

Chemical vs. Physical Acceleration of Cement Hydration

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Abstract

Cold weather concreting often requires the use of chemical accelerators to speed up the hydration reactions of the cement, so that setting and early-age strength development will occur in a timely manner. While calcium chloride (dihydrate – $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) is the most commonly used chemical accelerator, recent research using fine limestone powders has indicated their high proficiency for physically accelerating early-age hydration and reducing setting times. This paper presents a comparative study of the efficiency of these two approaches in accelerating hydration (as assessed via isothermal calorimetry), reducing setting times (Vicat needle), and increasing early-age mortar cube strength (1 d and 7 d). Both the CaCl_2 and the fine limestone powder are used to replace a portion of the finest sand in the mortar mixtures, while keeping both the water-to-cement ratio and volume fractions of water and cement constant. Studies are conducted at 73.4 °F (23°C) and 50 °F (10 °C), so that activation energies can be estimated for the hydration and setting processes. Because the mechanisms of acceleration of the CaCl_2 and limestone powder are different, a hybrid mixture with 1 % CaCl_2 and 20 % limestone powder (by mass of cement) is also investigated. Both technologies are found to be viable options for reducing setting times and increasing early-age strengths, and it is hoped that concrete producers and contractors will consider the addition of fine limestone powder to their toolbox of techniques for assuring performance in cold weather and other concreting conditions where acceleration may be needed.

Keywords: Acceleration; calcium chloride; cement hydration; early-age strength; limestone powder; setting time.

Introduction

On a cold winter's day, the sight of a ready-mix truck pouring and placing concrete likely surprises and perplexes the casual observer. Of course, it is only with special precautions [ACI, 2010] that concrete can be successfully delivered, placed, finished, and cured as temperatures approach (and perhaps even dip below) freezing. One of the major implications of producing concrete in cold weather is a delay in its setting times. For example, a reduction in temperature from 73.4 °F (23 °C) to 50 °F (10 °C) can effectively double the setting time of a given concrete mixture. Therefore, chemical accelerators are often employed to reduce/restore setting times (and increase early-age strengths) of cold weather mixtures. Calcium salts are often employed in this regard and when corrosion is not considered an overwhelming concern, calcium chloride still tends to be the accelerator of choice. According to the American Society of Concrete Contractors [ASCC, 2010], "calcium chloride is the most efficient and least expensive accelerator used in concrete. It is particularly useful when flatwork is placed in cold weather because both finishing and covering the slab with insulating blankets can be started earlier." For many concretes, ACI 318 permits a maximum water-soluble chloride ion content in concrete of 1 % by mass of cement, which roughly corresponds to a dosage of 2 % calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) by mass of cement [ASCC, 2010].

Surprisingly, even though its usage dates back well over 100 years [Ramachandran, 1981], the exact mechanism of how calcium chloride accelerates cement hydration remains elusive. Significant research efforts on this topic were conducted by Rapp in 1935 [Rapp, 1935], Rosenberg in 1964 [Rosenberg, 1964], and more recently by Juenger and colleagues in 2005-2006 [Juenger *et al.*, 2005; Peterson and Juenger, 2006]. The general consensus from these studies is that CaCl_2 is a catalyst for early-age cement (most prominently tricalcium silicate and dicalcium silicate) hydration and likely encourages the production of a more permeable (porous) calcium silicate hydrate gel (C-S-H) that permits faster diffusion of ions and thus a faster hydration of cement particles at early ages. At ages beyond a few days, however, the chloride is found to be incorporated in various hydration products (Friedel's salt, etc.) so that its influence goes beyond that of a simple catalyst. It is worth noting that it is the C-S-H gel formation that is responsible for linking together the cement particles into the percolated 3-D network that is responsible for setting in most ordinary portland cement (OPC) concretes. By accelerating hydration, CaCl_2 is able to concurrently and significantly reduce setting times.

While CaCl_2 exemplifies a chemical approach to accelerating cement hydration, physical approaches are also possible [Bentz, 2007]. The technology of seeding hydration with added C-S-H particles has moved from laboratory research to several commercial products in the past few years. Additionally, the ability of fine limestone particles to accelerate setting times has been explored in detail [Turpin, 2002; Gurney *et al.*, 2012; Bentz, 2014; Bentz *et al.*, 2016a]. The limestone particle (calcite) surfaces serve as ideal sites for the precipitation and growth of early-age cement hydration products and the virtually intact limestone particles are thus incorporated into the 3-D percolated structure that leads to setting [Bentz, 2014; Bentz *et al.*, 2016b]. In this way, the influence of fine limestone on setting is two-fold, accelerating hydration and actively participating in the 3-D network. By contrast, while CaCl_2 accelerates cement hydration (and perhaps even more cost effectively than the fine limestone), it does not participate directly in the 3-D network that produces setting. In this paper, the abilities of CaCl_2 , fine limestone powder, and a combination of the two to accelerate hydration, reduce setting times, and increase early-age (1 d and 7 d) strengths in mortars prepared at 73.4 °F (23 °C) and 50 °F (10 °C) are reported.

