



Formulation of low clinker blended cements and concrete with enhanced fresh and hardened properties

Federica Boscaro^{a,b}, Marta Palacios^{a,c}, Robert J. Flatt^{a,*}

^a Institute for Building Materials, ETH Zurich, 8093 Zürich, Switzerland

^b Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA

^c Eduardo Torroja Institute for Construction Science (IETcc-CSIC), Madrid, Spain

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ABSTRACT

Blended cements appear as the most promising way to massively produce cements with reduced environmental footprints. However, considering the generally lower early mechanical performance of highly blended cements, chemical admixtures are increasingly relied upon to increase early strength. However, in many cases this can negatively impact other properties as rheology and durability.

This paper proposes an approach to formulate low clinker cements and concrete using moderate alkali activation or gypsum to enhance early and long-term compressive strength, without inducing excessive alkali-silica reaction (ASR) expansion. It examines blended cements containing burnt oil shale along with limestone and fly ash or slag as supplementary cementitious materials. It optimizes the combination of polycarboxylate ether (PCE) superplasticizers with the strength enhancers. Along with the use of $\text{Ca}(\text{NO}_3)_2$ to drive PCE adsorption, this provides good rheology control, increased early and long-term compressive strength, as well as acceptable ASR expansion in cements with only 50% clinker.

1. Introduction

Portland cement production is responsible for about 5–8% of man-made CO_2 emissions [1]. One of the most effective solutions to substantially reduce its environmental footprint is clinker replacement with supplementary cementitious materials (SCMs) [2]. Much research has been conducted on identifying new sources of SCMs [3], on combining several types of SCMs and on investigating their effects on cement and concrete properties [4]. This led to the development of new binders among which calcined clay limestone cements (LC^3) represent a promising solution [5]. However, common SCMs show slower reactivity than alite, which results in lower early compressive strength of highly substituted binders [6]. Thus, the use of chemical admixtures is generally seen as an essential vector to increase the performance of low clinker cements and concrete [7].

The use of such chemical admixtures, as alkali solutions, is a well-established mode to increase the SCMs rate of reaction. They are a crucial component of the alkali-activated materials [8] and their effects on alite and Portland cement hydration have been widely investigated [9–11]. NaOH was found to increase the rate of reaction of alite and cement at 1 day, while generally reduced afterwards [9–11]. Kumar

et al. reported an earlier and faster precipitation of portlandite in NaOH doped alite [10]. Mota et al. measured higher compressive strength in alite mortars containing NaOH and Na_2SO_4 from 1 to 7 days [11]. However, it was found to be compromised up to 90 days in the NaOH system, while the opposite was observed in the Na_2SO_4 mix. As an alternative, the same authors showed that gypsum addition instead of the alkalis increases the rate of reaction and the maximum silicate peak of alite hydration and that although it delays the onset of the acceleration period, it enhances the early and long-term compressive strength with respect to plain alite [11].

Having underlined the positive effect of alkali salts, it should also be considered that such chemical admixtures can exhibit competitive adsorption processes with comb-shaped polycarboxylate ether (PCE) superplasticizers (SPs) which are the most efficient SPs in concrete technology. Specifically, the carboxylic groups of the PCEs compete with other ions for being adsorbed onto cement and SCMs surfaces, reducing the desired rheological properties provided by the polymer [12]. Flatt et al. argued that some superplasticizers can experience competitive adsorption with hydroxyl ions [13]. Some years later, Yamada et al. reported a reduction of adsorbed PCE in presence of Na_2SO_4 and demonstrated that this resulted in a decrease in paste fluidity [14].

* Corresponding author.

E-mail address: flattr@ethz.ch (R.J. Flatt).

Afterwards, the sulfate sensitivity was related to the molecular structure of PCEs [15,16]. Moreover, the sensitivity of PCEs to hydroxides was examined more in detail by Marchon et al. [17]. In particular, by investigating NaOH activated blended cements with 30% fly ash replacement, the authors developed a criterion that provides an indication of the adsorption behavior of PCEs in alkaline environment, which is based on the PCE adsorption equilibrium constant defined by the polymer structural parameters [17].

Apart from loss in fluidity, another topic of concern when dealing with alkali solutions lies in the potential risk of alkali-silica reaction (ASR) in concrete. Various factors affect this, such as solution concentrations of Ca^{2+} , K^+ , Na^+ and the presence and composition of SCMs. Studies have shown that ASR expansion is enhanced in presence of higher sodium relative content than potassium, which also leads to different ASR products [18,19], while calcium affects their presence and form [19–21]. On the other hand, it is also well-known that some SCMs mitigate the expansion. In this respect, fly ash is more effective than slag, which results from the aluminates fly ash releases. Indeed, these can interact with the silica network of the aggregates, reducing their dissolution and thereby mitigating ASR expansion [22–24]. Additionally, burnt oil shale has been found to reduce ASR expansion [25,26]. Bourdot et al. observed a positive effect with both reactive flint and siliceous limestone aggregates, which they attributed to alkali fixation by the pozzolanic reaction of micro-quartz contained in the SCM [25]. Further, finely ground glass powder has been reported to reduce ASR expansion [27,28].

This paper presents an approach to formulating low clinker cements and concrete, using weak alkali activation or gypsum to enhance strength development, without however inducing ASR. The alkali dosages used in this work are well below those in normal alkali activated systems as geopolymers. Apart from the lower dosages, the alkalis used (NaOH and Na_2SO_4) are combined with $\text{Ca}(\text{NO}_3)_2$ to drive PCE adsorption, something that is generally not done in ordinary alkali activation.

For this we use a low clinker cement, having a combination of three SCMs selected for the following reasons:

- An SCM which is predominantly latent hydraulic but with varying composition also giving pozzolanic character, requiring an alkali activation and capable in particular of releasing aluminate ions.
- Limestone, included to form reaction products with Portland cement and, potentially, with the above mentioned SCM which is characterized by a high alumina content.
- An additional SCM, specifically an aluminosilicate that can act as a ASR mitigation agent, included to counter the impact of an alkaline activator used to enhance the reactivity of the new binder.

