

Characteristics of Sorel cement prepared from impure materials

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Abstract: Production of potassium nitrate from potassium chloride and magnesium nitrate is related with the production of by-product, which is water solution of MgCl_2 having concentration (24–30) mass %. Along with magnesium chloride this solution contains also nitrates and potassium and calcium cations. This solution can be used as defrosting agent or as a component for the production of building material based on Sorel cement. Sorel cement is material originating from the reaction of MgCl_2 solution with solid MgO of suitable reactivity which depends on the temperature of calcinations of MgCO_3 and size of MgO particles. Sorel cement paste is prepared by mixing MgO and MgCl_2 in molar ratio 9 : 1 with the addition of water in appropriate amount. This cement settles in 2 hours and it can be treated within 24 hours, depending on the reactivity of MgO . This paper deals with the preparation and properties of Sorel cement made of by-product (MgCl_2) from the production of fertilizer KNO_3 and MgO prepared from Slovak magnesite (Jelšava) with high content of impurities. We will show that properties of this material are suitable for application in building industry.

Keywords: Sorel cement, impurities, Slovak magnesite, waste MgCl_2

Introduction

Sorel cement (also known as magnesia cement) is a non-hydraulic cement first produced by Frenchman Stanislas Sorel in 1867. The cement is a mixture of magnesium oxide with magnesium chloride with the approximate chemical formula $\text{Mg}_4\text{Cl}_2(\text{OH})_6(\text{H}_2\text{O})_8$. In use it is usually combined with filler materials such as sand or crushed stone. It is used for grindstones, tiles, artificial stone, and even artificial ivory. It can withstand (69–83) MPa, which is substantially more than standard Portland cement concrete.

Sorel cement is therefore based of the reaction of components in the system $\text{MgO-MgCl}_2\text{-H}_2\text{O}$. These reactions proceeds at ambient temperature under formation of crystalline phases marked on the base of ratio $n(\text{Mg}(\text{OH})_2) : n(\text{MgCl}_2)$ (Urwongse and Sorrell 1980; Li and Chau 2007):

1. **phase 5** — $\text{Mg}_3(\text{OH})_5\text{Cl} \cdot 4\text{H}_2\text{O}$ (resp., $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ [5 · 1 · 8]); phase 5 — corresponds to the molar ratio $n(\text{Mg}(\text{OH})_2) : n(\text{MgCl}_2) = 5 : 1$
2. **phase 3** — $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$ (resp., $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ [3 · 1 · 8]); phase 3 corresponds to the molar ratio $n(\text{Mg}(\text{OH})_2) : n(\text{MgCl}_2) = 3 : 1$
3. $\text{Mg}(\text{OH})_2$; $\text{Mg}_{10}(\text{OH})_{18}\text{Cl} \cdot 5\text{H}_2\text{O}$ are minor, and undesired phases.

Dominant component which governs the phase composition and kinetics of the whole process is the activity (reactivity) of MgO . This parameter

depends on the calcination temperature and size distribution of particles (Harper 1967).

The most common source of MgO is natural magnesite or basic magnesium carbonate, $(\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 5\text{H}_2\text{O})$. In this paper we will show that good quality material based on Sorel cement can be prepared from magnesium chloride originating as by-product from the production of potassium nitrate according to the reaction scheme published by Jurišová et al., 2013:



Magnesium oxide was prepared from natural Slovak magnesite. Its composition is given below.

Experimental

Composition of the solution containing as main component magnesium chloride was as follows (mass %): 30.0 % MgCl_2 ; 2.37 % CaO ; 3.25 % K_2O ; 2.40 % nitrogen (as NO_3^-).

Composition of burnt magnesia prepared from Slovak magnesite (Jelšava) was as follows (mass %): MgCO_3 — 85.7 %; CaCO_3 — 7.20 %, FeCO_3 — 4.36 %; SiO_2 — 1.93 %; MnCO_3 — 0.11 %. Before calcinations, magnesite was grinded. Particles having three different diameters (upper value is given) were obtained: 200 μm ; 100 μm , and 60 μm . Temperature of calcinations changed in the range 700 °C and 900 °C in the interval 50 °C. Rise of temperature was 10 °C · min⁻¹. When the desired temperature was reached, it was kept constant for

2 h. In each experiment, 1 kg of magnesite was calcined. Resulting samples were characterized by X-ray powder diffraction, scanning microscopy and by determination of their BET surface. Preliminary experiments had shown that samples calcined at the temperature 850 °C (or higher) are not sufficiently reactive. On the other hand, the samples obtained at the temperature of 750 °C (or lower) form in the system MgO-MgCl₂-H₂O preferably Mg(OH)₂, which is undesirable. On the base of these results we came to the conclusion that for preparation of Sorel cement the best material is MgO prepared at 800 °C. Its BET surface is 15.5 m².g⁻¹.

