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Prognosis and diagnostics of water-absorbing capacity of polydisperse materials by pH-metry data

Kseniya V. Ikonnikova^{a*}, Lyubov F. Ikonnikova^a, Ekaterina A. Koltunova^a

^aNational Research Tomsk Polytechnic University, 30 Lenin Avenue, 634050 Tomsk, Russia

Abstract

The work focuses on the solution of the problem concerning the diagnostics and prognosis of water-absorbing capacity of polydisperse materials. The relation of water absorption and acid-base properties of the surface is considered. The advantages of the research of acid-base properties of the surface by the pH-metry method are illustrated. The algorithm of the processing and interpretation of pH metric results to diagnose water absorption of powdery substances is suggested. The diagnostics is based on the research of velocity variation of mass transfer in the reaction zone in time. The change of pH suspension per unit of time is considered for the first time as an analytic signal of «WpH» mass transfer velocity. It is demonstrated that the velocity variation of mass transfer in the system “solid body-water” reflects the stopping mechanism of ion exchange and can be used for prognosis of hydrophobic behavior of the solid body surface. The introduced material in the given article will be useful for implementation in research, industrial and school laboratories.

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Keywords: material science; surface; water-repellent property; hydrophobic behavior; wetting ability; hydrophilic behavior; acid-base properties; functional groups; ion exchange.

1. Introduction

Thanks to their rich color gamma and magnetic properties the ferrioxide compounds find their application in different branches of industry: building and construction industry, medicine, criminalistics¹⁻⁵ and etc. Their

* Corresponding author. Tel.: +7-3822-56-34-70; fax: +7-3822-56-38-65.

E-mail address: ikonna@yandex.ru

production is based on the use of raw materials and waste from different production activities^{1,2}. Domestic industry requires ferrioxide raw materials. The main suppliers of these materials are China, Germany and the Czech Republic.

The alternative to these materials can be the use of iron-containing sludge from underground water purification which utilization is carried out by its burial. For example, each year about 600 tons of sludge with a high content of iron is accumulated at Tomsk water intake. Tomsk scientists have developed a special technological system which allows obtaining ferrioxide pigments of nanometric size from water treatment sludge⁶.

The method of pigment production using this technological scheme is energy-profitable and resource saving, which makes the product of technogeneous materials recycling ecologically and economically viable. The use of those pigments allows them to be independent on import procurement. Moreover, their cost will be lower.

Due to the diversity of performance features of iron oxide compounds the range of technical products made from these compounds is wide and specific. At present, the pigments made from iron-containing sludge of water treatment perform good results in building and construction industry:

- The production of paints, enamels, undercoating with good results concerning oil absorption power and high adhesion coating by any surface treatment;
- The preparation of sand-cement painted compositions of different application (for example, face and paving flag).

However, the quality of the industrial products of different industrial use depends on the compatibility of oxide and solvent^{7,9}. For example, to prepare paint-and-lacquer products (where the organic adhesive is used), compounds annealed up to 800°C demonstrate good results. Compounds annealed up to higher temperatures perform good results in cement-sand compositions where water is used as a tempering medium^{6,7}.

The possibility of these pigments application in dactyloscopy (criminalistic equipment of finger-printing) is considered. The relation between adhesional and “developing” properties of the pigment and compatibility of sweat-grease deposit of the fingerprint was also noted⁷. An old fingerprint (dried-up and containing only grease – stable part of sweat- grease deposit) is well developed by α -Fe₂O₃ pigment, while a recent fingerprint (containing only grease and water) is developed by Fe₃O₄ pigment.

It is to be noted that the relation between water-absorbing capacity of polydisperse substance and the quality of the generated product is inherent not only in oxide compound of iron¹⁰⁻¹⁵. Therefore, the issue concerning research and development of the diagnostics technique of the surface hydrophilization is vital. Usually, moisture- and water-absorption is determined by the gain in weight of the sample under the impact of water or air moisture. However, such a diagnostic technique is labor and time consuming. High volumes of the powdery substances production require the research of more express (rapid) diagnostic technique.

The aim of the given article is to study the possibilities of the water-absorbing capacity diagnostics of the ferrioxide compounds in accordance with pH-metry results of water suspensions. The pH-metry method has been chosen due to the range of its advantages¹⁶⁻¹⁹:

- price affordability to industrial, scientific and school laboratories;
- simplicity in maintenance and instrumental design;
- absence of the test-preparation stage and the rapidity of execution;
- availability of theoretical grounds for explanation of acid-base interaction in the system “solid body- water”.

The objective of this research is to determine the activity of the sample surface referring to distilled water and explanation of the causes of hydrophilic and hydrophobic behavior of the ferrioxide compounds surface.

