PREVENTION OF LOSS OF CEMENT ACTIVITY DURING TRANSPORTATION AND STORAGE

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Abstract
In this article discusses, the addition of 0.2% naphthalene soap or 0.1% oleic acid as a hydrophobizing agent to maintain the properties of cement during transportation and storage, and the production of commercially produced hydrophobized cements is studied.

Keywords: "M400" and "M500" brand cements, hydrophobic, naphthalene soap, oleic acid, clinker, moisture, water vapor absorption, sorption, rosin soap.

Introduction

It is known that cements with high quality characteristics lose activity during storage. For example, cements of the M400 and M500 grades lose a third of their activity after 6 months of storage. The loss of activity is more noticeable during storage of finely ground and fast-hardening cements with high grade properties. Therefore, their high factory characteristics are not fully realized in practice.

To preserve the properties of cement during storage and transportation, it is carefully protected from carbon dioxide and moisture present in the atmosphere. This is facilitated by packaging in special multi-layer bags impregnated with bitumen, metal barrels, special silos and containers, etc.

There are other methods. For example, at a large construction project in the Panama Canal zone, where the rainy season lasts 8 months and the relative humidity is often 100%, the inner surface of the silos is covered with special aluminum paint to reduce condensation. . The silo seams are sealed with bitumen compounds. For ventilation and movement of cement, the entrained air must be dried.

A less labor-intensive and cost-effective way to prevent a decrease in cement activity during storage and transportation is its hydrophobization.

In particular, cement is transported to the regions in an open way. During the pouring process, the water accumulated on the surface of the cement due to precipitation was removed using a pump, and the cement was sent for use as intended. There are also known cases when barges that failed to deliver cement to their destination on time stopped for the winter. In the spring, only minor damage to the top layer of cement was noted.

When simultaneously grinding cement with a waterproofing additive (regrinding), a coating of oriented large asymmetric molecules of the waterproofing additive is formed on the cement grains. This was determined in the laboratory by determining the wetting angle.

This layer is very small and at best equals the thickness of an additional waterproof molecule. For example, if the size of oleic acid molecules is 1.1 x 10^{-7} cm, and the diameter of cement grains is 5 x 10^{-3} cm, the ratio of the thickness of the hydrophobic film to the size of the cement grain will be 0.2 x 10^{-4} cm, which is approximately equal to the number of times less than the height of a 25-story building.

The hydrophobic coating formed on the cement grains prevents water from getting into them. But water vapor and carbon dioxide, even in small quantities, freely pass through this coating. Thus, when storing hydrophobized cements in the open air for 3-6 months, saturated with water vapor, the increase in mass is about 2-3%, and for ordinary cements - up to 20%. The increase in the presence of carbon dioxide in hydrophobic cement is calculated in hundredths or tenths of a percent, while for ordinary cements this figure is 8-12 times higher. A more detailed study of these capabilities of hydrophobic cement and the corresponding calculations confirmed the conclusion that the protective coating on the cement grains has not a solid, but a solid ("mesh") structure.

An analog of such a coating can be a fabric mesh coated with paraffin. Vapors and carbon dioxide freely pass through the holes of such a mesh, and the liquid phase of water stops, since the wetting angle at a right angle is greater than 90°, that is, the fabric coated with paraffin is not wetted by water. t flame An analogy can be made with oil that protects the feathers of waterfowl from getting wet.

The property of substances to absorb moisture from the atmosphere is called hygroscopicity. But the relationship of this term to cement is used only conditionally. Hygroscopicity in its simplest form is the absorption of moisture by the body. This process is reversed - when the vapor pressure decreases, previously absorbed moisture can evaporate. Due to the hygroscopicity of cement, the absorbed moisture enters into a chemical reaction with the cement clinker, the cement particles are irreversibly changed and cannot return to normal conditions.

The absorption of steam by cement is a complex process. In this process, not only pure steam is absorbed, but also capillary condensate is formed and a chemical reaction with cement occurs. At the same time, as a result of the decomposition of cement under the influence of water and the addition of water molecules to the ions of clinker minerals, new products are obtained with a hygroscopicity index different from that of unreacted cement particles.

The procedure for absorbing water vapor from the atmosphere and interacting with cement particles is divided into three successive stages.

The first stage is the absorption of water vapor by water-soluble components of cement. This is accompanied by the formation of a layer of concentrated aqueous solution on the surface of the particles. The vapor pressure of this solution is lower than the vapor pressure of water in the atmosphere and air in the spaces between the cement particles. At this stage, the characteristics of the hygroscopic absorption of water vapor are mainly influenced by the following conditions: relative air humidity, air temperature, cement temperature, specific surface area of cement, chemical and mineralogical composition, diffusion rate of fixed vapors. Air films surrounding the cement grains and, consequently, the degree of compaction of the cement powder and the

Volume 2, Issue 12, December - 2024 **ISSN(E):** 2938-3773

presence of convection currents of moist air. The initial degree of dryness of the cement powder is also important, since during the drying process the adsorbed vapors and gases disappear and the cement becomes hydrophilic.

