Formation of Lead-bearing Ferrite in Aqueous Suspension by Air Oxidation

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A Pb-bearing ferrite with spinel-type structure, $Pb_{0.19}Fe_{2.75}O_{4.0}$, was obtained by air oxidation of an aqueous suspension, with an initial Pb^{2+} : $Fe_{tot.}$ mol ratio of 0.30 : 1, at pH 12 and 65 °C. This Pb-bearing ferrite is formed by the transformation of an intermediate compound, which is stable in a nitrogen atmosphere, during air oxidation. The Curie point of the Pb-bearing ferrite was estimated to be *ca.* 400 °C. When the Pb^{2+} : $Fe_{tot.}$ mol ratio in the initial reaction solution was <0.20 : 1 at pH 12, α-FeO(OH) was formed together with the Pb-bearing ferrite.

As we have already reported,[1-3] magnesium-, cadmium-, and titanium-bearing ferrites can be formed by air oxidation of aqueous suspensions at 65 °C. When the Mg^{2+} or Cd^{2+} concentration in the initial solutions is low, the magnesium- or cadmium-bearing ferrite is readily formed.[1,2] When concentrations of these ions in the initial solutions are high, basic magnesium sulphate, cadmium hydroxide, and/or α-FeO(OH) are formed together with the ferrites.[1,2] Using this method, there was a limit to the Mg^{2+} and Cd^{2+} content of the magnesium- and cadmium-bearing ferrites that could be formed.[1,2] However, in the case of Ti^{4+}, an oxidized Fe_3O_4–$Fe_2[TiO_4]$ solid solution with spinel-type structure was synthesized at Ti : $Fe_{tot.}$ mol ratios of 0 : 1 to 0.5 : 1 in the initial solution, pH 9.0, and 65 °C.[3]

Kaneko and Katsura [1] suggested that Mg-bearing ferrite is not formed at pH values <8.0, where Mg^{2+} is not hydrolysed. The Cd-bearing ferrite is most readily formed at pH 10.[2] Kiyama [4] has established the range of temperature and alkalinity of the aqueous suspension over which Fe_3O_4 is formed as a stable species: it is readily obtained above 60 °C at pH 9—10. Tamaura *et al.*[5] have also studied the reaction conditions necessary for the formation of Fe_3O_4 in the presence of a dispersing reagent and suggested that the formation of α-FeO(OH) is completely suppressed by sucrose.

The formation of Fe_3O_4 or metal ion-bearing ferrite by air oxidation of aqueous suspensions, and the metal content in the resulting ferrite are therefore influenced by reaction conditions such as pH and metal-ion concentrations. In this paper, the formation of lead ferrite and its intermediate are reported.

EXPERIMENTAL

Reagents.—Guaranteed reagent grade $Fe[SO_4]{\cdot}7H_2O$ and $PbCl_2$ were employed for preparing reaction solutions.

Apparatus.—A beaker with a removable cover was used as the reaction vessel.[3] Glass, calomel, and platinum electrodes and a condenser were fitted to the reaction vessels as described in the previous paper.[3]

Procedure.—Except where mentioned, the experimental procedure was the same as that described earlier.[3] Initial solutions were prepared by dissolving $Fe[SO_4]{\cdot}7H_2O$ (15.0 g) and a desired amount of $PbCl_2$ in redistilled water (0.75 dm^3) at 65 °C under nitrogen. A CO_2-free sodium hydroxide solution (2 mol dm^{-3}) was added to initial solutions and the pH values were adjusted to 10 or 12. After the resulting suspension [a mixture of iron(II) and lead(II) hydroxide] had stood for 1 h at 65 °C in a nitrogen atmosphere, air oxidation was effected by passing through air at a rate of 3 dm^3 min^{-1} in place of nitrogen. The products obtained after air oxidation were separated from the solution, using magnetic attraction,[3] washed successively with redistilled water and acetone, and the washed products dried *in vacuo* at room temperature. *X*-Ray diffraction patterns and i.r. spectra (KBr disc) of the dried products were recorded. The Mössbauer spectra were obtained at room temperature; the Curie points of the products were measured *in vacuo*. When a weakly magnetic product was obtained after the oxidation reaction, the sample was filtered off, washed with redistilled water and acetone on the filter paper, and dried.

