

# Investigation of Interrelation between Deformation, Composition and Structural Characteristics of Magnesium Oxychloride Cements

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**Abstract.** The paper studies the process of volume deformation changes in magnesium cement at its hardening in accordance with its composition and structural peculiarities, which result from the roasting parameters of the raw materials. The study has been carried out with the aim of broadening raw materials sources for production of magnesia cements and construction materials through the use waste products of ore-dressing and processing enterprises. The mineralogical and phase composition of magnesium cements, obtained on the basis of magnesite with high content of impurity minerals from the mine dumps, has been studied by the X-ray phase analysis and derivatography. The roasting of the initial raw materials was carried out at various temperature conditions in order to get cements of different activities. The typical content of hydrated phases has been found for the hardened magnesian stone obtained from cements with different activity degrees. The characteristics of volume deformations developed in the magnesian stone have been described in relation to its phase composition. The influence of low- and high-activity crystals and calcium oxide crystals on the soundness and the structural integrity of magnesian stone has been covered.

## 1. Introduction

Magnesium oxychloride cement is the building material in the form of hardened mixture of magnesia powder and a special activator. Magnesia powder is the active substance in the form of fine magnesium oxide. To date, all magnesia powders (MP) are obtained by heat treatment of raw materials with the high content of magnesium, such as magnesites and dolomites.

The peculiarity of magnesium oxychloride cement is that water solutions of magnesium chloride or sulphate are used as activators. When magnesium oxide is activated with salt solutions, the compressive strength of the hardened magnesian stone reaches 30-70 MPa. Magnesium oxychloride cements activated with magnesium chloride are the most common, because they have the greatest strength.

The hardening process of magnesium oxychloride cement is accompanied by volume deformations. The uneven change in the volume of magnesium oxychloride cement during its hardening followed by the appearance of cracks is one of the significant drawbacks. This reason restrains widespread use of magnesium oxychloride cement in construction.

The causes that are responsible for appearance of cracks during magnesium oxychloride cement hardening have not been studied sufficiently to the present day. They are presumably related mainly to



the phase composition of the initial MP, the hydration peculiarities, and the kind of a hydrate that is formed in the magnesium cement stone.

Many researchers have shown that if magnesia powder is activated with water solution of magnesium chloride, the magnesium oxychloride cement is formed. It includes a mixture of  $\text{Mg}(\text{OH})_2$  and magnesium hydroxychlorides of the  $x\text{MgO} \times \text{MgCl}_2 \times y\text{H}_2\text{O}$  type. According to different sources, "x" varies in the range of 1 to 10, while "y" is in the range of 5 to 21 [1-4]. Recent studies have shown that the magnesium oxychloride cement of normal hardening is formed mainly by hydroxide, magnesium pentaoxyhydrochloride ( $5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O}$ ) and magnesium trioxyhydrochloride ( $3\text{MgO} \times \text{MgCl}_2 \times 8\text{H}_2\text{O}$ ). Its properties depend on the quantitative content of the named phases in the stone [5-7].

Moreover, magnesium pentaoxyhydrochloride exists both in the stable and in the metastable phase. The unstable phase of  $5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O}$  crystallizes, with transition to the stable  $3\text{MgO} \times \text{MgCl}_2 \times 11\text{H}_2\text{O}$  phase [8]. Pentaoxyhydrochloride has the stable existence region at medium concentrations of  $\text{MgCl}_2$  (activator with solution density of  $1.20 \text{ g/cm}^3$  or more) [9,10]. The mixtures of  $\text{Mg}(\text{OH})_2$  and  $5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O}$  or  $5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O}$  and  $3\text{MgO} \times \text{MgCl}_2 \times 8\text{H}_2\text{O}$  may be the equilibrium products of hardening of the magnesium oxychloride cement in such a system. At very low concentrations of  $\text{MgCl}_2$ ,  $\text{Mg}(\text{OH})_2$  is formed in the system. The activating of MP by highly concentrated solutions of magnesium chloride also contributes to the formation of the structure by pentaoxyhydrochlorides and trioxyhydrochlorides. The concentration rise of the activator agent contributes to the increase in the stable pentaoxyhydrochloride phase, and magnesium hydroxide in such systems is formed in small amounts or is altogether absent [11,12].