2. Experimental set up and methods

The pH signal of «pH_{susp}» water suspension is used as an analytic characteristics of water-absorbing capacity. The change of this signal characterizes the acid-base nature of the functional groups surface and kinetic stability of the surface towards moisture.

The pH metric research is carried out using a pH-150M device (a glass electrode of EGL-47-03 is used as a measuring instrument and a silver-chlorine electrode - as an auxiliary one). Inaccuracy of pH measurements does

not exceed ± 0.05 units of pH.

10 ml of distilled water (acidity is 6.7÷7.0 units of pH) is introduced into a potentiometric cell which capacity is 25 ml. After the potential stabilization of a glass electrode by continuous water stirring by means of a magnetic stirrer 0.2 g sample is introduced. Simultaneously a stopwatch timer is switched on. The first measurements of the aqueous suspension acidity are carried out every 5 minutes (till 3 minute contact – the response of the most powerful surface center). The next measurements are made with the step interval of 5-10 minutes. The measurements are over in 1.5 ÷ 2 hours (by the achievement of acid-base equilibrium)¹⁶.

3. Results and discussion

Specific surface of a solid body has a significant effect on the absolute value of the heterogeneous system index (coefficient)²⁰. Therefore, this article is only concerned with the change of «pH_{susp}», analytic signal, without taking into account the value of the specific surface.

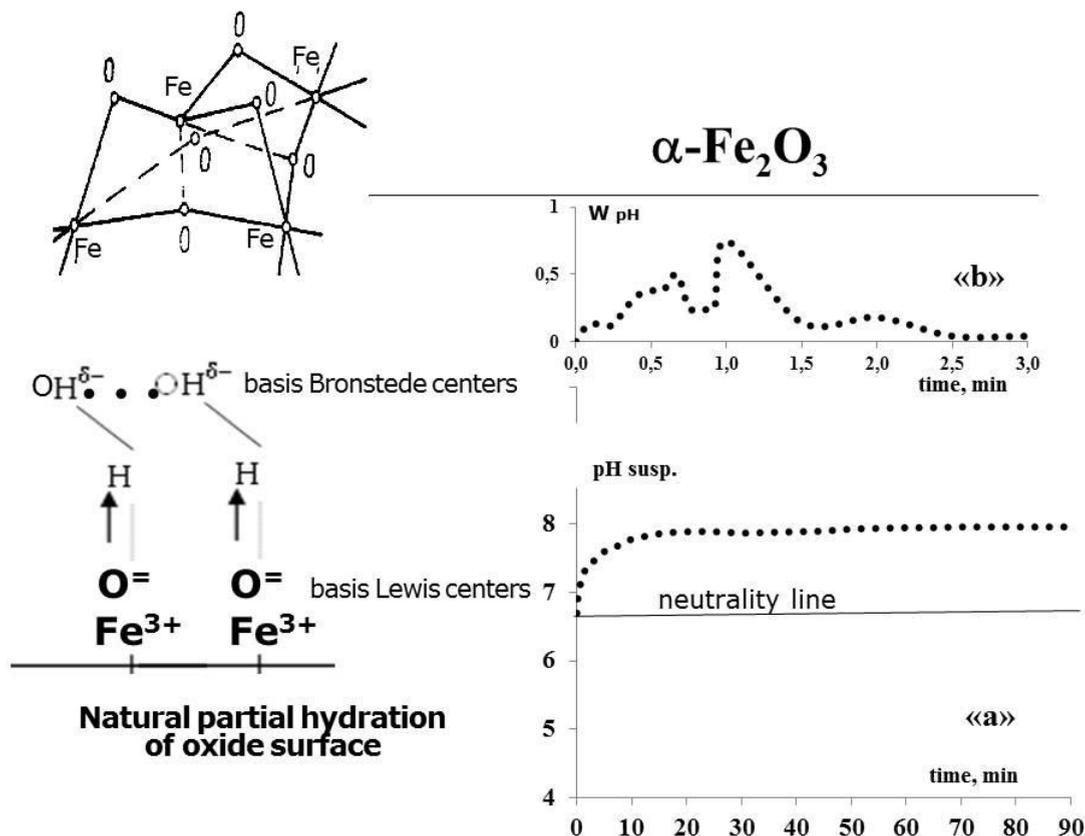
Two samples α -Fe₂O₃ and Fe₃O₄ of nanometric level of dispersion are chosen^{6,7}. They show the following differences in the course of suspension acidity variation in time:

- different location of kinetic curves of pH suspension relative to the neutrality level (relation «a», Figures 1 and 2);
- different velocity acceleration of reaction zone initiation and development on the phase boundary (mass transfer velocity). pH suspension is for the first time chosen as an analytic signal of mass transfer in this work. pH variation per unit of time $w_{pH} = \frac{\Delta p H_i}{\Delta \tau, \text{min}}$ is chosen as an indicator of mass transfer velocity. The experimental data show that significant variations in mass transfer velocity acceleration and deceleration are visible only within the first 3 minutes of the contact. The specified differences are primarily predetermined by the inner structure of the ferrioxide samples and can be explained by the impact of functional groups of naturally formed hydrate- hydroxyl coating on the moistening process.

