

Effect of additives on hydration and hardening of magnesia compositions

*Olga Miryuk**

Rudny Industrial Institute, Republic of Kazakhstan

Abstract. The article is devoted to the investigation of the influence of technological factors on the hydration and hardening of magnesia compositions. The objective – is investigation magnesia compositions with different additives. Factors which impact activity of magnesium oxide in compositions of different structure are investigated. Influence of liquid density on hardening of magnesium bindings is defined. Processes of hydration and hardening of magnesium bindings with participation of minerals – silicates are investigated. It is revealed that the addition of semi-aquatic calcium sulfate contributes to the hardening of magnesia binders. Defined effect of concentration calcium sulfate hemihydrate to the hardening of caustic magnesite. Here are proposed structures of sulphomagnesia compositions containing technogenic components. It revealed a beneficial effect on the hardening of ferrous component of the mixed magnesia binder. Composition of hydration products of magnesium binding with participation of ferriferous minerals is presented. Transformations of phases at hydration of magnesium binding are revealed. Influence of structure of bindings on transformations of hydrates is established. Results of research of magnesia bindings of long hardening are given. It is shown that the durability of stone of bindings is provided with dense structure of hydrates. In researches are used X – Ray and thermal methods, electronic microscopy.

1 Introduction

Magnesia binders reveal activate capacity in relation for various materials. This became background for getting mixed binders from caustic magnesite and mineral component [1 – 7]. The combination of caustic magnesite of natural and technogenic materials expands the range and increased the volume of magnesia binders. Magnesia compositions characterized by low energy intensity of production, intensive hardening and high strength. Containing of magnesium component in the composition of mixed binders is 50 – 70 %. Recourses of magnesia rocks are limited. It is necessary to reduce deficit caustic magnesite in the composition with mixed binders. The advantages of mixed binders are to improve the physical and mechanical properties while saving caustic magnesite and rational use of natural and technogenic raw materials. The purpose of the work is synthesis and investigation magnesia compositions with different additives.

* Corresponding author: psm58@mail.ru

2 Methodology

For experiments were used: caustic magnesite mark PMK – 75, building gypsum mark G – 5AII, minerals from geological collections, technogenic materials. In the experiments used minerals that are predominant in the composition of the studied technogenic materials (wastes from enrichment of skarn-magnetite ores, screening of granodiorite crushing, wastes from extraction of gold-copper ores, screening of plagioclase crushing, slag metallurgical).

Binding compositions were prepared by thoroughly mixing fine components. Strength properties were determined on samples with size 20x20x20 mm, made with dough of normal density. Magnesia composition hardened in air and in a humid environment, taking into account the objectives of the experiment.

The phase composition of the materials was determined using general purpose X-ray diffractometer type DRON-3M. The diffractometer is equipped with an BSV-24 type X-ray tube with CuK α -radiation. The diffractograms were processed using the difWin program. Thermochemical processes were studied by the differential thermal analysis method, which was carried out on a derivatograph of the «MOM» firm of the F.Paulik, I.Paulik and L.Erdey systems. The structure of the compositions was investigated using a JSM – 649OLV Energy scanning electron microscope.

3 Results and discussions

Structure of magnesium binders is unique by presence of magnesium oxide, which in comparison with calcium oxide is slightly soluble and slowly reacts with water. This is [2, 4] due to skinning effect $Mg(OH)_2$, which is prevent from water penetration into deep into the grain binder. Hardenings of magnesia materials, mixing with water, do not have much practical value.

With the introduction of salt (chloride or magnesium sulfate), into hardener significantly increased solubility of magnesium oxide, increases degree of supersaturation and accelerates the crystallization of brucite, forms hydro oxide salt.

Magnesia binders, mixing a solution of magnesium chloride hardens rapidly, are highly durable. Caustic magnesite, coupled with a solution of magnesium chloride activates siliceous, aluminosilicate and other substances. This capability is implemented in the magnesium binder compositions using natural and anthropogenic materials. Activity of MgO in compositions depends on many factors. The nature of these factors requires clarification.

3.1 Activity of magnesium oxide in magnesium compositions

The influence of the type of the liquid component on the hydration of the magnesia binder was investigated. The nature of changes in the content of basic hydrates was determined by the intensity (height) of the main diffraction reflections of hydrates using X – ray analys (Fig. 1). Increasing density of solution $MgCl_2$ in the limits 1150 – 1400 kg/m^3 for caustic magnesite limits or fully exclude formation of $Mg(OH)_2$; provides growth of containing magnesium pentahydrate oxychloride $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ («5 – form»), which is prevail in the composition of crystalline hydrate using solution with density 1250 – 1400 kg/m^3 (Fig. 1). A large proportion of the «5 – form» is formed in the early stages, providing a high rate of hardening stone.

