Microstructure of High C3A Portland Slag Cement Pastes, Modified with Accelerating Admixtures for Concrete

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Abstract. Modern concrete technology includes mineral additives and chemical admixtures usage. It is caused by their beneficial influence on properties of concrete mix and hardened concrete. Accelerating admixtures for concrete are commonly used for shortening of time demanded for demoulding and repeat use of forms in precast facilities. They allow to conduct works during low-temperature season. Main advantage of accelerating admixtures is enhancement of early strength of concrete. Alas they may cause decrease of long-term strength and durability of concrete or increase its shrinkage. One of the most popular mineral additives is ground granulated blast furnace slag (GGBFS). It is non-clinker main constituent of CEM II, CEM III and CEM V. GGBFS may be also used as additive with latent hydraulic properties for concrete. GGBFS as constituent of concrete increases consistency, long-term strength and durability, and decreases hydration heat evolution. Early compressive strength of concrete with GGBFS is lower than for Portland cement concrete. Accelerating admixtures and ground granulated blast furnace slag show advantages and disadvantages that can be equalized. In early terms calcium nitrate and crystal seeds enhanced compressive strength. Their efficiency is similar. Cement kiln dust also caused increase of compressive strength but not as much as former ones. Sodium hydroxide caused great increase of compressive strength after 12 hours but not in longer terms. In case of cements rich with C₃A the compressive strength in early stage of hardening is shaped by C-S-H phase and well-developed ettringite crystal skeleton. In spite of minor differences in non-modified and calcium nitrate modified cement pastes microstructure, the compressive strength of calcium nitrate modified mortars is significantly greater in comparison to non-modified ones. The greatest compressive strength was achieved by mortar modified with crystal seeds. Responsible for this increase is more well-developed C-S-H phase. Mortars modified with sodium hydroxide are weaker after 2 days of curing in comparison to non-modified mortar. It is caused by sparse ettringite crystal skeleton. Microstructures of non-modified and modified with cement kiln dust (CKD) cement pastes are similar. It is connected with similarity of chemical composition of CKD and Portland clinker. The compressive strength of CKD modified mortars is slightly greater than non-modified one.

1. Introduction

Modern concrete technology includes mineral additives and chemical admixtures usage. It is caused by their beneficial influence on properties of concrete mix and hardened concrete. Accelerating admixtures for concrete are commonly used for shortening of time demanded for demoulding and repeat use of forms in precast facilities. They allow to conduct works during low-temperature season [1, 2]. Main advantage of accelerating admixtures is enhancement of early strength of concrete. Alas
they may cause decrease of long-term strength and durability of concrete or increase its shrinkage [3-5]. One of the most popular mineral additives is ground granulated blast furnace slag (GGBFS). It is non-clinker main constituent of CEM II, CEM III and CEM V. GGBFS may be also used as additive with latent hydraulic properties for concrete [3]. Result of its reaction with water are C-S-H phase and other phases similar to results of Portland clinker hydration reaction [6]. GGBFS as constituent of concrete increases consistency, long-term strength and durability, and decreases hydration heat evolution [6, 7]. Early compressive strength of concrete with GGBFS is lower than for Portland cement concrete [8]. To conclude both accelerating admixtures and ground granulated blast furnace slag show advantages and disadvantages that can be partially or fully equalized.

In initial stage of slag cement hydration process Portland clinker hydration takes major part. During hydration GGBFS activity increases and additional amount of C-S-H phase is created [9-11]. Hydration of GGBFS starts with its reaction with alkalis dissolved from clinker (sodium and potassium oxides). Following step of this process is reaction of GGBFS with calcium hydroxide [6, 9, 12-14]. Microstructure of hardened slag cement pastes is more consistent in comparison to Portland cement pastes [7,15]. It contains more C-S-H phase and less Ca(OH)₂ [6]. Very small ettringite crystals are also present as result of reaction of aluminates contained in slag [15]. C-S-H phase created by slag cement is characterized by lower C/S ratio than for Portland cement [11, 16]. In initial stage of high C₃A cements hardening the compressive strength is shaped with ettringite crystals skeleton [17]. The influence of set and hardening accelerating admixtures on microstructure of cement pastes depends on their chemical composition. Modern accelerators act physically by incorporation of crystal seeds, which allow the hydration reaction start not only on the surface of cement grains but also in space between them. Such accelerators are not always causing decrease of long-term compressive strength. Resulting cement matrix is more consistent with those admixtures [4, 18]. Calcium nitrate, nitrite and chloride contain the same cations as C₂S and C₃S phases of Portland clinker. Those cations act as crystallisation seeds and accelerates hydration reaction of those phases [5]. Resulting microstructure of cement pastes is characterised by lower amount of gel pores and similar general porosity [19]. Sodium hydroxide increases pH value of water and allows glass phase of GGBFS to be dissolved and accelerate GGBFS hydration [5, 20, 21]. It also accelerates C₂S and C₃S hydration and hardening of cement paste. Beneficial effect of increased compressive strength may occur only in early phase of hardening [5]. Resulting C-S-H phase has lower specific surface area. There is no influence on general porosity of cement pastes [2, 5]. Cement kiln dusts (CKD) have pH value about 12. They contain alkali that accelerate hydration process of GGBFS [22]. Specific surface area of CKD is in range of 4000 – 14000 cm²/g. It allows faster dissolution of its constituents in water. Cement pastes with CKD are less porous [23].

