Binary and Ternary Shale Binders with High Replacement Levels

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Abstract. This paper investigates mortars with fifty percent cement replacement of supplementary cementitious materials in binary and ternary blends, according to DS/EN 197-5: 2021. A new standard that allows for up to 50% of cement replacement levels than previously. Different aspects ranging from rheology, mechanical properties, and mineralogical changes were measured. The selected shale was ground in a laboratory disk mill, blended and tested in binary blends (only shale), and together with limestone filler as ternary blends. As expected, the mechanical properties of these mortars are lower than the mortar made only with Portland cement. The binary binder, with 50% cement replacement by calcined shale alone, developed larger compressive strengths and larger reductions in portlandite than the ternary binder, due to the additional pozzolanic reactions. The replacement of one-third of the shale by limestone filler, with a total cement replacement of 50%, had the lowest compressive strength values but less superplasticizer demand for the target workability. This allows, when judged by the rheology and mechanical properties alone, a mixture of both SCMs might be beneficial, for example where no risk of corrosion would be expected (X0, XC1). Furthermore, one might consider the optimization of the relation between the calcined shale and limestone where CO_2 emissions are being reduced.

Keywords: Calcined Shale · Limestone · High Replacement · Strength · Mineralogy

1 Introduction

Today, the CO_2 footprint of materials from carbon-intensive sectors, such as the construction sector - which is responsible for large quantities of materials being extracted, transported, and discarded - is of societal interest [1].

Since the use of by-products of other industries provides an advantage for the environmental footprint, which has been used widely in the concrete industry in the past by utilizing for example fly ashes. Materials such as calcined clays and shales may have a financial and CO_2 penalty due to the necessary calcination step while having a wider distribution globally as an upside [2]. When implementing circular pathways for construction materials, the use of shales as a by-product of mining industries may become

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beneficial. Shales could then be used as secondary raw materials, where CO_2 footprints are being minimized and large scales of waste should be used. Shale, or more precisely calcined shales, are defined in DS/EN 197-1 as suitable for use in cementitious binders if the reactive SiO_2 content is larger than 25 mass %. It seems that majority of shales used in cement, according to literature [3–5], seem to originate from the energetic utilization of oil-shales, where the oil shale is used as a fuel, and the burnt (ashes) are utilized as pozzolan in specialized cement (CEM II/T after EN 197-1). Today, these types of binders could contain up to 50% of shale in CEM II/C-M cements due to a recent change in European standardisation (DS/EN 197-5:2021).

However, by-products from mines, which can produce significant quantities of mine tailings, are not used for energy production by burning off the hydrocarbons contained in oil-shale but could be used in cement as well in CEM II/Q cements. These types of shales need to be calcined to activate the pozzolanic properties of the clay fractions. In this work, we investigate the use of high replacements of cement by calcined shales in binary and ternary composite cement including also limestone filler.

2 Materials and Methods

2.1 Materials

The used cement was a CEM I 42,5 N. As calcined shale, a smectite rich shale from Germany was used and calcined at ca. 850 °C in CemGreens A/S pilot scale calciner and ground in a laboratory disk mill for three minutes.

Rollovit 30 from Lhoist Western Europe (Faxekalk A/S) was used as a calcium carbonate source with a particle size under 45 µm (>97% $CaCO_3$, Fig. 1).

CEN Standard Sand according to EN 196-1 from NORMENSAND GmbH, Germany and deionized water was used to make standard mortars with a replacement of 50% of the cement (Table 1).

Table 1. Mix design of the mortar samples (rheology tests) and mortar samples, all in [g].

	CEM I 45.5 N	shale	$CaCO_3$	water	normsand	SP
CEM I	450	–	–	225	1350	–
S3	225	225	–	225	1350	2.7
SL3	225	150	75	225	1350	1.0

The workability of the mortars was adjusted using Dynamon NRG-670 (Mapei) as super plasticizing admixture (SP), a modified acrylic-based polymer blends with accelerating properties intended for precast applications.

This SP was chosen as high cement replacement binders may display low early age strengths that may limit the productivity in precast plants.

