Perspective Technologies for the Disposal of Spent Adsorbents Based on Zeolites in Building Materials

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Abstract. This paper presents the results of investigations and substantiation of the possibility of disposal of spent adsorbents created on the basis of the modification of natural zeolite tuffs of the Holinsky deposit of East Transbaikalia, and used in industrial wastewater treatment technology, in building materials are presented. Effective technological methods of using zeolites and zeolite-like materials are considered: non-firing technologies (an extensive class of mixed binders), concrete, autoclave-free silicate products, ash-zeolite compositions; firing technologies (high-temperature: 1100-1200 °C artificial porous aggregates), ceramic materials of a wide range of applications, aluminosilicate component in the preparation of Portland cement clinker and binders, foams.

1. Introduction
In the practice of treating industrial wastewater from metallurgy, engineering, and transport industries from heavy metal ions and oil products, batch adsorption units with a fixed adsorbent layer are used. As a loading of adsorption filters, we proposed using natural zeolite tuffs of the Holinsky deposit of East Transbaikalia, and used in industrial wastewater treatment technology, in building materials are presented. Effective technological methods of using zeolites and zeolite-like materials are considered: non-firing technologies (an extensive class of mixed binders), concrete, autoclave-free silicate products, ash-zeolite compositions; firing technologies (high-temperature: 1100-1200 °C artificial porous aggregates), ceramic materials of a wide range of applications, aluminosilicate component in the preparation of Portland cement clinker and binders, foams.

Upon completion of the industrial wastewater treatment process in the adsorption treatment unit and regeneration stages, the idle (washed) adsorbent - zeolite-like material can be disposed of in the technologies for the production of building materials taking into account the specific properties of modifying agents.

In addition, the use of zeolite-containing rocks is due to the availability and expansion of the raw material base in order to create local building materials. It should be noted that certain types of binder do not require long transportation to the consumer and this helps to reduce their cost.

Perspective areas for the use of zeolites and zeolite-like materials in construction are: their use as an additive in the production of concrete, building binders, and ceramic products. The porous structure of the zeolites leads to the binding of large quantities of CaO and SO₃ in calcareous and calcareous-gypsous systems. In this case, the decomposition of zeolites into hydro (sulfo) - aluminates and gilrosilicate gel occurs much faster than other aluminosilicates. This is due to the fact that atomic and
flint oxygen tetrahedral units in zeolites are arranged alternately, more easily released, and more easily integrated into hydrate structures, supplying finished blocks. Due to this in cement compositions a fast synthesis of hydrosulfoaluminate phases is observed with the additional formation of a hydrosilicate gel. The high pozzolanic activity of binding not only CaO, but also SO₃, as well as the secondary porosity of the zeolite tuffs, helps to reduce or completely eliminate the destructive processes during the hydration of high-calcium ashes. Another feature of natural zeolites is that they bloat when heated (1100 - 1200 °C), which makes them a promising raw material, along with fusible clays, vermiculite and perlite to produce various kinds of porous thermal insulating materials [3].

2. Experimental investigations. Results and discussion
When zeolite tuffs are introduced into mixed binders, the durability of mortars and concrete based on them increases: sulfo and acid resistance increases, water resistance and frost resistance remain at the control level. The total porosity of the stone decreases with increasing age of hardening due to a decrease in the number of macropores, and the more intense, the higher the zeolite content in cements. The introduction of pre-calcined zeolite affects on the process of the mass blowout in cellular aerated concrete. At the same time, there is an increase in the water demand of the mixed binder in proportion to the amount of added additive. The main construction and technical properties of concrete with the replacement of up to 20% of Portland cement with fine-ground zeolitive tuff do not deteriorate compared with the properties of non-admixture concrete. In the case of the use of a complex calcareous -zeolite additive, the properties of concrete are significantly improved [4].