As part of a binder, mixing solutions of high density (1350 and 1400 kg/m^3), identified hydrated complex $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ («3 – form») – magnesium trihydrate oxychloride. Hydrate «3 – form» is formed by recrystallization of a small part of

«5 – form». There is no clear relationship between the concentration of $MgCl_2$ solution, and the degree of hydration of MgO . This indicates the dependence of activity MgO from content and structure of hydrates.

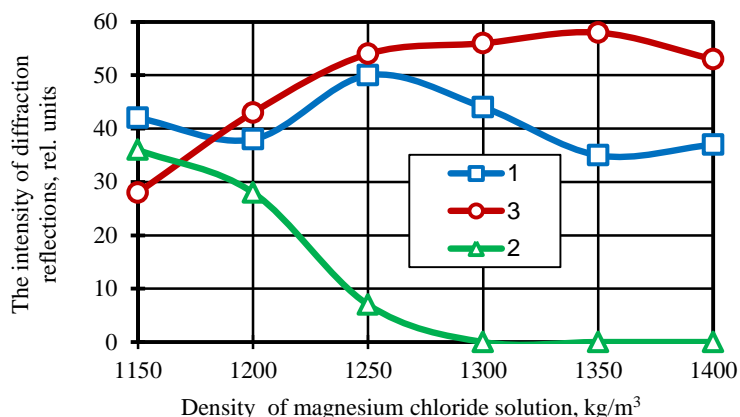


Fig. 1. Influence of sealer density on phase composition and strength of caustic magnesite stone (7 days): 1 – MgO ; 2 – $Mg(OH)_2$; 3 – $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$.

Along with salt solutions, magnesium binders are recommended to temper with acids solution HCl [7]. To obtain comparative characteristics was used $MgCl_2$ solution with density of 1250 kg/m^3 and complex solution (solution of $MgCl : HCl : H_2O - 2:1:1$, volumetric parts).

When tempering caustic magnesite with complex solution hydration level of MgO is increased on 6 %. In the cured binder is formed $Mg(OH)_2$. A content of magnesium pentahydrate oxychloride reduces on 28 %, which is lead to decreasing strength of the stone. Staying in the water samples twice reduces the proportion of the initial MgO ; provides a significant increase quantity of $Mg(OH)_2$. There is a part of hydrate $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ in the water.

According to the X – ray analysis, in the stone, which was hardened 28 days, save up to 30 % uncombined MgO .

The tendency of growth activity of MgO and increasing the degree of its transformation into hydrate oxychloride complexes safes when added to the caustic magnesite mineral component. Character of hydrate formation with participation MgO also depends on the composition of the mineral component. These approve results of investigations binders of caustic magnesite (35 %) and minerals – silicates (65 %), tempered with solution of magnesium chloride with density 1220 kg/m^3 (Table 1).

The highest degree of conversion of magnesium oxide is characteristic for compositions containing silicates insular structure (andradite and epidote), which are more prone to hydrolytic decomposition in a solution of magnesium chloride.

Another indication of the influence of material composition on hydration activity of magnesium oxide and the composition of hydrates is the nature of phases changes in mixtures MgO with Al_2O_3 and SiO_2 (additive content 45 %). Ratio of diffraction intensity reflections of magnesium oxide for binders consisting of MgO , « $MgO + Al_2O_3$ », « $MgO + SiO_2$ », respectively, equal to 1 : 0.5 : 0.3; the diffraction reflections of magnesium pentahydrate oxychloride – 1 : 3.6 : 4.3.

Important indicator of phase activity is hydration with prolong hardening. Here are investigated mixed binders, tempered with solution $MgCl_2$ with density 1250 kg/m^3 and which were hardened in various mediums during 5 years.

Table 1. Influence of minerals structure on phase content in hardened mixed magnesium binders.

