PERIÓDICO TCHÊ QUÍMICA
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CORROSÃO DE MAGNÉSIA DE MATERIAIS DE ENCHIMENTO

MAGNESIA CORROSION OF GROUTING MATERIALS

МАГНЕЗИАЛЬНАЯ КОРРОЗИЯ ТАМПОНАЖНЫХ МАТЕРИАЛОВ

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RESUMO

A questão da corrosão de magnésia de materiais de enchimento em poços de petróleo e gás é muito relevante na construção de poços de petróleo e gás, uma vez que os sais de magnésio podem levar à destruição da pedra de cimento à base de cimento Portland dentro de alguns meses. Ao fixar os intervalos poderosos de depósitos de sal representados por sais de magnésio, o uso de cimentos da magnésia é eficaz. No entanto, as camadas individuais e as camadas contendo os sais de magnésio dissolvidos não são cimentadas individualmente, mas se sobrepõem ao longo de todo o intervalo do orifício aberto com o cimento Portland, que pode ser destruído devido à corrosão de magnésia. A parte principal do trabalho é dedicada ao estudo da corrosão da pedra de cimento Portland em ambientes agressivos de magnésia. Como os indicadores quantitativos que caracterizam o grau de dano à pedra, são tomadas a espessura da camada danificada e o coeficiente de resistência da pedra, caracterizados pela relação da resistência à compressão ou à flexão das amostras de pedra, depois de estar em um ambiente agressivo com a resistência das amostras de controle no mesmo tempo de endurecimento. A resistência à corrosão da pedra de cimento foi avaliada após 8 semanas no ambiente de magnésia agressivo. Além disso, foi estudado o papel da concentração de $MgCl_2$ no mecanismo de danificação da pedra de cimento por corrosão. Propõe-se a redução em relação água/cimento e a adição de argila de da paligorsquite para reduzir a porosidade da pedra de cimento e a taxa de danos por corrosão. A cinética e os principais fatores que afetam o processo de corrosão foram considerados, uma análise de difração de raios X dos produtos de corrosão e da pedra de cimento não afetada foi realizada.

Palavras-chave: *corrosão de magnésia, pedra de cimento Portland, resistência à corrosão, profundidade de corrosão, paligorsquite.*

ABSTRACT

The issue of magnesia corrosion of grouting materials in oil and gas wells is very relevant in the construction of oil and gas wells since magnesia salts can lead to the destruction of Portland cement-based cement stone within few months. When fastening powerful intervals of salt deposits represented by magnesium salts, the use of magnesia cements is effective. However, individual layers and interlayers containing dissolved magnesium salts are not individually cemented, but overlap over the entire interval of the open hole with cement Portland cement, which can be destroyed due to magnesia corrosion. The main aim of the paper is to analyze the corrosion of Portland cement stone in aggressive environments of magnesia. As the quantitative indicators characterizing the degree of stone damage, the thickness of the damaged layer and the stone resistance coefficient are taken, characterized by the ratio of the compressive strength or bending strength of stone samples after being in an aggressive environment to the strength of control samples at the same hardening time. The corrosion resistance of cement stone was assessed after 8 weeks in an aggressive magnesia environment. Also, the role of $MgCl_2$ concentration on the mechanism of corrosion damage to cement stone was studied. The use of reducing the water-cement ratio and adding palygorskite clay to reduce the porosity of cement stone and reduce

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the rate of corrosion damage is proposed. The kinetics and the main factors affecting the corrosion process were considered, an X-ray diffraction analysis of corrosion products and unaffected cement stone was carried out.

Keywords: *magnesia corrosion, Portland cement stone, corrosion resistance, corrosion depth, palygorskite.*

АННОТАЦИЯ

Вопрос магнезиальной коррозии тампонажных материалов в нефтяных и газовых скважинах является весьма актуальным при строительстве нефтяных и газовых скважин, поскольку магнезиальные соли могут привести к разрушению цементного камня на основе портландцемента в течение нескольких месяцев. При креплении мощных интервалов соляных отложений, представленных солями магния, эффективно применение магнезиальных цементов. Однако, отдельные пласты и пропластки, содержащие растворенные соли магния, не цементируются индивидуально, а перекрываются по всему интервалу открытого ствола тампонажным портландцементом, который может разрушаться из-за магнезиальной коррозии. Основная часть работы заключается в изучении коррозии портландцементного камня в агрессивных магнезиальных средах. В качестве количественных показателей, характеризующих степень поражения камня, приняты толщина поврежденного слоя и коэффициент стойкости камня, характеризуемый отношением предела прочности на сжатие или изгиб образцов камня, после пребывания в агрессивной среде, к прочности контрольных образцов в одинаковые сроки твердения. Проведена оценка коррозионной стойкости цементного камня через 8 недель пребывания в магнезиальной агрессивной среде. Кроме этого, изучена роль концентрации MgCl2 на механизм коррозионного поражения цементного камня. Предложено использование снижение водоцементного отношения и добавки палыгорскитовой глины для уменьшения пористости тампонажного камня и снижения скорости коррозионного поражения. Рассмотрена кинетика и основные факторы, влияющие на процесс коррозии, проведен рентгеноструктурный анализ продуктов коррозии и непораженного цементного камня.

