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Ecological Binding Material of First Generation

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Abstract

Bentonite is clay rock, which is created by decomposition of volcanic glass. It is formed from mixture of clay minerals of smectite group, mainly montmorillonite, beidellite and nontronite. Its typical characteristics is, that when in contact with water, it intensively swells. First who used this term was W.C. Knight in 1887. The rock had been named after town Fort Benton in American state Montana. For its interesting technological properties and whiteness has wide technological use. Bentonite is selectively mined and according to its final use separately modified, which results in high quality product with specific parameters.

In the beginning of 21st century belong bentonite moulding mixtures in foundry to always perspective. Mainly increased ratio of ductile cast iron castings production cannot be ensured without the need of quality bentonite. Great area of scope remains to further research of moulding materials, which return also to bentonite producers.

Keywords: Bentonite, Moulding mixture, Nitrification, Ecological aspect

1. Introduction

Term „bentonite“ is today applied to rocks, which perished to „bentonitization“, mainly on „clayed“ products of volcanic activity [7]. In places of these rock's occurrence, characterized by heavy sorptive capability, high interchange of cations, swelling, plasticity and binding capacity, deposits of bentonite are being created [1]. Bentonite can be also considered as residual rock, in which smectite is found in such amount, when additive of sand or dust grains can be 20%, or materials of cementation nature up to 10%, including other clay materials – kaolinite, illite, glaukonite etc. [2]. Petrographically bentonite is not created with just one sort of rock, but is mineral material of clay look, which is directly or non-directly connected to volcanism [3].

Bentonite is clay foundry binder, which consists of minimal 75% montmorillonite mineral. The rest consists of other aluminosilicates, mainly kaolinite and illite, glaukonite, chlorite, vermiculite, quartz, anatase and others. Fragments of older rocks as

quartzite, sandstone, decalcified clays, gneiss can be also found there [4, 5]. All of these minerals and rocks, which can be present in bentonite, are considered as harmful substances, negatively influence technological properties, which depend from montmorillonite presence [6, 7, 8, 9]. Therefore bentonites from different locations significantly differ from each other and only 30% of world production is being used for foundry purposes [10]. Clay binders belong to the most spread foundry binders. They are mostly present in natural sands and are used in clean state to bind washed sands and sometimes artificial materials [11, 12].

2. The significance of bentonite

The significance of bentonite for our foundry industry is very great, for long years almost all technical metals are being poured into bentonite mixtures and development of modern foundry moulding machines in the world always counts with

bentonitemoulding mixtures [13, 14]. Main reason of dominant position of bentonite mixtures by moulds production is reversibility of binding properties, which enables repeated usage of these materials. Present global production of castings is estimated on 80 mil. tons. From this production, 60 – 70% is poured into raw bentonite moulds. We are talking about first generation mixtures, where binding is result of capillary pressure and van der Waals forces (moulding mixtures with clay binder). The beginning of usage of this technology in Europe falls down to 30's of last century [14].

On the contrary to significant tendency of other production processes used for mould production for pouring increase, the processes of bentonite-based moulds production will keep dominant position in future. Deciding advantages of bentonite moulds usage, or processes of mould production are:

High binding capacity and plasticity of bentonite binder is reached by low amount of free water, which make possible to pour castings into raw moulds

Relatively low costs on moulding mixture linked to relatively low costs on raw material

High degree of re-using of moulding mixture (cca 95 – 98%), low specific consumption of moulding material on sound castings (0,1 – 0,3 ton / ton on sound castings)

Possibility for closed circulation of materials creation.

High productivity of production technique used, enabling control and managing the quality of moulding mixtures

High and stable quality of castings (good surface, stabile accuracy, castings without errors) ensured by modern ways of compression

Today, also the state of the art methods of moulds production count with bentonite mixture, which brings a lot of technical, economical and mainly ecological advantages.

In praxis, clay minerals are being used for their valuable properties, coming from fine structure, significant dispersity degree, great specific surface capable of ion exchange etc. From these, significant technological parameters as plasticity, swelling, binding capacity, sorptive capability for gases, steam, solutions and heat resistance and other come out. From clay minerals, mostly used are illite, kaolinite, montmorillonite, attapulgite and halloizite. Other clay minerals such as montronite, beldelliteetc are only side substances of given minerals, and are minimally used [15].

