INFLUENCING OF FOUNDRY BENTONITE MIXTURES BY BINDER ACTIVATION

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Although new moulding processes for manufacture of high quality castings have been developed and introduced into foundry practice in recent years, the green-sand moulding in bentonite mixture still remains the most widely used technology. Higher utility properties of bentonite binders are achieved through their activation. This contribution is aimed at finding a suitable activating agent. A number of sodium salts and MgO based agents has been chosen. In the framework of the experiment the swelling volume of chosen agents was tested and technological parameters of a bentonite mixture with a binder activated with the studied agents were determined.

Key words: foundry, bentonite, green sand, activation, swelling volume

INTRODUCTION

Bentonite all the time represents the most widely used binder. It is estimated that more than 70 % of iron alloys castings (primarily of graphitizing cast irons) is produced with the use of these mixtures worldwide and the use is extended for light alloys castings too [1].

According to the structure the montmorillonites (MMT), which form the basic component of bentonites (more than 75 %) included into stratified clays (phylosilicates) [2].

Montmorillonites have a typical triple layer structure. Between two silicate tetrahedrons $(SiO_4)^{4-}$ the octahedron $(AlO_6)^{-}$ occurs.

Individual layers are bound by weak van der Waals forces. In montmorillonites the partial isomorphic substitutions of central atoms are in the coordination tetrahedron (Si⁴⁺ – Al³⁺) or the octahedron (Al³⁺ – Mg²⁺). Thus the surface becomes electrically charged with a negative sign (O²⁻). This structural effect is a cause of the extraordinary sorption capacity (high surface activity). The negative charge is partially compensated in the spaces of the exchange base by cations, most commonly by Ca²⁺ – Mg²⁺ but by Na⁺ too. Cations are bound between particles by different forces which allows to rank the ability of the ion exchange [3, 4]:

 $Li^{\scriptscriptstyle +} - Na^{\scriptscriptstyle +} - H^{\scriptscriptstyle +} - K^{\scriptscriptstyle +} - Mg^{2 \scriptscriptstyle +} - (Ba^{2 \scriptscriptstyle +},\,Ca^{2 \scriptscriptstyle +},\,Sr^{2 \scriptscriptstyle +}) - Rb^{\scriptscriptstyle +}.$

Replacement of $Ca^{2+} - Mg^{2+}$ ions for Na⁺ ones in bentonite mixtures is technologically significantly advantageous and it is called the soda-activation process. Water is then consumed not only for the formation of lyosphere on the surface of particles – the intermicellar swelling but the intramicellar swelling too (between basal planes) [5]. The soda-activation process can be simply expressed by an equation as follows:

 $Ca^{2\scriptscriptstyle +} \text{ - } MMT + 2 \text{ } Na^{\scriptscriptstyle +} \leftrightarrow 2 \text{ } Na^{\scriptscriptstyle +} \text{ - } MMT + Ca^{2\scriptscriptstyle +}$

The soda-activation can be done with any sodium salt (Na⁺) but the quantitative course of the reaction from left to right will be determined by the solubility of calcium salts (Ca²⁺).

Therefore the anionic part of the sodium salt is decisive for the efficiency. Therefore it is not possible to successfully natrificate with NaCl or water glass, whose calcium salts are well soluble in water. Sodium carbonate is most commonly used with regard to minimum solubility of CaCO₂ in water [5, 6].

From the point of view of economy the widely available sodium carbonate (Na_2CO_3) is used. Multivalent (Ca^{2+}, Mg^{2+}) less hydrated cations operate coagulatingly while on the contrary the monovalent hydrated cations (Na^+) operate dispersingly, i.e. they prevent the agglomeration of particles (increasing swelling). Among the main reasons of the soda-activation are included as follow:

- (i) high swelling more swelling bentonite has a higher strength in the water condensation zone (wet tensile strength) what allows to reduce the bentonite content;
- (ii) the susceptibility of bentonite mixtures to overmoistening decreases (higher resistance to scabs);
- (iii) the reduction of heat stress of the mould from braked thermal expansion of the base sand (SiO_2) . During dehydration the montmorillonitic clays begin to shrink under lower temperatures (the reduction of stress and the increase of the resistance to defects caused by stress);
- (iv) the growth of the binder thermostability (temperature of the clay dehydroxylation) [4, 6, 7].

This contribution is aimed at finding a suitable activating agent. A number of sodium salts and MgO based agents have been chosen. In the framework of the ex-

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periment the swelling volume of chosen agents was tested and technological parameters of a mixture with a bentonite binder activated with the studied agents were determined.