Later, the molar ratio of  $6 > \text{MgO}/\text{MgCl}_2 > 4$  has been established for a system with an excess of  $\text{MgCl}_2$ , at which the stable phase of magnesium pentaoxyhydrochloride predominates [13-17].

However, none of the studies discussed above has shown how the phase composition of the magnesium oxychloride cement affects its propensity to volume deformations during hardening and operation.

The second possible reason for the unevenness of volume deformation of the magnesium oxychloride cement is the fact that at different degrees of crystallization magnesium oxide is significantly different in activity and properties. Consequently, the hydration and formation of the structure on the basis of different MP will differ in character.

Earlier, while studying calcination characteristics of high-magnesia raw materials, it has been found that the magnesia powder used in construction should be of medium activity and have the  $\text{MgO}$  crystallite size of 38 ... 43 nm. The magnesium oxychloride cement on the basis of such MP hardens gradually. This leads to volume shrinkage of the magnesian stone due to evaporation of the mixing water at the initial hardening time. With the formation of the crystalline framework the shrinkage deformations slow down. Then they gradually transform into expansion deformations due to the slow growth of magnesium hydroxychloride crystallites.

If the roasting time and/or roasting temperature of the raw material are insufficient, crystallites of magnesium oxide have the size less than 38 nm. Such crystallites of magnesium oxide have high activity, characterized by their rapid interaction with the chlorides and hence rapid hardening due to the high growth rate of magnesium hydroxychloride crystallites. Thus it creates a highly stressed expanding block structure prone to cracking. The cement, obtained at excessively high temperatures and/or long roasting times, contains magnesium oxide crystallites of the size up to and exceeding 50 nm in its composition. Even a small amount of such crystallites in the cement powder causes the appearance of internal expansion stresses in the magnesium oxychloride cement, due to its hydration with volume increasing by 2.5 times at later hardening stages.

Besides, roasting of the lumpy magnesia raw material, non-uniform in the fractional composition, can lead to instability of the cement formulation on its basis. This could be due to the possible formation of crystallites with the size less than 38 nm and more than 50 nm in the MP simultaneously [18].

The third cause of the appearance of volume deformations in the magnesium oxychloride cement is relevant, if the raw materials for the MP are waste products of the refractory or mining industry. Usually it is low-grade magnesite with high content of impurity minerals of dolomite and calcium carbonate. For magnesium oxychloride cements the admixture of calcium oxide, formed during decomposition of dolomite and calcite, is considered harmful and should be limited to 5%. The negative effect of calcium oxide on the quality of the magnesium oxychloride cement is confirmed by many researchers [19,20]. The action of calcium oxide hydration is similar to that of hydration of the grains with crystallite size more than 50 nm; it causes uncontrolled extensions in the structure of the magnesium oxychloride cement.

To avoid the appearance of uncontrolled deformations caused by low- and high-activity MP crystallites or impurities of calcium oxide, it is advisable to modify the process of cement production according to the developed recommendations. These recommendations imply the use of technological methods that include physicochemical treatment of raw materials in the form of preliminary grinding followed by granulation (in the presence of intensifier additives, if it is necessary) [21].

Thus, assuming that by changing the conditions for roasting of magnesium rocks for cement production, it is possible to achieve predictable (adjustable) volume deformations of the magnesium oxychloride cement on their basis.

## 2. Research objectives

The present research aims to reveal the relationship between the phase composition of the magnesium oxychloride cement and the nature of the deformations that arise during its hardening.

The main objectives of this research are:

1. Study of the deformation processes of magnesium oxychloride cements on the basis of the magnesium oxychloride cement obtained at various temperatures.
2. Investigation of the mineralogical and phase composition of the samples of the activated solidified magnesium oxychloride cement at the time when their deformation changes end.
3. Investigation of the uniformity of the volume deformations of the magnesium oxychloride cements in order to determine the effect of crystallites with sizes less than 38 nm / more than 50 nm and calcium oxide.
4. Identification of the causes of deformation changes in the resulting magnesium material.

## 3. Materials and methods

Satka magnesium deposit of unregulated fractional composition was chosen as the raw material for MP. Chemical composition (%):  $\text{SiO}_2$  – 0.2;  $\text{Al}_2\text{O}_3$  – 0.25;  $\text{Fe}_2\text{O}_3$  – 0.43;  $\text{CaCO}_3$  – 10.66;  $\text{MgCO}_3$  – 15.73;  $\text{Mn}_3\text{O}_4$  – 0.01,  $\text{CaMg}(\text{CO}_3)_2$  – 60%.

