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Magnesium-Containing Slurry as Technogenic Alternative Raw Material for Magnesium Oxychloride Cement

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Abstract. It has been shown experimentally that a waste of magnesium metal production is a realistic alternative to naturally occurring cement raw materials. The waste is the carnallite slurry forming during the chlorination stage. The slurry contains magnesium oxide (MgO) and magnesium chloride (MgCl₂) in a mass ratio close to their optimal ratio when preparing Sorel cement. It is found that the magnesium oxide in the slurry is highly reactive. MgO extracted from the slurry and MgCl₂ solution are mixed forming homogeneous magnesium oxychloride cement (MOC) paste in which bonding crystalline structures typical for Sorel cement are formed during hardening.

1. Introduction

Magnesium oxychloride cement (MOC) are widely used in the construction industry. Traditional MOC raw materials are natural minerals such as magnesite, dolomite, and brucite. However, the shortage of naturally occurring cement raw materials, arising environmental challenges associated with waste management, as well as the high cost of caustic magnesia binders require to find alternative raw materials for manufacture of magnesium-based cements. The excellent solution for that is using magnesium-containing technogenic raw materials [1,2] with a special focus on a MgO- and MgCl₂-containing waste such as the carnallite slurry forming during the chlorination stage of magnesium metal production.

The aim of this study was to determine chemical, phase, and radionuclide compositions of the slurry forming during magnesium metal manufacturing, VSMPO-AVISMA Corporation, Russia; to study the hydration kinetics of MgO containing in the slurry, binding properties of MgO and the slurry, and to develop technology for recovering and recycling the carnallite slurry to MOC powder.

2. Research methods

The slurry for the study was prepared (regeneration) by mechanical crushing, grinding to a particle size varying between 100–200 µm and fractionating. A laboratory unit for fractionation consisted of a jaw crusher and ball mill equipped with a cyclone for dust collection. Screen size gradation was used to fractionate the powder. The slurry prepared for the study was stored in hermetic containers to avoid the hydration of MgO containing in the slurry.

Quantitative determination of the chemical composition of the slurry was investigated by chemical and X-ray diffraction analyses. Chlorides of alkali metals were determined by flame spectrophotometry; magnesium-containing compounds were determined by complexometric titration.



X-ray diffraction analysis was also used to reveal the phase state of individual compounds containing in the slurry. X-ray patterns of the studied slurry samples were shot on auto-diffractometer STADI- (STOE, Germany), copper $K\alpha$ radiation, an interval of angles 2θ from 5° to 80° , step of 0.02° . The compounds were identified according to "Base powder standards JCPDS-ICDD PDF2" (ICDD, USA, Release 2003).

Reactivity of MgO extracted from the slurry, was determined by the degree of its hydration at temperatures of 40, 60, and 80°C in systems $\text{MgO}-\text{H}_2\text{O}$ and $\text{MgO}-\text{MgCl}_2-\text{H}_2\text{O}$. Magnesium oxide was extracted from the slurry by hydroleaching the soluble salts (MgCl_2 , KCl , NaCl); the formed heterogeneous mixture was separated by filtration, the resulting residue after the filtration was washed by water, then by acetone, made it air-dried and kept in hermetic containers. According to X-ray diffraction analysis the MgO content in the residue was 97 % wt. The hydration of MgO was investigated by thermogravimetric analysis. Derivatograms of hydrated MgO samples were filmed with derivatograph Q-1500D. The investigated samples were heated in air medium in crucibles to a temperature of 700°C at rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The sample mass was 1000 mg, the sensitivity of DTA-250, both TGP and TG – $500\ \mu\text{V}$. The product compositions after the hydration were determined by X-ray diffraction analysis and infrared spectroscopy.

The experimental values of the degree of MgO hydration were calculated according to derivatograms. To do this, the established ratio of the mass loss in the samples were related to stoichiometric amounts of products after thermal decomposition of crystallohydrate structures $\text{Mg}(\text{OH})_2$ and $3\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$. The rate of the MgO hydration in the investigated mixtures was calculated according to the results of kinetic studies on the equations of Kolmogorov–Erofeev and Sakovich [3].

