

DIFFERENTIAL THERMAL ANALYSIS OF HYDROUS FERRIC OXIDE FORMED BY DIRECT NEUTRALIZATION OF FERRIC CHLORIDE SOLUTION

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Abstract

Differential thermal investigation was made of amorphous hydrous ferric oxides, precipitated on neutralization of ferric chloride solution under different laboratory conditions, ranging from 0°C to 85°C in temperature, and from 3 to 12 in pH. Each of the differential thermal curves obtained shows an endothermic peak due to the release of adsorbed water, followed by a exothermic peak due to crystallization of anhydrous ferric oxide to hematite. The temperature corresponding to the exothermic peak varies in the range from 240°C to 460°C according to the temperatures and pH values of the solution from which the hydrous ferric oxide is precipitated.

Introduction

The author primarily attempted to investigate hot spring deposits composed mainly of hydrous iron oxide. Almost all of these deposits were found to be "amorphous", on X-ray powder photographs. Differential thermal analysis is an efficient means for identifying these amorphous materials. In view of establishing a standard for the identification, differential thermal curves for synthetic "amorphous" hydrous iron oxides were examined. The synthetic hydrous ferric oxides were formed by direct neutralization of ferric chloride solution, under various laboratory conditions.

This investigation is incomplete, and should be continued further. It is especially important to examine amorphous iron oxide prepared from various ferric solutions differing in the counter anion, and those formed by the oxidation of ferrous salts. The effects of coexisting ions should also be investigated.

Of the differential thermal curves for synthetic iron oxides, considerable information is obtained from literature, e. g., from the papers by J. L. Kulp and A. F. Trites (1951)¹⁾, and M. A. Geith (1952)²⁾.

Equipment and Procedure

For the differential thermal analysis, equipment and technique as described by T.

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Sudo (1953) was used. A dual thermal couple was used, one of its terminals being placed in a calcined alumina, the other in the sample to be examined. The sample was heated at the rate 10°C per minute. A straight line relationship was obtained between time and temperature in the interval between 100°C and 1000°C . All samples were prepared by grinding them to 200-300 mesh to minimize variations due to particle size.

X-ray powder patterns of the samples were taken with iron radiation. Amorphous hydrous ferric oxide specimens were prepared in the following procedure.

1/10 molar ferric chloride solution was warmed or cooled to a desired temperature, at which the solution was kept constant while precipitation reaction was taking place. 1:10 NH_4OH solution was added carefully to the above ferric chloride solution to a desired pH, with occasionally testing with pH test paper. The pH value of the supernatant liquid was then measured exactly by a glass electrode pH meter. The precipitate was filtered and thoroughly washed with water until filtrate became free from Cl^- (for AgCl test). The washed precipitate was dried under infra-red ray at 35°C overnight, and slightly wet specimen was ground and thermally analyzed.

Thermal Behavior of the Synthetic Amorphous Hydrrous Ferric Oxides

Curves 2, 3, and 4 represent the thermal behavior of the amorphous hydrous ferric oxides precipitated at $0 \pm 2^{\circ}\text{C}$, by adding 1:10 NH_4OH solution to 1/10 molar ferric chloride solution to pH 3.4 (curve 2), to pH 7.6 (curve 3), and pH 8.6 (curve 4), respectively.

Curve 2 shows a major endothermic reaction occupying the interval between 100°C and 230°C , with the peak at 150°C . This reaction is probably due to the release of adsorbed water. It is followed almost immediately by a major exothermic reaction culminating in a sharp peak at 240°C . This reaction is caused by the crystallization of the amorphous anhydrous ferric oxide to hematite. Two X-ray powder photographs proved that the material was amorphous at 220°C , and consisted of hematite at 300°C .

Curve 3 is almost identical to curve 2.

Curve 4 shows an endothermic peak due to the release of adsorbed water, similar to those in curve 2 and 3. However, the exothermic peak due to the crystallization of amorphous ferric oxide to hematite is of different feature from those in the above two curves. It starts from 250°C and culminates in a peak, which is much broader than those in curve 2 and 3, at 320°C . The material was proved from its X-ray photographs, to be amorphous ferric oxide at 230°C , and hematite at 400°C . A step-

like course in the curve around 300°C perhaps may be, though it is not confirmed, due to the dehydration of lepidocrocite which was present contaminating the sample.

Curve 5 and 6 represent the thermal behavior of the samples precipitated at 12°C, pH 7.2 and at 15°C, pH 7.3, respectively. The sharp crystallization exothermic peak lies slightly above 300°C.

Curves 7, 8, 9, 10, and 11 are for the samples (amorphous hydrous ferric oxide except the case of curve 7, where the sample became crystalline by aging) precipitated at $30 \pm 2^\circ\text{C}$. by adding 1:10 NH_4OH solution to pH 3.9 (curve 7), to pH 5.9 (curve 8), to pH 7.6 (curve 9), to pH 9.5 (curve 10), and to pH 11.6 (curve 11), respectively.

Curve 8 shows a crystallization exothermic reaction culminating in a sharp peak at 260°C.

The exothermic reaction in curve 9, 10, and 11 are characterized by the peaks of smaller amplitudes than in curve 8. The temperatures corresponding to the peaks are 330°C, 330°C, and 420°C, respectively, higher than that in curve 8.

