Interaction between α-, β- or γ-FeOOH and water at 60 °C, 80 °C, and 100 °C

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The influence of temperature (60 °C, 80 °C, and 100 °C) and time (4 weeks, 8 weeks, and 12 weeks) on phase composition and stability of polymorphous modifications of α-, β-, and γ-FeOOH (goethite, akaganeite, and lepidocrocite) in aqueous suspension was investigated by X-ray phase analysis and infrared absorption spectral analysis. It has been found that β- and γ-FeOOH is transformed to stable α-FeOOH or stable α-Fe$_2$O$_3$ (hematite) and, to a certain extent, to γ-Fe$_2$O$_3$ (maghemite). The degree of crystallinity increases. The presented infrared spectra of the starting materials as well as of the products of their heating (in the wavenumber range 250—4000 cm^{-1}) indicate the transformation of hydroxyl water to surface-bonded water.

С помощью рентгенофазового анализа и ИК-адсорбционного спектрального анализа наблюдалось влияние температуры (60 °C, 80 °C и 100 °C) и времени (4 недели, 8 недель и 12 недель) на фазовый состав и устойчивость полиморфных модификаций α-, β- и γ-FeOOH (гетит, акаганеит и лепидокрокит) в водной суспензии. Обнаружено, что протекает превращение β- и γ-FeOOH в устойчивый α-FeOOH или в устойчивый α-Fe$_2$O$_3$ (гематит) и частично в γ-Fe$_2$O$_3$ (магемит). Повышается степень кристалличности. Из приведенных ИК-спектров исходных материалов и продуктов их нагревания (в интервале 250—4000 см$^{-1}$) очевидно превращение гидроксильной воды в поверхностно связанную.

Iron(III) hydroxide-oxides are products of hydrolysis of dicalcium ferrite, calcium ferrite, and calcium ferrite-aluminates which represent the essential component of the ferritic phase of portland cement. Besides Ca(OH)$_2$, colloidal X-ray amorphous gel, polymorphous modifications of FeOOH of different degree of arrangement of crystal structure and crystallinity in different stage of dehydration, cryptocrystalline or even crystalline hydrate of iron(III) oxide of varying composition or polymorphous dispersion modifications of iron(III) oxide may arise.

The hydration of dicalcium ferrite $2CaO \cdot Fe_2O_3$ and calcium ferrite $CaO \cdot Fe_2O_3$ gives rise to instable hydration products of composition $2CaO \cdot Fe_2O_3$ $5H_2O$, $2CaO \cdot Fe_2O_3 \cdot 2H_2O$, $CaO \cdot Fe_2O_3 \cdot H_2O$, $4CaO \cdot Fe_2O_3 \cdot 13H_2O$, and $3CaO \cdot Fe_2O_3 \cdot 6H_2O$ as well as to other hydrates of nonstoichiometric composition with varying content of hydrate water. While considerable amounts of Al_2O_3 pass from calcium aluminates into solution in the form *e.g.* of $Al(OH)_4^-$ ions [1] and the metastable product is transformed into stable $3CaO \cdot Al_2O_3 \cdot 6H_2O$, only small amounts of Fe_2O_3 pass from calcium ferrites into solution as $Fe(OH)_4^-$, $FeOH^{2+}$, and $Fe_2(OH)_2^{4+}$ ions [2, 3] or in alkaline medium as FeO_2^- ions according to the equation [4]

$$FeO \cdot OH + H_2O + OH^- \rightarrow FeO_2^- + 2H_2O$$

A gradual decrease in concentration of $Ca(OH)_2$ in solution brings about that $4CaO \cdot Fe_2O_3 \cdot 13H_2O$ as well as cubic $3CaO \cdot Fe_2O_3 \cdot 6H_2O$ hydrolyzes to give colloidal iron(III) hydroxide [5, 6] or $Fe_2(OH)_2^{4+}$ ions which polymerize to yield the $[Fe(OH)_x^{(3-x)+}]_n$ polycations [7, 8].