2. Materials
For preparation of cements following constituents were used:
- Portland clinker with specific surface area of 3000 cm²/g. chemical and phase composition of clinker are given in table 1 and 2 respectively.
- Anhydrite as set regulator. Amount of anhydrite results in 2% of SO₃ in cement. Chemical composition of anhydrite is given in table 3.
- Ground granulated blast furnace slag with specific surface area of 3870 cm²/g. activity index according to EN-15167-1 is 62,8% after 7 days and 88,3% after 28 days. Amorphous phase content is 98,5%. Chemical composition of GGBFS is given in table 4.

| Table 1. | Chemical composition of Portland clinker [% of mass]. |
|----------|----------------------------------------------|
| SiO₂     | 20.25                                       |
| Al₂O₃    | 6.83                                        |
| Fe₂O₃    | 3.23                                        |
| CaO      | 65.66                                       |
| MgO      | 1.39                                        |
| SO₃      | 0.69                                        |
| Cl⁻      | 0.01                                        |
| Na₂O     | 0.15                                        |
| K₂O      | 1.02                                        |
| Na₂Oeq   | 0.82                                        |
| CaOfree  | 2.80                                        |
| ign. loss| 0.15                                        |
| non. solv.| 0.52                                       |

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### Table 2. Phase composition and modules of Portland clinker [% of mass].

|     | C₂S | C₃S | C₃A | C₄AF | Lime saturation factor (LSF) | Silica modulus (SR) | Alumina Ratio (AR) |
|-----|-----|-----|-----|------|-----------------------------|---------------------|-------------------|
|     | 10.90 | 64.40 | 13.50 | 7.30 | 0.88                        | 2.01                | 2.11              |

### Table 3. Chemical composition of anhydrite [% of mass].

|     | SiO₂ | CaO | MgO | SO₃ | Na₂O | ign. loss |
|-----|------|-----|-----|-----|------|-----------|
|     | 0.61 | 40.16 | 0.40 | 54.83 | 0.02 | 2.71      |

### Table 4. Chemical composition of ground granulated blast furnace slag [% of mass].

|     | SiO₂   | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Cl⁻ | Na₂O | K₂O | Na₂Oeq | CaO_free | ign. loss | n.solv. |
|-----|--------|-------|-------|-----|-----|-----|-----|------|-----|--------|----------|-----------|---------|
|     | 37.35  | 7.30  | 1.22  | 43.90 | 5.73 | 0.62 | 0.03 | 0.55 | 0.56 | 0.92    | 0.17      | 0.17      | 4.92    |

For preparation of cement pastes and mortars following constituents were used:

- Portland slag cement CEM II/B-S containing 35% of ground granulated blast furnace slag,
- Water-cement ratio was equal 0.5. Amount of water was reduced by its amount in admixtures,
- CEN standard sand,
- Accelerating admixtures (table 5),

### Table 5. Chemical composition of Cement Kiln Dust [% of mass].

| Symbol | Characteristics                                      | Dosage                          |
|--------|------------------------------------------------------|---------------------------------|
| NaOH   | 20% solution of sodium hydroxide (NaOH)              | 5% of NaOH acc. to mass of cement|
| CN     | 20% solution of calcium nitrate (Ca(NO₃)₂·4H₂O)      | 2% of (Ca(NO₃)₂·4H₂O) acc. To cement mass |
| CKD    | Cement kiln dust, composition is given in table 6.    | 10% of mass of cement           |
| CS     | Accelerating admixture containing crystal seeds.     | 4% of mass of cement            |

### Table 6. Chemical composition of Cement Kiln Dust.

|     | SiO₂   | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Cl⁻ | Na₂O | K₂O | Na₂Oeq | CaO_free | ign. Loss | n.solv. |
|-----|--------|-------|-------|-----|-----|-----|-----|------|-----|--------|----------|-----------|---------|
| CKD | 18.24  | 4.83  | 2.33  | 56.63 | 1.56 | 2.02 | 1.40 | 0.39 | 3.66 | 2.80 | 15.90 | 10.30 | 2.01 |

### 3. Methods

Mortars for compressive strength tests were prepared according to standard EN-196-1. Samples were cured in 20±1°C and RH=60% in climatic chamber for 12 hours. Samples were cured in water of temperature 20±1°C until test. Tests were conducted after 12 and 24 hours and 2, 7 and 28 days. Cement pastes for initial setting time examinations were prepared according to EN-196-3 standard. Tests were conducted with automatic Vicat’s apparatus in temperature 20±1°C. Cement pastes for microstructure observations were prepared according to EN-196-3 standard. Water-cement ratio was established on 0.5. samples were formed as cuboids with dimensions of 5×5×25 mm. Samples were cured in 20±1°C under damp cloth for 48 hours. 1 hour before the test samples were air-dried in room with temperature 20±1°C. observations were conducted with SEM QUANTA FEG 250 microscope with EDS detector and software allowing determination of chemical composition in points. Observations were conducted with magnification × 100 to × 40000.

