

DOCTORAL THESIS

EFFECT OF LIMESTONE ON THE DEVELOPMENT OF PROPERTIES OF MULTI-COMPONENT SLAG – LIMESTONE CEMENTS

In the era of sustainable development policy, the cement industry, responsible for around 5-7% of all anthropogenic carbon dioxide emissions, faces the need to reduce CO₂ emissions in the cement production process. For this reason, as well as economic reasons, mineral additives, such as fly ash, granulated blast-furnace slag, or limestone, are increasingly used in the production of cement. It can be assumed that due to the limited quantities of the most frequently used non-clinker main components of cement (granulated blast-furnace slag and fly ash), the use of limestone as a main component of cement will be more widespread in Poland. Increased use of limestone in cement is also included in an amendment to the EN-197-1 standard, introducing multi-component Portland CEM II/C cements with higher limestone content as well as a new group of multi-component CEM IV cements.

Limestone has a beneficial effect on a number of cement properties, which is mainly related to its physical effects. Due to the high fineness in comparison to clinker, which results from its high grindability, limestone acts as a micro-filler, sealing the cement paste structure. In addition, fine limestone grains can act as nucleation seeds of cement hydration products. At the same time, the addition of limestone to cement may negatively affect the mechanical properties of mortars, reducing compressive strength and tensile strength.

The aim of the doctoral thesis was to determine the influence of limestone on rheological and mechanical properties and heat of hydration of Portland limestone cement CEM II/A, B-LL and multi-component slag-limestone cements CEM I/A,B,C M (S-LL) and CEM VI (S LL).

In the research, two technological possibilities of using LL limestone in cement were used: homogenisation of separately ground limestone LL, clinker and granulated blast furnace slag, and mixing of ground limestone with Portlands slag cement (CEM II/A,B-S) and slag cement (CEM III/A) that are produced industrially.

The scope of the dissertation includes a literature study and research carried out in four stages. In the first stage, tests of rheological and mechanical properties as well as heat of hydration of Portland-limestone cements obtained by homogenization of four industrially produced Portland cements with two types of LL limestone, ground to two specific surfaces, were carried out. The second stage includes research on rheological properties and heat of hydration of Portland-slag cements obtained as a result of homogenization of four types of Portland cement with two types of granulated blast furnace slag, one of which has been ground to two specific surface areas. The third stage examined the rheological properties and heat of hydration of multi-component slag-limestone cements obtained by homogenizing three Portland cements with two types of granulated blast furnace slag and two types of LL limestone with two different specific surface areas. The last stage included research on rheological properties, heat of hydration and mechanical properties of slag and

lime multi-component cements obtained by homogenizing Portland slag cements and slag cement with two kinds of limestone.

The addition of limestone to cement in the amount of 5-10% of cement mass did not show a significant effect on both mechanical and rheological properties of mortars with Portland limestone CEM II/A, B-LL cement and multi-component slag-limestone cements CEM II/A,B,C M (S- LL). Increasing the content of limestone above 10% in the composition of Portland-limestone cement or multi-component cement had a negative effect on the mechanical properties of mortars. The influence of limestone on the rheological properties of mortar was dependent on the type of limestone, which can be attributed to a clearly different particle size distribution of the limestones used. Limestone characterized by discontinuous particle size distribution decreased rheological properties, whereas limestone with symmetrical distribution and low content of coarse grains did not affect rheological properties.

The specific surface area of a particular type of limestone did not have a significant impact on the investigated properties of Portland limestone cements and multi-component slag-limestone cements. It can be concluded, that the use of high specific surface area limestones is not economically and technologically sound.

Addition of ground granulated blast furnace slag to Portland cement CEM I in an amount of 6-30% of cement mass causes a reduction of the yield stress and an increase in the plastic viscosity of the mortars, while the type and specific surface of the MGŻW have no noticeable effect. In the case of multi-component Portland cement CEM II/A,B,C-M (S, LL) and multi-component cement CEM VI (S, LL) it can be noted, however, that the type of blast furnace slag affects the mortar yield stress. In mortars with the addition of blast furnace slag SH, with high activity and specific surface area, the yield stress is comparable to the yield stress of Portland cement mortar CEM I. In the case of mortars with slag SZ, with a lower activity and surface area relative to SH slag, the yield stress decreases along with the increase in blast furnace slag content.

Limestone and ground granulated blast furnace slag show a synergy effect in relation to the compressive strength of mortars with multi-component slag-lime cements. Increasing the total content of slag and limestone in the cement composition did not cause a proportional drop in strength.

The results of the conducted research indicate the possibility of using limestone in both Portland limestone CEM II/A, B-LL cements as well as multi-component slag-limestone cements CEM II/A,B,C M (S-LL) and CEM VI (S, LL).