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INFLUENCE OF INORGANIC ADDITIVES ON THE WATER RESISTANCE OF A MAGNESIUM BINDER

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Magnesium-based binders are widely used worldwide. Magnesia cements are employed in the production of xylolite, fibrolite, various structural elements, artificial marble, bases for finished floors, plasters, heat-insulating foamed and gas concretes, refractory ramming masses, grindstones, and more. They are characterized by several advantageous properties, including high mechanical strength at the initial stages of hardening; increased flexural strength compared to other types of binders; a compact structure of the hardened cement combined with low true density; low thermal conductivity; high adhesion strength to aggregates in magnesia concretes and mortars; and relatively high resistance to corrosive media. Furthermore, the relatively low energy costs for firing (unlike lime and Portland cement production) make the use of magnesite and dolomite particularly appealing. A distinguishing feature of magnesia binders compared to traditional ones is the use of magnesium chloride solutions (instead of water) in combination with caustic magnesite or dolomite. This study investigates inorganic additives capable of stabilizing the phase composition of hardening magnesium cements through the incorporation of mineral bischofite brine into the magnesium mixture. The research identifies specific inorganic additives that enhance frost and water resistance, thereby broadening the application range of magnesium-based binders formulated with bischofite mineral brine.

Keywords: magnesium-based binder, mineral bischofite brine, hydration products, inorganic additive, water resistance.

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Introduction

Magnesia binders are used for the production of xylolite, fiberboard, various structural elements, artificial marble, bases for finished floors, plasters, thermal insulating foam and aerated concrete, fire-resistant ramming masses, grindstones, etc. [1]. They are characterized by the following useful properties: high mechanical strength during the initial period of hardening; increased bending strength as compared with other types of binders; compact structure of hardened cement combined with low true density; low thermal conductivity; high adhesion strength to aggregates in magnesium concrete and mortars; and fairly high resistance to aggressive environments [2]. In addition, the obvious advantage of using magnesite and dolomite is the relatively low firing costs (in contrast to the production of lime and Portland cement) [3]. A characteristic property of magnesium binders, in contrast to traditional ones, is the addition of magnesium chloride solutions (rather than water) to caustic magnesite or dolomite.

Unavailability of magnesite deposits as well as high cost of imported magnesite limit possibility of its application as raw material for magnesia binders obtaining in Ukraine. But dolomite, an inexpensive and wide-spread mineral, can be used as an alternative magnesite [4]. In Ukraine, there are dolomite deposits within the boundaries of Donetsk folded region, Ukrainian crystalline board and Carpathian folded region. Ukrainian Reserves Balance takes into account 5 dolomite deposits and 2 explored and blocked-out reserves [5]. Four deposits and two reserves of them are in Donetsk region (including largest in Europe deposit «Olenivske») which is about 69.4% of total reserves. In addition, there is a deposit is in Dnipropetrovsk region containing 30.6% of total reserves. Total reserves of dolomite deposits in Ukraine include 670 million tons. It should be emphasized that Ukrainian Reserves Balance takes into account the deposits of metallurgical dolomite only, which are less than 60% of total Ukrainian dolomite reserves.

Magnesium chloride solution is used for mixing magnesia binders. In our opinion, the brine of mineral bischofite $MgCl_2 \cdot 6H_2O$ can be applied for its preparing [6]. Due to hygroscopicity of bischofite, the underground solution method is used for mineral mining. Mentioned above process is the easiest way to extract the salt from depth. Water solution being obtained has the same properties as a crystalline bischofite has. A rather strong brine has the density of 1.30–1.38 g/cm^3. Thus, substitution of crystalline magnesium chloride by brine of natural bischofite will allow reducing the binder cost. In Ukraine, bischofite deposits are placed in north-west part of Dniprovsko-Donetsk region [5]. There are promising resources of bischofite raw ore in Chernihiv region (deposit «Novopodilske») containing about 1171.7 million tons.

