Theoretical and experimental studies of energetics of the dolomite decarbonization process

V I Vinnichenko¹, A N Riazanov², R Z Rakhimov³ A A Riazanov² and O V Vinnichenko⁴

¹ Cool Clean Researches & Technologies, 37 Rue Sainte Catherine, Le Cannet, 06110, France
² Ufa State Petroleum Technological University, 1 Kosmonavtov st., Ufa, 450064, Republic of Bashkortostan, Russia
³ Kazan State University of Architecture and Engineering, 1 Zelenaya st., Kazan, 420043, Tatarstan, Russia
⁴ Kharkiv National University of Civil Engineering and Architecture, 40 Sumska st., Kharkiv, 61002, Ukraine

*E-mail: vvinnichenko@ukr.net

Abstract. One of the known advantages of magnesia binders is a significant reduction in energy consumption for the production of such binders compared to the production of lime and Portland cement. The theoretical costs of thermal energy for firing dolomite, which amount to 220-230 kcal/kg (for Portland cement – 420-430 kcal/kg), are almost halved under equal conditions of raw material moisture and furnace efficiency. This study examines the screening of dolomite waste and coal waste materials as raw materials for the production of dolomite cement. Coal preparation wastes in this case are both the initial raw material and, in part, can be used as fuel to ignite the raw charge. Theoretical and experimental studies of the influence of the organic component of coal waste on the process of decarbonization of dolomite have been carried out. The results of thermodynamic studies show that the participation of carbon and its gasification products in the reactions of dissociation of magnesium carbonate makes it possible to reduce the temperature of the beginning of the decomposition reaction of MgCO₃ and CaCO₃. The energy feasibility of obtaining dolomite binders has been theoretically substantiated.

Introduction
Dolomite rocks are one of the most common varieties of mineral commodities slightly developed by the construction industry. They may be used for the production of various types of binders and construction materials thereunder [1-2]. But nowadays such materials are actually not produced by the domestic industry, although a large number of construction materials and products based on magnesium carbonate (magnesites) and double calcium and magnesium carbonates (dolomites) are supplied from abroad. Various types of finishing and heat-insulating materials are made with the application of such binders [2-4]. One of the magnesia binder advantages is much less energy costs for the production thereof as compared with the production of lime and Portland cement [5]. Less gaseous pollutants are released under the dolomite firing [6-7].

The principal advantages of magnesia binders are: high mechanical strength with fast growth thereof in the initial period of hardening, better ultimate bending strength values as compared with...
other binders, dense structure of hardened magnesia stone under low true and average density, low heat conductivity, high bond strength with aggregates when making magnesia concretes and mortars, as well as high corrosion resistance [8-12]. The hardening products of some magnesia binders are known to have an extremely high resistance to seawater, alkali soil water, saline, and alkali solutions, much higher than the resistance of the hardening products of special Portland cement types [12]. The above properties indicate the advisability of developing technologies for making such binders and materials thereunder [9].

On the other hand, much coal-based waste has been accumulated. The problem of industrial waste disposal and recycling is still extremely pressing. The ecological danger of coal waste piles is widely covered [13-15]. They are both the initial commodities and at the same time they may be partially used as fuel for the construction materials industry under the integrated application of waste. In addition, waste disposal enables to solve the environmental problems, improve the lands by removing the waste piles therefrom, and reduce harmful emissions.

Theoretical and experimental energy costing for the dolomite binder firing is the aim of the paper.

1. Theoretical

1.1. Theoretical costs of heat energy

Theoretical costs of heat energy for dolomite clinker formation are the costs of heat for dissociation of MgCO₃, a certain amount of CaCO₃, and impurities dehydration [7] will be ‘equation 1’:

\[ q_\text{th} = G^C_{\text{CaCO}_3} \Delta H_1 + G^C_{\text{MgCO}_3} \Delta H_2 + G^C_{\text{ASJH}_2} \Delta H_3 \]  

(1)

where \( G^C_{\text{CaCO}_3}, G^C_{\text{MgCO}_3}, G^C_{\text{ASJH}_2} \) are the content of calcium carbonate, magnesium carbonate and aluminosilicates respectively in dolomite per 1kg of clinker, \( \Delta H_1, \Delta H_2, \Delta H_3 \) are the enthalpy of the reactions of decarbonization of calcium carbonate, magnesium carbonate, aluminosilicate impurity.

Theoretical costs of heat energy for dolomite firing are (220-230) kcal/kg of clinker. For comparison, theoretical heat consumption for firing Portland cement clinker is (420-430) kcal/kg of clinker, on average. Actual fuel consumption for firing depends on the commodity moisture and efficiency of the heat generating unit. Fuel consumption for firing dolomite clinker is reduced by 47% as compared to Portland cement clinker, i.e. almost twice under equal conditions of the initial moisture content of the commodity and the furnace efficiency.

1.2. Thermodynamic studies

Procedure [17] was applied therefor. Initial data were taken from [17-19]. Thermodynamic analysis was made to theoretically determine the effect of the carbon involvement and gasification products thereof in the mixture on the magnesium carbonate dissociation. The following reactions are considered:

- 1. \( \text{MgCO}_3 = \text{MgO} + \text{CO}_2 \)
- 2. \( \text{MgCO}_3 + \text{C} = \text{MgO} + 2\text{CO} \)
- 3. \( \text{MgCO}_3 + 2\text{OH}^- = \text{MgO} + \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2 \)
- 4. \( \text{MgCO}_3 + \text{CO} + 0.5\text{O}_2 = \text{MgO} + 2\text{CO}_2 \)

The results obtained are indicated in ‘figure 1’.

