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MONTMORILLONITE: A COMPARISON OF METHODS FOR ITS DETERMINATION IN FOUNDRY BENTONITES

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Preliminary Note – Prethodno priopćenje

A comparison and estimation of usefulness of a quantitative analysis of montmorillonite in foundry bentonites, was the aim of this research. The investigations were made by means of three different techniques: methylene blue (MB) adsorption method, Cu(II)-triethylenetetramine complex (Cu(II)-TET) adsorption method, and infrared spectroscopy (FTIR) method. Tests were performed for 9 kinds of bentonites originated from various producers. The achieved results indicated that, the results obtained by the FTIR method were, in general, even 10 % lower than the ones obtained by other methods. The best correlation with the data given by the producers were obtained for the Cu(II)-TET method. In addition, this method was characterised by the smallest value of standard deviations. A very essential advantage of the Cu(II)-TET method is a much shorter time needed for the analysis and its easier execution, which is important under production conditions

Key words: foundry, green sands, bentonite, montmorillonite, FTIR

Montmorilonit – usporedba metoda za njegovo određivanje u ljevaoničkim bentonitima. Cilj ovog istraživanja je bila procjena upotrebljivosti kvantitativne analize montmorilonita u ljevaoničkim bentonitima. Istraživanja su provedena pomoću tri različite tehnike: adsorpcija metilenskog modrila (MB), adsorpcija Cu(II)-trietilentetramin kompleksa (CU(II)-TET), i infracrvena spektroskopija (FTIR). Ispitivanja su provedena na 9 vrsta bentonita koji potječu od različitih proizvođača. Rezultati dobiveni FTIR metodom u prosjeku su za čak 10,0 % niži od rezultata dobivenih ostalim metodama. Najbolja korelacija s podatcima od proizvođača dobivena je primjenom Cu(II)-TET metode. Osim toga, kod te metode najmanje su vrijednosti standardnih devijacija. Vrlo važna prednost Cu(II)-TET metode je znatno kraće vrijeme potrebno za anaalizu i lakše provođenje, što je značajno u proizvodnim uvjetima.

Ključne riječi: ljevaonica, svježa kalupna mješavina, bentonit, montmorilonit, FTIR

INTRODUCTION

Currently, approximately 70-80 % of casting production of ferrous alloys is done with sands containing bentonite (green sands). Information on an amount of active bentonite in moulding sands, after shakeout of casting, is necessary in the rebounding process of bentonite sands – under real casting house conditions. It decides how much of fresh bentonite should be added to moulding sands, thereby influencing their technological properties and cost of the rebounding process [1]. A standard method of an active bentonite estimation in moulding sands normalised in the Polish foundry plants and in the majority of European ones is based on the methylene blue adsorption [2]. This is a time-consuming method and therefore the results are available for a technologists some hours after the introduction of rebound sands into the circulation. This is specially important in the case of a variable casting production (it mainly concerns casting sands), which causes different sand overheating degree, thus causing various amounts of inactive bentonite in a whole sand volume. Therefore several companies which are dealing with a bentonite or mixtures bentonite – lustrous carbon carrier production for the foundry industry, perform intensive investigations in order to develop a reliable and simultaneously fast method of the active bentonite (montmorillonite) estimation in moulding sands. In order to do that, the spectrophotometric determination method, which is applying triethylenetetramine complex (Cu(II)-TET) used in geology for checking clays activity, was also introduced. This method is much faster and much simpler from the analytical point of view, than the methylene blue adsorption method. Tests of applying the infrared spectroscopic method (FTIR) are also undertaken. This method allows for a very fast determination of active bentonite, which is essential under production conditions. However, it has certain limitations related to some admixtures present in bentonite, causing distortions of the final result [3–6].

Investigations in this field aimed at the development of the proper analytical method as well as the correct in-

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terpretation of the obtained results have been performed, for a couple of years already, in the Department of Engineering of Foundry Processes, Faculty of Foundry Engineering, AGH - University of Science and Technology.

DETERMINATION METHODS OF THE MONTMORILLONITE CONTENT

Spectrophotometric method of the methylene blue adsorption. This method is based on measuring methylene blue adsorption on montmorillonite particles contained in bentonite [7, 8].

The methylene blue cation is easily adsorbed by clays, including also montmorillonite. The adsorption process has three stages [8]. The absorption was measured by the VIS ODYSSEY DR/2 500 spectrophotometer of the HACH Company, with an automatic wave length calibration, at a wave length of 470 nm. The result is given as a number of mg of methylene blue adsorbed by 1 gram of the tested sample. The following reagents were used: tetrasodium pyrophosphate (produced by SIGMA), methylene blue (produced by CHEM), demineralized water.

Cu(II) – triethylenetetramine complex (Cu-TET) adsorption method. This method is based on measuring the copper complex adsorption on montmorillonite particles contained in bentonite [9].