The hydration of $2CaO \cdot Fe_2O_3$ and $CaO \cdot Fe_2O_3$ and compounds of the series of solid solutions $2CaO \cdot Fe_2O_3$ with Al_2O_3 arisen by isomorphous substitution of aluminium for iron or the hydration of calcium aluminate-ferrites at laboratory temperature, at 60 °C and 80 °C as well as under hydrothermal conditions at 100 °C results in hydrolytic decomposition of the formed calcium ferrite or calcium ferrite-aluminate hydrates [9—11].

Ryžak [12] prepared goethite and lepidocrocite or their mixtures by crystallization and transformation of "gel" precipitates obtained at 20 °C, 40 °C, and 80 °C and at pH = 4.8 and pH = 12. *Fischer* and *Schwertmann* [13] investigated the mechanism of formation of hematite in aqueous suspension of amorphous iron(III) hydroxide at 70 °C and 100 °C on the basis of kinetic measurements and infrared spectroscopy as a function of temperature and pH of medium. Christensen [14] prepared goethite from amorphous iron(III) hydroxide under hydrothermal conditions at 100—200 °C and pH = 0.8—10.8.

The infrared spectra of amorphous iron(III) hydroxide-oxide, polymorphous modifications of FeOOH (α-goethite, β-akaganeite, γ-lepidocrocite, δ-ferroxyhite), ferrihydrite ($Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$), hematite ($\alpha$-$Fe_2O_3$), maghemite ($\gamma$-$Fe_2O_3$), and ferrites have been presented and interpreted in [7, 15—25].

The aim of this study was to investigate the influence of temperature and time on stability and transformation of individual polymorphous modifications of FeOOH from monomineral starting materials by X-ray phase analysis and infrared absorption spectral analysis. These investigations are a part of the study of hydration process of ferrite phase of the clinker of portland cement.

Experimental

Goethite was prepared by precipitating dilute solution of $FeCl_3$ with concentrated solution of NaOH up to pH = 12 at laboratory temperature according to [26]. Akaganeite was obtained by hydrolytic precipitation of dilute solution of $FeCl_3$ by the method according to [27] modified by slow addition of NaOH solution up to pH = 4.5 at laboratory temperature. Lepidocrocite was made ready by precipitation and oxidation of cooled solutions of $FeSO_4$ $7H_2O$, $Na_2S_2O_3$, and NH_4Cl by KIO_3 solution by the method according to [28]. By repeated intensive stirring with distilled water and centrifugation the precipitates were deprived of undesirable adsorbed ions and dried at 25 °C. After X-ray phase analysis, the air-dry and, to a certain extent, crystallized crystallinic gels of individual polymorphous modifications of FeOOH in aqueous suspension (mass ratio = 1 : 10) were put into teflon crucibles and allowed to react in hydrothermal pressure vessels for 4 weeks at 60 °C, 80 °C, and 100 °C. In order to attain or at least to approximate to the equilibrium composition, the phase transformations were so investigated that the product formed at 60 °C was identified and heated again in aqueous suspension for further 4 weeks at 80 °C. This heating was also repeated at 100 °C. The phase composition of the products was identified by an X-ray diffractograph Philips (goniometer PW 1050, radiation Fe K_a, angle interval ⟨5°—35°⟩, evaluation of linear diffraction intensities according to ASTM). The infrared spectra were taken with an instrument Perkin—Elmer, model 457. The samples were measured by the KBr method. The concentration of samples was 0.6 mg for 300 mg of KBr and the diameter of pellets was 13 mm.

