A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 59 2014 Issue 3
DOI: 10.2478/amm-2014-0175

P. JELÍNEK*, ST.M. DOBOSZ**, J. BEŇO*, K. MAJOR-GABRYŚ**

THE BEHAVIOR OF BENTONITE BINDERS FOR THE ELEVATED AND HIGH TEMPERATURES

ZACHOWANIE BENTONITÓW ODLEWNICZYCH W PODWYŻSZONYCH I WYSOKICH TEMPERATURACH

Bentonite binders rank among the most widespread applied systems for the production of molds. Their resistance to high temperatures (thermal stability) is mainly defined by genesis of binders, chemical composition and the content of Montmorillonite. The aim of this contribution is to compare selected bentonite binders commonly used in the foundries of the Central European region, in different ways of the thermostability determination as a result of changes of the mechanical strengths of the bentonite bonded sand mixture.

Keywords: bentonite, thermostability, DTA/TG analysis, XRFS analysis, mechanical properties, bentonite soda – activation

Masy formierskie z bentonitem jako materiałem wiążącym stanowią najbardziej rozpowszechnioną technologię otrzymywania form odlewniczych. Ich odporność na wysokie temperatury (stabilność termiczna) jest uzależniona od pochodzenia minerologicznego, składu chemicznego oraz zawartości montmorylonitu w bentonicie. Celem tego artykułu jest porównanie stabilności termicznej wybranych bentonitów – powszechnie stosowanych w odlewniach w regionie Europy środkowej – mierzonej różnymi metodami. Kryterium oceny tych metod jest zmiana wytrzymałości mechanicznej mas formierskich wiązanych bentonitem.

1. Introduction

Bentonite as a natural and abundant soil is being widely used in large range of industrial applications. That's why many scientific centers conduct research connected to this material [1-18].

The task was initially elaborated by authors in previous publication [1].

In practice there are a lot of various methods usually used for the bentonite thermal stability determination. One group of the methods is based on application of instrumental analytical methods, DTA/TG analysis and/or X-Ray Diffraction analysis especially.

Another way of the thermal stability evaluation are based on comparison of the mechanical properties of the green molding mixture prepared from as-received bentonite (compression strength, splitting strength, wet tensile strength – WTS), with preheated bentonite at a defined temperature. Annealing temperature is usually derived from DTA/TG analysis and it is selected to be close to bentonite temperature of dehydroxylation. Generally, the range of annealing temperature is 500-650°C with different firing time (0-3 h) [8, 13,19-21].

The objectives of this study are: I) evaluation of basic physical and chemical properties of bentonites from Czech and Slovak region commonly used in foundry industry II) evaluation of thermal stability of bentonites samples with employing of DTA/TG analysis, III) evaluation of thermal stability of bentonites samples by determination of mechanical properties of molding mixtures prepared from studied bentonites, IV) mutual assessment of applied method for evaluation thermal stability.

2. Materials and methods

Four soda activated foundry bentonites were used for the experiments within this research. The studied bentonites were *Sedlec* and *Sabenil* from West Bohemian's and North Bohemian's region respectively, one bentonite *Bentovet K* from Central Slovakia region and finally one bentonite *Keribent R* represented a mixture of bentonites of various locality.

General parameters (Table 1) were determined: a) moisture under temperature of 105°C up to constant weight, b) pH and conductivity of water suspension (1:10 solid-liquid ratio), c) loss on ignition of dried samples (105°C up to constant weight) at 900°C/2 h. Cation exchange capacity (CEC) and montmorillonite content in the samples were determined according to Holtzer et al. [22].

Chemical composition were determined using energy dispersive fluorescence spectrometer (XRFS) SPECTRO XEPOS

---

* VSB – TECHNICAL UNIVERSITY OF OSTRAVA, DEPARTMENT OF METALLURGY AND FOUNDRY ENGINEERING, 17. LISTOPADU, 708 33, OSTRAVA CZECH REPUBLIC
** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING, DEPARTMENT OF MOULDING MATERIALS, MOULD TECHNOLOGY AND FOUNDRY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

(SPECTRO Analytical Instruments GmbH) equipped with 50 W Pd X-ray tube. The samples for analysis were prepared in the form of pressed tablets (wax was used as a binder) for this measurement (Table 2).

Thermogravimetry and differential thermal analysis (DTA/TG) were conducted using NETZSCH STA 429 CD (Gerätebau GmbH equipment). The samples were analyzed in air atmosphere with the heating rate of 15°C min^{-1} from 25°C to 1000°C.

