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The Mechanism of Disintegration of Cement Concrete at High Temperatures

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Abstract **– Concrete is a composite material composed of a binder, aggregates, water and additives. Mixing of cement with water results in a number of chemical reactions known as cement hydration. Heating of concrete results in dehydration processes of cement minerals and new hydration products, which disintegrate the microstructure of concrete. This article reviews results of research conducted with Portland and alumina cement with conventional and refractory concrete aggregates. In civic buildings such common fillers as gravel, granite, dolomite or expanded clay are usually used. It is important to point out the differences between fillers because they constitute the majority of the concrete volume.**

Keywords **– Aggregate, concrete, dehydration, disintegration mechanism, high temperature, Portland cement.**

I. Introduction

This review examines hydraulic binders – cements, which harden and remain strong both in the air and in water. Portland cement and its varieties, slag and pozzolanic cements, alumina cement and expansive cement are considered to be hydraulic binders. Aggregates are another component of concrete. Fine aggregate is such an aggregate, the coarsest particles of which are no greater than 4 mm, while coarse aggregate is such an aggregate, the coarsest particles of which are at least 4 mm and the finest particles are no smaller than 2 mm. By their origin aggregates are classified into natural, artificial, from industrial waste and from secondary raw materials.

Water or aqueous solutions form a liquid phase in concrete mixtures. Physical and chemical processes result in mixtures acquiring cohesive and certain rheological properties when mixed with water. Water plays an important role in hydration processes. Water for the preparation of construction mixtures should meet certain requirements, namely, it cannot contain any impurities, which lead to corrosion of the hardened concrete, organic impurities, which slow down hydration processes of binders, limiting the content of chlorides, sulphates, alkalis, phosphates and nitrates, which leads to sulphate or alkaline concrete corrosion.

In some cases, when concrete is not dried, concrete degradation due to explosive spalling caused by thermal stresses and water vapour pressure can be observed. Anderberg indicates that surface cracking increases with the higher moisture content in concrete, due to its impermeability, compression from external load, speed of temperature change, asymmetric distribution of temperature. Fragmentation mechanisms are related to vapour pressure. When concrete is heated, free water heats up and evaporates, in case there are no conditions for water to evaporate (pores are closed), the pressure increases greatly [1].

The authors present the following conclusions: [18], [19].

Concrete bursting takes place at the temperature of 200 °C to 325 °C.

Additives are added to regulate the hardening processes or to obtain technological properties. They are divided into mineral and chemical additives. Chemical additives are chemical substances added into mixtures in small quantities during preparation. By the nature of their action, chemical additives are divided into several groups: those regulating rheological properties, intensity of the setting and hardening, special and multi-functional additives. Mineral additives are finely ground natural rock or industrial waste, which are added when mixing mixtures, and they are divided into active additives and mineral fillers. The listed concrete components are important in designing concrete having respective properties.

There are no raw materials, except for expanded clay, suitable for the production of refractory concretes in Lithuania, therefore, the major share of the necessary refractory components is imported into the country, namely, the sodium silicate bar for the production of a liquid glass binder, also alumina cement, chamotte, mullite, vermiculite, bauxite, refractory clay and other substances [10].

In order to reduce the price of refractory concrete, Portland cement should be used instead of special alumina cement. A variety of cements is produced depending on the mineral composition of cement clinker, additives and received cement properties. 5 cement types are distinguished: CEM I – Portland cement, CEM II – composite Portland cement, CEM III – slag cement, CEM IV – pozzolanic cement and CEM V – composite cement.

The aim of the work is to review the impact of different cements and aggregates on the concrete disintegration mechanism at high temperatures and identify the occurring processes.

II. The Mechanism of Disintegration of Portland Cement at High Temperatures

The hardening of Portland cement occurs in aqueous environment. Cement minerals form new hydrated compounds with water. There are three key products forming during cement hydration:

- calcium hydrosilicates (C-S-H),
- calcium hydroxide (CH),
- calcium hydro sulpho-aluminate – trisulphate (AF_t) or monosulphate (AF_m) form.

The hardening process of Portland cement takes a long time. Strength properties of the composite increase faster when curing at temperatures ranging from 20 °C to 35 °C and can reach the necessary strength in 4–5 day of hardening.

When treating Portland cement stone at high temperatures, $Ca(OH)_2$ crystal hydrates, the size of which is 10^{-6} m, lose water when heated and transform to CaO crystals, the characteristic size of which is 10^{-9} m [7].