As foundry binders, three groups of clay minerals are being used:

- Illite clays (most common binder in natural sands)
- Kaolinite clays (belong to high heat resistant clays, binder of fire clay mixtures for drying – burning)
- Montmorillonite clays (smectites) create main part of bentonites (raw bentonite mixtures)

Montmorillonite has typical three-layer structure, between two silicate tetrahedron $[\text{SiO}_4]_4$, gibbsite octahedron (AlO_6) is placed – Fig. 1. In octahedron and tetrahedrons atoms are bounded with strong covalent binding and each layer are bounded with weak Van der Waals forces.

As a result of allotropic substitution of central atom in coordinate tetrahedron, e.g. Si^{4+} for Al^{3+} or in octahedron Al^{3+} for Mg^{2+} in grid with lower-powerful cations, on surface of elements free valencies are being created. In montmorillonite, the surface is saturated with negative ions (O_2^- , OH^-). This structural

effect is cause of extraordinary sorptive capability of montmorillonite. Negative charge is compensated with cations, mainly Ca^{2+} , Mg^{2+} , Na^+ . Cations are bounded with different strength between layers, which allows to create a sequence of ion exchange; Li after Na after H after Mg after (Ba, Ca, Sr) after Rb. Therefore we are speaking about Ca, Mg bentonites (calic, north-czech bentonites) and Na bentonites (sodium bentonites, USA) [10].

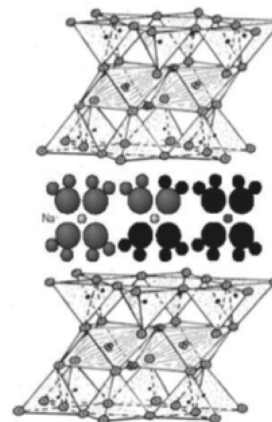


Fig. 1. Scheme of montmorillonite structure

Montmorillonite (smectite) plays main role in group of three-layered minerals. The strength of binding, reached inside every accumulated layer allows placing of water molecules, coming to expansion in c – axis (inner part – crystal case swelling). By ion integration, charged in different orientation into octahedron coordination, electroneutrality of whole grid is disturbed. To compensate these different charges, ions are connected to the grid or between separated layers. These “exchanged ions” significantly influence behaviour (activation) of bentonite in sense of practical application in foundries.

Because of their layer form, crystals of montmorillonite have lameral structure – Fig. 2, thickness of these crystal leaves reaches 1 nm. Diameter of these leaves is in range 100 – 800 nm. Montmorillonite crystals are known for its thickness, capacity to yield and wide surface layer [16, 17].

Water molecule has polar character with dipole properties, which allows their mutual association, with help of H – binding, chains of planar and dimensional orientation are being created – Fig. 2.

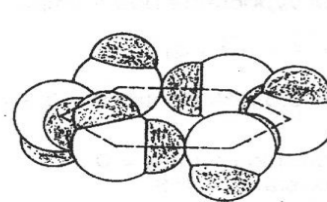


Fig. 2. Planar association of water molecules [6]

When talking about water in clay minerals, we talk about two forms:

Molecule water – represents cca 10% of mineral weight, occurs in in places between layers (intercrystalic swelling) or as

absorbed on surface bundles (packets, intercrystalline swelling) and pores between particle bundles

Grid water – hydroxylated in form of OH- groups, as part of crystal grid

It is not possible to make dehydration quantitative up to temperature 110°C, total evaporation of molecule water will be done by temperature 250 – 300 °C. Action is completely reversible. Water, bounded in form of OH- groups usually escapes by temperature 300 °C. Dehydroxylation is irreversible action, connected with process of degradation of plastic properties of clays [1]. With help of thermal analysis it is possible to identify different types of clay binders [11].