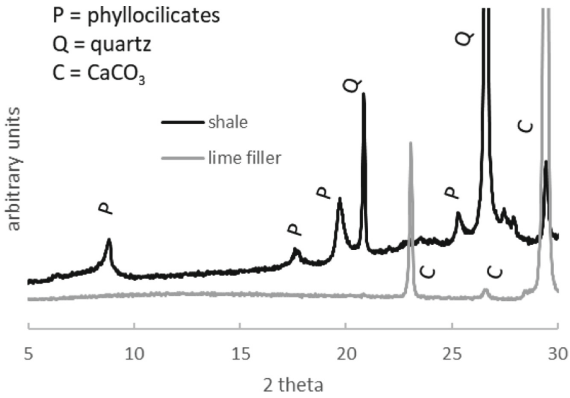

Fig. 1. Powder XRD diffractogram for the shale and limestone filler.

2.2 Methods

Powder X-ray Diffraction (XRD) is a method to observe the mineralogical composition for materials. The instrument used is an X'Pert PRO with a Cu Kα radiation source with a voltage of 45 kV and a current of 40 mA. The instrument measured the sample between 5 and 69 2ϴ. As the sample is spinning with a revolution time of 16:00 s, and a step size of 0:017 2ϴ. For the measurements, a divergence slit of 1°, a beam mask spacing of 10 mm and an anti-scatter slit of 6.6° were used. The data is evaluated with Malvern Panalytical's HighScore software version 4.9.

Workability. Mortars were mixed according to DS EN 196-1 and tested with a brass cone on a flow table with 15 hits per test before the slump flow was measured in two perpendicular directions and averaged. The target value was a slump flow between 17 and 18 cm.

Calorimetry. The method used is inspired by standard DS/EN 196-9:2010. A Testo 176T4 data logger that can measure 4 different temperatures simultaneously, one per channel. The wire used is a thermal wire type T, Cu CuNi class 2.

One channel was used as the temperature reference and three were running with the same mortar mixture. All four channels were placed in a polystyrene box to isolate the samples thermically from the room temperature with a minimum thickness of 24 mm at the bottom and more cover on the other sides. The box was hosted in a temperature-controlled lab without windows with a target temperature of 18 °C. The mortar mass, time of addition of water and starting of the data logger of each sample were noted to enable the calculation of the heat release per gram cement and peak time. The time from when the water is added to the mortar and transport to the data logger was less than 30 min. This means that the initial part of the hydration, dominated by calcium aluminate hydrates was not recorded. After ca. three days of hydration, the temperature recorded corresponded to the room temperature.

All data displayed is the average of the three mortar samples and corrected by the average temperature of the reference channel to avoid overall reductions through possible noise in the signals.

Mechanical Properties. The mechanical strengths were tested after DS/EN 196-1. The samples were cured for the first day in the mold covered by a metal plate. Afterwards the samples were stored in deionized water until the desired age for strength measurements.

3 Results and Discussion

The heat release per gram of cement for the reference mortar and the two binary mixtures is shown in Fig. 2 and suggest that the hydration is accelerated for both binder types: binary and ternary. In the same tests without SPs and lower replacement rates, the acceleration was almost identical for both binders [6]. In this case, the additional acceleration for the shale only binder might be due to the accelerating properties of the superplasticizer (Table 1) that is almost three times higher in concentration. This does not only affect the start of the acceleration period, but also the quantity of heat released.

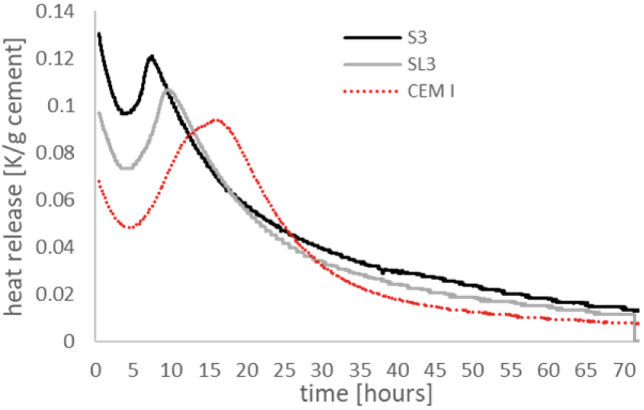

Fig. 2. Heat release over time as measured by the datalogger in an insulated, semi-adiabatic set-up for the three binders investigated; S = binary shale, SL ternary = shale and limestone, CEM I = Portland cement.

