

# EFFECT OF CALCIUM AND MAGNESIUM OXIDES ON THE PROPERTIES OF EXPANDING CEMENTS AND PLUGGING MORTARS

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*Досліджено вплив добавок оксидної форми розширення на фізико-механічні властивості цементів і тампонажних розчинів. Встановлено, що введення добавки оксиду кальцію призводить до менш значного падіння міцності цементного каменю і тампонажного розчину та більшого розширення, ніж введення оксиду магнію. Визначено вплив добавок на формування кристалічної структури продуктів гідратації*

*Ключові слова: оксидне розширення, цемент, розширливий тампонажний розчин, фізико-механічні властивості, мікроструктура*

*Исследовано влияние добавок оксидной формы расширения на физико-механические свойства цементов и тампонажных растворов. Установлено, что введение добавки оксида кальция приводит к менее значительному падению прочности цементного камня и тампонажного раствора и большего расширению образцов, чем введение оксида магния. Установлено влияние добавок на формирования кристаллической структуры продуктов гидратации*

*Ключевые слова: оксидное расширение, цемент, расширяющийся тампонажный раствор, физико-механические свойства, микроструктура*

## 1. Introduction

Expanding cements are enjoying the biggest demand among all special types of cements [1]. This trend is evident in other developed countries [2].

Expanding cements provide concretes and solutions with increased watertightness. This allows increasing use of such materials for cementing wells during natural gas and oil extraction [3]. Expanding additives make it possible to prevent cracking of concretes at hardening [4].

Special features of using such cements in the different fields of construction determine different requirements to them, especially to the capability of expanding. The fundamental question is what residual changes in the volume of hardened expanding cement or concrete take place after the shrinkage process. In this regard, the following new definition of the expanding cements is proposed – expanding cements are the inorganic binding materials that exhibit changes in volume controlled over time and space.

One of the important directions of using expanding cements is the plugging-back of oil and gas wells for the purpose of insulating productive oil and gas layers from aquifers, as well as to separate these layers from one another at multi-layer deposits of oil or gas [5]. To obtain a denser layer of cement to the outside of the pipe space, not only the expanding of the plugging-back material is required but also

its strength in the course of well operation. From this point of view, determining the optimal materials for the manufacture of expanding plugging-back materials is a relevant task.

## 2. Literature review and problem statement

Two types of additives of the oxide form of expanding are employed in the manufacture of plugging mortars. These are calcium oxide [2, 6] and magnesium oxide [7].

At a significant content of these additives in the expanding cements, a reduction of strength of the cement stone occurs. A special feature of applying plugging-back cements is the fact that they are fed into a well, first, without fillers, second, with the amount of water that considerably exceeds the standard need in water to ensure the required mobility [8]. All this leads to a certain change in both the processes of setting and the expanding processes. Given the fact that the operation of a well can last for quite a long time and often under conditions of aggressive impact of different origin, the strength of the cement stone plays a significant role in the longevity of the well itself.

Plugging expanding cements [9] are used for the cementation of oil and gas wells with complicated mining and geological conditions (alternating productive layers and aquifers, existence of a significant pressure difference in closely-spaced

layers, etc.). Standard plugging portland cements of type I and II, plugging slag sand cements, and expanding additives are applied for the production of these cements.

It should be noted that the observation and accurate inspection of a wellbore condition is impossible [10]. This extremely complicates the study of cement under operating conditions. The temperature and pressure gradually increase with the deepening of an oil wells, which naturally affects the process of cementation and quality of the resulting cement stone. It is known [11] that a temperature increase due to the depth of drilling varies in different oil fields.

Currently, the standards on plugging cements regulate a strength indicator at bending in the age of 2 days. But the exploitation of wells lasts over considerable time and strength of the cement stone plays a significant role. Therefore, there is a need to investigate the effect of oxides of calcium and magnesium on the physical-mechanical properties of cements (at normal density) and plugging mortars, which will make it possible to optimize the choice of compositions for plugging expanding mortars. It is especially important to identify features in the hardening of cements and plugging mortars over the early period of this process, exactly when the materials expand.

### 3. The aim and objectives of the study

The goal of present research was to determine essential characteristics of cements and plugging mortars and to compare character of the expansion processes when using additives of the oxide form of expansion.

