Shotcrete using ternary binder made from coal combustion products: from lab tests to an application

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Abstract. The paper presents a ternary binder development and its utilization in shotcrete. The binder is made from fluidized bed combustion (FBC) fly ash, siliceous fly ash, and Ca(OH)\textsubscript{2} addition, now available under the name Sorfix. XRD and TGA identified ettringite and C-S-H as two main hydration products. In addition, thermodynamic modeling verified robustness in terms of space-filling capabilities when varying input oxide composition.

Since alkali-free accelerators produce mostly ettringite in Portland-based systems, a fraction of Portland cement was advantageously replaced with the ternary binder, forming early ettringite as well. Extensive testing led to 45\% replacement of Portland cement, following J2 curve for early strength gain used commonly in shotcrete tunnel linings. The shotcrete was successfully tested in a mock-up experiment in a 2 m\textsuperscript{3} batch. Primary lining of a newly built metro D in Prague served for the full-scale application, utilizing over 1000 tons of Sorfix and saving over 700 tons of CO\textsubscript{2}.

1. Introduction
Coal combustion products (CCP), such as fly ash or flue-gas desulfurization gypsum, are produced in high quantities around the world. CCP serve for various purposes, such as mineral admixture for concrete [1]. During 2010, 780 Mt of CCP were generated worldwide with an average utilization rate as 53\% [2]. There are two useful fly ashes which emerge from coal burning, particularly:

- Siliceous fly ash.
- Fluidized bed combustion (FBC) fly ash. It emerges from co-combustion with limestone, binding SO\textsubscript{2} into anhydrous CaSO\textsubscript{4}.

Hydration of FBC fly ash itself yields C-S-H, ettringite and gypsum as the main hydration products [3]. Volume expansion commonly occurring due to ettringite growth prevents simple addition to Portland-based binders. Ettringite is known from other systems widely used since 1970s in China; two common binders include calcium sulfoaluminate (CSA) cements and CSA-belite cements [4, pp. 341-361]. It has been documented that common hydrated products cover
ettringite, monosulphate, strätlingite, amorphous Al(OH)$_3$, and also portlandite and C-S-H with belite addition. As discussed further, the newly designed ternary binder Sorfix produces similar phases such as the CSA cement, which proved 40 year durability and excellent performance [4, pp. 341-361].

2. Materials
Design, development and properties of the ternary binder Sorfix have been previously summarized [5], together with years-lasting monitoring of volume changes and compressive strength evolution showing no detrimental strength loss or excessive shrinkage [6]. Let us recall the basic constituents of the ternary binder; FBC fly ash originates from fluidized bed combustion power plant Tisová ($d_{50}=36.3$ $\mu$m, Blaine 603 m$^2$/kg) while fly ash class F comes from Počerady ($d_{50}=44.9$ $\mu$m, Blaine 484 m$^2$/kg). Their chemical compositions are summarized in Table 1.

| Chemical composition of FBC and fly ashes (wt. %). |
|-----------------------------------------------|
|            | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | Na$_2$O | K$_2$O | TiO$_2$ | SO$_3$ |
| FBC ash    | 31.4    | 26.2       | 4.9        | 21.9| 0.24    | 0.36   | 5.5     | 8.0    |
| Fly ash    | 52.4    | 35.0       | 5.1        | 1.8 | 0.41    | 2.1    | 1.5     | 0.2    |

Binder composition was optimized for workability, for reasonable 28 day compressive strength. Further optimization focused on volumetric stability which was achieved in accelerated aging test (curing 28 days in 95°C water). Superplasticizer ensured a feasible workability on a specified water/binder ratio. Table 2 summarizes the optimal design of the paste, yielding 32 MPa average compressive strength at the age of 28 days. Bulk density of paste is 1710 kg/m$^3$ and the initial volume fraction of water yields 0.47 for this particular paste. Strength increase up to 50 MPa is further possible increasing superplasticizer dosage and lowering the water content.

| Paste composition for the ternary binder (wt. %). |
|-----------------------------------------------|
|            | FBC fly ash | Siliceous fly ash | Ca(OH)$_2$ | Water | Superplasticizer |
|            | 0.313       | 0.313              | 0.094      | 0.263 | 0.017            |