The high activity of zeolitive tuffs in binding lime and gypsum, full compliance with regulatory requirements for active mineral additives confirm the effectiveness of the use of natural zeolites in cements. On the other hand, the presence of channels in the structure of zeolites, as well as the high secondary porosity of tuffs, increases the water demand of zeolite-containing cements. Fine-grained zeolite accelerates the formation of a moment-resisting space frame, the setting time is reduced [5]. The introduction of zeolite in mortar leads to an increase in binding power to the plastered surface and reduces efflorescence [6].

From the point of view of obtaining the greatest mechanical strength, the addition of zeolites in an amount of 10% to cements improves grindability, reduces the true and bulk density of the powders. The effectiveness of the use of zeolites in cements increases when combined with aluminosilicate glasses (ashes, slags). In this case, it is possible in the manufacture of non-autoclaved aerated concrete of grades D 500-D 700 to completely replace the siliciferous component with crushed zeolite-containing tuff [7].

Zeolite can also be used as an additive to concrete, which protects against ionizing radiation and concrete preservatives used in the hardening of radioactive waste. The presence of zeolite in their composition can significantly reduce the leaching of such a long-lived isotope as Sr-137 from the composition. The most effective in this case is zeolite - klinoptilolite [8].

The high content of klinoptilolite and pozzolanic activity characterize zeolites as a material with not only sorption, but also cementing properties. The introduction of ground zeolite in an organic mineral binder in an amount of 20-25% by weight of cement allows to reduce the total cement consumption in the composition, reduces the density of the solution from 1.83 to 1.72 g/cm³ while increasing strength and frost resistance by 25-30% [9].

It has been proved that the introduction of zeolitive tuff increases the rheological characteristics of a mixed binder [10]. Water-cement paste of normal density immediately after preparation has a plastic strength of the order of (0.1-0.15)·10⁵ Pa, at the moment of the time of initial setting 1.5·10⁵ Pa, and at the moment of the time of final setting - 5·10⁵ Pa. The kinetics of the change in the plastic strength of paste of normal density over time on Portland cement M 400 with additives of 20, 30% zeolitive tuff is shown in Figure 1. In the induction period, characterized by intense dispersion of particles, zeolite-containing cements exhibit higher values of plastic strength. Therefore, the introduction of 20% zeolite reduces the time of technological operations from 4.5 to 3 hours, and 30% - to 1.5 hours.
Figure 1. Kinetics of plastic strength maturing of zeolitive Portland cements in paste of normal consistency: 1 - control formulation, 2.3 – with additives of 20% and 30% zeolitive tuff respectively.

Cement is considered resistant to this medium if the resistance coefficient after 6 months ($RC_6$) ≥ 0.9. It is proved that the introduction of 20% zeolitive tuff to the cement increases $RC_6$ to 0.93-0.95 in solutions of gypsum and magnesium sulfate, respectively. Thus, zeolite-containing cements are characterized by greater durability compared to pure clinker [11].

The manifestation of the hydraulic activity of zeolites of the Holinsky deposit was studied [12]. The results obtained indicate that when mixing the ground powder of a zeolite-containing rock with water, the strength of the samples is determined only by the physical drying processes of the finely dispersed material and therefore the zeolite cannot be used as an independent binder. The dispersion of zeolite-containing rocks does not significantly affect on the strength indicators. Cement paste has a normal density of 26-28% on average, and when zeolite is added to the composition this value increases to 38% due to its high water demand. When using binders, the speed of their setting and hardening has a great importance. With the introduction of zeolite in the composition of cement, the setting time is reduced by an average of 1.5 hours, which meets the regulatory requirements.

Considering that the important properties of raw mixes when using them in a dry method for producing clinker are flowability and caking. The caking properties of zeolite-containing raw mixes are less. Thus, the prospects of using zeolites instead of the clay component of clinker can be traced. The best results from a technological and economic point of view are achieved when replacing 30-50% of the clay component with zeolitive tuffs. However, zeolite rocks can completely replace the clay component of clinker provided that iron-containing corrective additives — pyrite cinders — are used in an amount of 0.9–2.3% of the total mass of the raw material mixture, since there are no iron oxides in the chemical composition of zeolites [4].