The specific surface of calcium oxide is large, therefore it becomes saturated with moisture from the environment and rehydrates. During the second hydration, $Ca(OH)_2$ volume increases by 44 %. This phenomenon leads to complete disintegration of cement stone [15].

The scientists [10] conducted a research. Portland cement (CEM I 42.5) was used in tests. Water-cement ratio was 0.25. Cement samples were left to harden for 7 days under normal conditions. Later, they were calcined at various temperatures ranging from 300 °C to 1200 °C and kept for 3 days under humid conditions. Samples disintegrated after calcination at the temperature of 600 °C and storage under humid conditions for 3 days (Fig. 1).

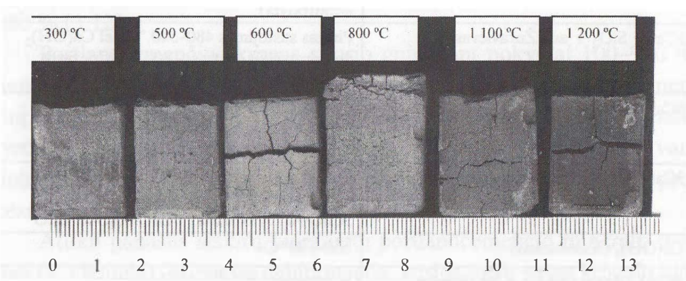

Fig. 1. Portland cement samples after calcination and storage for 3 days under humid conditions [10].

Having calcined samples at high temperatures and protected them from moisture effects, different results were obtained. The samples did not disintegrate, but their compressive strength decreased (Fig. 2).

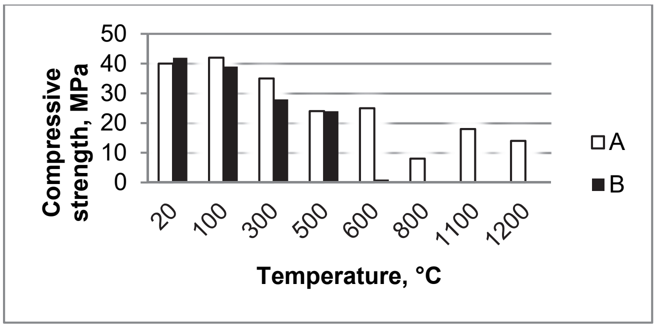

Fig. 2. Portland cement rock compressive strength: A – heated at high temperature and protected from moisture, B – heated at high temperature and left for 3 days in humid conditions [10].

The scientists conducted research with various Portland cements having different tricalcium aluminate C_3A content. The first sample had $C_3A > 9$ % and the second – $C_3A < 1$ %. The samples were kept under normal conditions for 28 days. Later, they were calcined at temperatures up to 620 °C and cooled under normal conditions. The research results confirmed the above-described mechanism that having reached 530 °C to 560 °C, portlandite $Ca(OH)_2$ decomposes resulting in the formation of lime (CaO). Later, while cooling, lime absorbs water from the environment and hydrates once again. Portlandite hydrated for the second time is less crystallized than the primary one, and its thermal decomposition temperature becomes lower. In the case of sample content ($C_3A > 9$ %) only part of it decomposes to form portlandite and larnite, while the decomposition is total in the case of the powdered sample with content ($C_3A < 1$ %) [8].

The researcher [11] examined four concretes of different composition at different temperatures. He used Portland cement with composition C_3S – 38.95 %, C_2S – 30.55 %, C_3A – 9.91 %, C_4AF – 11.98 % in the tests. Crushed limestone and river stone, the largest particles of which were 15 mm, were used as aggregate. 70 × 70 × 70 cubic samples were prepared for tests, and were kept in water for 28 days, later dried at ambient temperature for 6 days and kept in the oven at 105 °C for one day. Samples were heated and kept at the desired temperature for 2 hours. Temperature rising speed was 20 °C/min. Surface cracks (Fig. 3), weight losses and compressive strength were recorded. Up to 800 °C, weight losses increased gradually up to 10 %. From 800 °C to 1200 °C the loss of concrete weight increased rapidly and totalled 40 %. W/C ratio had no impact on weight losses. Compressive strength decreased by 60 % at 800 °C, and the sample disintegrated at 1200 °C.