With regard to the SCM presenting both pozzolanic and latent hydraulic character, we used burnt oil shale, as blends of Ordinary Portland cement, burnt oil shale and limestone represent the second most used cement in Switzerland and show a very high potential for further replacements based on performance, availability and cost. We combined burnt oil shale with fly ash and/or slag. However, tests on additional blended cements containing other reactive SCMs would be worth investigating to prove a wider applicability of the approach proposed in this study.

In the first part of this paper, we illustrate how competitive processes play out between activators and superplasticizers in the highly blended cements here studied, in terms of rheology behavior, hydration kinetics and strength development. From this, specific formulations are selected to investigate the issue of ASR, demonstrating that the inclusion of 10% fly ash mitigates ASR for activator dosages allowing to double compressive strength at 24 h.

In the second part of the paper, we move on to presenting approaches allowing to more efficiently and insightfully formulate low clinker cements and concrete in terms of rheological performance, using one of the

activated blended cements studied here.

This largely extends the results and discussions presented in two recent conferences papers [29,30] here summarized with additional insights. Furthermore, we extend the compatibility study by Marchon et al. [17] to more complex systems characterized by: – including more than one SCM, – containing higher amounts of SCMs, – being activated by a broader range of admixtures. In doing so, we apply the concept of adsorption equilibrium constant of PCEs [17] to pre-select molecular structures. Such structures and dosages are refined by using correlations between yield stress, adsorption and PCE molecular structure [31] to determine dosages needed to achieve targeted rheological and strength performance in paste and concrete.

2. Materials and methods

2.1. Materials

Table 1 and Table 2 show respectively the mineralogical and chemical composition of the commercial Portland cement CEM I 52.5R (OPC, LafargeHolcim), limestone (LL), burnt oil shale (BOS), ground granulated blast furnace slag (SL) and siliceous fly ash (FA) used in this study as determined respectively by Rietveld refinement (performed with the software HighScorePlus 4.8) of XRD measurements (X'pert Pro PANalytical) and X-Ray fluorescence. The data of CEM II/B-M(T-LL) 42.5 N (Optimo 4, LafargeHolcim, here abbreviated as Op) are provided by the supplier. This commercial cement contains BOS and limestone, but in lower percentages than the novel quaternary cement investigated in this paper.

The exact mineralogical composition of BOS is variable depending on the firing temperature. Fig. 1 summarizes the main phases that can be found, as discussed by Kruspan et al. [32]. The BOS investigated in our work contains mainly amorphous phases, quartz, illite and anhydrite.

The particle size distribution of the powders dispersed in isopropanol was measured by laser diffraction (Malvern MasterSizer S for OPC and SCMs; CILAS 920 L (CILAS, France) for Op provided by the supplier). Table 3 reports the D_{v50} and the BET specific surface area (SSA_{BET}), which was determined by nitrogen adsorption technique (Micromeritics Tristar II 3020).

NaOH pellets (99.4% purity, VWR), granular Na_2SO_4 ($\geq 99.0\%$

Table 1
Mineralogical composition of Op, OPC and SCMs in % (w/w).

	Op	OPC	LL	BOS	FA	SL
Alite	49.1	67.6	–	–	–	–
Belite	5.6	6.4	–	–	–	–
C_3A	4.4	4.6	–	–	–	–
C_4AF	7.9	8.7	–	–	–	–
Gypsum	2.7	4.6	–	–	–	–
Hemihydrate	0.4	–	–	–	–	–
Anhydrite	2.0	–	–	14.8	–	–
Quartz	3.0	–	–	16.2	1.1	–
Calcite	16.6	–	100 ^a	8.5	–	–
Dolomite	0.3	–	–	–	–	–
Hematite	0.6	–	–	3.5	1.1	–
Illite	0.7	–	–	15.4	–	–
Portlandite	0.6	–	–	0.7	–	–
Free lime	0.2	0.4	–	4.2	–	–
Periclase	0.6	–	–	–	–	–
Arcanite	1.1	–	–	–	–	–
Feldspar	0.2	–	–	–	–	–
Gehlenite/Akermanite	0.4	–	–	–	–	–
Ca-Langbeinite	0.4	–	–	–	–	–
Mullite	–	–	–	–	3.6	–
Lorenzite	–	–	–	–	0.1	–
Amorphous	3.2	7.7	–	36.7	94.1	100

^a This value is rather high and unexpected. At least 90–95% (w/w) should be calcite while other minerals may be present as minor compounds (considering the XRF results). However, a detailed discussion of this is beyond the scope of this study.

Table 2
Chemical composition of Op, OPC and SCMs in %(w/w).

	Op	OPC	LL ^a	BOS ^a	FA ^a	SL ^a
CaO	57.5	62.8	53.76	28.69	6.55	40.99
SiO ₂	20.1	20.2	1.9	34.2	48.73	36.82
Al ₂ O ₃	5.2	4.7	0.92	10.74	23.50	10.68
Fe ₂ O ₃	3.2	3.1	0.4	6.65	10.59	0.41
MgO	1.7	2.1	0.35	1.9	1.54	8.54
MnO	0.04	–	–	0.1	0.1	0.1
TiO ₂	0.3	–	0.06	0.57	1.16	0.71
P ₂ O ₅	0.19	0.19	–	0.29	0.48	–
K ₂ O	0.97	1.03	0.06	2.0	2.5	0.61
Na ₂ O	0.15	0.22	–	0.19	0.48	0.2
SO ₃	3.0	3.5	–	9.6	0.67	2.64
L.O.I.	7.65	2.16	42.5	5.0	3.7	–1.7 ^b

^a XRF of the SCMs was performed on fused samples. The chemical composition and L.O.I. considering dried powders was calculated by: - subtracting to 100% (w/w) the L.O.I. obtained on fused samples to obtain the L.O.I. on dried powders, - multiplying the L.O.I. for each oxide content, both measured on fused samples, to obtain the oxide content for dried powder.

^b The negative value is attributed to the oxidation of sulfides to sulfates.