The samples of cement pastes were prepared with MgO and MgCl₂ at the molar ratios ranging from 9 : 1 to 5.5 : 1. The amount of water was added for keeping proper consistency. All used compositions are summarized in Table 1.

After homogenization the Sorel paste was casted into plastic moulds. Height of paste was 3 cm. For each composition, 5 samples of Sorel cement samples were made. Hardening of the mixture was observed after 1 h. The reaction is exothermic and we observed small heating of the samples. After 24 h, the moulds were dismantled and the samples were hardening in open air. After eight days their compressive strength was measured by MICRO-EPSILON UMZ-3k. Plane of cleavage was studied by SEM and the phase composition by the powder X-ray diffraction.

Results and discussion

It was found that quality, i.e. good mechanical properties, is determined mainly by the content of phase 5, Mg(OH)₂ and unreacted MgO particles. Presence of Mg(OH)₂ and unreacted MgO particles has a negative influence on the stability of the system, because these components react slowly with CO₂ under the formation of magnesium carbonate which can destroy resulting Sorel concrete. Theoretical composition of needle like phase 5 which is responsible for the strength of Sorel cement is n(MgO) : n(MgCl₂) : n(H₂O) = 5 : 1 : 13. For phase 3 this ratio is 3 : 1 : 11. Needles of phase 5 grow quite quickly and they form close-fitting structure with minimum pores. Ideal composition corresponds to that of phase 5. Thus there should be no surplus of water with respect to the formation of this phase (Matković et al. 1977). High activity (reactivity) of MgO increases the rate of hardening of the cement paste. On the other hand it requires the addition of water with respect to optimum which results in the formation of undesired Mg(OH)₂. Thus it is necessary to make a compromise between the activity of MgO, amount of used water and the ratio between MgO and MgCl₂. It is important that the resulting material contains no MgCl₂ which is hygroscopic. These conditions can be achieved by using a small surplus of MgO with respect to the stoichiometry of phase 5.

Tab. 1. The composition of aggregate materials of Sorel cement prepared from MgO (magnesite calcined at a temperature 800 °C) and MgCl₂ solution prepared as a by-product production of KNO₃ fertilizers.

Sample	1	2	3	4	5	6
MgO particle size [μm]	200	200	100	100	60	60
n(MgO)/n(MgCl ₂)	9/1	7/2	8/1	6/1	7/1	5.5/1
MgO [g]	200	200	200	200	200	200
MgCl ₂ [g]	48	61	56	72	61	86
Solution of MgCl ₂ (30 wt. %) [g]	160	205	188	240	205	286
H ₂ O [g]	55	32	27	37	33	44
n(H ₂ O)/n(MgCl ₂)	18.4	15.2	15.3	15.1	15.0	15.0

Tab. 2. Crystalline phases and the compressive strength of the samples after seven days of hardening on air. Composition of the samples is listed in Tab. 1. The main crystalline phase in all cases is phase 5, to a lesser extent phase 3.

Sample	1	2	3	4	5	6
MgO	+++	++	+	-	-	-
Mg(OH) ₂	++	++	+	+	+	-
MgCl ₂	++	+++	+	-	-	+
Compressive strength [MPa]	82.3	68.6	95.4	110.4	120.5	98.5