Results and discussion

X-ray phase analysis

A. Simple heating

$\theta = 60$ °C

Goethite   — goethite with slight portion of maghemite
Akaganeite   — akaganeite with small portion of goethite
Lepidocrocite — lepidocrocite with slight portion of goethite

$\theta = 80$ °C

Goethite   — goethite with small portion of maghemite
Akaganeite   — mixture of akaganeite and goethite
Lepidocrocite — lepidocrocite with small portion of goethite

$\theta = 100\ °C$

Goethite	— goethite with slight portion of maghemite and hematite
Akaganeite	— mixture of goethite and hematite with slight portion of maghemite
Lepidocrocite	— mixture of goethite and hematite with slight portion of maghemite

B. Gradual heating

$\theta = 60\ °C\ \rightarrow\ 80\ °C$

Goethite	— goethite
Akaganeite	— goethite with smaller portion of hematite
Lepidocrocite	— hematite with smaller portion of goethite

$\theta = 80\ °C\ \rightarrow\ 100\ °C$

Goethite	— goethite (relatively high degree of crystallinity)
Akaganeite	— hematite with small portion of goethite
Lepidocrocite	— hematite with small portion of goethite

It is obvious from the presented results of X-ray phase composition of the products that the thermal treatment by direct simple heating of the starting materials to 80 °C and 100 °C under given conditions results in partial decomposition of goethite giving rise to maghemite or hematite while it is stabilized by gradual heating even at 60 °C. In comparison with the published data [2, 4], the temperature of partial decomposition of goethite by simple heating is somewhat lower. Akaganeite and lepidocrocite behave in a different manner at the described kinds of heating and it seems that the time (at further heating) has the decisive influence on transformation, *e.g.* of lepidocrocite to hematite. The transformation of amorphous iron(III) hydroxide and lepidocrocite into goethite proceeds by dissolution and reprecipitation [29]. A higher concentration of amorphous iron(III) hydroxide-oxide in aqueous suspension (*e.g.* in hydrating pastes), agglomeration, nucleation, and crystallization of gel particles enhance the formation of hematite by the mechanism of internal dehydration [30].

Infrared spectral analysis

We present a series of complete infrared spectra in the wavenumber range 250—4000 cm^{-1} the interpretation of which enables us to elucidate the origination of hematite that is the most stable phase in the Fe_2O_3—H_2O system.

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Goethite

There are two distinct bands at 1635 cm^{-1} and 3420 cm^{-1} in the spectrum of goethite. They correspond to bending and stretching vibrations of bonds of the O—H groups in the sorbed molecular water. The bands at $\bar{v} = 1380$ cm^{-1}, 1465 cm^{-1}, 1530 cm^{-1}, or 3180 cm^{-1} may be assigned to the stretching vibration $v(OH)$. The characteristic and distinct bands of goethite with wavenumbers of 790 cm^{-1} and 890 cm^{-1} appear in the region of bending vibrations of O—H or of the bonds between O—H and atoms of Fe (Fe—OH bonds). The band at $\bar{v} = 630$ cm^{-1} has not been yet assigned b,ut it may correspond to the stretching vibration stressing the Fe(III)—O bond. The most conspicuous band of goethite is the broad, intensive band at $\bar{v} = 405$ cm^{-1} (with shoulders at 375 cm^{-1}, 425 cm^{-1}, and 450 cm^{-1}) which corresponds to vibrations of the Fe—O skeleton. Other bands of the spectrum of goethite appear at $\bar{v} = 270$ cm^{-1}, 285 cm^{-1}, and 305 cm^{-1}. The doubled band at $\bar{v} = 3300$ cm^{-1} and 3700 cm^{-1} indicates two types of asymmetric stretching vibrations of the OH groups which are energetically differently bonded in the structure. The band $v(OH)$ becomes visible in the $\bar{v}$ region 3600—3750 cm^{-1} provided hydroxides without hydrogen bonds are present. It is also valid for the group of weaker bands in the $\bar{v}$ range 1300—1800 cm^{-1} (bands at $\bar{v} = 1380$ cm^{-1}, 1460 cm^{-1}, 1630 cm^{-1}, and 1740 cm^{-1}) while the band at $\bar{v} = 1630$ cm^{-1} indicates the presence of molecular water the contribution of which to the band intensity is very small [7, 18, 21]. If this band is missing, only hydroxides are present. The O—H bonds in water and FeOOH can be distinguished. We may deduce from intensity of the three bands corresponding to bending vibrations of O—H and Fe—O in goethite in the $\bar{v}$ region 400—1000 cm^{-1} (bands at $\bar{v} = 630$ cm^{-1}, 790 cm^{-1}, and 890 cm^{-1}) that the starting material is, to a great measure, a crystallite product when compared with data published in paper [17]. The weak but characteristic band at $\bar{v} = 673$ cm^{-1} (better shoulder) is also described in paper [25]. Some bands which are assigned to stretching vibrations of the bonds in the Fe—O skeleton are also present in this region. Further bands in the spectrum of goethite corresponding to those vibrations appear in the $\bar{v}$ region 250—400 cm^{-1} (Fig. 1) and are consistent with the published data [22, 23].