Materials and Experimental Procedures

Materials

A locally available Type I/II ordinary Portland cement (OPC) conforming to the ASTM C150 specification [ASTM, 2014] with a 3.7 % limestone (91.0 % CaCO₃) addition by mass was used in this study. The primary grey limestone powder (LS) was obtained from a commercial aggregate production plant, supplied as the dust of fracture passing through a #100 (150 μm) sieve, having an estimated CaCO₃ content of 98.1 % ± 0.6 % based on TGA measurements [Bentz *et al.*, 2016a]. For comparison purposes, a more expensive and white 3800 yd²/lb (7 m²/g) limestone powder with a CaCO₃ content of 98 % [Gurney *et al.*, 2012] was used in two mortar mixtures in this study (LS2 in Table 1). Cement oxide composition and other available characteristics of the raw materials are provided in Table 1.

PSDs of the OPC and LS powders were measured using laser diffraction with isopropanol (refractive index 1.378) as the dispersant. The values of D₁₀, D₅₀, and D₉₀ that characterize each PSD are presented in Table 1. Densities of the raw materials reported in Table 1 were measured using helium pycnometry (coefficient of variation of less than 1 %). The specific surface area of the powders was determined by the multipoint Brunauer-Emmett-Teller (BET) method, using nitrogen as the sorbent gas (typical coefficient of variation of 2 % for three replicate specimens [Gurney *et al.*, 2012]). The specific surface area of the primary limestone powder is of the same order as that of the portland cement, but much finer limestone powders such as LS2 in this study (or even approaching 5425 yd²/lb or 10 m²/g to 10850 yd²/lb or 20 m²/g [Gurney *et al.*, 2012]) are also readily available, albeit at a premium cost.

Calcium chloride dihydrate (CaCl₂·2H₂O) in granule (not flake) form was purchased from a chemical supplier. It has a quoted density of 3120 lb/yd³ (1850 kg/m³) and an assay of greater than 99 %. In its dihydrate form, there are 0.755 lb CaCl₂ per lb of dihydrate (75.5 mass %). In this study, quoted dosages (1 %, 2 %, etc.) are based on the CaCl₂ portion of the dihydrate only.

Mortar Mixtures

The mortars delineated in Table 2 were prepared following the mixing procedures given in ASTM C109 [ASTM, 2014], using a blend of four different size silica sands. In each mixture with CaCl₂ granules or limestone powder, the additive was used to replace an equivalent volume of the finest of the four sands (F95) in the mortar mixture, to avoid any dilution effects that would occur if the accelerator were used to replace cement and/or water. The LS2_05 mixture was formulated using LS2 (finer) to match the same surface area as that provided by the first (coarser) limestone, when the latter is used at the 20 % level. The LS2_13 mixture was intended to match the setting time of the coarser limestone at the 20 % level. For all of these mixtures, the additive was in each case pre-blended with the cement for 30 min using a three-dimensional laboratory mixer that simultaneously rolls and tumbles the (mixing) container. For the two mortars with the higher limestone (coarser) powder contents, a small dosage of a high range water-reducing admixture (HRWRA, non-retarding Type F, dosage provided in Table 2) was required to moderately increase the flow to an acceptable level (> 100).

The fresh mortars were characterized by measuring their temperature (± 0.2 °F or ± 0.1 °C), unit (cup) weight and air content (ASTM C185), and flow (ASTM C1437); results for these are provided in Table 3. After the flow table measurement, the mortar was returned to the mixing bowl and remixed for 30 s, following which specimens were prepared for the measurement of isothermal calorimetry to 7 d (73.4 °F or 23 °C), setting time (ASTM C191), and mortar cube compressive

Table 1: Characterization of raw materials.