For the analysis of samples before air oxidation, 0.025 dm^3 of the suspension under nitrogen was extracted by syringe without air contamination and centrifuged at 1 500 revolutions per min. The precipitates thus obtained were washed several times with oxygen-free acetone to remove as much water as possible in order to prevent oxidation, and dried under nitrogen overnight. The dried products were sealed with Cellophane tape before *X*-ray diffraction patterns were obtained. The i.r. spectra of the dried products were obtained as Nujol mulls.

Chemical Analysis.—The Pb^{2+} content in the products was determined by ethylenediaminetetra-acetate titration after separating the Pb^{2+} from the sample solution as $Pb[SO_4]$. The samples taken from the suspension before air oxidation were dissolved in HCl (5 mol dm^{-3}). The Fe^{2+} and Fe^{3+} contents of the samples were determined by means of 2,2′-bipyridyl.[6] The products obtained after air oxidation were dissolved in H_2SO_4 (3 mol dm^{-3}) and the Fe^{2+} and Fe^{3+} contents determined by the method mentioned previously.[1,2] The SO_4^{2-} content of the products was determined by means of *X*-ray fluorescence, using $Na_2[SO_4]$ as an internal standard. The analytical precision of the *X*-ray fluorescence method is ±0.2 wt.%.

RESULTS AND DISCUSSION

Reaction Conditions for the Formation of Lead-bearing Ferrite.—In the *X*-ray diffraction pattern of the product obtained at pH 12 at a high Pb^{2+} concentration in the initial solution (Pb^{2+} : $Fe_{tot.}$ ratio of 0.30 : 1), only broadened peaks typical of spinel-type compounds were seen. In the electron micrograph, only the ferrite particles were observed, and the particle size was estimated to be *ca.* 10 nm. The broadening of the peaks in the *X*-ray diffraction pattern is due to the formation of small particles of spinel-type compounds. In the i.r. spectra, only the bands due to the ferrites (560 and 360 cm^{-1}) [7,8] were seen. However, in the i.r. spectra of the products obtained at Pb^{2+} : $Fe_{tot.}$ ratios $<0.20:1$, key bands for α-FeO(OH) (890 and 795 cm^{-1}) [9] were seen. In the *X*-ray diffraction patterns, at pH 10 and at high Pb^{2+} concentrations (Pb^{2+} : $Fe_{tot.}$ ratios from 0.15 : 1 to 0.20 : 1), peaks (ASTM 22–65) for $PbO{\cdot}nH_2O$ were seen together with peaks (2θ 37.0 and 47.0°) which were not assigned, and with broadened peaks of the spinel-type compound. When Pb^{2+} concentrations were low (Pb^{2+} : Fe_{tot} ratios of 0.02 : 1 to 0.07 : 1 at pH 10 and 0.02 : 1 to 0.05 : 1 at pH 12) the peaks for α-FeO(OH) were seen. Thus, the spinel-type compound is most readily formed at a Pb^{2+} : $Fe_{tot.}$ ratio of 0.30 : 1 in the initial solution and at pH 12 and 65 °C. We call the spinel-type compound formed under these conditions ' the optimum lead ferrite.'

Chemical Composition, Curie Point, Mössbauer Spectrum, and I.r. Spectrum of the Optimum Lead Ferrite.—Table 1 gives the Pb^{2+}, Fe^{2+}, Fe^{3+}, and SO_4^{2-} content of the optimum lead ferrite. The analytical values given in the table were determined for a sample weighing 149.94 mg. As seen in the table, the SO_4^{2-} : Pb^{2+} mol ratio in the optimum lead ferrite is 0.020 2 : 1, which shows that the Pb^{2+} ions determined in this compound do not form $Pb[SO_4]$, but are taken into the optimum lead ferrite. From the Pb^{2+}, Fe^{2+}, and Fe^{3+} content given in Table 1, we can estimate the chemical formula as $0.104\,PbFe_2O_4{\cdot}0.361\,Fe_3O_4{\cdot}0.119\,Fe_2O_3$ ($Pb_{0.19}Fe_{2.75}O_{4.0}$), provided that the lead ferrite has a spinel-type structure. The calculated weight from the chemical formula is 142.6 mg. This value is very close to that obtained before the chemical analysis.

