Composite binders for concrete with reduced permeability

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Abstract. Composite binder consisting of cement (55%), acid fly ash (40%) and limestone (5%) has been designed. It is obtained by co-milling to a specific surface of 550 kg/m², it has an activity of 77.3 MPa and can produce a more dense cement stone structure. Integrated study revealed that the concrete on the composite binder basis provides an effective diffusion coefficient $D$. So we can conclude that the concrete layer protects buildings from toxic effects of expanded polystyrene. Low water absorption of the material (2.5% by weight) is due to the structure of its cement stone pore space. Besides lime powder prevents the penetration of moisture, reduces water saturation of the coverage that has a positive effect on useful life period. It also explains rather low water vapor permeability of the material – 0.021 mg/(m²-hour-Pa).

1. Introduction.
In modern construction concrete and reinforced concrete are ones of the most commonly used construction materials, foam materials are most commonly used heat insulators. At the same time, it is well known that the materials from foamed polymers have ecological and fire hazard, and, in the absence of adequate protection, also have short time of exploitation.

It is obvious, that influence of interior and exterior climatic conditions on polystyrene foam should be avoided. This problem can be solved by the internal arrangement of insulation between two structural concrete (reinforced concrete) layers [1,2].

However, concrete is cellular material and the evaporation of styrene from polystyrene occurs continuously, and when the temperature rises, this process significantly accelerates. So, only the infusion of special admixtures, which treat concrete pores and strengthen its structure, is able to neutralize the environmental and fire hazard of polystyrene, as well as to increase its durability by preventing the penetration of atmospheric moisture (which is very important for the monsoon climate of the south of the Russian Far East).

Thus, the development of high gas, water and steam impermeability concrete, able to protect both cellular polystyrene from moisture, and a building from styrene vapors is an urgent task.

2. Design of composite binding material
To achieve this goal the composite binders obtained by co-grinding cement, hyperplasticizer, ash and limestone in the vario-planetary mill have been designed.

Fly ash of the Primorye Territory's largest thermal power plants: Vladivostok TPP and Artem TPP, Primorye SRPS and Partisansk SRPS was used as a component of the composite binder. An important factor is the capacity of dry separate ash extraction that is currently implemented at these power plants. The use of man-made products in the manufacture of building materials contributes to the
solution of the following main objectives: saving energy and raw resources; waste management; improvement of the environmental situation in the regions. It should be noted that revenues in the seaside ash dumps are one of the largest in the Far Eastern Federal District. In particular, the annual flow of ash in the ash dumps of the Primorsky Territory is from 2.5 to 3.0 mn tons per year, Khabarovsk Territory is up to 1.0 mn tons. Thermal power plants fly ash is an effective material for the production of fine and active mineral admixtures. These waste substances do not require special preparation when infused into the concrete.

Mineral powder from limestone Dinnogorsk deposit (Primorye) of "Spasskcement" production (MP-1) was employed.

The obtained composite powder had a specific surface area equal to 600 m$^2$/kg (determinations were performed on surface meter PSH-11), particle size is 0.15-500 micron, the average particle diameter is shifted to 0.65-11.2 mm, density is 930 kg/m$^3$ (Figure 1).

Co-grinding of cement with ash and limestone can increase the activity of binding to 70.2 MPa. The increase in strength is due to the improvement of co-grinding of cement stone structure.

This is due to the fact that the floured active mineral components that contribute to an earlier binding of portlandite, intensify the process of hydration of clinker minerals [3,4].

At the same time, the larger particles act as nucleation sites and act as microfiller reducing shrinkage deformation and improving performance of the composite. A characteristic feature of the structure of cement stone with floured admixtures is substantially smaller number of microcracks.

The structure of the cement stone on the composite binder is denser than conventional Portland cement. It is a very dense packing of the grains in the total mass of new formations. Co-grinding of components leads not only to increase of the ultimate compressive strength, but also increases the rate of maturing of the samples with admixtures.

In order to determine the optimum particle size intergrinding of cement with hyperplastisizer, ash and limestone (in a ratio of composition number 7) to different specific surface: 500, 550, 600, 700, 800, 900 m$^2$/kg was produced.