### 4. Results

Initial setting time of non-modified and modified with accelerating admixtures is given in figure 1. All accelerators have shortened the initial setting time. The most efficient is sodium hydroxide which shortened initial setting time by 50%. Efficiency of calcium nitrate and cement kiln dust is similar,
those admixtures have shortened initial setting time by about 15%. Crystal seeds based accelerator have shortened initial setting time by about 30%.

![Figure 1. Initial setting time of non-modified and modified cements.](image)

Compressive strength results are given in figure 2. In early terms (12 hours to 7 days) calcium nitrate (CN) and crystal seeds (CS) enhanced compressive strength. Their efficiency is similar. Cement kiln dust (CKD) also caused increase of compressive strength but not as much as former ones. Sodium hydroxide (NaOH) caused great increase of compressive strength after 12 hours but in longer terms its influence is opposite. After 28 days compressive strength of both non-modified and modified with CS and CN mortars is similar. CKD caused slight decrease of compressive strength. Sodium hydroxide caused evident decrease of compressive strength by about 50%.

![Figure 2. Compressive strength of mortars.](image)

After 48 hours of curing the compressive strength of mortars differs in according to accelerator used. Attempt to explanation with microstructure observations was made. Because of scanning electron microscopy and energy dispersive spectroscopy method were used only chosen points of samples were observed.

Microscopic images and microanalysis in points of non-modified pastes are shown on figure 3. In observed points C-S-H phase and long thin crystals of ettringite are visible. Ettringite in such shape is responsible for compressive strength of high C3A cement pastes in early terms [3, 6, 15]. In every sample the non-hydrated cement grains coated with thin layer of hydration products are visible. Single portlandite (Ca(OH)2) hexagonal crystals are present in samples.

In samples of modified with crystal seeds (CS) paste the C-S-H phase in form of honeycomb, long and thin ettringite crystals and single hexagonal portlandite crystals are present. It seems to be more
C-S-H phase in comparison to reference sample (figure. 4), which complies with results given in [24]. Well-developed C-S-H phase and ettringite crystal skeleton are responsible for the greatest compressive strength of mortars with CS in comparison to non-modified and modified with other accelerating admixtures mortars.

Morphology of C-S-H phase in cement paste modified with calcium nitrate (CN) does not differ in comparison to non-modified one. There is less ettringite and its crystals are shorter and thicker (figure 5). In spite of minor differences in pastes microstructure, the compressive strength of CN modified mortars is significantly greater in comparison to non-modified ones.

Modification of mortars with sodium hydroxide (NaOH) cause decrease of compressive strength after 48 hours of curing. Ettringite crystals are shorter and thicker (figure 6). Crystal skeleton created by ettringite is not well-developed [3, 6, 15]. C-S-H phase morphology and presence single of hexagonal portlandite crystals is similar to reference sample.

Microstructures of non-modified and modified with cement kiln dust (CKD) cement pastes are similar (figure 7). It is connected with similarity of chemical composition of CKD and Portland clinker [25, 26]. Difference occurring in both samples is presence of calcite in form of rosette crystals. Their presence is caused by large amount of carbon contained in cement kiln dusts. Calcite crystals in such amount are not visible in any other sample (single calcite crystal was observer in CS modified hardened paste).

Figure 3. Microstructure and microanalysis of non-modified cement paste.
1 – C-S-H phase, 2 – ettringite, 3 – portlandite.
Figure 4. Microstructure and microanalysis of crystal seeds (CS) modified cement paste.  
1 – C-S-H phase, 2 – ettringite, 3 – calcite.

Figure 5. Microstructure and microanalysis of calcium nitrate (CN) modified cement paste.  
1 – C-S-H phase, 2 – portlandite.
Figure 6. Microstructure and microanalysis of sodium hydroxide (NaOH) modified cement paste. 1 – C-S-H phase, 2 – ettringite, 3 – portlandite.

Figure 7. Microstructure and microanalysis of cement kiln dust (CKD) modified cement paste. 1 – C-S-H phase, 2 – ettringite, 3 – calcite.
5. Conclusions
In case of cements rich with C₃A the compressive strength in early stage of hardening is shaped by C-S-H phase and well-developed, connected, long and thin ettringite crystal skeleton.

In spite of minor differences in non-modified and calcium nitrate modified cement pastes microstructure, the compressive strength of calcium nitrate modified mortars is significantly greater in comparison to non-modified ones.

The greatest compressive strength was achieved by mortar modified with crystal seeds. Responsible for this increase is more well-developed C-S-H phase.

Mortars modified with sodium hydroxide are weaker after 2 days of curing in comparison to non-modified mortar. It is caused by sparse ettringite crystal skeleton.

Microstructures of non-modified and modified with cement kiln dust cement pastes are similar. It is connected with similarity of chemical composition of CKD and Portland clinker. The compressive strength of CKD modified mortars is slightly greater than non-modified one.

Observations made for calcium nitrate and cement kiln dust modified pastes are not sufficient to explain compressive strength differences.

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