Technical magnesium chloride (bischofite  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) was used as an activator.

Since low-grade magnesite with a high content of impurity minerals, as well as non-standardized fractional composition was selected as the raw material, the combined roasting method was used to produce the magnesium powder. Based on the evidence for the influence of some salts on various magnesium deposits, potassium chloride was chosen as the intensifier additive [22]. In the presence of this additive the roasting temperature of about 600 °C was required to produce the magnesium oxychloride cement. Thus, it helps to avoid the decomposition of calcium carbonate and the calcium component of dolomite, which occurs at temperatures in the range of 700-850 °C.

To determine the temperature dependence of the volume deformations of the magnesian stone for obtaining the magnesium oxychloride cement, three types of this cement were used, obtained by roasting of raw materials at temperatures of 550, 600 and 650 °C for 1 hour. The additive was introduced as the 4% water solution during the wet granulation process. In addition, the magnesium oxychloride cement obtained by roasting at 800 °C for 1 hour without additives was studied. Under these conditions, roasting was carried out for magnesium rocks in lump and finely ground form. The finely ground form was subjected to wet granulation.

Raw materials, samples of magnesium oxychloride cements and hardened magnesium oxychloride cements were subjected to complex study using thermal analysis, X-ray phase analysis and standard methods. Thermal analysis of the minerals was carried out by a "Luxx STA 409" derivatograph system of the German company "Netsch". The rate of temperature rise was 10 °C / min; the maximum heating temperature was 1000 °C. Platinum crucibles were used for the test, heated in a nitrogen atmosphere. The X-ray phase analysis was performed on a DRON-3M device upgraded with a PDWin attachment at the 30 kW voltage, the 10 mA current, and the 1 mm width of the output slit. The surveys were conducted within the angular interval 6-70 °.

To determine the physicochemical properties of the magnesium oxychloride cement, the following techniques were used.

The normal thickness for the cement was determined according to the procedure of GOST 1216-87 "Magnesium caustic powders" with a Vicat apparatus.

Investigation of volume deformations was carried out by a Schwindmessgerät Typ B shrinkage measuring devices in accordance with GOST 24544-81, DIN 52450. The weight of the cement sample was 100 g. The amount of the activator was equal to the water/powder ratio of the least active magnesia powder. Formation of the samples was carried out in non-removable formwork. The measurement of deformations was begun from the moment of activating the magnesium oxychloride cement.

The uniformity of the volume of the hardening binder was determined by the method of TU 5744-001-60779432-2009 on the samples in the form of flat plates.

#### 4. Experimental

Preliminary experiment for determination of the crack appearance was carried out on the samples in the form of flat plates. The samples were hardened for 24 hours in air. Then they were placed in water. After 24 hours the samples were tested for the appearance of cracks under a microscope. Microcracks were found in the samples of MP obtained by roasting at 800 °C (both in lumps and in granules). In addition, these samples underwent collapsing after the 6th day of storage in air.

Quantitative changes in volume deformations were carried out by the instruments for shrinkage measuring. Measurements were taken every minute during the first hour after activating. The subsequent measurement frequency was once in half an hour. The measurements were carried out for 28 days.

The graphs show that the volume deformations of the magnesium oxychloride cement obtained with the use of additives are similar in character. The deformation nature of MP, roasted in lump, has no regular pattern. This phenomenon is explained by the presence of grains with sizes more than 50 nm in the magnesia powder. Such grains are hydrated at later times of hardening. This way, chaotic deformations of expansion can be caused, as well as subsequent shrinkage, sometimes. Shrinkage deformations at the initial hardening time are typical for all types of magnesium oxychloride cements. It is explained by the evaporation of chemically unbound water from the colloidal system. At the beginning of the setting, due to the gradual formation of the crystallite framework, the shrinkage deformations slow down. Then they gradually transform into expansion deformations due to the slow growth of magnesium hydroxychloride crystallites.