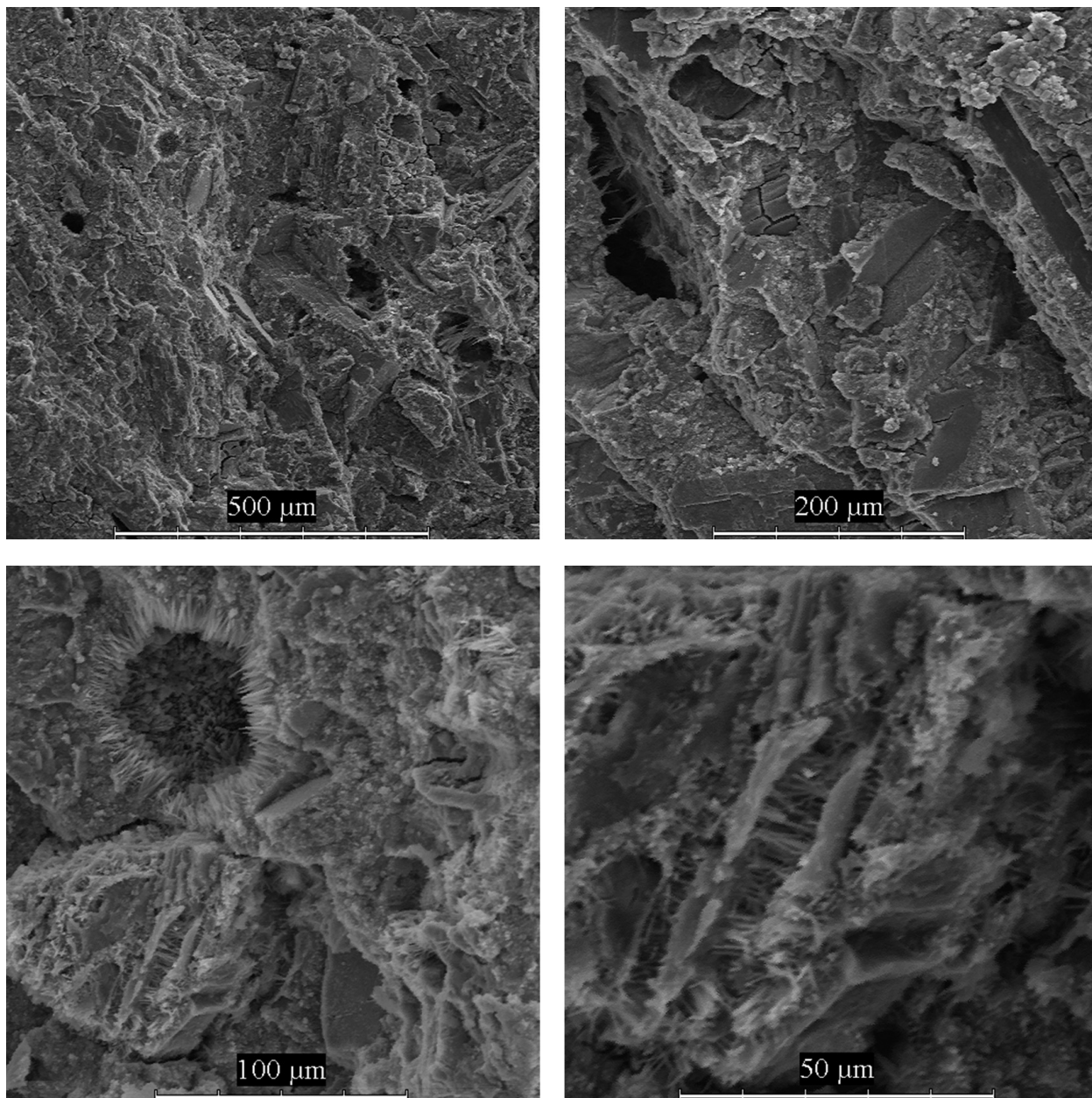


Fig. 1. Picture of the material of example 1 which is after seven days compact. There are visible unreacted MgO particles and visible fibrous microstructure of the phase 5.

As mentioned above, reactivity of MgO can be influenced mainly by calcination temperature. For example, according to paper (Matković et al. 1977), MgO obtained by calcinations in the temperature interval (750–1000) °C yields mainly phase 5 and only small amount of $\text{Mg}(\text{OH})_2$. On the other hand when the calcinations temperature is low (600–700) °C, dominant phase is $\text{Mg}(\text{OH})_2$ and only small amount of phase 5 is formed. It is interesting that when the samples of homogenized mixture corresponding to the composition of phase 5 were kept in a closed container, only phase

5 was formed regardless of the activity of MgO. In this case, the reactivity of MgO influences only the rate of hardening of cement.

Parameters used for the preparation of Sorel cement in this work are summarized in Tables 1 and 2. Tab. 2 illustrates the presence of crystalline phases in the material and the measured compressive strength of the test piece. Every value of the compressive strength is the averaged value of the measurements of five samples. Measurement error for this parameter is within $\pm 5\%$.

As can be seen from Fig. 1, Sorel cement materials

made from MgO and the by-products of KNO₃ fertilizer have a compact microstructure. Fibrous nature of phase 5 which is the bearer of high material strength can be seen as well.

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