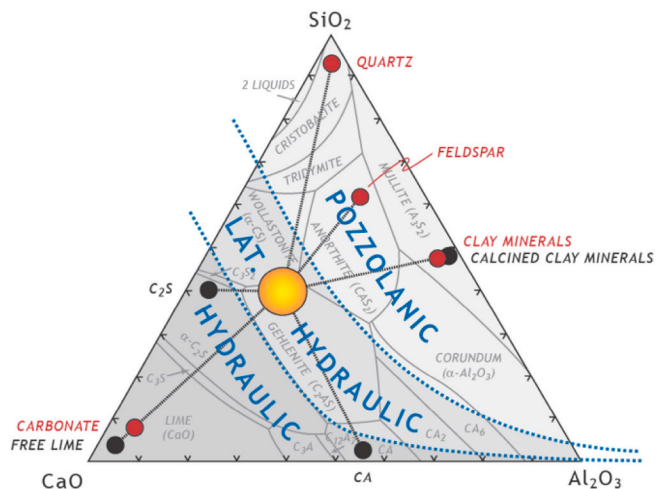


Fig. 1. CaO-Al₂O₃-SiO₂ ternary diagram showing the most important mineral phases present in the oil shale (red dots), the ones formed by the firing (black dots) and the composition of BOS if the unburned oil shale is fully transformed into glass (yellow dot). Reproduced from [32] with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Median diameter D_{V50} and SSA_{BET} of OPC and SCMs.

	Op	OPC	LL	BOS	FA	SL
D _{V50} [μm]	13.5	11.70	7.40	6.06	14.40	14.93
SSA _{BET} [m ² /g]	1.60	1.01	2.19	5.53	1.50	0.72

purity, Sigma-Aldrich), Ca(NO₃)₂•4H₂O (>99.0% purity, Sigma-Aldrich) and gypsum were used as activators. Lab grade gypsum (>98% purity, ACROS Organics) having D_{V50} and SSA_{BET} of 55.29 μm and 0.50 m²/g, was used for the cement pastes and mortars experiments, while industrial ground gypsum (99% purity, FG200, Saint-Gobain Formula), with D_{V50} and SSA_{BET} of 16.73 μm and 0.77 m²/g, was used for concrete.

Table 4 shows the characteristics of the four non-commercial PCEs (Sika Technology AG) used in this study. PCE1, PCE2 and PCE4 are methacrylic-based polymers synthesized by esterification, while PCE3 is maleic-based made by copolymerization. The adsorption equilibrium constant K^{*}_{A,1} was calculated according to [17]. For the experiments on

Table 4
Molecular parameters of the PCEs used. C/E is the charge density, expressed as N-1, indicating the carboxylate functions per side chain. n is the number of repeating structural units. N is the number of monomers in the backbone per repeat unit (B). P is the amount of monomers in a single side chain (SC).

PCE	C/E	B M _w [g/mol]	SC M _w [g/mol]	n	N	P	K [*] _{A,1}
PCE1	3.2	5250	1000	15	4.2	23	102
PCE2	6.3	5250	1000	8	7.3	23	533
PCE3	3.1	n.a.	1200	4	4.1	27	615
PCE4	2.6	5250	1000	17	3.6	23	67

mortars and concrete, defoamer and biocide were added. The dosages are expressed as % of active polymer by weight of binder (bwb).

2.2. Methods

2.2.1. Sample preparation

Two blended cements were prepared:

- MF: composed by 50% OPC, 20% LL, 20% BOS and 10% FA.
- MS: composed by 50% OPC, 20% LL, 20% BOS and 10% SL.

Three different activators were used: NaOH, Na₂SO₄ and gypsum. The first two were additionally combined with Ca(NO₃)₂. All the three were dosed to obtain an equivalent cation concentration.

The pastes were prepared at a liquid/binder (l/b) of 0.35. 330 g of blend were mixed with the liquid at 200 rpm for 30 s and at 800 rpm for 4 min with a 4-bladed propeller stirrer (Eurostar power control visc, IKA®-Werke GmbH & Co. KG, Staufen, Germany). The NaOH and Na₂SO₄ solutions and the gypsum suspension were prepared with ultrapure water (UPW, ρ = 18.2 MΩ·cm, TOC about 1–2 ppb, provided by a water purification system (Milli-Q A+) from Millipore, Merck & Cie). Ca(NO₃)₂•4H₂O was added as the last component of the liquid. For the alkali activated mixes, PCE was included as first into the liquid batch, while admixed with the activated suspension for the gypsum activated systems. Prior fluidity loss tests, the pastes were mixed at 200 rpm for 1 min.

Delayed addition of all the admixtures was used in specific cases: 80% of the total water was mixed with the binder at time 0, while the remaining 20% with the PCE and activators was added after 2 min.

Mortars were prepared according to ASTM C305–11 at constant l/b of 0.45 using deionized water. The binder to sand (siliceous, 0–4 mm) ratio was 0.5. PCE was added as first component of the liquid, followed by the alkali solution and Ca(NO₃)₂. For gypsum activated mortars, gypsum was added after the PCE and water.

Concrete for rheological and mechanical studies was prepared at l/b of 0.5 using 0–32 mm pre-wetted aggregates (LafargeHolcim), using only NaOH, combined with Ca(NO₃)₂, as activator (Table 5). The procedure used for wetting and their water absorption coefficient at 24 h

Table 5
Mix formulations for 1 m³ of concrete prepared for the rheological and mechanical studies.

Components	MS_0_0.3PCE1	MS_1_0.4PCE1	MS_1_0.45PCE4
Sand 0–1 mm [kg/m ³]	304	304	–
Sand 0–2 mm [kg/m ³]	–	–	228
Sand 0–3 mm [kg/m ³]	190	190	–
Sand 0–4 mm [kg/m ³]	–	–	570
Sand 1–4 mm [kg/m ³]	285	285	–
Gravel 4–8 mm [kg/m ³]	266	266	152
Gravel 8–16 mm [kg/m ³]	361	361	456
Gravel 16–32 mm [kg/m ³]	494	494	494
Total aggregates [kg/m ³]	1900	1900	1900
Binder [kg/m ³]	300	300	353
NaOH [% bwb]	–	1	1
Ca(NO ₃) ₂ [% bwb]	–	1	1
PCE [% bwb]	0.3	0.4	0.45

can be found in [33]. Concrete was prepared in delayed addition of 2 min of PCEs and, when present, the activators. 80% of the total water was mixed with the binder and aggregates for 2 min at 45 rpm, while the remaining 20% including the admixtures for 3 min at the same speed. Concrete was mixed again for 1 min prior fluidity loss measurement.

