Physicochemical and physicomechanical studies of dolomite binder

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Abstract. To obtain dolomite cement, it is proposed to use screenings of dolomite stone and coal waste. Both physicochemical and physicomechanical studies of cement samples are carried out. It is shown that, in contrast to the existing dolomite binders, the proposed cement has the ability to harden when mixed with water.

1. Relevance
According to literature analysis the magnesia binders have a number of significant advantages, i.e. quite fast setting, quick hardening, effective protection against the harmful effects of electromagnetic and high frequency radiation. There are significant reserves of dolomite stocks in Ukraine, with technological off-quality waste of dolomitic stone screenings being largely accumulating at mining combines, refractory making plants and metallurgical enterprises. Amount of waste in the piles is approaching millions of tons, with the quantity thereof constantly increasing, thereby generally resulting in environmental pollution and ecological problems [1]. On the other hand, the technology for the production of binders from dolomite waste has advantages over the Portland cement technology: lower fuel consumption for heat treatment; reduction in energy and operating costs, since crushing of raw materials and the use of expensive crushing equipment is no longer required; release of land plots used for landfills; the production process uses only one-component raw materials, such as dolomite, which does not require corrective additives; the firing temperature of dolomite cement is lower than that of Portland cement, therefore, the furnaces should not be lined with expensive refractory materials. All this makes it possible to reduce the production cost of dolomite cement at least twice as compared to Portland cement. In addition, the thermal processing of raw materials for the production of dolomite binders produces less greenhouse gases.

2. Problem setting
Currently, there is no unified and generally accepted theory of cement hardening [2,3]. The first theoretical concept of cement hardening was proposed by Le Chatelier. In accordance with his theory (crystallization theory), the cement hydration occurs through the solution [4]. Due to higher solubility of clinker minerals as compared with the formed crystalline hydrates, the latter, forming supersaturated solutions, are released from the cement-water suspension thereby forming a crystalline aggregate. The main position of Le Chatelier's theory of the fact that cement hydration occurs through the mortar is the starting point in current concepts for the hardening of mineral binders. According to the V. Michaelis theory (1893 - colloid theory), water directly interacts with the surface of cement
minerals, and the hydration processes proceed without dissolution thereof (topochemical mechanism) [5]. Michaelis did not deny the occurrence of crystalline hydrates formation in the process of cement hardening, but paid less attention thereto. In 1923 A.A. Baikov tried to combine these theories (unified colloid chemical theory) [6]. He identified three periods: dissolution (before the start of setting); colloidation (hydration) and crystallization with the formation of a crystalline aggregate. The main position of Baikov's theory, current theoretical concepts are adhered to, is the ability of a significant part of the binder to hydrate according to the topochemical scheme.

P.A. Rehbinder divides the hardening process into three stages: dissolution of unstable clinker phases in water and separation of crystals; the formation of a coagulation structure; growth and aggregation of crystals [7].

As far as the magnesia binder is concerned, the forming Mg(OH)\textsubscript{2} layer is known to prevent from the diffusion of water into MgO grains. The process is strongly accelerated, if salt electrolyte is dissolved in water. For caustic magnesite to form an artificial stone, it is tempered with FeSO\textsubscript{4}, MgSO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4}, NaHSO\textsubscript{4}, FeCl\textsubscript{2}, ZnCl\textsubscript{2} and mainly MgCl\textsubscript{2} • 6H\textsubscript{2}O solutions [8-18, 46].

Regarding the process of curing magnesia binder M. Sorel [13], and then other researchers [14-18] found that when the magnesia binder hardened with an aqueous solution of magnesium chloride, an artificial stone is formed with different properties depending on the compounds formed. In theory, magnesium chloride reacts with MgO to form oxychlorides like nMgO ∙ MgCl\textsubscript{2} mH\textsubscript{2}O. According to various scientists, n ranges from 3 to 7, and m - from 6 to 17 [14-29]. When magnesium oxide is mixed with highly concentrated solutions of MgCl\textsubscript{2}, the structure of magnesia stone is usually formed mainly by 5- and 3-hydroxychlorides, since the formation and appearance of magnesium hydroxide in it becomes energetically unfavorable.

The composition of the end products in magnesia cement is determined by ratio of initial components, since under insufficient solution content in conditions of high density of structure and under a significant change in MgCl\textsubscript{2} concentration due to crystalline hydrates formation, the phase transitions of metastable compounds into stable ones may be stopped at one of the stages, and only 3MgO ∙ MgCl\textsubscript{2} ∙ 11H\textsubscript{2}O or 5MgO ∙ MgCl\textsubscript{2} ∙ 13H\textsubscript{2}O may be the end products, as well as mixtures thereof or mixtures of these oxychlorides with Mg(OH)\textsubscript{2} or MgCl\textsubscript{2}.

