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# COMPOSITE BINDERS BASED ON NATURAL RAW MATERIALS AND WASTE PRODUCTS OF THE BAIKAL REGION

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## ABSTRACT

The further development of civilization is decelerated by lack of energy resources. This is especially significant for the construction industry. Considerable energy savings can be achieved by using specially prepared raw materials. Examples of these raw materials are volcanic rocks of the Republic of Buryatia. The modern complex approach to solving problems also requires additional development of resource-saving technologies, which imply the widespread use of associated industrial products, designed to significantly reduce the energy intensity of cement and concrete production without a fundamental change in technology. The paper deals with the use of natural pearlite and fly ash of Gusinoozersk thermal power plant (TPP) to obtain composite binders. It was investigated that natural pearlite and fly ash can be used as part of a multi-component fine cement and low water requirement binder (LWB). Compositions of binders were obtained with super plasticizers based on sulphonated naphthalene-formaldehyde polycondensates - C-3 and based on polycarboxylates - Sika Viscocrete. It is shown that the mechanism of action of these additives on the properties of the composite binders appears in the range up to 15 nm.

**Keywords:** Portland cement, composite binders, pearlite, mechanical activation, multi-component fine cement, super plasticizer, electrostatic, steric effects.

## INTRODUCTION

It is known that cement is the most expensive component of a concrete mixture, the cost of which depends on the cost of the concrete itself. The question of saving cement for the production of concrete is one of the important issues of modern construction. Improving the quality of concrete requires the use of new composite binders (CB), which have improved physical and mechanical characteristics, instead of the ordinary Portland cement (OPC).

Currently, using silicate and aluminosilicate materials, which is rich in the Republic of Buryatia (quartzite, pearlite, zeolite, volcanic slags) on existing production facilities can will organize the production of cement-low and cement-less composite binders and construction materials and products based on them: wall blocks and panels of aerated concrete, effective thermal insulation materials and products with using the activation modification of raw material in efficient mills.

To achieve these purposes tis necessary carrying out fundamental and applied research on complex use of pearlite raw materials for the production composite binders, materials and products based on them. The research carried out to obtain composite binders (CB) using pearlite materials: multi-component fine cement (MCFC), low water requirement binder (LWB), which allows developing recommendations on the efficient use pearlite raw materials (Lesovik, Zhernovoj and Glagolev2009; Sulimenko and Urkhanova 2006; Sulimenko and Urkhanova 2006; Urkhanova, Bardakhanov and Lkhasaranov 2011; Khozin, Khokhryakov, Bituev and Urkhanova 2011).

Recently, in Russia, the environmental aspects of the development of technology and technology have been paid more attention, and therefore actively renewed work related to the utilization of ashes of thermal power plants by the construction industry. In accordance with this, the possibility of obtaining composite binder using fly ash from Gusinoozersk TPP was investigated.

## MATERIALS AND METHODS

In current research to obtain composite binders were used Portland cement CEM I 32, 5, vitrified (VP) and crystallized (CP) pearlite of "Mukhor-Tala" deposit (Republic of Buryatia), super plasticizers C-3® and Sika Viscocrete®. Pearlite applies to magmatic rocks and is one of the volcanic glass. Structural water content in pearlite is 1 ... 6%. In vitreous pearlite content of glass phase was 60-80%, in the crystallized pearlite - 30-50%. The total reserves of pearlites from the Mukhor-Tala volcano are a few tens of millions of cubic meters.

LWB was obtained with consistent milling of pearlite rocks (0-70 weight %), fly ash (0-50 weight %) with OPC and super plasticizer C-3® (1-2 weight %). Specific surface area of LWB is 450-480 $m^2$/kg. From these binders were prepared samples with dimensions 20*20*20 mm. Samples were stored in molds at t = 20-22 °C, relative humidity of 90-95%, and without the molds above the water for a period of 28 days.

Physical and mechanical properties of binders were determined in accordance with Russian national standards GOST 310.2-76, 310.3-76 GOST, GOST 310.4-81.

The structure of LWB was studied using a scanning electron microscope JEOL-JSM-6510LV.

