Effect of industrial by-products incorporated in composites on strength and leaching parameters due to microbiologically induced corrosion

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Abstract. The durability of cement-based materials is an increasingly important characteristic for civil engineering structures due to the growing demand for their long service life and minimal maintenance. Mortars and concrete with high acid resistance are required for the construction and the repair of sewer structures, in which biogenic sulphuric acid attack is the major degradation mechanism. Important progress has been achieved in this regard with hybrid binders and materials known as supplementary cementitious materials (blast furnace slag, silica fume, fly ash etc.). These mainly industrial wastes and by-products increase many important properties of concrete structures such as acid resistance, permeability, strength and many more. This study investigates the effect of industrial by-products such as blast furnace slag and fly ash on strength and leaching parameters of composites exposed to bacterial influence. The medium with bacteria A. thiooxidans was used for microbiologically induced corrosion and the experiments were conducted during the period of 9 months. The sample with 95 wt. % of slag was found more resistible in bacterial environment compared to the sample with hybrid binder.

1. Introduction

It is a well-known fact that concrete structures made with ordinary Portland cement (OPC) deteriorate when exposed to various acidic environments. Cement-based materials can come into contact with different aggressive acidic media, which can be harmful to cementitious materials and these includes biogenic mineral and organic acids [1,2].

Sewer networks and wastewater systems worldwide suffer with significant corrosion and deterioration due to sulphuric acid attack, resulting in large economic losses [1,3]. Sulphuric acid in sewer systems is generated by sulphur-oxidising bacteria and it has been identified as the corroding acid [1,4,5]. This acid can also be present in groundwater or produced from the oxidation of sulphur bearing compounds in back fill, such as pyrite [1,6]. The dissolution of hydrogen sulphide can also contribute to formation of sulphuric acid with a low pH on the concrete walls of geothermal wells [1,7]. Therefore, biogenic sulphuric acid is a major cause of biodegradation and microbiologically induced corrosion (MIC) of concrete and cement-based materials. MIC often leads to a reduction in strength, serviceability and even loss of the structure [1].

Increased resistance to microbiologically induced corrosion can be achieved by, among other things, the addition of supplementary cementitious materials (SCM) or hybrid binders [8,9,10]. Both
hybrid binders and supplementary cementitious materials (SCMs) have been added to concrete and mortars as a partial replacement of cement to lower cement consumption and improve fresh and as well as hardened properties [11]. Hybrid binders are based on the blend of alkali-activated aluminosilicates with less than 30% of Portland cement clinker. Typical mixtures of hybrid binders contain fly ash and clinker, activated with Na₂SO₄ and Na₂CO₃ [12,13] or blast furnace slag with metakaolin and clinker, activated with Na₂CO₃ and K₂CO₃ [12,14]. From economic point of view are industrial by-products such as fly ash or slag interesting materials for binder mass production, even though the composition and quality of fly ash and blast furnace slag can be changing [12]. Granulated blast-furnace slag is nowadays commonly used pozzolanic material, which is often used in combination with Portland cement for many different applications. Cement based materials made with blast furnace slag have many advantages, including improved durability, workability and better sulphate resistance, particularly at higher levels of replacement [15,16,17].

The current experiment was conducted to verify the difference in microbiologically induced corrosion between samples made with high share of different waste materials. Two mortar mixtures one with hybrid binder made with slag and fly ash and the other with 95 wt. % of blast furnace slag and 5 wt. % of Portland cement were subjected to biogenic sulphuric acid for 270 days. Leaching trends of Ca²⁺ ions along with degradation depth, compressive strength and degree of hydration of samples were evaluated.