Ключевые слова: *магнезиальная коррозия, портландцементный камень, коррозионная стойкость, глубина коррозии, палыгорскит.*

1. INTRODUCTION:

To improve the quality of the fastening of wells, it is inevitable to regulate the technological properties of cement slurries using various chemicals (Agzamov *et al.*, 2006; Agzamov *et al.*, 2018). However, the expansion of the drilling zone led to the development of a significant number of fields, in the context of which there are formations represented by solid magnesia salts or solutions of these salts, which reduce the integrity of the well support (Kravets *et al.*, 1979; Agzamov and Izmukhambetov, 2005; Tolkachev *et al.*, 2010). The thickness of magnesia saline deposits varies from several to a thousand meters (Zhuravlev, 1972; Karabalina and Tankibaeva, 1989; Palilu *et al.*, 2019).

The amount and composition of salts in the reservoirs in each individual region vary widely. Typically, saline deposits are represented by bischofite ($MgCl_2 \cdot 6H_2O$), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), kieserite ($MgSO_4 \cdot H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$). The temperature of salt formations in some regions reaches 160°C, which enhances the aggressiveness of salts (Mukhin *et al.*, 1976). In salt deposits, brine-forming strata with abnormally high pressures, consisting of saturated saline and containing chlorides, calcium, magnesium, sodium and potassium sulphates and other salts, are often found. As a rule, the presence of magnesia salts in the section creates serious complications when fastening wells, manifested in: increasing the diametre of the well; the formation of gaps between the cement ring and the wall of the well; plastic flow of salts; thickening of grouting mortar; increasing pressure on the cementing head; destruction of cement stone; inter-reservoir flows and increased water cut of well products; crushing of intermediate or production strings, premature corrosion of casing strings, etc. (Mukhin et al., 1976; Akhmadeev and Danyushevsky, 1981; Danyushevsky *et al.*, 1987).

In wells cemented with Portland cement, casing corrosion is usually observed in places where grouting stone is absent, since Portland cement, having a high pH (more than 12.0), ensures the formation of a protective passivation film on the metal surface (Maksutov *et al.*, 1970; Zagirov, 1982; Tolkachev *et al.*, 2013). It should be noted that the practice of well construction, depending on the thickness of aggressively active sections, uses various types of grouting materials. To fix the intervals represented by magnesium-containing salts, magnesia cements are used, which are shut with aqueous solutions of magnesia salts (Trupak, 1956; Tolkachev *et al.*, 2010; Wang *et al.*, 2019; Calvo *et al.*, 2019), the effectiveness of which is confirmed by practice. At

the same time, aqueous solutions of magnesia salts and magnesia cements have a low pH (less than 7). Therefore casing strings under these conditions require additional protection (Tolkachev *et al.*, 2013).

If there are separate layers and interlayers in the section of the well containing dissolved magnesia salts, there is no practice of using technology for individual cementing of these zones, and cementing is usually carried out along the entire open hole interval with Portland cement, which is the weakest link in the well support and can be destroyed from due to magnesia corrosion (Shahraki et al., 2017; Kujur et al., 2018; Liu et al., 2019a). Therefore, despite the danger of magnesia corrosion in relation to Portland cement, even with a small amount of magnesium, a sufficiently large number of wells under these conditions are cemented by this grouting material. The main aggressive component in the corrosion of cement stone in contact with magnesium salts or their aqueous solutions is magnesium cation (Zaitsev *et al.*, 2016; Xu *et al.*, 2017a; Xu *et al.*, 2017b). As a result of chemical reactions of components of an aggressive environment with cement hydration products, and first of all with calcium hydroxide located in the pore fluid, reaction products are formed that are either removed from the cement stone as a result of diffusion or, precipitating, remain in its pores.

Thus, the main aim of the study is to research the main factors affecting the corrosion process of Portland cement stone in aggressive magnesia media by an experimental method using X-ray crystallography of corrosion products and unaffected cement stone.

