

# Preparing particulate magnetites with pigment properties from suspensions of basic iron(III) sulphates with the structure of jarosite

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The transformation of a suspension of hydronium jarosite,  $\text{H}_3\text{O}^+\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ , into  $\text{Fe}_3\text{O}_4$  (magnetite) of pigment quality is described. The process consists in the neutralization of the hydronium jarosite suspension in  $\text{FeSO}_4$  aqueous solutions with  $\text{NH}_3$  and subsequent thermal treatment of this mixture at controlled pH and temperature.

## 1. Introduction

Various precipitates of basic iron(III) sulphates, consisting principally of jarosites,  $\text{Me}^+\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$  where  $\text{Me}^+$  stands for a monovalent cation such as  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}_3\text{O}^+$ , occur frequently as waste products of the removal of iron(II) and iron(III) compounds from industrial hydrometallurgic extracts obtained by the treatment of non-ferrous metal ores (e.g. in Zn and/or Cu metallurgy). Subject to the conditions of their production, such precipitates may also contain some crystal modifications of iron oxide or oxide-hydroxide, most frequently haematite and goethite.

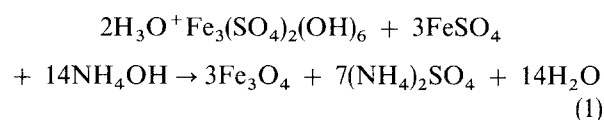
Basic sulphates of the jarosite type feature a number of favourable properties when employed for the separation of iron from hydrometallurgic extracts. Such a precipitation of  $\text{Fe}^{3+}$  ions is highly selective and only minor percentages of other metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , etc.) are entrained in the precipitate. Further, the jarosite precipitates are readily filterable.

The main drawbacks of this process can be found both in the cost of auxiliary chemicals and in the problem of jarosite disposal, because it can be stored under controlled conditions only (e.g. in an acid environment) due to its limited resistance against hydrolysis.

Therefore, the exploitation of jarosite by-products of the treatment of polymetallic ores and their reprocessing into commercial products represent an opportunity for improving the economical efficiency of the whole process of treatment. Up to now, a number of methods have been published for processing jarosite into marketable, iron oxide-based materials [1–8].

In our previous work [5], the reprocessing of ammonium jarosite into haematite-based iron pigments was described, which employed both thermal decomposition and hydrothermal treatment, resulting in red iron pigment and micaceous iron oxide, respectively. Other alternatives can be sought in the transformation of ammonium jarosite by reacting it with a suitable iron(II) salt to produce a black iron pigment based on magnetite ( $\text{Fe}_3\text{O}_4$ ). It was found [9, 10] that a neutralized mixture of hydronium jarosite (or a

mixture of other alkali jarosites) with a solution of iron(II) sulphate, or more precisely a mixture containing  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  compounds in the ratio of  $\text{Fe}^{3+}:\text{Fe}^{2+} = 2:1$ , does react in aqueous media to produce black ferroso-ferric oxide solids according to the equation



However, if such black precipitates are to be used as black pigments, a number of additional requirements should be met, particularly as to the size of primary magnetite particles produced by the reaction of solid jarosite with iron(II) sulphate solution [9]. The magnetite precipitates formed by the reaction of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in aqueous media often consist of very small particles showing poor crystal structure, a feature reflected in insufficient thermal stability and additional unfavourable physical properties that make such powders unsuitable for use as pigments (e.g. due to their high oil absorption, low hiding power, unacceptable colour shade, insufficient thermal stability, etc.). The methods described in the literature up to now for the conversion of jarosite into  $\text{Fe}_3\text{O}_4$  (magnetite) have generally led to such inferior products [4].

## 2. Experimental procedure

### 2.1. Hydronium jarosite preparation

Hydronium jarosite was obtained as the by-product of the air oxidation of a concentrated iron(II) sulphate solution into ferric sulphate, carried out within the temperature range between 120 and 140 °C (under the corresponding water vapour pressure) in acid solution. The method is described in a pending patent application [11] and has been used for manufacturing iron(III) sulphate solution used as a flocculant. The solid product formed in addition to the dissolved iron(III) sulphate, hydronium jarosite, also contained iron(III) oxide-hydroxide (goethite) as the only admixture, not exceeding 20 wt %.