4. Hydrophobic behavior of α -Fe₂O₃ surface

It is known^{16, 20-22}, that the reaction zone in the region of the surface emerges and develops not on the whole surface but only in some special points (active surface centers).

Active surface centers in α -Fe₂O₃ haematite, according to the minimum electrostatic energy realization principle, are Fe³⁺ cations in the octahedral site on oxygen (Figure 1). The density of the negative charge is increased in this surrounding (surface with the basis Lewis centers)^{8, 16-21}.

Fig.1. Diagram of active centers of $\alpha\text{-Fe}_2\text{O}_3$

Surface and the change of pH suspension course ($\text{pH}_{\text{susp.}}$) and mass transfer velocity (W_{pH}) in time

Due to the partial hydration of the real surface on the primary Lewis centers^{16-21, 24-26}, natural hydrate-hydroxyl coating of the water molecules absorbed from air is formed ($\text{O}^{2-} \dots \text{H}^+ / \text{OH}^-$) secondary basis Brondstedt centers).

By contact with water the processes of ion-exchange absorption occurs¹⁶, and suspension alkalization is observed (Figure 1, relation «a»).

Water supply to active centers of water molecules surface and their diversion in H^+ reaction products or OH^- ions medium forms the dominant direction of diffusion flux and determines the acceleration and deceleration of the mass transfer velocity at every certain period of time. The velocity acceleration for $\alpha\text{-Fe}_2\text{O}_3$, haematite is slower and more discrete than its deceleration set (Figure 1, relation «b»). It is connected with the hydrogen bonds formation between the basis centers of Brondstedt type. The shielding hydrate-hydroxyl surface film offers resistance to the moistening process, and prohibits the further diffusion of water molecules in porous adsorbent space. The accessible surface and the level of volumetric filling by water molecules of oxide pores, which determines the hydrophobic behavior of its surface, are decreased. This mechanism of mass transfer velocity decrease refers to external diffusive one^{16,27}.

5. Hydrophilic behavior of Fe_3O_4 surface

There are two active surface centers in Fe_3O_4 protoxide-oxide of iron^{1,2} that is explained by the structure of $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]_4\text{O}_4$ inverted spinel.

Coulomb energy of attraction and repulsion of anions and cations in the crystal as well as cation sizes determine the advantage of Fe^{2+} cations location in the tetrahedral site of the spinel and Fe^{3+} location in the octahedral site. The

decrease of the iron atoms shielding by oxide atoms enhances its accessibility to the interaction with other atoms and functional groups. Therefore, the active centers of Fe_3O_4 surface are Fe^{2+} cations preferring a tetrahedral site by oxygen. In this case the density of the positive charge of the surface is enhanced^{16,20,25,26} and primary Lewis acid centers are formed (Figure 2).

The fresh-formed surface with split bonds possesses excessive energy, therefore, almost instantly there is saturation of bonds due to the water molecules absorption from ambient medium ($\text{Fe}^{2+} \dots \text{OH}^-/\text{H}^+$) as coating by OH^- ions and water molecules is more energy-profitable than ion chemical^{8, 16, 20-24} adsorption O^{2-} . In this case its acid function is guaranteed due to the formation of acid Bronstedt centers. Therefore, there is suspension acidification (Figure 2, relation «a») – the curve of the pH suspension change is lower than the curve of the neutrality level).

The shielding surface film is not formed and the acceleration of mass transfer velocity is abrupt (Figure 2, relation «b»). The velocity decrease is slow and discrete, that is connected with the change of the conditions of reagent and product transportation due to the interaction zone displacement inside the porous space of the substance. The development of ion-exchange reaction at regions of grains with different depth changes the conditions of reagent and product transportation.

By achieving some (critical) concentration, the two-dimensional hydrate-hydroxyl coating undergoes the phase transition. There is a group of three-dimensional liquid phase islands on the surface. Liquid phase islands flow together forming a continuous layer and the hydration process takes place. Then, the hydration process deepens inside the solid body and the velocity changes discretely due to the stage-by-stage increase-decrease of the surface available to interaction. Such consequence in acceleration and deceleration of mass transfer velocity corresponds to the mechanism of volume filling of porous adsorbent space with adsorbate solution (mechanism of pore-diffusion resistance) as accepted in the literature^{16, 27} and characterizes the hydrophilic behavior of the solid body surface.