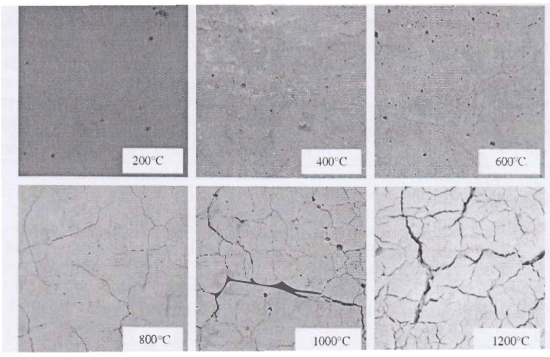

Fig. 3. Surface cracks at different temperatures [11].

III. The Impact of Alumina Cement on the Disintegration Mechanism at High Temperatures

Alumina cement is a rapidly hardening hydraulic binder [13]. Alumina cements are classified by Al_2O_3 content and can be divided into four groups: containing 40 % Al_2O_3, 50 % Al_2O_3, 70 % Al_2O_3 and 80 % Al_2O_3.

Various reactions occur in water and alumina cement paste. Cement minerals having different activity levels take part in these reactions. Water molecules are absorbed locally in the mineral surface – active centres of crystals – in the initial hydration stage. Mixing cement with water and observing through the microscope, separate new formations can be seen, which eventually expand and cover the surface of the crystal [4], [10].

Free as well as physically and chemically linked water is discharged during the first heating. Water emits from cement rock in stages: 110 °C to 120 °C, 180 °C to 200 °C, 280 °C to 300 °C [5]. First of all, at up to 100 °C, free water is discharged, followed by CAH_{10} dehydration at 120 °C and C_2AH_8 dehydration at 200 °C, with dehydration of AH_3 at 300 °C in the end. Crystal hydrates C_3AH decompose at 337 °C. After dehydration, $C_{12}A_7$ forms at the temperature of 500 °C to 800 °C, which transforms to CA, CA_2 and C_2AS minerals after heating at 1000 °C [10].

Cements, the temperatures of operation of which are below 1300 °C, are usually used with chamotte aggregates and low alumina content alumina cement. The composition of conventional cement of such type is 25 % of alumina cement and 75 % of (0 to 10) mm fraction chamotte. The following are the main properties of concrete:

- the maximum operating temperature – 1300 °C;
- compressive strength after curing at 110 °C – 25 MPa;
- residual strength after heating at 800 °C – 30 %;
- density after curing at 110 °C – 1900 kg/m^3.

However, after the heat treatment at temperatures higher than 1100 °C, when reactions in solid phases and sintering processes occur in the chamotte concrete structure, compressive strength of the concrete increases significantly and reaches 50 MPa to 60 MPa [10].

IV. The Impact of Additives on the Mechanism of Disintegration of Cement Concrete at High Temperatures

To improve characteristics of concrete, various additives are mixed in the composition of the concrete. The scientists [3], [16] examined concrete with micro silica and determined that increasing the content of SiO_2 micro silica in the composition of the binder, the need for water increases substantially. This shows that micro silica absorbs a large amount of water. The time of the start and end of setting depends on micro dust content. Having added 1 % SiO_2 micro silica into the mixture, the start of the setting is registered at 150 min. Having added 3.2 % of micro dust, the start of the setting is registered at 600 min. Compressive strength depends on SiO_2 micro silica content and the duration of hardening. In 2–3 days of hardening, the weakest sample is with the highest content of SiO_2 micro silica, however, in 6–7 days of hardening such samples acquire the maximum compressive strength [3]. The scientists [16] observed that during ultrasonic testing, exposing concrete at temperatures ranging from 400 °C to 800 °C, the speed of ultrasonic propagation slowed down by half from 3800 m/s to 1800 m/s.

The researcher [2] examined the impact of the sodium silicate (liquid glass) and its solution on the properties of heat-resistant concrete. The expansion of the sample was determined to depend on the density of liquid glass. A lower density of liquid glass was observed to less expand the material at 500 °C to 600 °C. These reactions occur as a result of the bloating of liquid glass films unreacted during the hardening process. The durability of concrete changes depending on the content of sodium silicate in the concrete. Reducing the content from 6.5 % to 3.7 % thermal stability increases from 13 to 20 thermal cycles, while their residual strength accounts for 79 % to 87 % [2].

The scientist [17] examined the impact of polypropylene and metal fibers in high-strength concretes at high temperatures. Portland cement CEM I with the strength class of 52.5 and the aggregate superplasticizer Cimfluid 2002, polypropylene and metal fibers were used in the tests. Samples of 4 types were produced: without fiber, with polypropylene fiber, with metal fiber and with metal and polypropylene fibers. The loss of weight in the temperature range from 300 °C to 600 °C was determined to change evenly, but it was greater in concretes with polypropylene fiber. Mechanical strength properties of concrete with polypropylene and metal fibers are worse than those of concrete with metal fiber, but better than concrete without fiber [17].