## 2.2. Reaction of hydronium jarosite with iron(II) sulphate

The reaction between hydronium jarosite and iron(II) sulphate was studied employing a gas-heated stainless steel reaction vessel of 7 dm<sup>3</sup> working volume, equipped with a propeller stirrer and gas and liquid inlets. The applied temperature control system allowed one to maintain a chosen reaction temperature within the range  $\pm 1$  °C. The neutralizing agent (i.e. aqueous ammonia, approx. 13 wt %) as well as iron sulphate solution were fed in using metering peristaltic pumps. During the course of reaction, pH values and redox potentials were monitored with a glass electrode and a Pt–Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell, respectively. One of the two parameters could be kept constant using a feedback control arrangement for ammonia addition.

Two methods were used to carry out the reaction between hydronium jarosite and iron(II) sulphate, differing from each other in the method of iron(II) sulphate addition. In the first one (method A), hydronium jarosite as a wet filter cake (500 g, i.e. jarosite dry substance 300 g) was mixed with distilled water (1.2 dm<sup>3</sup>) and iron(II) sulphate solution was added in an amount that exceeded the quantity given by Equation 1 by 5 to 80%. The total volume of the addition was always made up to 1.5 dm<sup>3</sup> with water. The reaction mixture was then heated up to 90 °C within 30 min. During the following 30 min the pH value was adjusted to 6.5 by aqueous ammonia solution (13 wt %). The remaining ammonia (up to 0.9 dm<sup>3</sup>) was added during the next 2.5 h at the same temperature. After the neutralizing agent had been added, the reaction mixture was stirred for an additional 6 h at 90 °C. During the latter period the excess of iron(II) compound was oxidized by air oxygen and the pH value of the reaction mixture restored to 6.5. Samples were withdrawn at various points of the course of reaction and the intermediates and the final product of reaction were analysed as to their phase and chemical compositions.

In the other method (method B) the suspension of hydronium jarosite (500 g of filter cake, 1.2 dm<sup>3</sup> water) was heated up to 90 °C (the same temperature as in method A) and then neutralized to a pH value between 6.75 and 7.25 in the absence of iron(II) sulphate. After the required pH had been achieved, slow addition of iron(II) sulphate solution was started and the total amount, exceeding the Fe<sub>3</sub>O<sub>4</sub> stoichiometry by 50%, was added within the following 2.5 h. The preselected pH value of reaction mixture (in the range of 6.75 to 7.25 units) was kept by the controlled addition of ammonia using a pH-stat. Finally, the reaction mixture was heated to 90 °C for an additional 5 h regardless of any change in its pH value. Samples of intermediates and the final product were withdrawn and analysed. At the end of the reaction, the products of either method were separated from soluble by-products by decantation and filtration, washed and dried at 90 °C in an air oven.

All the obtained samples were phase-analysed using the powder X-ray diffraction (XRD) method. The particle size of magnetite was determined using transmission electron microscopy. The Fe(II)/Fe(III) ratios

of products were determined using common chemical methods. The final products of the two methods of preparation were also evaluated in terms of their possible use as pigments.

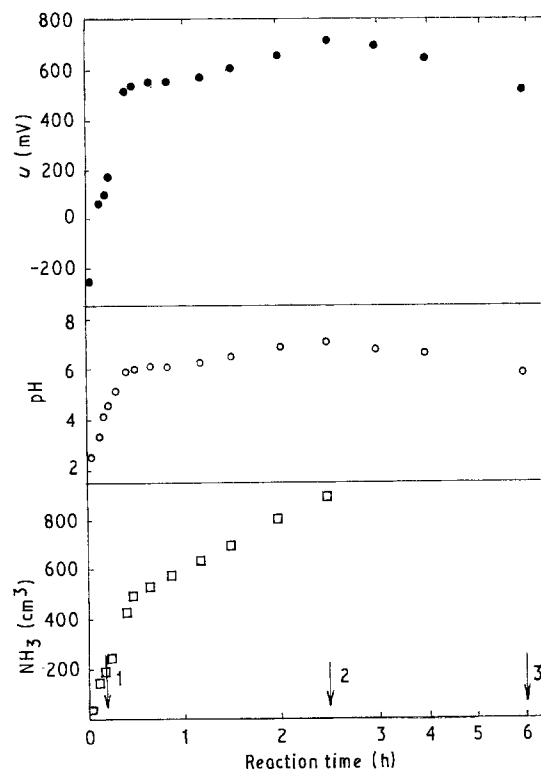


Figure 1 Pt–Pt/Hg<sub>2</sub>Cl<sub>2</sub> voltage, pH value and NH<sub>3</sub> (13 wt %) usage versus time courses during the preparation of C 55 iron black by method A: (1) sample C 55/1, (2) sample C 55/2, (3) sample C 55.