	OPC	Limestone LS	Limestone LS2
SiO ₂ (mass %)	19.8	-	-
Al ₂ O ₃	4.81	-	-
Fe ₂ O ₃	3.14	-	-
CaO	63.4	-	-
MgO	2.75	-	-
SO ₃	2.91	-	-
LOI	2.71	-	-
Total alkalies ^a	0.54	-	-
C ₃ S	58.9	-	-
C ₂ S	11.6	-	-
C ₃ A	7.38	-	-
C ₄ AF	9.46	-	-
D ₁₀ (μm ^b)	1.5	1.8	0.86
D ₅₀ (μm)	10.7	6.4	2.2
D ₉₀ (μm)	32.9	34.4	5.5
BET surface area yd ² /lb (m ² /g)	873 (1.61)	835 (1.54)	3830 (7.06)
Specific gravity	3.16	2.74	2.71
BET surface area m ² /cm ³	5.09	4.22	19.13

^aNa₂O + 0.658K₂O ^b1 μm=3.94 x 10⁻⁵ in

Table 2: Mixture proportions of mortars with different limestone and CaCl₂ additions.

MIX ID	OPC	LS_20-LS_30-LS_40	CaCl ₂ _1-CaCl ₂ _2-CaCl ₂ _3	Hybrid	LS2_05-LS2_13
Cement (g ^c)	710	710	710	710	710
Limestone (% by mass of cement)	0	21.7-37.1-59.3	0	21.7	4.74-12.8
CaCl ₂ (% by mass of cement)	0	0	1-2-3	1	0
Cement (g)	710	710	710	710	710
Limestone powder (g)	0.00	154.1-263.4-421	0	154.1	33.6-90.9
CaCl ₂ ·2H ₂ O (g)	0	0	9.4-18.8-28.2	9.4	0
F95 Fine sand (g)	401	254.2-150.1-0	387.7-374.5-361.2	241.0	368.2-313.5
Graded sand C778 (g)	305	305	305	305	305
20-30 sand C778 (g)	305	305	305	305	305
S16 coarse sand (g)	594	594	594	594	594
HRWRA (g)	0.0	0.0-1.29-3.54	0.0	0.0	0.0
Water (g)	284	284	284	284	284
Limestone (% vol. of powders)	0.0	20.0-30.0-40.6	0.0	19.7	5.2-13.0
CaCl ₂ ·2H ₂ O (% vol. of powders)	0.0	0.0	2.2-4.3-6.4	1.8	0.0
Water (% total volume)	25.28	25.28	25.28	25.28	25.28
Sand volume fraction	0.55	0.50-0.46-0.41	0.54-0.54-0.53	0.49	0.54-0.52
w/p ratio (by mass) ^d	0.40	0.33-0.29-0.25	0.39-0.39-0.38	0.33	0.38-0.35

^c454 g = 1 lb ^dpowder includes cement and limestone powder or CaCl₂

Table 3: Properties of fresh mortar including temperature, unit weight and air content (ASTM C185), and flow (ASTM C1437, only at 73 °F/23 °C).

MIX ID	OPC	LS_20	LS_30	LS_40	CaCl ₂ _1	CaCl ₂ _2	CaCl ₂ _3	Hybrid	LS2_05	LS2_13
Temperature °F (°C) (Room/Chamber)	71.6/52.9 (22.0/11.6)	77.7/50.9 (25.4/10.5)	72.5 (22.5)	75.6/52.5 (24.2/11.4)	75.0/52.3 (23.9/11.3)	69.3/52.9 (20.7/11.6)	76.6 (24.8)	76.1/51.3 (24.5/10.7)	73.4 (23.0)	73.8/50.4 (23.2/10.2)
Specific gravity (Room/Cold)	2.22/2.22	2.27/2.28	2.28	2.26/2.26	2.23/2.21	2.23/2.18	2.21	2.27/2.26	2.22	2.24/2.23
Air content (%) (Room/Cold)	4.2/4.0	2.3/1.8	2.1	3.1/3.0	3.3/4.2	3.2/5.4	4.2	2.0/2.6	3.9	3.2/3.8
Mortar flow (%)	135	118	108	106	131	136	105	123	126	118

strength (ASTM C109) at ages of 1 d and 7 d. Two sets of three mortar cubes were prepared for each mixture; one set of three cubes was broken upon demolding at an age of 1 d, while the second was stored in limewater in a sealed container at 73.4 °F (23 °C) and then broken at an age of 7 d.

According to the ASTM C191 test method, the single-operator standard deviation for initial time of setting (taken as the time when a penetration of 1 in or 25 mm is first achieved) is 12 min. For calorimetry measurements, the average absolute difference between replicate specimens was previously measured to be 1.03×10^{-5} BTU/(lb·s) (2.4×10^{-5} W/g (cement)), for measurements conducted between 1 h and 7 d after mixing [Bentz and Ferraris, 2010].