Concrete for the ASR test were prepared using 0–22.4 mm dry reactive aggregates (Aarekies Brienz AG). The l/b was kept at 0.5. Table 6 shows the mix proportions. All the mixes were prepared in direct addition of the PCE with the exception of the alkali activated ones where delayed addition of all the admixtures was used as described above.

2.2.2. Calorimetric measurements

Calorimetric measurements were conducted at 23 °C using isothermal calorimeters: TAM Air (TA Instruments - Waters LLC, New Castle, DE, USA) for cement pastes, I-Cal 8000 HPC (Calmetrix, Arlington, MA, USA) for mortars. The tests started about 5 min and 7 min after the beginning of the hydration for respectively cement pastes and mortars. The first 30 min of the measurements were discarded.

2.2.3. Spread flow test and flow table spread

Spread flow tests were conducted on cement pastes at 10 and 60 min after mixing by filling a mould placed on a humidified glass surface. For cement pastes, a cylindrical mould of 5 cm diameter and volume of 99 cm³ was used, while for mortars a tronco-conic one with a volume of 340 cm³. The mould was filled after 8 min from the start of the mixing and lifted after 1 min of rest. Two perpendicular diameter were measured. The yield stress of cement pastes was calculated according to the empirical equation:

$$\tau_0 = \left[\frac{225\rho g V^2}{128\pi^2 R^5 \left(1 + \frac{225}{128\pi} \sqrt{3} VR^{-3} \right)} \right] - \lambda \frac{R^2}{V} \quad (1)$$

where R is the radius of the spread flow, ρ the density of the sample, V its volume, g the gravitational acceleration and λ the surface tension, of which the effect can be neglected for most flow spreads considered in this paper [15].

The flow table spread (FTS) of concrete was performed according to SN EN 12 350–5 using a tronco-conic mould (200 mm height x 200 mm bottom diameter x 130 mm smaller diameter). The flow table was shocked 15 times and two perpendicular diameters were taken.

2.2.4. Compressive strength

The compressive strength was measured according to EN 196 on mortar specimens of 40x40x40 mm and on concrete samples of 15x15x15 cm. The cubes were demoulded after 1 day and stored at 20 °C/95%RH.

2.2.5. ASR measurements

The concrete performance test was conducted according to SIA MB 2042 [34]. Three prisms of 70x70x281 mm were casted for each mix design. They were stored at 20 °C/95%RH until demoulding after 1 day. Afterwards they were placed at 60 °C/100%RH for 48 weeks. The Swiss

norm considers concrete formulations suitable against ASR if after 12 months (48 weeks) the expansion does not exceed 0.300‰ and no single value is >0.350‰. Intermediate limits are reported in the results but are not further explained here, while their single values limit are not reported.

3. Results

3.1. Coupled effects of activators and PCEs on hydration kinetics, rheology and ASR

Due to the similarity of the hydration and rheology results obtained for MF and MS, only the data on MF pastes and mortars are shown here, while the corresponding results for MS are reported in the supplementary material.

3.1.1. Cement pastes

Fig. 2 shows the effect of activators addition on the hydration kinetics of MF pastes: both the alkalis and gypsum accelerate the rate of reaction with respect to the non-activated system [30]. Further, alkalis increase the cumulative heat at 24 h, but values are then lower than the reference after 50 h. As far as gypsum goes, it leads to less heat release than all the other systems [30].

Fig. 3 represents the cumulative heat at 24 h and the yield stress obtained for several MF pastes [30]. It highlights the effect of activators (gypsum and alkalis combined with Ca(NO₃)₂), and different PCEs. Among the three PCEs, PCE1 is found to provide the highest cumulative heat at 24 h, while PCE3 the lowest. Competitive adsorption appears to take place in the weakly alkali activated systems in presence of all the PCEs, because higher dosages of these polymers are necessary to reach a comparable yield stress to the one of the non-activated MF. However, Ca(NO₃)₂ improves the rheological behavior, which can be understood because of the favorable role of calcium ions on PCE adsorption. On the contrary, lower competitive adsorption is observed in the gypsum activated samples. Gypsum is added as a suspension and it is not fully dissolved, in contrast to NaOH and Na₂SO₄, which are included as solutions. Therefore, in the case of the alkali salts, the anions in solutions are expected to be in higher amounts and, consequently, to lead to higher competitive adsorption. For this reason, an extra source of calcium ions, in the form of Ca(NO₃)₂, was added in combination with the alkali salts.

From this ensemble of results, PCE1 is selected for mortars preparation as it represents the best compromise between good initial fluidity and highest cumulative heat at 24 h.

3.1.2. Mortars

Boscaro et al. demonstrated that the alkali activators combined with Ca(NO₃)₂ substantially increase the compressive strength at 24 h of mortars prepared with the MF binder in comparison to the non-activated system [30]. The authors reported that this effect was more enhanced in presence of NaOH than Na₂SO₄, while gypsum provided only slightly higher strength than the reference MF [30].

Table 6

Mix formulations for 1 m³ of concrete prepared for the ASR test.