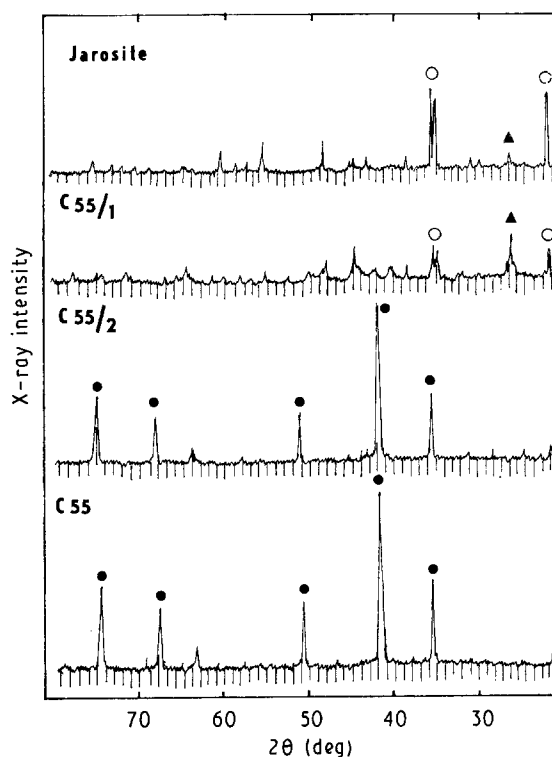


Figure 2 XRD diagrams of the initial jarosite, the intermediates and the final product of method A: (●) Fe<sub>3</sub>O<sub>4</sub>, (▲)  $\alpha$ -FeOOH, (△)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (○) jarosite.

### 3. Results and discussion

The conditions of preparation of samples according to method A can be found in Fig. 1. Fig. 2 shows the powder XRD diagrams of the intermediate samples as obtained in the reaction times indicated in Fig. 1. The particles of intermediates withdrawn at various reaction stages are shown in Fig. 3.

According to the XRD data (see Fig. 2), the initial sample employed for magnetite preparation consisted of about 80% hydronium jarosite and 20% goethite ( $\alpha$ -FeOOH) mixture. Fig. 2 also shows the progressive changes in solid phase structure taking place during the whole period of reaction. The continuing neutral-

ization of the mixture containing both suspended jarosite and dissolved iron(II) sulphate led primarily to the progressive disappearance of the jarosite phase accompanied by a corresponding increase in goethite percentage. However, very small particles of goethite were formed (sample C 55/1). Moreover, a part of trivalent iron was present as an XRD-amorphous solid.

The transformation of less stable iron oxide/oxide-hydroxide phases into goethite taking place in iron(II) sulphate solutions has been discussed in a number of studies [12–15]. Evidence was provided in these studies of the fact that in aqueous media the