A. Simple heating

$\theta = 60\,°C$: bands at $\bar{v} = 3180$ cm^{-1} and 3420 cm^{-1} are approximately of equal intensity like the group of bands at $\bar{v} = 1300$—1800 cm^{-1} and other characteristic bands in the spectrum of goethite

$\theta = 80\,°C$: intensity of the band at 3180 cm^{-1} and bands in the $\bar{v}$ group 1300—1800 cm^{-1} decreases

$\theta = 100\,°C$: all bands in the spectrum are relatively the least intensive

B. Gradual heating

$\theta = 60\ °C \rightarrow \ \ 80\ °C$:   bands at $\bar{v} = 3180\ cm^{-1}$ and $3400\ cm^{-1}$ do not essentially change, other bands are more conspicuous (narrower, more intensive)

$\theta = 80\ °C \rightarrow 100\ °C$:   a comparison with the intensity of bands of goethite obtained by simple heating shows that the general character becomes more expressive, which indicates that goethite with perfecter crystal structure arises in the course of time (after 12 weeks).

Akaganeite

There are four bands in the spectrum of akaganeite among which the bands at $\bar{v} = 635\ cm^{-1}$ and $685\ cm^{-1}$ characterize akaganeite while the most conspicuous doubled band at $\bar{v} = 425\ cm^{-1}$ and $475\ cm^{-1}$ (with inverse intensity ratio in comparison with the preceding doubled band) almost suggests the band of goethite. Original akaganeite has only one (in comparison with further two polymorphous modifications of FeOOH) intensive, asymmetric band at $\bar{v} = 3420\ cm^{-1}$. The doubled character of the band as stated in paper [23] is not evident. In contrast to statement in paper [24], the band at $\bar{v} = 275\ cm^{-1}$ is missing (Fig. 2).
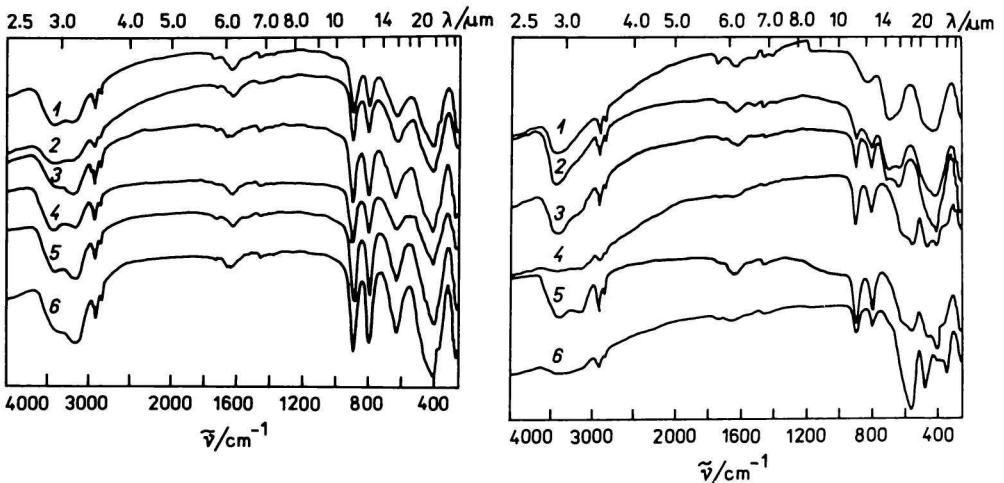