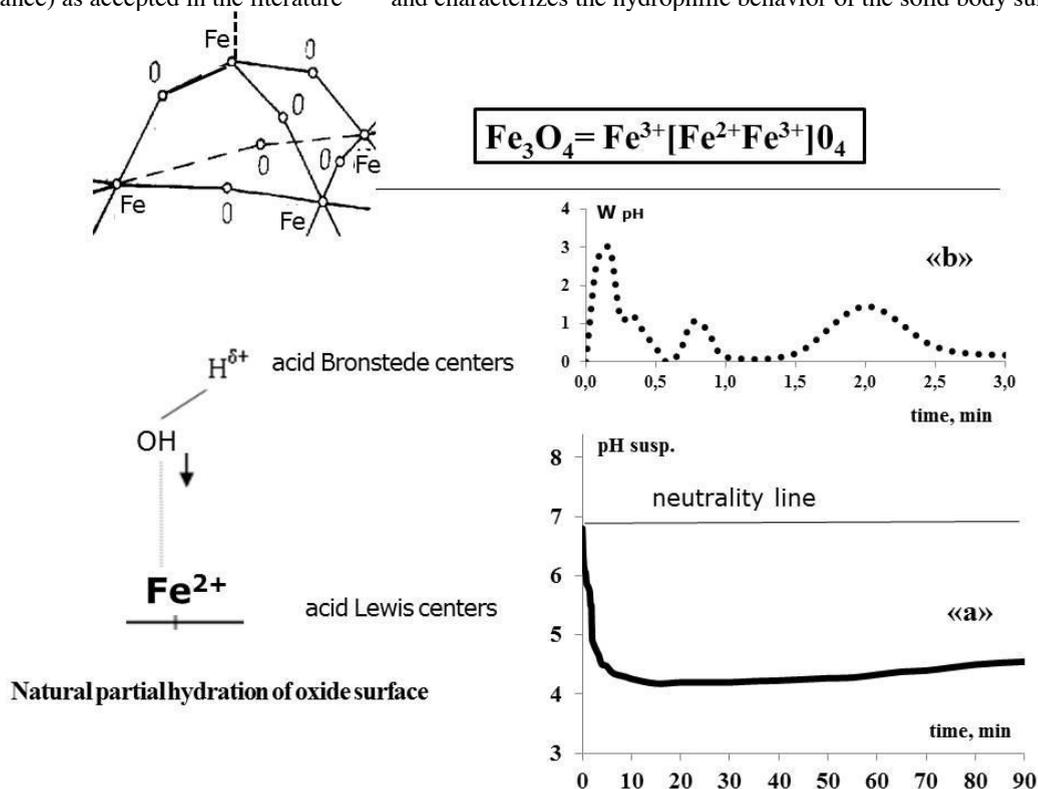


Fig.2. Diagram of active centers of Fe_3O_4 .

Surface and the change of pH suspension course ($\text{pH}_{\text{susp.}}$) and mass transfer velocity (W_{pH}) in time

Thus, the diagnostics of water-absorbing capacity of the solid body surface has been carried out for the first time.

This diagnostics is based on the difference of mass transfer velocity acceleration and deceleration. The variation of pH water suspension per unit of time is used as an analytic signal of mass transfer velocity. The inhibition mechanism of ion exchange reaction has been considered. This mechanism explains the causes of hydrophobic and hydrophilic behavior of the solid body surface. The acceleration of ion exchange for α -Fe₂O₃ haematite is long and discrete, and the deceleration is abrupt, that is determined by the processes of external diffusion braking and characterizes the hydrophobic behavior of the surface. The mass transfer acceleration for Fe₃O₄ magnetite is abrupt and deceleration is slow and discrete that testifies the hydrophilic behavior of the surface.

6. Conclusions

It has been shown, that moisture absorbing power of a solid body is predetermined primarily by the type of functional groups of naturally formed hydrate-hydroxyl coating. The recommendations to mathematical processing of the pH-metry research results of acid-base interaction in the system “solid body-water” for obtaining the data concerning mass transfer velocity have been developed. The physicochemical model of stopping, mechanism description of acid-base interaction has been suggested. It has been shown, that the use of the pH-metry results simplifies and speeds up the process of diagnostics of the surface hydrophilization which proves to be economically viable and of low cost.

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- Research supervisor: Ikonnikova L.F., PhD, associate professor, National Research Tomsk Polytechnic University.