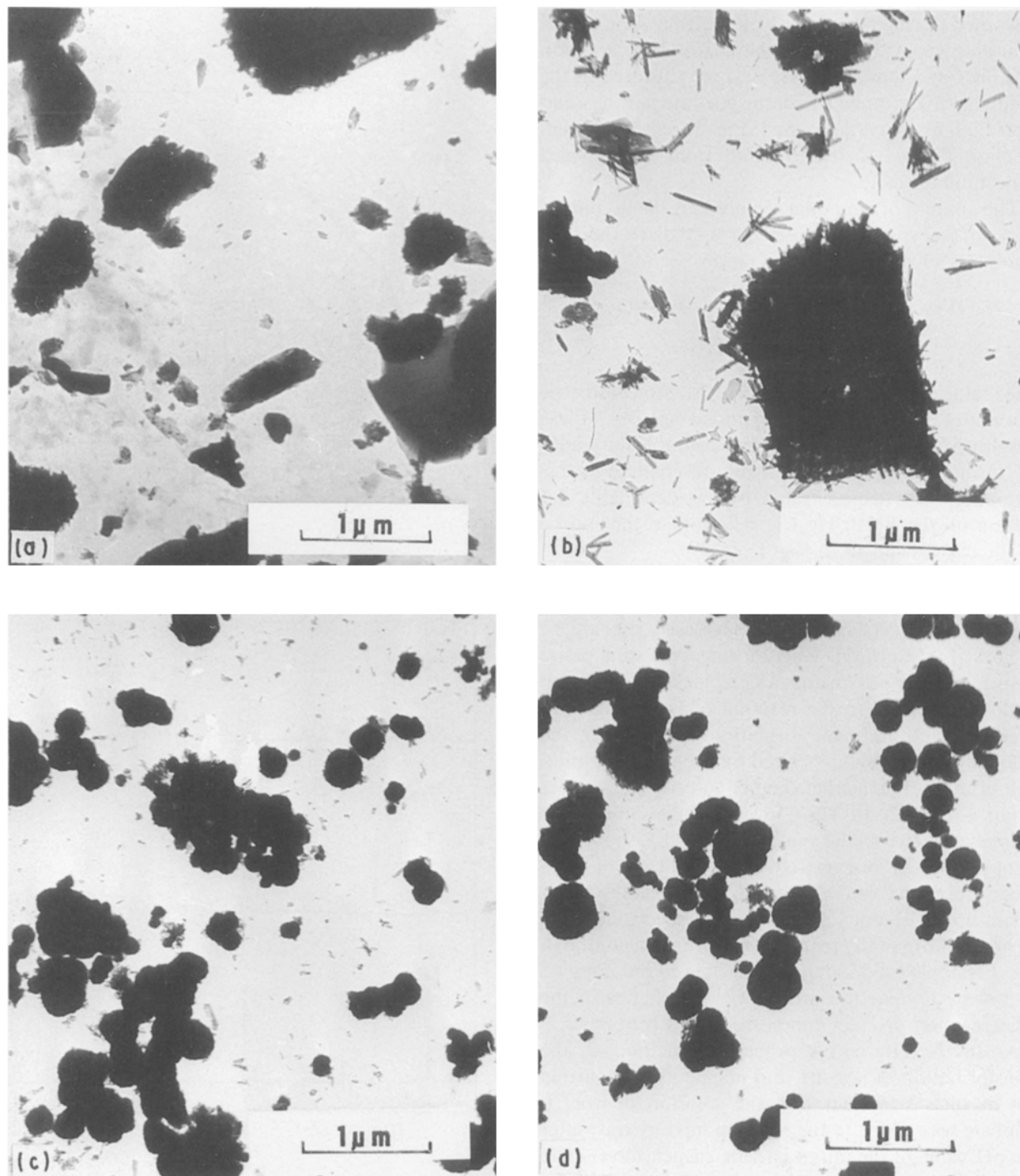
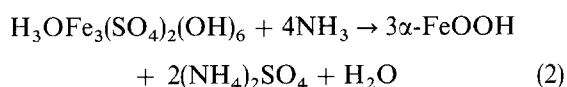


Figure 3 TEM micrographs of the initial jarosite, the intermediates and the final product of black iron pigment preparation with method A: (a) initial jarosite, (b) C 55/1, (c) C 55/2, (d) C 55.

formation of more stable phases (particularly  $\alpha$ -FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is accelerated in the presence of Fe<sup>2+</sup> ions and takes place through the process of unstable solid phase dissolution and the subsequent crystallization of a more stable solid from the mother liquor. One should add, however, that while the solubility products of both the initial and resulting solids can be as low as  $\sim 1 \times 10^{-40}$ , these transformations are fast and show an autocatalytic reaction course, suggesting the existence of an unstable soluble intermediate.

One can assume a similar overall mechanism for the process of recrystallization of very small particles of stable phases, resulting in the formation of bigger and more stable crystals. It therefore, seems logical that the most stable phase of the given system (i.e.  $\alpha$ -FeOOH) is formed during the process of neutralization to pH values at which the Fe<sup>2+</sup> ions remain in the solution and the Fe<sup>3+</sup> ions hydrolyse and are captured in the solid phase. The small size of the goethite particles and their high aspect ratio as well (Fig. 3) reflect the high reaction rate of their formation from decomposed hydronium jarosite.