The samples prepared from molding mixture were made in order to evaluation termostability of studied bentonites by comparison of the mechanical properties of the molding mixture prepared from as-received and preheated bentonite The samples were prepared by 5 min homogenization of the mixture of the studied bentonite with silica sand in the constant weight ratio 8:100 and an appropriate amount of water which assured the constant compactibility 38±2% using MK 00 sand mill. Then the mixtures were processed into the standard cylinders (Ø 50, height 50 mm) to obtain the samples for the determination of technological parameters.

Compression strength were measured using testing machine WADAP the LRU-1 type, wet tensile strength was measured using testing machine +GF+, the SPNF type.

TABLE 1

General properties of bentonites

Properties		Bentonites			
		Keribent R	*Sabenil*	*Sedlec*	*Bentovet K*
Content of MMT	[%]	68	65	62	75
CEC	[mmol/100g]	66,87	64,28	60,88	74,9
Moisture	[%]	6,93	7,16	10,63	8,21
pH	[-]	10,16	10,44	10,21	10,59
Conductivity	[μS/cm]	675	1422	886	1456

TABLE 2

Chemical composition of bentonites (selected elements)

	Composition/Bentonite			
	Keribent R	*Sabenil*	*Sedlec*	*Bentovet K*
Na_2O	<1.000	2.000	<1.000	2.500
MgO	2.500	3.200	1.600	2.200
K_2O	1.140	0.970	2.370	1.680
CaO	2.380	4.630	1.700	1.480
Fe_2O_3	8.410	12.70	14.800	2.150
LOI	13.600	16.300	11.900	12.600

LOI . . . loss on ignition (2h, 900°C)

3. Results and discussion

Values of montmorillonite contents in the studied bentonites are summarized in Table 1. The highest content of montmorillonite was found for bentonite *Bentovet K* (75%), The MMT content of the rest bentonite samples ranged from 62% (*Sedlec*) to 68% (*Keriben R*) what correlates with the determined CEC values (Table 1). Natural moisture of the samples determined at 105°C was very different, ranged from 6.9% (*Keribent R*) to 10.7% (*Sedlec*)

The conductivity differs significantly and falls into the range from 675 to 1456 μS/cm, measured for samples *Keribent R* and *Bentovet K*, respectively. The values of pH and conductivity are connected with the fact that all bentonite samples are activated by soda.

Although the samples *Keribent R* and *Sedlec* should be rich on the Na content (the samples are soda activated bentonites), the chemical analysis performed by XRFS showed the amount of Na_2O bellow the detection limit. The lower content of Na_2O measured for the sample Keribent R, Sedlec is in good agreement with the measured conductivity of their water suspensions (see Table 1). The LOI values for the samples *Keribent R, Sedlec, Bentovet K* and reached the values typical for content of water present in the interlayer space of montmorillonite (approx. 12 wt.%). The highest LOI value was observed for the sample *Sabenil* (16.3 wt.%) what signalizes presence of thermal unstable phases up to 900°C (for example carbonates).

Simultaneous thermal analysis was used for the characterization of changes occurred during the heating of the samples and the DTA and TG curves measured up to 1000°C are shown in Figs. 1 and 2. Both TG as well as DTA curves has a shape typical for this kind of materials.

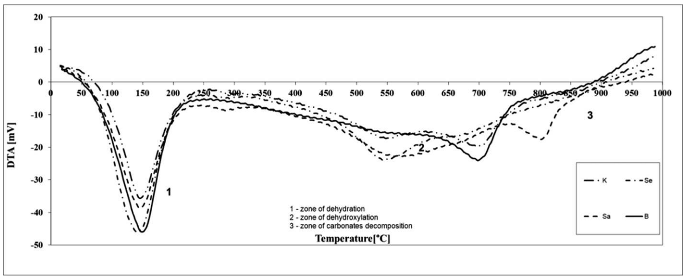

Fig. 1. DTA analysis of as-received bentonites

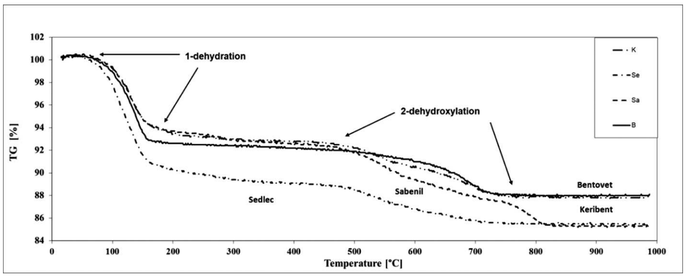

Fig. 2. TG analysis of as-received bentonites

The first endothermic process occurred during the heating of the studied bentonites is reflected by the presence of the intensive peak with the maximum about 130-150°C (dehydration) observed on the DTA curves and the significant loss of mass observed on the TG curves.