## RESULTS AND DISCUSSIONS

The results of a comprehensive study of pearlites give reason to assume that incorporation into the composite binders of ultrafine and fine-of pearlite lead to the realization of a dense structure and high technical properties of artificial stone (Lesovik, Zhernovoj and

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Glagolev2009; Sulimenko and Urkhanova 2006; Sulimenko and Urkhanova 2006; Urkhanova, Bardakhanov and Lkhasaranov 2011; Khozin, Khokhryakov, Bituev and Urkhanova 2011).

It was investigated the possibility of using vitrified (glass phase content 60-80%) and crystallized (glass phase content - 20-40%) pearlites of Mukhor-Tala deposit to obtain LWB (Table 1).

**Table-1.** Characteristics of LWB with the use pearlite rocks of Mukhor-Tala deposit.

| Indicators | Vitrified pearlite | | | Crystallized pearlite | | | LWB-100 |
|---|---|---|---|---|---|---|---|
| | LWB-30 | LWB-50 | LWB-70 | LWB-30 | LWB-50 | LWB-70 | |
| Standard consistence, % | 27,5 | 25,8 | 25 | 26,6 | 26,2 | 25,8 | 20 |
| Initial setting, min<br>Final setting, min | 170<br>245 | 150<br>220 | 130<br>210 | 135<br>270 | 130<br>255 | 120<br>245 | 120<br>205 |
| Compressive strength, MPa<br>3 days<br>28 days | <br>35<br>57 | <br>50<br>73 | <br>58<br>82 | <br>17<br>28 | <br>29<br>48 | <br>37<br>57 | <br>60<br>90 |

In LWB it is possible to replace 50-70% of OPC on the vitrified pearlite with the achievement of the compressive strength exceeding the strength of the OPC. Compressive strength of LWB with 30-50% of crystallized pearlite is comparable to the compressive strength of OPC. This is confirmed by the known data: the mineral additive is more active, when it has less orderly structure.

As a result of mechanical action on a binary system of "an ionic crystal - a surfactant» irreversible interaction carried out on the donor-acceptor mechanismanion and cation surfactant with a newly formed surface of the crystals due to the presence on it at the time of the formation of specific electron σ- centers of donor and acceptor type . Furthermore, when a mechanical impact the degradation of the surfactant occurs with appearance of free radicals.

The use of fly ash in the composition of composite binders leads to a change in setting time and physical and mechanical parameters (Table-2, Figure-1).

With co-grinding, the highest values were obtained with a fly ash content of 30%. Nevertheless, an increase in ash fly ash content of up to 50% makes it possible to significantly save material costs for obtaining binder and concrete on its basis, and may be expedient with a feasibility study.

Replacement of part of Portland cement to fly ash when co-grinding leads to partial dispersion grains of cement. This contributes to a significant increase in the number of active sites per unit volume of clinker and mineral filler grains of silica in the composite binder. The fly ash acts as an active component, participating in the processes of the structure formation of the mixed binder and thereby increasing the physical and mechanical properties of the binder.

**Table-2.** Characteristics of composite binders using fly ash of Gusinoozersk TPP.

| Показатель | Binder with C-3 | | | Binder with Sika Viscocrete | | | OPC |
|---|---|---|---|---|---|---|---|
| | 10% | 30% | 50% | 10% | 30% | 50% | |
| Standardconsistence, % | 30 | 28 | 27 | 27 | 25 | 24 | 28 |
| Initial setting, min<br>Final setting, min | 130<br>290 | 140<br>300 | 150<br>310 | 140<br>300 | 150<br>320 | 160<br>330 | 90<br>245 |