Temperature Study

Because accelerators are most often employed under cold weather conditions, seven of the mortar mixtures of Table 2 (specifically OPC, LS_20, LS_40, CaCl₂_1, CaCl₂_2, Hybrid, and LS2_13) were repeated at a temperature of 50 °F (10 °C), using the built-in temperature control of the isothermal calorimeter and a walk-in chamber to house the mortar mixer, automated Vicat instruments, and curing containers for the mortar cube specimens. For these mixtures, flow was not measured to avoid exposing the material to the higher temperature laboratory that contains the flow table. As seen in Table 3, the measured mixture temperatures were all in the range of 50 °F (10 °C) to 53 °F (11.7 °C). For one mixture, a thermocouple was inserted in a companion setting specimen and a temperature of $50.5 \text{ °F} \pm 0.2 \text{ °F}$ ($10.3 \text{ °C} \pm 0.1 \text{ °C}$) was measured throughout its setting process, suggesting that the assumption of a constant temperature of 50 °F (10 °C) for the curing of the calorimeter and setting time specimens is a valid one. Air contents are generally similar for corresponding mixtures prepared at the two temperatures, with an indication that mixtures with CaCl₂ have a slight tendency to entrain additional air at low temperatures (this could potentially impact measured compressive strengths for these mixtures).

Measurements at two temperatures allowed for a comparison of the activation energies determined for the hydration (calorimetry) and setting processes when using CaCl₂ and limestone powder as accelerators. For setting times and calorimetry results, the following equation can be used to solve for the apparent activation energy when applying an Arrhenius-based approach, based on measurements at two temperatures (50 °F/10 °C and 73.4 °F/23 °C in this study) [Bentz, 2014]:

$$E_A = \frac{-\ln\left(\frac{t_1}{t_2}\right)R}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (1)$$

where E_A is the apparent activation energy (typically in SI units of kJ/mol), t_1 and t_2 are the times (setting or calorimetry data points), R is the universal gas constant [8.314 J/(mol·K) in SI units],

and T_1 and T_2 are the two temperatures (in K). For example, initial setting times of 2.5 h and 5 h at 73.4 °F/23 °C (296.15 K) and 50 °F/10 °C (283.15 K), respectively, would correspond to an activation energy for setting of 37.2 kJ/mol according to equation (1). For the calorimetry, a time shift factor (t_2/t_1) that gives the best overlap of the time-transformed heat flow calorimetry curves is first determined and then equation (1) is again applied to determine the activation energy for hydration. For E_A for setting, combined standard uncertainties were calculated in accordance with the propagation of uncertainty outlined in NIST Technical Note 1297 [Taylor and Kuyatt, 1994].

Results and Discussion

Isothermal calorimetry results

Plots of the heat flow and cumulative heat release, the latter normalized per unit volume of mixing water, are provided in Figures 1 and 2 for the results obtained at 73.4 °F (23 °C) and 50 °F (10 °C), respectively. In every case, the accelerators both accelerate and amplify the early-age hydration peaks, the first peak being indicative of silicate hydration and the second peak/shoulder usually being attributed to the depletion of gypsum and a renewed activity of the aluminate phases [Taylor, 1997]. In this regard, interestingly, the second peak/shoulder is missing entirely from any of the systems containing CaCl_2 (including the hybrid), as x-ray diffraction data on a system with 2 % CaCl_2 has indicated the persistence of gypsum to at least 5 d, with the presence of chlorides leading to the formation of Friedel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) and other chloroaluminate phases that reduce the consumption of sulfate (gypsum). Based on the mixtures investigated in this study, at both temperatures, CaCl_2 provides a greater acceleration/amplification of the early-age hydration reactions than either of the fine limestone powders (at the dosages investigated). However, both the chemical and physical approaches do provide significant acceleration in comparison to the 100 % OPC control.

