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Research paper

Energy Efficiency of Binder Application in Concrete

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Abstract

Theoretical calculation of the thermal effect of formation of minerals of binders is carried out. The dependence allowing calculating the thermal effect of formation of minerals of lime, gypsum, slag cement, portland cement, dolomite cement is presented. The formula also takes into account the effect of organic components in the mixture. A comparative analysis of the energy efficiency of different types of binder in concrete is carried out. It is shown that the use of slag cement in the production of concrete mix is twice as effective as portland cement. This is due to the presence in the slag of calcium oxide, which does not need energy to carry out the endothermic decarbonization reaction. Lime in the concrete composition has a rate of energy consumption is five times greater. This means, industrial waste which contains calcium oxide (slag, ash and others) can replace natural materials with high efficiency.

Keywords: *binders in the composition of concrete, cement clinker, energy, lime, slag, theoretical calculation, thermal effect of clinker formation.*

1. Introduction

Concrete is currently the most used material in construction. The main attention is paid to increasing the efficiency of the use of resources, materials, energy. Concrete must be characterized by: high physical and mechanical properties, high environmental parameters for the use of materials of secondary origin.
Reducing energy costs and energy saving in various sectors of the national economy and industry, including construction - this problem is becoming increasingly relevant in the world.
From 1973 to 2016, world fuel consumption increased from 3,740 Mtoe to 5,257 Mtoe. And the emission of carbon dioxide increased from 15,000 to 30,000 (Mt of CO^2) [1].
This issue is especially relevant for the Ukrainian economy, since in Ukraine the energy intensity of industrial production is 2.6 times [1] above the global indicators. The fuel consumption and emissions into the environment of carbon dioxide have a directly proportional relationship. Therefore, energy saving is a very urgent problem in the production of building materials.

2. Energy Intensity of Concrete Production

2.1. Energy Intensity of Concrete Production.

Concrete is an artificial and durable stone used in the manufacture of construction works. Components for its preparation are: binders (cement, lime, gypsum), aggregates (crushed stone), sand, water and additives (fig.1). Different types and brands of concrete are obtained by changing the ratio between components, the use of a variety of types of components, the use of special additives, as well as improving the technological methods of preparing a concrete mixture. The process of preparation of a concrete mix seems to be simple: the components are mixed together in machines which are called mixers.

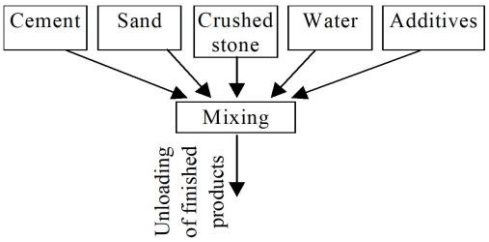


Fig. 1: Scheme preparation of concrete mixtures.

The concrete mix has a liquid consistency (Fig. 2). In this case, very complex reactions occur between the binder, water and additives. The transformation of a concrete mixture into an artificial stone is a complex physicochemical process. Simpler it looks like this. When hydrated, clinker minerals of tricalcium aluminate, alite and belite interact with water. As a result of the interaction, hydroaluminates, calcium hydrosilicates and hydrated lime are formed, which remains inside the cement stone. Slaked lime protects steel reinforcement from the appearance of rust. The resulting hydration products are gel and pore space. Gradually, the gel thickens and is transformed into spatial bonds of crystalline neoplasms. The structure begins to harden. This is the first stage of the process. It is called grasping. At the next stage, the material strength increases which is called hardening. The process of hardening of concrete mainly depends on the mineral composition of cement clinker, the fineness of cement grinding, the type and brand of cement, the amount of water, the temperature of hydration, fractional composition, type of aggregates of concrete, type and quantity of additives.

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Fig. 2: Concrete mixture [2].

As a result of the reactions, compounds appear that promote a gradual transition from a liquid species to a solid stone. The binder serves to connect all components of the concrete mix to a solid stone.



Fig. 3: Concrete is a solid stone [2].

The total energy intensity of production of concrete consists of energy costs for: the preparation of concrete mix components and the production of concrete. The energy consumption for the production of such a component as cement is 50-70% of the energy intensity of concrete [3].
Save energy in the production of concrete can be reduced energy costs for the production of cement. Wastes from industrial production (slag, coal processing waste, coal combustion ash and the like) reduce fuel and electricity consumption in cement production.
Slag contains calcium oxide, which is able to participate in the reactions of clinker minerals formation. And in this case, the thermal energy is not spent on the decarbonization of calcium carbonate. Slag can reduce fuel consumption for burning clinker, due to the presence of calcium oxide. Energy is not expended on the re-carbonization of $CaCO_3$. At the same time, carbon dioxide emissions into the atmosphere are declining. Replacing natural materials with slag (or other materials containing calcium oxide) has an environmental effect- reduction of carbon dioxide emissions into the environment,the liberation of lands from dumps,-preservation for future generations of natural resources.The consumption of high-quality fuel is also reduced if one of the organic components is present. Coal particles in the composition of the cement raw meal also contribute to increased productivity of raw and cement mills, intensification of alite formation.