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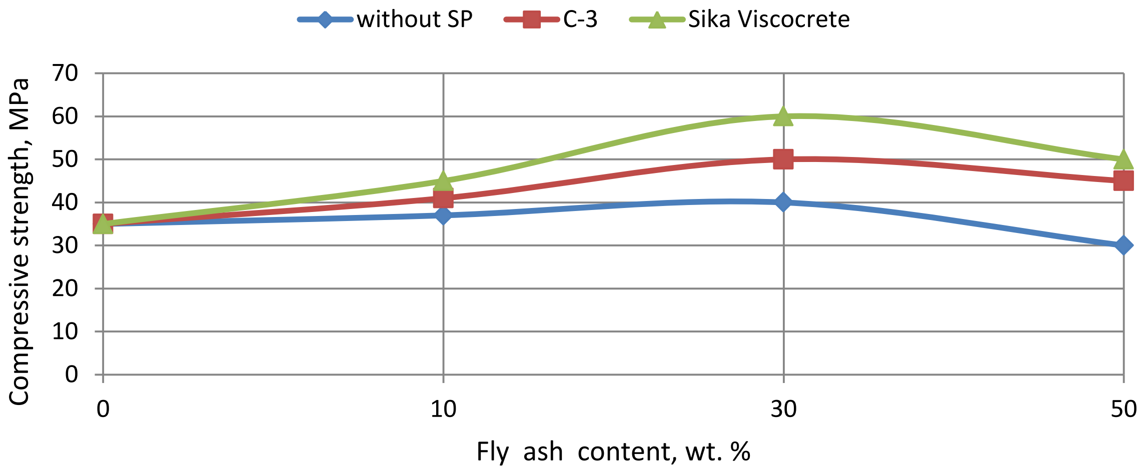
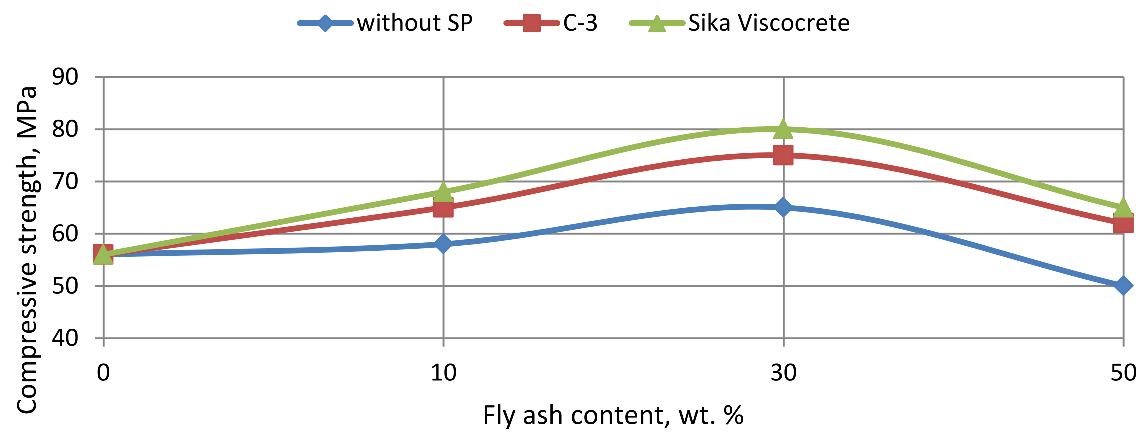



(a)




(b)

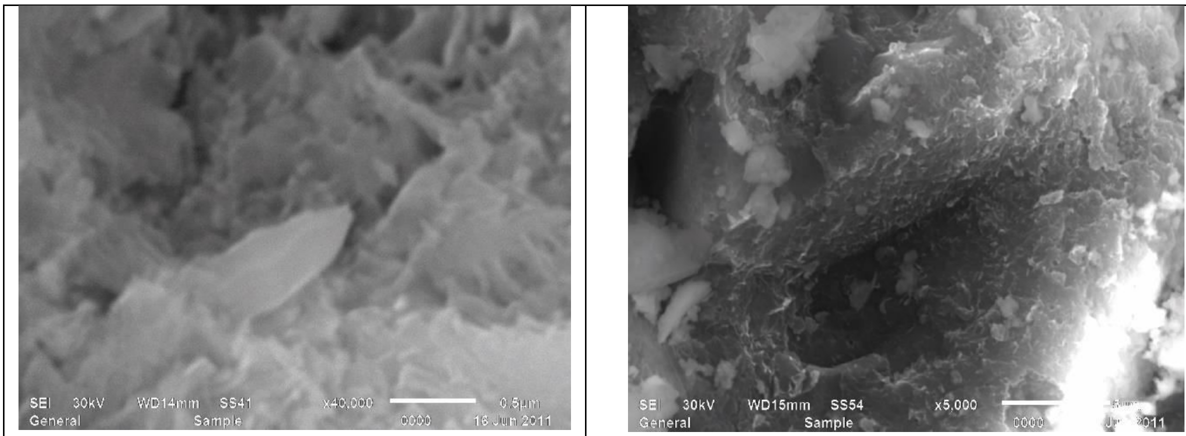
**Figure-1.** Compressive strength of composite binders: a - 3 days, b - 28 days.