In the majority of scientific works devoted to magnesian binder based on dolomite and materials based on it, much attention is paid to the problems of improving the quality of binders and materials [30-52].

The use of saline solutions negates the advantages of dolomite binder production due to the high price of this salt compared to water.

Modern theoretical and practical data suggest research on obtaining a magnesia binder that can harden in water.

3. **Research hypothesis**

Under aqueous conditions, magnesium oxide hydrates so slowly that this method has not found wide application, but when it is mixed with saline solutions (most often with a solution of MgC12 6H2O), the process is accelerated. An increase in the solubility of the Mg (OH) 2 layer appearing on the MgO surface and the involvement of magnesium oxide in the hydration process can be achieved due to the formation of minerals in the binder during its heat treatment, obtained by joint firing of dolomites and coal waste. The minerals formed during firing play the role of a salt mixture, and the interaction reactions proceed through the formation of calcium and magnesium hydroxides, which take part in the hardening process.

4. **Theoretical**

We have investigated the thermodynamic conditions for the decomposition of dolomite in a mixture with silicon dioxide - SiO2. The changes in the Gibbs free energy (ΔG) in the temperature range from 900 to 1500K are calculated.
The possibilities of forming the following connections are thermodynamically considered: calcium and magnesium oxides (reaction 1); calcium carbonate and magnesium oxide (reaction 2); β-wollastonite and magnesium oxide (reaction 3); α-wollastonite and magnesium oxide (reaction 4); magnesium silicate and calcium oxide (reaction 5); 2Ca SiO2β and magnesium and silicon oxides (reaction 6); 2Ca SiO2γ and magnesium and silicon oxides (reaction 7); clinoestatite (reaction 8); diopside (reaction 9); ackermanite (reaction 10); mervenite (reaction 11); monticellite (reaction 12).

Possible reactions in the mixture of dolomite and coal enrichment wastes are presented below:

1. \(CaCO_3 + MgCO_3 + SiO_2 = CaO + MgO + SiO_2 + 2CO_2\)
2. \(CaCO_3 + MgCO_3 + SiO_2 = CaCO_2 + MgO + SiO_2 + CO_2\)
3. \(CaCO_3 + MgCO_3 + SiO_2 = \beta CaO SiO_2 + MgO + 2CO_2\)
4. \(CaCO_3 + MgCO_3 + SiO_2 = \alpha CaO SiO_2 + MgO + 2CO_2\)
5. \(CaCO_3 + MgCO_3 + SiO_2 = MgO SiO_2 + CaO + 2CO_2\)
6. \(CaCO_3 + MgCO_3 + SiO_2 = 1/2(2CaO SiO_2β) + MgO + 1/2SiO_2 + 2CO_2\)
7. \(CaCO_3 + MgCO_3 + SiO_2 = 1/2(2CaO SiO_2γ) + MgO + 1/2SiO_2 + 2CO_2\)
8. \(CaCO_3 + MgCO_3 + SiO_2 = 1/2(MgO SiO_3) + CaO + 1/2SiO_2 + 2CO_2\)
9. \(CaCO_3 + MgCO_3 + SiO_2 = 1/2(CaO MgO 2SiO_2) + 1/2CaO + 1/2MgO + 2CO_2\)
10. \(CaCO_3 + MgCO_3 + SiO_2 = 1/2(CaO MgO 2SiO_2) + 1/2MgO + 2CO_2\)
11. \(CaCO_3 + MgCO_3 + SiO_2 = 1/3(3CaO MgO 2SiO_2) + 2/3MgO + 2CO_2 + 1/3SiO_2\)
12. \(CaCO_3 + MgCO_3 + SiO_2 = CaO MgO SiO_2 + 2CO_2\)

Table 1 shows the results of the thermodynamic identification of the Gibbs energy of these reactions.

| Reaction No | \(\Delta G\), kCal/Mol at, K |
|-------------|-----------------------------|
|             | 900            | 1000 | 1100 | 1200 | 1300 | 1400 | 1500 |
| 1           | -3117.40       | -10808.88 | -18378.13 | -25824.91 | -33149.16 | -40350.89 | -47430.16 |
| 2           | -9470.24       | -13368.47 | -17189.48 | -20931.18 | -24591.86 | -28170.08 | -31664.62 |
| 3           | -200670.00     | -203732.10 | -206650.40 | -209421.80 | -212043.90 | -214514.50 | -216831.90 |
| 4           | -201508.40     | -204777.40 | -207899.00 | -210870.70 | -213690.30 | -216356.20 | -218866.80 |
| 5           | -187658.60     | -190663.00 | -193522.70 | -196235.00 | -198797.90 | -201209.60 | -203468.60 |
| 6           | -107364.40     | -112886.10 | -118286.00 | -123563.20 | -128717.10 | -133747.30 | -138653.40 |
| 7           | -111561.80     | -117501.50 | -123331.10 | -129053.00 | -134669.40 | -140182.40 | -145593.80 |
| 8           | -103807.00     | -111089.00 | -118537.00 | -126149.40 | -133924.60 | -141886.60 | -149959.30 |
| 9           | -194460.30     | -197254.90 | -199909.60 | -202421.30 | -204787.20 | -207005.00 | -209072.80 |
| 10          | -31607.10      | -39722.50 | -47821.10 | -55920.30 | -64002.70 | -72074.90 | -80137.50 |
| 11          | -26189.05      | -34010.30 | -41812.61 | -49598.91 | -57385.21 | -65149.51 | -72876.81 |
| 12          | -224951.00     | -230422.50 |             |             |             |             |             |