Components	MS_1	MF_0	MF_0.5	MF_1	MF_0.9	MF_G	Op
Sand 0–4 mm [kg/m ³]	716	770	770	770	770	770	716
Gravel 4–8 mm [kg/m ³]	269	269	269	269	269	269	269
Gravel 8–16 mm [kg/m ³]	358	358	358	358	358	358	358
Gravel 16–22.4 mm [kg/m ³]	448	394	394	394	394	394	448
Binder [kg/m ³]	392	389	389	389	389	389	401
NaOH [% bw]b]	1	–	0.5	1	–	–	–
Na ₂ SO ₄ [% bw]b]	–	–	–	–	0.9	–	–
Ca(NO ₃) ₂ [% bw]b]	1	–	0.5	1	0.5	–	–
Gypsum [% bw]b]	–	–	–	–	–	4	–
PCE4 [% bw]b]	0.45	0.2	0.25	0.45	0.2	0.2	0.2

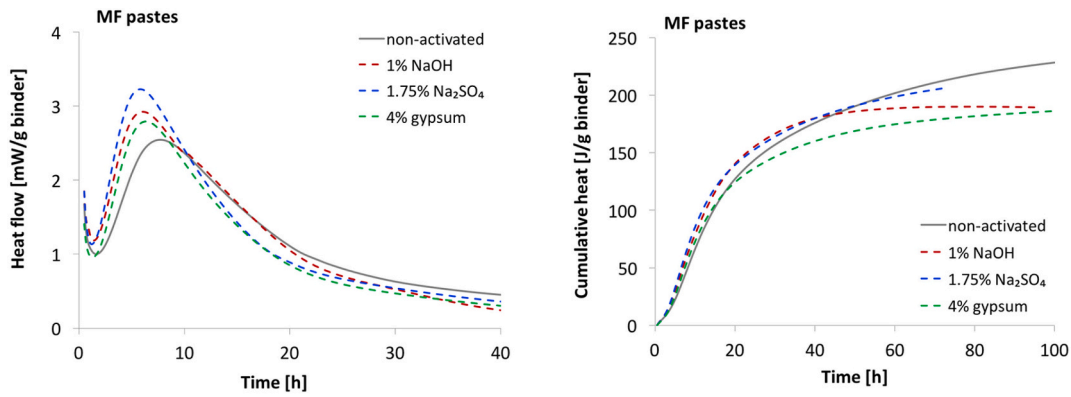


Fig. 2. Hydration kinetics of cement pastes with and without the activators. Modified from [30] with permission.

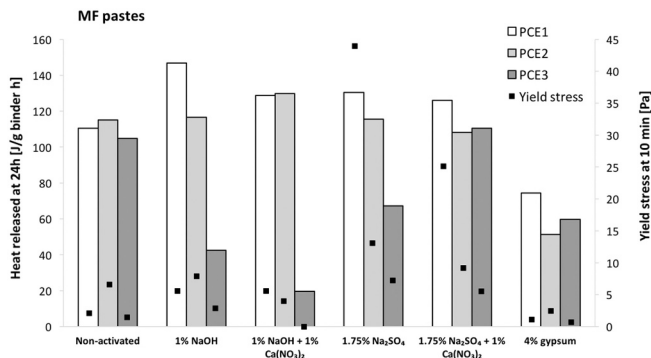


Fig. 3. Cumulative heat at 24 h and yield stress at 10 min of cement pastes with and without activators and with three different PCEs. The admixtures are added in direct addition. The dosage of PCEs in the non-activated samples corresponds to 0.2% bwb, while in all the activated systems is 0.4% bwb. Modified from [30] with permission.

Based on the results reported by Boscaro et al., we selected to only measure long-term strength of the weakly alkali activated samples combined with $\text{Ca}(\text{NO}_3)_2$ as these showed the best early strength gains. These longer-term strength measurements are reported in Fig. 4. The first and most important observation here is both NaOH and Na_2SO_4 combined with $\text{Ca}(\text{NO}_3)_2$ increase the compressive strength with respect to the non-activated MF up to 90 days for the dosages considered. Although the relative benefit decreases over time, it nevertheless always remains positive. Furthermore, it can also be observed that NaOH provides a higher increase up to 2 days, while Na_2SO_4 becomes more effective from 7 days on.

From these results, the following formulations are selected to

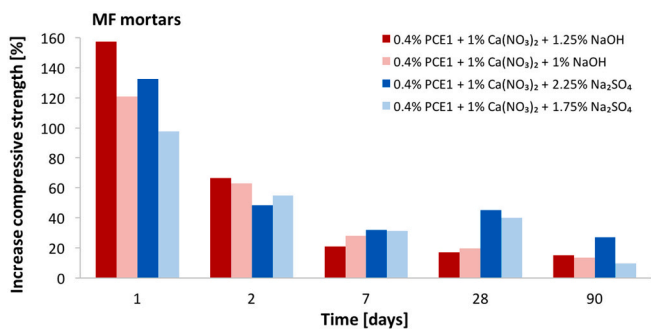


Fig. 4. Compressive strength increase from 1 to 90 days of mortars in presence of activators at different dosages with respect to the non-activated system. The admixtures are added in direct addition.

investigate the ASR risk in concrete and are compared with the commercial cement Op: non-activated MF (MF_0), alkali activated MF and MS (MF_1; MF_0.9; MF_0.5; MS_1) and gypsum activated MF (MF_G).

3.1.3. Concrete: ASR test

The results of the concrete performance test are shown in Fig. 5. The reference (MF_0) passes the test, showing better performance than the sample prepared with the commercial cement Op (a CEM II/B-M(T-LL) 42.5 N). Similarly, it is observed for MF_G at 48 weeks. More interestingly, Fig. 5 shows that for the higher dosage of NaOH and $\text{Ca}(\text{NO}_3)_2$, MS and MF exceed the norm limit at 48 weeks, whereby MS_1 leads to much higher expansion than MF_1. Further, the expansion of MF_1 is only slightly higher than the limit at 48 weeks. This points to the beneficial effect of having fly ash rather than slag in the mix, even if only 10% of the total binder. Moreover, when the dosage of NaOH, Na_2SO_4 and $\text{Ca}(\text{NO}_3)_2$ are reduced to obtain a practice-relevant compressive strength of about 12 MPa at 24 h in mortars and a comparable initial spread flow to the one of MF_0_0.225PCE4 (Table 7), the alkali activated MF pass the test as indicated in Fig. 5 (MF_0.5 and MF_0.9). This further underlines the benefit of fly ash to mitigate ASR, while using alkali activators in blended cements.

An interesting insight into optimizing activator dosages is obtained by plotting the compressive strength of mortars at 24 h as function of the expansion due to ASR measured on concrete at 48 weeks. Indeed, as shown in Fig. 6 both values are linearly related, making it easy to determine the maximum strength that can be obtained for our systems without exceeding the ASR test limit. As shown in Fig. 6, for our mixes this corresponds to 14 MPa, thus offering a very respectable activation without ASR.

