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SPECTROPHOTOMETRY APPLICATION FOR THE MONTMORILLONITE CONTENT DETERMINATION IN MOULDING SANDS WITH BENTONITE

1. INTRODUCTION

More than 70% of iron castings are made in moulding sands with bentonite. After filling a mould with liquid cast iron a part of montmorillonite contained in bentonite undergoes a thermal degradation, losing its binding properties (bentonite deactivation process), forming chamotte. The moulding sand separated from casting is subjected to rebounding and once more introduced into the production process. Rebounding is done by addition of fresh high-silica sand and bentonite [1–3]. In order to determine the required bentonite amount to be introduced in the rebounding process the knowledge of the actual montmorillonite content (active bentonite, active clay) is needed.

For the determination of the active binder content in moulding sands with bentonite the method of ‘the determination of active clay in moulding sand is done by means of the methylene blue adsorption method’ [4] is being applied in the current foundry practice. However this method is not accurate, since it is based on visual, subjective, colorimetric measurements. Therefore the montmorillonite content in bentonite is the most often determined by spectrophotometric methods. Usually – in spectrophotometry – the absorbance (A) measurement in solution containing the examined substance sample is used for the determination of the substance concentration [2]. The determinations can be performed either by means of the methylene blue or the Cu(II)-triethylenetetraamine complex (Cu-TET) adsorption [1–3, 5–8]. The methylene blue method is highly time consuming and requires a very precise adhering to analytical procedure, which under industrial conditions

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is often very difficult. The new Cu-TET method is less time consuming and uses the bentonite ability for the cation exchange when the copper complex of triethylenetetraamine is applied [3, 5–8].

Bentonites from various producers (Süd-Chemie, ZGM Zębiec S.A.) as well as samples of model moulding sands bound by these bentonites were tested in the study. The montmorillonite content was estimated by the Cu-TET method in samples of a room temperature and in samples hold at temperatures of 400 °C and 700 °C.

2. SPECTROPHOTOMETRY

Spectrophotometry deals with an electromagnetic radiation influence on matter. UV and VIS spectrophotometry deals with absorption of a visible and ultraviolet radiation by particles [2]. Absorption and emitting of energy can occur – in a micro-world of atoms and particles – only by determined portions, it means by quantum. Thus, energy changes of a particle or atom is described by an equation:

$$\Delta E = E_e - E_i = h\nu \quad (1)$$

where:

- ΔE – energy change of a particle or atom,
- E_e, E_i – quantised energies of the end and initial state,
- h – the Planck constant,
- ν – frequency.

A particle or atom can absorb or emit the radiation of a determined wavelength, and this constitutes the basis of spectrophotometric methods. Energy of UV or VIS quantum radiation is contained within a range: 1–100 eV. It corresponds to transfers within electronic energy levels of particle or atomic external envelopes. A change of an electron energy level causes usually changes in oscillation and rotational energy levels, which in effect broadens absorption bands. The radiation beam of intensity I_0 and a wavelength λ , after passing via the absorbing medium, decreases its intensity to I .

The Lambert–Beer's law determines relations between a light flux and a concentration of absorbing solution:

$$\lg\left(\frac{I_0}{I}\right) = K_b \cdot c \quad (2)$$

where:

- I – intensity of radiation passing through the solution,
- I_0 – intensity of a beam of radiation,
- $\lg(I_0/I)$ – determined as optical density or absorbance,
- K_b – proportionality coefficient,
- c – concentration of the absorbing component.

Absorption coefficient ε is a value characteristic for each dissolved substance depending on the light wavelength, temperature and the kind of solvent. Absorbance of coloured solutions, at steady-state measurement conditions, is proportional to the concentration of the given substance.

$$A = \varepsilon \cdot l \cdot c \quad (3)$$

where:

- A – absorbance,
- ε – molar absorption coefficient,
- l – thickness of absorbing layer,
- c – concentration of absorbing substance in solution.

Another quantity, which can determine the radiation absorption, is transmittance (permeability), T [3]:

$$T = \frac{I}{I_0} \quad (4)$$

The block diagram of the spectrometer used in investigations is presented in Figure 1. Usually measurements are performed for standard concentrations of the examined coloured substances and the extinction function is experimentally determined. The graphical representation of this dependency is called the standardization curve. The concentration of the given component in the examined solution is graphically estimated from the standardization curve, which satisfies the Lambert–Beer’s law [2].