V. Concrete Aggregates

Aggregates are an inert component of mixtures constituting the major share of the volume of the mixture – up to as much as 95 %. The main purpose of aggregates is to fill up the volume in the mixture, reduce the content of binders and improve technical properties of concrete [12], [13].

The structure and properties of the product depend on the concentration of aggregate properties in the mixture. Aggregates usually fill up the volume of the product, while one or another binder, the content of which in the mixture is usually a few times smaller than the content of the aggregate, only binds together the particles of the aggregate in the product. The properties of components, particles of the aggregate, its shape and layout, the roughness of the surface and other properties necessary for the evaluation of durability of the hardened composite should be evaluated in the production of composite mixtures. Usually the aim is to receive a mixture of the optimum structure and a product of the necessary quality. Aggregates most commonly used in concrete include sand, gravel, dolomite, granite, and expanded clay.

Sand is a fine concrete aggregate, the fraction size of which ranges from 0 mm to 4 mm. Natural sand is a sedimentary rock with differing mineral composition, quartz for the most part. The particles come in different forms, such as angular, rubbed, etc.

Gravel is a chunky concrete aggregate, the fraction size of which is from 4 mm. Gravel is a sedimentary rock, which just like sand has a differing mineral composition depending on the prevailing rock.

Dolomite is a carbonate class calcite group mineral. Its crystals are shaped as a tringonic syngony, rhombohedron or a polygon. They can be of different shades from light grey to dark grey with hardness of 3.5 to 4.0 according to the Mohs scale.

Granite is an intrusive igneous rock, which crystalizes from a high temperature melt in the crust of the earth, therefore, the walls of the minerals are grown together and strongly bonded, with the porosity of intact granite accounting for mere 0.01 %. This is the reason why granite is resistant to high temperature effects, has low water absorption ratio (of 0.2 % to 0.5 %) and is virtually impervious to water. Its hardness ranges from 5.5 to 7.0 according to the Mohs scale.

Expanded clay is granules of clay baked at high temperatures, which are as many as four times lighter than analogues found in nature. The clay of different layers dug out in quarries is mixed, super cooled, dried, crushed and fed into a ball oven. Clay raw material expands there at the temperature of 1150 °C, forming a hard outer surface and granules with a porous internal structure.

The aggregate takes up to 95 % of concrete volume, thus it is important to know how different aggregates affect concrete in case of fire. Thermogravimetric studies were used for this purpose in our research. The temperature rising speed was 10 °C/min. The dependence of weight losses on temperature is illustrated in Fig. 4.

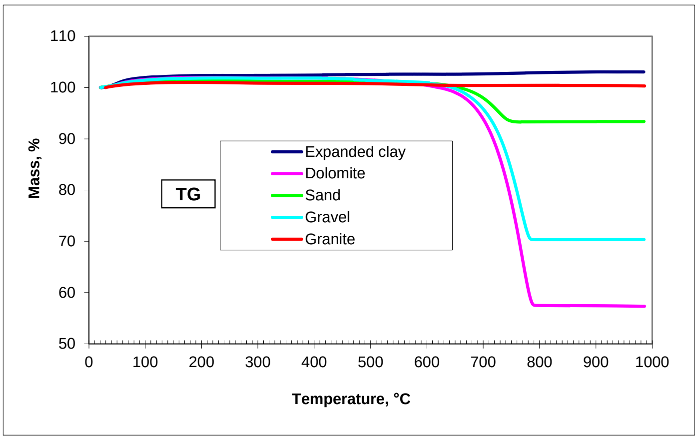

Fig. 4. Dependence of weight loss on temperature in different aggregates.

The largest weight losses of about 40 % were observed in dolomite, because calcium and magnesium carbonates decompose. At lower temperature decarbonisation of magnesium carbonates occurs and at higher temperature – decarbonisation of calcium carbonates. The process begins at the temperature starting from 680 °C and completes at 800 °C [20]. Slightly lower losses of about 30 % were observed in gravel and about 10 % in sand. They also contain calcium and magnesium carbonates, because decomposition occurs at the same temperature. Weight losses in granite and expanded clay were not recorded, thus these aggregates can be said to be inert to temperature. However, literature emphasizes that at 573 °C quartz changes its lattice structure from alpha to beta, thus increasing its volume. Therefore, a dilatometer, which measures material deformation (expansion) caused by temperature, was used for this issue. The temperature rising speed was 10 °C/min. Concrete samples with different aggregates were prepared for tests. Sand was used as a fine aggregate, while gravel, expanded clay, granite and dolomite were used as a coarse aggregate. The dependence of deformation (expansion) on temperature is illustrated in Fig. 5.