Fig. 1. Infrared absorption spectra of goethite.
1. Original; 2. after heating at $\theta = 60\ °C$; 3. $80\ °C$; 4. $100\ °C$; 5. $60\ °C \rightarrow 80\ °C$; 6. $80\ °C \rightarrow 100\ °C$.

Fig. 2. Infrared absorption spectra of akaganeite.
1. Original; 2. after heating at $\theta = 60\ °C$; 3. $80\ °C$; 4. $100\ °C$; 5. $60\ °C \rightarrow 80\ °C$; 6. $80\ °C \rightarrow 100\ °C$.

A. Simple heating

$\theta = \ \ 60\ °C$: band at $\bar{v} = 3420\ cm^{-1}$ does not change, bands of goethite arise

$\theta = \ \ 80\ °C$: band at $\bar{v} = 3420\ cm^{-1}$ does not change, other bands of akaganeite nearly vanish, the typical bands of goethite are distinct

$\theta = 100\ °C$: intensity of band at $\bar{v} = 3420\ cm^{-1}$ considerably decreased, goethite is partially transformed to hematite

B. Gradual heating

$\theta = 60\ °C \rightarrow \ \ 80\ °C$: intensity of band at $\bar{v} = 3420\ cm^{-1}$ is alike, other bands at $\bar{v}/cm^{-1}$ 475 and 565 or 460 and 625, 790, 890 evidence the transformation of akaganeite to goethite and hematite

$\theta = 80\ °C \rightarrow 100\ °C$: original band at $\bar{v} = 3420\ cm^{-1}$ is little distinct, intensity of bands of goethite is lower whereas intensity of bands of hematite is higher.

Lepidocrocite

The spectrum of lepidocrocite in the wavenumber region 1635 cm^{-1}, 3180 cm^{-1}, and 3420 cm^{-1} exhibits bands which indicate chemically and physically bound water. Of course, the bands at $\bar{v} = 745\ cm^{-1}$, 1020 cm^{-1}, and 1140 cm^{-1} are characteristic of lepidocrocite. They correspond to bending vibrations of the Fe—OH groups. Further typical bands appear at $\bar{v} = 475\ cm^{-1}$ and 540 cm^{-1} (broad, doubled) and an intensive and relatively narrow band at $\bar{v} = 365\ cm^{-1}$ and a weaker band at $\bar{v} = 265\ cm^{-1}$ are also visible (Fig. 3).
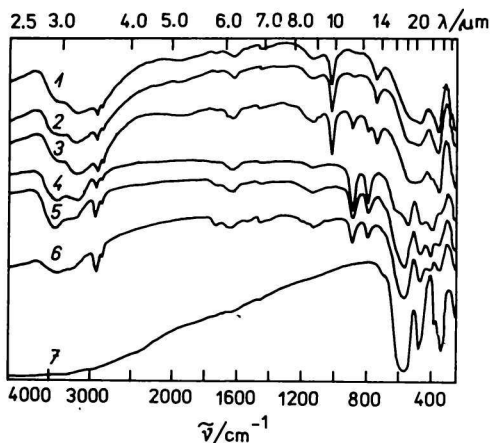

Fig. 3. Infrared absorption spectra of lepido-
crocite.
1. Original; *2.* after heating at $\theta = 60\ °C$;
3. 80 °C; *4.* 100 °C; *5.* 60 °C→80 °C;
6. 80 °C→100 °C; *7.* α-Fe$_2$O$_3$ (hematite).

