

## **KINETICS OF THERMAL TRANSFORMATIONS OF PRECIPITATED MAGNETITE AND GOETHITE**

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### **Abstract**

The aim of the present study was to determine the kinetic equations for the thermal transformations of precipitated iron oxides and hydroxides, namely for the process of thermal dehydroxylation of goethite and consecutive of hematite crystal structure growth as well as for the oxidation of magnetite to maghemite and its thermal transformation into crystalline hematite. The investigations have been carried out using thermogravimetry (TG/DTG/DTA), X-ray powder diffractometry (XRD) and high temperature powder diffractometry (HT-XRD). This presentation contains the continuation of our earlier works.

**Keywords:** kinetics of iron oxides transformation, thermal analysis of iron oxides

### **Introduction**

The global market for iron oxides for pigment applications is estimated today to be over one million tons per year. The largest use of iron oxide pigments is for coloring construction products such as roof tiles and paving blocks. Three principal iron oxides are mainly used as pigments: goethite, magnetite and hematite. These principal semi-products used for iron oxides pigments manufacturing are obtained mainly by precipitating oxidation of iron(II) salts solutions as for example solution of waste coppers from titanium dioxide production. The knowledge of the thermal behaviour of precipitated iron oxides and oxyhydroxides have importance in final treatment of produced in industrial scale iron oxide pigments. This paper deals with thermal transformations and kinetics of these transformations on example of goethite and magnetite, which can be used as precursors for the preparation of red hematite phase.

### **Experimental**

The method for obtaining the precipitated iron oxyhydroxide (goethite),  $\alpha$ -FeOOH and magnetite,  $(\text{FeO})_x \cdot \text{Fe}_2\text{O}_3$  and the detail experimental conditions are discussed in our other paper [1].

The investigation of crystal structure of products obtained by oxidative/hydrolytic process and obtained during their thermal treatment semi-products were carried

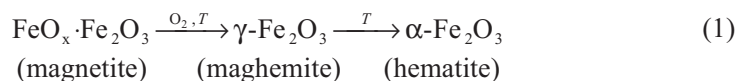
out by X-ray diffractometry using  $\text{CuK}_\alpha$  radiation on a Philips PW 1710 goniometer, equipped with high temperature camera Anton Paar HTK 10. The thermal transformations of iron oxides and kinetics of thermal transformations have been investigated using thermogravimetry (thermoanalyser MOM 1500 C) and high temperature X-ray diffractometry. The crystal dimensions and morphology have been measured by transmission electron microscopy using Tesla BS-350 instrument.

The extent and rate of goethite dehydroxylation as well as the rate of thermal oxidation of magnetite in static air atmosphere have been investigated using the thermogravimetric method. The extent of thermal transformations of maghemite to hematite and the rate of consecutive to goethite dehydroxylation the transformation of amorphous  $\text{Fe}_2\text{O}_3$  microparticles to crystalline hematite phase have been investigated using high temperature X-ray diffractometry.

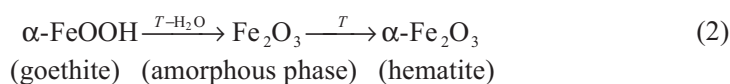
TG/DTG/DTA curves of precipitated goethite and magnetite in static air atmosphere were recorded in the temperature range from room temperature to 1300 K. The measurements have been carried out using standard ceramic crucibles for 100 mg samples. The experiments have been carried out using goethite samples having the following particles size: mean length of 5  $\mu\text{m}$  and width about 0.8  $\mu\text{m}$  and with particles size distribution as is shown in our parallel paper [1]. The magnetite samples used in experiments consisted of spherical particles with mean diameter about 1  $\mu\text{m}$ .

## Results and conclusions

As it was shown earlier [2-4] the precipitated magnetite undergoes the following cycle of thermal transformations in air atmosphere



In other side the precipitated goethite after dehydroxylation stage forms amorphous  $\text{Fe}_2\text{O}_3$  phase which particles at higher temperature grow forming crystalline hematite phase



Although in both above processes the final product of transformations is the same –  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) but the optical properties of red pigments prepared by goethite and magnetite thermal treatment are essentially different. The aim of the present work is to set the kinetics and kinetic equations for describing the above transformations.

The results of kinetic elaboration of thermogravimetric and HT XRD measurements are shown and discussed below. The kinetic experimental results have been elaborated using the Coats–Redfern method applied to the Avrami–Erofeev A3 model

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{\Delta E}{RT}\right) (1-\alpha) [-\ln(1-\alpha)]^{2/3} \quad (3)$$

The integral Coats–Redfern equation has following form

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\left(\frac{k_0 R}{\beta E}\right) \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (4)$$

and this linear equation in the form

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = a_0 + a_1 \left(\frac{1000}{T}\right) \quad (5)$$

has been used for kinetic parameters estimation of selected kinetic model.