EXPERIMENTAL PROCEDURE

Natural $Ca^{2+} - Mg^{2+}$ bentonite of the North Bohemia provenance was chosen for the experiment. Different sodium salts (Na₂CO₃; Na₂SO₄; Na₂HPO₄ × 12 H₂O; NaH₂PO₄ × 2H₂O, NaOH) and Mg based agents (pure MgO; CCM65 – technical MgO; 70 % MgO) were chosen as activating additives whose positive effect on bentonite swelling is known for applications in the construction industry [8].

Bentonite swelling was evaluated as a change of the volume of 2 g of the bentonite sample with the addition of the activating agent (1 - 5 % related to the binder) in water in a 50 ml burette after 24 h of sedimentation.

Activation of all bentonite mixtures with the aid of additives took place in such a way that the additive was mixed in a water solution. Bentonite and sand were charged in a sand mill and after a minute the water solution with the activating agent was added.

The samples of the testing bentonite molding mixture 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 45 ± 3 % using LM-1 sand mill. After the maturation for 24 hours the mixture was mixed again in the sand mill for 5 minutes and the mixture moisture was treated for compactibility of 45 ± 3 %. Mechanical properties of the mixture activated in such a way were determined and compared with those ones of the non-activated mixture. Compactibility was determined on the device +GF+, the PRA Sand Rammer type. Mixture moisture was determined through loss in weight under temperature of 130 °C on the device of the AND MX-50 type.

The prepared mixtures were processed into the standard cylinders (\emptyset 50 mm, 50 mm height) to obtain the samples for the determination of technological parameters. The parameters include compression, split-

ting and wet tensile strength, were measured on the samples prepared using molding mixtures.

Compression and splitting strength were measured using testing machine WADAP the LRU-1 type, wet tensile strength was measured using testing machine +GF+, the SPNF 5401 type.

RESULTS AND DISCUSSION

Swelling volume

Swelling is a process when the clay due to water uptake from its neighbourhood increases its volume. The process continues as long as the clay is completely saturated. The results of swelling tests of studied agents are summarized in Figure 1.

The highest values of swelling were measured for 4 % of the addition of pure MgO (swelling 27,3 ml). With industrial MgO (CCM65) the swelling was significantly smaller. The highest value represented the swelling 7,2 ml with 4 % of the solution. Pure MgO has a much better swelling ability than CCM65 but it takes high acquisition costs.

The next activating agent which showed higher swelling is $Na_2HPO_4 \times 12H_2O$. The highest swelling was found with the addition of 1 % of the agent (17,9 ml); with growing concentration of the agent the swelling decreased (5 % - 8,8 ml). Similar course was observed also with the addition of Na₂CO₂. These activating agents were then chosen for the combination with pure MgO. Conversely, the worst swelling ability was found with the addition of NaOH where its value gradually decreased (1 % - 6.5 ml; 5 % - 0.3 ml). From the results of swelling of bentonite binders with different activating agents were chosen those ones that showed the highest abilities of swelling. Pure MgO which showed the highest swelling ability was combined with 2 % and 3 % of Na₂CO₃ and Na₂H- $PO_4 \times 12H_2O$. The highest swelling volume of these combined agents was determined for 2 % of Na_2CO_2 + MgO with maximum swelling value (19,6 ml) with the addition of 5 % of this agent into the binder. The values are reported in Figure 2.



Figure 1 Influence of selected simple activation agents on swelling volume



Figure 2 Influence of selected combined activation agents on swelling volume

A similar character was found also with the addition of a combined agent of 3 % of $Na_2CO_3 + MgO$ with maximum 19 ml with the addition of 5 % of the agent. Almost linear character of the growth of the swelling volume was also found with the addition of the agent of composition 2 % of $Na_2HPO_4 \times 2H_2O+MgO$ with maximum value of the swelling volume 12,9 ml with maximum concentration in the binder (5 %). The addition of 3 % of $Na_2HPO_4 \times 2H_2O$ showed the maximum values with the addition of 2 % (10,5 ml) of the agent, the growing concentration of the agent in bentonite caused a slight decrease.

Technological parameters of bentonite molding mixtures

In the next part of the experiment the influence of the activating agents on properties of moulding mixtures bonded with bentonite was evaluated. Values of individual technological parameters of bentonite mixtures activated with different agents are summarized in Table 1.

The highest values of compression strengths have been measured for the combination of additives and pure MgO. Activating agents with 3 % solution of Na- $_2CO_3$ and Na $_2HPO_4 \times 2H_2O$ combined with MgO showed the mean compression strengths of 178 kPa and 182 kPa. In total, the mean values of compression strength of the activated bentonite mixture ranged 158 – 182 kPa. The highest values of splitting strength which determines the real binding properties of bentonites and it is given by the mixture resistance against deformation in a direction transverse to the axis of the cylinder test sample were determined for the mixture activated with 2 % MgO.