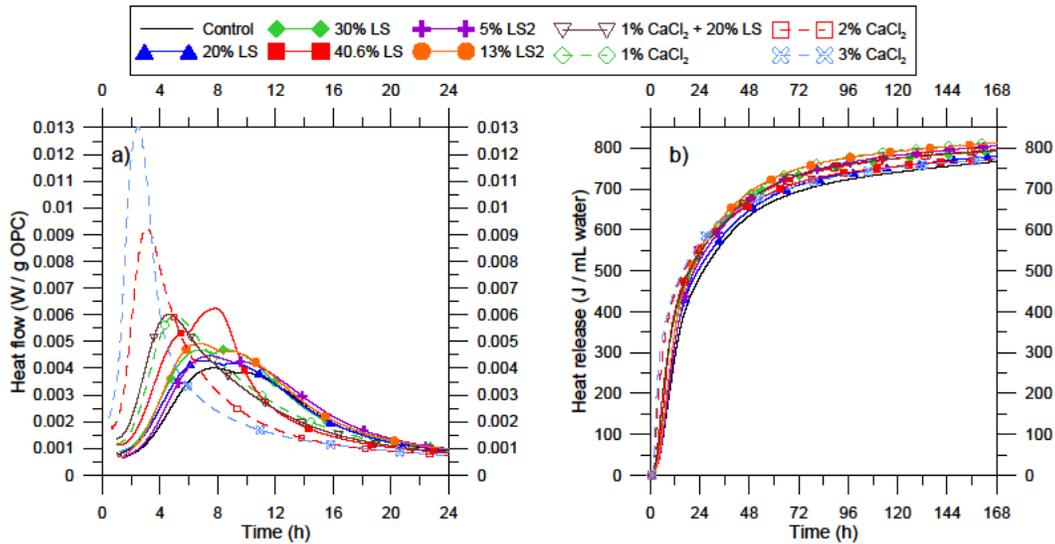


Figure 1: Heat flow and cumulative heat release normalized per unit volume of mixing water measured for the ten mortar mixtures at 73.4°F (23 °C). Calorimetry results are reported in SI units as provided by the calorimeter (1 W/g = 0.43 BTU/(lb·s) and 1 J/mL = 0.028 BTU/oz.).

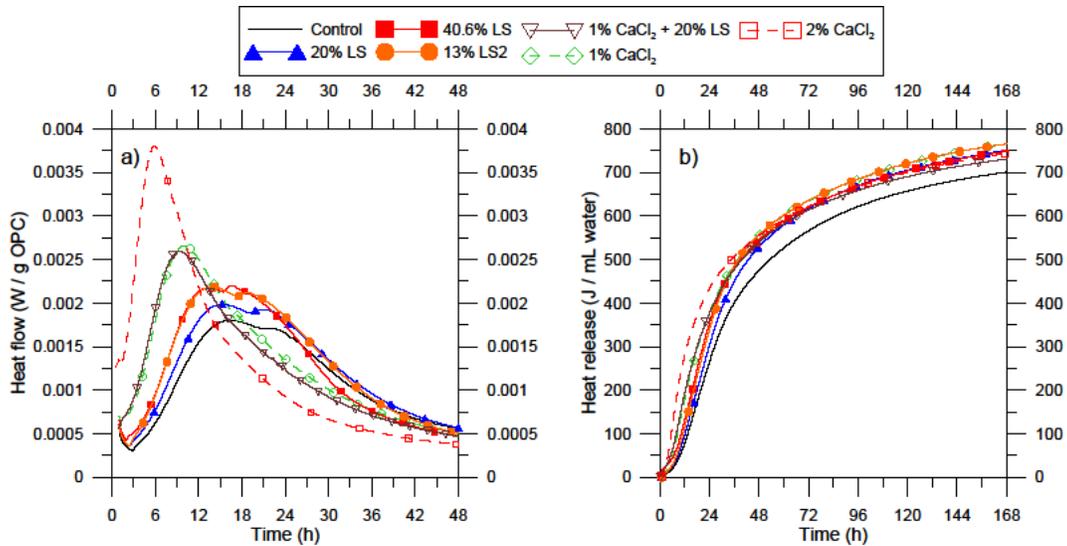


Figure 2: Heat flow and cumulative heat release normalized per unit volume of mixing water measured for seven of the mortar mixtures at 50 °F (10 °C).