TABLE 1

The Fe^{2+}, Fe^{3+}, Pb^{2+}, and SO_4^{2-} contents of the air-oxidation product at a Pb^{2+} : $Fe_{tot.}$ mol ratio of 0.30 : 1, pH 12, and 65 °C

Ion	Amount (mmol) in a 149.94 mg sample	Mol fraction Ion/$Fe_{tot.}$	SO_4^{2-}/Pb^{2+}
Fe^{2+}	0.361	0.236	
Fe^{3+}	1.17	0.764	
Pb^{2+}	0.104	0.067 9	
SO_4^{2-}	0.002 11	0.001 37	0.020 2

Figure 1 shows the temperature dependence of the magnetization of the optimum lead ferrite. Curve A was obtained by increasing the temperature from room temperature to 700 °C, and curve B by decreasing the temperature from 700 °C to room temperature. Curve A is not a typical smooth magnetization curve, but is formed from two different curves, as shown by broken lines A′ and A″. Curve B is not identical with curve A. These results indicate that the sample decomposed on heating *in vacuo*. The decomposition temperature is estimated to be *ca*. 400 °C from curve A. Curve A′ shows the temperature dependence of the magnetization of the lead ferrite formed in solution. The Curie point of this lead ferrite is estimated to be at *ca*. 400 °C. Curve A″ corresponds to one of the decomposed products and its Curie point is at 570 °C. This value is approximately equal to that of stoicheiometric Fe_3O_4 (at 585 °C [10]), which shows that one of the decomposed products is Fe_3O_4. Curve B is also formed from two different curves (B′ and B″). These two curves show the temperature dependences of the magnetization of the two decomposed products. Curve B″ corresponds to Fe_3O_4. The Curie point for curve B′ (at 270 °C), which corresponds to the other decomposed product, is considerably different from that for curve A″ (at 400 °C), corresponding to the lead ferrite. Thus, the optimum lead ferrite seems to decompose at *ca*. 400 °C *in vacuo* into Fe_3O_4 and some ferromagnetic compound with a Curie point of *ca*. 270 °C.

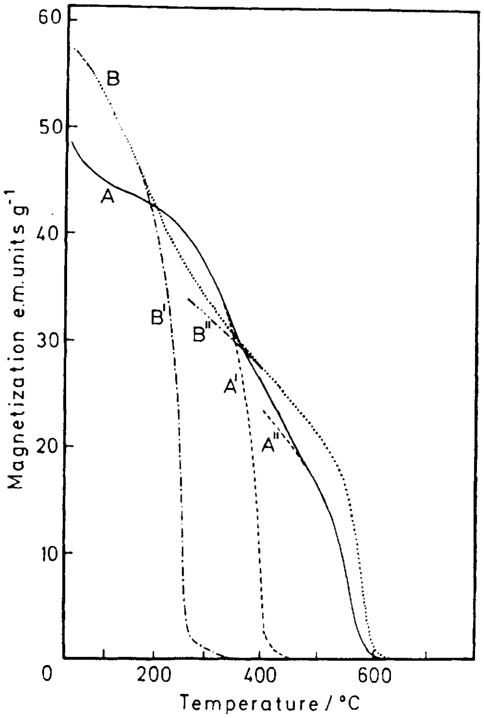

FIGURE 1 Temperature dependence of the magnetization of the product obtained after air oxidation at a Pb^{2+} : $Fe_{tot.}$ mol ratio of 0.30 : 1 in the initial solution at pH 12 and 65 °C. Curves A and B were obtained by increasing the temperature from room temperature to 700 °C, and decreasing the temperature from 700 °C to room temperature, respectively. Curve A is formed from curves A′ and A″. Curve B is formed from curves B′ and *B*″. 1 e.m.u. — 79.58 A m^{-1}

In the *X*-ray diffraction pattern of the sample obtained by heating the optimum lead ferrite at 500 °C for 2 h *in vacuo*, two peaks unlike those of spinel-type compounds were observed together with peaks corresponding to the spinel-type compound. These two peaks were not assigned, but seem to correspond to a ferromagnetic compound with a Curie point of 270 °C, whose existence is suggested from curve B′ in Figure 1.

The peaks in the Mössbauer spectrum of the optimum lead ferrite were broadened, compared with those of the Fe_3O_4 formed by air oxidation of the aqueous suspension. This broadening seems to be due to the fact that the Pb^{2+} ions are situated on the lattice points in a lead ferrite with a spinel-type structure. The values of the effective magnetic field in the tetrahedral and octahedral sites estimated from the Mössbauer spectrum are 484 and 448 kOe,* respectively. These values are lower than those of stoicheiometric Fe_3O_4 (494 and 461 kOe[11]). This lowering of the effective magnetic field is in good agreement with the fact that the Curie point of the lead ferrite (400 °C) is lower than that of stoicheiometric Fe_3O_4 (585 °C), as mentioned above.