In addition to free water, the zeolite adsorbs lime from the solution, while the zeolite silica reacts with lime, forming silicates and hydroxides of Ca and Mg, which also become additional crystallization centers, as a result of which the masonry mortar is compacted and hardened [13].

Zeolite can also be used as an additive in building mixtures with bactericidal properties that inhibit the growth of fungi and bacteria [14]. In addition, a known composition with the addition of zeolites of 2.4-6.5%, used for the conservation of dumps of industrial and household waste [15]. The technology of adding zeolite to road concrete mix based on a nano-modified binder based on bitumen was studied [16]. The possibility of using zeolites in road concrete mix is due to the high adsorption ability and activity that manifests itself during mechanical activation, which makes it possible to improve the interaction at the phase boundary “bitumen - rubber crumb”.

Zeolite is also added to the anti-corrosion coatings applied to building materials [17]. At the same time, the zeolite present in the composition, acting as a sorption carrier, retains phosphate on the treated surface. At the same time, it prevents the formation of slippery films on roads and protects building and road materials from the harmful effects of exhaust gases, sorbing them. With the addition of zeolite of more than 10-15%, which based on klinoptilolite and montmorillonite, in the anticorrosion coating based
on polyethylene, it is possible to increase the corrosion resistance of carbon steels in contact with oil products [18].

The use of zeolitic tuffs in pressed products as silicate brick can be considered in the following areas: small dosages (up to 3-5%) in a traditional silicate mass in order to increase the raw and grade strength; complete replacement of quartz sand as part of a calcareous silica binder; and finally, obtaining calcareous-zeolite autoclave-free silicate bricks in steaming chambers.

The grinding time of a zeolite-containing binder is reduced by 30% compared with a calcareous-siliceous binder. When the tuff content in the mixture is up to 2.5%, a certain increase in the strength of autoclaved samples is observed. A further increase in tuff in the mixture reduces the strength of the finished product, probably due to the formation of less durable hydroaluminates, hydrogranates, and aluminum-substituted calcium hydrosilicates [19].

To assess the influence of the type of zeolite on the properties of autoclave-free wall stone, zeolites of the Holinsky deposit were used. The compressive strength of samples from a pure binder (sand is absent) compares well with data on the absorption of lime by zeolites. In accordance with regulatory requirements, an ordinary brick must withstand at least 15, and the front brick must withstand 25 cycles of alternate freezing-thawing without reducing strength by more than 25%. It was established that autoclave-free zeolite-containing bricks withstand 35 cycles of frost resistance, and autoclave ones did not withstand 15 cycles as well [20].

According to various researchers, the thermal conductivity of dry silicate bricks and stones ranges from 0.35 to 0.7 W / (m °K) and is linearly dependent on their average density. It has been proven that the thermal conductivity of zeolite-containing products is lower than that of a full-body silicate brick of 0.7 W / (m°K) and ranges from 0.463–0.684 W / (m°K) depending on the type of aggregate used and the average density of the stone [4].

It was confirmed [19] that in the production of steamed silicate brick on zeolitic tuffs of Holinsky deposit with additives - hardening accelerators (sulfates and chlorides), the compressive strength of an artificial stone on a calcareous-zeolite binder is increased. The optimum can be considered 3% NaCl, 5% CaCl₂ and 5% CaSO₄ · H₂O. At the same time, the maximum strength of cast products immediately after heat and moisture treatment reaches 15-20 MPa, and after 6 months the strength increases by 45%. A linear dependence is observed of increasing up to 80% of the raw strength of bricks with the introduction of 3.5% zeolite in the silicate mass. Increasing the dosages of zeolite into the silicate mass of autoclaveable products is not advisable, as this leads to the formation of aluminum-substituted tobermorite [4].

