Studying compression strength of XD3 concrete samples after addition of calcium nitrate inhibitor and superplasticizers

Shaymaa Abbas ABDULSADA

PhD student in Faculty of Materials Science and Engineering, University of Miskolc, Hungary.
Lecturer at Faculty of Engineering, University of Kufa, Iraq. Research Interests: Corrosion Engineering, Metallurgy Engineering, Heat Treatment of Metals, Casting of Metals.

Tamás I. TÖRÖK

Professor of Chemical Metallurgy and Surface Technologies at University of Miskolc, Hungary.
First Secretary of HUNKOR, the Hungarian Corrosion Society, and former President of ASM International Hungary Chapter.
Recent Research Interests: Corrosion Phenomena, Protective Coatings, Metals Surface Treatments and Surface Engineering.

SHAYMAA ABBAS ABDULSADA ▪ Faculty of Materials Science and Engineering, University of Miskolc, Hungary ▪ qkosha86@uni-miskolc.hu

TAMÁS I. TÖRÖK ▪ Faculty of Materials Science and Engineering, University of Miskolc, Hungary

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Abstract

This research paper presents an analysis of the compression strength properties of concrete samples in the function of their calcium nitrate inhibitor content. This low cost inorganic inhibitor was added to the concrete mix in concentrations of 1% and 3% by weight of cement in addition of two different superplasticizers (MapeiDynamon SR 31 and Oxydtron). The compressive strengths of the so prepared samples were checked according to the relevant European standard and were within the acceptable limits, so this inhibitor does not weaken this important property of the concrete samples. Moreover, the MapeiDynamon SR 31 superplasticizer even showed higher (acceptable) values compared to the other type of superplasticizer due to the difference between their ability in reducing the ratio of water of the concrete samples.

Keywords: calcium nitrate inhibitor, compression strength, superplasticizers, concrete samples

Kulcsszavak: kalcium-nitrát uinhibitor, nyomószilárdság, plasztifikáló adalékok, beton minták

1. Introduction

Corrosion of steel rebar in reinforced concrete structures is a serious problem which might cause significant human and economic losses. One of the most important reasons of corrosion in reinforced concrete is chloride attack. The main sources of chlorides are seawater and de-icing salts. Also, there are other sources of chlorides for example from gravels, sand, cement, water (being used for preparing the mixture of fresh concrete) and sometimes from (contaminated) steel rebar. In the subsistence of chloride, the protective passive stratum of steel is locally destroyed and the unprotected steel areas start dissolve. The formation of corroding products (rust) involves a substantial volume increase, i.e. the volume of corrosion products is greater than that of original steel bar. Therefore expansive stresses are induced around corroded steel bars causing possible cracking, spalling of concrete cover and loss of bond between steel and concrete, thus reducing the serviceability of concrete structures [1-9].

There are several methods used to minimize corrosion of steel in concrete, one of these is to use inhibitors. Among the available methods, the uses of corrosion inhibitors are cost-effective and easy to handle. Inhibitors are added to fresh concrete while migrating inhibitors are usually proposed for concrete repair. Inhibitors, such as zinc oxide, molybdates and borates, carboxylate ions, quaternary ammonium salts, and other organic compounds were studied [10].

The hardening process of concrete is one of the important factors which effects on the compressive strength of concrete. The binder in concrete is cement. The cement matrix is formed during the hydration process and binds the aggregates together. The basic elements in the production of Portland cement are limestone (CaCO_3), silica (SiO_2), alumina (Al_2O_3), iron oxide

(Fe_2O_3) and other substances in minor quantities. To produce cement clinker, the raw materials are mixed, ground and burned in a rotary kiln at about 1450°C . The constituents react to form new minerals. The four major minerals in cement clinker are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The minerals in the clinker begin to react when water is added. This series of chemical reactions is called the hydration process, and consists of various phases. It starts immediately, and the dominant reactions occur on the first day [11, 12]. However, the chemical reactions continue for months, or even years, slowing down gradually. In engineering practice, the hydration process is often supposed to be 'finished' after around 28 days when the representative strength is reached. It is presented schematically in Fig. 1 according to Locher [13].

In cement hydration process, there are some amounts of calcium hydroxide (CH) remaining in the cement structure. Those remaining CH can be replaced by consuming them with silica to form additional calcium silicate hydrates (C-S-H) which is the main contribution of cement strength [14, 15]. This silicon dioxide (silica) can be found through the pozzolanic material known as pozzolan.