Mineral	The intensity of the diffraction reflections of phases, rel. units					
	MgO (0.148 nm)		Mg(OH) ₂ (0.157 nm)		5Mg(OH) ₂ ·MgCl ₂ ·8H ₂ O (0.196 nm)	
	7 days	80 days	7 days	80 days	7 days	80 days
	No	100	87	100	93	100
Andradite	43	35	29	30	93	100
Epidote	53	44	33	33	116	114
Albite	66	47	no	no	139	161
Diopside	64	52	23	25	91	99

By the data of X – ray analysis, stone crystal foundation of air hardening are form hydrate oxychloride complexes, formed on initial stages of hydration. Presence of 20 % free MgO indicates on not full realization binding properties of component. This can serve as recourse for further hydro formation. In the stone of water hardening saves up to 5 – 10 % of initial MgO; contains Mg(OH)₂, formed by the decay of a significant amount of hydrates.

Replacement of magnesium chloride by complex temper (solution MgCl₂ : HCl : H₂O – 2:1:1, volumetric parts) for the mixed binder is accompanied by a slight slowing of the hydration MgO in the initial period of hardening; formation of Mg(OH)₂ in the stone of binder; formation hydrate oxychloride complexes in amounts comparable with the content of these phases in the composition, tempered with MgCl₂ solution. Staying samples of hardened binder in water accelerates the hydration of MgO and helps to complete the process to 28 days of hardening. As part of the stone increases number of Mg(OH)₂ and reduced the proportion of 5Mg(OH)₂·MgCl₂·8H₂O.

With complete elimination of magnesium chloride from the structure of temper and use of hydrochloric acid solution with density 1050 kg/m³ hydration activity of magnesium oxide is changed slightly. In this case MgO in the mixed binders also differs by high speed of hydration. Strength values of samples based on HCl solution are reduced nearly threefold compared with salt temper. However, staying samples in water within 60 days provided the increase of strength on 40 % compared with similar samples of air hardening. Hardening of the stone in the water promoted complete hydration and participation of MgO in the formation of hydromagnesium. This confirms the reduction intensity of the diffraction reflections of minerals and invariability of reflexes Mg(OH)₂ on diffraction patterns of binder with various degrees of hydration of MgO.

Therefore, changing the recipe of magnesia binders allows you to adjust the type and amount of hydrates, affect the construction and technical properties and durability of materials. The greatest increase in the hydration activity of magnesium oxide in magnesia compositions is achieved by the addition of minerals. It has been revealed that according to the degree of participation in hydration processes, comprising 25 – 60 %, the minerals – silicates are located in the series: albite → epidote → andradite → diopside. The effect of minerals is as follows: an increase in the degree of conversion of MgO to magnesium hydroxychlorides; minimization of Mg(OH)₂; predominance of 5Mg(OH)₂·MgCl₂·8H₂O. Purposeful selection of a salt solution for magnesia compositions provides an increase in the degree of hydration of magnesium oxide, the formation of hydrates, more resistant to exposure to the aquatic environment.

3.2 Investigation of sulfomagnesium compositions

The advantage of adding calcium sulfate to magnesia binder is mentioned in work [5]. For optimization the concentration of gypsum component investigated series of compositions «caustic magnesite – semi-aquatic calcium sulfate», tempered by solution of $MgCl_2$.

With the introduction semi-aquatic calcium sulfate reduced water demand, prolonged time of setting binder. Replacement to 60% of caustic magnesite semi-calcium sulfate does not reduce the strength of the compositions, which in some cases exceed the benchmark on 25% (Fig. 2). Hardening of sulfomagnesium binder takes place at the initial hydration of MgO . Activity MgO rises with increasing of gypsum component. In the structure of hydrates dominated $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$. In low magnesium binders also formed $Mg(OH)_2 \cdot MgCl_2 \cdot 2MgCO_3 \cdot 6H_2O$.

Hardening sulfomagnesium binders is occur in initial hydration of magnesium oxide, which activity rises with increasing portion of building plaster (Table 2). The highest degree of hydration of MgO is typical for the first 7 days, later reactive ability of phase reduced. Effect of temper concentration on the activity of MgO sulfomagnesium binders is inexpressively. In the structure of new formations is prevail $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$. With In the process of hydration of binders with a low content of the magnesia component a complex carbonate-containing hydrate $Mg(OH)_2 \cdot MgCl_2 \cdot 2MgCO_3 \cdot 6H_2O$ is formed. Intensive formation of magnesium hydrate complexes provides high strong characteristics of sulfomagnesium binder.

High values of hydration activity and strength of sulfomagnesium binder let use it as an activator of hardening. Were investigated compositions based on sulfomagnesium binder and anthropogenic materials in the component ratio 50 : 50, %. As temper were used magnesium chloride and sulphate solutions with density 1250 kg/m^3 . Caustic magnesite was a control composition.

The introduction of technogenic component reduces the volume of solution on 32 – 37 % compared with the caustic magnesite.