2. MATERIALS AND METHODS:

In studies of the durability of concrete and cement, the corrosion processes of Portland cement are classified into several types (Kind, 1955; Babushkin and Ratinova, 1968; Moskvin *et al.*, 1980; Rakhimbayev *et al.*, 2012; Rakhimbayev, 2012; Rakhimbayev and Tolypina, 2015). Corrosion of the first type is associated with the gradual hydrolysis of cement hydration products, and the leaching of calcium hydroxide. A decrease in calcium hydroxide violates the stability of cement stone hardening products, leading to their subsequent hydrolysis and dissolution. In borehole conditions, this type of corrosion is characteristic of injection wells (Kind, 1955; Agzamov *et al.*, 2011). Corrosion of the second type is charactersed in that in the surface layers of cement stone in contact with the aggressive environment; there is an intensive destruction of the structural elements of hydrated cement stone. In this case, the process of destruction of the surface layers can be complete while maintaining intact stone in the adjacent layers. As a rule, this type is characteristic of the interaction of cement stone with acidic environments. About downhole conditions, this is observed under the action of dissolved hydrogen sulfide or carbon dioxide on the well support (Kind, 1955; Babushkin and Ratinova, 1968; Agzamov *et al.*, 2011).

The third type of corrosion is characterised by the fact that crystalline products accumulate in the pores and capillaries of the cement stone, which are the result of chemical reactions of an aggressive environment with the constituent parts of the cement stone. The growth and accumulation of corrosion products can lead to the development of tensile stresses on the pore walls and destroy the structural elements of the stone. One of the signs of this type of corrosion is the destruction of stone with an increase in volume, which is preceded by an accelerated, in comparison with control samples, increase in strength. In borehole conditions, this type of corrosion can be observed when sulfate media or gaseous hydrogen sulfide acts on a cement stone (Babushkin and Ratinova, 1968; Agzamov *et al.*, 2011).

The damage to the cement stone caused by $Mg(SO_4)_2$, according to (Kind, 1955), at low salt concentrations in water is caused by sulfate corrosion, which is dangerous only for Portland cement. At high concentrations of $Mg(SO4)_2$, magnesia-gypsum corrosion is observed, which is also dangerous for other types of cements. This means that with an increase in the Mg^{+2} cation in the solution, it is magnesia corrosion that prevails, the mechanism of which differs from the types of corrosion described above. There are several opinions regarding the corrosion mechanism of Portland cement in magnesia media. When the cement stone comes in contact with an aggressive magnesia medium, chemical reactions occur between the dissolved salt and calcium hydroxide located in the pores of the cement stone and near its surface according to the Equation 1:

$$Ca(OH)_2+MgCl_2 \rightarrow Mg(OH)_2\downarrow+CaCl_2 \text{ .....(Eq. 1)}$$

Calcium chloride, being a readily soluble product, dissociates into ions, and the Ca^{2+} cation is released into the environment. Chlorine ion remains in the pores of the cement stone and can diffuse further into the cement stone. Depending on the concentration of the aggressive substance, the composition of the cement stone hardening products, its structural characteristics during

magnesia corrosion, the meeting of the flows of aggressive ions with calcium hydroxide, and their subsequent neutralization can occur in different places. It can be outside the cement stone, either inside the stone near its surface or inside the stone at a considerable distance from the surface of the stone. Accordingly, a different mechanism of magnesia corrosion can be observed.

A decrease in calcium hydroxide in the pores of the cement stone upset the equilibrium between solid hardening products and dissolved $Ca(OH)_2$, leading to the dissolution and hydrolysis of hardening products and leaching of new portions of calcium hydroxide. In this case, leaching corrosion is observed, leading to the destruction of cement stone due to leaching of calcium hydroxide from it. The corrosion rate will depend on the diffusion rate of calcium cations from the cement stone, i.e., on the porosity of the formed leached layer, which in turn depends on the initial porosity of the cement stone. If cement stone hardening products are easily soluble, for example, highly basic calcium hydro silicates, their hydrolysis occurs quickly, and the zone of penetration of aggressive ions narrows. In this case, the corrosion of cement stone can take place according to the acid mechanism, that is, the destruction of the stone is carried out in layers, and the destruction can achieve full development when stored in closely spaced intact layers of cement stone with almost no change in structure and composition (Moskvin *et al.*, 1980; Kravtsov *et al.*, 1987; Amanbayev *et al.*, 2019; Orynbayev *et al.*, 2019).