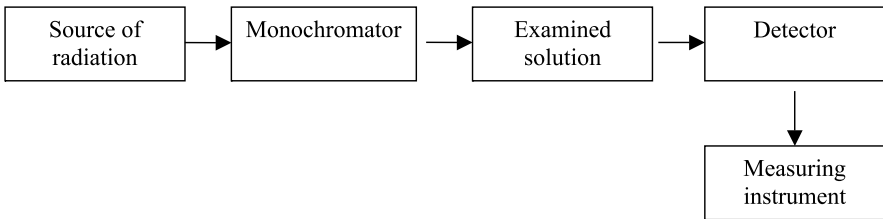


Fig. 1. Block diagram of a spectrophotometer

3. METHODOLOGY

Materials applied in testing

Spectrophotometric examinations were performed on samples of model moulding sands with bentonites from various producers (Tab. 1).

Model moulding sands being mixtures of bentonite samples with high-silica sands, as matrices, were prepared at assuming that there was 6% of bentonite in an initial mixture. The proper amounts of bentonite and high-silica sand, as components of model moulding sands, were determined on the bases of stoichiometric calculations.

Table 1. Sample characteristics

Sample	Colour	Wetness in 110 °C [%]	Remarks
GEKO S bentonite	Pink	9.7	Süd-Chemie
GEKO B bentonite	Beige	6.0	Süd-Chemie
Special bentonite	Cream	8.3	ZGM Zębiec S.A.
Bentonite-carbon mixture Kormix 75 (75% bentonite, 25% carbon carrier)	Grey	6.6	ZGM Zębiec S.A.

In order to obtain used foundry sands and to determine the high temperature influence on the montmorillonite content, the tested samples of model moulding sands were hold in the laboratory furnace for two hours at temperatures of 400 °C and 700 °C.

Cu-TET spectrophotometric method

The Cu(II) – triethylenetetraamine complex adsorption method (Cu-TET) is bases on measuring the copper complex adsorption on montmorillonite particles contained in bentonite [6]. To determine the active bentonite content in a moulding sand, water in proportion 1:20 was introduced into the weighted amount of the properly prepared moulding sand – bound with bentonite – and the whole mixture was dispargated by ultrasounds. Into the suspension obtained in such way 10 ml of 0.01M solution of Cu(II)-triethylenetetraamine was added and topped-up with water to the mark of 50 ml. Then the whole was centrifuged until the clear solution required for the photometric measurement was obtained. Spectrophotometric determination was performed at the wavelength of 620 nm in 10 mm processing tray versus water as a zero test. The adsorbed amount of Cu (II) complex was determined from the measurement difference. Then, the percentage montmorillonite content in bentonite was determined and calculated into the active bentonite content in the moulding sand.

Equipment

The following equipment was used in examinations:

- Spectrophotometer of the Hach Company, type DR 2500 Odyssey;
- Ultrasound device of the Polsonic Company, model Sonic 3;
- Laboratory centrifuge MPW-350;
- Laboratory furnace, type SNOL 7,2/1300.

4. THE OBTAINED RESULTS AND THEIR DISCUSSION

As the first stage of examinations the montmorillonite content in the bentonite samples were estimated by means of the spectrophotometric Cu-TET method. 5 analytic determinations were in succession performed for each sample. Using dependencies contained in the Lambert-Beer's law the absorbance (A) values were determined, in addition to which for the given absorbance measuring series the relative standard deviation (v) was calculated.

It was contained in the range: 0.38÷4%. Then, the Cation Exchange Capacity (CEC) and the montmorillonite content in bentonite (M) versus the bentonite standard were calculated for each sample. The averaged results are listed in Table 2.

Table 2. List of average values of: A, CEC and M for bentonite samples

No.	Sample	A	CEC [mmol/100g]	M [%]
1	GEKO S	0.029	85.5	89.9
2	GEKO B	0.077	64.8	70.6
3	Special	0.045	77.9	82.0
4	Kormix 75	0.083	59.3	64.6

At the further stage of investigations the model moulding sands with bentonites were prepared and the montmorillonite content in individual sands was measured. Figure 2 graphically presents the montmorillonite content in bentonite samples and in model moulding sands.