To accomplish the set goal, the following tasks had to be solved:

- to establish the effect of oxides of calcium and magnesium on the physical-mechanical properties of cements and plugging mortars;
- to determine the character of the expansion processes of cement and plugging mortars at introduction of oxides of calcium and magnesium.

### 4. Materials and methods for the study of influence of oxides of calcium and magnesium on the physical-mechanical properties and expansion processes of cements and plugging mortars

#### 4.1. The examined materials and equipment used in the experiment

Experimental samples of cements and plugging mortars were prepared using the plugging cement of type I, lime of grade 2 and caustic magnesite of brand PMK-87 (VAT Kombinat "Magnesite", Russian Federation).

The oxides of calcium and magnesium were pre-grounded to a residual on the sieve No. 008 in the range of 8–12 %.

Electron-microscopic studies were conducted on electron raster microscope Tesla-VS-242 (Czechoslovakia). We examined surface of the chippings from the hydrated samples. Surface magnification was 2500.

#### 4.2. Procedure for determining the indicators of samples' properties

The examined compositions were prepared by the agitation of dosed components in laboratory ball mills with a

small amount of grinding bodies to prevent additional grinding of the mixture.

Normal density and the periods of setting the cements and plugging mortars were determined in the WIKA gauge at normal density for the former and at water/cement ratio 0.5 for the latter.

Content of the additives of oxides of calcium and magnesium was 0, 10 and 20 % by weight.

The expansion processes were studied by determining a height of the mould with dimensions of the working space  $\varnothing=30$  mm,  $H=20$  mm, which was filled with the appropriate material. The height of the mould was measured with an accuracy of 0.1 mm until full completion of the expansion process. Expansion values were determined as the arithmetic mean of 3 experiments under equal conditions. Error of the experiment was 2.8 %.

### 5. Results of study of the effect of oxides of calcium and magnesium on the physical-mechanical properties and expansion processes of cements and plugging mortars

Results of the study into physical-mechanical properties of cements with the additive of calcium oxide are given in Table 1.

Table 1

Effect of a calcium oxide additive on the properties of cements

No. of composition	Cement composition, % by weight		ND, % by weight	Setting period, hours-min.		Strength at compression, MPa, in the age, days		
	Cement	Calcium oxide		Start	Finish	1	3	28
1	100	0	25.0	0–32	0–50	15.0	33.1	41.8
2	90	10	30.0	0–33	1–05	8.8	31.0	33.3
3	80	20	35.0	0–34	1–25	6.0	19.8	28.4

The data represented indicate that an increase in the content of a calcium oxide additive leads to a monotonous growth of the cement water consumption. The effect at the start of the setting is not very much expressed, but the period of its finish is somewhat extended. Most likely, this is due to the higher water consumption of calcium oxide, which leads to a monotonic increase in the required amount of water at increased calcium oxide content in the cement.

More interesting are the details of the impact of calcium oxide on the strength of cements. With the increased content of additive it is monotonically decreasing, the fall is especially pronounced at the age of 1 day (by almost 2 times).

Such a significant drop in strength no longer occurs over the later periods of hardening. One may assume that the products of hydration begin to participate over time in the formation reactions of calcium hydrosilicates and, thereby, somewhat increase the overall strength of the cement stone.

In general, the introduction of calcium oxide leads to a significant decrease in the strength of the cement stone, which is an indirect confirmation of the expansion processes occurring in the system.

Results of the study into properties of cements with a magnesium oxide additive are given in Table 2.

Table 2

Effect of a magnesium oxide additive on the properties of cements

No. of composition	Cement composition, % by weight		ND, % by weight	Setting period, hours-min.		Strength at compression, MPa, in the age, days		
	Cement	Magnesium oxide		Start	Finish	1	3	28
2	90	10	28.0	0-34	0-55	9.3	21.3	20.0
3	80	20	34.0	0-38	1-00	5.5	1.9	5.0

Magnesium oxide affects the physical-mechanical properties of cement more significantly than calcium oxide. The cement water consumption grows, setting start time is extended while its finish period somewhat increases. The strength indicators of cements with a magnesium oxide additive are significantly reduced. Over the all periods of hardening in the examined range of hardening time, the introduction of magnesium oxide leads to a significant drop in the strength of cements.

Significantly different is also the character of the expansion of cements with the additives of oxides of calcium and magnesium (Fig. 1).