The corrosion rate is also determined by the diffusion of aggressive fluids, i.e. the process has diffusion control. The higher the concentration of the solution of magnesia salt, the denser the structure of the membrane formed on the surface of the stone, and the retardation effect depends on its density, strength, and permeability. Another mechanism of damage is associated with the formation of magnesium hydroxide in the pores of cement stone by replacing the calcium cation with magnesium cation. According to (Trupak, 1956), this reaction is accompanied by an increase in the volume of corrosion products, leading to volumetric destruction of the stone. The possibility of volumetric destruction of Portland cement stone upon contact with a magnesia medium was also indicated in the works of V. Danyushevsky (Akhmadeev and Danyushevsky, 1981; Danyushevsky *et al.*, 1987). He noted that osmotic pressure, due to the presence of a semi-permeable shell in the surface layers of cement stone, and leading to the development of high pressures inside the stone, contributing to its destruction, is a reinforcing factor of magnesia corrosion. In his opinion, magnesium hydroxide (solubility 18.2 mg/l) can accumulate at the border of a cement stone or inside a stone near the surface, forming a semi-permeable septum, leading to osmotic effects.

According to (Kind, 1955), in $MgCl_2$ solutions, cement stone corrosion proceeds more slowly than in $Mg(SO_4)_2$ solutions having a similar concentration of Mg^{2+} ions. This is due to the effect of clogging the pores of the cement stone with magnesium hydroxide deposited on the surface of the cement stone and in pores adjacent to the surface. With a high porosity of the cement stone, the effect of the formation of a mud layer decreases, and the active corrosion of the cement stone under the influence of $MgCl_2$ begins to appear when the salt content in the solution is about 2%, which corresponds to about 5000 mg/l of $MgCl_2$ ions (Kind, 1955). If the flow of calcium hydroxide is insufficient due to the low rate of hydrolysis of the hardening products and the low concentration of calcium hydroxide, for example, in slag cement, and the number of aggressive ions is large, then a deeper penetration of magnesium cations into the stone and the formation of poorly soluble precipitate of magnesium hydroxide at a larger thickness inside cement stone.

Thus, when exposed to aggressive environments containing magnesium cations, several types of corrosion can be observed. In particular, it can be corrosion of the first type associated with the leaching of calcium hydroxide from cement stone, corrosion of the second type (acid), as well as corrosion of the third type, accompanied by the accumulation of corrosion products in the pores of the cement stone. During experimental studies, an aqueous solution of $MgCl_2$ with a concentration of 10% was used as an aggressive medium. The ratio of the volume of aggressive liquid and the volume of cement stone was 10:1, with a weekly update of the aggressive solution. The tested cement samples were prepared from Portland cement solutions with a water-cement ratio (W/C) of 0.4; 0.5; 0.6, which are solid in both water and air. Weekly, three samples were taken from the solution, which was tested for bending and compression. In addition, the depth of corrosion was determined at the fracture of the samples, and the phase composition of hardening products and corrosion products was determined in various layers of cement stone.

3. RESULTS AND DISCUSSION:

The applicability of this method to assess the effect of the aggressiveness of magnesium salts on cement stone is conditioned by the fact that during the reaction of the sample with the medium, hydrolysis and leaching of cement hardening products occur, thereby increasing the pore space and decreasing the strength of the stone (Cano *et al.*, 2015; Thomas *et al.*, 2015; Zhang *et al.*, 2019; Liu *et al.*, 2019b). The depth of corrosion is equal to the penetration depth of magnesium ions and was measured as the boundary of the resulting white products. The effect of H/C on the tensile strength of a cement stone installed in an aggressive environment during compression is shown in Figure 1, which shows that with a decrease in the initial water content of a solution, the strength of a Portland cement stone increases over time (Lee and Lee, 2019; Nikolopoulou *et al.*, 2019).

At the same time, the effect of hardening conditions and the composition of cement stone on the change in the strength of the stone was clearly manifested only due to the change in W/C. This is due to the fact that in the cement stone in the first weeks of hardening, hydration processes actively continue, which competes with destructive corrosion processes (Zhang *et al.*, 2019). Since the structural processes associated with the hydration and hardening of Portland cement during this period proceed faster than corrosion processes, it is not possible to single out the role of the latter during this period. This is quite obvious and does not contradict the basic provisions of hydration and hardening of cements (Danyushevsky et al., 1987; Agzamov et al., 2011; Kravtsov et al., 1987).

The decrease in W/C always reduces the porosity of the cement stone. It increases the corrosion resistance of the cement stone, which confirms the assumption of diffuse control of the process. At the fracture of the samples (Figure 2), zones of different colors are visible. The depth of the corroded zone increases with time. Moreover, with increasing W/C, the depth of the corrosion zone grows (Figures 3 and 4).