Thermodynamic analysis of the waste organic component affecting dissociation reactions of magnesium carbonate has revealed that reaction 1 is thermodynamically possible at temperatures above 600 K, and MgO presence is thermodynamically possible in reactions 2,3,4 at lower temperatures, with the organic component containing in the waste.

The thermodynamic studies results indicate that the involvement of carbon and the products of gasification thereof in the dissociation reactions of magnesium carbonate enable to reduce the temperature of starting the decomposition reaction of MgCO₃.
2. Experimental
The possibility and advisability of joint application of waste coal and dolomite waste to obtain binders is first determined by the nature of the behavior under heating of the organic component of the waste coal. Gravity concentration waste of the Belorechensk concentrating mill and Krasnoyarsk dolomite were used for making the studies.

The process of thermal oxidative breakdown ‘Figure 2’ characterized by the release of gaseous volatile products is within the temperature range of (100-366.8) °C.

Figure 1. Action of temperature on Gibbs energy

Figure 2. Waste coal heating pattern.

Under further heating the processes of thermal breakdown of the organic mass of waste is intensified accompanied by the release of volatile substances and resins, occurring together with the dehydration of aqueous oxides of aluminosilicates. The character of the effect i.e. two maxima on the
DSC curve indicates that the composition of the organic component is inhomogeneous. On the DTA curve, intense exothermic effects with a maximum at 480 °C and 550 °C correspond to this process. The process ends at 654.4 °C, therewith a 9.73 % weight loss is observed due to volatile organic compound release. The process of thermal breakdown of the organic component within 654.4-980 °C temperature range is known as semicooking with the formation of a liquid phase – the plastic state of coal – with the subsequent transformation thereof into semicoke.

Thermal transformations of dolomite upon heating are shown in ‘figure 3’.
The deflections of the DTA curve after heating above 750 °C indicate the stepwise process of dolomite decarbonization. The intense endothermic effect at 815.9 °C corresponds to the magnesium carbonate dissociation, while the endothermic effect with a maximum at 919.8 °C corresponds to the calcium carbonate dissociation. Energy consumption for endothermic decarbonization reactions of magnesium and calcium carbonates is 758.2 J/g (Area – 758.2 J/g).

Waste coal adding to the dolomite, the character of thermal effects is significantly changing, although the features of thermochemical transformations of the waste organic component remain. The exothermic effects seen on the DTA curve ‘Figure 4’, ‘Figure 5’, ‘Figure 6’ at 486.4 °C, 489.0 °C and 485.8 °C are due to thermal oxidative breakdown of the organic component of the waste coal.

![Figure 5. Heat pattern of dolomite:waste coal mixture as 1:2.](image)

![Figure 6. Heat pattern of dolomite:waste coal mixture as 1:3.](image)

According to the heat patterns analysis the decarbonization process is intensifying. Comparison of the heating curves of dolomite ‘Figure 3’ and a mixture of dolomite and waste coal ‘Figure 4’, ‘Figure 5’, ‘Figure 6’ indicated a temperature decrease at the start of carbonate dissociation. While in the
dolomite/mixture series as 1:1, 1:2, and 1:3, the temperature at the start of dissociation is: (742.3-734.6-709.5-687.1) °С.

The endothermic process of the decarbonization effect ‘Figure 4’, ‘Figure 5’, ‘Figure 6’ of MgCO₃ and CaCO₃ with the waste is seen to undergo significant changes. First, the curve has two distinct peaks ‘Figure 4’: one is the decarbonization of MgCO₃ at 822.4 °C and the second one is the decarbonization of CaCO₃ at 882.2 °C. The waste coal in the mixture increasing to 1:3, there is one exothermic peak ‘figure 6’ at 849.3 °C.

Combustion of the waste organic component at the required temperature and oxygen results in exothermic transformations and is accompanied by a change in the internal heat content of the system. This is confirmed by a significant reduction of area occupied by curves on the heat patterns that are recording endothermic reactions from the point of starting the heat absorption to the point of end thereof.

A very interesting dependence is seen when analyzing the heat required for the decarbonization reaction.

The total heat energy used for decarbonization of calcium and magnesium carbonates is:
- dolomite – 758.2 J/g ‘Figure 3’;
- dolomite:waste mixture as 1:1 – 430.3 J/g ‘Figure 4’;
- dolomite:waste mixture as 1:2 – 331.4 J/g ‘Figure 5’;
- dolomite:waste mixture as 1:3 – 262.5 J/g ‘Figure 6’.

Exothermic reactions in dolomite and waste mixture provide for the requirement in endothermic processes in heat energy.

3. Results

The energetic advisability of obtaining dolomite binders has been theoretically substantiated.

The thermodynamic studies results have shown that carbon and gasification products thereof involved in the dissociation reactions of magnesium carbonate enables intensification of the carbonization process.

Comparative studies of the behavior under heating of waste coal, dolomite and waste/dolomite mixture have been carried out. Decrease in the demand of energy of endothermic processes of dolomite decarbonization is found to be due to exothermic reactions of waste coal and dolomite mixture.

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