At later times of hardening, the MP obtained at a roasting temperature of 550 °C shows stable and active growth of expansion deformations. On the graph illustrating the cement obtained at 600 °C this process is less pronounced and ends within 28 days. For the MP obtained at 650 °C this effect is not observed, and a slight shrinkage process continues in the stone. In addition, the formation of salts is observed on the surfaces of the magnesium oxychlorides samples obtained by low-temperature roasting. Thus, it can be concluded that in the process of hydration in such a magnesium oxychloride cement,  $\text{Mg}(\text{OH})_2$  crystallites are formed. They do not bind the anions of magnesium chloride. Magnesium hydroxide is a fairly active compound and can undergo carbonization processes over time. These processes are accompanied by an increase in volume and can be indicated by a sharp increase in 5 days in the volume of the 550 °C cement sample.

The X-ray analysis has been carried out to control the phase composition of the samples of hardened cements. According to it, all the samples contain magnesium hydroxide compounds ( $d = 4.77, 2.365, 1.794 \text{ \AA}$ ), magnesium pentaoxyhydrochlorides ( $d = 7.7, 4.17, 2.43, 2.39 \text{ \AA}$ ), and magnesium trioxyhydrochlorides ( $d = 8.3, 3.88, 2.46, 4.08, 2.71 \text{ \AA}$ ), the residues of magnesium carbonate ( $d = 2.737, 1.697, 2.101, 1.935 \text{ \AA}$ ) and dolomite ( $d = 2.883, 1.785, 2.191, 1.110 \text{ \AA}$ ), as well as ferruginous residues in the form of  $\text{FeOOH}$  ( $d = 4.18, 2.45, 2.69, 1.720 \text{ \AA}$ ) and  $\alpha\text{-FeO}_2$  ( $d = 2.694, 2.513, 1.842, 2.203 \text{ \AA}$ ).

To analyze the quantitative content of key phases in the magnesium oxychlorides cements samples, thermal analysis by derivatography method has also been carried out. According to the derivatogram data, the summary table of the quantitative content of the phases in the samples has been compiled (Table 1).

**Table 1.** Quantitative content of the phases in the samples.

	$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{CaMg}(\text{CO}_3)_2$	$\text{Mg}(\text{OH})_2$	$5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O}$	$3\text{MgO} \times \text{MgCl}_2 \times \text{H}_2\text{O}$
550°C	2	2	6,2	20	48	24
600°C	2	2	6	9,6	45	34
650°C	2	1,5	5,0	6,4	64	21
800°C	2	-	4,0	12	34	27

Based on the data obtained during the study, the following conclusions can be drawn. The magnesium oxychloride cement, obtained on the basis of magnesia powder of low-temperature roasting, has the highest content of magnesium hydroxide in its composition. As the roasting temperature rises, the presence of the magnesium hydroxide phase in the magnesium oxychloride cement is reduced. However, in the stone of the magnesium oxychloride cement, obtained at a temperature of  $800^\circ \text{C}$ , the amount of magnesium hydroxide increases. This phenomenon can be explained by the presence of  $\text{MgO}$  crystallites with different degrees of activity in the powder.

The amount of calcium carbonate for all samples remains unchanged. It is approximately equal to the amount of calcium carbonate in the initial material, since its decomposition temperature is higher than the roasting temperature of this MP. The residue of undecomposed magnesium carbonate is present in the samples of the  $550^\circ \text{C}$  and  $600^\circ \text{C}$  MP.

Dolomite is present in all samples. As roasting temperature increases, its amount decreases. The oxyhydrochloride phases are the main minerals formed in the stone of the magnesium oxychloride cement; they form a large part of the structure of all the test samples. The  $5\text{MgO} \times \text{MgCl}_2 \times 13\text{H}_2\text{O} / 3\text{MgO} \times \text{MgCl}_2 \times \text{H}_2\text{O}$  ratio varies from 3/1 to 1/1 in different samples. It is correlated to the  $\text{MgO} / \text{MgCl}$  ratio in the samples.

The additional phases present in the powders of different roasting are the residues of the initial minerals of calcium carbonate, magnesium carbonate and dolomite. They are inert and do not react with the activators.

Magnesium hydroxide is a sufficiently active compound. It can be subjected to carbonation processes accompanied by an increase in volume over time. At the same time, oxyhydrochloride phases tend to slightly change the volume during hydration, which does not lead to significant shrinkage.

The unstable phase composition of the magnesia powder, obtained at insufficient roasting, causes non-simultaneous hydration processes. As a consequence, weakly crystallized crystallites of magnesium oxide primarily form magnesium hydroxide. Crystallites of magnesium oxide of normal activity form compounds of pentaoxyhydrochloride and trioxyhydrochloride at a later date. Lastly, hydration of low-active magnesium oxide crystals and carbonation processes of hydroxide constituents occur. Together, these phenomena cause destructive deformations in the hardened stone.