The second stage is capillary condensation, i.e. the gradual transformation of steam into liquid in the capillaries. When the liquid phase begins to form in the pores, menisci are formed in them. In this case, the pore walls are moistened and the vapor pressure above the menisci is lower than above the surface. If the walls are hydrophobic, then the inverse relationship is observed. In cement capillaries, the concavity of the liquid meniscus (if it is ordinary cement) or convexity (if it is hydrophobized cement) promotes or hinders vapor condensation. As the vapor pressure increases, condensation occurs in increasingly larger pores. The maximum sorption value, corresponding to saturated steam, is characterized by filling the entire pore volume with liquid.

The third stage is the chemical interaction of the absorbed moisture and cement. This process takes a long time and can continue until the clinker in the cement is completely consumed.

All three phases can intersect. Capillary condensation of steam is directly related to its absorption, and the reaction rates of clinker with water in cement depend on the degree of moisture condensation. Experimental calculations of water vapor absorption in cements at 100% and 75% relative humidity are presented in the following tables (see Table 1 and Table 2, respectively).

Table 1 – Water vapor absorption by cements at 100% humidity

Type of cement tested	Sorption of water vapor by different grades of cement at 100% humidity, over time (day).															
	1	2	3	6	10	13	18	23	30	40	50	65	80	90	100	200
Normal (control)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
same but hydrophobic 0.2% rosin soap	8,2	8,6	10,4	11,3	14,8	16,2	16,3	16,3	15,5	16,7	18,4	22,6	22,3	21,4	25,4	40,5
the same, but hydrophobic 0.2% soaponaft	8,2	11,6	15,8	14,3	16,6	26,4	34,9	34,2	33,8	35,4	38,7	38,9	41,1	40,2	38,3	42,5
same but hydrophobic 0.2% oleic acid	8,2	7,4	8,3	9,2	13,3	16,9	18,2	19,2	20,8	22,7	23,7	25,9	24,9	27,4	29,2	32,5

Note: The weight gain of the control cement samples is taken as 100%.

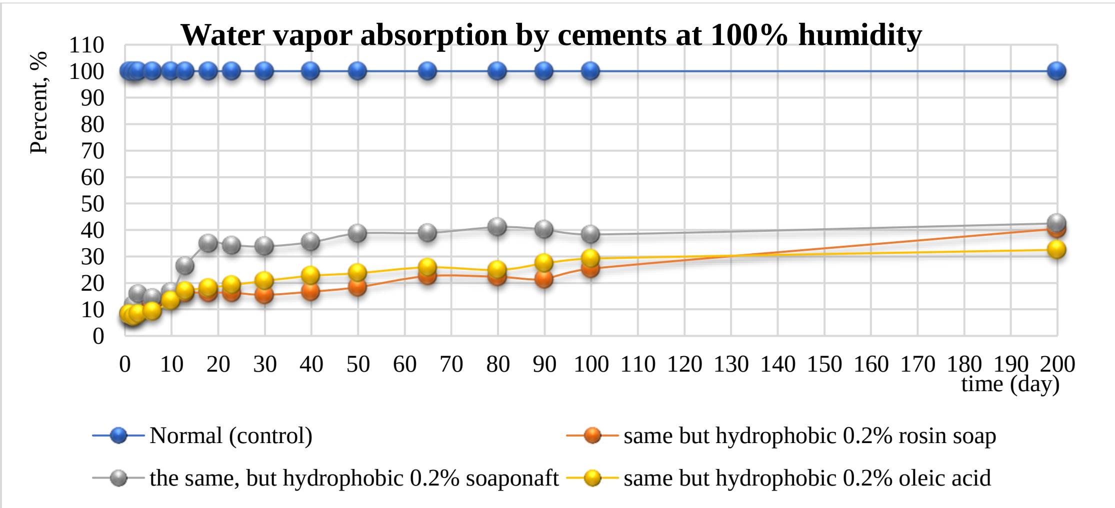
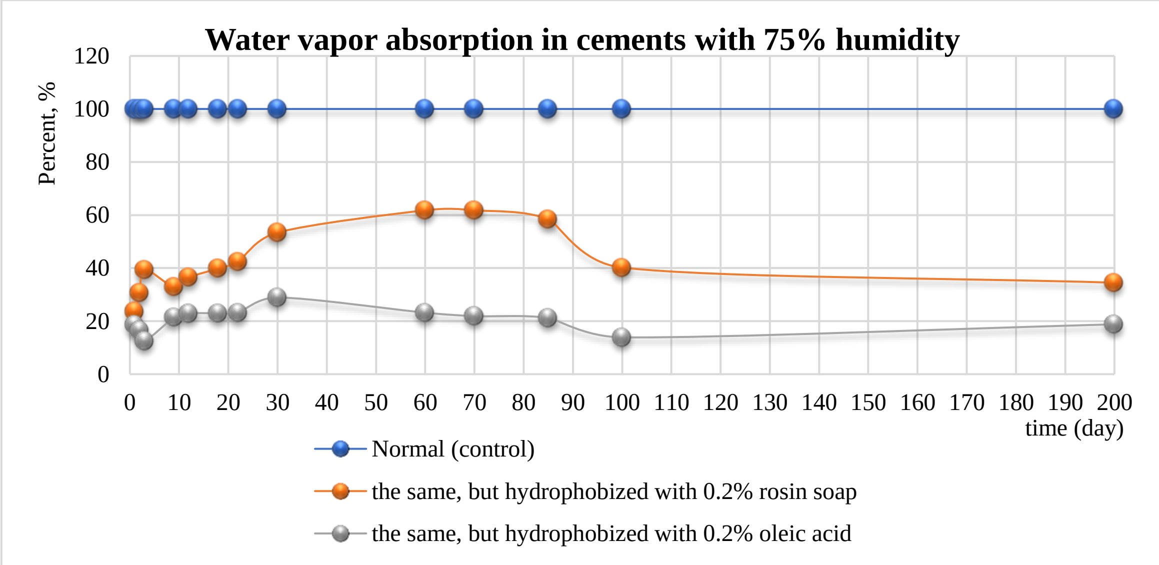