Absorption measurements were carried out by the same equipment as in the case of the methylene blue method but at a wave length of 620 nm. The result was given as a consumption of Cu(II)-TET complex in mmol/l, and than recalculated into the cation exchange capacity, CEC, (mmol/100 g). The following reagents were used: copper sulphate (VI), anhydrous, analytically pure (produced by MERCK Company), triethylenotetramine pure >97 % (produced by FLUCKA), demineralised water.

Infrared Spectroscopy method (FTIR). Infrared spectrometry belongs to analytical methods enabling to investigate samples in all three states of matter. The selection of the proper measuring technique for the given sample depends on the purpose, which we would like to achieve: quantitative or qualitative analysis, as well as on the sample size, its state of aggregation and the possibility of the components interaction in the analysed sample.

For minerals containing montmorillonite the characteristic SiO band occurs at the wave number of app. 1 040 cm^{-1}. Vibrations of OH groups have the maximum at the wave number of app. 3 630 cm^{-1}. In order to determine the montmorillonite content the mutual relations of the band intensity (peak heights) and surface areas below the band related to stretching vibrations of Si-O in the ratio to the band corresponding to stretching vibrations of OH group - were analysed [10].

Investigations of samples performed by the FTIR method was done by means of the Excalibur FTS 3 000 spectrometer of the BIO-RAD Company with the DTGS detector. Samples for testing were prepared by the pellet technique with potassium bromide (KBr). Investigations were performed by the transmission technique. Bands were recorded as the absorbance function, within the wave number range 4 000–400 cm^{-1} at a resolution of 4 cm^{-1}. The montmorillonite content was calculated on the basis of the medium spectrum.

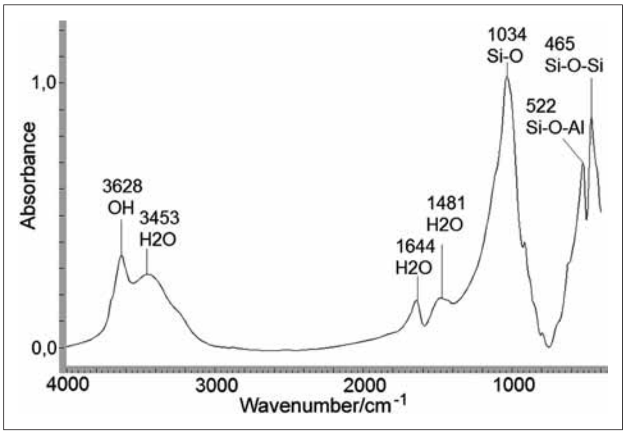

Figure 1 Typical bentonite spectrum obtained by the infrared spectroscopy method

The typical bentonite spectrum obtained by the FTIR technique is presented in Figure 1.

Two methods were applied for the quantitative analysis of the obtained spectra:

1) Determination of the relation in between the intensity of Si-O and O-H bands Si-O band at a wave number app. 1 040 cm^{-1} and O-H band at a wave number app. 3 630 cm^{-1} is obtained for the standard of the known montmorillonite content (German VDG Ref. Bentonite is treated as the reference). The relations of the height of analytical bands for the reference and investigated sample is calculated according to equation (1):

$$\frac{SiO_{reference}}{OH_{reference}} = A \quad \frac{SiO_{investigated}}{OH_{investigated}} = B \qquad (1)$$

2) Determination of the relation between surface areas below Si-O and O-H bands.

The procedure is analogical as in the case 1, with the only difference, that this time the surface areas under the respective bands are taken into account (in the established wave number range). The values obtained for the standard bentonite are considered the reference values. The mutual relations of surface areas obtained for analytical bands for the reference and investigated sample are calculated according to equation (1).

MATERIALS USED IN EXPERIMENTS

Bentonites from various producers, applied in the majority in the Polish foundry plants: S&B Industrial Minerals: Bentonite S, Bentonite E, Süd-Chemie: Geko B, Geko S, Geko Optimum, CETCO Szczytno: bentonite A, bentonite B, bentonite C, ZGH Zêbiec: bentonite Specjal, Standard: German VDG Ref. Bentonite (Bavarian) – methylene blue adsorption 360 mg/g; CEC 70,04 mmol/l, 75 % montmorillonite.

THE OBTAINED RESULTS AND THEIR DISCUSSION

In the sets of results of the montmorillonite content (for each sample 6-10 measurements were performed by the given method), obtained by each of the method, arithmetic means "x", standard deviations "s" and relative standard deviations "v" – were calculated. Investigations of mutual dependencies of the average results of the montmorillonite content carried out by various methods, was performed by means of the linear regression analysis.

The obtained results are shown in Table 1.

The comparison of the accuracy of the montmorillonite determination by various methods indicated even larger differences than the comparison of average values. The relative standard deviation of the results from the IR spectroscopy was in the range: 1,4 to 12,7 %, from the MB method usually did not exceed 2 %, (only for Bentonite E it was above 4 %), from the Cu (II)-TET method to 1,5 % (exceptionally above 2 %) at a small montmorillonite content.