In the i.r. spectrum of the optimum lead ferrite, a band at 360 and a band at 560 cm^{-1} with a shoulder (at 690 cm^{-1}) were observed. The band at 560 cm^{-1} corresponds to the vibrations of the oxygen ions along the tetrahedral bond, and the lower one at 360 cm^{-1} is due to the motion of the oxygen ions in a direction almost perpendicular to the first one.[8] Waldron [8] reported that the i.r. spectrum of Fe_3O_4 has no shoulder, but that the spectra of $MgFe_2O_4$ and $MnFe_2O_4$ have shoulders at 735 and 645 cm^{-1}, respectively. The shoulder appears when divalent metal ions are situated in tetrahedral sites and the distance between the tetrahedral sites and the oxygen increases slightly.[8] The appearance of the shoulder in the i.r. spectrum of the optimum lead ferrite indicates that Pb^{2+} is situated in the tetrahedral sites.

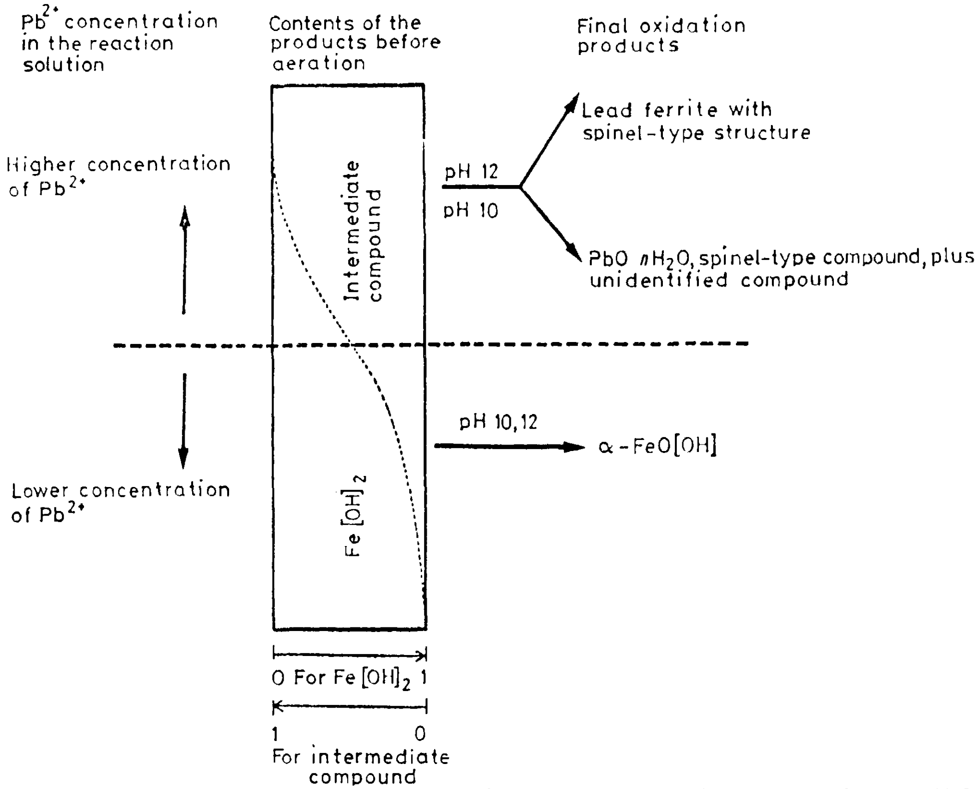

FIGURE 2 Schematic representation of air oxidation at 65 °C of aqueous suspensions prepared from $Fe[SO_4]$ and $PbCl_2$