Dehydroxylation of montmorillonite clays, influenced by heat exposition of mould leads to creation of different bentonite types in unified bentonite mixtures:

Active bentonite – has original binding properties and can be quantified with MM test – adsorption of methylene blue

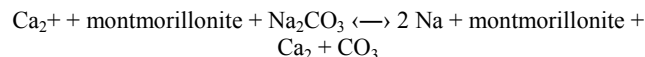
Dead bentonite – dehydroxylated clay, is part of oolitized cases of silicate sands and washed-away parts of unified bentonite mixtures

Passivated bentonite – hydrofobized after adsorption “Cover effect” of pyrolyzed gases of carbon additives and organic core binders

Latent bentonite – active bentonite, placed in intergranular places (outside of grain case) as a result of insufficient mixing of mixture [10]

By charge compensation, cations are bounded between particles with different force, what enables us to create a sequence of ion exchange. Therefore we can make exchange of Ca²⁺ - Mg²⁺ ions for Na⁺, what is technologically very advantageous for bentonite mixtures. This process is called natrification.

Process of natrification can be described by schematic equation:



Natrification can be done with every sodium salt, but quantitative progress of reaction from left side to right will be given by solubility of sodium salts, therefore regarding the effectiveness, anion part of sodium salt will decide. We cannot successfully nitrify with waterglass or NaCl. Mostly used is Na₂CO₃, due to minimal solubility of reaction product, CaCO₃ in water. Other, also important condition is ion diameter of cation. The smaller the diameter, the higher the effectiveness – Fig. 3.

In technical praxis is used bentonite, which consists mainly of mineral montmorillonite, and also already mentioned minerals as quartz, limestone, illite. The quality of montmorillonite present in bentonite, limits its chemical – physical properties [29, 30]. Mostly present form of montmorillonite (beidelite) is Ca and Mg form, less present is Na form. Prevailing exchangeable kation has significant influence on bentonite properties. Bentonites expand in different way in water environment with influence of interlayer absorption of water (12 x increase of volume). Following areas of usage could be described very roughly [18, 21]:

- Sorbents – food industry, agriculture, catalytic converter, decontaminators (cca 30%)
- Dispersant – additives to drilling scavengings, building suspensions, stabilizers of paints (cca 20%)

- Binders, filling, putty – foundry industry, building industry, pharmacy, paper industry, textile industry (cca 40%)
- Other – materials for specific needs (cca 10%)

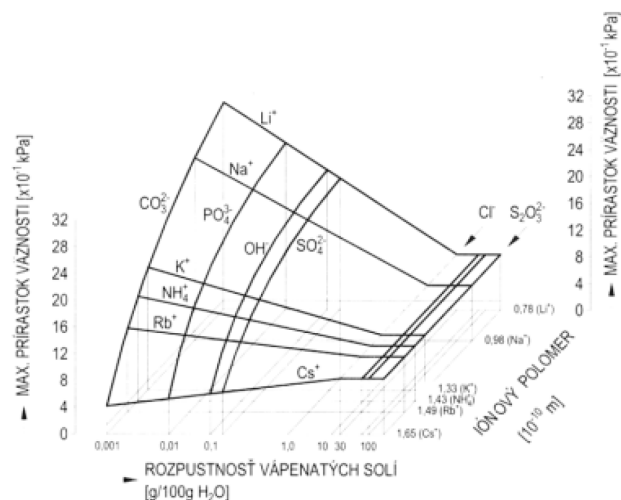


Fig. 3. Effectiveness of different salts on ion exchange by montmorillonites

In chemical production, bentonite is used mainly in catalytic chemistry, is used as bearer of catalyzers, catalyzer itself mainly for organic synthesis and petrochemistry. Oil industry as first had widely spread the area of bentonite usage: production of engine fuel with catalytic cracking from heavy oil products, production of petrol/gas, dehydrogenation of paraffinic carbohydrates, production of synthetic ethanol by hydration of ethylene, production of synthetic rubber etc. Bentonites create important part of different industry deodorants, which serve to remove the odor, these complex substances can contain except for sulphates, chlorides, nitrate and mixtures of organic acids also additives of bentonite or vermiculite [19]. Different forms of bentonite are also part of detergents and cleaning substances, for these purposes are suitable natural bentonites and synthetically natrified bentonites, for dry cleaning H-bentonites are used [20, 21].