The introduction of additives C-3 and Sika Viscocrete improves the compressive strength by 10-15%, while the super plasticizer based on polycarboxylates - Sika Viscocrete showed better results. In addition to the water-reducing effect, which contributes to the increase in physical and mechanical characteristics, superplasticizers significantly affect the processes occurring in the cement system through various effects. Given their different chemical nature, the mechanism of action of the superplasticizer S-3 is based on the electrostatic effect, and Sika Viscocrete - on the steric effect (Ohta, Sugiyama and Tanaka 1997; Uchikawa and Hanehara 1997; Kaprielov, Batrakov and Sheynfeld 1999). The results indicate that the chemical additives superplasticizers significantly influence the properties and structure of the adsorption and diffusion layers of cement particles and are manifested in the range upto 15 nm (Yukhnevskiy 2010).

The phase composition of LWB samples based on pearlite, according to electron microscopy showed significant content of calcium hydrosilicate type CSH (I). Intensity of the peaks attributed to the lime decreases during hydration cement-low binders in comparison with cement. In the cement stone observed crystalline structure with germinating and fastened together needlelike crystals of tobermorite, ettringite, $C_2SH(A)$, and so on. There are pores of different diameters, and inclusions of unreacted amorphous grains of cement and pearlite particles.

In the initial cement stone, after 28 days of hardening, less coagulated gel, needle crystals and hexagonal plates of calcium hydrosilicates, as well as calcium hydrosulfoaluminates on the surface of non-hydrated cement grains, are observed. In LWB all cement particles are surrounded by crystalline hydrates of colloidal size and needle crystals.

The "coagulated gel" formed by hydrosilicate composition formed during further hydration reactions fills the pores in the physical structure of the hardened stone, causing an increase in its density. The fragment of the surface of LWB-70 after 28 days of hardening shows a more dense structure of the stone (Figure-2, b): needle crystals - calcium hydrosilicates and calcium hydrosulfoaluminates are identified on the surface.




(a) (b)

**Figure-2.** Microstructure after 28 days of hardening: a – OPC, b – LWB-70 based on pearlite

The results of electron microscopy of composite binder on the basis of fly ash showed a change in the microstructure of the cement stone at the age of 2, 7 and 28 days of hardening (Figure-3).