Despite availability of great raw reserves, the magnesia binders are not applied widely in Ukraine yet. It is known that high strength of air hardening magnesia cements is the result of magnesium oxychloride formation [7]. However, it should be noted that magnesium oxychloride materials are high-hygroscopic. Oxychlorides are decomposed under moist curing to form loose low-bonded structure. This leads to a considerable decrease of mechanical strength and limits a possibility of magnesia cements application by air conditions with relative humidity less than 60%. To expand the fields of application of magnesia binders, first of all, it is necessary to give them water-resistance. Taking into account all of the above, our study examines inorganic agents capable of stabilizing the phase composition of hardening magnesia cements. In addition, in this work, a brine of the mineral bischofite $MgCl_2 \cdot 6H_2O$ is used to add to the magnesium mixture.

Experimental

For obtaining caustic binder, the natural dolomite (deposit «Olenivske», Donetsk region, Ukraine) fired in an electric furnace at 700^{0}C for 2 h was used. Besides, caustic magnesite (deposit «Satka», South Ural) was applied in our research. Chemical composition of dolomite and magnesite being used is presented in Table 1.

As an additive to caustic dolomite or magnesite, the brine of mineral bischofite (deposit «Novopodilske», Chernihiv region, Ukraine) was used with the density of 1.20 g/cm^3. The content of basic components in bischofite was as follows (wt.%): $MgCl_2$ 36.20; $CaSO_4$ 0.05; KCl 0.31; and NaCl 0.59.

The materials listed below were applied as admixtures:

1) dehydrated and condensed superphosphate (PLC «Sumychimprom», Sumy, Ukraine), a product of thermal treatment of simple or double superphosphate at 225–280^{0}C for 3–4 h;

2) fine ground electrothermophosphoric slag, a waste of electrothermal phosphorus production containing (wt.%): CaO 46.02; MgO 3.20; Al_2O_3 4.42; SiO_2 41.08; Fe_2O_3 0.32; SO_3 0.52; P_2O_5 2.21; F 2.28; and MnO 0.30. Slag is present in the amorphous form and consists of 98% wollastonite glass and the little pseudowollastonite;

3) aluminophosphate binder (Al_2O_3/H_3PO_4=1:4) prepared by thermal treatment of aluminium hydrate and orthophosphoric acid mix at 180–200^{0}C;

4) aluminochromphosphate binder, a water solution of mixed aluminum and chromium phosphates with total formula $Al_2O_3 \cdot xCr_2O_3 \cdot xCrO_3 \cdot yP_2O_5 \cdot nH_2O$ (research-production company «SVK», Dnipro, Ukraine).

The dimensions of the samples were 2×2×2 cm. The samples based on caustic dolomite were placed in the water after 7 days of air hardening and were examined after 28 days of moist curing. The samples in terms of caustic magnesite after 28 days of air curing were saturated by water for 48 h, and then were subjected to the cyclic freezing and thawing (–15; +20^{0}C). To determine phases present in the samples, the hydration products were tested by X-ray powder diffraction and differential thermal analysis.

Table 1

Chemical composition of dolomite and magnesite being used

Raw material	Content, wt.%					
	CaO	MgO	Al_2O_3	SiO_2	Fe_2O_3	ignition loss
dolomite	34.40	17.60	0.50	0.77	0.29	44.9–45.7
magnesite	0.28–1.60	45.42–46.44	0.40–0.77	0.25–1.78	0.80–1.45	50.80–51.90

Results and discussion

Water-resistant binders based on caustic dolomite

There are a few data [8,9] concerning the fact that the properties of magnesia cement are improved in the presence of alkali metals and magnesium water-soluble phosphates. In addition, it is known that hydrolysis process of polyphosphates is accelerated via the catalytic action of some metal ions. In this case, final products of polyphosphates hydrolysis are not different from hydrolysis products in water. Based on mentioned above facts, it was assumed that under conditions of rehydration and hydrolysis process of condensed phosphates, the products of their hydrolysis would interact with caustic dolomite forming water-insoluble compounds. New compounds being formed will not destroy cement structure owing to described process proceeds rather slowly. Moreover, it is known that magnesia cement water-resistance can be increased by addition of reactive silica as silicagel, rottenstone, opoka, ground quartz sand, tobermorite and others.