At the fracture of the samples shown in Figures 2 and 3, layer-by-layer destruction of the stone, characteristic of the second type of corrosion, is visible. At the same time, a loose white layer about 1 mm thick was formed on the surface of the cement stone, the composition of which, according to the X-ray phase analysis, showed the predominance of brussite $Mg(OH)_2$, which is a reaction product of $MgCl_2$ and $Ca(OH)_2$. The middle zone of the sample (non-corroded) in its phase composition corresponds to the composition of the control sample of cement stone (Illampas et al., 2019; Liu, 2019; Samsykin *et al.*, 2019). Between these layers inside the stone, a damaged (corroded) layer is distinguished, with a partially changed composition of the phase composition (Table 1). A quantitative analysis of the XRD results, the names of minerals, hardening products, and corrosion products were obtained by processing the diagrams in the TopasDiffrac licensed program. The comparison was carried out by changing the amount of non-hydrated cement minerals, cement hydration products, and corrosion products.

The table shows that in the central non-corroded part of the samples, there are not hydrated cement minerals and their hydration products (Elsayed *et al.*, 2018; Khatami and O'Kelly, 2018; Sögaard *et al.*, 2018; Wu and Zhang, 2018). The presence of corrosion products is not observed. In the middle (corroded) layer, the number of clinker minerals decreased with a simultaneous increase in hydration products. In particular, the number of minerals included in the composition of the initial cement decreased from 76.7% to 27.2%. An increase in the proportion of hardening products may indicate an increase in cement hydration processes with a decrease in pH. Other researchers noted this effect. In particular, some works suggested hardening cement stone when mixing it, for example, with water with dissolved carbon dioxide or dissolved hydrogen sulfide. This is because calcium hydroxide released during hydration of clinker minerals is more quickly neutralized by an acidic medium, and, as a result, causes accelerated hydration of cement minerals to maintain the required concentration of calcium hydroxide solution (Agzamov *et al.*, 2011; Hou *et al.*, 2018; Song *et al.*, 2018; Le and Sun, 2018).

The amount of Portlandite (calcium hydroxide) in these layers does not differ significantly. In the non-corroded layer, this is due to the onset of equilibrium between the solid phase and the pore liquid, and in the corroded layer it is associated with the hydrolysis of the hardening products due to the constant binding of calcium hydroxide from the pore liquid due to the reaction with magnesium chloride (Zou *et al.*, 2018; Liu *et al.*, 2018; Junxiang *et al.*, 2018). In the surface layer of cement stone, calcium hydroxide (oxide) completely went into solution and bound with aggressive ions, due to which only insoluble or poorly soluble compounds remained in this layer, which play a significant role in inhibiting the

corrosion process. These include aluminum and magnesium hydroxide, as well as silicon oxide and a small amount of carbonates. Aluminum hydroxide, which has a larger size than aluminum oxide, reducing pore size, acts as an additional agent that reduces the permeability of the cement stone layer near the border with the aggressive environment. Magnesium hydroxide, in this case, acts as a semipermeable membrane and a binding agent for silicon oxide.

Analysis of the results allows to clarify the idea of the mechanism of corrosion of cement stone in a magnesia medium. A significant value of the content of brussite in the surface sediment (Table 1) indicates the second type of corrosion, during which exchange reactions occur between the components of the cement stone and the mortar, and the resulting reaction products are deposited on the cement surface and in the pores (Moskvin et al., 1980; Rakhimbayev, 2012; Rakhimbayev *et al.*, 2012; Rakhimbayev and Tolypina, 2015;). Corrosion, in this case, can come with braking due to the partial compaction of cement stone with corrosion products. At the same time, no signs of volumetric destruction due to the accumulation of corrosion products inside the cement stone were noted, which may indicate a reaction between calcium hydroxide and magnesium chloride at the surface of the cement stone. This may be evidenced by a small amount of corrosion products in the middle (damaged) layer.

The experiments confirmed that the factors determining the kinetics of the corrosion process are the diffusion rate, the porosity of the stone, and the compaction of the cement stone with reaction products. Since one of the factors determining the kinetics of the corrosion process is the porosity of the stone, an addition of salt-resistant clay – palygorskite in an amount of 3% was used to reduce it. In this case, the W/C of the solution was maintained equal to 0.5. The experiments showed (Figure 5) that corrosion also occurs in layers, but the boundaries of the layers are less noticeable, and the corrosion process slows down. A layer of brussite $Mg(OH)_2$, less than 1 mm thick, also formed on the surface of the cement stone. The results of determining the tensile strength of Portland cement stone and the depth of corrosion of samples containing palygorskite are shown in Figures 6 and 7.