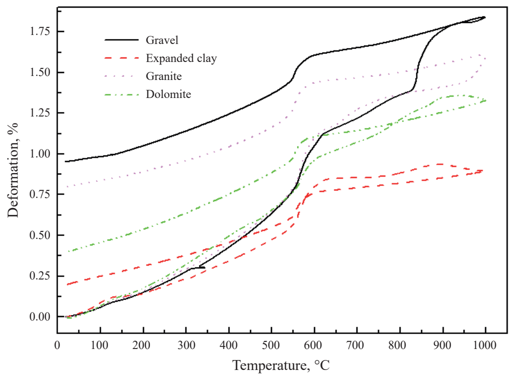

Fig. 5. Dilatometric curves of specimens with different types of aggregates.

Dilatometry well illustrates the expansion process occurring at 570 °C. All concrete samples contained quartz, and its content was dependant on the selected aggregate. Quartz content was the greatest in concrete samples with gravel and granite aggregates, therefore the greatest deformations of as much as 1.8 % were observed. Concrete samples with dolomite and expanded clay aggregates demonstrated lower deformation (expansion) because only the quartz contained in sand acted there.

Refractory materials are of different composition and properties. During operation, they have to retain their structure and volume, not to melt or disintegrate at certain specified temperatures. Such aggregates are used in the production of refractory concretes, mortars and fillers [9].

Chamotte materials are made of a mixture of sintered, refractory clay and a binder. Refractory clay consists of about 28 % to 34 % $A_{12}O_3$, 45 % to 55 % SiO_2 and 2 % to 5 % other oxides. The more $A_{12}O_3$ and the less other oxides are there in clay, the more heat resistant it is.

Dinas is made of natural quartzite with at least 97 % of SiO_2. Lime milk (1.5 to 2.5) % and sulphite lye or sulphite solubles are used as a binder. The mixed mass slowly calcines at a temperature of about 1430 °C. At the end of calcination, quartz mineral transforms to tridymite or cristobalite. Dinas is used at temperatures up to 1600 °C to 1650 °C.

Magnesite products are made by pressing calcined magnesite containing at least 85 % of MgO. The highest magnesite operating temperature is 1550 °C to 1800 °C.

Chromite ($FeO \cdot Cr_2O_3$) and magnesium aluminium spinel ($MgO \cdot Al_2O_3$) obtained from bauxites and calcined magnesite are heat-resistant materials. Chromite forms at the temperature of 2180 °C. Crushed chromite is used as an aggregate, and it is used at a temperature below 1500 °C to 1700 °C.

Bakor (baddeleyite-corundum) heat-resistant materials are made of technical aluminium oxide and zirconium natural mineral ($ZrSiO_4$). Poor zirconium ZrO_2 is received by sintering it with alkaline earth metal oxides or carbonates. That way the obtained $Zr(OH)_2$ transforms to ZrO_2 when additionally heated. The highest operating temperature is 1500 °C to 1700 °C.

Carborundum products are made of the mixture of enriched quartz sand and petroleum coke. Their heating at the temperature of 2000 °C to 2200 °C results in the formation of artificial carbide (SiC). The highest operating temperature is 1650 °C to 1680 °C [9].

VI. Conclusion

The use of Portland cement in the production of refractory concretes is complicated because of lime (CaO) forming during dehydration. Additional additives are necessary to bind the discharging lime (CaO).

Alumina cement is more suitable for the production of refractory concretes than Portland cement. Based on the research presented in scientific literature, concrete with alumina cement should be calcined at a temperature of more than 1100 °C. Then, reactions having occurred in solid phases allow using concrete at high temperatures.

Chamotte, dinas, magnesite products, chromites, bakor and carborundum products may be used as aggregates of refractory concrete, they withstand high thermal stresses up to 1700 °C. These aggregates are expensive to be used for normal concrete used in construction.

Dolomite is a more suitable aggregate for normal concrete, as its deformation is the lowest. Expanded clay is a more suitable aggregate for lightweight concrete, because it does not deform at high temperatures. These aggregates have lower expansion rate during heating of concrete at high temperature due to fire.

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