Rheological properties of belite-rich cement doped with sulfur

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Abstract. Reactive belite cement based on clinker doped with sulfur is a new type of low-energy cement that is still in the laboratory testing phase. In terms of application, one of the desired properties of new cement is its well-defined rheological behavior in fresh state. The chemical composition of the belite cement was determined by wet chemistry analysis, the phase composition of the belite cement clinker by quantitative X-ray powder diffraction analysis and microscopic point counting and specific surface by Blaine method. Rheological properties were determined by rotational rheometer in flow and oscillation regime. Shear and time dependent rheological parameters were calculated from flow curves. Stability of belite cement paste was judged based on the critical strain determination in amplitude sweep test. Setting was evaluated by Tussenbrock needle penetration test and oscillation time test on rheometer. The properties of the laboratory belite cement were correlated to industrial cement CEM I, CEM II/A-LL and CEM III/A. Reactive belite cement pastes show good flow properties both due to small amount of alite and larger amount of rounded belite grains and clusters. Belite rich cement show decent stability comparable to CEM III and very good dispersing efficiency of PCE based HRWR.

1. Introduction

The cement industry is one of the primary producers of greenhouse gas CO₂. Around 7% of global anthropogenic CO₂ emissions are related to the production of Portland cement, mainly due to the limestone and clay burning at around 1450°C [1].

There are several alternative clinker systems that deserve serious attention with respect to global reductions in concrete-related CO₂ emissions. Reactive belite-rich Portland cement clinkers (RBPC) is one of them. RBPC belong to the same family as ordinary Portland cement (OPC) in terms of clinker phase composition, which comprises C₂S-C₃S-C₃A-C₄AF phases. Unlike sulfobelite cements the RBPC doesn’t contain Klein’s compound. The main difference in phase composition between RBPC and OPC lies mainly in the belite/alite ratio. For RBPC the belite is the most abundant phase, as opposed to alite in OPC.

The RBPC manufacture leads to lower specific energy consumption and CO₂ emissions. Furthermore, there is an advantage of requiring less high-grade limestone as a raw material. The burning temperature for RBPC is about 100°C lower than for OPC, which can lead to somewhat lower kiln heat consumption and permit more use of low-grade kiln fuels [2].

Staněk and Sulovský [3] discussed the mechanism of activation during preparation of belite-rich clinkers with an increased Ca:Si ratio in the structure of C₂S and partial substitution of SiO₄²⁻ by SO₄²⁻. Activation was done by sulfate ions, which substitute SiO₄ in the structure of belite causing an increase of Al₂O₃ incorporation in the belite and increased CaO:SiO₂ ratio in belite. The sulfur doping stabilizes alite M₁ modification in the clinker.
There are several papers on rheology of sulfobelite cement but only few about belite cement without Klein’s compound. The behavior of belite-cement in presence of polynaphthalene sulfonate and polycarboxylate types of high-range water-reducers (HRWR) was already discussed in [4]. Authors reported that lower reactivity and rounded particles of belite cement compared to ordinary cement causes lower shear thickening response regardless of the w/c and type of HRWR in use.

2. Experimental

2.1. Materials and methods
Belite clinker doped with sulfur was prepared in laboratory scale. Common materials for cement production were used for raw meal preparation: limestone, clay shale, quartz sand, iron ore tailings and FGD (flue gas desulfurization) gypsum as the source of SO$_3$. Raw materials were ground in laboratory ball mill in amount of 10 kg on fineness characterized by sieve residue 12% on 0.09 mm sieve. Tablets were prepared from homogenized raw meal and burnt in Kanthal furnace at 1350°C for 60 min. Clinker was quenched rapidly in the air on piece of metal outside the furnace. Quantitative phase composition of clinker determined by XRD with Rietveld refinement and by point counting in light microscope is given in table 1. In case of point counting method, the quantitative composition (wt. %) was calculated from area and specific gravity of clinker phases.