With the same porosity of the stone (due to the same W/C), the corrosion rate of the stone obtained from cement with the addition of palygorskite decreased by 17% compared to the control samples. This is attributed to a slowdown in the diffusion of aggressive ions into the stone due to the clogging of its pores with swollen, salt-resistant clay. A study of the behavior of cement stone in media with different concentrations of magnesium chloride showed that a concentration of 10% is most interesting for considering the corrosion process, since the corrosion front is at the grouting stone – solution, and second-type corrosion is observed. When the concentration of the aggressive medium is more than 10%, in the experiment with 20%, the corrosion front moves inside the stone, and the corrosion passes to the third type, and, also, $MgCl_2$ begins to crystallize on the surface of the samples (Figure 8).

At concentrations of aggressive medium less than 10%, the corrosion front extends beyond the cement stone, and corrosion occurs only due to the leaching of $Ca(OH)_2$.

4. CONCLUSIONS:

1. The relationship of the kinetics of corrosion damage to Portland cement stone with its structural properties is shown, which makes it possible to control the corrosion rate by reducing the water-cement ratio of the cement slurry.

2. The possibility of reducing the rate of corrosion of cement stone in a magnesia medium using palygorskite additive, which acts as a pore colmatant, has been shown.

3. A change in the mechanism of damage to cement stone in magnesia media depending on the concentration of Mg^2 cation has been theoretically substantiated and experimentally shown.

4. Corrosion damage to the cement stone has a layered character, from the intact sample to the corroded layer, which differ in phase composition, and the kinetics of the lesion is characterised by a slowdown in the corrosion rate.

5. It has been shown that on the open stone surface from Portland cement at high concentrations of $MgCl_2$ crystallisation occurs with the formation of a layer that reduces the corrosion rate.

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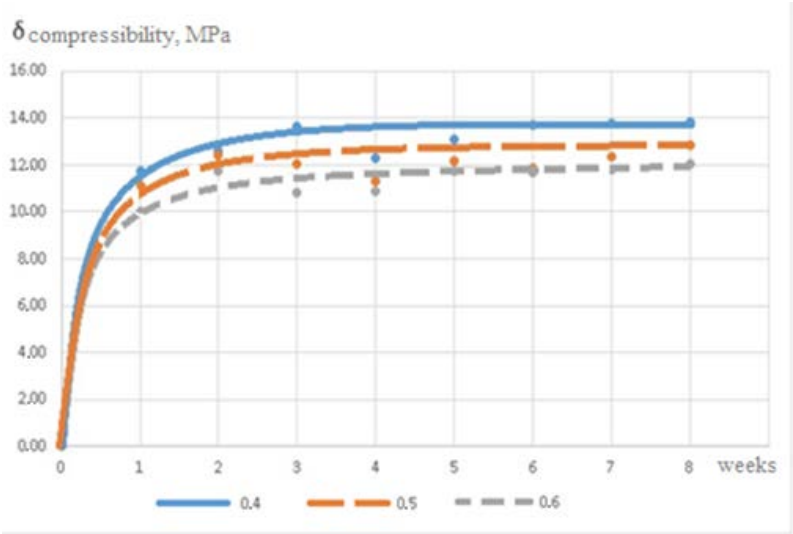


Figure 1. *Influences of W/C on cement stone strength in an environment of* $MgCl_2$

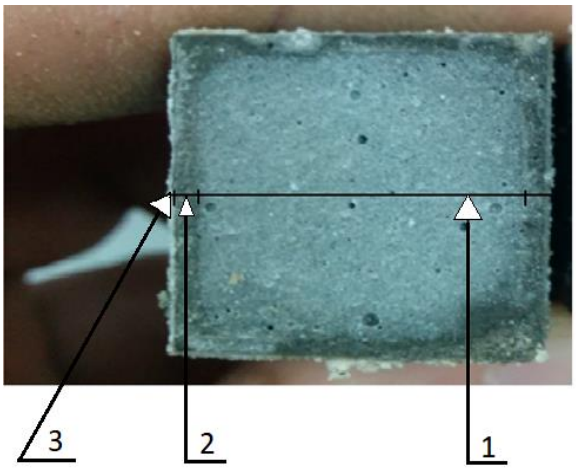
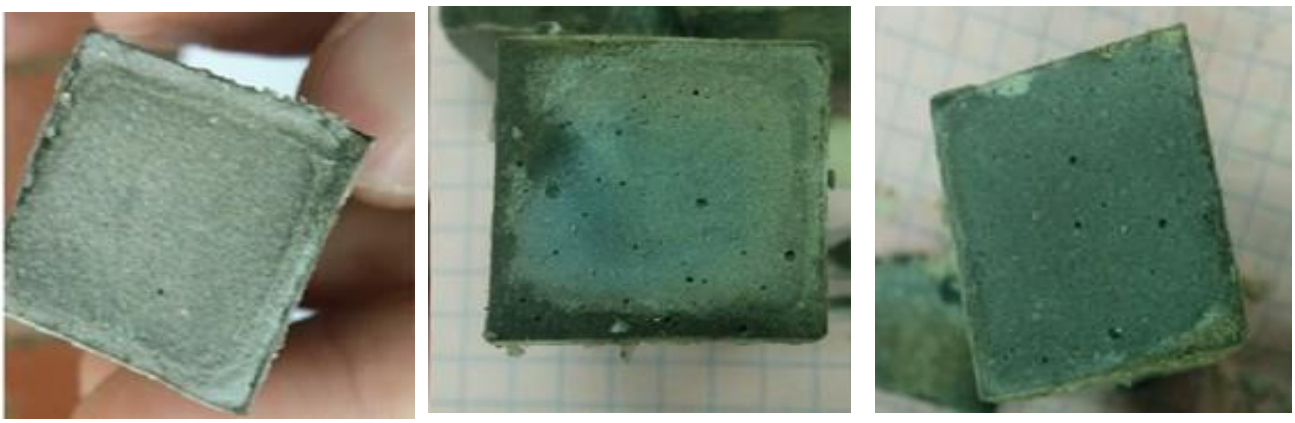