The role of MgO in the formation of crystallohydrate structures was revealed experimentally according to X-ray diffraction analysis. Normal density magnesium mixture, start and final moments of its setting, formed when mixing MgO with MgCl_2 solution, and the slurry – with water, were determined in accordance with GOST 310.3–76 using Vika tool. Binding properties of MgO and the slurry were estimated by the compressive strength values of the laboratory samples of magnesium stone, shaped in the form of cylinders, diameter and height 20mm and seasoned for 3, 7, and 28 days for strength developing. The samples were subjected to destruction under dynamic load test on a hydraulic press 2NG–10 with evenly increasing speed of 1 mm/s.

Toxicological tests of the slurry were carried out in the Center of State Sanitary and Epidemiological Supervision, Sverdlovsk region. The natural radioactivity of the slurry was determined by the method of γ -spectrometry.

3. Results and discussion

Methods of chemical analysis identified the substance composition of the slurry, which is composed of 98.4 wt. % of NaCl , KCl , MgCl and MgO . Impurity compounds containing in the slurry are SiO , FeO , AlO and CaCl_2 and BaCl_2 $4.0\cdot 10^{-1}$, $2.7\cdot 10^{-1}$, $9.0\cdot 10^{-2}$, $2.0\cdot 10^{-3}$ $4.3\cdot 10^{-4}$ wt. % respectively.

When studying several sets of the slurry samples taken at the site for dehydration of carnallite melting in VSMPO-AVISMA Corporation, Russia, it was revealed that the vertical cut of the slurry ingot is a "layer cake" and each layer is differently coloured: white (upper layer), grey (middle layer) and yellow (bottom layer). The differently coloured slurry samples were analyzed to detect quantitative content of the main chemical compounds and their phases by chemical and X-ray diffraction analyses (table 1).

The white layers were characterized by high content of the water-soluble chemical compounds MgCl_2 , KCl and NaCl , which, when cooling the slurry melting, "were getting salted out" to the upper parts of the ingots. MgO was almost absent in the upper parts.

The grey layers were presented by magnesium components (MgO , MgCl_2), their contents were 35.0 и 27.3 wt. % respectively according to chemical analysis.

Table 1. Mass fraction (%) of main chemical compounds in the differently coloured layers and in the averaged sample.

Slurry color	Chemical analysis				X-ray diffraction analysis			
	MgO	MgCl ₂	NaCl	KCl	MgO	KCl·MgCl ₂ ·6H ₂ O	KCl·MgCl ₂	NaCl
White	0.7	47.4	2.7	18.1	^a	8.0	80.5	5.9
Grey	35.0	27.3	1.7	10.0	31.4	51.5	^a	3.8
Yellow	56.6	18.1	1.1	6.3	72.6	46.2	^a	1.3
Averaged	42.3	27.9	2.0	16.6	63.3	34.6	^a	2.2

^a the compound is not presented in the studied sludge sample

The yellow layers were characterized by high MgO content. MgO precipitated to the bottom parts because of its higher density in comparison to other chemical compounds.

According to X-ray diffraction analysis the chemical composition of white coloured layers is characterized by the presence of three separate phases: the separate phase NaCl ($d = 0.282$ and 0.199 nm), the phase of anhydrous carnallite KCl·MgCl₂ (0.285 ; 0.248 ; 0.246 and 0.175 nm), and the phase of hexaquacarnallite KCl·MgCl₂·6H₂O ($d = 0.333$; 0.298 ; 0.239 ; 0.234 nm). The chemical composition of the grey and yellow coloured slurry layers are also characterized by the presence of three separate phases: the phase of hexaquacarnallite KCl·MgCl₂·6H₂O, the phase NaCl, and the phase MgO ($d = 0.211$; 0.149 ; 0.122 nm).

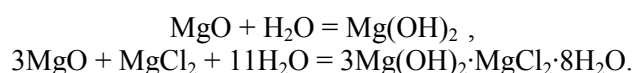
The uneven distribution of chemical compounds along height and across volume of the slurry ingot forming in a mold is explained by sedimentation and stratification of the chemical components of the slurry in mixers and molds during cooling and crystallisation of the slurry melting.