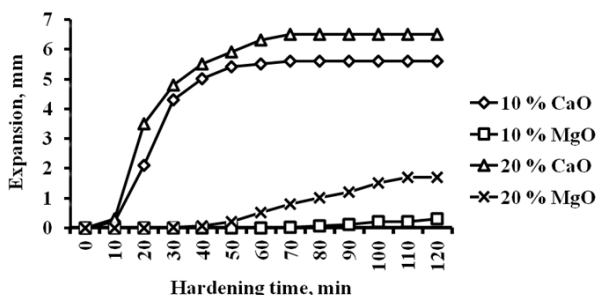


Fig. 1. Effect of oxides of calcium and magnesium on the expansion of cement slurry with normal density

Cements with a calcium oxide additive are characterized by a significantly larger expansion compared to the magnesium oxide additive. It is logical that with an increase in the content of additives, the mixture exhibits an increase in the indicators of expansion.

It should be noted that the introduction of calcium oxide leads to an earlier start of the expansion process, practically in 10 minutes from the moment of mixing the mixture with water. At the same time, expansion of the samples with magnesium oxide starts in about 40 minutes.

This process finishes earlier in the cements with a calcium oxide additive (60-80 min.) compared with magnesium oxide (110-120 min.).

Results that were obtained in the study of influence of calcium oxide on the plugging mortars are given in Table 3.

The introduction of a calcium oxide additive leads to a reduction in terms of setting: both the start and finish of this process. The fall in the values of strength is significantly less than in the cements at normal density of cement slurry.

The effect of magnesium oxide on the physical-mechanical properties of plugging mortars has a slightly different character (Table 4).

Table 3

Physical-mechanical properties of plugging mortars with a calcium oxide additive

Calcium oxide content, % by weight	W/C, % by weight	Setting period, hours-min.		Strength at compression, MPa, in the age, days		
		Start	Finish	1	3	28
10	0.5	4-50	5-50	1.2	6.1	14.3
20	0.5	2-15	5-15	1.0	5.1	10.1

Table 4

Physical-mechanical properties of plugging mortars with a magnesium oxide additive

Magnesium oxide content, % by weight	W/C, % by weight	Setting period, hours-min.		Strength at compression, MPa, in the age, days		
		Start	Finish	1	3	28
10	0.5	2-50	5-40	1.4	5.9	10.1
20	0.5	1-20	3-30	1.5	4.8	5.6

A significantly more pronounced reduction in the setting periods take place, especially early in the process, but the drop in strength is considerably larger.

The impact of oxides of calcium and magnesium on the expansion of plugging mortars is displayed in Fig. 2.

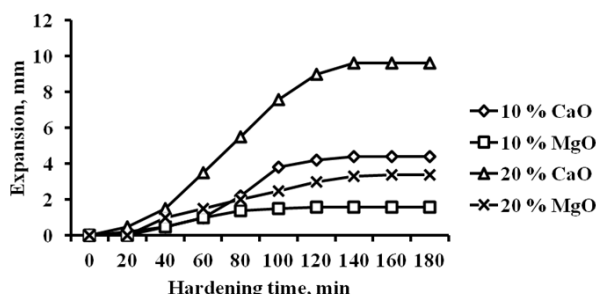


Fig. 2. Impact of oxides of calcium and magnesium on the expansion of plugging mortars

In order to compare efficiency of the expansion of cements with the examined additives, we studied kinetics of the expansion of the given cements at temperatures of 22, 45, and 75 °C. The appropriate additives were introduced in the amount of 20 % by weight to the plugging Portland cement at a water/cement ratio of 50 % by weight when introducing calcium oxide, and 55 % by weight when introducing magnesium oxide. Such a difference is explained by the need to provide the mortar with required mobility.

The data obtained on the kinetics of expansion of plugging mortar with a calcium oxide additive at different temperatures are given in Table 5.

**Table 5**  
Expansion kinetics of the plugging mortar with a calcium oxide additive at different temperatures

Hardening period, min.	Enlargement of the sample linear size, %, at temperature °C		
	22	45	75
0	0	0	7.5
20	0.5	1.0	7.8
40	1.5	2.2	9.8
60	3.5	4.5	9.8
80	5.5	6.8	9.8
100	7.6	8.9	9.8
120	9.0	8.9	9.8
140	9.6	8.9	9.8
160	9.6	8.9	9.8
180	9.6	8.9	9.8

It should be noted that at all of the examined values of hardening temperatures of the plugging mortar, the sample expansion occurs in 20 minutes after mixing. There is a difference in the intensity of the course of the processes with a rise in the temperature, at which the materials hardened.