Specific gravity of the clinker determined by pycnometer method is 3299 kg/m$^3$. Cement was prepared by grinding the clinker with 2% of gypsum in laboratory ball mill. Specific gravity of the cement was 3259 kg/m$^3$ and specific surface 400 m$^2$/kg. SO$_3$ content in the cement was 3.93 wt. %.

Particle size distribution (PSD) of the belite cement was determined by a laser diffraction method using CILAS 920L laser particle size analyzer. The range of the analyzer is 0.3–400 μm. Sample was treated with ultrasound (60 s) before measurement and dispersing medium was isopropyl alcohol. PSD of RBPC is given in figure 1.

Setting of the belite-rich cement was monitored by oscillation test monitoring evolution of complex modulus ($G^*/τ$) on rotational rheometer, Tussenbrock needle penetration test ($τ/t$), semiadiabatic (T/t) and isothermal (heat flow/t) calorimetry. Calorimetric methods were used for correlation of rheological properties with heat evolution during early hydration.

Flow parameters calculated using Bingham [5] and Herschel-Bulkley model were tested by rotational rheometer DHR-1 (TA Instruments) using geometry of coaxial cylinders. Samples were pre-sheared with 150 s$^{-1}$ for 60 seconds and the logarithmic sweep was used with 5 points/decade, 5 sec of steady state sensing and 5 sec of averaging time. Yield stress - $τ_y$ (Pa), plastic viscosity $ν_{pl}$ (Pa.s) and thixotropy/rheopexy (Pa/s) were determined from hysteresis loops of ascending and descending curves in 1 s$^{-1}$ – 150 s$^{-1}$ – 1 s$^{-1}$ shear rate region.

| Table 1. Quantitative phase composition of the clinker. |
|------------------------------------------------------|
| XRD | Point counting |
| vol. % | wt. % |
|β-C$_2$S | 86.5 | 84.7 |
|C$_3$S | 7.4 | 8.2 |
|C$_3$A cub. | 1.4 | 0.5 |
|C$_3$A orth. | 0.9 | - |
|C$_4$AF | 2.4 | 5.1 |
|CaO | 1.4 | 1.5 |
Linear viscoelastic region and critical strain (%) was determined in oscillation regime by monitoring storage and loss moduli (G’ and G”) in chosen region of oscillation strain γ (%) and frequency 1 Hz. Geometry of parallel plates with cross-hatched surface was used. All rheological and calorimetric testing was done on cement pastes with w/c = 0.32 at 25°C. From two to four measurements were performed for each sample to keep standard deviation below 5%. For each sample, the measurement started after 5 minutes after adding of water.

3. Results and Discussion

3.1. Setting of RBPC

Setting of the RBPC paste was followed by combination of needle penetration Tussenbrock method, oscillation test on rotational rheometer monitoring evolution of complex modulus (G*/t), semiadiabatic (T/t) and isothermal (heat flow/t) calorimetry (figure 2 and 3).

In case of Tussenbrock test, threshold shear stress is related to penetration resistance calculated from the depth of indentation of needle. It shows slow increase of shear stress up to 190 min followed by steeper trend till the end of setting at 270 min. Different trend comparing to needle penetration test was found for setting test done on rotational rheometer (figure 2). Evolution of G* related to setting f cement paste is strongly affected by structural break down, since the measurement is continuous and the bonds formed during setting is continuously broken by oscillatory movement of the upper plate. The values are more related to dynamic than to static yield stress; as can be seen in the case of needle penetration test. Both static and dynamic yield stresses are critical for many field applications [6]. Despite the fact that geometry of parallel plates with cross-hatched surface was used, the test is limited by the adherence of the measured material to the plate. The course of the curve is gradual without significant acceleration of the increase in the values associated with the onset of setting.