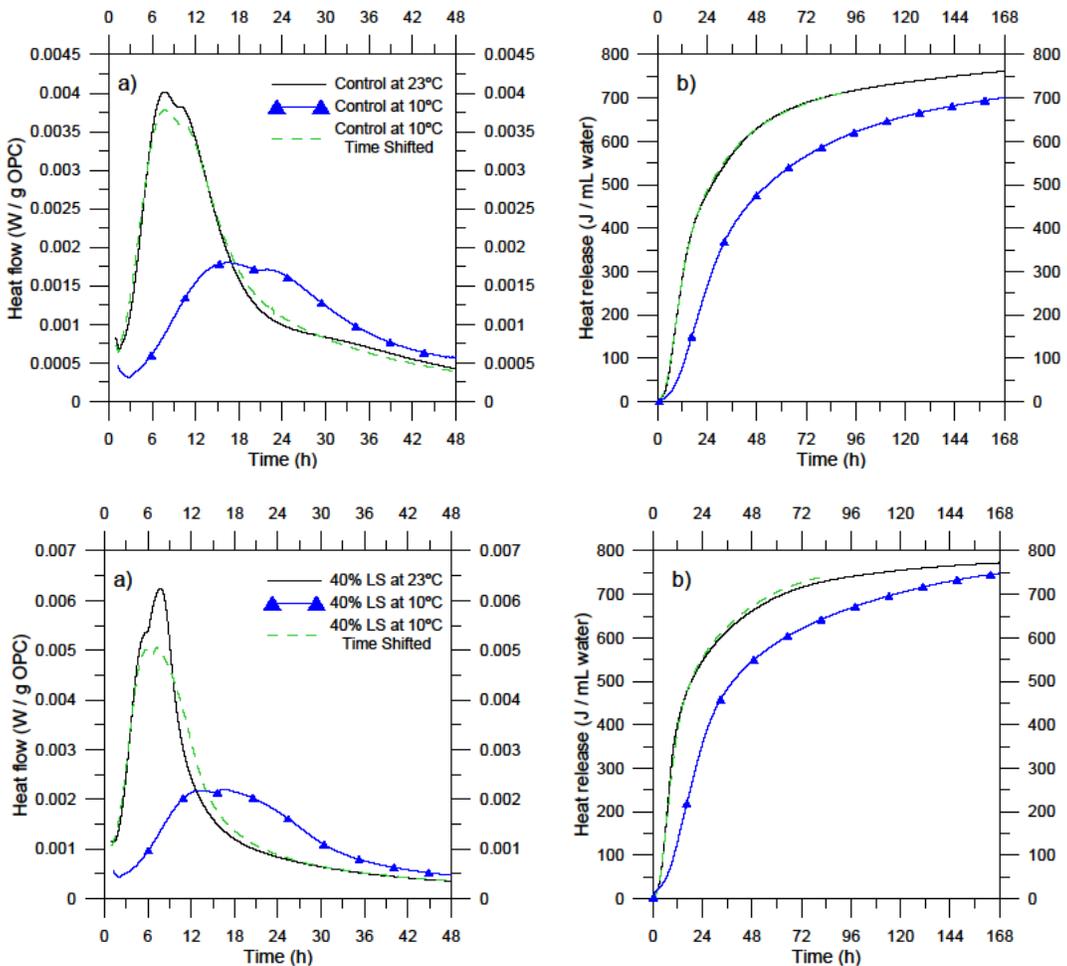


Figure 3. Superposition of 50 °F (10 °C) and 73.4 °F (23 °C) isothermal calorimetry data for heat flow (left) and cumulative heat release normalized per mL water (right) for the control (top) and 40 % LS (bottom) mortars.

Apparent activation energies for early-age hydration, based on superposition of the calorimetry data via a time shift factor (as illustrated for two of the mortar mixtures in Figure 3), are included in Table 4 below. In general, even though limited to a constant (single) value of the activation energy for all hydration times, a good overlap (superposition) of the cumulative heat release data from the two temperatures could be obtained for the first 48 h of the hydration process (as shown in Figure 3). Previously, Thomas (2012) has measured an apparent activation energy (based on calorimetry data) of 51 kJ/mol for tricalcium silicate hydrated either in pure water or in a CaCl₂ solution (2 % by mass of cement) for the first 24 h of hydration. Similarly, in Table 4, for early-age hydration, the mixture with 1 % CaCl₂ exhibits an apparent activation energy equivalent to that found for the OPC control mortar, while that of the 2 % CaCl₂ system is only slightly higher. The mixtures with limestone powder also exhibited an apparent activation energy in good agreement with that measured for the OPC control (about 40 kJ/mol), with the exception of the 40 % LS system where a higher value of about 45 kJ/mol was obtained. 40 kJ/mol is also the default value recommended by the ASTM C1074 standard test method concerning estimation of concrete strength by the maturity method.