Further heating caused next obvious change of both DTA as well as TG curves which is connected with the loss of crystalline water (process called as dehydroxylation). Apparent on-set temperature of dehydroxylation enables dividing the tested samples into two earlierly mentioned groups: i) less thermally stable – so-called “soft” bentonite of probably mineral origin, and ii) thermally stable – so-called “hard” bentonite of probably volcanic origin. The on-set temperature of dehydroxylation of *Sabenil* and *Sedlec* occurs at lower temperature (544 and 582°C, respectively) and thus these bentonites belong to the less thermally stable group. The samples *Bentovet K* (thermally stable group) show significantly higher apparent on-set temperature of dehydroxylation (701°C). The DTA curve of the sample *Keribent R*, shows the curves of both sample, thus shows two maxima (548°C and 692°C), it can suspiciously explained that sample *Keribent R* represents the mixture of two various bentonites as *Bentovet K* and *Sabenil.*

The dividing of the samples to the above mentioned groups is in good agreement with Heller et al. [12].

As a main reason for the lower thermal stability of certain bentonites the authors mentioned a substitution of aluminium by iron in the octahedral sheets.

The results of DTA/TG analysis correlate with Fe content in individual samples of bentonites according to results of XRFS analysis. Temperature of dehydroxylation is also connected with MMT content of samples (Table 1).

Generally, it is well known, that thermostability, can be improved by soda-activation process. Soda activation with the aid of soda (0-4%) supports the growth of wet tensile but at the same time the thermostability too measured with two processes The sample *Bentovet K* was selected in order to study of these phenomenon. Relation between compression strength and wet tensile strength on degree of soda activation (0-4%) and thermostability of bentonite sample were evaluated as a ratio of values of compression and wet tensile strength of molding mixture prepared from as-received and preheated sample of bentonite *Bentovet K.* (Fig. 3).

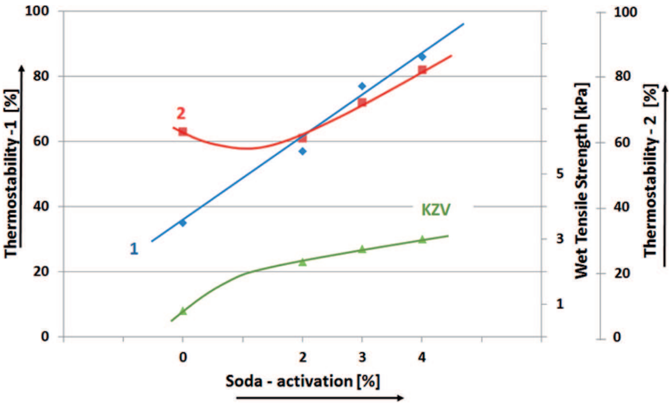

Fig. 3. Thermostability of the Slovak bentonite Bentovet K (measured by a method through the compression strength – 1); measured through the wet tensile strength – 2) in dependence on the Soda – activation degree)

From the Fig. 3 it is obvious a positive effect of soda-activation on thermo stability of the sample of bentonite *Bentovet K*. With 4% of soda per bentonite the value achieved up to 80%. Furthermore, thermo stability evaluated by the change of wet tensile strength is in good correlation with values of thermo stability evaluated by the change of compression strength, ie. Both values show the same trend. General view of compression strength values of molding mixtures prepared from studied bentonites is summarized in Fig. 4. Termostability was evaluated by the change of wet tensile strength. There were no considerable differences in the binding property with the same mixture composition and moisture 2.5% (compatibility 40%). More than 55% of thermostability showed *Keribent R* and *Bentovet K* bentonites but the last one showed the lowest binding property. The lowest thermo stabilities have the *Sabenil 65* and *Sedlec* bentonites which are the materials of very similar mineralogical and chemical composition. Then the high thermo stability and on the contrary the lower binding property need not to bring savings in binder consumption in the GSS systems.

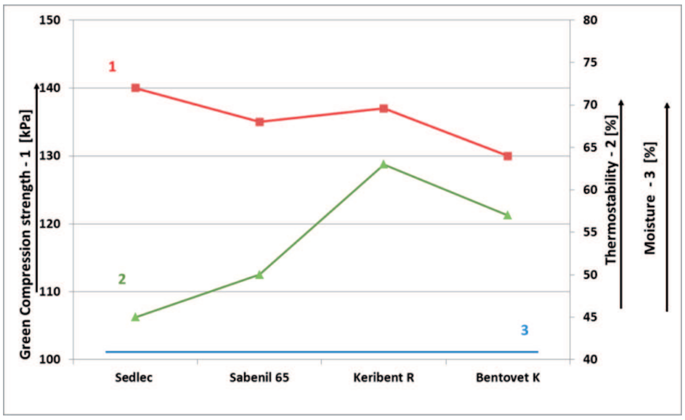

Fig. 4. Thermostability and binding property in compression of different bentonites

All tasks elaborated above are also important in contest of rebonding molding sands with bentonites [23, 24].