Two different calorimetric methods were used to describe the beginning of the hydration of RBPC (figure 3). The belite cement was compared to three industrially produced cements CEM I 42.5 R, CEM II/A-LL 42.5 R and CEM III/A 42.5 N (Hranice plant). Due to preparation of the sample,
the semiadiabatic method measurement starts up to 5 minutes after the addition of water. In case of isothermal calorimetry, the measurement starts within few seconds after addition of water and the large exothermic signal related mainly to initial reactions of aluminate phase and tempering heat is monitored. The period of slow reactions characterized both by slow development of T and heat flow resp. in time is followed by main exothermic peak related to hydration of C₃S and formation of portlandite (CH) and C-S-H. The onset of the C-S-H formation is related to the start of the setting of cement pastes. In terms of length of dormant period and start of the setting, the RBPC is very similar to CEM I, it means there is no dilution effect of supplementary cementitious materials as it is for CEM II and III. The important fact is that the RBPC contains small amount of C₃S which is the main contributor of the heat at this acceleration period of hydration. Belite hydration takes place at later times and thus not affecting setting process. Isothermal calorimetry is able to monitor very subtle differences of the rate in which the heat is dissipated due to its sensitivity, which is in the range of μm, and the ability to separate individual exotherms compared to semiadiabatic calorimetry. On the other hand, semiadiabatic calorimetry reflects more the autocatalytic nature of the reactions.

![Figure 2. Setting of the RBPC, Tussenbrock needle test and oscillation time test.](image)

![Figure 3. Period of slow reactions, semiadiabatic and isothermal calorimetry.](image)

3.2. Rheological parameters and stability of RBPC compared to industrial cements
Rheological parameters yield stress and plastic viscosity were calculated from flow curves using the Bingham model (figure 4). Stability of the cement paste was tested by amplitude sweep test to determine critical strain (%) [7], which is defined as the cut-off point between linear and nonlinear regions of strain sweep (figure 4). The mechanisms for the strain of the yield stress and the critical strain of linear viscoelastic region of cement pastes were investigated by Roussel [8]. RBPC parameters were correlated to industrial type of cements. It has been previously published [9–13] that in case of OPC strain was $10^{-5}$ to $10^{-1}$, while the frequency was kept constant at 1 Hz until the structure broke down. In
view of previous studies, the RBPC show decent values of critical strain revealing promising stability of the material. Results of amplitude sweep show that stability of the RBPC paste is closer to CEM II and CEM III than to CEM I.

![Figure 4](image.png)

**Figure 4.** Yield stress, plastic viscosity and critical strain of RBPC and industrial cements.

Yield stress, as an important parameter of cementitious material qualifying flowability [14], of RBPC is close to CEM I and CEM III and plastic viscosity is similar to CEM III. RBPC, same as other belite cements [4], is expected to improve rheology of cement-based materials because of the rounded grains of C₂S and their relatively lower reactivity at early age compared to C₃S.

### 3.3. Rheology of RBPC with PCE superplasticizer

The role of various dosage of PCE superplasticizer on RBPC rheology was determined by rotational rheometer calculating rheological parameters yield stress, plastic viscosity and rate index with Herschel-Bulkley model from flow curves. SP positively decreases values of yield stress, plastic viscosity and thixotropy with increasing dosage (figure 5). Several instrumental approaches how to determine thixotropy have been proposed through last decades [8, 15–18]. Shear-thinning behavior of the paste [4, 19, 20] (rate index values >1) is more pronounced with increasing dosage of SP. In terms of plasticization, PCE SP works similarly to OPC. RBPC show very good dispersing efficiency of PCE based HRWR, which compatibility with OPC based materials has been discussed intensively [21–23].
Figure 5. Rheological parameters of RBPC with various dosage of PCE superplasticizer.

4. Conclusion
Prior pilot testing and market introduction of the new low-energy cement, the good workability in fresh state is one of the crucial parameters of the material. This study proved that RBPC has good flow properties comparable to industrial cement due to its high belite content. Setting and heat evolution during period of slow reactions of RBPC is ruled by the presence of alite and its relatively small content. Setting reactions were followed by four different methods showing pros and cons of each. Amplitude sweep tests revealed improved stability of RBPC compared to CEM I. Testing PCE based HRWR compatibility, the RBPC showed decent dispersing efficiency and predictable shear-dependent behavior.

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