Setting time results

Measured initial setting times at the two curing temperatures are provided in Table 4, along with the estimated apparent activation energy for the setting process. As expected, all of the accelerators decreased the initial setting time, but to varying degrees and with different effectiveness at the two investigated temperatures. At 73.4 °F (23 °C), for example, 1 % CaCl₂ and 30 % LS produced similar reductions in setting time, while 40 % LS and 2 % CaCl₂ were also found to provide similar performance. While the finer limestone (LS2) did not achieve the setting time reduction provided by the dust-of-fracture limestone powder when compared at equal surface areas (5 % LS2), the finer particles did allow a reduction of the limestone powder content from 20 % to about 13 %, with a similar setting time within the variability of the test method (2.47 h vs. 2.37 h). As indicated by their reduced apparent activation energies for setting, the CaCl₂ additions were particularly effective at reducing the setting times in the 50 °F (10 °C) mixtures. For each mixture, the apparent activation energy observed for setting was lower than that found for hydration based on the isothermal calorimetry results, in general agreement with previous studies [Bentz, 2014].

Table 4: Setting time results at 73.4 °F (23 °C) and 50 °F (10 °C) for the 10 mortar mixtures.

MIX ID	OPC	LS20	LS30	LS40	CaCl ₂ _1	CaCl ₂ _2	CaCl ₂ _3	Hybrid	LS2_05	LS2_13
73.4 °F/23 °C setting time (h)	3.06	2.37	2.15	1.64	2.10	1.50	1.10	1.62	2.79	2.47
50 °F/10 °C setting time (h)	5.56	4.53		3.60	3.76	2.53		3.23		4.66
Setting time app. activation energy (kJ/mol ^e)	31.9 (4.0) ^f	34.8 (5.1)		42.0 (7.2)	31.4 (5.9)	28.2 (8.3)		36.9 (7.4)		34.0 (4.9)
Hydration (calorimetry) app. activation energy (kJ/mol)	39.8	39.8		44.7	39.8	42.2		42.2		38.5

^e1 kJ/mol = 0.447 BTU/lbmol

^fNumber in parentheses indicates calculated combined standard uncertainty [Taylor and Kuyatt, 1994].

Strength results

Measured mortar cube average compressive strengths are provided in Table 5 for the various mixtures at 1 d and 7 d, and at each investigated curing temperature. All of the accelerators produced some strength increase relative to the 100 % OPC (no accelerator) control mortar, at both ages and at 50 °F (10°C) or 73.4 °F (23 °C). At both curing temperatures, the greatest 1 d strength increases were provided by the 2 % CaCl₂, 40 % dust-of-fracture limestone powder, and the hybrid mixture that combined 1 % CaCl₂ with 20 % dust-of-fracture limestone powder. At 7 d, the greatest strength increases were provided by the 1 % CaCl₂ and the hybrid system, with the strength of the hybrid mixture cured at 10 °C being especially notable at about 9200 psi (over 63 MPa).

While the 1 d strengths measured at 50 °F (10 °C) for all 7 mixtures were less (1/3 to 5/8) than their corresponding value measured at 73.4 °F (23 °C) (as to be expected), one of the more surprising results of this study was obtained when comparing the 7 d strengths achieved at 50 °F (10 °C) and 73.4 °F (23 °C). For the OPC control mixture and for many of the mixtures containing limestone powder, and particularly for the hybrid system, after only 7 d of curing in limewater, the strengths obtained at 50 °F (10 °C) exceeded those measured at 73.4 °F (23 °C). While it has been well documented by Carino and Lew (1983) and many others that the ultimate strength of a mortar or concrete increases as the curing temperature is lowered, to achieve this crossover prior to or at 7 d is surprising to say the least. However, repeat experiments have confirmed this result and further investigations are now underway to determine the cause of the strength enhancement provided by low temperature curing in the mortar mixtures with added limestone powder. Of course, portland cements have changed significantly since the 1983 study of Carino and Lew, as cement fineness has increased by about 32.5 yd²/lb (60 m²/kg), tricalcium silicate and alkali contents are generally increased, and most cements (including the one used in this study) now contain 3 % to 4 % (interground) limestone powder [Bentz *et al.*, 2011].