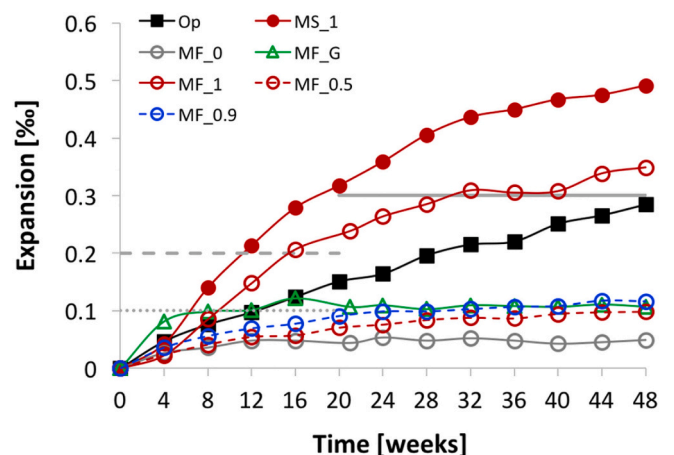


Fig. 5. Expansion of concrete prisms due to ASR over 48 weeks.

Table 7

Spread flow and compressive strength of mortars with and without alkali activators. The dosage in % of PCE4 is indicated in the sample name, while the activator ones are: MF_0 contains no activators, MF_0.5 includes 0.5% of NaOH and Ca(NO₃)₂, MF_0.9 0.9% Na₂SO₄ and 0.5% Ca(NO₃)₂, MS_1 1% NaOH and Ca(NO₃)₂. The activated mortars are mixed in delayed addition of the admixtures.

	MF_0_0.225PCE4	MF_0.5_0.25PCE4	MF_0.9_0.3PCE4	MS_1_0.45PCE4
Spread flow at 10 min [cm]	18.9 (± 2.3 ^b)	17.2 (± 2.3 ^b)	19.1 (± 2.3 ^b)	18.1 ± 1.7
Compressive strength at 1d [MPa] ^b	8.2 ± 1.6	12.4 ± 0.9	11.1 ± 0.4	17.2 ± 3.1

^a The spread flow error reported for mortars MF binder is an upper value obtained on mortars prepared with the same binder, but PCE1, and reported by Boscaro et al. between 1.1 and 2.3 cm [33].

^b The error on compressive strength is based on a standard deviation on six samples.

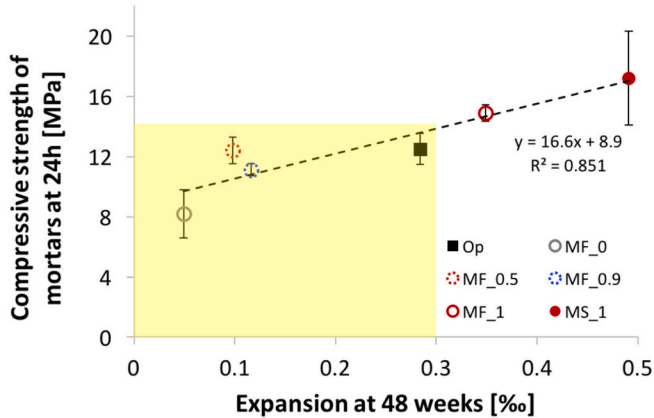


Fig. 6. Compressive strength of mortar cubes at 24 h as function of the ASR expansion of concrete prisms measured at 48 weeks. MF_1 data point is plotted based on the expansion measured on MF_1 and the strength of MF_1_0.4PCE1 prepared in direct addition of all the admixtures.

3.2. Optimization strategies to formulate low clinker cements and concrete

Based on the optimized competitive adsorption presented in Sections 3.1.1 and 3.1.2, the admixture formulation containing 1% NaOH, 1% Ca (NO₃)₂ and 0.4% PCE1 is used to design a low clinker concrete for conventional construction. Table 8 presents the rheological properties and compressive strength obtained in delayed addition of the admixtures. Delayed addition simplifies the system, preventing the perturbations of ettringite nucleation by PCE that impact the dispersing properties of such polymers [12,35,36]. Results show good initial rheological performance. However, the flow loss at 1 h is not suitable for conventional construction, where changes of <5% would be desired.

To resolve this issue, an alternative PCE characterized by somewhat different molecular parameters than PCE1 is needed. To identify such a polymer, we use a simple approach allowing to select the new PCE based on cement paste-scale test results, followed by a fine-tuning of the dosage in concrete. For this, we make the following considerations:

- Relating rheological performance in cement pastes to that in concrete:

According to Roussel and Coussot, for large flows the yield stress (τ)

Table 8

FTS, flow loss and compressive strength over 90 days of concrete prepared in delayed addition of the admixtures, using PCE1.

	MS_0_0.3PCE1	MS_1_0.4PCE1
FTS at 10 min [cm]	51.5	53.5
Flow loss at 1 h [%]	10.7	15.9
Compressive strength at 1 day [MPa] ^a	8.0 ± 0.2	17.2 ± 1.1
Compressive strength at 28 days [MPa] ^a	38.0 ± 1.1	43.0 ± 1.7
Compressive strength at 90 days [MPa] ^a	43.0 ± 0.9	47.0 ± 3.4

^a The error on compressive strength is based on a standard deviation on three samples.

is proportional to the radius of the spread flow (R) by a power relation [37]:

$$\tau \propto \frac{1}{R^5} \tag{1}$$

By considering the interpolated relation for both small and large spread radius proposed by Flatt et al. [38], we can use an exponential rather than a power-law relation:

$$\tau = \exp(b - aD) \tag{2}$$

where a and b are fitting parameters and D is the spread diameter.

Consequently, the yield stress in concrete (τ_c) can be related to the one in paste (τ_p) by a coefficient of proportionality β :

$$\tau_c = \beta \cdot \tau_p \tag{3}$$

By using Eq. (1) and Eq. (3), we apply a simple proportion that relates the spread flow obtained in pastes and concrete for two different PCEs, maintaining the same dosage in paste and concrete:

$$D_{px} = D_{p1} \cdot \frac{D_{Cx}}{D_{C1}} \tag{4}$$

where D_{p1} and D_{px} are the spread diameters measured in pastes for PCE1 and a new PCE_x, while D_{C1} and D_{Cx} are the FTS obtained in concrete with the two PCEs.