The results of determination of compressive strength of cement samples are shown in Table. 1.

| Table 1. The results of determination of compressive strength (MPa) cement samples |
| Age of sample,  | The specific surface area of the composite binder, m$^2$/kg |
|-----------------|----------------------------------------------------------|

Figure 1. A general view of the composite binder; 200x magnification (a) and 400 x magnification (b)
The optimal activity of the binder is 550-600 m$^2$/kg. Increased activity in excess of these values has a negative effect on the structure. Using a binder with increased activity significantly speeds up the process of setting - setting of the mixture ends after 35-40 min., while the developing temperature at 95-97°C. Fast setting of airbrick prevents the formation of evenly distributed spherical particles in the macrostructure of cement stone. Electron microscopy revealed the presence of heterogeneity macrostructure and irregularly shaped cells [5,6].

The results to determine the sponginess of the samples of the cement stone are given in Table 2. It follows that at the insignificant (less than 2%) difference in total sponginess samples differ by the distribution pattern of different diameter pores.

**Table 2. Research porosity of the cement stone**

| Composition | technological (macroscopic level) | capillary (microscopic level / submicroscopic level) | gel (supramolecular level) | general |
|-------------|----------------------------------|-----------------------------------------------|------------------------|---------|
| 1           | 2.4                              | 4.6/8.3                                       | 18.2                   | 33.5    |
| 2           | 3.0                              | 1.7/7.5                                       | 21.6                   | 33.4    |
| 3           | 4.2                              | 1.1/5.0                                       | 23.5                   | 33.8    |
| 4           | 4.0                              | 1.9/4.3                                       | 24.4                   | 34.6    |
| 5           | 4.0                              | 1.7/7.5                                       | 21.6                   | 34.4    |
| 6           | 4.2                              | 1.1/6.0                                       | 23.5                   | 34.8    |
| 7           | 3.0                              | 1.9/4.8                                       | 24.4                   | 34.1    |

Analysis of the microstructure (Figure 2) showed that the cement stone with optimal dosage of components differs by denser matrix consisting of low basic calcium hydrosilicates, while the cement stone without any admixtures (Figure 2a) contains a highly basic calcium hydrosilicates and hexagonal plates of portlandite.

The highest technical effect is achieved due to the synergistic action of man-made pozzolanic admixtures (fly ash) and natural materials of sedimentary origin (limestone) when the content of cement - 55 wt.%, limestone - 5 wt.% and the ash - 40 wt.%. Such composites have a compressive strength of up to 57.3 MPa when the strength of the control of the composition (without any admixtures) is 50.5 MPa.

Earlier, it was revealed that the infusion of mineral supplements in the initial binding activates the hydration process. In composite binders hydration products redistribution of crystalline phases of both non-hydrated clinker minerals ($S_3S$, $C_2S$, $C_4AF$), quartz and calcite and hydration products (CH – portlandite, $3S_3A$:$3CaSO_4$:$32H_2O$ - ettringite) occurs [7,8].

Hydrate structure of the composite binder is represented by two types - the primary and secondary structures. The primary structure is represented by amorphous interporous space formed by the solution mechanism, wherein the composition of the products in the pore space depends on the chemistry of the large particles which surround a pore.

The results show a clear synergistic effect of components of the material composition of binder on the mineralogical composition of the hydration products and the rate of interaction of clinker minerals with water, on the morphology of hydration products and micro-porosity of the stone.
Replacement of the cement by different admixtures of natural and anthropogenic origin accelerates hydration and leads to formation of new products that enhance the density of the cement stone, and as a result, increase the strength and impermeability [9,10].

Realization of the potential capabilities of fiber-reinforced concrete is only possible when the optimum structure of the material is created. The formation of the structure is determined by the following main parameters: the type and quality of raw materials; technology of preparation of concrete mixtures; the quantitative relationship between the fiber-reinforced concrete components of the mixture.

As a result of tests on the device "Agama-2M" air permeability of concrete parameter $a_c$ was found to be $0.0253 \text{ cm}^3 / \text{s}$. In Table. 7 of GOST 12730.5 corresponding mark on the permeability is W14 (Table. 3).