The most critical phase in the production of ceramics is the sintering process, which determines the quality of the finished product. Zeolite-containing tuffs sinter more easily than clays. However, it must be borne in mind that the zeolite framework does not contain iron oxides, therefore, the higher degree of zeolitization of rock, the higher the temperature is required until the material reaches the pyroplastic state.

Ceramic wall and facing materials on zeolite tuffs are usually obtained by semi-dry pressing with preliminary grinding. Zeolite-containing tuffs have an increased moisture content of the press powder for semi-dry pressing, equal to 13-30%, in contrast to traditional clay materials (8-12%). In addition, products based on them have greater mechanical strength [21]. Firing of highly zeolitized rocks with a content of 60% klinoptilolite, 27% montmorillonite allows obtaining sufficient mechanical strength of products even at 950 °C with a wide sintering interval (up to 150 °C) and high fire shrinkage. Zeolite can be used as an additive in the production of glaze [22].

The known ability of zeolites to swell at high temperatures due to the presence of structural OH-groups makes them suitable for the production of foams. Zeolites swell at high temperatures from 900 °C during prolonged exposure (Figure 2). Further heating of klinoptilolite tuffs to 1000-1200 °C is accompanied by intensive glass formation, with dissolution of the residual crystalline phases in the melt that are completely assimilated at 1300 °C.
Figure 2. Dependence of bubble radiuses in the structure of a klinoptillolite type zeolite on the blowout time.

In the absence of other sources of high-temperature gas formation in the rock, the zeolite can swell only in the presence of divalent cations. The rate of expansion of klinoptilolite and montmorillonite tuffs is presented in Table 1. In addition, the presence of Ca$^{2+}$, Na$^+$ and K$^+$ affects the rate of expansion of zeolites. Cations of Na$^+$ and K$^+$ prevail in the Holinsky and Shivyrtuisky deposits of zeolite-containing tuffs (Eastern Transbaikalia) [23].

| Deposit of East Transbaikalia | Zeolite content, % | Density of samples, g/cm$^3$ | Density of samples after firing at 1200 °C, g / cm$^3$ |
|-------------------------------|-------------------|-----------------------------|---------------------------|
| Holinsky                      | 71                | 2,28                        | 1,4                       |
| Shivyrtskoe                   | 91                | 2,32                        | 1,25                      |

To reduce the density of the foam, it is necessary to use granules of small diameter. The granulometric analysis of zeolite-containing tuffs of the Holinsky deposit showed that the diameter of zeolite granules $d = 2$ mm is more prevalent [24]. Thus, the starting material must be milled. As can be seen from Figure 3, an increase in the fineness of grinding of zeolite less than 0.25 mm does not lead to a decrease in the density of bloating agent.

Figure 3. Dependence of density change of the foam based on klinoptilolite type zeolites depending on the pellet diameter.
3. Conclusion
The main construction and technical properties of concrete with the replacement of up to 20% of Portland cement with fine-ground zeolitic tuff do not deteriorate compared with the properties of non-admixture concrete. In the case of the use of a complex calcareous-zeolite additive, the properties of concrete are significantly improved, and it is possible to use low-quality lime. Adding zeolitic tuffs to cements improves grindability, reduces the true and bulk density of powders. The normal density of the cement paste increases with the amount of tuff added. When zeolite tuffs are introduced into mixed binders, the durability of mortars and concrete based on them increases.

Firing of highly zeolitized rocks allows obtaining sufficient mechanical strength of ceramic products based on them with a wide sintering range and high fire shrinkage. An important factor is the fineness of grinding of zeolite, which affects both the sintering process. The ability of zeolites to bloat during high-temperature heating above 900 °C determines the appropriateness of its use in the production of foams, however, to increase the intensity and lower the temperature of swelling of zeolites, it is necessary to introduce adjunctive additives.

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