The amount of ammonia required for the decomposition of jarosite to goethite corresponds to the stoichiometry of the following equation:



The value of pH attained after the stoichiometric amount of ammonia had been added (see Fig. 1) was roughly 5.5, i.e. within the range favourable for goethite formation [15]. The jarosite-to-goethite transformation was demonstrated by an identifiable flat section on the Pt-Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell voltage-time curve at 100 mV, as shown in Fig. 1.

With the subsequent addition of ammonia up to the stoichiometric amount given by Equation 1, the voltage of the Pt-Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell increased quickly to 550 mV (Fig. 1). In this reaction stage, the solid phase acquired a dirty brown and later a black colour, which could be assigned to the reaction of Fe<sup>2+</sup> ions with goethite resulting in the formation of Fe<sub>3</sub>O<sub>4</sub>. In the following period, characterized by progressive formation of magnetite, neither the pH value of the mother liquor nor the Pt-Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell voltage showed any significant increase, the values of 6.3 and 550–570 mV being achieved, respectively. The addition of 12% excess ammonia caused the pH and *E* values to increase up to 7.1 units and 720 mV, respectively. Prolonged heating of the reaction mixture after point 2 in Fig. 1 (sample C 55/2) had been achieved did not lead to any Fe<sub>3</sub>O<sub>4</sub> particle growth or any change in the solid reaction product composition and properties.

As to the alternative process of method B, the transformation of jarosite into magnetite was carried out in such a manner that the solution of iron(II) sulphate was added to the reaction mixture only after the pH value of the initial jarosite suspension ( $\sim$  pH 2) had been adjusted to a preselected value (7.25 for the present case) and maintained within the time interval of A to C in Fig. 4. Figs 5 and 6 show XRD

diagrams and the TEM micrographs, respectively, of intermediate product particles. As seen from Figs 4 and 5, the transformation of jarosite into goethite had already taken place before the pH value of 7.25 could be attained. However, unlike the previous case, goethite particles were not acicular, but appeared as clusters of smaller particles of varied shape. Further, the

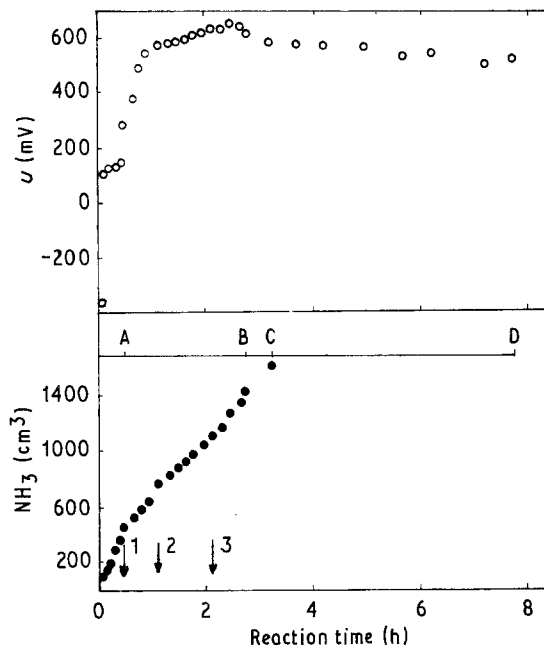


Figure 4 Pt-Pt/Hg<sub>2</sub>Cl<sub>2</sub> voltage and NH<sub>3</sub> usage versus time courses during the preparation of C 56 iron black by method B: (1) C 56/1, (2) C 56/2, (3) C 56/3; AB = FeSO<sub>4</sub> addition interval (12 cm<sup>3</sup> min<sup>-1</sup>), AC = time interval of constant pH value of 7.25, CD = extended heating period, without keeping the pH value constant.