## 5. Conclusions

In the presented results of the study, a relationship between the phase composition of the magnesian stone and the nature of the deformations that arise during its hardening has been established.

In the initial period of hardening shrinkage deformations in the magnesian stone are the result of the removal of the chemically unbound water from the system. They cease at the end of the setting time. Gradual formation of the crystalline framework slows down shrinkage deformations. The subsequent transition to expansion deformations is also explained by the continued slow growth of magnesium hydroxide and magnesium oxyhydrochloride crystallites.

A significant amount of weakly crystallized  $\text{Mg}(\text{OH})_2$  crystals is formed in the magnesium oxychloride cement on the basis of the powder that is obtained by low-temperature roasting in the presence of intensifier additives. It can subsequently lead to an increase in the volume due to carbonization.

Magnesia powders obtained by roasting at optimal temperatures (600-650 °C) have normal activity. They are hydrated mainly with the formation of oxyhydrochloride phases, accompanied by a slight increase in volume. The main shrinkage in the activated magnesia powder proceeds mainly to the end of setting, when it is in the viscous-plastic state. Thus, it does not cause cracks in the hardening material.

The powder obtained by roasting the granulated raw material without additives at a moderate temperature (800 °C) is mainly composed of magnesium oxide crystallites of increased activity. Also it has inclusions of magnesium oxide crystallites with different degrees of roasting. Magnesian stone based on such a powder is quickly activated and has significant expansion deformations at the initial time of hardening. With further hardening, the process of increasing expansion deformations continues over a long period with lesser intensity. Magnesium oxide crystals of medium and low activity gradually continue the hydration reaction.

Magnesia powder, obtained without the use of recommended modifications of the roasting process, has crystals of low activity in its composition, as well as harmful impurities of calcium oxide. Hydration of such formations in the later stages of hardening of the magnesian stone leads to chaotic volume expansions of the structure with its subsequent destruction.

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## References

- [1] Biliuski H, Matcovic B, Mazuranic C and Zumic T 1984 *Amer. Ceram. Soc* **67** pp 266–9
- [2] Nanazashvili I 1990 *Building materials and wood-cement compositions* **470**
- [3] Yanshin A 1960 *Refractories* **11** pp 505–15
- [4] Matcovic B, Popovic S, Rogic V and Zunic J 1977 *Amer. Ceram. Soc.* **60** pp 504–7
- [5] Chumak V 2003 *Building Materials* **9** pp 10–11
- [6] Rogic V and Matkovic B 1972 *Cement (Zagreb)* **16** pp 61–9
- [7] Catherine S 1987 *Industrial minerals* **2** pp 43–8
- [8] Bergman G and Vyrodov I 1958 *ZhPKh* **3** pp 119–24
- [9] Bergman G and Vyrodov I 1959 *ZhHKh* **32** pp 504–9
- [10] Vorobiev V and Kolokolnikov V 1960 *Manufacture of mineral binders* **304**
- [11] Vyrodov I 1960 *ZhPKh* **33** pp 2399–404
- [12] Filatkin A 1937 *Building Materials* **2** pp 39–41
- [13] Gordon R and Beinlich A 1946 *J. Amer. Cer.Soc. Bull.* **29** pp 208–22
- [14] Maravelaki-Kalaitzaki P and Moraitou G 1999 *Cem. And Concr. Res.* **29** pp 1929–35
- [15] Mayska M and Jindrich D 1997 *Ctramis-Silikaty* **41** pp 121–3
- [16] Averina G F, Chernykh T N and Kramar L Ya 2016 *Trends in the Development of Science and*

*Education*

- [17] Vayvad A 1971 *Magnesian astringents* (Riga: Science) 315
- [18] Beruto D T, Vecchiattini R and Giordani M 2003 *Thermochimica Acta* **1** pp 25–33
- [19] Noll W 1950 *Angew. Chem* **62** pp 567–72
- [20] Haul R A and Heystek H 1952 *Am. Mineralogist* **5** pp 166–79
- [21] Hedvall J A 1953 *Z. anorg.allg.Chem.* pp 22–33
- [22] Chernykh T N, Orlov A A, Kramar L Ya and Averina G F 2015 *Perspective Materials in Engineering and Construction: PMTC* pp 427–30