The averaged (regenerated) slurry sample was obtained by mixing representative differently coloured slurry layers in equal mass ratio, then the mixture was crushed, grinded and thoroughly mixed towards grey powder with definite particle sizes. According to X-ray diffraction analysis the chemical components in the averaged sample were presented the same phases as in the grey and yellow coloured slurry layers, however they were evenly spread throughout the sample. The mass ratio MgO:MgCl₂ for the recovered slurry was 1: 0.66 which is close to the optimal ratio of these components while forming magnesium cement from caustic magnesite and magnesium chloride solution ($1 : 0.62 \pm 0.65$).

Thus, the results of these studies showed the necessity of regeneration of the original slurry to achieve homogeneity and constancy of the chemical composition, especially magnesium components, throughout the slurry.

Because of high sensitivity of the magnesium binding materials technology to MgO reactivity, as well as the lack of understanding the mechanism of underlying processes of magnesium cement formation, especially when using technogenic materials, we investigated the reactivity of MgO extracted from the regenerated slurry. The background for such research was the developing knowledge of the kinetics of the MgO hydration in the system MgO–H₂O and MgO–MgCl₂–H₂O at different temperatures.

The MgO hydration in the investigated systems was described by the following equations:



The values of the MgO hydration degree were evaluated in accordance with the endothermic effects in the derivatograms of hydrated samples. It was found the values got higher with temperature rose and were significantly higher for the system MgO–MgCl₂–H₂O (table 2). The fact indicates that technogenic MgO has higher reactivity when it interacts with MgCl₂ solution, which is in good agreement with the scientific report data concerning the reactivity of caustic magnesia binder [4, 5].

Table 2. Values of the MgO hydration degree (α , %) in the investigated systems at different temperatures and exposure time 6 h.

	Temperature, °C		
	40	60	80
MgO–H ₂ O	4.1	17.2	34.4
MgO–MgCl ₂ –H ₂ O	22.5	61.8	75.3

The values of the hydration rate constants calculated by mathematical treatment of kinetic curves of MgO hydration degree in the investigated systems [4] are given in Table 3.

Table 3. Values of the MgO hydration rate constants in systems MgO–H₂O and MgO–MgCl₂–H₂O.

	Process temperature, °C		
	40	60	80
MgO–H ₂ O	$3.077 \cdot 10^{-5}$	$5.026 \cdot 10^{-2}$	$1.871 \cdot 10^{-1}$
MgO–MgCl ₂ –H ₂ O	$2.513 \cdot 10^{-2}$	$1.827 \cdot 10^{-1}$	$2.964 \cdot 10^{-1}$

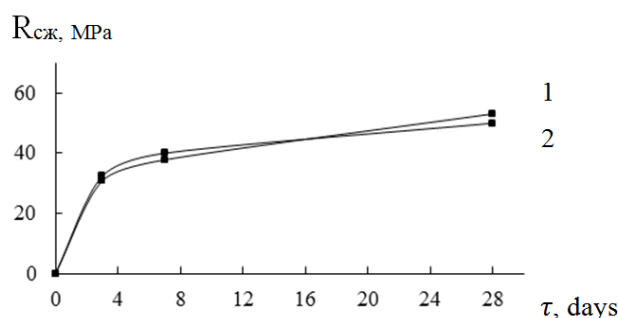
The values of the hydration rate constants got higher when temperature rose; the values for the system MgO–MgCl₂–H₂O appeared to be higher by 1000, 10, and 1.5 times at temperatures 40, 60, and 80 °C respectively.

Study of hydration kinetics has shown that MgO containing in the slurry is highly reactive and, being mixed with MgCl₂ solution, forms magnesium mixture with following forming crystallohydrate structures, which are the basis for magnesium cement.