The dependence of the Gibbs function change in the temperature range of (900 - 1500) K is represented by a diagram in Figure 1.
Figure 1. Dependence of Gibbs energy on temperature in 1-12 reactions.

An analysis of the results obtained shows that there is a thermodynamic probability of the formation of compounds during firing, capable of solidifying when mixed in water.

5. Characteristics of original materials

Dokuchaevsky dolomitic stone screenings (DSS) and waste coal (WAC) from Belorechensk processing plant are used as raw stock, with the chemical composition of DSS (mass %) being CaO – 28.89; MgO – 19.02; SiO₂ – 6.37; Fe₂O₃ – 0.85; Al₂O₃ – 1.21; ignition loss – 42.81, and that of WAC (mass %) CaO – 3.8; MgO – 1.3; SiO₂ – 55.3; Fe₂O₃ – 10.9; Al₂O₃ – 20.6; SO₃ – 2.8; K₂O – 2.6; Na₂O – 1.0.

X-ray patterns of dolomite screening and waste coal are shown in Figure 2 and Figure 3, respectively.

Figure 2. X-ray pattern of dolomitic stone screening.
6. Experimental results
The prepared composition of DSS to WAC being as 1:1; 1:2, 1:3 was isothermally fired in a muffle furnace at 1000°C for 1 hour. After being fired the resulting material was cooled down in the muffle to 150-180°C for 6-8 hours. Afterwards the material was grounded in a ball mill up to a specific surface area of 3200-3300 cm²/g.

The X-ray diagram of the obtained dolomite binder is shown in Figure 4.

The results of X-ray analysis show that the binder contains compounds capable of hydrating when tempered with water, and having hydraulic properties. Then the binder and sand mixture was mixed with water. The water-cement ratio was taken considering cone flow of 109-110 mm on the shaker table.

The strength properties were determined with 40x40x160 mm and 31.6x31.6x31.6 mm samples with a binder-to-sand composition as 1:3. The samples were heat- and moisture-treated at 95°C according to 2+8+2h steam curing regime, with the prior exposition thereof to air for 2-3 hours. The physical and mechanical properties of the binder are given in table 2.

Dolomite binder samples with DSS-WAC composition of 1:3 are seen from table 2 to have the best strength properties characterized by strength of 4.0MPa after 28 days of leaving in moist room, and that of 21.0MPa after heat- and moisture-treated.
Table 2. Physical and mechanical properties of dolomite binder.

| Mixture composition | True density, kg/m³ | Normal consistency of paste, % | Setting time | Distance b/n Le Chatelier mold indicator stems, mm | Water cement ratio | Compressive strength, MPa |
|---------------------|--------------------|-------------------------------|--------------|----------------------------------|-------------------|----------------------|
| DSS                 | 50                 | 2520                          | 38           | 0-38 3-40                       | 3.5               | 0.40                 | 6.82                 |
| WAC                 | 34                 | 2480                          | 33           | 0-40 3-35                       | 2.7               | 0.45                 | 6.91                 |
|                     | 25                 | 2390                          | 30           | 0-46 3-47                       | 2.0               | 0.40                 | 9.13                 |

Therefore, the usage of DSS - WAC mixture under the heat treatment enabled to get a binder capable of hardening when mixed with water.

7. Results
- 1. Principles of binding properties found in the dolomite binder when mixed with water are theoretically verified and experimentally confirmed.
- 2. The research in making a dolomite binder by mutual firing of dolomitic stone screenings and waste coal with further grinding thereof to a specific surface area of 3200-3300 cm²/g. The minerals capable of interacting with water and acting as a saline grout are found in the products of firing.
- 3. The dolomite binder was mixed with water at a water-cement ratio of 0.4-0.45.
- 4. Both physical and mechanical and physical and chemical studies have been carried out. The compressive strength of a dolomite binder in the cement to sand composition as 1:3 after being heat- and moisture-treatment is 14-21 MPa.

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