range still fall short of those for goethite samples directly precipitated from Fe(III) salt solutions (140 m^{2}g^{-1} upwards), but they

are more comparable with products from hydrolysis and oxidation of Fe(II) salt
solutions 80-120 m^2g^{-1}), as found by Crosby et al (7, 8). At the lowest
concentrations, $10^{-5}-10^{-4}$M, and with no goethite (or δ-FeOOH convertible to
goethite) present initially, the Fe(II) salts hydrolyse and oxidise to form
mainly γ-FeOOH, lepidocrocite. But at somewhat higher concentrations and with
goethite (or ferrihydrite, δ-FeOOH) present initially, the products are mainly
goethite, α-FeOOH, suggesting that there has been some crystal growth on the
added goethite ("seeding out") which would reduce its surface area.

The magnitude and variation of the $\sum SO_4^{2-}$ in Table 2 show that sulphate is
an important factor in the formation of Green Rusts. It is likely that the
sulphate comes out of solution at the same time as the iron(II) hydroxide to
form basic sulphate precipitates, which react with the surface of the iron(III)
oxyhydroxide. Since the Green Rusts have comparatively low surface areas, the
higher concentrations of sulphate evidently promote coagulation and crystal
growth with loss of surface and porosity.

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