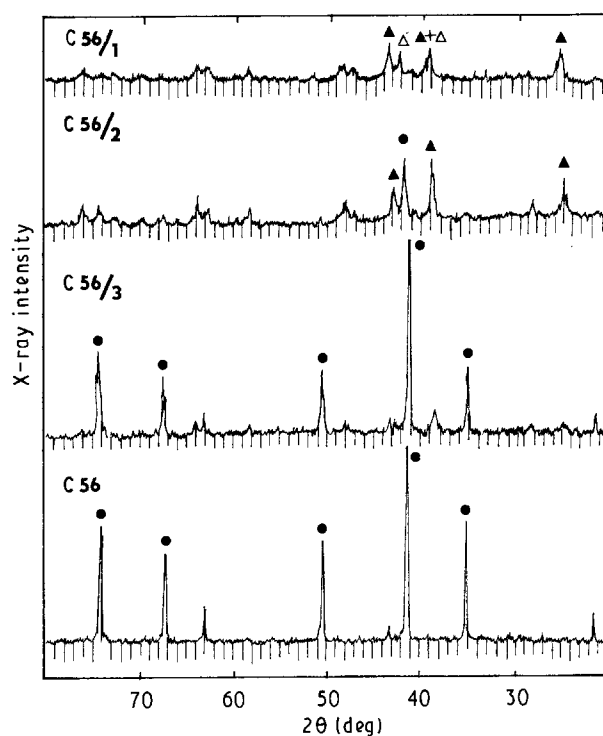


Figure 5 XRD diagrams of intermediates and the final product of reaction during the preparation of black iron oxide by method B: (●) Fe<sub>3</sub>O<sub>4</sub>, (▲)  $\alpha$ -FeOOH, (△) jarosite.