The activated mixture showed mean strength of 44 kPa. The mixture activated with Na_2CO_3 , MgO, $Na_2HPO_4 + MgO$ where 3 % of the activating agent were



used showed on average the same values. The values of these mixtures were 39 kPa. Probably the most important test with regard to the effectiveness of the activating agent is the determination of wet tensile strength. This test simulates conditions on the mould face during casting before contact with liquid metal and therefore it characterizes the mixture susceptibility to casting defects. A technological optimum value is between 2,0 - 4,0 kPa Mixtures activated with the additions of 2 % and 3 % MgO and CCM65 showed very low values..

The values were similar to those ones of the nonactivated mixture. Mixtures activated with combination with MgO and activating agents Na_2CO_3 , Na_2HPO_4 showed the low values too. The highest wet tensile strength value has been measured for 3 % Na_2H - $PO_4 \times 2H_2O$, the value showed 4,3 kPa.

CONCLUSION

This contribution has been focused on the study of the influence of different activating agents on properties of the bentonite binder or bentonite bonded moulding mixtures.

From the obtained results it is evident that a suitable and fully satisfying activating agent is represented by the commonly used Na_2CO_3 (3 %). Another option is the use of phosphate based salts the use of which may, however, bring environmental problems. Carried out experiments didn't confirm earlier published dependency of wet tensile strength on the swelling volume.

Influence the ion kind with which the activating process is carried out is recognisable of the MgO addition as an activating agent hasn't been unambiguously confirmed.

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Sample	Compactibility	Compression strength	Splitting strength	Wet tensile strength
	/ KPd	/ KPd	/ KPd	/ KPd
Non activated mixture	45	98,3	26,0	0,56
2 % Na ₂ CO ₃	44	84,0	28,7	2,73
3 % Na ₂ CO ₃	43	161,7	39,0	3,13
2 % Na ₂ HPO ₄ × 12 H ₂ O	45	168,3	34,6	3,30
3 % Na ₂ HPO ₄ × 12 H ₂ O	46	160,0	33,0	4,30
2 % NaH ₂ PO ₄ ×2H ₂ O	44	173,3	36,0	2,33
3 % NaH ₂ PO ₄ ×2H ₂ O	44	158,3	32,0	3,50
2 % MgO	44	175,0	44,0	0,67
3 % MgO	45	170,0	38,0	0,56
2 % CCM65	44	173,0	34,0	0,66
3 % CCM65	46	152,0	27,0	0,43
2 % Na ₂ CO ₃ + MgO	46	158,3	35,0	1,50
3 % Na ₂ CO ₃ + MgO	46	178,3	34,0	1,90
2% Na ₂ HPO ₄ ×12H ₂ O + MgO	46	171,7	35,0	1,20
3 % Na ₂ HPO,×12H ₂ O + MgO	46	182,0	40,0	1,47

REFERENCES

- [1] W. Tilch; C. Grefhorst; W. Kleimann, Bentonite als Formstoffbinder-eine praxisnahe Bewertung der Eigenschaften, Giesserei-Praxis (2002) 2, 53-62 (in German)
- [2] Report of The clay Minerals society nomenklatur committee: Revise classification of clay minerals, Clays and Clay Minerals, 39 (1991), 3, 333-335.
- [3] M. Holtzer, B. Grabowska, A. Bobrowski, S. Żymankowska-Kumon, Methods of the montmorillonite content determination in foundry bentonites, Archives of Foundry Engineering 9 (2009) 2, 69-72.
- [4] P. Jelínek, Pojivové soustavy slévárenských formovacích směsí, P. Jelínek, Ostrava, 2004, pp. 36-39 and 48 (in Czech)

- [5] F. Boylu, Optimization of foundry sand characteristics of soda-activated calcium bentonite, Applied Clay Science 52 (2011), 104-108.
- [6] P. Jelínek, Slévarenská technologie, VŠB-TU Ostrava, Ostrava, 1986, pp. 128-156 (in Czech)
- [7] G. Solenicki, I. Budic, I. Kladaric, D. Novoselovic, Compressive stresses of mould mixture, Metalurgija 53 (2014) 4, 591-593.
- [8] C. Karagüzel; T. Çetinel; F. Boylu; K. Çinku; M. S. Çelik, Activation of (Na, Ca) - bentonites with soda and MgO and their utilization as drilling mud, Applied Clay Science 48 (2010), 398-404.
- Note: The responsible translator for English language is František Urbánek, Brno, Czech Republic