2.2. The Thermal Effect of the Formation of Cementing Minerals

The most common binders - cement, lime, gypsum - are obtained by heat treatment of materials. The starting materials for the production of lime are the materials represented by calcium and magnesium carbonates with impurities of aluminosilicates. The raw materials of cement production include calcium carbonates and aluminosilicates. Gypsum binders are prepared from two-water gypsum with insignificant impurities of carbonates and (or) aluminosilicates.
One of the most important characteristics of the initial raw meal used in the technological process for the production of binders is the theoretical energy expenditure (theoretical thermal effect) on the physicochemical processes of the formation of minerals. The determination of the theoretical thermal effect of clinker formation is the most difficult. The process of clinker formation is a combination of endothermic and exothermic transformations. Endothermic is the process of decomposition of the primary components of the initial mixture - carbonates and aluminosilicates. The formation of new clinker compounds is an exothermic process, since it occurs with the release of thermal energy. If the initial components of the cement raw meal contain gypsum, the calcium and magnesium carbonates participate in endothermic processes with the release of gaseous carbon dioxide. The decomposition of aluminosilicates and two-water gypsum releases water vapor. The determination of the thermal effect of clinker formation is based on the Hess law, which, as is known [4], says that the magnitude of the thermal effect of chemical reactions at constant pressure depends only on the type and state of the starting materials and final products, but does not depend on the path of the transition. Several approaches to compiling methods for calculating the thermal effect of clinker formation are known in the literature [5-13]. In accordance with the procedure [5], the thermal effect of the formation of clinker minerals consists of the following values: heat consumption for heating the raw materials to the dehydration reaction temperature; heat consumption for dehydration of minerals; heating of the material to the decarbonization temperature; heat consumption for decarbonization of carbonate compounds, heat consumption for heating the products to the maximum process temperature, heat consumption for the formation of the liquid phase, minus heat from the exothermic reactions of clinker formation, and heat from clinker cooling and gases. Later E. Khodorov [5] suggested that the clinker formation process is a hypothetical circular cycle and can be represented as the production of clinker, water and carbon dioxide at 0°C, heating them to the temperature of clinker minerals formation and then cooling to 0°C. But since the heat costs for heating and cooling are equal and opposite in sign, the thermal effect of clinker formation is equal to the sum of all the partial effects of reactions at 0°C. The authors [7] presented a scientifically grounded methodology, which takes into account the thermodynamic characteristics of all participants in the reaction. This approach made it possible to more accurately determine the thermal effect of clinker formation than was previously done. They propose to take into account the heat content of gases leaving the process: water vapor and carbon dioxide. Based on the fact that there are a lot of disagreements in the existing methods, and that none of them takes into account the heat of burn-out additives. The authors of [8] propose the heat of clinker formation to be determined experimentally on thermographic curves. Undoubtedly, the proposed method is the most accurate, which in itself does not reduce the importance of theoretical studies. The above formulas for the theoretical thermal effect of clinker formation make it possible to determine the thermal effect of the formation of only Portland cement clinker. All known techniques do not take into account the presence of organic matter in the feed mixture. To determine the thermal effect of the formation of minerals of binders - lime, cement clinker, semi-aqueous gyp-

sum - the dependence can be applied [14-15], kJ/kg of the finished product:

$$q = [G_{CaCO_3} \cdot (\Delta H_t)_1 + G_{MgCO_3} \cdot (\Delta H_t)_2 + G_{CaSO_4 \cdot 2H_2O} \cdot (\Delta H_t)_3 + + G_{AS_2H_2} \cdot (\Delta H_t)_4 + \sum G_i \cdot (\Delta H_i)] + L_1 - 0.01[C_3S(\Delta H_t) + + C_2S \cdot (\Delta H_t)_5 + C_4AF \cdot (\Delta H_t)_6 + C_3A_3\overline{CS} \cdot (\Delta H_t)_7 + + C_{12}A_7 \cdot (\Delta H_t)_8 + \sum M \cdot E] - L_2 - n \cdot Q \cdot \eta \quad (1)$$