- Selection of the dosage of the new PCE for a target initial spread flow:

We assume that PCE adsorption is proportional to dosage, independently of the molecular architecture. This is based on the observation by Marchon et al. that many PCEs adsorb in a constant fraction of dosage at low dosages [31]. Moreover, those authors demonstrated for a CEM I 42.5 that in delayed addition of PCE the linear relation between adsorbed PCE and spread diameter depends on the molecular structure. Consequently, they expressed D as:

$$D = D_0 + \alpha_{PCE} \cdot c_{ads} \tag{5}$$

where D_0 is the spread diameter with no PCE, c_{ads} the amount of PCE adsorbed and α_{PCE} indicates the dependence of the spread diameter on the molecular architecture which the authors found scales as $(P/N)^{0.2}$ [31].

Based on the above, it can be concluded that for any pre-specified spread diameter, the product of dosage C and $(P/N)^{0.2}$ must have a defined value. In other words, for two mixes respectively using PCE1 and PCE4, but showing the same spread, the following equality must hold:

$$\left(\frac{P_1}{N_1}\right)^{0.2} \cdot C_1 = \left(\frac{P_4}{N_4}\right)^{0.2} \cdot C_4 \tag{6}$$

where P_i and N_i relate to the molecular structure of PCE_i, while C_i is its dosage.

We use Eq. (4) to calculate the spread flow that should be obtained with PCE4 on pastes, if for the same dosage the FTS on concrete should reach 47.5 cm. In this calculation we consider that with PCE1 dosage at 0.4%, a spread flow of 14.2 cm is obtained in pastes (D_{p1}), while the FTS in concrete is 53.5 cm (D_{C1}). This leads to the conclusion that PCE4

should be dosed in such a way as to give a flow spread of 12.6 cm in paste. The dosage of PCE4 needed for this is calculated based on Eq. (6), giving 0.39%. As shown in the first column of Table 9, this dosage leads to an initial spread flow of 10 cm, rather close to the expected value of 12.6 cm defined above. In concrete the dosage is slightly adjusted to 0.45% to achieve the desired performance. Related results with that dosage are shown in the last column of Table 9. In particular, it can be seen that not only is the FTS acceptable, but that the fluidity retention is much improved with respect to PCE1 (6–7% instead of 16%, see Table 8). Comparing the mechanical performance of the activated concrete prepared with PCE1 (see Table 8), results in presence of PCE4 are not affected (Table 9). In short, PCE4 provides about 17 MPa already at 1 day, along with good strength values at 28 days, acceptable initial rheology and retention thereof.

4. Discussion

4.1. Coupled effects of activators and PCEs on hydration kinetics, rheology and ASR

In the first part of this paper the effects of several PCEs combined with activators were presented and results in particular of rheology highlighted the presence of competitive adsorption between these two types of activators. For example, Fig. 3 shows that to reach similar yield stresses as the reference, higher PCE dosages are needed when alkaline activators are used. Such results are consistent with previous publications reporting on competitive adsorption [12,14,17,39,40]. Na₂SO₄ leads to a larger reduction of yield stress than NaOH that we interpret to be related to the divalent nature of sulfate ions. Among PCE1, PCE2 and PCE3, the latter suffers the least from competitive adsorption, which is most likely due to its higher value of $K_{A,1}^*$ [17]. Along with this, the more specific type of molecular architecture should not be overlooked, since PCE3 is a maleic-based polymer, while PCE1 and PCE2 are methacrylic ones. This different backbone chemistry results in different chelating abilities, being higher in the maleic-based PCE due to the proximity of the carboxylic functions [41]. However, competitive adsorption is observed to a lower degree in the gypsum activated systems. This may be related to the lower solubility of gypsum in comparison with Na₂SO₄, that would lead to a lower concentration of sulfate ions in solution, which may compete with PCEs on being adsorbed onto cement surfaces.

It is also worth noting that Ca(NO₃)₂ improves the dispersing properties of MF pastes in presence of alkali activators, regardless of which PCE is used. This is consistent with results by Yamada et al., who demonstrated that the negative effect of Na₂SO₄ on rheology of cement pastes is reduced by providing Ca²⁺ ions, which causes gypsum precipitation thereby reducing the sulfates in solution [14]. It is therefore reasonable to conclude that Ca(NO₃)₂ increases the adsorption of PCE in

Table 9

Spread flow or FTS, flow loss and compressive strength over 28 days of cement pastes and concrete prepared in delayed addition of the admixtures, using PCE4.

	MS_1_0.39PCE4 Paste ^a	MS_1_0.45PCE4 Concrete ^a
Spread flow / FTS at 10 min [cm]	10.0 ± 0.5	49.8 ± 3.5
Flow loss at 1 h [%]	34.4 ± 6.0	6.5 ± 11.4
Compressive strength at 1 day [MPa]	n.a.	17.4 ± 1.2
Compressive strength at 2 days [MPa]	n.a.	22.8 ± 2.1
Compressive strength at 7 days [MPa]	n.a.	32.9 ± 2.5
Compressive strength at 28 days [MPa]	n.a.	43.8 ± 3.3

^a The spread flow error for cement pastes represents an average of the error on such measurements and here it is considered constant over the range of measured spread flows. For concrete it corresponds to the standard deviation of two samples. The flow loss is expressed as the percentage variation and the error is calculated accordingly. The error on compressive strength is based on a standard deviation on three samples.

activated MF pastes through a similar process, as also suggested for MS pastes by Palacios et al. [29].