At a temperature of 22 °C, maximum enlargement in the size of the sample occurs after 140 minutes of hardening, at 45 °C – in 100 minutes. The expansion process finishes after 40 minutes at a temperature of 75 °C. If one takes into account the fact that during plugging of wells it is important that the process of expansion occurs at a time when the crystalline structure of cement stone forms, then it is possible to conclude that the use of calcium oxide is appropriate only when plugging the wells, which are characterized by low and normal temperatures (up to 45 °C).

The data obtained on the expansion kinetics of cement mortar with a magnesium oxide additive are given in Table 6.

**Table 6**  
Expansion kinetics of the plugging mortar with a magnesium oxide additive at different temperatures

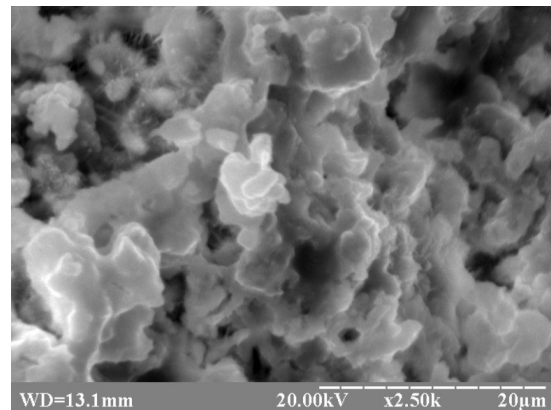
Hardening period, min.	Enlargement of the sample linear size, %, at temperature °C		
	22	45	75
0	0	0	0
20	0	0	0.5
40	1.0	1.1	1.4
60	1.5	1.9	2.1
80	2.0	2.2	2.5
100	2.5	2.8	3.0
120	3.0	3.1	3.5
140	3.3	3.5	3.6
160	3.4	3.5	3.6
180	3.4	3.5	3.6

The results presented indicate that the expansion process in the plugging mortars with a magnesium oxide additive starts in 20–40 minutes after the introduction of water to the mortar, however, at all temperatures the value of this expansion is negligible. With a rising in temperature, at 45 and 75 °C, there is a certain intensification of the expansion process, but also very small. It is possible that the process

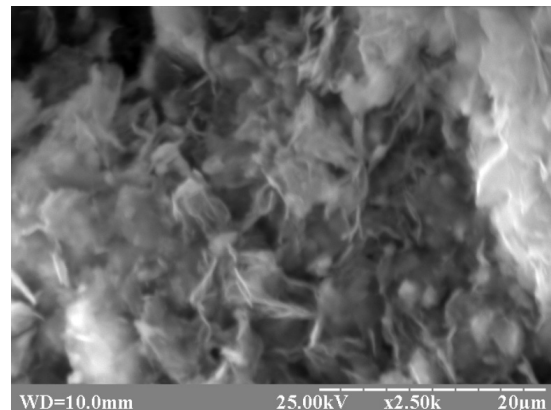
of increasing the volume of new formations (magnesium hydroxide) is levelled off due to a large volume of water introduced to the system.

We examined the microstructure of cement stone over the early setting periods in the age of 1 day, that is, at the time when the maximum expansion of a plugging mortar occurs. The cement stone was studied from the plugging mortars with different additives that hardened at temperatures of 22 °C and 75 °C.

The microstructure of cement stone from the plugging mortar with a calcium oxide additive, hardened at a temperature of 22 °C, is represented by a significant amount of gel, calcium hydroxide, and a small amount of thin needle-shaped crystals of calcium hydrosilicates (Fig. 3, *a*).



*a*



*b*

**Fig. 3.** Microstructure of the cement stone at the age of 1 day at a temperature of 22 °C, with additives of oxides: *a* – of calcium; *b* – of magnesium

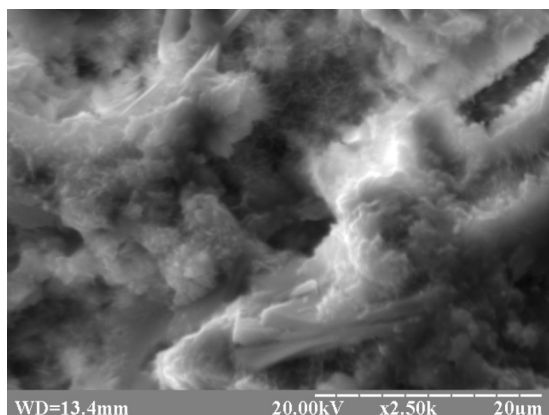
At a temperature of 75 °C, physical appearance of the samples of plugging mortar with a calcium oxide additive changes (Fig. 4, *a*). Its thickness exhibits separate filamentous formations and the accumulation of well-formed crystals of calcium hydrosilicates. A process of the portlandite formation is initiated: one observes the formations that are of lamellar form characteristic of portlandite.