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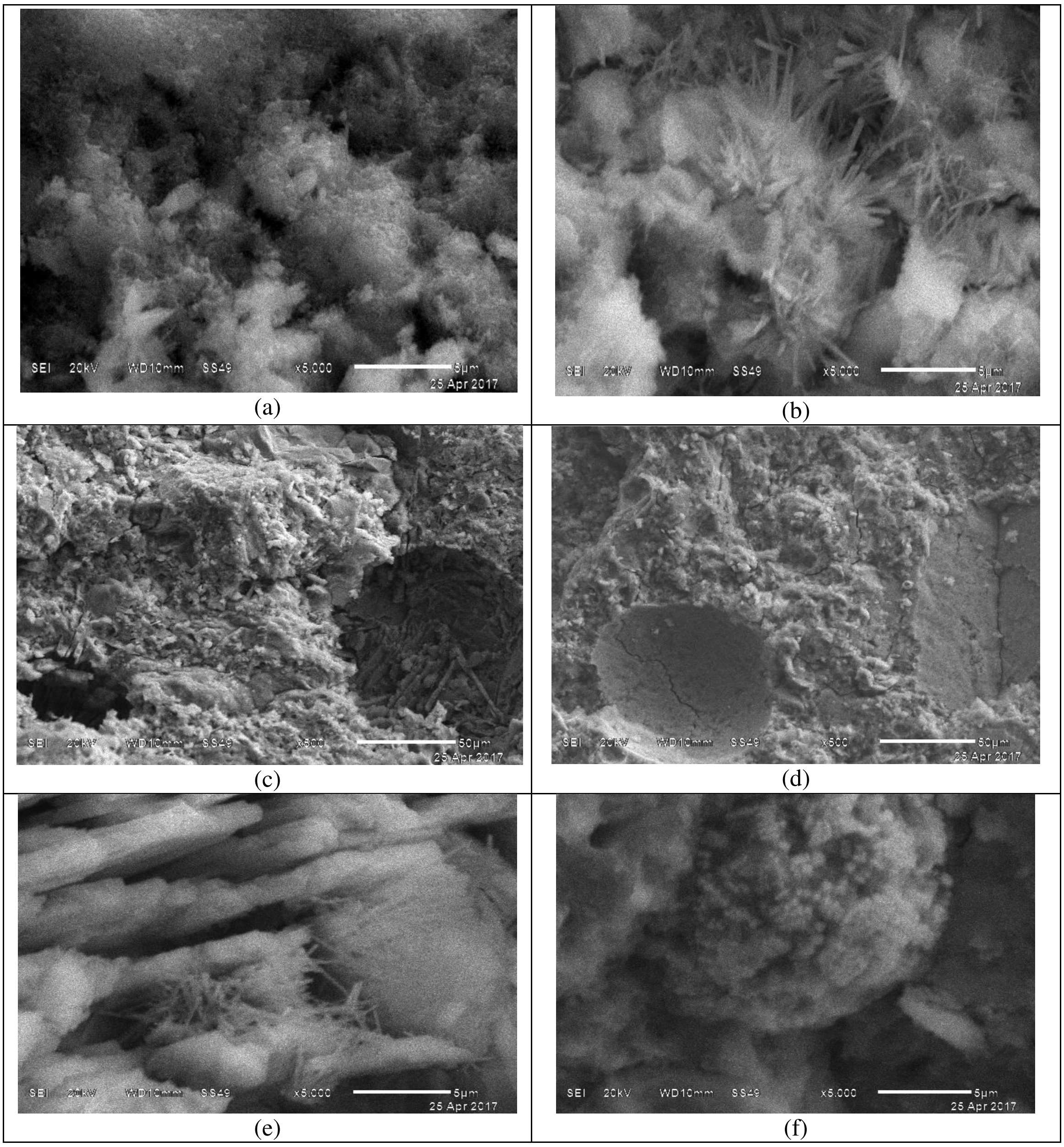


**Figure-3.** Microstructure (x1000) of OPC (a, c, e) and LWB-70 (b, d, f, fly ash - 30%) at the age of hardening 2 (a, b), 7 (c, d) and 28 (e, f) days

The structure of the composite binder stone in the early days of hardening (Figure-3 b) showed the presence of thin needle crystals calcium hydrosilicates. At the age of 28 days hardening (Figure-3 d, e) the structure of the composite binder stone is denser with finely dispersed evenly distributed crystals of calcium hydrosilicates. On the fragment of the composite binder (Figure-3 e), particles of fly ash are densely bonded to the products of hydration of clinker minerals. Thus, the introduction of fly ash promotes the directed formation of a high-strength stone structure from calcium hydrosilicates and a decrease in the content of calcium hydroxide.

## CONCLUSIONS

Introduction of pearlite leads to rapid strength development in the early stages of hardening; so, the strength of 3 daily conglomerates with an additive of ultrafine pearlite from 5 to 15% in comparison with the base cement higher to 58-64%;

Increase in strength is related to the reduction consumption of water and the acceleration of the pozzolanic reaction and formation CSH(I);

When a surfactant is added to the composite binder composition, the W/B ratio is reduced, the rheological properties of the binders are improved, and their strength is increased. The introduction of 0.6% additive Sika ViscoCrete® leads to an increase in the strength of the composite binder by 10% compared to the composite binder with C-3. The addition of Sika ViscoCrete has a greater water-reducing effect than the C-3: a decrease in the W/B ratio to 60% is observed;

The introduction of fly ash promotes the directed formation of a high-strength stone structure from calcium hydrosilicates and a decrease in the content of calcium hydroxide.

Thus, research has shown promising the use pearlite raw materials of "Mukhor-Tala" deposit for the production of composite binder. This will expand resource base for the production of construction materials and products, increase the range of proposed materials, use some capacity of currently idled construction industry enterprises.

In the industrial production of composite binders, it is possible to use efficient grinding aggregates, for example, a centrifugal elliptic mill, a ball planetary mill where, at optimal energy inputs, sufficient energy is transferred to the materials to be processed to increase their reactivity.

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