

Analysis of possibility of using indicator method to study functional groups of surface of new components of building materials

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Abstract. The current trend to increase the volume of construction of public and industrial facilities the need for new modern building materials is as high as ever. The physicochemical and mechanical properties of the materials obtained are especially important, the improvement of which is often provided by the introduction of new additives into the composition. Using the indicator method to study the surface of new components of building materials can help to assess the impact of the nature of their surface on the final product.

1. Introduction

Currently, there is a constant growth in the construction of housing, public and industrial facilities, resulting in a need to provide the construction industry with highly efficient and relatively cheap building materials. Reduction of material intensity of production of building materials, which is determined by the amount of raw materials spent on their production, to the total volume of output, can be achieved by involving various industrial wastes or new functional materials [1-3].

The important step in the search for new raw materials for the production of building materials is to analyze its physico-chemical properties. The main feature of solid industrial waste is their chemical heterogeneity of the surface, which is determined by its defects and the presence of different functional groups [4-7]. According to modern ideas, the surface of solids is functional and represents a set of acid and basic Lewis and Brensted centers. Therefore, the study of the distribution spectra of adsorption centers allows predicting the reactivity and sorption capacity of the surface and other properties of solids used in the construction industry for the production of cements, fillers of composites, composite and other materials [8-11].

Based on the above, the purpose of this work was to analyze the adsorption method of Hammett indicators to study different types of raw materials.

2. Method of Hammett indicators adsorption

In order to determine the distribution and concentration of acid-base centers at the surface of solids we use the method of adsorption of Hammett indicators (indicator method). However it means that we may investigate the distribution of surface centers and the correlation between the adsorption by specific surface centers and the activity of the surface as a whole. The indicator method is based on the adsorption of monobasic indicators from an aqueous medium by a solid surface [5]. In analytical



conditions, the indicator is adsorbed both at Brensted centers and at Lewis centers, where water molecules are adsorbed by a coordination mechanism in accordance with the corresponding pK_a value. As a result, quantitative determination gives the total content of Lewis and Brensted centers of the corresponding strength at the surface of solids [6, 12, 13].

For neutral centers, $pK_a = +7$. With increase in pK_a , the donor properties of the metal atoms in the fuel shales and ash become stronger; with decrease in pK_a , the acceptor properties become stronger. As the acceptor properties of the atom become stronger, the surface acidity of the Brensted center increases ($pK_a < 7$). Breakaway of a hydrogen atom from a Brensted center is possible in the form of a proton H^+ , the radical H^\cdot , or the negatively charged ion H^- . When an electron passes from the hydrogen atom to an orbital of the oxygen atom as a result of proton breakaway, a basic Lewis center is formed. The adsorption of water (acceptor) molecules of acidic type is possible at the Lewis center. Further strengthening of the element–oxygen bond leads to the formation of a free Lewis base. With increase in donor properties of the atom, at the surface, the basic Brensted centers ($pK_a > 7$) give rise to acid Lewis centers with breakaway of an OH^- group. At these centers, water molecules (donors) are adsorbed by a coordination mechanism. The water molecules may give rise to two Brensted center of acid and basic type [6].

UV and visible spectrophotometry may be used for quantitative determination of such acid–base centers (mg-equ/g or mg-equ/m²). The acid–base indicators with a pK_a value in the range from -0,3 to 14,2 were used. The list of standard indicators and their values of ionization constants is presented in table 1.

Table 1. Characteristics of the acid–base indicators

Indicator	pK_a
O-nitroaniline	-0.3
Brilliant green	1.5
Fuchsin (base)	2.1
Xylenol orange	2.6
Methyl orange	3.5
Bromophenol blue	4.1
Methyl red	5.0
Bromocresol purple	6.4
Phenol red	8.0
Phenolphthalein	9.5
Alizarin yellow	11
Indigo–carmine	12.8
Ethylene glycol	14.2

A sample (mass of 0.02 g.) is placed for 2 hours in an aqueous indicator solution with a known pK_a value. To take account of the influence of the pH at contact of the sample with the solution on the optical density, the material is also placed in distilled water for 2 hours and then the indicator solution is added and the optical density is measured. A spectrophotometer (PE5400UF) with a wavelength corresponding to the maximum absorption of each indicator is used for photometry of the solutions. The change in the optical density (ΔD) after adsorption of the indicators on the surface of the powders is found by the equation:

$$\Delta D = \left(|D_0 - D_1| \pm |D_0 - D_2| \right)$$

The content of active centers, which is equivalent to the quantity of adsorbed acceptor, is calculated from the formula:

$$q_{pKa} = \frac{C_{ind} \cdot V_{ind}}{D_0} \left(\frac{|D_0 - D_1|}{\alpha_1} \pm \frac{|D_0 - D_2|}{\alpha_2} \right),$$

where C_{ind} - the concentration of indicator solution, mg-mole/ml; V_{ind} - the volume of indicator solution used in the analysis, ml; D_1 - the optical density of the indicator solution before sorption; D_2 - the optical density of the indicator solution after sorption; D_0 - the optical density of the quiescent indicator solution. A minus sign corresponds to change in D_1 and D_2 in the same direction relative to D_0 ; that is, D_1 and D_2 are less than D_0 . A plus sign corresponds to change in D_1 and D_2 in opposite directions relative to D_0 ; that is $D_1 > D_0$ and $D_2 < D_0$, or $D_1 < D_0$ and $D_2 > D_0$.