where: $G^C_{CaCO_3}$, $G^C_{MgCO_3}$, $G^C_{CaSO_4 \cdot 2H_2O}$, $G^C_{AS_2H_2}$, $\sum G_i$ - the content of calcium carbonate, magnesium carbonate, gypsum, aluminosilicates and other components of the raw material, respectively, kg / kg; $(\Delta H_t)_1$ – the enthalpy of calcium carbonate calcination reaction, kJ per 1 kg of calcium carbonate; $(\Delta H_t)_2$ – the enthalpy of the reaction of calcination of magnesium carbonate, kJ per 1 kg of magnesium carbonate; $(\Delta H_t)_3$ - enthalpy of the reaction of dehydration of calcium sulphate bicarbonate; $(\Delta H_t)_4$ – enthalpy of the dehydration reaction of the aluminosilicate component of the raw mixture, kJ / kg of the alumosilicate component; (ΔH_i), - enthalpy of other compounds, kJ / kg; L_1 – a coefficient that takes into account the enthalpy of the formation of a melt; kJ / kg of melt; L_2 - coefficient which takes into account the enthalpy of melt sealing, kJ / kg of melt; C_3S, C_2S , C_4AF , $C_3A_3C\overline{S}$, $C_{12}A_7$ – the content of alit, belit, four calcium aluminferrite, calcium sulfoaluminate and twelve calcium sevenaluminate in the composition of clinker, % by weight of clinker; $(\Delta H_t)_5$, $(\Delta H_t)_6$, $(\Delta H_t)_7$, $(\Delta H_t)_8$, E – respectively, the enthalpy of exothermic reactions of formation of alite, belit, four calcium aluminferrite, calcium sulfoaluminate, dinuclear setium aluminate, and other compounds, kJ per kg of the corresponding mineral; n amount of organic constituent of the raw mix, kg / kg; Q - calorific value of the organic component of the raw mixture, kcal / kg; η - efficiency of combustion of the additive. It is assumed that the heat content of gases released as a result of chemical reactions is taken into account in calculating the heat balance of a specific heat unit in which the process is carried out, taking into account the actual temperature and heat capacity of the exhaust gases. The dependence takes into account the mineralogical composition of the raw feed mixture and the phase composition of the final product of heat treatment. Moreover, in this case, energy costs are taken into account for the decomposition of various small components of the raw mix, as well as the release of energy during the formation of impurity minerals and combustion of the burning additive. The source material for the production of lime consists only of calcium carbonates and magnesium with small impurities. Therefore, the theoretical energy costs for burning lime are equal to the thermal effect of the calcining reaction of the source material in the calculation per unit of burned lime. The theoretical thermal effect of the calcium oxide formation reaction is estimated to be 42500 calories [13]. Theoretical energy expenditure for the formation of CaO minerals per 1 kg of product - lime: 42500: 56 = 758.9 kcal / kg of lime, where 56 is the molecular weight of calcium oxide. When the cement clinker is fired in the furnace, almost all the components specified in formula (1) are present. The mixture undergoes endothermic decomposition reactions of carbonates requiring the addition of heat. In addition, in the mixture there are exothermic processes of formation of clinker minerals alite, belit, alum ferrites, etc., which emit heat. Therefore, the total energy effect of the formation reactions of cement clinker minerals is less than the effect of lime formation reactions. Theoretical energy expenditure on the formation of minerals of cement clinker is 400-420 kcal / kg clinker [5], that is, on average, 1.8 times smaller than that of calcium oxide. For gypsum it is: 140 kcal/kg of semi-gypsum plaster. The actual energy consumption of the process of producing the binders depends on the efficiency of the equipment in which the firing process is carried out, kcal/kg:

$$q_a = \frac{q}{\eta_f} \quad (2)$$

where: q - the thermal effect of the formation of minerals of binders - lime, cement clinker, semi-aqueous gypsum, kcal / kg, η_f - efficiency of the firing process.

When using a dry production method, the efficiency is, as a rule, less than 0.5. Then the thermal energy consumption for production is estimated to be (kcal/kg) for: lime - 1500, cement clinker 800, dolomite clinker 450 [14-15], gypsum - 280.