Superplasticizers are preferred in concrete preparation for their ability to reduce the water requirement while maintaining workability and enable the improvement of strength. Fig. 2 illustrates the working mechanism of superplasticizer. Cement particles are dispersed by repulsive force generated by negatively charged superplasticizers (Fig. 2/b) as, for example, in our case by a modified acrylic polymer Mapei Dynamon SR 31, and the entrapped water would be released. Therefore, the flow characteristics of concrete are improved [16].

Fig. 1 Scheme of the hydration process according to Locher [13]. (Top) The development of the individual components and (bottom) schematic sketches of the material structure at 4 corresponding stages in time

1. ábra Hidraulikus kötés folyamata Locher szerint [13] Az egyes összetevők (fázisok) kialakulása (felül), és a megszilárduló anyag szerkezetének változása vázlatosan az időben (alul)

Fig. 2 Action of superplasticizer on cement particles. (a) Flocculated cement particles; (b) dispersing cement particles by the repulsive force generated by negatively charged superplasticizer; (c) releasing of entrapped water [16]

2. ábra Plasztifikáló adalék hatása a klinker ásványsemmekre. (a) Flokkulálódott részecskék; (b) Cement/klinker részecskék diszpergálódása a negatív felületi töltésű plasztifikáló adalék hatására; (c) A fizikailag megkötődött víz felszabadulása [16]

The main purpose of this paper is to present the results of an experimental study on the compressive strengths to monitor and evaluate the effect of calcium nitrate inhibitor and superplasticizers of test samples prepared from concrete type XD3.

2. Materials and methods

2.1 Materials and preparation of samples

Portland slag cement CEM II/A-S 42.5R was used in this study conforming to the standard EN 197-1 [17] and it was received from CRH Magyarország Kft. company in Miskolc, Hungary. Aggregates (fine and coarse) were used according standard EN 12620 [18] and it was also received from the CRH Magyarország Kft. company. This type of cement chosen because it is very workable, has a progressive increase in its initial strength, has very good cement density and its resistance to chemical reactions is high. Calcium nitrate as a inorganic inhibitor and two types of superplasticizers (Mapei Dynamon SR 31 and Oxydtron) were used. Tap water was used for both making and curing the specimens.

Concrete mixes were designed in accordance with the European mix design method (XD3 class) to have compressive strength C35/45 at age of 28 days. Two times three samples were prepared (with the two different plasticizers) and the two sets of three plus three samples contained in 0%, 1%, 3% the calcium nitrate inhibitor as shown in Table 1. The concrete cubes so prepared for compressive strength testing had dimensions of 70×70 mm. The molds were thoroughly cleaned and oiled before casting to avoid adhesion with the concrete surface. Mixing of materials was done manually after that water added to the mix with continued mixing, then the mix was put in the molds.

The specimens were taken out from the molds after 24 hours hardening, then were immersed in tap water for 28 day as shown in Fig. 3.

Symbol of Mix	Type of Mixtures	
	Type of Admixture	Concentration of Calcium Nitrate Inhibitor
A3 (Reference)	Mapei Dynamon SR 31	without
B3	Mapei Dynamon SR 31	1% by weight of cement
C3	Mapei Dynamon SR 31	3% by weight of cement
A4 (Reference)	Oxydtron	without
B4	Oxydtron	1% by weight of cement
C4	Oxydtron	3% by weight of cement

Table 1 The concrete mixtures (specimens) prepared for this study
1. táblázat Betonminták összetétele a jelen vizsgálatokhoz

Fig. 3 Curing of compressive strength specimens in tap water

3. ábra Nyomószilárdság mérésére előkészített próbák érlelése csapvizben

2.2 Compressive strength test

The concrete compressive strength was measured by using a compressive strength testing machine (Kispesti Vas és Fém KTSZ) as shown in Fig. 4. The cubes were removed from the curing water at age of 28 days after that tested by compressive strength machine as shown in Fig. 5. The reported values are the average of three specimens for each age (nine for each mix).

Fig. 4 Machine of compressive strength while sample testing
4. ábra Berendezés a nyomószilárdság mérésére

Fig. 5 Specimens before and after compressive strength testing
5. ábra Betonminták a nyomószilárdság mérése előtt és után

3. Results and discussion

After adding calcium nitrate as a corrosion inhibitor, the results of compressive strength measurements was presented in Fig. 6 and Table 2.