2. Material and methods

2.1. Materials and exposure conditions

Three different types of cementitious materials, namely: ordinary Portland cement of strength grade 52.5 R (OPC), fly ash (FA) and blast furnace slag (BFS), were used. The samples were prepared according to standard STN EN 196-1 [18]. Two mixtures were designed for the experiment, in the first mixture (H-B) the Portland cement was replaced by hybrid binder by 100 wt. % and in the second mixture (C-BFS) the OPC was replaced by blast furnace slag by 95 wt. % The test specimens have been designed in cooperation with cement factory plant and the dimensions of samples were approximately 160 mm × 40 mm × 40 mm.

| Components | Sample H-B | Sample C-BFS |
|------------|------------|---------------|
| Fly ash    | 3.36       | 39.55         |
| Blast furnace slag | 39.24 | 38.95         |
| Clinker    | 66.13      | 21.69         |
| Blast furnace slag | 39.55 | 57.15         |
| Portland cement | 57.15 | 19.01         |
| CaO        | 51.42      | 26.39         |
| SiO₂       | 10.11      | 8.33          |
| Al₂O₃      | 2.72       | 7.19          |
| Fe₂O₃      | 2.10       | 4.02          |
| MgO        | 0.87       | 0.54          |
| K₂O        | 0.53       | 1.07          |
| SO₃        | 1.50       | 1.47          |
| Other      |            | 1.11          |

Used hybrid binder is produced according to patent application on the base of industrial by-products and wastes [12,19]. The content of clinker is under 30%. Mineralogical composition of fly ash in the hybrid binder is quartz SiO₂, mullite Al₅Si₂O₁₀, hematite Fe₂O₃, magnetite Fe₃O₄, granulated
blast furnace slag is fully glassy and clinker is composed typically by C₃S 69 % wt., C₃A 11 % wt., C₄A 9 % wt., and C₄AF 8 % wt. Highly alkaline waste water from red mud pond is used for activation of fly ash and granulated blast furnace slag [12]. Blast furnace slag used for the mixture C-BFS is resistant to mold and is defined as a fungistatic building material according to CSN 72 4310 [20]. BFS is suitable as an antifungal admixture for cements, concretes, mortars, dry plaster mixtures, building binders, cement-containing mixtures and building materials. Blends with BFS are also characterized by increased chemical resistance, especially to sulphate and chloride ingress. Chemical composition of main components of hybrid binder, blast furnace slag and Portland cement is given in table 1.

In the experiment, the bacterial culture of sulfur-oxidizing bacteria Acidithiobacillus thiooxidans, originated from the local sources (the shaft Pech, the locality Smolník, Eastern Slovakia) was used. The selective nutrient medium by Waksman and Joffe (pH 4.0) was used for the preparation of the active bacterial culture as well as for the isolation and cultivation of A. thiooxidans in the presence of the samples. The prepared samples were exposed to the medium of activated bacteria for 270 days. The volume ratio of solid samples to the liquid phase was set to 1:10. Experiment was carried out in covered tanks under aerobic atmosphere at laboratory temperature. pH value of the liquid phase was kept on an optimal level of 4.0. The dissolved concentrations of calcium ions in leachates were regularly measured through experiment [21].

2.2. Experimental techniques for investigation

Several test methods were used in this study to investigate the effect of aggressive bacterial medium and its consequences on durability properties of tested samples.

X-ray fluorescence analysis (XRF) was used to analyse the chemical composition of the leachates. SPECTRO iQ II equipment (Ametek, Germany) has been fitted with silicon drift detector (resolution of 145 eV at 10 000 pulses) and the samples were measured using standard procedure at two voltages and corresponding currents. The concentrations of the measured elements were calculated from the calibration methods for liquids [21].

The compressive strength tests were carried out according to the methodology described in the standard EN 196-1 [18]. Compressive strength of first set of specimens was determined after the 28 days curing period and the compressive strength of second set of samples was determined after 270 days of bacterial exposure by using the instrument ADR 2000 (ELE International, England). The samples before and after the bio-corrosion experiment were researched also by thermal analysis. Simultaneous DSC/TG analysis was performed by using the STA 449 F3 Jupiter (Netsch, Germany). The samples of 9 mg were heated in Al₂O₃ crucibles in the temperature range 26-800 °C, at heating rate 30 K/min under nitrogen atmosphere.