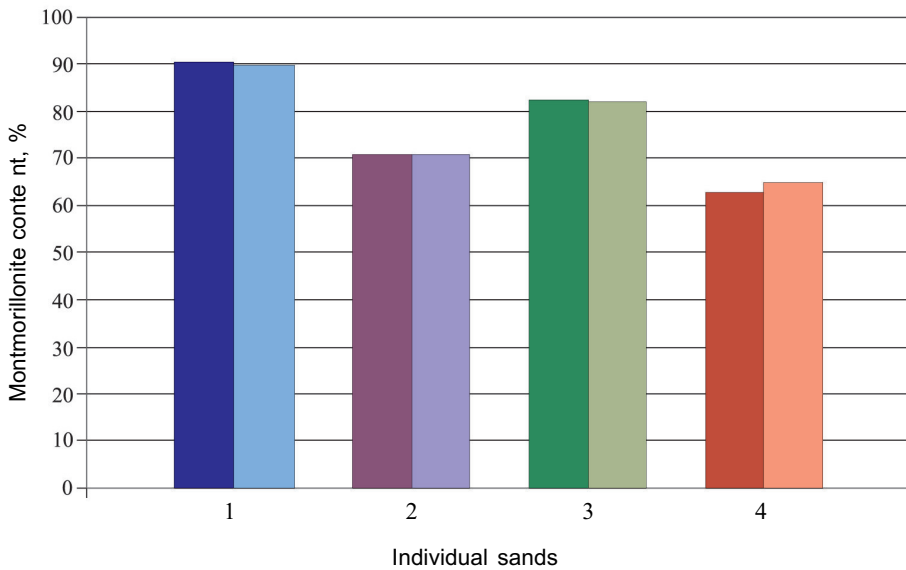


Fig. 2. List of the montmorillonite content in the given samples: bentonite (on the left), model moulding sand (on the right)

As can be seen from the data given in Figure 2, M values (montmorillonite content) calculated for pure bentonites as well as for the model moulding sands are very similar. Thus, it can be stated that the quartz matrix presence in the model moulding sands does not

disrupt the measurements. The Cu(II)-triethylenetetraamine complex is suitable for the application in moulding sands.

During the final stage of investigations the montmorillonite content was determined by the Cu-TET method in samples of model moulding sands hold in temperatures of 400 °C and 700 °C. The active bentonite contents in moulding sands are listed in Table 3.

Table 3. Calculation of the active bentonite content in model moulding sands, at the given temperature

Model moulding sands	Active bentonite content in a moulding sand [%]		
	Initial moulding sand	$T_{hold} = 400\text{ °C}$	$T_{hold} = 700\text{ °C}$
Moulding sand bound with bentonite, GEKO S	5.4	5.4	1.5
Moulding sand bound with bentonite, GEKO B	4.2	4.1	0.5
Moulding sand bound with bentonite, Special	4.9	4.8	0.2
Moulding sand bound with a bentonite-carbon mixture, Kormix 75	3.7	3.4	1.3

The active montmorillonite content in the tested moulding sand samples, up to a temperature of 400 °C – in practice – does not change (within the measurement error limit), which means that it is not undergoing any deactivation. Whereas in a temperature of 700 °C the montmorillonite deactivation occurs, which manifests by the decrease of its content.

5. CONCLUSIONS

The spectrophotometric method of the Cu(II)-triethylenetetraamine complex for the determination of the montmorillonite content in moulding sands at various temperatures was applied in investigations.

It was indicated, that the determined montmorillonite content in bentonite for the bentonites under investigation and for the model moulding sands with bentonites, are comparable, which proves that the quartz matrix, does not disrupt the measuring methodology and the applied spectrophotometric method is suitable for the moulding sands.

In addition, it can be stated that up to a temperature of 400 °C, the active montmorillonite content does not change in the tested samples, which indicates that there is no deactivation process. Whereas in a temperature of 700 °C the montmorillonite deactivation occurs, which manifests by the decrease of its content.

This deactivation process is of a significant meaning since it lowers the binding property of bentonite and causes an increased tendency to moulding sands ridging. The deactivation degree increases with an increase of a temperature of the liquid casting alloy poured into a mould cavity, with a mass increase, and specially with an increase of a casting wall

thickness and a length of time of a casting being hold in a mould (all these parameters cause moulding sand overheating). However, investigations concerning the montmorillonite deactivation in moulding sands require further examinations with taking into account broader temperature ranges.

Due to the developed spectrophotometric Cu-TET method the time shortening of the active bentonite determination in moulding sand will be possible and – to this end – obtaining by the foundry plant the fast information concerning the required amount of the fresh bentonite addition. The optimisation of bentonite additions at the moulding sand rebounding will result in lowering the casting production costs.

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