![Figure 2](image)

**Figure 2.** The micrographs neoplasms: a - cement stone without admixtures; b - cement stone on the basis of the composite binder

**Table 3.** The permeability of fine concrete depending on the composition of the binder

| № Composition | Binder, kg | Material consumption per 1 m$^3$ | Parameter air permeability of concrete $a_c$, cm$^3$/s | Mark on the water permeability $W$ |
|---------------|------------|-------------------------------|------------------------------------------------------|----------------------------------|
| 1             | 415        | -                             | 0.0565                                               | W10                              |
| 2             | 210        | 178 27                        | 0.0253                                               | W14                              |
| 3             | 200        | 186 29                        | 0.0289                                               | W14                              |
| 4             | 190        | 194 31                        | 0.0402                                               | W12                              |
| 5             | 180        | 202 33                        | 0.0465                                               | W12                              |
| 6             | 170        | 210 35                        | 0.0423                                               | W12                              |

As test results show admixtures of fly ash and limestone at all dosages reduce water permeability of concrete. Thus, a clear link between the properties of concrete and structural features of the cement
stone is revealed. Increase in the number of low basis hydrosilicates of calcium and increased gel and less capillary sponginess especially at the submicroscopic level determine the growth of the strength and reduction of the concrete permeability [11,12].

3. Results.
The results of the experiment on water vapor permeability for the created concrete are shown in Table 4. Obtained results show the better characteristics compared to the standard concrete (0.03 mg/(m-h Pa)).

**Table 4.** The vapor permeability of fine concrete depending on the composition of the binder

| № Composition | Binder, kg | Ash, kg | Screenings crushing of granite, kg | Sand, kg | Water, l | Slump | Vapor permeability of concrete, mg/(m-h Pa) |
|---------------|------------|---------|----------------------------------|---------|----------|-------|--------------------------------------------|
|               | Cement     | Limestone | Hyperplasticizer | 10-12 |          |       |                                           |
| 1             | 415        | -        | -                                | 1000    | 762      | 220   | 0.032                                      |
| 2             | 210        | 178      | 27                               | 0.022   | 0.021    |       |
| 3             | 200        | 186      | 29                               | 0.026   | 0.025    |       |
| 4             | 190        | 194      | 31                               | 0.027   | 0.026    |       |
| 5             | 180        | 202      | 33                               | 0.030   | 0.029    |       |
| 6             | 170        | 210      | 35                               | 0.032   | 0.030    |       |

Results of water absorption on the basis of fiber-reinforced concrete developed on designed composite binder are shown in Table 5.

**Table 5.** The vapor permeability of fine concrete depending on the composition of the binder

| № Composition | Binder, kg | Ash, kg | Screenings crushing of granite, kg | Sand, kg | Water, l | Slump | Water absorption |
|---------------|------------|---------|----------------------------------|---------|----------|-------|-----------------|
|               | Cement     | Limestone | Hyperplasticizer | 10-12 |          |       | % by weight kg/m³ |
| 1             | 415        | -        | -                                | 1000    | 762      | 220   | 6.1             |
| 2             | 210        | 178      | 27                               | 60.75   | 2.5      |       |
| 3             | 200        | 186      | 29                               | 63.18   | 2.6      |       |
| 4             | 190        | 194      | 31                               | 77.76   | 3.2      |       |
| 5             | 180        | 202      | 33                               | 109.35  | 4.5      |       |
| 6             | 170        | 210      | 35                               | 123.93  | 5.1      |       |

Rather low water absorption of the material is due to the structural features of its pore space described previously.
Besides lime powder prevents the penetration of moisture, reduces water saturation coverage that has a positive effect on service life. This also explains the rather low water vapor permeability value of the material.

As a result of an experiment on evaluating the diffusion constant, the average value of the thickness of the concrete neutralized layer $X$ is set, see the following formula:

$$X = \frac{\sum_{i=1}^{n} X_i}{n}$$

where $n = 10$- number of measurements (Table. 6).

The standard deviation:

$$S = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X)^2}{n-1}}$$

The calculation is performed with the reliability of 95% and the probability of the risk $2\beta = 0.05$.