Based on the thermal analysis results, the degree of hydration α of the samples was calculated using Bhatty’s method [19] following the equations (1) and (2).

\[ W_H = Rh + Rx + 0.41 \text{ (Re)} \quad \% \]  \hfill (1)

\[ \alpha = \frac{W_H}{0.24} \quad \% \]  \hfill (2)

Equation (1) shows the calculation of the chemically bound water \( W_H \) from relative mass losses in the particular regions on the TG curve Rh (calcium-silicate hydrates), Rx (portlandite) and Re (carbonates). The value 0.41 is conversion factor to calculate the chemically bound water derived from the carbonated portlandite. In equation (2), the value of 0.24 represents the maximum chemically bound water required to entirely hydrate a cement particle. This value can vary between 0.23 and 0.25 according to different authors [22,23,24]. For Bhatty, the constant value of 0.24 is used in the equation. Regarding the final calculation presented by such a method, the degree of hydration is directly proportional to chemically bound water as only a conversion factor equal to 0.24 is considered [24].
The degradation depths of samples, after the biogenic sulphuric acid exposure, were evaluated using equation (3), by dividing the total amount of leached calcium by the theoretical initial total calcium content of specimens [21,25].

\[
\text{Degradation depth} = \frac{c(Ca)_L (mg/cm^2)}{c(Ca)_I (mg/cm^3)} (cm)
\]

Where \(c(Ca)_L\) is the amount of leached-out \(Ca^{2+}\) ions per unit area (mg/cm\(^2\)) of the sample and \(c(Ca)_I\) represents an initial calcium content in the sample per 1 cm\(^3\) of sample.

The calculation of the degradation depth (DD) of samples assumes that all portlandite (CH) was dissolved from the surface layers of samples after the 270-day leaching and that the \(Ca^{2+}\) ions were fully leached out in a degradation depth [21,25]. Considering the leached-out concentrations of \(Ca^{2+}\) ions, assuming that they originate from the decomposition of portlandite, DD of tested specimens with different share of pozzolanic materials were calculated, according to Roziere et al. [25]. The theoretical DD could actually estimate the degradation depth of samples and based on this assumption degradation depths could predict the deterioration stage of material.

3. Results and discussion

The more intensive leaching trend of \(Ca^{2+}\) ions was observed for the sample C-BFS with 95 wt. % of blast furnace slag compared with the sample H-B with hybrid binder (figure 1).

![Figure 1. Dissolving trends of calcium during bio-corrosion simulation.](image)

The increasing leaching of \(Ca^{2+}\) ions was observed continuously for both samples placed in the bacterial environment until the end of the experiment at 270 days. For both samples, the H-B and the C-BFS, the highest value of concentration of \(Ca^{2+}\) ions was observed at the end of the exposure (531.2 and 790.1 mg/L, respectively).

The leaching trends were similar, even though the C-BFS sample had higher leaching performance of calcium ions throughout the experiment compared with the H-B sample. It is important to note, that the specimen C-BFS had 2.3 higher initial calcium content than the specimen H-B (table 2), so it was expected that the values of total leached out \(Ca^{2+}\) ions would be higher. However, the dissolved amount of calcium from the C-BFS sample was only 1.5 times higher. This points to the higher stability of the C-BFS sample in bacterial environment even though the absolute mass of the calcium dissolved was higher when compared to the H-B sample. This is in accordance with the degradation depths as reported in table 2.
Although the most intensive Ca\textsuperscript{2+} leaching was observed for sample C-BFS exposed to bacterial medium for 270 days, sample with hybrid binder H-B was observed to have higher degradation depth (0.525 mm). The value of degradation depth of specimen H-B had increased for 35% compared to the C-BFS specimen. Sample made with blast furnace slag was more durable against the influence of biogenic sulphuric acid, from the degradation depth point of view. Compressive strengths of investigated samples made with pozzolanic materials after 28 and 270 days are shown in figure 2. An initial value (28-day) of compressive strength was higher for the sample H-B made with hybrid binder. In comparison the compressive strength after 28 days of curing in water for sample C-BFS was only 12.50 MPa. Results for both samples after 270 days of exposure to the biogenic sulphuric acid produced by *A. thiooxidans* were visibly different. The 270 day compressive strength for specimen with 95 wt.% had increased by 72% from 12.50 to 44.76 MPa. For the sample H-B the decrease by 24% in compressive strength was observed. The decrease in compressive strength of H-B sample could manifest a bio-deterioration process due to bacterial exposure. Increase in compressive strengths of C-BFS specimen with slag addition, after 270 days of exposure to the biotic environment, can likely resulted in an additional hydration process, which was probably more intensive compared to the biological corrosive process. Corrosion as well as hydration processes takes place at the same time, yet after 270 days long biological exposure the hydration process exceeds the corrosion one.