Symbol of Mix	Compressive Strength in MPa at 28 day
A3 - Reference (for comparing)	38
B3	41
C3	46
A4 - Reference (for comparing)	30
B4	32
C4	38

Table 2 Results of compressive strength test for samples with calcium nitrate inhibitor
2. táblázat Kalcium-nitrát inhibítort is tartalmazó teszt minták nyomószilárdság értékei

As it is illustrated in Fig. 6 the samples without inhibitor has significantly lower compressive strength. In the samples with Dynamon SR 31 there was not much reduction observed in the compressive strength (about 38 MPa as average for 3 samples tested at age 28 days). While the samples with Oxydtron caused a greater decrease in compressive strength (about 30 MPa as average for 3 samples tested at age 28 days) than Dynamon SR 31 admixture.

(Without this admixtures (Dynamon SR 31 and Oxydtron)

the given type of concrete should have a compression strength of C35/45 MPa at age 28 days.).

Fig. 6 Compressive strength of concrete samples with calcium nitrate inhibitor after immersion in tap water for 28 days
6. ábra Kalcium-nitrát inhibítort is tartalmazó betonminták nyomószilárdság értékei 28 napig csapvízben érlelés után

Comparing the effect of superplasticizers we found that Dynamon SR 31 caused reduction in water during the hardening process of concrete more than Oxydtron and this reduction in water caused increase in compressive strength of concrete and also decreased the porosity as a consequence of a series of chemical reactions (called hydration) of cement with water to form the binding material. The major compounds of cement (tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF)) begin to react with water within a few minutes and absorb the water then do not generate much strength, but can stiffen the mix and reduce workability, so if there's high quantity of water in the concrete that means the hydration components will be larger and these will decrease the capillary porosity and finally cause decrease in strength of concrete because the compressive strength depends also on the capillary porosity. So Dynamon SR 31 superplasticizer in this case more advantageous than Oxydtron superplasticizer.

By using calcium nitrate as corrosion inhibitor in conc. 1% and 3% by weight of cement and Dynamon SR 31 superplasticizer, the compressive strength increased considerably by 8% for 1% addition and 21% for 3% addition, respectively. While after using calcium nitrate inhibitor with 1% and 3% by weight of cement and Oxydtron superplasticizer, the compressive strength effected with an increase 7% for 1% addition and 27% for 3% addition, respectively.

The increase in compressive strength after adding calcium nitrate was due to that this admixture can accelerate the setting time and/or foster the development of higher early strength (calcium nitrate is a multifunctional admixture for concrete, i.e. it can work as setting accelerator for hydration process and as corrosion inhibitor). Calcium nitrate accelerates the hydration process because it has the same Ca^{2+} ion like the cement clinker minerals C_3S and C_2S . And, in presence of the water soluble calcium nitrate additive the crystallization processes can progress more intensively. The observed higher compressive strength with 3% calcium nitrate additive compared to the case with 1% can be attributed to the different compositions of the amorphous calcium silicate hydrate binders (CSH-gels) that will precipitate around the cement grains. An increased calcium

concentration in the pore water when calcium nitrate is also present may stabilize the CSH-gel causing a higher Ca/Si molar ratio and thus leading to the formation of polysilicate anions with shorter average length. The replacement of cement by calcium nitrate on the other hand, will lead to a CSH-gel with a lower Ca/Si ratio and longer length of the polysilicate anions, in addition to the formation of more gel due to the pozzolanic reaction [19-22]. Another contributing factor may be a change in morphology of calcium hydroxide due to a lower solubility caused by a higher Ca^{2+} concentration in the pore water, which agrees with several of researchers [23].

4. Conclusion

After testing the XD3 concrete samples with or without calcium nitrate inhibitors and two types of plasticizers we can conclude the following points:

- The compressive strength without calcium nitrate was higher in samples with Dynamon SR31(A3) than samples with Oxydtron (A4)
- The samples B3 and B4 (with 1% inhibitor) showed increase in compressive strength about 8% and 7% respectively.
- The compressive strength of the sample C3 (with 3% calcium nitrate inhibitor + Dynamon SR 31superplasticizer) was increased by 21%.
- The sample C4 (with 3% calcium nitrate inhibitor + Oxydtron superplasticizer) was the one that increased the most in the compressive strength after the addition of the inhibitor, where the increase was about 27%.

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