Specification limits are determined by the formulas:

$$t_1 = X - L \cdot S$$
$$t_2 = X + L \cdot S$$

Table 6. The average value of the thickness of the concrete neutralized layer $X$, cm

| № sample | $X_i$ | $X_i \cdot X$ | $(X_i - X)^2$ |
|----------|------|----------------|--------------|
| 1        | 7    | -1.4           | 1.96         |
| 2        | 6.5  | -1.9           | 3.61         |
| 3        | 11   | 2.6            | 6.76         |
| 4        | 10.5 | 2.1            | 4.41         |
| 5        | 7.5  | 0.9            | 0.81         |
| 6        | 8.5  | 0.1            | 0.01         |
| 7        | 10   | 1.6            | 2.56         |
| 8        | 9.5  | 1.1            | 1.21         |
| 9        | 7    | -1.4           | 1.96         |
| 10       | 6.5  | -1.9           | 3.61         |
| All      | 84   |                | 26.9         |

$$X = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{84}{10} = 8.4$$
$$S = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X)^2}{n-1}} = \sqrt{\frac{26.9}{10-1}} = 1.73$$

$$t_1 = X - L \cdot S = 8.4 - 3.39 \cdot 1.73 = 2.54 \text{ mm}$$
$$t_2 = X + L \cdot S = 8.4 + 3.39 \cdot 1.73 = 14.26 \text{ mm}$$

Diffusion permeability of concrete is calculated by the upper boundary of the tolerance, i. e, the depth of carbonation takes equal 14.3 mm.

According to the results of chemical analysis of the concrete reaction vessel of concrete $m_0$ in relative terms is calculated by the formula:

$$m_0 = 0.4C\rho f = 0.4 \cdot 210 \cdot 0.6 \cdot 0.6 = 30.24$$

where $C$ - cement content, g in 1 cm$^3$ of concrete; $\rho$ - the number of basic oxides in the cement based on CaO in weight relative values; $f$ - a degree of neutralization of concrete, equal to the ratio of quantity of basic oxides, which undergo reaction with carbon dioxide to the total amount of cement (average $f = 0.6$).
The effective diffusion coefficient of carbon dioxide in concrete \( D' \), cm² / s, is calculated from the formula:

\[
D' = \frac{m_0 X^2}{2C \tau} = \frac{30.24 \cdot 0.84^2}{2 \cdot 0.1 \cdot 14 \cdot 24 \cdot 3600} = 1.34 \cdot 10^{-4} \text{ cm}^2/\text{s}
\]

The result revealed that the developed concrete provides an effective diffusion coefficient \( D' \), so we can conclude that the concrete layer protects buildings from toxic effects of styrofoam.

4. Conclusion
Developed composite binder consisting of cement (55%), acidic fly ash (40%) and limestone (5%) has been designed. It is obtained by co-milling to a specific surface of 550 kg / m² and it has an activity to 77.3 MPa and it can produce a more dense cement stone structure.

It was found that the combined effect of mechanical and chemical activation (the presence of limestone particles) increases the pozzolanic activity of acidic ashes. It has a catalytic effect on the reaction activity of the surface of ash and sand during mechanical conversion in vario planetary mill. Furthermore, the infusion of limestone increases the alkalinity of the concrete, which leads to the formation of more hydration products of cement per unit of time.

It was found that the addition of fly ash and limestone at all dosages reduces water permeability of concrete. Thus, it revealed a clear link between the properties of concrete and structural features of the cement stone. Increase in the number of low basis hydrosilicates of calcium and increased gel and less capillary sponginess especially at the submicroscopic level determine the growth of the strength and reduction of the concrete permeability.

Integrated study revealed that the concrete, developed on designed composite binder provides an effective diffusion coefficient \( D' \). So we can conclude that the concrete layer protects buildings from toxic effects of expanded polystyrene. Rather low water absorption of the material (2.5% by weight) is due to structural features of its pore space of cement stone. Besides lime powder prevents from penetration of moisture, reduces water saturation coverage that has a positive effect on service life. This also explains the rather low water vapor permeability of the material values - 0.021 mg / (m-h-Pa).

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