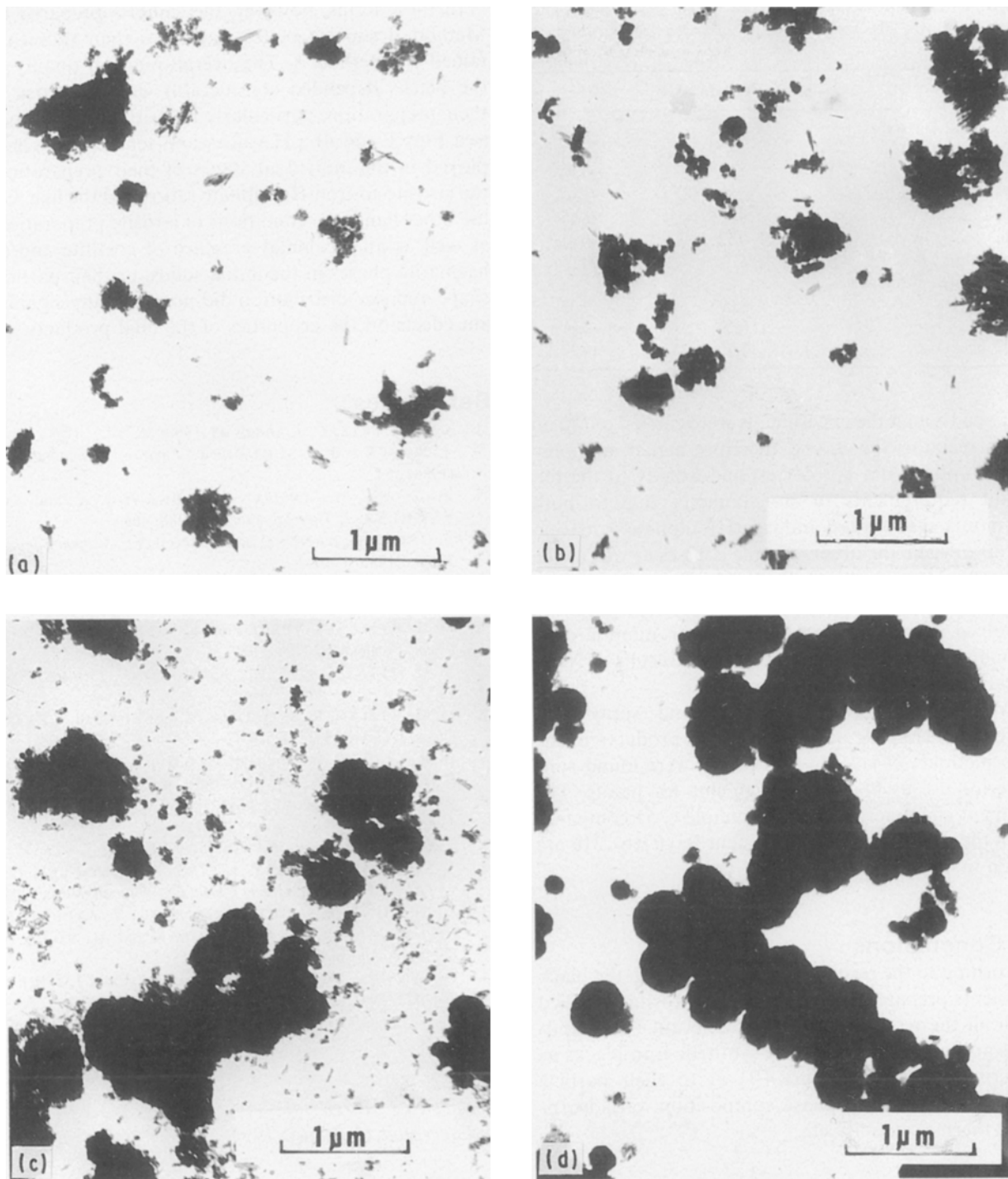


Figure 6 TEM micrographs of intermediates and the final product of reaction during the preparation of black iron oxide by method B: (a) C 56/1, (b) C 56/2, (c) C 56/3, (d) C 56.

above-mentioned plateau was much more pronounced in this case (see Fig. 4), and corresponded roughly to the period of jarosite neutralization according to Equation 2, or jarosite-to-goethite transformation.

In that reaction stage the pH value reached 7.25 after the rest of the ammonia had been added according to Equation 1, and slow addition of iron(II) sulphate ( $12 \text{ cm}^3 \text{ min}^{-1}$  within time interval A to B in Fig. 4) was commenced. From the very beginning, magnetite was being formed as small spherical particles. In that period, the Pt-Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell voltage fluctuated within the range 550 to 570 mV. The magnetite particles got bigger with the progressive addi-

tion of iron(II) sulphate and simultaneously their crystal structure improved. The percentage of small particles decreased at the same time.

An intermediate sample withdrawn at the end of FeSO<sub>4</sub> solution addition consisted mainly of magnetite, in which only hardly XRD-detectable amounts (i.e.  $\sim 2 \text{ wt } \%$ ) of goethite and haematite were present (sample C 56/3). Prolonged heating of the mixture without keeping the pH value constant (Fig. 4, C to D) led then to apparent reduction in the occurrence of small particles (see Fig. 6, samples C 56/3 and C 56), but no marked growth or shape changes of the other magnetite particles were observed. The final pH value of the reaction mixture was 6.9.

TABLE I Comparison of properties of commercial black pigment Bayferrox 316 with magnetite prepared from hydronium jarosite

	Bayferrox 316	C 55
Retention (+ 316 mesh)	0.06	0.09
Density (g cm <sup>-3</sup> )	4.67	4.51
Surface area (m <sup>2</sup> g <sup>-1</sup> )	7.4	21.8
Oil absorption (g/100 g)	16.82	17.97
pH value	4.5	6.1
Soluble salts (wt %)	0.52	0.31
Conductivity (μS)	185	174
Chromacity coordinates		
y (%)	2.09	2.22
z (%)	0.29	0.11
Fe <sup>2+</sup> (wt %)	17.2	16.34

Even though the experiments were carried out in an open reaction vessel, and therefore actual ammonia consumptions did not correspond exactly to the relevant requirements of stoichiometry due to both ammonia evaporation and iron(II) sulphate oxidation by air oxygen, the observed time courses as well as the related pH values and Pt–Pt/Hg<sub>2</sub>Cl<sub>2</sub> cell voltages could be employed for interpretation of the processes involved in the transformation of hydronium jarosite to magnetite, in due relation with the results of XRD spectrometry and TEM microscopy.

Moreover, thoroughly washed and spray-dried magnetite samples, obtained as final products in the two methods of jarosite processing, were found suitable for use as black iron pigments for paints. The pigment characteristics of our sample C 55 compared with the commercial black pigment Bayferrox 316 are given in Table I.

#### 4. Conclusions

According to the results of thorough testing, the black pigments prepared from hydronium jarosite complied with all the requirements set by relevant ISO standards and generally resembled synthetic iron blacks as described in the literature [9] as to their particle shape, chemical and phase composition, oil adsorption, thermal stability etc.

In these terms, however, the samples prepared by Method B showed better properties than those obtained by Method A. The overall pigment quality of the blacks depended considerably on the course of their preparation, particularly as to the time periods (see Figs 1 and 4), pH values and temperatures employed in the individual stages of their preparation, the jarosite-to-iron(II) sulphate ratios and the like. On the other hand, the conditions of jarosite preparation, as well as an incidental presence of goethite and/or haematite phases in the initial solids, or their particle shape and size distribution did not exert any significant effects on the properties of the final products.

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