The evaluation of the effect of crystallization additives on long term durability of self-compacting concrete

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Abstract. The article deals with the influence of crystallisation additives on the life of self-compacting concrete (so-called SCC concrete) in case of exposure to aggressive gases. The effect of crystallization additives on the properties of such modified composites is generally tested during exposure of liquid media, in this case the attention is focused on influence of selected types of aggressive gases (CO$_2$ and SO$_2$). The impact of individual types of aggressive gases is assessed on the basis of a set of physico-mechanical and physico-chemical analyses.

1. Introduction
In common concrete, as well as self-compacting concrete, one way to limit the adverse influence of aggressive substances from the external environment is to use additives for 'secondary crystallization' (hereinafter referred to as 'crystallization materials'). The article analyzes the effect of these types of additives on the long life of SCC concrete in selected types of aggressive gases. The results obtained after the annual and one-year exposure of SCC concrete in aggressive environments are presented.

The use of crystallization materials results in slowing down the degradation of concrete and thus increasing its service life. By contrast to conventional solutions (bitumen strips, plastic foils, etc.), crystallization materials cause changes to the internal structure of concrete.

Self-compacting concrete (SCC) is a high-performance type of concrete. It is a type of concrete that shows both sufficient mobility and resistance to segregation while it is still fresh. Self-compacting concrete is able to fill the form and to flow past even closely spaced reinforcing bars. The fact that SCC does not need to be compacted leads to the relatively higher homogeneity of the resulting concrete structure [3].

The interaction of crystallization additives in the capillary porous structure of ‘standard’ concrete types has been studied by many authors [1, 2]. In the case of SCC and with respect to the fact that they are new and highly progressive materials, the situation is different. The effects of crystallization additives on the capillary porous structure of self-compacting concrete represent an area that has not yet been explored properly.

The effect of aggressive environments on the developed SCC concrete was evaluated by a set of physico-mechanical and physico-chemical analyses.

2. Methods and experiments
The methodical procedure used for conducting experiments is described in the following text. The composition of the SCC followed on from its previous development at the Institute of Technology of Building Materials and Components, as well as the knowledge mentioned in [3]. For the composition of SCC, refer to the table below:
Table 1. Composition of the SCC concrete.

| Component                        | Component amount [in kg per m³ of concrete] |
|----------------------------------|--------------------------------------------|
| Cement CEM I 42.5R               | 390                                        |
| Aggregate 0-4 mm                 | 545                                        |
| Aggregate 4-8 mm                 | 850                                        |
| Aggregate 8-16 mm                | 210                                        |
| Fly ash                          | 180                                        |
| Water                            | 200                                        |
| Plasticizer Visocrete 1035 (0.9% of cement weight) | 3.50                                      |
| Xypex Admix C-1000NF (1% of cement weight)                  | 3.90                                      |

Additionally, concrete samples of the same composition, but without the crystallization additive, were made. The samples were subjected to a test that would allow a correct assessment of the effect of the additive on the SCC properties of both fresh and hardened concrete. In particular, the following determinations were made:

- Determination of the consistency of fresh SCC concrete – L-box test carried out according to ČSN EN 12350-10,
- Determination of water absorption according to ČSN 731357,
- Determination of capillary attraction according to ČSN 731357-2.

To determine the effect of aggressive gases on SCC concrete modified with crystallization additive and without it, the test samples were divided into several sets, namely:

- Set I – the test specimens of this set were left in laboratory conditions (t=20±2°C, φ=50±10%) throughout the experiment, i.e. for one year. Test samples of this set were considered as reference,
- Set II – the test samples were exposed for 360 days to sulfur dioxide, the concentration of 3%, t=20±2°C, φ=50±10%,
- Set III – test specimens were exposed for 360 days to carbon dioxide, the concentration of 3%, t=20±2°C, φ=50±10%.

The samples were placed in the test environment at 28 days of age. The concentration of aggressive media was monitored and maintained at a constant level throughout the experiment. To determine the effect of aggressive media on SCC concrete modified with crystallization additive and without it, the following set of experiments took place:

- Determination of tensile strength of surface layers of concrete was performed according to ČSN 731318,
- Determination of compressive strength of concrete was made according to ČSN EN 12390-3.

Microstructure analysis using electron scanning microscope, differential thermal, X-ray diffraction analysis and SEM microscopy. Value of pH was also evaluated. These assays were performed according to the methodology described in [4].

3. Results

3.1. Determination of the characteristics of fresh concrete
For the results of the determination of the consistency of the tested SCC, refer to table 2. Values shown represent the arithmetic mean of three measurements.
Table 2. Workability of SCC.

| Mix designation                  | Investigated parameter | T$_{500}$ [s] | Slump-flow [mm] | L-box, flow rate |
|----------------------------------|------------------------|---------------|-----------------|-----------------|
| SCC without crystallization additive | Values                | 1.7           | 680             | 0.84            |
|                                  | Classification         | VS1           | SF2             | PL2             |
| SCC with crystallization additive | Values                | 1.8           | 675             | 0.82            |
|                                  | Classification         | VS1           | SF2             | PL2             |

It has been proven that the modification of SCC concrete by the crystallization additive has no significant influence on the workability of fresh concrete.

3.2. Characteristics of the capillary porous structure of concrete

The effects of the crystallization additive on the characteristics of the capillary porous structure of SCC were assessed by determining absorptivity and capillarity. The results are summarized in Table 3. The values shown represent the mean of six measurements.