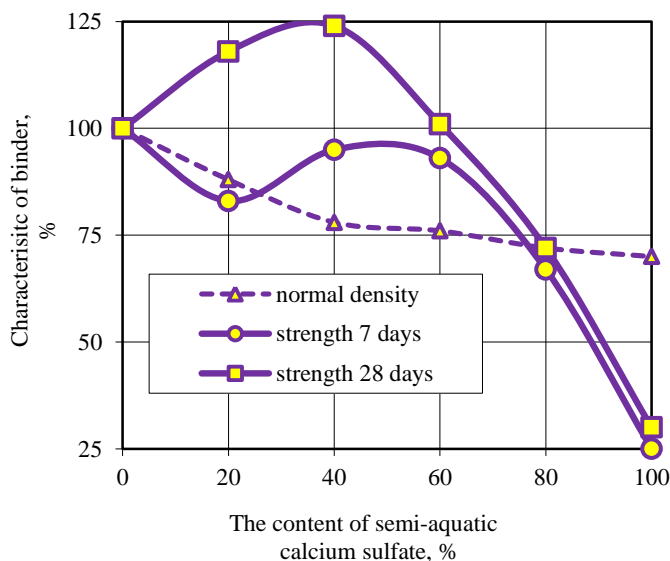


Fig. 2. Influence of semiaquatic calcium sulfate on properties sulfomagnesium composition.

Table 2. Containing phases in the hardened sulfomagnesium binder (40 % CaSO₄·0,5H₂O).

Density of solution MgCl ₂ , kg/m ³	Age, days	The intensity of the reflection phase in the diffraction pattern, relation of units	
		MgO (0.148 nm)	«5 – form», (0.196 nm)
1240	1	102	190
1240	90	90	185
1200	7	98	165
1240	7	96	210
1280	7	97	260

The greatest influence on the hardening mixed binders has composition of salt solution. The use of MgCl₂ solution provides increased hydration activity MgO, contributes to the intense stone hardening and increases its strength on 12 – 70 %. The high strength characteristics of three-component binders – is the result of a joint magnesium – chloride and sulfate activation of hardening anthropogenic material. Activity of technogenic component depends on the structure and chemical properties of minerals. The greatest strength is achieved with the introduction of wastes from enrichment of skarn-magnetite ores and screening of plagioclase crushing.

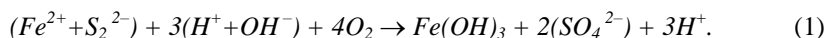
3.3 Hardening of magnesia compositions containing ferrous component

The range of the magnesia cement extends at the expense of compositions from the caustic magnesite and filler. Preference of ferriferous by-product additives in the magnesia cement is noted [7, 10].

For receiving the binding materials used the caustic magnesite, chemical reactants, and natural minerals. Binding materials added water to a mix of magnesium chloride. Phase structure of the hardened compositions was estimated by X – ray and differential thermal methods. Stone structure of the binding materials was investigated by the means of electronic microscopy.

Nature of curing of binding materials depends on the maintenance of MgO. The analysis of diffraction patterns revealed that with increase in a share of Fe₂O₃ MgO hydration is accelerated. In comparison with binding materials, which containing SiO₂ and Al₂O₃, in composition the Fe₂O₃ hyperactivity of MgO. The extent of transformation of Fe₂O₃ in hydrates 5 – 18 %. Basis of the hardened binding materials forms 5Mg(OH)₂·MgCl₂·8H₂O. Place the figure as close as possible after the point where it is first referenced in the text. If there is a large number of figures and tables it might be necessary to place some before their text citation.

Pyrites Fe[S₂] – the widespread sulfide of crust. Possibility of introduction 70 % of pyrites in magnesium knitting is proved. As a part crystalline hydrates prevails 5Mg(OH)₂·MgCl₂·8H₂O. 40 – 60 % of pyrites are involved in hydrate formation of the binding materials. Processes of hydrolysis and the oxidations of pyrites accelerated in MgCl₂ solution are presented by the scheme:



Exothermic effect at 550°C characterizes oxidation of pyrites (Fig. 3). Pentahydroxichloride of magnesium remains in composition of long-term curing. The microconglomerate structure of a stone from particles of various morphology promotes consolidation and increase of stability of structure to destructive processes (Fig. 4).