Shotcrete composition is summarized in Table 3, yielding concrete strength class of C25/30. In this particular mix design, ternary binder Sorfix makes 45% of the total binder mass. Wet mix from a concrete plant was transported to a construction site. An alkali-free accelerator was added in the nozzle as 7.5% mass of the total binder.

| Shotcrete mix design |
|----------------------|
| Component            | Mass (kg/m$^3$) |
| CEMI 42.5 R          | 250             |
| Ternary binder Sorfix| 200             |
| Water                | 180             |
| Aggregate 0-2 mm     | 250             |
| Aggregate 0-4 mm     | 760             |
| Aggregate 4-8 mm     | 480             |
| High-Range Water Reducer | 4             |
| Alkali-free accelerator | 33.8 (7.5%)     |
3. Results and discussion

3.1. Volume phase evolution

Four overlapping techniques were used to deduce volumetric phase evolution: XRD, deconvolution of DTG, SEM/EDX mappings and porosimetry [5]. Seven phases were distinguished, namely non-reactive crystalline phases, calcium hydroxide, amorphous glass, ettringite, C-S-H globules, gel and capillary porosity, see Fig. 1.

![Phase evolution due to hydration of ternary binder Sorfix](image)

**Figure 1.** Phase evolution due to hydration of ternary binder Sorfix [5].

XRD analysis quantified the amount of calcium hydroxide, non-reactive crystalline phases, and amorphous content. DTG deconvolution yielded C-S-H gel amount and ettringite [5]. Volume fractions stemmed from mass fractions and known densities of particular phases [5]. The density of C-S-H gel is assumed as 2000 kg/m$^3$ for saturated LD C-S-H [7]. The total measured porosity is divided into the capillary and gel porosity parts, where the gel porosity is calculated as 37% of the LD C-S-H gel (packing density 0.63) [8].

3.2. Thermodynamic modeling and binder robustness

Thermodynamic modeling contributes to the design and optimization of cementitious binders, yielding hydrated phase composition in solid solution [9]. The non-stoichiometric method, often called “Gibbs free energy minimization approach” assumes no chemical reactions’ system and a stable equilibrium condition is reached on the minimization of the Gibbs free energy.

GEM-Selektor provides such a software package, containing a built-in thermodynamic database and Cemdata18 database for Portland cements, blended systems and alkali-activated materials [9]. It is possible to simulate phase assemblage in the Sorfix ternary binder and to explore sensitivity in terms of oxide composition.

The simulation took 100 g of the ternary binder interacting in water environment. First, it was necessary to assess dissolved components in the solution, which may form a hydrate assemblage. Fig. 1 provides an indication of dissolution from the components when hydration proceeds for 60 days. It transpires that 45% of fly ashes and 62% of Ca(OH)$_2$ had reacted by that time. Further estimations yielded that FBC fly ash reacted by 80% and siliceous fly ash by only 15%. The reactions have impact on SiO$_2$, CaO and SO$_3$ availability in the pore solution.

The ternary binder was simplified in the GEM-Selektor, leaving out Fe$_2$O$_3$ and TiO$_2$ contribution, increasing unreacted part by 2% vol. Further volume reduction occurred due to chemical shrinkage, estimated as 5% at 60 days of hydration.
Predictions of GEM-Selekto are summarized in Fig. 2. The column ‘XRD+DTG’ represents identified phases from Fig. 1 at the age of 60 days under sealed curing. The column ‘GEMS’ gives phase assemblage without further adjustments. In this particular case, 14% less volume in C-S-H + ettringite is predicted, however, a new gibbsite phase is revealed unnoticed previously. This might stem from gibbsite’s amorphous nature when Na concentration is low.

Sorx robustness is assessed by variations around default oxide composition by +50% and -50%. The ternary systems remain relatively stable in the ranges of oxide availability; C-S-H and ettringite still present the two main hydration products. Different hydrates contribute to space-filling properties, which guarantees certain engineering properties, for example elasticity or strength.