It has been established experimentally that MgO takes part in the forming crystallohydrate structures of magnesium cement. MgO samples were gauged by MgCl₂ solution with different mass solid: liquid ratios (S:L) to form homogeneous MOC paste. It was found that optimal parameters for the homogeneous MOC paste formation with following hardening and the crystallohydrate structures forming: the mass ratio MgO and MgCl₂ solution (1.2 g/cm^3) - 1.96, temperature - 80 °C, and time of pre-heating the reaction mixture - 30 min, under these parameters the start and final setting time were 20 and 60 min. respectively, and they correspond to the normative values for caustic magnesite binders.

Laboratory samples formed from the paste and seasoned for strengthening for 3, 7, and 28 days had a maximum compressive strength of 18.7; 31.2 and 53.1 MPa respectively.

Kinetic studies of strengthening of the laboratory samples showed that the process of forming crystallohydrate structures ran intensively during the first 7 days and by the finish of the period the magnesium cement gained 60 % of the grade strength (Figure 1). After 28 days forming crystallohydrate structures of magnesium cement was almost completed and the compressive strength of the cement was maximal.

**Figure 1.** Relation between ultimate compressive strength and hardening time for the laboratory samples formed from the mixture of MgO and MgCl₂ solution at S:L = 1.96 (1) and slurry with water at S:L = 0.43 (2).

Forming crystallohydrate structures in the samples aged of 28 days of hardening time was confirmed by the presence in the X-ray diffraction lines $d = 0.478, 0.237, 0.180, 0.157$, and 0.148 nm, corresponding to the hydrated form of the composition $\text{Mg}(\text{OH})_2$ and $d = 0.240, 0.226$, and 0.198 nm corresponding to the crystallohydrate composition $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ (Figure 2).

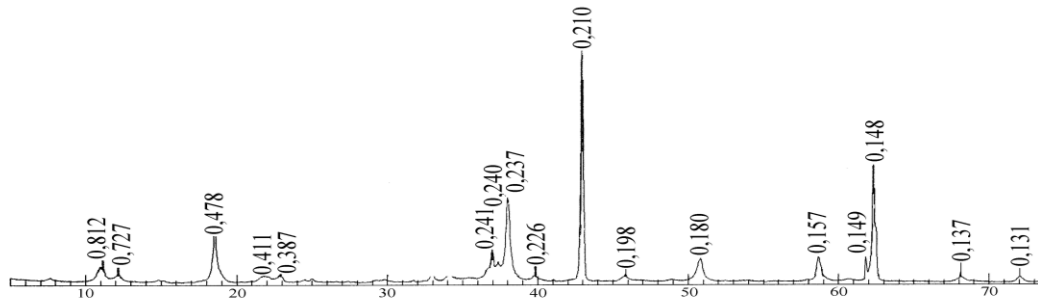


Figure 2. X-ray pattern of the sample, formed from MgO , gaged with MgCl_2 solution ($\rho = 1.20 \text{ g/cm}^3$) and aged 28 days.

Presence of the hydrated form in the magnesium “stone” was also evidenced by the intensive absorption band appeared in the IR spectrum of the studied sample in the region of 3.500 to 3.700 cm^{-1} , typical for stretching vibrations of associated OH-groups.

Thus, the mixing MgO with MgCl_2 solution resulted to the formation of strong magnesium structures; this fact indicated high reactivity of MgO in the reactions of forming and hardening of magnesium cements.

The binding properties of the slurry were studied in the system slurry– H_2O , since MgCl_2 containing in the slurry interacts with water and forms the internal solution of magnesium chloride, the last and MgO take part in the formation of magnesium-based cement. The optimal mass ratio of water and slurry (S: L) was determined experimentally. The laboratory samples of magnesium-based cement, formed from homogeneous MOC paste with different ratios S:L, were tested for strength characteristics (Figure 3).