2.3. The Energy Component of the Binder in the Composition of the Concrete

The component energy consumption for the production of binder, which is in the concrete, is determined as follows. If, for example, for the production of 1 m3 of cement concrete is consumed "c" (kg) of cement, the cement contains "k" clinker (kg clinker / kg of cement), and the specific heat consumption on the burning out is "q" (kcal / kg clinker) then energy consumption per 1 m^3 of cement concrete is determined, kcal/m^3 of concrete:

$$Q_b = c \cdot k \cdot q_a, \quad (3)$$

kJ / m^3 of concrete:

$$Q_b = 4{,}187 \cdot c \cdot k \cdot q_a, \quad (4)$$

kWh / m^3 of concrete:

$$Q_b = 1{,}163 \cdot 10^{-3} c \cdot k \cdot q_a \quad (5)$$

When using lime in the production of concrete, "k" expresses the activity of lime. For gypsum concrete, "k" indicates the content of calcium sulfate hemihydrate in the construction gypsum. Fig. 4 shows the dependence of the energy component in 1 m^3 of concrete for binders: building gypsum, slag cement, dolomite cement, portland cement, lime. The calculation is carried out with a content of 1 m^3 of concrete 330 kg of binder. The content of clinker in slag Portland cement was taken at 40%, in Portland cement 80%, in dolomite cement 80%. The lime activity is accepted at 0.9. It can be seen from Fig. 4 that lime is the most energy-intensive astringent. Portland cement during firing consumes energy significantly less. Gypsum, slag Portland cement and dolomitic cement can be attributed to energy-saving binders. The heat consumption for the production of slag Portland cement is approximately 5 times less than for lime production. The total energy consumption for the production of concrete consists of energy costs for the production of concrete components, transportation of components, preparation of concrete mix.

The formula for energy consumption for the production of concrete takes the form, kWh/м^3:

$$Q_c = Q_b + Q_s + Q_a + Q_m, \quad (6)$$

where: $Q_c, Q_в, Q_s, Q_a, Q_m$ - accordingly, energy consumption per 1 m^3 of concrete, for the production of binders, aggregates, additives and preparation of a concrete mixture.

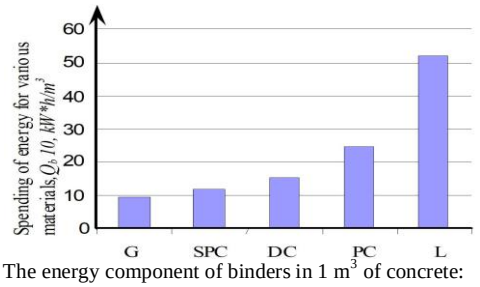


Fig. 4: The energy component of binders in 1 m^3 of concrete:
G - Gypsum, SPC - Slag cement, DC - Dolomite cement, PC - Portland cement, L – Lime.

The energy intensity of concrete production is reduced [17] by: fine cement grinding, the use of disperse fillers, effective plasticizing additives, compliance with technology, improving the quality of aggregates, minimizing transportation costs, using multicomponent cements, reducing cement consumption. Since in the total costs of energy for the production of concrete, the cost of energy for the production of cement is (50-70)%, then reducing the consumption of cement is the most important problem in improving the efficiency of concrete production. Scientists around the world are working on this problem [18-24]. They invent new compounds, improve the quality of concrete, replace natural components with industrial waste. A lot of attention is paid to slags - waste of the metallurgical industry. In the composition of slags there are the same oxides as in the cement clinker: calcium oxide, oxides of silicon, aluminum and iron in different ratios. Slag takes part in the reactions of hydration of a concrete mixture. Advantages of slag application: do not contain calcium carbonate. And, therefore, do not pollute the environment with carbon dioxide. In terms of output, slags are equated to the needs of the building materials industry. Therefore, they can replace some of the natural materials used in the production of concretes. The disadvantages of slag are slow hardening. This problem is also solved by fine grinding of slag and activation of its binding properties with the help of additives.

3. Conclusion

A relationship has been shown that makes it possible to determine the thermal effect of the formation of minerals during firing of binders taking into account the content of organic matter in the composition of the feed mixture.
A comparative analysis of the energy consumption for the production of lime, portland cement, dolomite cement, slagportland cement and gypsum was carried out. It is shown that the use of slagportland cement in the manufacture of concrete mix is two times more energy efficient than Portland cement, and five times more profitable than the use of lime.
It is shown that the use of natural components in the production of concrete contributes to an increase in the consumption of thermal energy. The best alternative to natural materials is industrial waste. They contribute to reducing fuel consumption and reducing greenhouse gas emissions.
Reduction of calcium carbonate in the composition of the initial mixture or its replacement with calcium oxide instead of calcium carbonate helps to reduce heat consumption for burning cement clinker.
The use of waste containing calcium oxide (slag or ash) in the production of binders and concretes has a fourfold ecological and economic effect:
- it reduces consumption of expensive fuel,
- reduces environmental pollution by gas emissions,
- releases land from the industrial waste,
- retains natural resources for future generations.

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