From the hydration point of view, both alkali activators and gypsum were found to accelerate the hydration of MF pastes, but to decrease the cumulative heat respectively before 24 h or after about 50 h. This is consistent with previous studies [9–11] and could be related to the presence of aluminum ions in solution which passivate C₃S hydration [42–45]. In our study the aluminum may be provided by both clinker and/or BOS, FA and SL. Importantly, we found that moderate concentrations of NaOH and Na₂SO₄ added in combination with Ca(NO₃)₂ not only largely enhance the early compressive strength, but also substantially increase the long-term strength of MF mortars and MS concrete. For the Na₂SO₄ activated system, the result is in agreement with Mota et al. who reported increased strength over 90 days of alite mortars doped with 0.725 M Na₂SO₄ [11]. In contrast to our results, those authors found that with respect to plain alite, samples including 1.45 M NaOH showed lower strength from 7 days on. These authors attributed the increase in mechanical performance to a change in the microstructure. In particular, they observed a more homogeneous distribution of portlandite and a modification of the C-S-H morphology in presence of alkalis, going from a convergent needle-like structure in plain alite to a divergent and a foil-like configuration in respectively the Na₂SO₄ and NaOH systems [11]. Therefore, we infer that a microstructure densification and potentially different phase assemblage may be responsible for the increased strength from 1 to 90 days of the alkali activated mortars here investigated. The related activation mechanism of MF and MS by NaOH and Na₂SO₄ solutions is topic of a future publication based on the PhD of the first author of the present publication [33].

Formulations where competitive adsorption was satisfactorily managed were tested against ASR (Fig. 5). We demonstrated that MF activated by 1% NaOH and 1% Ca(NO₃)₂ exceeds the limit set by the norm. However, it can be noted that this admixture dosage provides a doubling of compressive strength at 24 h with respect to reference, which is more than what would be needed in practice. Additionally, expansion results show that samples including fly ash (MF) show much less expansion than those with slag (MS), even if either of those SCMs is only used in an amount of 10% of the total binder. We attribute this beneficial effect of FA to its higher alumina content (Table 2) that can hinder the dissolution of reactive silica [22–24]. We speculate that a slight increase of FA content in the MF binder may allow to pass the ASR test. In this paper however, we chose another approach, which is to reduce the activator dosage, enough to pass the test, but not too much so as to maintain enough activation. As shown in Fig. 5, a reduction of the dosage by a factor two allows to pass the test. Such mixes still give a very respectable compressive strength of 12 MPa at 24 h. A more effective optimization of the activation dosage can be achieved based on Fig. 6, which shows that compressive strength at 24 h and ASR expansion of our systems are linearly related. Specifically, for our mixes 14 MPa should be achievable at 24 h while still passing the ASR test. Such correlations may prove very effective in determining on a case-by-case basis how to best exploit the potential of alkali activation in blended cements at early age without running into problems related to ASR. However, more data points on other blended cements ought to be measured in order for this correlation to hold in other systems.

4.2. Optimization strategies to formulate low clinker cements and concrete

Section 3.2 presents approaches to efficiently formulate low clinker cements and concrete from cement pastes to concrete. We demonstrated that a combination of equations can be successfully applied to gain a desired rheological performance in low clinker concrete by selecting molecular parameters and dosage of PCE on the pastes. Our results confirm that Eq. (6) proposed and tested by Marchon et al. in OPC pastes in delayed addition of PCEs [31] holds also in much more complex systems with high clinker replacements and in presence of several

activators that bring about competitive adsorption issues for PCEs.

In the specific case presented in this paper we aimed at reducing the initial fluidity of concrete while increasing the fluidity retention. For this, we selected a new PCE (PCE4) characterized by a marginally lower C/E ratio than PCE1 having slightly lower N and same P . The reasoning was that in our system competitive adsorption is quite pronounced. Therefore, a large amount of PCE may not be initially adsorbed and remains in solution. This non-adsorbed fraction should therefore remain available over time to adsorb as additional surfaces are created by early hydration [46,47]. This improves the fluidity retention and is expected to be enhanced at lower C/E ratios. This is why it could be expected that PCE4 would provide slightly lower initial fluidity but keep low the fluidity loss than with PCE1. Such concepts can help to identify candidate structures and their dosages can then be rapidly estimated with paste tests according to the procedure we outlined. This can save a lot of time and therefore make the optimization of admixture selection for activated blended cements much more efficient.

Importantly, although we have found these assumptions to hold in our case study where we used delayed addition of PCE, NaOH and Ca $(\text{NO}_3)_2$ activators, it might not be the case in direct addition of PCE and with other chemical activators. Such questions would be worth investigation in further research.

5. Conclusion

In the present paper we presented a straightforward approach to formulate low clinker cements and concrete in presence of multiple chemical admixtures. We developed optimization strategies using highly substituted low clinker cements containing 20% limestone, 20% burnt oil shale and 10% fly ash or slag as SCMs.

In the first part of the paper, we demonstrated that competitive adsorption can be mitigated by optimizing PCE molecular architecture and dosage, alkali activator type and an extra addition of a soluble calcium salt, without compromising compressive strength development at early and long term ages. By using such an approach to select specific formulations, we showed that ASR can be mitigated by using 10% fly ash instead of slag in alkali activated concrete providing double compressive strength at 24 h with respect to the non-activated system.

In terms of ASR, acceptable expansions can be achieved by decreasing the alkali activator dosage while still maintaining very good compressive strengths at 24 h. The linear relation between strength and expansion appears as a useful tool to determine maximum early strength performances that may be obtained without ASR becoming critical. However, in addition to our data on the commercial binder (Op), data points on further blended cements must be collected to prove the applicability of this correlation to other systems.

Moreover, it can be expected that higher fly ash dosages, would allow higher activator dosages, raising early strength without causing excessive ASR expansion. Such combination therefore appears to be important levers to activate in order to enhance the performance of blended cements.

In the second part of this work, we presented an optimization strategy to formulate weakly alkali activated concrete composed by a highly replaced blended cement, aiming at targeted rheological and mechanical properties over time. This was possible by using new and state of the art equations relating yield stress, spread flow and PCE adsorption, as well as the molecular structure and dosage of such polymers. This also offers efficient procedures to optimize the mix design of admixed blended cements to achieve high clinker replacement without compromising rheology, strength or inducing excessive ASR expansion. Such increased efficiency can play a fundamental role in facilitating the use of low clinker cements and thereby assisting the construction cement in reducing CO_2 emissions and costs.

CRediT authorship contribution statement

Federica Boscaro: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Data curation, Visualization, Writing – original draft. **Marta Palacios:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition. **Robert J. Flatt:** Supervision, Formal analysis, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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