The below drawing (Fig. 1) shows the thermoanalytical curves (in the temperature range from room temperature to 800 K) for the dehydroxylation reaction of precipitated goethite. This reaction progresses in the temperature range from 470 to 570 K. Figure 2 shows the TG/DTG/DTA curves for thermal oxidation reaction of precipitated magnetite which proceeds in the temperature range from 400 to 570 K leading to the maghemite formation as an intermediate product.

The results of elaboration of thermogravimetric data for goethite dehydroxylation reaction using the selected kinetic models: A2, A3, R3, D1, F1 and D4 are shown in Fig. 3. The best data fitting has been achieved for the Avrami–Erofeev

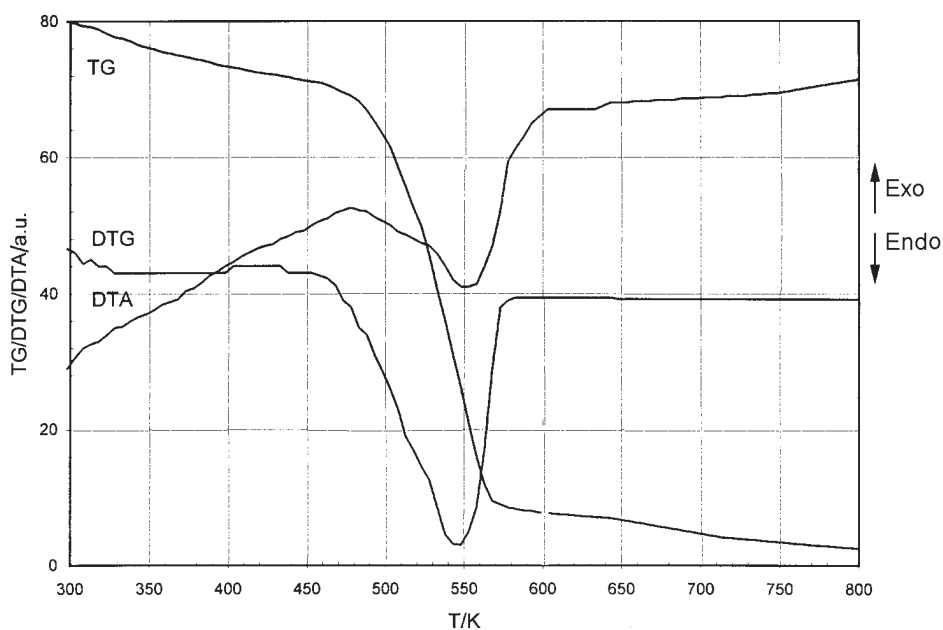


Fig. 1 TG/DTG/DTA curves of precipitated goethite

model. The results of kinetics elaboration by a similar way of thermogravimetric data for the magnetite oxidation reaction are shown in Fig. 4.