A. Simple heating

$\theta = 60\ °C$: in comparison with the spectrum of original lepidocrocite, intensity of the bands of molecular and O—H water only slightly changes. Other bands of spectrum indicate the transformation of lepidocrocite to goethite

$\theta = 80\ °C$: degree of transformation of lepidocrocite to goethite increases and the relatively more intensive band at $\tilde{v} = 545\ cm^{-1}$ gives evidence of arising hematite

$\theta = 100\ °C$: bands in the wavenumber region $3200\ cm^{-1}$ and $3400\ cm^{-1}$ do not essentially change. Lepidocrocite disappears and a part of goethite is transformed to hematite

B. Gradual heating

$\theta = 60\ °C \rightarrow 80\ °C$: intensity of bands at $\tilde{v} = 1120\ cm^{-1}$, $3200\ cm^{-1}$, and $3400\ cm^{-1}$ decreases, band at $\tilde{v} = 1020\ cm^{-1}$ disappears, and bands of goethite become more distinct. The dominant band of hematite at $\tilde{v} = 560\ cm^{-1}$ and its weaker bands at $\tilde{v} = 345\ cm^{-1}$ and $475\ cm^{-1}$ arise, while intensity of the band of goethite at $\tilde{v} = 405\ cm^{-1}$ decreases

$\theta = 80\ °C \rightarrow 100\ °C$: intensity of the bands of hematite increases to the detriment of the bands of goethite

The spectrum of anal. grade Fe_2O_3 (hematite) contains hardly visible bands in the wavenumber region 3200—$3400\ cm^{-1}$. The spectrum of hematite is characterized by three intensive bands at $\tilde{v} = 340\ cm^{-1}$, $475\ cm^{-1}$, and $570\ cm^{-1}$ among which the band at $\tilde{v} = 570\ cm^{-1}$ predominates.

A small portion of maghemite in thermally treated samples cannot be identified in the spectra because of insufficient distinctness of their characteristic bands which in addition coincide with the bands of hematite [24], goethite [7], and lepidocrocite [31], which is not in agreement with the statement in paper [25]. This series of infrared spectra shows evident shift in bands with progressing transformation of polymorphous modifications of FeOOH in aqueous suspension because of thermal treatment of the samples.

All spectra also contain bands at $\tilde{v} = 2860\ cm^{-1}$, $2930\ cm^{-1}$, and $2960\ cm^{-1}$ (shoulder). This fact may be due to the presence of hygroscopic water in FeOOH molecules and KBr pellets. The mechanism of dehydration and polymorphous transformations in the samples may be interpreted on the basis of change in infrared spectra as successive degradation of the OH groups chemically bonded in the structure with simultaneous increase in concentration of molecules of the water physically bound on the surface of particles. By the use of infrared spectroscopy we may distinguish the individual polymorphous modifications of FeOOH from each

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other because the difference in structural relation between hydrogen and oxygen atoms manifests itself in the wavenumber of bending vibrations which give more information than stretching vibrations (irrespective of the fact that bending vibrations may vary according to the strength of the hydrogen bond between the OH group and metal atom). In comparison with the data published in papers [13, 17], it is obvious that the prepared starting materials exhibit much more intensive bands, which indicates a relatively higher degree of crystallinity. For instance, the complete spectrum of lepidocrocite or a detailed interpretation of individual types of bands in the spectra of α-, β-, and γ-FeOOH has not yet been presented in literature.

Conclusion

On the basis of our results, we may state that a gradual transformation of the thermally treated crystallinic polymorphous modifications of β- and γ-FeOOH gives rise to goethite as intermediate which gets stabilized by direct simple heating, while it is transformed to maghemite and subsequently to hematite by prolonged heating at increased temperature. The rapid transformation of initially gel-like iron(III) hydroxide-oxide to hematite due to hydration and the hydrolysis of the ferrite phases of portland cement may obey similar mechanism. The pieces of knowledge resulting from this study will contribute to elucidation of the processes accompanying solidification and hardening of the ferrite phases at 25 °C or increased temperature in the medium heated by steam.

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