3. Examples of use of analyzed methods

method of adsorption of Hammett indicators can be used to study materials of various types: industrial waste of thermal processing of hydrocarbons, which are used for the production of Portland cement (Figure 1), various functional materials (Figure 2), etc.

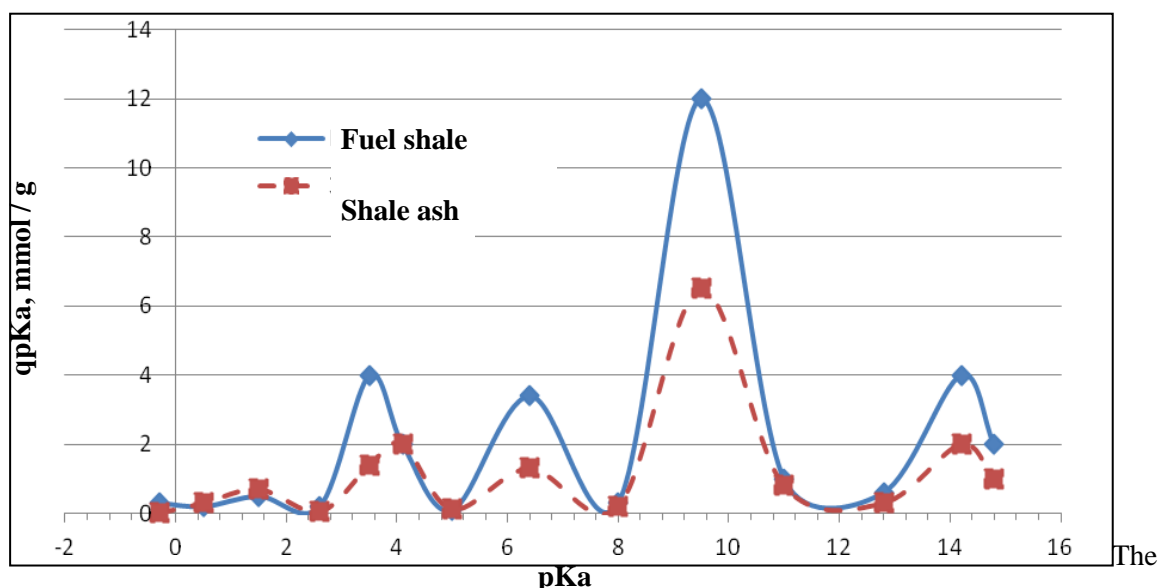


Figure 1. Distribution of acid–base centers at the surface of Baltic Basin fuel shales and shale ash [6]

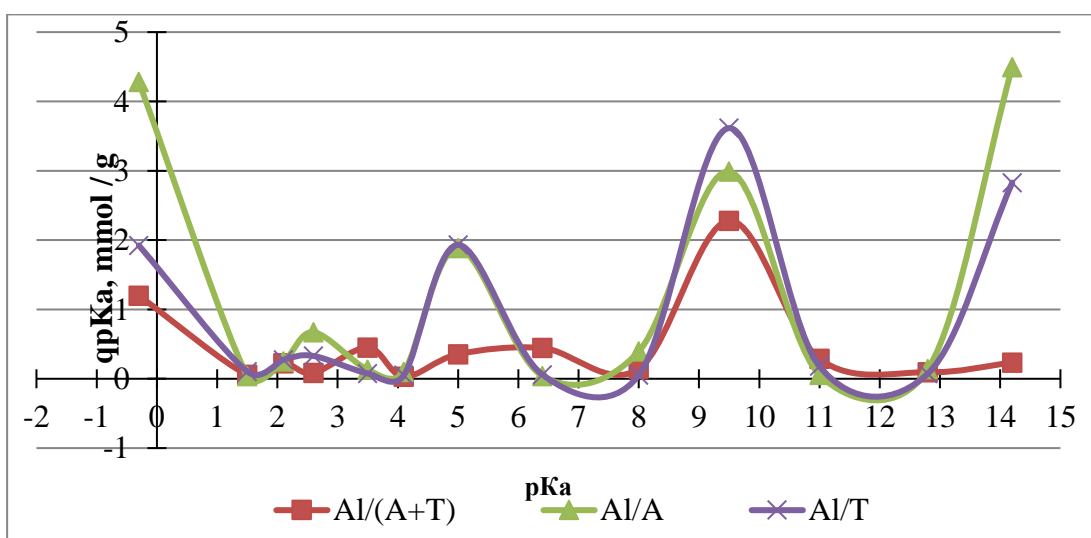


Figure 2. Distribution of acid-base centers on the surface of adsorption-modified aluminum powders with various cationic modifiers.

For example, in the work [13] using the Hammett indicator method, the acid-base properties of dispersed aluminum were studied and the change in the composition of the donor-acceptor centers of the powder caused by the adsorption of Quaternary ammonium compounds was established (Fig. 2). The obtained data on the nature of the surface of the studied samples allow expanding the understanding of the evolution of the acid-base properties of the surface of aluminum powder in the process of adsorbed interaction with ammonium compounds.

4. Conclusions

Taking into account all the above mentioned aspects, it can be concluded that the indicator method is an effective and promising method for the study of new components for building materials. This method will allow studying the nature of the surface of additives and linking the surface properties of the material with the physical, chemical and mechanical characteristics of the obtained building materials based on new additives.

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