3. Decrease of ecological strain

Decrease of ecological strain by casting production is nowadays most observed task of foundry development in area of moulding and core mixtures.

For bentonite mixture this means to solve two main problems:

- Waste
- Working environment

Waste is accompanying phenomenon not only for bentonite moulding mixtures. For cast iron castings it is enough 1 – 2% of new material for reviving into mixer. This makes from this method most ecologically process, because in comparison to present used technologies, after shaking out stay not only opening material but also binding material. So costs for revival of bentonite mixtures are surely lowest from other used technologies. Unfortunately, mentioned 1% of new material is

valid only for non-core production. When we use cores, into revival counts also the sand from cores, which cannot be eliminated. In parameter comparison of bentonite mixtures [22] average revival (including sand from cores) 4,1% is stated. In foundry is valid the law of material preservation: Every bought kg of material must be in foundry produced as a casting or as a waste. Third possibility – production of for example paving brick from waste sand – did not take over yet.

Unfortunately, for materials for reviving of moulding mixture or for core production applies only second variant – waste. There are a lot of ways of regeneration and usage at least opening material, back to moulding or core mixture. An example, that it can be fulfilled is in Foundry Component in Netherlands. Here they had to adjust both technologies (CB core production – amine and bentonite mixture) on the same granularity of opening material 0,22 mm. Wit producer they had to adapt such regeneration, that waste bentonite mixture should be used as opening material for cores. Pleasing is, that it was fulfilled. From [21] comes out, that under our conditions, mostly used granularity of opening material for revival of bentonite mixture is 0,22 mm, while for core production is commonly used 0,27 – 0,30 mm. So regressive usage of regenerate is strictly eliminated. Example from Component will soon find its successors. The reason is extremely low amount of bought and waste sand and from this related savings. Under Slovak conditions there is interesting example from foundry BeskydFryland in Ostravice, where for non-core production they use just pure bentonite, without carbonic additive and opening material with granularity 0,14 mm. There is no problem with toxicity of waste mixture and with emissions during pouring.

There are three main sources of waste sand toxicity:

- Additives of moulding mixture – mainly their heat dissociation
- Residues from cores – dissociation of core binders, chemical composition of binders
- Unwanted additives – e.g. hydraulic oil

Additives of moulding mixture are mostly on the basis of stone coal for cast iron castings. There is problem with methodology of measurement because with different temperatures comes to different liberation of harmful additives as benzene, toluene, ethylbenzene, xylene (BTEX). Laboratory results are shown on Fig. 4. As a source, Ecosil with content of pyrolyzed (bright) carbon 20% was used. It can be seen, that in different layers of moulding mixture, according to distance from castings, different amount of benzene would be created.

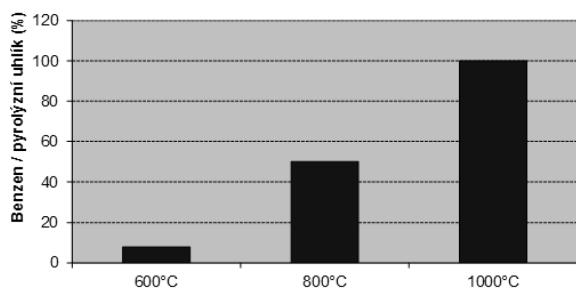


Fig. 4. Dependence of proportional amount of benzene on % of pyrolyzed carbon by different temperatures

Unfortunately shows up, that today in Clariant, used selected stone coal and natural resins as source of pyrolyzed (bright) carbon are optimally selected and no other additives with significantly lower emission development can be found – Fig. 5.