Figure 2. *A sample of cement stone after 14 days in a medium of magnesium chloride. 1 – non-corroded part; 2 – corrosion zone; 3 – precipitate of magnesium hydroxide on the surface of the sample*



a) *b)* *c)*

Figure 3. *Samples of cement stone after 28 days in an aggressive environment a – W/C = 0.6; b – W/C = 0.5; c – W/C = 0.4*

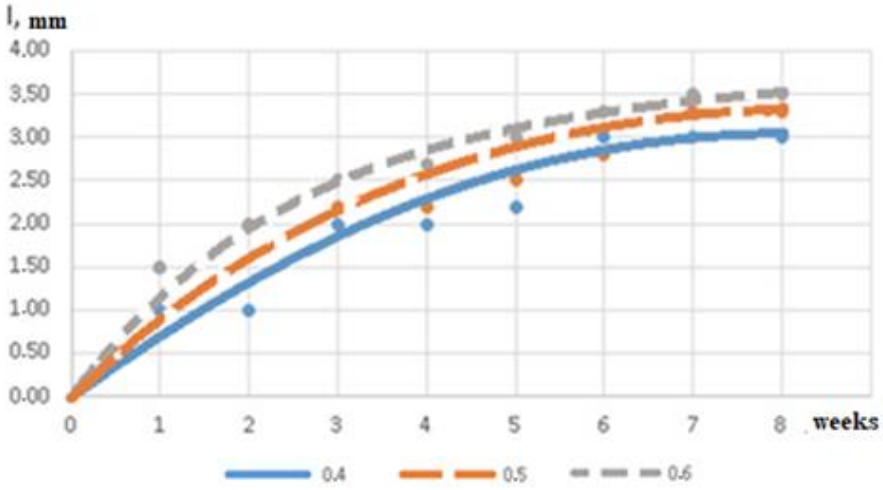


Figure 4. *The effects of W/C on the depth of corrosion of cement stone in a medium of $MgCl_2$*