Regression equations indicate that the montmorillonite content obtained by spectrophotometric methods (MB and Cu(II)-TET) are comparable to the producers' data (within limits of error). The best correlation was obtained for the Cu(II)-TET method (Figure 2). Quite good correlation was also obtained for the FTIR method based on measuring the intensity and the surface area below peaks. However, the correlation between results obtained by the spectrophotometric methods MB and Cu(II)-TET (Figure 3) was quite poor. The reason of the poor correlation of the results obtained by the FTIR method and the results obtained by other methods can be the dependence of this methods on particle sizes in analysed samples as well as the presence of contaminations (e.g. feldspars, kaolinite, mullite), which can disturb the FTIR method analysis.

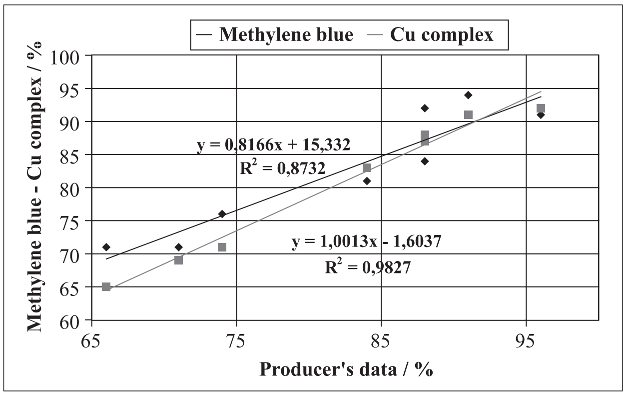

Figure 2 Comparison of the results of the montmorillonite content (%) obtained by spectrophotometric methods with the results supplied by the bentonite producers

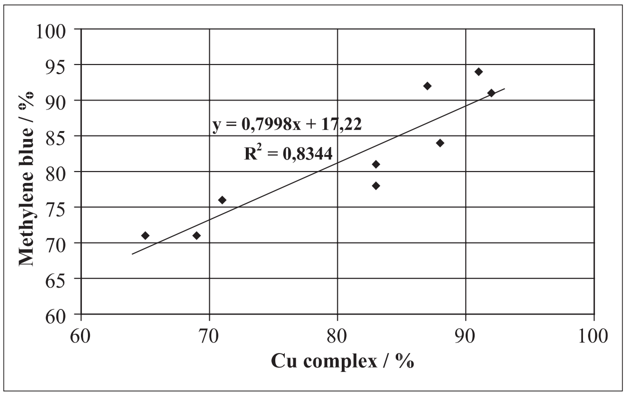

Figure 3 Comparison of the results of the montmorillonite content (%) obtained by the spectrophotometric methods (MB and Cu(II)-TET)

CONCLUSION

On the basis of broad studies concerning the determination of the montmorillonite content in foundry

Table 1 **The obtained results and the data supplied by the bentonite producers**

Sample	Producer's data	Methylene blue method MB			Complex method Cu(II)-TET			FTIR method (peak height)			FTIR method (surface area)		
	X/ %	X/ %	s	ν	X/ %	s	ν	X/ %	s	ν	X/ %	s	ν
Bentonite S	91	94	0,80	0,79	91	0,72	0,80	84	1,40	1,67	80	4,89	6,10
Bentonite E	74	76	3,35	4,36	71	1,79	2,48	72	4,15	5,91	69	3,30	4,80
Geko B	71	71	1,15	1,62	69	1,05	1,50	77	1,15	1,50	73	1,22	1,68
Geko S	88	84	1,02	1,19	88	0,86	0,98	83	1,17	1,36	84	4,67	5,50
Geko Optimum	96	91	0,77	0,85	92	0,41	0,45	87	1,74	2,01	84	1,63	1,95
Bentonite A	88	92	1,92	2,10	87	0,95	1,09	75	3,95	5,27	83	2,19	3,03
Bentonite B	84	81	0,91	1,14	83	1,26	1,55	75	3,99	5,32	66	5,36	8,16
Bentonite C	66	71	1,44	2,03	65	1,77	2,71	70	6,83	9,80	64	8,03	12,70
Special	80	78	1,70	2,20	83	1,09	1,30	60	0,90	1,50	54	1,75	3,22
Standard	75	-	-	-	-	-	-	-	-	-	-	-	-

X – arithmetic mean, s – standard deviation; ν – relative standard deviation / %

bentonites performed by various methods, it can be stated that:

– The adsorption method of the Cu(II)-TET complex can be fully utilised for the determination of the montmorillonite content in foundry bentonites. This method is much faster (2–3 times) than the currently applied method based on measuring the methylene blue adsorption.

Simultaneously it provides the results, which correlate well with the data supplied by the bentonite producers. Therefore it seems appropriate to implement this method in the foundry plants.

– The infrared spectroscopy (FTIR) method, based both on measuring the peaks intensity and surface areas, can eventually be applied for the determination of the smaller montmorillonite content (70–75 %), due to the fact that bentonites contain substances, which disturb the obtained spectrum. This method should rather be used for comparative analyses of the same kind of bentonite.

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