Table 3. Absorptivity of SCC.

| Mix designation                          | Absorptivity [%] |
|------------------------------------------|------------------|
| SCC without crystallization additive     | 5.9              |
| SCC with crystallization additive        | 3.7              |

These results document the positive effect of the crystallization additive on the capillary-pore structure, respectively on the sorption properties of concrete. This aspect is highly perspective in terms of the concrete’s resistance to aggressive environments.

3.3. Determination of the effects of aggressive environments on SCC

As already mentioned above, the effects of selected types of aggressive environments on tested SCC was investigated by both physico-mechanical and physico-chemical analyses. The results of the determinations of strength characteristics (i.e. tensile strength of surface layers and compressive strength) are listed in the following tables. For the sake of clarity, the results that were obtained after a one year exposure in aggressive environments and then after two years exposure in these environments, are shown below. The values shown represent a mean of six measurements (figures 1-4).
Figure 1. Tensile strength of surface layers - SCC without crystallization additive.

Figure 2. Tensile strength of surface layers - SCC with crystallization additive.

Figure 3. Compressive strength - SCC without crystallization additive.

Figure 4. Compressive strength - SCC with crystallization additive.

The knowledge obtained during the testing of strength parameters has been further extended and supplemented by X-ray diffraction analysis, differential thermal analysis and by pH determination. The findings obtained by these methods are captured in the following tables.
### Table 4. Results of X-ray diffraction analysis

| Mix designation          | Exposure conditions                  | Identified mineral                                      | Time of exposure – one year                             |
|--------------------------|--------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| SCC without crystallization additive | Laboratory conditions – reference environment | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, calciumhydroxysilicate, traces of portlandite, monosulfate, quartz, feldspar |
|                          | Sulfur dioxide                       | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, calciumhydroxysilicate, gypsum, ettringite, quartz, feldspar |
|                          | Carbon dioxide                       | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, traces of calciumhydroxysilicate, monosulfate, quartz, feldspar |
| SCC with crystallization additive | Laboratory conditions – reference environment | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, calciumhydroxysilicate, carbonate complexmonosulfate, quartz, feldspar |
|                          | Sulfur dioxide                       | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, calciumhydroxysilicate, traces of portlandite, monosulfate, quartz, feldspar |
|                          | Carbon dioxide                       | Calcite, calciumhydroxysilicate, portlandite, quartz, feldspar | Calcite, calciumhydroxysilicate, monosulfate, quartz, feldspar |

### Table 5. Results of pH determination

| Mix designation          | Exposure conditions                  | pH value                                      | Time of exposure – one year                             |
|--------------------------|--------------------------------------|----------------------------------------------|--------------------------------------------------------|
| SCC without crystallization additive | Laboratory conditions – reference environment | 12.1                                         | 11.9                                                   |
|                          | Sulfur dioxide                       | 12.0                                         | 9.8                                                    |
|                          | Carbon dioxide                       | 12.1                                         | 10.7                                                   |
| SCC with crystallization additive | Laboratory conditions – reference environment | 12.2                                         | 12.1                                                   |
|                          | Sulfur dioxide                       | 12.1                                         | 10.4                                                   |
|                          | Carbon dioxide                       | 12.1                                         | 11.9                                                   |
4. Conclusions

Negative effect of selected types of aggressive gases is particularly more noticeable on the tensile strength of the surface layers of concrete, less significantly in the case of compressive strength. The fact that the surface layers of concrete are primarily interfered has also been proved by physico-chemical analyzes. Of the tested types of aggressive gases, the most dynamic effect is caused by the sulfur dioxide. One year long exposure to this environment caused in the SCC concrete sample without the crystallization additive in virtually complete destruction of the surface layers of the concrete, the depth of concrete distortion was approximately 5 mm. The one year exposure in the sulfur dioxide resulted in a decrease in compressive strength of approximately 40%. The deterioration of mechanical properties of SCC concrete without crystallization additives was also confirmed by physical-chemical analyses. By these analyses was showed the occurrence of corrosion neoplasms, especially in the surface layers of concrete (formation of gypsum etc).

In the case of SCC concrete modified by the crystallization additive, the decrease of these parameters was significantly lower. The tensile strength of the surface layers in this case decreased by about 60% due to the one year exposure to sulfur dioxide. Decrease in compressive strength after one year long exposure did not exceed 20%. For concrete modified by the crystallization additive, the incidence of corrosion neoplasms in their microstructure was relatively low.

The impact of carbon dioxide on the properties of SCC concrete was lower than that of sulfur dioxide. For example, in the case of concrete tensile strength of the surface layers, SCC concrete without a crystallization additive there has been a relative increase. This effect is due to the formation of calcium carbonate crystals which compact the matrix structure of the surface layers. In the case of modified concrete, this effect was not detected. This observation, together with the results of physico-chemical analyzes, indicates that the crystallization additives limit the penetration of carbon dioxide into the concrete structure.

Another aspect, which documents the positive effect of crystallization additives on the durability of self-compacting concrete, is parameter of pH value. It has been shown that for concrete modified by additives the decrease of concrete alkalinity is reduced. This is particularly positive in terms of the ability of the concrete to protect reinforcement against corrosion.
It can be stated that the crystallization additives positively affect the resistance of self-compacting concrete not only to the action of liquids but also to the action of aggressive gases.

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