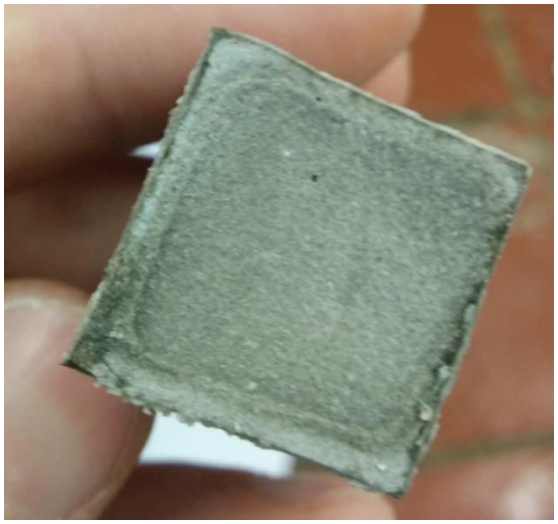


Figure 5. *Corrosion of Portland cement with palygorskite*

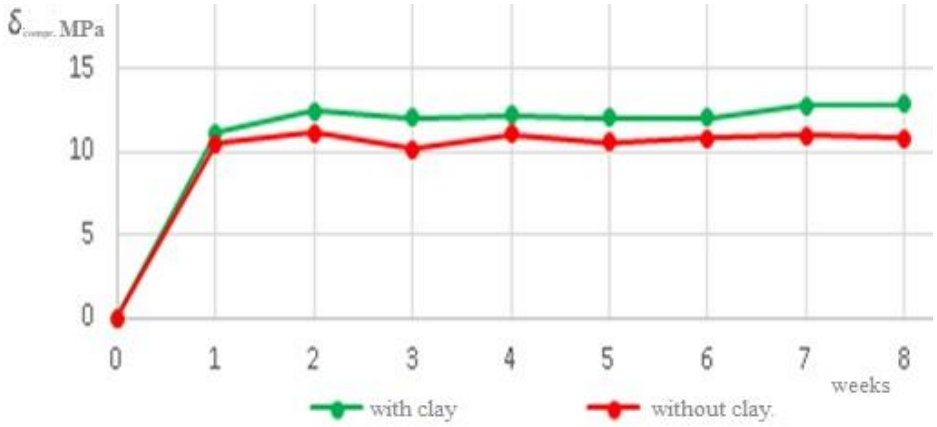


Figure 6. *Effect of palygorskite additive on the strength of Portland cement stone in $MgCl_2$*

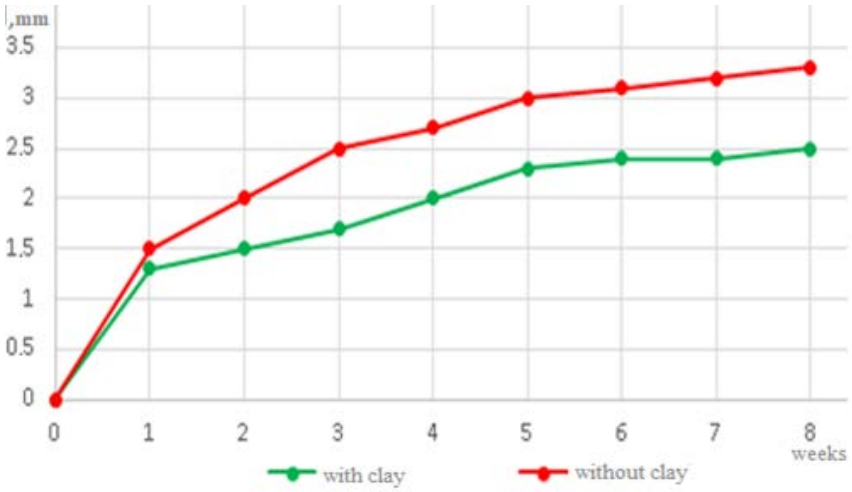


Figure 7. *The effect of palygorskite additive on the corrosion depth of Portland cement stone in $MgCl_2$*

Figure 8. *Crystal formation of magnesium chloride on a stone surface*

Table 1. *The results of quantitative X-ray phase analysis*

Zone	Formula	Name of compound	%
Non-corroded layer	C_3S	monoclinic (NISHI)	47.21
	C_2S (sum α, β, γ)	dicalcium silicate	14.59
	C_4AF	tetracalcium aluminaferrite	12.67
	C_3Acubic	tricalcium aluminate	2.22
	$Ca(OH)_2$	portlandite	2.18
	C_3S_3H	xonolite	7.66
	$C_5S_6H_5$	тobermorite	7.4
	$MgCO_3$	magnesite	6.02
Corroded layer	C_3S	monoclinic (NISHI)	7.17
	C_2S (sum α, β, γ)	dicalcium silicate	11.46
	C_4AF	tetracalcium aluminaferrite	7.32
	C_3Acubic	tricalcium aluminate	1.2
	$C_{12}A_7$	mayenite	2.69
	$Ca(OH)_2$	portlandite	2.01
	$C_5S_6H_5$	тobermorite	19.54
	C_3S_3H	rosenhahnite	17.75
	C_6S_3H	gammaDellaite	12.65
	$(Mg,Fe)_2Al_4Si_5O_{18}$	cordierite	9.49
	C_2AS	gehlenite	4.57
	SiO_2	quartz	0.44
	$MgCO_3$	magnesite	3.05
	$CaCO_3$	vaterite	1.1
Precipitation	C_3S	monoclinic (NISHI)	1.24
	C3Acubic	tricalcium aluminate	0.29
	C_4AF	tetracalcium aluminaferrite	0.84
	$C_3ACs_3H_{31}$	ettringite	1.71
	$Mg(OH)_2$	brucite	54.70
	SiO_2	silicaLeBail	29.01
	$Al(OH)_3$	nordstrandite	8.63
	$CaCO_3$	calcite	3.58
	MgO	periclase	0.19