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THERMAL PROPERTIES OF AKAGANÉITE (β-FeOOH)

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A method is described for the preparation and thermal investigation of akaganéite (β-FeOOH). Its thermal properties were investigated by means of a derivatograph. The thermal stability was studied during its heating in the air and also in aqueous suspension. At a characteristic temperature the akaganéite is converted to hematite.

The β-modification of FeOOH was first prepared and described by Weiser and Milligan [1]. The compound was prepared by the hydrolysis of iron (III) chloride solution. The occurrence of β-FeOOH in natural deposits was presumed by Heller et al. [2], but an actual deposit was described only in 1959 by van Tassel [3] and later by Mackay [4]. The mineralogical nomenclature "Akaganéite" was originally given by Nambu after the deposit at Akagané in Japan.

Although the compound β-FeOOH has long been known and various natural deposits have been described, its properties have not yet been studied in sufficient detail. This is primarily due to the difficulties in preparing large quantitites, while the amounts of akaganéite found in natural deposits are usually too small and in addition contaminated with other minerals.

Up to now the thermal properties of akaganéite have been investigated only by Chandy [5] who studied the thermal transformation of β-FeOOH during its heating under normal atmospheric conditions. The differential thermal curve of akaganéite has not previously been published.

One of the authors of this paper (J. B.) systematically investigated the compounds obtained by the precipitation of Fe^{3+} from solution with alkaline substances and studied the conditions under which akaganéite formed. He prepared an amount of akaganéite which was sufficient for the study of its thermal and other properties.

The following method of preparing pure akaganéite was found to be best. A dilute solution of $FeCl_3$ (0.01 M) was heated to boiling and a previously determined amount of KOH solution (0.5 – 1.0 M) was added in order to obtain a pH of 5 to 7. The solution was boiled for one hour, the precipitate was filtered, washed with hot water and then dried at laboratory temperature. The final product was a practically pure β-FeOOH sometimes containing a small amount of hematite or goethite, depending on the actual pH of the final solution within the above range.

The product (needed for thermal investigation by the authors of this paper) was identified by X-ray diffraction: the results were compared with the *d*-values of β-FeOOH published by Rooksby [5].

The thermal investigation was made by means of a Paulik–Paulik–Erdey derivatograph. The size of samples and the DTA, DTG and TG response were chosen according to the water-loss and the intensities of the endothermic and exothermic peaks. A fast accompanying reaction – due to crystal conversion – was observed during the analysis. This resulted in the splitting of some of the sample from the platinum crucible. In order to obtain reproducible results, the crucible was covered and this reaction was controlled by Al_2O_3 addition (ratio 1 : 1).

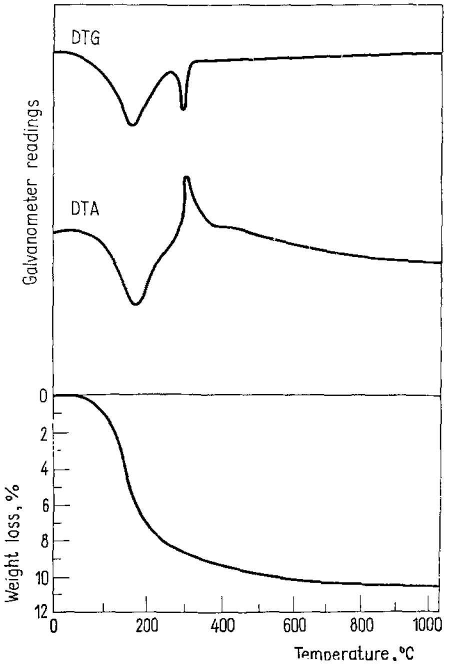

Fig. 1. Thermal curves of synthetic akaganéite

The thermal properties of synthetic akaganéite revealed by the derivatograph (Fig. 1) are comparable with those of synthetic goethite (Fig. 2).

A marked difference between these compounds is shown up by the different shapes of the DTA and DTG curves in the range 270° to 400°; this can be considered the decisive diagnostical range for akaganéite.

The DTA curve of goethite shows an endothermic peak at 350° which according to DTG and TG curves corresponds to water release from the OH groups. At almost the same temperature (310°) occurs the exothermic peak reaction of akaganéite. In the thermal range 250–360° the DTG curve of akaganéite shows endothermic deviation, which according to the TG curve corresponds to loss of weight, evidently due to water release from the OH groups.

The endothermic effect mentioned is related to the change of crystal structure from that of β-FeOOH (probably tetragonal $C_{4h}^5 - I4(m)$) to α-Fe_2O_3 (trigonal $D_{3d}^6 - R3c$). The exothermic effect does not appear during the change of α-FeOOH (rhombic $D_{3d}^{16} - Pbnm$) to α-Fe_2O_3. It is probable that the transition of α-FeOOH to α-Fe_2O_3 proceeds via another labile compound (e.g. γ-Fe_2O_3), but this was not proved either by Chandy [5] or by the authors of this paper.

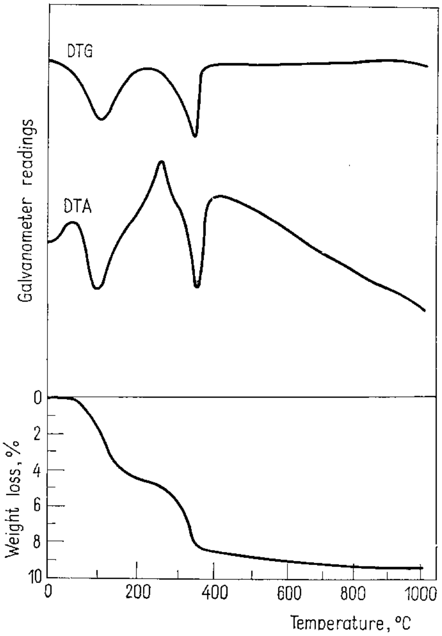

Fig. 2. Thermal curves of synthetic goethite

In both cases the total loss of weight (after subtracting the hygroscopic water) approaches very closely the theoretical value corresponding to the loss of water during the reaction 2 FeOOH → $Fe_2O_3 + H_2O$, i.e. 10.17%. According to the results of the analysis this water loss for akaganéite was 10.50% and for goethite 9.20%.

The thermal stability of akaganéite was investigated by prolonged heating in the air and also in aqueous suspension. Akagenéite heated at 100° in air showed practically no change. After long heating at 200° (approximately 25 hours) traces of hematite (β-Fe_2O_3) appeared in the X-ray diffraction patterns. With shorter heating (3 hours) at 250° the akaganéite was converted quantitatively to hematite.

During heating at 100° in aqueous suspension in a closed vessel, the akaganéite changed completely to hematite. In this case a temperature of 80° is considered as the upper limit of stability (in an almost neutral medium). Details of the preparation, the stability limitations and other properties of akaganéite will be published in a separate paper.

References

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