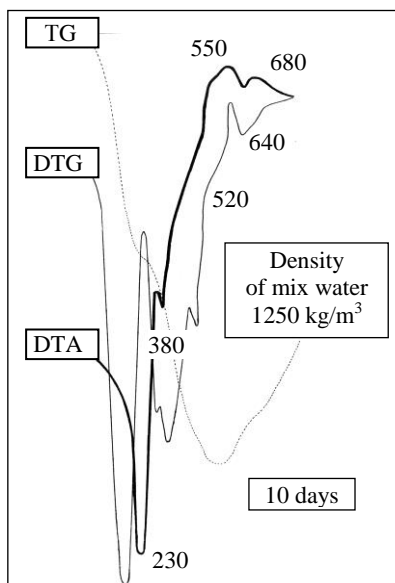


Fig. 3. Thermogram of magnesium composition stone with 70% of pyrites.

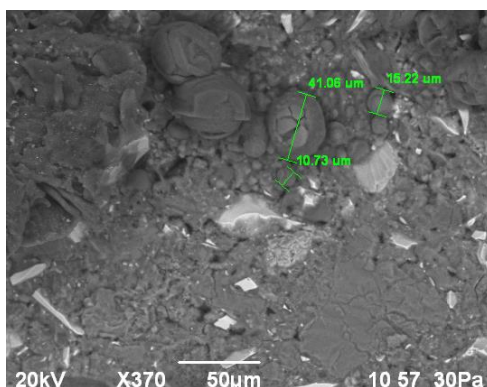
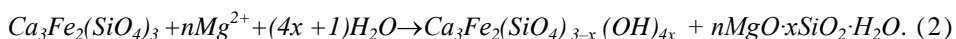


Fig. 4. Microstructure of magnesium composition stone with 70% of pyrites after 10 years curing.

Andradite $\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$ – the widespread scans mineral, provides stable curing of the binding materials. Compositions from 30 – 60 % of andradite are investigated. The main hydrate phase is $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$.

General scheme of probable transformation of andradite:



Hydrate of $\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ is formed after 1 days of curing. Intensive formation of hydro-oxchloride carbonate magnesium is promoted the increase in a ratio of $\text{MgCl}_2:\text{MgO}$ in the binding materials. The extent of andradite transformation in the hydrates, defined by X – ray method, was made 20 – 23 % for 7 days.

Therefore, magnesium compositions, containing pyrites are characterized by high hydration ability, the formation of hydrates, strengthening the structure of materials.

High strength properties of pyrites-containing binders are provided by the activating effect of sulfate-ions on the hydration ability of MgO ; optimization of the ratio of crystalline and amorphous hydrates.

4 Conclusions

For the first time magnesia compositions, containing minerals, present in technogenic materials, were studied. It has been established, that the introduction of minerals contributes to an increase in the activity of MgO; the predominance of $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, which provides high strength properties of the stone; the formation of $\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$; competition in the formation of hydrate complexes.

It is shown, that a change in the composition and density of the salt solution enhances the effect of minerals on the hardening of magnesia compositions. The dependence of the composition, amount and stability of hydrates on the concentration of MgO and MgCl_2 , the type and activity of the mineral was determined.

Proved high reactivity of iron supplements for hardening magnesia compositions. The nature of the influence of minerals has been revealed, hydrate formation schemes have been proposed based on common technogenic wastes minerals (pyrites, andradite). Reactionary ability of a ferriferous component provides high activity of magnesium composition of oxychloride curing, variety of crystal and gel hydrates.

The possibility of obtaining magnesia compositions with a high content of calcium sulfate (40 – 60 %). Efficiency of sulfomagnesium compositions determined by the possibility of replacing part of caustic magnesite by gypsum binder and technogenic component, with saving high technical characteristics of material.

The development of mixed magnesia binders using technogenic wastes is aimed at expanding the resource base and increasing the durability of efficient building materials.

References

1. Z. Xiangming, L. Zongjin, *Const. Build. Mat.* **27**, 382 (2012)
2. M. Jianli, Z. Youcai, W. Jinmei, W. Li, *Const. Build. Mat.* **24**, 79 (2010)
3. D. Zhu, L. Zongjin, *Cem. Conc. Comp.* **27**, 11 (2005)
4. V. N. Zyryanova, E.V. Lytkina, G.I. Berdov, *Tech. Technol. Silic.* **17**, 2 (2010)
5. Z. Li, C. K. Chau, *Cem. Conc. Comp.* **37**, 866 (2007)
6. K. Yildirim, M. Sümer, *Comp. Eng.* **52**, 56 (2013)
7. O. A. Miryuk, *ARPN J. Eng. Appl. Sciences*, **13**, 545 (2018)