Considering all mentioned above, heat-treated superphosphate (as phosphate-containing agent) and electrothermophosphoric slag (as reactive silica containing agent) were selected to increase magnesia binder water-resistance in this study. It should be noted that under normal conditions, finely ground electrothermophosphoric slag has no binding properties, but can be activated by additives of chloride, sulfate or carbonic acid salts of alkali- and alkaline-earth metals. Calcite and magnesium chloride can be such activating agents in caustic dolomite-based magnesia binder. The results of investigations of influence superphosphate and electrothermophosphoric slag on magnesia cement properties are given in Table 2.

It is concluded arom the obtained results that superphosphate and electrothermophosphoric slag can be applicable for the preparation of water-resistant magnesia binders. Under moist curing conditions, the additive-free cements samples are destroyed. However, admixture-containing samples demonstrated highly good results: superphosphate-containing cements have a softening ratio of 0.70–0.94 and water-resistance coefficient of 0.9–1.5 (depending on agent content), while cements containing electrothermophosphoric slag exhibited softening ratio of 0.74–0.80 and water-resistance coefficient of 1–1.2.

It was ascertained that main hydration products of air-hardened additive-free cements are magnesium pentahydrooxychloride $5MgO \cdot MgCl_2 \cdot 13H_2O$ (the most stable phase which provides high strength of magnesia oxychloride materials [10]) and magnesium hydroxide $Mg(OH)_2$. The following endothermic effects are presented on the thermogram of a given sample:

– at 180^0C and 620^0C corresponding to decomposition of $5MgO \cdot MgCl_2 \cdot 13H_2O$;

– at 420^0C corresponding to dehydration of $Mg(OH)_2$;

– at 910^0 corresponding to decomposition of $CaCO_3$.

As a result of the investigation of hydration products derived from additive-free binder after 28 days of moist curing, we determined that the intensity of diffraction peaks for magnesium oxyhydrochlorides on the XRD-pattern considerably decreases. On the thermogram of given samples, endothermic effects corresponding to magnesium oxychlorides decrease too. The results confirm water-solubility of magnesium oxychlorides. This fact result in a strength decrease and moist-nonresistance of caustic dolomite based cement.

From the results of studies on agent-containing magnesia binders, it is revealed that magnesium oxychlorides are formed in the presence of admixtures both at air curing and at moist one, i.e. these agents stabilize phase composition of hardening caustic dolomite. It should be noted that XRD-patterns of agent-containing binders (Fig. 1) after 28 days of

Table 2

Physical and mechanical properties of caustic dolomite-based binders

Content of agent, wt.%		Water-cement ratio	Setting time, hour-minute		Compressive strength after 28 days of hardening, MPa		
					air curing	moist curing	
superphosphate	electrothermophosphoric slag		initial set	final set		wet samples	dried-out samples
–	–	0.42	4–20	5–05	92.0	–	–
3	–	0.41	3–50	4–24	81.6	57.2	73.3
5	–	0.40	4–00	4–30	77.5	69.8	85.7
7	–	0.38	4–04	4–36	61.2	58.0	91.8
–	10	0.38	2–53	3–40	61.3	45.0	52.0
–	20	0.34	3–00	3–55	75.5	58.9	81.5
–	30	0.33	3–23	4–00	51.0	40.8	60.7

moist hardening do not differ from those of an additive-free air-hardening binder. On the XRD-pattern of binder containing 5 wt.% of superphosphate after 28 days of moist curing (Fig. 2a), the endothermic effects corresponding to magnesium oxychlorides (at 220^{0}C and 640^{0}C) as well as magnesium hydroxide (at 440^{0}C) are observed. However, the endothermic effect for $Mg(OH)_2$ decreases in comparison with the thermogram of additive-free binder. Moreover, a new endothermic effect at 280^{0}C appears.