The overall mineralogy is also very similar for all binders investigated (Fig. 3). The hydrate phase assemblage is characterized in all binders by ettringite, monocarbonate and some hemicarbonate, portlandite, calcite and anhydrous phases from the shale and clinker minerals. Note that the portlandite (CH) quantities are not only reduce due to pozzolanic reactions, but also because less clinker minerals are present to form calcium hydroxide as hydrate phase.

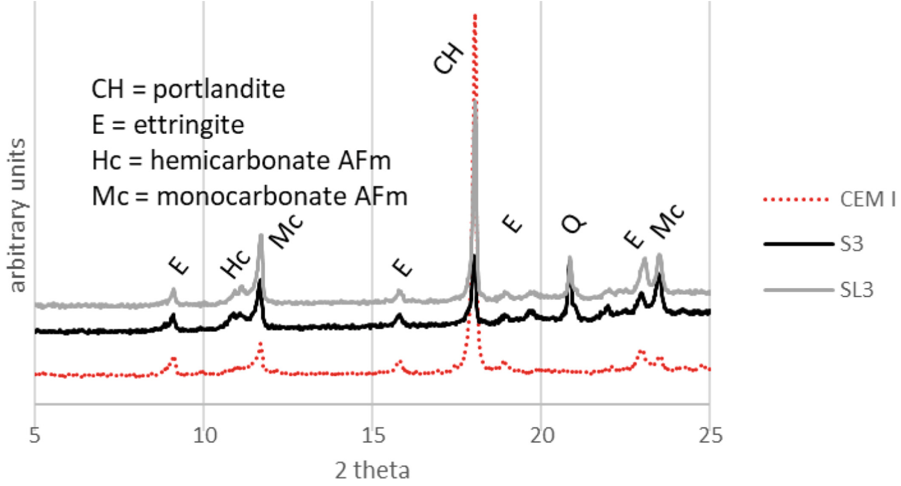

Fig. 3. Powder XRD patterns after 91 days of hydration for the reference CEM I and the binary (S) and ternary shale (SL) binders. The key phases are indicated on the diagram.

Figure 4 shows the changes between one week and 3 months of curing for the binary binder (S3; a) and the corresponding ternary binder (SL3; b). The extra curing time leads to higher intensities for monocarbonate and hemicarbonate, while the ettringite quantities are comparable. It seems that the binary binder consumes more portlandite in pozzolanic reactions as the intensities after three months of curing are the lowest observed in this study. The portlandite reduction in the ternary blend is much lower between the two measurements times (Fig. 4b).

The compressive strength development for the tested binders displays very similar development (Fig. 5). The overall strengths are lower than the reference Portland cement mortar, as expected based on the very high replacement levels. The binary binder displays somewhat higher strength when compared to the ternary binder. However, the difference between them is barely larger than 3 times the standard deviation for the binary binder, suggesting a significant difference if the background data would be normally distributed. However, the number of samples is too low to confirm a normal distribution. Overall, the binary and ternary binders perform quite similar.

Unfortunately, this may be especially the case for early age strength which determine when samples can be demoulded. This would require possibly a cement with faster strength developments.