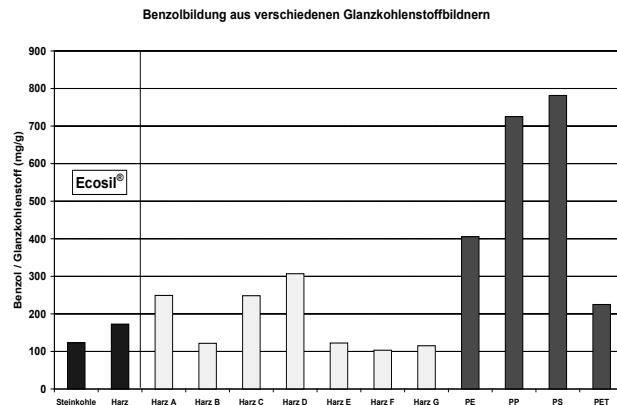


Fig. 5. Benzene formation by 1000 °C in different carrier of bright carbon

The same problem is being solved by all competition. New way of surface improvement is being searched, not only with use of classical carriers of bright carbon. In Czech republic are set in production new products of companies Clariant, Keramost and Šimeček. From executed measurements on mixtures from companies comes out, that emissions of BTXE were successfully decreased in half by preserving the surface of cast iron castings. As bonus is decrease of annealing losses, humidity and emission of gases, which helped to remove some casting errors – for example from excessive amount of pyrolyzed carbon, explosive penetration etc. Precise values are shown in references [23 - 25]. Important source of emission after pouring, and also of toxicity of wastes, is organic binder of cores. From data /1/ it is clear, that average amount of sand from cores is same as addition of new opening material into mixer. In some foundries no new opening material is being added into mixer – all opening materials comes from cores. Average CB cores contain 1,2 % of binder, which is few times bigger source of BTXE as additives in moulding mixture, which are 1,5 – 3 %. From stated it is clear, that organic binded cores are minimally the same source of pollutants as carrier of bright carbon. When we would be forced to eliminate these emissions, not only non-toxic additives would have to be solved, but it would be needed to change the whole technology of core production from basics.

The result of development for binder producers is present renaissance of anorganic binding systems. New generation of binders is represented with purchasing names Geopoli, Cordis, Inotec and others. Producers somehow forget about bentonite mixtures – up to now used anorganic binders on basis of modified waterglass are probably the worst, what should come to bentonite mixtures. Therefore, the main areas of success are cores for die castings or mould production from the same mixture. It is being estimated, that 70% of cast iron castings is being produced into bentonite mixture – there is still wide area for searching for new solutions. From harmfulness against bentonite point of view, used

technology of core productions can be divided in three groups – Table 1.

Table 1.
Groups of core technologies and needed amount of harmless opening material

Technology of core production	Casemixture CB-Amine	resol CO ₂ , alfaset	furane, water glass
Needed additive of new opening material to sandfromcores	0 – 10 %	20-33 %	50 and more %

Percent of requested addition of new (or harmless) opening material is result of experiences of author by solving errors as thorns in gray and ductile cast irons. Not only from reason of decreasing of emissions or amount of harmful substances in waste. Very common unwanted substance is hydraulic oil. If there is not excessive amount, it can also improve some properties of moulding mixture. The earlier-born remember additives of as fakol or rexol, which were stopped from being used for hygienic reasons. Hydraulic oil does not belong to moulding mixture, that is still true. In small amount it is harmful with development of unwanted emissions and in greater amount can cause casting errors. Another common bad habit is to pour the trash after cleaning of workshop into returning material – harmfulness will show immediately on moulding mixture properties. It comes to disturbance of bentonite natrification and to ability to bind the water. The correction needs few rounds of intensive revival. Third, unfortunately very often, case is mixing with returning materials from other technologies. It is so harmful, that it comes to significant worsening of bentonite mixture properties. When binder from other technology is organic, it will surely come to emission increase – similar as with using the sand from cores.

4. Conclusions

By non-core production, harmful substances from bentonite mixtures can be decreased with available products on less than 50% of present state. When new materials and knowledge would be consistently realized, it can reach almost 0. Problem comes with core production. Thanks to adsorbing ability of bentonite or new additives, emissions into workplace could be significantly decreased. Harmful substances stay in mixture.

Interesting solution is reducing of emissions of carbohydrates (BTEX) with use of oxidation [26]. This method was developed in USA and shows interesting results. Thanks to present used or new anorganic binders of cores, these cores are not very suitable into bentonite mixtures. But also without use of anorganic cores, emission decrease in half during pouring is very good result of present state.

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