Table 2 – Water vapor absorption in cements with 75% humidity

Type of cement tested	Sorption of water vapor by different types of cement at 75% humidity, over time (days)												
	1	2	3	9	12	18	22	30	60	70	85	100	200
Normal (control)	100	100	100	100	100	100	100	100	100	100	100	100	100
the same, but hydrophobized with 0.2% rosin soap	23,6	30,7	39,4	32,9	36,5	39,9	42,5	53,4	61,8	61,8	58,4	40,2	34,5
the same, but hydrophobized with 0.2% oleic acid	18,7	16,5	12,5	21,4	22,9	23	23,2	28,9	23,2	21,9	21,2	13,9	18,8

Note. The weight gain of the control cement samples is taken as 100%.



It is also necessary to pay attention to and compare the laboratory calculations for the best doses of waterproofing additives of three classes:

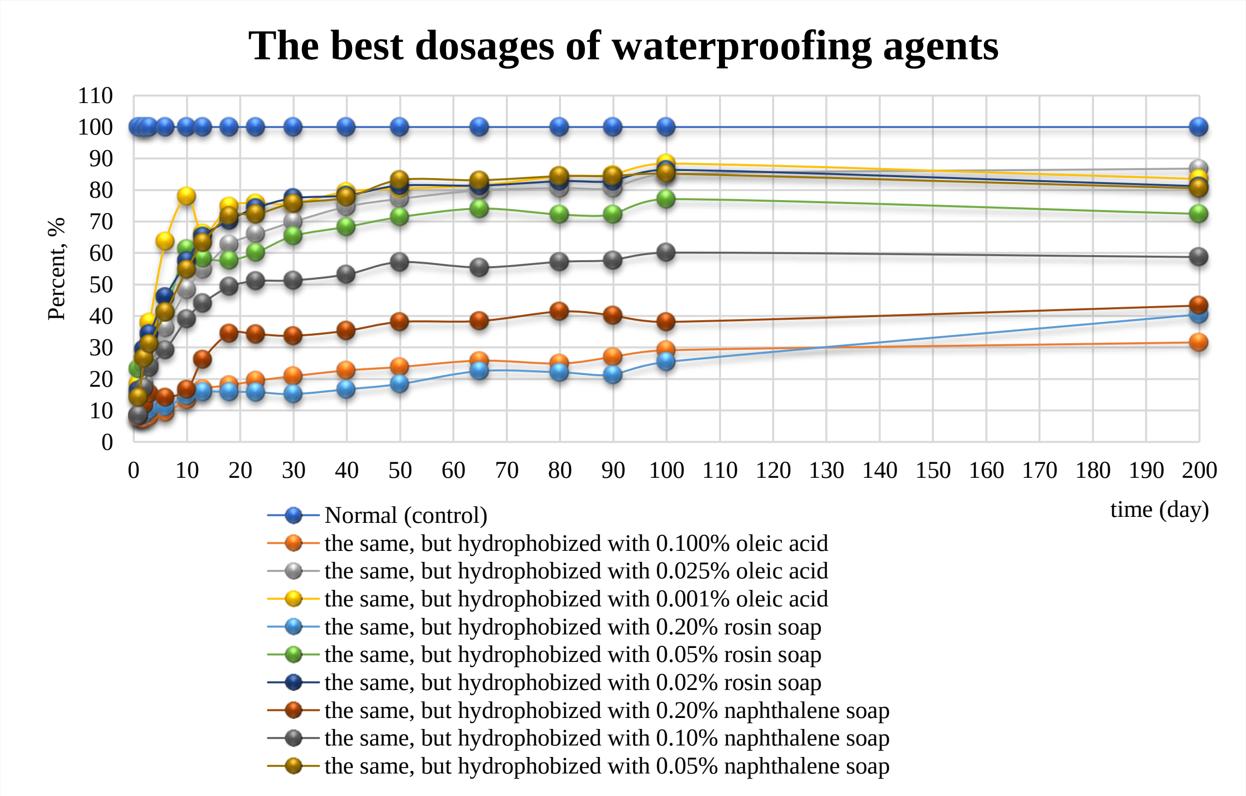
- fatty acids (oleic acid);
- resin acids (rosin soap);
- naphthenic acids (naphthalene soap)