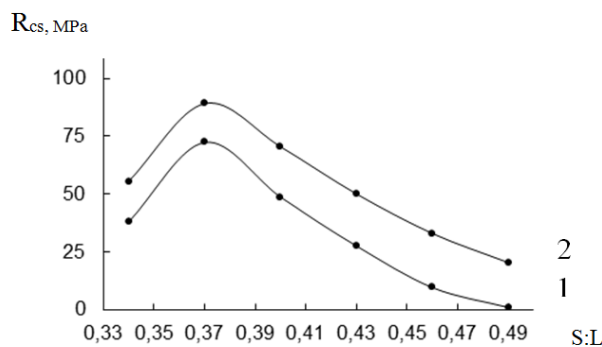


Figure 3. Relation between ultimate compressive strength and (R_{cs}) and the ratio S:L for magnesium stone samples, formed in the system sludge – H_2O at 1) 3-day hardening time and 2) 28-day hardening time.

High values of the ultimate compressive strength were achieved for samples of 3- and 28-day hardening time when the ratio of the MOC paste was S:L = 0.37 (72.3 and 89.1 MPa, respectively). However, the setting time for such MOC paste was less than 5 min. With the ratio, the paste cannot be used in the technological process, for example, to prepare wood-mineral composition because of very short lifetime of the MOC paste.

The ratio of W:T = 0.43 is likely to be considered the optimal ratio when the start and finish of hardening time for the magnesium mixture is 20 and 40 min, respectively, this is typical for the formation of the magnesium mixture on the basis of caustic magnesite and magnesium chloride

solution. The ultimate compressive strength values for samples of 3- and 28-day hardening time were 32.4 and 50.0 MPa respectively.

Hardening the magnesium-based cement formed in the system at the optimum ratio of S: L ran intensively during the first 7 days (Figure 1, curve 2). Similar shapes of the kinetic curves describing the hardening the magnesium paste in the open air indicated that adding water into the slurry resulted to forming the internal MgCl_2 solution, which took part in gauging MgO containing in the slurry with forming hydrated structures.

The formation of hydrated compounds containing in magnesium-based cement, produced on the basis of the slurry and water at the optimum mass ratio, was confirmed by X-ray diffraction analysis. In the X-ray diffraction pattern of the 28-day hardening sample there was a number of both diffraction lines typical for the hydrated compounds $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ and diffraction lines, $d = 0.238, 0.192$ and 0.183 nm, typical for the crystallohydrate $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. However, the concentration of magnesium pentoxihydrochloride was significantly lower in compared with trioxihydrochloride indicating involving MgO into the hydration as an intermediate metastable phase.

Mineral binders used in the construction material industry should comply with the radiation safety criteria in according to radiation safety standards of Russian Federation NRB-99/2009. Specific effective radioactivity of the slurry was $430 \text{ Bq} \cdot \text{kg}^{-1}$ so the waste can be referred by radiation safety to the materials of class II. Composite mixture of the slurry and sawdust with weight ratio 1:1 showed $290 \text{ Bq} \cdot \text{kg}^{-1}$. Such construction mixes refer to the class I of danger on radiation safety so they are suitable for the manufacturing construction materials for residential and public buildings.

The toxicological tests of the slurry and its mixture with sawdust, weight ratio 1:1, has shown that they are non-toxic. MgO and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are potentially hazard in the slurry and its dust. While using, the cement doesn't emit any chemical components to the air exceeding the threshold limit values (TLV). Sanitary-epidemiological conclusion certificate No.66.01.10.530 T. 000055.06.01 (issued 02.07.2001) confirmed the compliance of the material to the state sanitary-epidemiological regulations.

The experimental results of the balance experiments to determine output of effective fractions when regenerating slurry, magnesium components and their mass ratio have provided the basis for developing novel technology and the unit to recycle the slurry to the MOC powder.

4. Conclusion

The comprehensive study has proved that the carnallite slurry forming during the chlorination stage can be used to produce magnesite binder materials. It is found that the magnesium oxide in the slurry is highly reactive and, being mixed with magnesium chloride solution, it forms a homogeneous MOC paste with the subsequent formation of hydrate crystal structures which are the MOC basis. The characteristics of the slurry comply with radiation and sanitary-and-epidemiological safety requirements of Russian Federation because there is no any emission of the chemical components exceeding the maximum permissible concentrations in the atmospheric air. The studied technogenic raw material is alternative substitution of acoustic magnesites in manufacturing wood mineral composites for construction industry.

5. References

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