It is known that the hydrolysis of heat-treated superphosphate is intensified in $MgCl_2$ solution: P_2O_5 and Ca^{+2} concentrations are greater than those in water. It can be concluded from our data that $Mg(OH)_2$ interacts with products of superphosphate hydrolysis forming a new complex compound. Therefore, protective colloids are formed and magnesium oxychlorides have complicated composition. On the thermogram of binder containing 20 wt.% of electrothermophosphoric slag (Fig. 2b), not only endothermic effects for magnesium oxychlorides (at 180^{0}C and 580^{0}C) and $Mg(OH)_2$ (at 400^{0}C) but also a new endothermic effect at 240^{0}C are observed. In our opinion, this effect corresponds to dehydration of calcium hydrosilicates which results from activated electrothermophosphoric slag hardening.

Thus, X-ray amorphous water-insoluble complex compounds are formed at hardening the agent-containing binders. The presence of these compounds provides high strength and water resistance of caustic dolomite-based cement. This phenomenon can be described in the following way. Gel being formed fills space between magnesium oxychlorides crystals. In due time, gel «ages», crystallizes, and, consequently, is compacted. This process leads to the structure strengthening and in the phase composition stability of hardening binder and high service properties under moist curing conditions are provided.

Water-resistant binders based on caustic magnesite

As a result of our investigations, the influence of some admixtures on the properties of caustic magnesite based binder has been established (Table 3). It is ascertained that the addition of selected agents (not only superphosphate and electrothermophosphoric slag, but also aluminophosphate and aluminochromphosphate binders) has a positive effect on water resistance (softening ratio depending on the kind of admixture is equal to 0.54–0.94) and gives the hydraulic properties to magnesia binders. Moreover, all samples with phosphate-containing admixtures have withstood 50 freezing-thawing cycles (freeze resistance factors after 50 cycles are equal to 0.55–1.29).

Conclusions

Thus, inorganic additives have been identified that increase the water and frost resistance of magnesium binders. Due to the use of additives that improve performance properties, the limits of use of magnesium chloride cement in wet conditions are

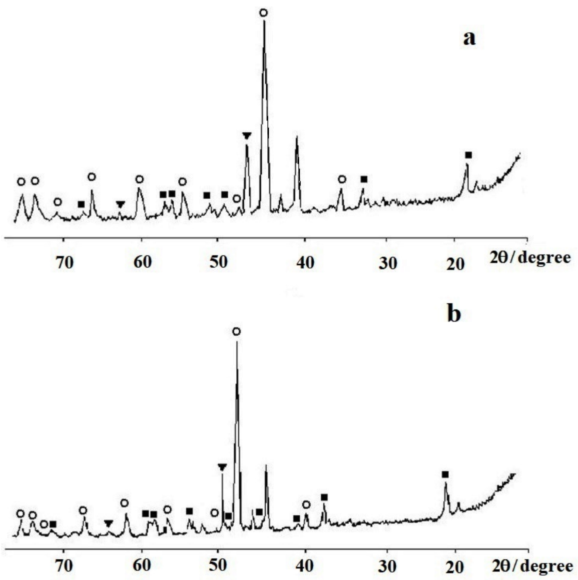

Fig. 1. XRD-patterns of magnesia binders containing superphosphate (a) and electrothermophosphoric slag (b) after 28 days of moist curing: ■ – $5MgO \cdot MgCl_2 \cdot 13H_2O$; ○ – $CaCO_3$; ▼ – $CaMg(CO_3)_2$