The results of the experiment are presented in the following table (see Table 3).

Table 3 - The best dosages of waterproofing agents

Type of cement tested	Sorbtsiya vodianogo para v zavisimosti ot dozirovki i vida hydrophobisiruyushchih dovavok pri lajnosti 75%, cherez vremya (day)														
	1	2	3	6	10	13	18	23	30	40	50	65	80	90	100	200
Normal (control)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
the same, but hydrophobized with 0.100% oleic acid	8,2	7,4	8,2	9,4	13,3	16,8	18	19,4	20,9	22,7	23,8	25,8	24,9	27	29,1	31,6
the same, but hydrophobized with 0.025% oleic acid	14,7	18,5	24,9	36,2	48,3	54,7	62,7	66	69,9	74,7	77,2	79,9	80,6	80,6	85	86,8
the same, but hydrophobized with 0.001% oleic acid	18,3	26,6	37,9	63,7	78	66,1	74,8	75,8	75,7	79,5	80,4	81,5	84,3	84,8	88,4	83,5
the same, but hydrophobized with 0.20% rosin soap	8,2	8,7	10,2	11,1	14,6	15,9	15,9	15,8	15,2	16,7	18,4	22,5	22,1	21,3	25,4	40,5
the same, but hydrophobized with 0.05% rosin soap	23,2	24,3	31,4	41,3	61,4	58,3	57,7	60,1	65,4	68,3	71,4	74,1	72,2	72,2	77,1	72,4
the same, but hydrophobized with 0.02% rosin soap	16,3	29,4	34,3	46,1	57,4	65,2	70,4	74,3	77,4	78,3	81,4	81,4	82,8	82,8	86,4	81,2
the same, but hydrophobized with 0.20% naphthalene soap	8,2	11,7	15,4	14,2	16,6	26,2	34,4	34,2	33,7	35,3	38,1	38,4	41,4	40,2	38,1	43,3
the same, but hydrophobized with 0.10% naphthalene soap	8,6	17,2	23,6	29,2	39,1	44,1	49,3	51,1	51,3	53,2	57,1	55,4	57,2	57,7	60,1	58,7
the same, but hydrophobized with 0.05% naphthalene soap	14,2	26,6	31,1	41,2	54,7	63,3	71,8	72,3	75,8	77,6	83,2	83,1	84,4	84,4	85,2	80,5

Note. The weight gain of the control cement samples is taken as 100%.



After the cement has been hydrophobized, its ability to absorb moisture from the atmosphere is significantly reduced. The special arrangement of asymmetric polar molecules of hydrophobic surfactants, with hydrocarbon radicals facing outward, promotes the formation of hydrophobic coatings on the cement particles. In this regard, hydrophobized cements usually do not sinter during long-term storage and transportation.

For example, hydrophobized cements of industrial production containing 0.2% naphthalene soap or 0.1% oleic acid as a hydrophobizing agent were stored in sealed paper bags in refrigerated chambers with wooden floors. The bags were stacked in two rows high, with no gaps between the rows. In addition to the four-layer bags that are usually used in such cases, "double" packaging was also used, i.e. the paper bags were placed one inside the other. A year later, during the report on the condition of the cements, control samples of plain cement were noted in both packaging methods (both double packaging failed to protect the cement from caking). The hydrophobized cement retained its fluidity in both types of packaging, and no lumps were found.

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