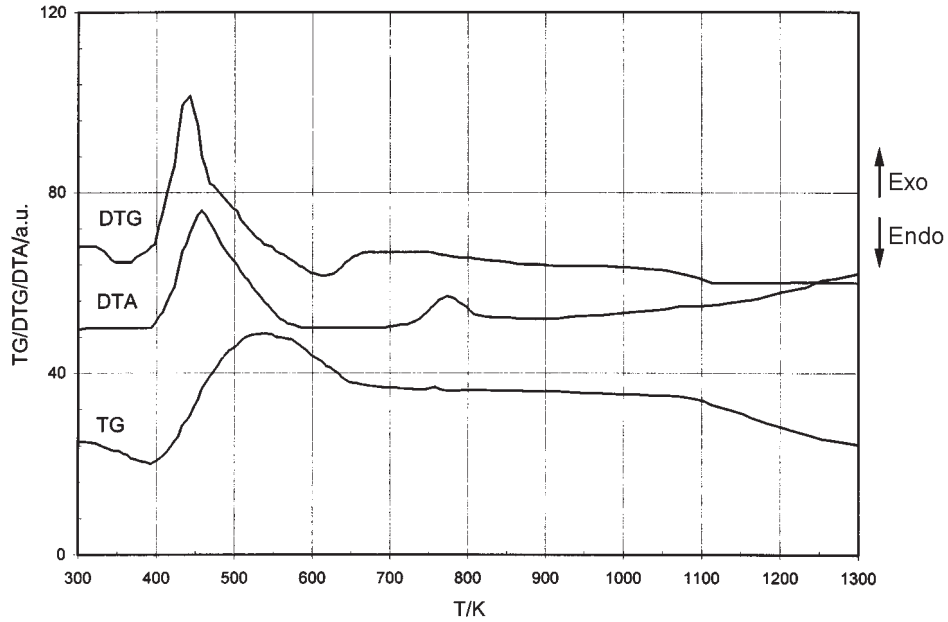


Fig. 2 TG/DTG/DTA curves of precipitated magnetite

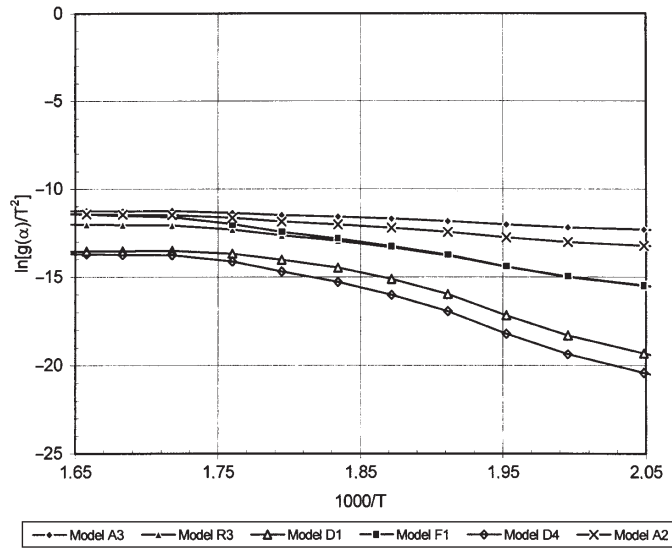


Fig. 3 Results of rate fitting for goethite dehydroxylation reaction by selected kinetic model

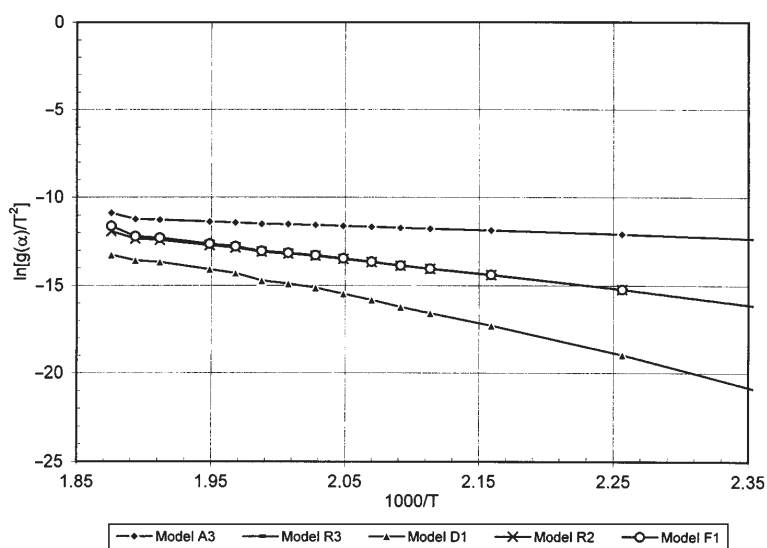


Fig. 4 Results of rate fitting for magnetite oxidation reaction by selected kinetic models

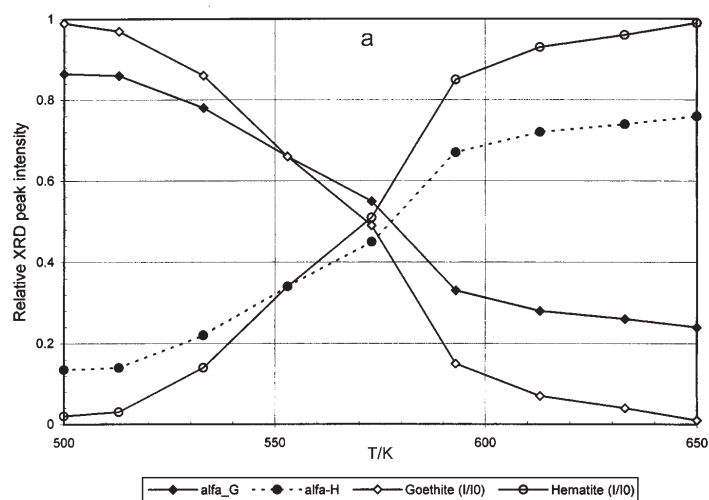
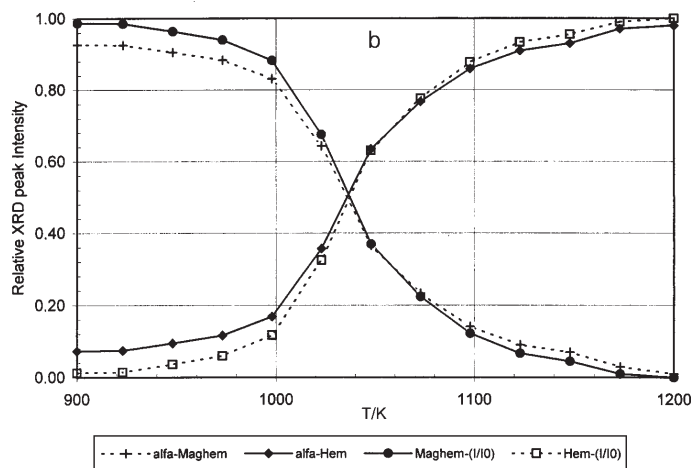