Hydration phases form at excess/deficiency of considered oxides. Zeolite P originates in CaO deficient systems, which is stimulated by low FBC or Ca(OH)2. Deficiency in SiO2 leads to strätlingite instead of C-S-H. Abundance of SiO2 creates Zeolite P on behalf of aluminates.

3.3. Mock-up shotcrete
The mock-up shotcrete started from 2 m³ wet-mix concrete, summarized in Table 3 [10]. A truss-tunnel frame imitated a tunnel profile, the height was approximately 5 m, see Fig. 4 left. Shotcrete exhibited fallout under 10%, which signalizes good adhesion and workability. Desired J2 curve was fulfilled, needle penetration test was used for early age assessment while drilled cores led to 28 day compressive strength, see Fig. 3. The mock-up test proved anticipated behavior in terms of workability, spraying and strength gain.

3.4. Tunnel lining in Prague metro D
Construction of the Metro D line in Prague began with a geological survey in June 2019. Shotcrete similar to the mock-up experiment has been used for primary lining and temporary structures, see Fig. 4 right. Up today, over 1000 tons of Sorfix replaced CEM I, saving over 700 tons of CO2. This was calculated from substituted clinker CO2 direct emissions [11] and
additional limestone decomposition as $1000 \times 0.612 / 0.783 - 130 \times 44 / 74 = 704$ t, electricity for grinding is assumed to remain the same. Only minor technological adjustments were necessary, for example excessive transport time of fresh mix led to small slump loss which could be corrected by plasticizer or water addition.
4. Conclusions
The paper presented design of a ternary binder named Sorfix, yielding mainly ettringite and C-S-H due to hydration. Thermodynamical modeling proved robust capillary-filling capabilities even under large oxide variations. The advantage of early-age ettringite formation was utilized in a shotcrete, where Sorfix replaced 45% of Portland cement. The shotcrete successfully fulfilled technological and material requirements in a mock-up experiment and in Prague metro D’s primary lining, saving over 700 tons of CO₂ and utilizing over 1000 tons of coal combustion products.

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References
[1] Robl T, Oberlink A and Jones M 2017 Coal Combustion Products (CCP’s): Characteristics, Utilization and Beneficiation. 1st ed. (Woodhead Publishing Limited)
[2] Heidrich C, Feuerborn H J and Weir A 2013 Proceedings of World of Coal Ash
[3] Li X G, Chen Q B, Huang K Z, Ma B G and Wu B 2012 Construction and Building Materials 36 182-187
[4] Lea F M 2019 Lea’s chemistry of cement and concrete fifth edition. ed (Oxford, England: Butterworth-Heinemann) ISBN 0-08-100795-7
[5] Hlaváček P, Sůlč R, Šmilauer V, Rößler C and Snop R 2018 Cement and Concrete Composites 90 100–107 ISSN 0958-9465 URL https://www.sciencedirect.com/science/article/pii/S0958946518302245
[6] Škvára F, Sůlč R, Snop R, Peterová A and Šídlova M 2018 Cement and Concrete Composites 93 118–126 ISSN 0958-9465 URL https://www.sciencedirect.com/science/article/pii/S0958946518300957
[7] Jennings H M 2008 Cem. Concr. Res. 38 275–289
[8] Hlobil M, Šmilauer V and Chanvillard G 2016 Cement and Concrete Research 83 188 – 202
[9] Lothenbach B, Kulik D A, Matschei T, Balonis M, Baquerizo L, Dihessa B, Miron G D and Myers R J 2019 Cement and Concrete Research 115 472-506 ISSN 0008-8846 URL https://www.sciencedirect.com/science/article/pii/S00088846193027073
[10] Sovják R, Pesková S, Šmilauer V, Mára M, Růžička P, Černá Vydrová L and Konvalinka P 2019 Case Studies in Construction Materials 11 1–12 ISSN 2214-5095 URL https://www.sciencedirect.com/science/article/pii/S2214509518304200
[11] Henrich C 2012 Sustainability - oddíl věnovaný České republice / slovensku 2012 Tech. rep. Buzzi Unicem