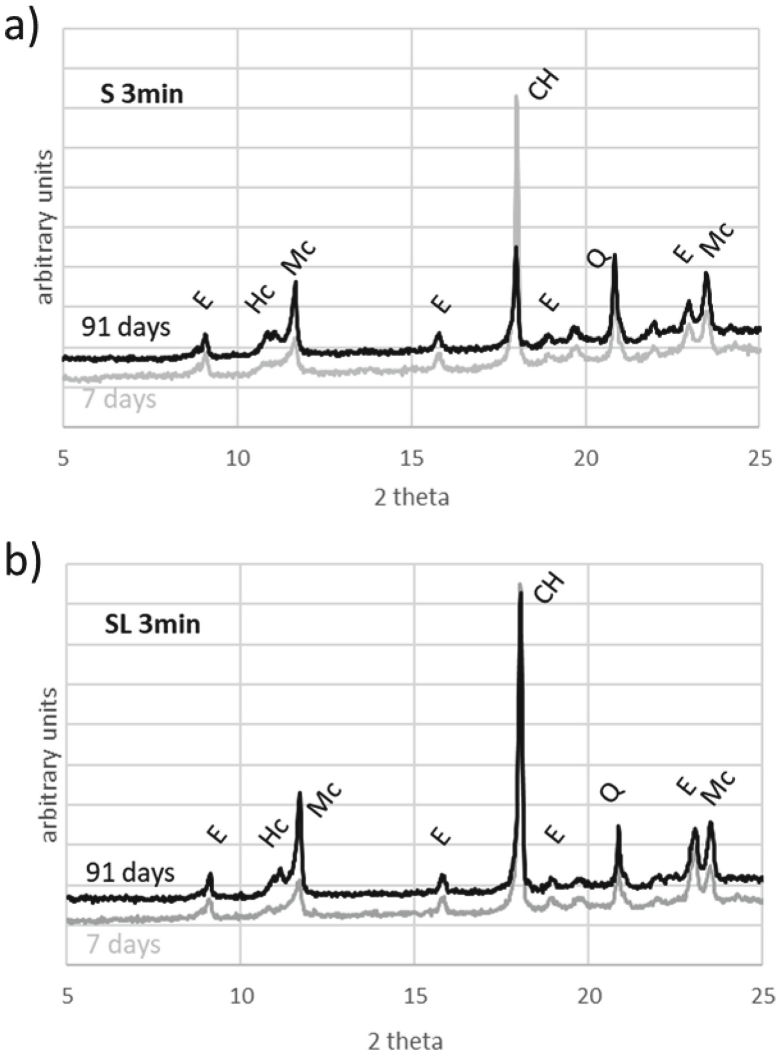

Fig. 4. Powder XRD patterns after 7 and 91 days of hydration for the finer binary (S; a) and ternary shale (SL; b) binders. The key phases are indicated on the diagram.

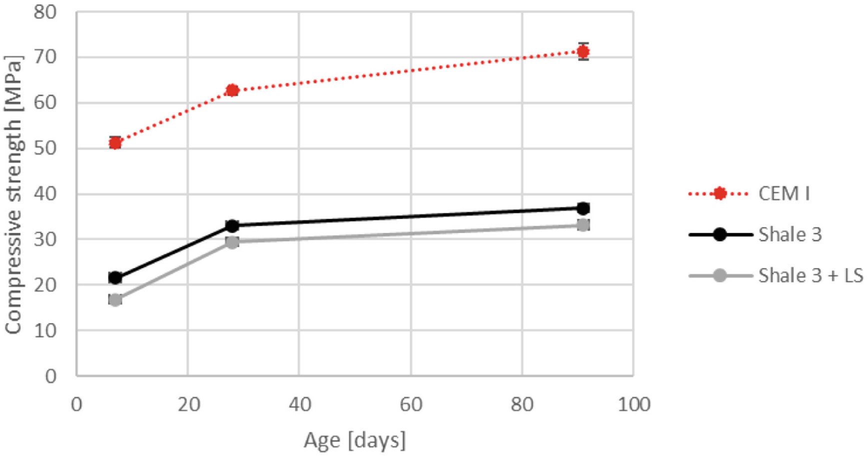

Fig. 5. Compressive strength development of the investigated binary (S) and ternary (SL) mortars.

4 Conclusions

The compressive strength was larger for the binary binder, where also the calcium hydroxide appeared to more reduced, indicating a higher pozzolanic reactivity.

All of the tested mortars, with 50 mass % replacement, have relatively low early age strengths, which may reduce the use in for example applications, such as precasting, where the productivity of each production line may require faster demoulding schedules.

The replacement of shale with limestone filler yields slightly lower mechanical results but may improve the CO_2 footprint. This may be desirable where early mechanical strengths are not crucial but overall CO_2 budgets need to be reduced due to e.g. limitations in the CO_2 quantities used in a construction.

It will be interesting to follow how the recent addition to standardized cements of the Portland cement family, CEM II/C-M cement, will be utilized in the industry in the future.

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