Microstructure of the cement stone, which was obtained from the plugging mortar with a magnesium oxide additive has a physical appearance different from the previously examined sample with a calcium oxide additive.

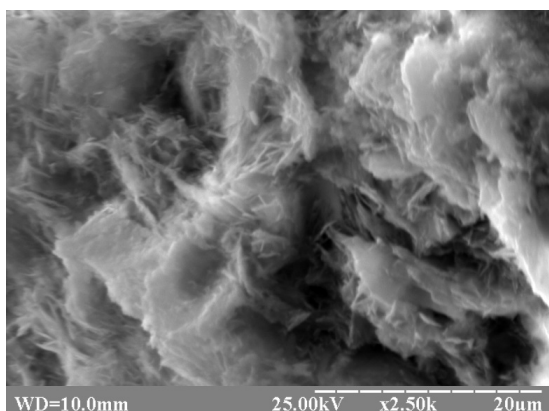
At a temperature of 22 °C, one may observe on the surface of the chipping of the cement stone with a magnesium



oxide additive a large number of formations with characteristic shape (Fig. 3, *b*). Increasing the hardening temperature of the plugging mortar with a magnesium oxide additive to 75 °C changes a physical appearance of the cement stone sample (Fig. 4, *b*). Against the background of arrays of hydrate formations of calcium silicates and embryos of portlandite crystals, formed in different places, it is possible to see a large number of fibres with different size, which are located throughout the entire thickness of the sample.



*a*



*b*

Fig. 4. Microstructure of the cement stone at the age of 1 day at a temperature of 75 °C, with additives of oxides: *a* – of calcium; *b* – of magnesium

#### 6. Discussion of study results into the effect of oxides of calcium and magnesium on the physical-mechanical characteristics and expansion of cements and plugging mortars

The effect of oxides of calcium and magnesium on the strength of cements at compression at the age of 1 day of hardening is similar in character. The indicators of strength decrease by 41.3–38.0 % when introducing the additives in the amount of 10 % by weight, and by 60.0–63.3 when introducing the additives in the amount of 20 % by weight.

At the age of 3 days, the character of curves of strength dependence at compression on the concentration of an additive in cement remains the same, however the effect of magnesium oxide leads to a more significant reduction of this indicator. Thus, a decrease in the strength when introducing an additive in the amount of 10 % by weight is, respectively

for Cao and MgO, 6.3 and 35.6 %; when introducing an additive in the amount of 20 % by weight – 40.2 and 64.0 %.

When analyzing strength at the age of 28 days and the character of this indicator's dependence on the concentration of additives that are introduced to cement, it can be concluded that the introduction of a magnesium oxide additive leads to a more significant decrease in strength. Accordingly, when introducing the additives in the amount of 10 and 20 % by weight, a decrease in strength is 32.1 and 64.1 % compared with calcium oxide: 20.3 and 52.2 %.

The results obtained make it possible to assume that the introduction of calcium oxide to cement at first leads to the formation of a large quantity of calcium hydroxide (increasing the volume of the hardening mortar). Then it gradually begins to participate in the formation of calcium hydrosilicates. This leads to some decrease in the rate of strength fall with an increase in the content of calcium oxide in cement.

Regarding the role of magnesium oxide in the hardening of cement, most likely, after the formation of hydroxide magnesium it does not participate in the formation of crystalline framework of the cement stone. A large number of loose flakes forms that over a wellbore long operation can be gradually removed out of the cement stone.

The expansion value of cements with a calcium oxide additive is larger than that of magnesium oxide by several times. The beginning of this process starts earlier when introducing calcium oxide (in 10 minutes after mixing with water versus 40 minutes in the cements with a magnesium oxide additive). The end of this process also occurs later, in, respectively, 70 and 110 minutes and is, at an additive in the amount of 10 and 20 % by weight, respectively: at the age of 1 day – 7.7 and 23.1 %; at the age of 3 days – 10.3 and 25.0 %; and at the age of 28 days – 17.3 and 39.9 %.