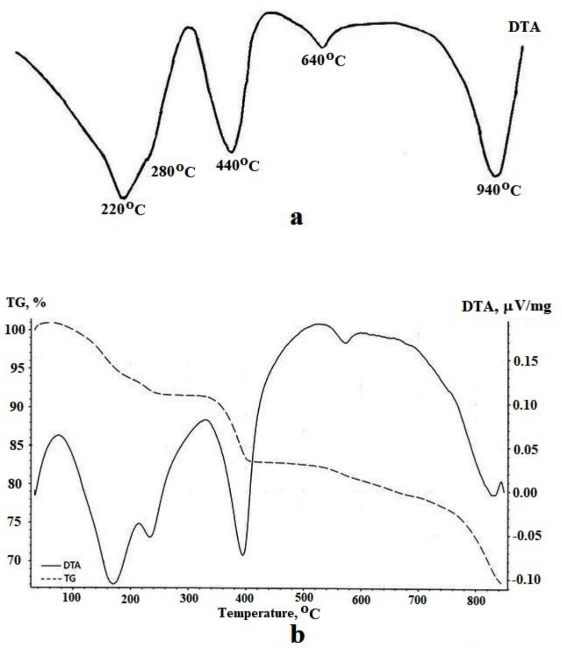

Fig. 2. Thermograms of magnesia binders containing superphosphate (a) and electrothermophosphoric slag (b) after 28 days of moist curing

significantly expanded. In addition, the possibility of using a brine of the bischofite mineral $MgCl_2{\cdot}6H_2O$ as an additive to the magnesium mixture has been shown.

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ВПЛИВ НЕОРГАНІЧНИХ ДОБАВОК НА ВОДОСТІЙКІСТЬ МАГНЕЗІАЛЬНОГО В'ЯЖУЧОГО

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У всьому світі застосовують в'яжучі речовини на основі магнію. Магнезіальні цементи використовують для виготовлення ксилоліту, фіброліту, різних конструкційних елементів, штучного мармуру, основи для готових підлог, штукатурок, теплоізоляційних піно- та газобетонів, вогнетривких набивних мас, точильних каменів тощо. Вони характеризуються такими корисними властивостями: висока механічна міцність на початковому етапі твердіння; підвищена (у порівнянні з іншими видами в'яжучих) міцність на вигин; компактна структура затверділого цементу в поєднанні з низькою істинною щільністю; низька теплопровідність; висока адгезія щодо наповнювачів в магнезіальних бетонах і розчинах; досить висока стійкість до впливу корозійних середовищ. Крім того, очевидною перевагою використання магнезиту і доломіту є відносно низькі витрати на випал (на відміну від виробництва вапна і портландцементу). Характерною властивістю магнезіальних в'яжучих на відміну від традиційних є замішування каустичного магнезиту або доломіту розчинами хлоридів магнію, а не водою. У цьому дослідженні розглядаються неорганічні агенти, здатні стабілізувати фазовий склад магнезіальних цементів, що твердіють, з використанням добавки до магнієвої суміші розсолу мінерального бішофіту. Внаслідок дослідження обрано неорганічні добавки, які підвищують морозо- і водостійкість, що розширює межі застосування в'яжучих на основі магнію, з використанням розсолу мінерального бішофіту.

Ключові слова: магнезіальне в'яжуче, розчин мінерального бішофіту, продукти гідратації, неорганічні добавки, водостійкість.

Table 3

Physical and mechanical properties of caustic magnesite based binders

Content of agent, wt.%				Compressive strength, MPa		Amount of being with-stood freezing-thawing cycles	Compressive strength after 50 freezing-thawing cycles, MPa	Freeze resistance factor
aluminophosphate binder	aluminochrom-phosphate binder	superphosphate	electrothermo-phosphoric slag	after 28 days of air hardening	after saturation by water for 48 h			
–	–	–	–	54.0	50.8	24	–	–
3	–	–	–	63.6	34.3	50	30.1	0.87
–	3	–	–	52.8	48.9	50	27.3	0.55
–	–	5	–	36.9	28.0	50	36.0	1.29
–	–	–	20	66.7	61.0	38	–	–

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