4. Conclusion

Thermostability, natural property of clay minerals, depends on genesis, source and chemical composition of clay. The substance of thermo stability is dehydroxylation of montmorillonite, loss of water liberated from the octahedral network (2OH → H2O + O). Relation between MMT contntet of bentonite sample and thermostability was confirmed on the basis of MMT evaluation and DTA/TG analysis. The highest temperature of dehydroxylation (701°C) was found for the sample Bentovet K (75% MMT) in comparison with the sample Sedlec (62% MMT, 544°C).

The results of DTA/TG analysis correlate with Fe content in individual samples of bentonites according to results of XRFS analysis For the sample with the lowest value of Fe content (Bentovet K) the highest dehydroxylation temperature (701°C) was obtained according to results of DTA/TG analysis.

Termostability of bentonite binders can be assessed as a ratio of mechanical properties of molding mixtures prepared from as-received and preheated bentonite samples.

Furthermore, thermo stability evaluated by the change of wet tensile strength is in good correlation with values of thermo stability evaluated by the change of compression strength Wet tensile strength can be improved by soda-activation process of bentonite binder.

Process of bentonite soda – activation admittedly doesn't lead to substantial changes of binding properties but besides the growth of thermostability it significantly influences mechanical properties during overmoistening (the growth of WTS). Some experience in practice is leading to mixing of both bentonite kinds (Ca+Na – bentonites) for the purpose of the moisture stabilization. Practical results of measurements of thermo stability of foundry bentonites have proved an importance of the ion exchange (Soda – activation). Besides thermo stability the dispersion ability and the binding property too are important.

If the questions are the "hard" bentonites then the high thermo stability need not to bring lower bentonite consumption in the GSS.

The nature has played a decisive role in thermo stability of montmorillonites, therefore for obtaining the required properties the mixing of bentonites from different localities is a possible way.

Acknowledgements

This work was elaborated within the research project TA02011314 supported by the Technology Agency of the Czech Republic.

REFERENCES

[1] P. Jelinek, St.M. Dobosz, J. Beno, K. Major-Gabryś, China Foundry (2013) /in printing/.
[2] S. Guggenheim, R.T. Martin, Clays and Clay Minerals,**43**, 255-256 (1995).
[3] C. Paluskiewicz, et. al., Journal of Molecular Structure **880**, 109-114 (2008).
[4] V.J. Inglezakis, et. al., Desalination **210**, 1-3, 10, 248-256 (2007).
[5] H.A. Patel, et. al., Applied Clay Science **35**, 3-4, 194-200 (2007).
[6] J. Madejova, et.al., Vibrational Spectroscopy **40**, 80-88 (2006).
[7] F. Bergaya, et. al. Handbook of clay science. Oxford, Elsevier, 2006.
[8] P. Lichý, et.al. 20^{th} Anniversary international conference on metallurgy and materials, 890-896 (2011).
[9] W. Tilch, et. al., Giesserei – Praxis **2**, 53-62 (2002).
[10] F. Boylu, Applied Clay Science **52**, 1-2, 104-108 (2011).
[11] M. Klinkenberg, et.al., Applied Clay Science **33**, 3-4, 195-206 (2006).
[12] L. Heller, et al., Clay Minerals Bulletin **4**, 213-230 (1961).
[13] R. Gauglitz, H.E. Schwiete, Berichte Deutsche Keramik Ges **38**, 43-49 (1964).
[14] P. Wu, C. Ming, China Spectrochimica Acta Part A **63**, 85-90 (2006).
[15] C. Grefhorst, Giesserei **93**, 5, 26-31 (2006).
[16] V.I. Kaplun, et al., Litějnoje proizvodstvo **6**, 12-15 (2006).
[17] L. Calarge, et.al., Journal of South Americans Earth Sciences **16**, 187-198 (2003).
[18] L. Stoch, Minerały ilaste, Wyd. Geologiczne, Warszawa, 1974.
[19] P. Jelínek, J. Beňo, V. Matějka, Slévárenství **54**, 5-6, 178-182 (2011).
[20] P. Jelínek, et al., Slévárenství **38**, 1, 31-35 (1995).
[21] F.C. Kvaša, Litějnoje proizvodstvo **10**, 13-15 (2006).
[22] M. Holtzer, et.al., Archives of Foundry Engineering **9**, 4, 69-72 (2009).
[23] J. Jakubski, et. al., Archives of Metallurgy and Materials **58**, 3, 961-963 (2013).
[24] J. Jakubski, et. al. Archives of Metallurgy and Materials **55**, 3, 843-849 (2010).

Received: 20 March 2014.