It is seen here that the amplitude of the reaction peak decreases as the peak temperature increases. The increase in the pH value of the mother solution at the time of precipitation effects in raising the peak temperature of the thermal curve, broadening the peak width, and decreasing the peak amplitude. It appears further that this variation depends on the particle size and crystallinity of the sample. Generally speaking, the increase in particle size (or crystallinity) tends to raise the peak temperature, to broaden the peak width, and to lessen the amplitude, so that the area under the curve is kept constant. So then, the higher is the pH value at the time of precipitation, the higher are the particle size and the crystallinity of the sample.

Curves 12, 13, 14, 15, 16, and 17 represent the thermal behavior of the samples (amorphous hydrous ferric oxide) precipitated at $50 \pm 2^\circ\text{C}$, by adding 1:10 NH_4OH solution to pH 4.3, 7.1, 8.5, 8.6, and 12.0 respectively. The crystallization exothermic peaks lie at 240°C, 330°C, 380°C, 330°C, 330°C, and 410°C, respectively.

Here the same relation as in the case of the precipitation at 30°C is seen to be held.

Curves 19, 20, 21, 22, 23, and 24 represent the thermal behavior of the samples precipitated at 70°C, by adding 1:10 NH_4OH solution to pH 3.8, 6.4, 6.6, 6.8, 8.8, and 11.9, respectively. The crystallization exothermic peaks lie in the curves (excluding curve 19) at 350°C, 380°C, 450°C, and 440°C, respectively.

Curves 27, 28, 29, and 30 represent the thermal behavior of the samples precipitated at 85°C, the final pH of the solution being 3.3, 7.2, 8.1, and 11.4, respectively. The crystallization exothermic peaks in the curves (excluding curve 27) lie at 390°C, 450°C, and 460°C, respectively.

Here again, both in the precipitations at 70°C and 85°C, the same relation as in the precipitation at 30°C holds good, excepting the case of curves 19 and 27.

So far, the effects of pH of the mother solution upon the thermal behavior of the sample of amorphous ferric oxide precipitated at a given temperature has been discussed. It is now to discuss on the effects of temperature of the precipitation of the sample from the mother solution of a given pH, upon the thermal behavior of the sample.

The curves 3, 5, 6, 9, 13, 14, 18, 25, and 28, which represent the thermal behavior of the samples precipitated from solutions with approximately same pH around 7.3 (7.0-7.6), at 0°C, 12°C, 15°C, 30°C, 50°C, 50°C, 60°C, 80°C, and 85°C, respectively. It is clearly seen that the higher is the temperature of precipitation, the higher is the peak temperature. This relation holds good throughout the whole range of pH value.

It should be noticed that the crystallization exothermic peak for the amorphous ferric oxide precipitated in the range between 30°C and 60°C is broad in width and small in amplitude, showing that the sample is of relatively large particle size and probably high in crystallinity; whereas the crystallization exothermic peak for the sample precipitated below 30°C or at 70°C is sharp and is large in amplitude, showing that the sample is relatively small in particle size and probably low in crystallinity.

Curves 1, 7, 19, and 27 represent the thermal behavior of the samples precipitated at pH below 4.0. In these cases, the samples are of very small. With the samples of such a small size, it required long time (a few days) for their filtration and washing; and the aging of the samples was inevitable. Such aging proceeds more quickly when they are wet. The X-ray powder photographs of the samples for the curves 1, 19, and 27 showed that they were mixtures of hematite and poorly crystallized lepidocrocite. In the case of curve 7, the amorphous ferric oxide was found to be converted into hematite by aging.

Acknowledgment

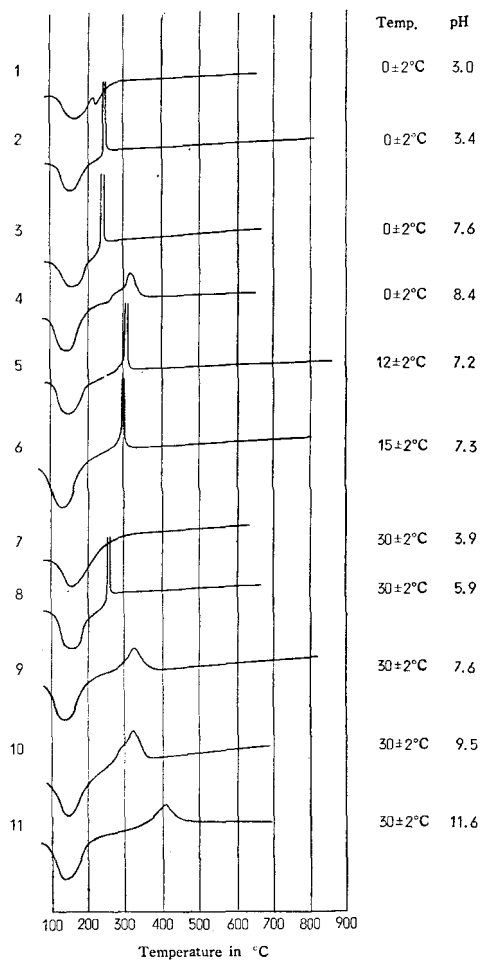
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