Similar results were obtained when studying the plugging mortars with additives of oxide of calcium and magnesium. In the presence of magnesium oxide, there is a slight increase in the strength of plugging mortars in the first 24 hours of hardening (by 7.7–15.4 %). However, further reduction in the strength of plugging mortars with this additive proceeds more essentially compared with calcium oxide. Thus, on day 3 of hardening, a reduction in strength compared with an additive-free mortar is 13.2–29.4 %, and at the age of 28 days – 41.6–67.6 %.

Therefore, the introduction of magnesium oxide to the plugging mortar does not lead to a significant expansion of the cement stone in a range up to 300 minutes of hardening. This fact casts doubts on the feasibility of using the given additive in the production of expanding plugging cements.

The most effective is the use of calcium oxide, which expands gradually at temperatures of 22 °C and 45 °C.

The expansion process of both additives finishes quite early at a temperature of 75 °C. Using calcium oxide is not appropriate because the early expansion of the mortar while the formation of structure of the cement stone has not started yet does not lead to the formation of a strong contact between the metal column and the cement mortar. The plugging mortar with a magnesium oxide additive under conditions of the diluted plugging mortar also does not yield a significant expansion.

Thus, under conditions of low and normal temperatures of a wellbore, it is expedient to use the calcium oxide additive, at moderate temperatures – none of the examined additives.

All this indicates that during hardening of the plugging mortar with a calcium oxide additive, with increasing tem-

perature there occurs a substantial acceleration of the hydration processes of the expanding additive, which leads to the formation of crystalline calcium hydrosilicates. This agrees well with the results of research into kinetics of the expansion of plugging mortars with a calcium oxide additive at temperatures of 45 °C and 75 °C, which are given in Table 5, 6.

Similar to the previous case, when using magnesium oxide, there is also a certain decrease in the rate of fall in strength of the samples over a period of hardening. But the overall decline in the strength characteristics of cements with magnesium oxide is so significant that it questions the feasibility of using magnesium oxide as an expanding additive for the plugging mortars.

It is known that magnesium oxide hydration leads to the formation of magnesium hydroxide in the form of plates, fibers or flakes. The physical appearance of the new formations of magnesium hydroxide in the examined stone resembles a mixture of plates and fibers located throughout the thickness of the sample.

All this testifies to the fact that with an increase in the temperature of hardening, the character of the course of the magnesium oxide hydration process changes. A rise in temperature leads to the formation of the larger mass of hydroxide of the latter due to the formation of smaller fibers instead of the large lamellar ones. Total weight of the new formations increases – the expansion of the hardening mass of the plugging mortar also grows, but these new formations of magnesium hydroxide do not possess strength and, in general, the cement stone essentially loses strength in comparison with a calcium oxide additive. This once again confirms inappropriateness of using magnesium oxide as an additive in the manufacture of expanding plugging cements.

## 7. Conclusions

1. We established that the additives of oxide of calcium and magnesium lead to a decrease in the strength of stone at increasing the content in cements. The largest fall in strength occurs in materials containing magnesium oxide. This is due to the fact that during the hydration of cements with the given additive, there occurs the formation of magnesium hydroxide flakes, which do not have sufficient strength. At hardening of cements with a calcium oxide additive, there forms calcium hydroxide, which subsequently participates in the formation of calcium hydrosilicates.

2. It was determined that the cements with a calcium oxide additive are characterized by a much larger expansion compared to the magnesium oxide additive. In addition, the introduction of calcium oxide leads to an earlier beginning of the expansion process. This process also finishes earlier in such cements.

The expansion process of plugging mortars is also largely affected by a calcium oxide additive. Examples of the materials with this additive yield a significantly greater increase in volume compared with the magnesium oxide additive. The expansion kinetics is considerably impacted by the temperature at which this process takes place. With an increase in temperature higher than 45 °C, the intensity of expansion shifts toward the earlier stage of hydration, which makes it inefficient to use both additives in the plugging mortars.

Thus, the use of magnesium oxide as the expanding additive in the production of plugging mortars is impractical due to the negligible expansion under conditions of the diluted plugging mortars and the negative influence on the strength of cement stone.

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