Intermediate Product formed before Air Oxidation.—In the *X*-ray diffraction pattern of the sample taken from the suspension before air oxidation at a $Pb^{2+} : Fe_{tot.}$ ratio of 0.02 : 1 in the initial solution and pH 12, peaks (ASTM 13–89) due to $Fe[OH]_2$, along with several peaks which were not assigned (2θ 39.4, 41.0, and 80.7°), were observed. However, in the pattern of the sample taken from the suspension at a ratio of 0.30 : 1, no peaks for $Fe[OH]_2$ were seen, but strong peaks at 39.4, 41.0, and 80.7° were found. In the i.r. spectrum of the suspension sample at a ratio of 0.02 : 1, a very strong band from $Fe[OH]_2$ was seen at 490 cm^{-1}.[12] However, in the spectrum of the sample at a ratio of 0.30 : 1, the band for $Fe[OH]_2$ was considerably diminished, and the bands at 560 and 330 cm^{-1} appeared. Thus, when the Pb^{2+} concentration in the initial solution is high ($Pb^{2+} : Fe_{tot.}$ ratio of 0.30 : 1), no $Fe[OH]_2$ is formed in the suspension before air oxidation. In its place, a compound corresponding to the peaks at 39.4, 41.0, and 80.7° in the *X*-ray diffraction pattern is formed. The bands at 560 and 330 cm^{-1} in the i.r. spectrum are in the region typical of Fe_3O_4 bands. This suggests that the compound formed before air oxidation has lattice vibrations similar to Fe_3O_4.

Table 2 gives the Fe^{2+}, Fe^{3+}, Pb^{2+}, and SO_4^{2-} contents of the precipitate and the supernatant obtained before air oxidation, and the content of the supernatant after air oxidation at a $Pb^{2+} : Fe_{tot.}$ ratio of 0.30 : 1 in the initial solution, at pH 12. The values in the table are given as mol ratios to the total iron initially added to the reaction solution. As seen here, neither iron nor lead(II) ions were detected in the supernatant before air oxidation. All Fe^{2+} and Pb^{2+} ions present in the initial solution were precipitated before air oxidation. The compound formed before air oxidation dissolved in the HCl solution, but not in a H_2SO_4 solution. In the i.r. spectrum of the compound formed before air oxidation,

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* Throughout this paper: 1 Oe = 1 $cm^{-\frac{1}{2}}$ $g^{\frac{1}{2}}$ s^{-1}.

bands which seemed to be due to SO_4^{2-} were seen.[13] The SO_4^{2-} ion is apparently incorporated into the compound formed before air oxidation. Thus, before air oxidation, some species which is significantly different from the spinel-type compound is formed, and all Pb^{2+} ions present in the initial solution are taken into this compound. However, as mentioned previously, after air oxidation, only the lead ferrite with spinel-type structure was formed at a $Pb^{2+} : Fe_{tot.}$ ratio of 0.30 : 1 and pH 12 (the optimum lead ferrite). Thus, the compound formed before air oxidation is stable in a nitrogen atmosphere, but transformed to the lead ferrite with spinel-type structure during air oxidation at pH 12. The transformation of the intermediate compound formed before air oxidation into the lead ferrite is accompanied by the release of the Pb^{2+} ions into the supernatant. Approximately $\frac{2}{3}$ of the Pb^{2+} present in the initial solution is released during air oxidation at pH 12.

TABLE 2

The Fe^{2+}, Fe^{3+}, Pb^{2+}, and SO_4^{2-} contents * of the suspension before air oxidation at a $Pb^{2+} : Fe_{tot.}$ mol ratio of 0.30 : 1 pH 12, and 65 °C, and after air oxidation

Ion	Before air oxidation Precipitate	Supernatant	After air oxidation Supernatant
Fe^{2+}	1.00	0.00	0.00
Fe^{3+}	0.00	0.00	0.00
Pb^{2+}	0.30	0.00	0.22
SO_4^{2-}	0.22		

* Values given as $Ion/Fe_{tot.}$ mol fractions.

At pH 10, the same intermediate compound as that at pH 12 was formed at a high Pb^{2+} concentration ($Pb^{2+} : Fe_{tot.}$ ratio of 0.20 : 1). However, as mentioned previously, after air oxidation, $PbO \cdot nH_2O$ and another compound corresponding to the peaks at 37.0 and 47.0° in the *X*-ray diffraction patterns were formed together with the spinel-type compound. The $PbO \cdot nH_2O$ formed during air oxidation dissolved only slightly owing to its low solubility at pH 10. However, the $PbO \cdot nH_2O$ seemed to have dissolved at pH 12, and the Pb^{2+} ions which were not taken into the lead ferrite were present in the supernatant after air oxidation.

At low Pb^{2+} concentrations, α-FeO(OH) was formed after air oxidation at both pH 10 and 12. The reason for this is not well understood. In the case of Cd^{2+}, α-FeO(OH) was formed at certain Cd^{2+} concentrations.[2]

The relationships between the intermediate product formed before air oxidation, the final oxidation products, the concentration of Pb^{2+}, and the pH of the reaction solutions are summarized in Figure 2.

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