Fig. 5a Kinetics of goethite to hematite thermal transformation determined by HT-XRD

The kinetic model for the growth of hematite phase during thermal treatment of precipitated goethite has been elaborated using high temperature X-ray powder diffractometry data. Experimental results for this transformation are shown in Fig. 5a. Using the shown in this drawing relative XRD peak intensity ( $I/I_0$ ) measurements for the most intensive goethite peak and for the hematite phase made in the temperature range from 500 to 650 K were calculated the values of reaction extent  $\alpha$  vs. temperature at a heating rate of  $0.05 \text{ K s}^{-1}$ . As we can see the reaction proceeds with maximal



**Fig. 5b** Kinetics of maghemite to hematite thermal transformation determined by HT-XRD

rate at temperature close to 570 K. In the next step using the same as for thermogravimetric measurements procedure the best kinetic equation for this transformation has been selected.

In Fig. 5b the results of HT XRD measurements for the maghemite-hematite thermal transformation are shown. The diffractometric measurements of the most intensive maghemite and hematite peaks have been made at temperature ranging from 900 to 1200 K. This reaction has attained the maximal rate at temperature 1040 K. Above temperature 1170 K the transformation of maghemite into hematite structure is practically completed.

**Table 1** Results of kinetics elaboration for iron oxides thermal transformations

No.	Reaction	$a_0$	$a_1$	$R$	$s$	$k_0/s^{-1}$	$E/kJ\ kmol^{-1}$
1	Goethite dehydroxylation	-6.7888	-2.6662	0.9649	0.0944	0.4233	22.167
2	Magnetite oxidation	-6.2562	-2.6080	0.9532	0.0811	0.6747	21.682
3	Goethite-hematite transformation	-6.0292	-3.2857	0.9465	0.1284	0.6018	27.317
4	Maghemite-hematite transformation	-7.0477	-6.2601	0.9484	0.1349	0.4043	52.046

All the results of kinetic measurements for the thermal transformation of samples of precipitated goethite and magnetite have been finally elaborated using the Avrami-Erofeev kinetic model (A3). The results of these calculations are summarized in Table 1. This table contains the values of regression parameters ( $a_0$ ,  $a_1$ ) for the linear form of Eq. (5) and essential statistics for these equations: multiple correlation coefficient  $R$  and residual standard deviation  $s$ . According to the Coats-Redfern

simplification Arrhenius parameters were also calculated estimated for A3 kinetic model:  $k_0$  and  $E$ .

## Conclusions

The above results of investigation of complex cycle of iron oxides thermal transformation have importance for industrial scale processes of iron oxide and iron oxides pigments preparation especially in their final thermal treatment stage. All measurements have been carried out using the conditions prepared in laboratory and precipitated using oxidative/hydrolytical procedure synthetic goethite and magnetite. The principal aim of the applied experimental and calculation procedures was to give a consistent qualitative and quantitative description for iron oxides thermal transformations.

## References

- 1 K. Przepiera and A. Przepiera, Kinetics and Reactivity of Solids, P. IV/17, CCTA 8, Zakopane, Sept. 3–8, 2000.
- 2 K. Przepiera, Podstawy otrzymywania strąconych pigmentów żelazowych, Thesis, Technical University of Szczecin, Szczecin 1995.
- 3 A. Przepiera, K. Przepiera, M. Wiśniewski and W. Dąbrowski, J. Thermal Anal., 40 (1993) 1131.
- 4 A. Przepiera, K. Przepiera, M. Wiśniewski and M. Jabłoński, Mat. Sci. Forum, 133–136 (1993) 599.