Table 5: Mortar cube compressive strength results (in psi/MPa)

	OPC	LS20	LS30	LS40	CaCl ₂ -1	CaCl ₂ -2	CaCl ₂ -3	Hybrid	LS2_05	LS2_13
1 d @ 23°C	3950/27.3 (2.8 %)§	4620/31.9 (3.1 %)	4950/34.1 (3.4 %)	5170/35.7 (2.8 %)	4780/32.9 (11.6 %)	4990/34.4 (2.0 %)	4710/32.5 (3.8 %)	5190/35.8 (1.0 %)	4400/30.4 (3.2 %)	4740/32.7 (3.7 %)
7 d @ 23°C	7240/49.9 (0.7 %)	7580/52.2 (3.2 %)	7260/50.1 (2.6 %)	8050/55.5 (3.0 %)	9040/62.3 (6.8 %)	8800/60.7 (2.0 %)	8270/57.0 (1.2 %)	8750/60.4 (0.4 %)	7300/50.3 (2.1 %)	7300/50.3 (1.7 %)
1 d @ 10°C	1430/9.9 (11.0 %)	1780/12.3 (0.1 %)		2530/17.4 (1.7 %)	2210/15.3 (1.1 %)	2620/18.0 (1.2 %)		2530/17.3 (0.5 %)		2060/14.2 (0.8 %)
7 d @ 10°C	7400/51.0 (1.6 %)	7660/52.8 (2.4 %)		7590/52.3 (2.2 %)	8040/55.4 (2.8 %)	7610/52.5 (3.4 %)		9200/63.4 (1.5 %)		7450/51.4 (3.9 %)

§Number in parentheses indicates coefficient of variation for testing three specimens for each mortar mixture.

Summary and Prospectus

The above results have indicated that both CaCl₂ and fine limestone powder can function as effective accelerators of cement hydration, setting, and strength development when used as a replacement for fine sand. To summarize the performance attributes of both materials individually and in combination, Table 6 provides cost and performance information for several of the dosages employed in the present study. Material costs were obtained as estimates from industry representatives and no delivery costs were included in the cost analysis. For example, sand that costs \$15/ton at the quarry (as assumed in Table 6) could easily cost \$25/ton for delivered material. Understandably, a locally available limestone powder could be more economical in comparison to

a concrete sand being delivered from a far distance. Furthermore, for the 40 % LS system, the cost of any needed HRWRA was not included in the analysis of Table 6.

In general, the values in the Table indicate that both CaCl₂ and fine limestone powder can function as effective accelerators, and at similar costs. The range of reductions in setting times and increases in early age strengths are similar for the two classes of materials. When a reduced chloride level is prescribed for a concrete, the hybrid approach consisting of 1 % CaCl₂ along with 20 % LS represents an attractive option both in terms of performance and cost, as it nominally matched the setting time and 1 d strength performance of the 2 % CaCl₂ mortar in this study, while providing a significantly greater boost to the 7 d strengths at the 10 °C curing temperature. When chlorides are entirely prohibited by a specification, due to concerns with reinforcement corrosion, groundwater contamination, etc., the fine limestone powder may serve as an effective replacement to provide necessary acceleration for cold weather concreting. Then, the casual observer can rest assured that the concrete being poured on a cold winter's day will meet its setting time and strength performance specifications.

Table 6: Performance of accelerators at various dosages relative to 100 % OPC control.

	1 % CaCl ₂	2 % CaCl ₂	20 % Dust-of-fracture LS	40 % Dust-of- fracture LS	13 % High purity LS	Hybrid 1 % CaCl ₂ 20 % LS
Estimated accelerator cost	\$0.30/lb ^h (\$0.14/kg)	\$0.30/lb	\$50/ton (\$55.12/metric ton)	\$50/ton	\$150/ton	
Cost per dosage ⁱ	\$2.30	\$4.60	\$2.14	\$4.29	\$5.29	\$4.44
Setting time reduction at 73.4 °F/23 °C (min)	60	95	40	85	35	85
1 d strength gain at 73.4 °F/23 °C (%)	21	26	17	31	20	31
7 d strength gain at 73.4 °F/23 °C (%)	25	22	5	11	1	21
Setting time reduction at 50 °F/10 °C (min)	110	180	60	120	55	140
1 d strength gain at 50 °F/10 °C (%)	55	82	24	76	43	75
7 d strength gain at 50 °F/10 °C (%)	9	3	4	3	1	24

^hCost estimate for calcium chloride dihydrate (75.5 % CaCl₂ by mass)

ⁱDosage computed for a mixture with a cement content of 600 lb/yd³ (356 kg/m³), with accelerator replacing sand that costs \$15/ton (\$16.53/metric ton) (no delivery charges included in analysis).

Acknowledgements

The authors gratefully acknowledge Mr. Max Peltz (NIST) for performing the PSD, helium pycnometry, and BET surface area measurements on the powders used in this study and Dr. Scott Jones (NIST) for assistance with some of the mortar mixtures. The authors also acknowledge Pontificia Universidad Católica de Chile and the Chilean Ministry of Education (MINEDUC) through their agreement PUC1202 for funding Franco Zunino's internship at NIST.

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