### Table 2. Calculated degradation depths of samples.

| Composite sample | Leached out Ca\textsuperscript{2+} (mg/cm\textsuperscript{2}) | Initial amount of Ca\textsuperscript{2+} (mg/cm\textsuperscript{2}) | Degradation depth (mm) |
|------------------|-------------------------------------------------------------|---------------------------------------------------------------|------------------------|
| H-B              | 4.611                                                       | 87.707                                                       | 0.525                  |
| C-BFS            | 6.858                                                       | 199.422                                                      | 0.344                  |

Regarding processes that take place in the presence of mineral admixtures, as complexity increases, use of additional techniques is required in understanding their development in a better way. The use of differential thermal and thermogravimetric analysis (DSC/TG) is proposed as one of the most effective tests for the evaluation of hydrated compounds and hydration degree [24]. Hydration degree is an important parameter and also it is linked with the evaluation of the compressive strength of cement-based materials. The various regions of dehydration (Rh), dehydroxylation (Rx) and decarbonation
(Rc) that correspond to the hydrated compounds are defined according to the limit temperatures selected (table 3).

**Table 3. Temperature regions of the decomposition of main hydration products.**

| Region | Temperature (°C) |
|--------|-----------------|
| Rh     | 105-400         |
| Rx     | 400-500         |
| Rc     | 500-800         |

TG curves of studied samples with the Rh, Rx and Rc decomposition regions are shown in the figure 3.

![TG curves of the samples after the experiments.](image)

**Figure 3.** TG curves of the samples after the experiments.

The relative values of each decomposition region from TG curves of samples, the chemically bound water and the degree of hydration calculated according to Bhatty [22] are shown in table 4.

**Table 4.** Chemically bound water and degree of hydration of studied samples.

| Sample | Exposure time (days) | Weight losses in regions (%) | Chemically bound water and degree of hydration according to Bhatty (%) |
|--------|----------------------|------------------------------|---------------------------------------------------------------|
|        |                      | Rh  | Rx  | Rc  | W_B | α     |
| H-B    | 0                    | 1.18| 0.50| 2.58| 2.74| 11.41 |
|        | 270                  | 3.82| 3.18| 2.82| 8.16| 33.98 |
| C-BFS  | 0                    | 1.74| 0.31| 0.96| 2.44| 10.18 |
|        | 270                  | 5.74| 3.18| 1.71| 9.62| 40.09 |

The degree of hydration calculated according Bhatty was higher for the H-B sample after 28 day curing in water, which is consistent with the compressive strength measurements. After the bacterial influence, the degree of hydration as well as the chemically bound water increased for the both mixtures, and the C-BFS sample showed higher degree of hydration (40.09 %), which is again consistent with the strength development. Sample C-BFS had higher compressive strength after 270 days of bacterial exposure, which relates to higher amount of hydration products.
4. Conclusion
The influence of biogenic sulphuric acid on cement composites with incorporated industrial by-products on leaching of calcium ions, degradation depth, strength development and degree of hydration were investigated in this paper. The following conclusion can be drawn based on the experimental analyses and results:

- Chemical composition of leachates confirmed the corrosive process was taking place, because of the significant leaching of Ca$^{2+}$ ions.
- Evaluation of damaged depth according to leaching of calcium ions showed better resistance of sample with the addition of BFS compared to the sample made with hybrid binder in the aggressive biotic environment.
- Investigation of compressive strength of samples showed the increase in compressive strength for sample with 95 wt. % of blast furnace slag after 270 days of bacterial exposure and decrease in compressive strength for the sample with hybrid binder. Assumption that hydration was a dominant process compared to deterioration, due to increasing trend in compressive strength for sample with slag can be made.
- Results from thermal analysis completed the compressive strength results and confirmed that the degree of hydration is linked with the development of strength of studied samples.
- Evaluation of durability of samples made with different industrial by-product showed better resistance of sample made with 95 wt. % BFS in the terms of all studied parameters.

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