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Development of Calcined Clay/Calcium Sulfate Blends for Robust Performance of LC3 Concrete

Denise Antunes da Silva
Paula Bran Anleu

September 2025

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ORNL/TM-2025/4195

Buildings and Transportation Science Division

DEVELOPMENT OF CALCINED CLAY/CALCIUM SULFATE BLENDS FOR ROBUST PERFORMANCE OF LC3 CONCRETE

Denise Antunes da Silva
Paula Bran Anleu

September 2025

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CONTENTS

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We gratefully acknowledge Nina Bei, supported by the National Graduate Student Internship (NGSI) appointment administered by the Oak Ridge Institute for Science and Education (ORISE), for contributions to experimental work.

ABSTRACT

This report documents the development of robust blends of calcined clays (CCs) with calcium sulfate (gypsum) for application in limestone calcined clay cement (LC3) systems. The U.S. cement industry faces supply chain constraints and high energy intensity, motivating the need for alternative supplementary cementitious materials. Calcined clays are abundant and highly reactive when properly processed, but their variable physical and chemical characteristics can negatively impact hydration balance, rheology, and admixture demand in LC3 concretes. To address this, five calcined clays, two Portland cements, ground limestone, gypsum, and a polycarboxylate dispersant were procured. Isothermal calorimetry and mini-cone flow tests were used to determine sulfate and dispersant demand. Results show that the addition of approximately 6.7% gypsum, relative to the calcined clay weight, consistently balanced sulfate consumption across the LC3 systems studied. Dispersant demand, however, varied significantly with clay source, demonstrating the need for tailored admixture strategies. These findings confirm that supplying CC–gypsum blends directly to concrete producers is a viable approach to overcoming current manufacturing constraints, enabling reliable fresh and hardened performance of LC3 concretes, and supporting broader adoption of calcined clays in the U.S. market.

1. INTRODUCTION AND OBJECTIVES

The U.S. Portland cement industry imports around 24% of the cement it consumes[1] and is projected to grow by 20% by 2034[2]. It is also one of the most energy-intensive sectors, consuming 10x more energy than its economic share[3]. Increasing the availability of alternative substitutes for Portland cement in concrete would reduce the nation's dependence on imports, hence strengthening supply chains and driving the costs down besides offering energy-saving potential.

Calcined clay represents the largest opportunity to reduce cement use in concrete due to its availability. Ordinary clays containing 40 to 60% of kaolinite develop strong pozzolanic activity if calcined to temperatures not higher than 850^{o}C. This calcination temperature is importantly lower than the Portland cement kilning, making calcined clay a lower energy-intensive substitute to cement. When used in combination with limestone to produce LC3 cements (limestone calcined clay cements), the cement

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[1] https://www.nasdaq.com/press-release/us-housing-market-faces-4-million-home-shortage-realtorcomr-calls-lawmakers-let.
[2] https://www.expertmarketresearch.com/reports/united-states-cement-market.
[3] https://www.eia.gov/todayinenergy/detail.php?id=11911#.

replacement can be as high as 50%[4]. However, physical and chemical characteristics of calcined clays alter the fresh and hardened performance of concrete. The addition of a source of calcium sulfate ensures chemical balance in the system, reducing negative effects on engineering properties of concrete related to the presence of calcined clays. The required type and content of calcium sulfate for chemical balance may vary as a function of the characteristics of the raw materials in the mix. Chemical admixtures can also modify the sulfate demand of the system.

The purpose of this report is to describe steps taken towards the development of robust blends of calcined clays (CC) and sources of sulfate that can be supplied directly to concrete producers to enable increased partial replacement of Portland cement. Due to the configuration of manufacturing plants, concrete producers are unable to add calcium sulfate during the production of concrete. Supplying blends of CC and calcium sulfate (gypsum) that provide robust fresh and hardened performance to ready-mix concrete would overcome this technical barrier for the widespread use of CCs by the U.S. concrete industry.

The specific objectives of this project included:

1. To procure and characterize selected CCs, gypsum, hemihydrate, ground limestone, and two types of Portland cement.
2. To identify blends of CCs and calcium sulfate for adequate rheologic and heat of hydration behavior of LC3 pastes.
3. To evaluate the mechanical performance of LC3 mortars.

The research reported here was developed in collaboration between the Oak Ridge National Laboratory (ORNL) and a multinational manufacturer of minerals that include quality kaolin and kaolin crudes. It is the company's objective to supply a cost-effective calcined clay to the U.S. concrete industry that reduces the energy demand of concrete while maximizing its natural resource efficiency. However, because of contract expiration, the objective #3 listed above could not be accomplished. In addition, some tasks related to objectives #1 and #2 were not performed, for the same reason.

2. MATERIALS AND METHODS

2.1 MATERIALS

Samples of two Portland cements, five calcined clays, one ground limestone, one calcium sulfate dihydrate (gypsum), one calcium sulfate hemihydrate, and one polycarboxylate-based dispersant were used in the experiments performed at ORNL.

The characteristics of the five calcined clays are described in Tables 1 and 2. Testing included thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence (XRF), particle size distribution (PSD) by laser diffraction and dry sieving, N_2 adsorption to measure specific surface area (SSA) according to the Brunauer-Emmett-Teller (BET) method, and density (loose and packed). Major oxide chemistry was determined by XRF analysis performed using a Rigaku Primus IVi XRF with loss on ignition (LOI) normalization and fused pellet preparation using a 5/0.5 ratio of flux ($LiBO_2/Li_2B_4O_7/LiI$) to un-ignited sample. The minimum reliable detection limit is 0.1%. XRD results were obtained using a Panalytical X'Pert Pro model unit. Mineralogy percentages are estimated based on the XRD results as

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[4] Sharma, M.; Bishnoi, S.; Martirena, F.; Scrivener, K. (2021) Limestone calcined clay cement and concrete: a state-of-the-art review. Cement and Concrete Research 149, 106564.

well as stoichiometric calculations based on XRF results. Particle size distribution was measured using a Malvern Mastersizer laser light scattering instrument.

Table 1. Characteristics of five calcined clays (CCs).

	CC1	CC2	CC3	CC4	CC5
Bulk Density Loose (lb/ft^3)	18.42	60.06	53.63	50.75	20.16
Bulk Density Packed (lb/ft^3)	26.47	71.36	66.49	69.54	26.34
Particle Size Distribution by Laser Diffraction (% volume)					
<20 micron	97.80	10.14	39.20	62.44	96.60
<10 micron	82	7	30	48	76
<5 micron	55	4	20	32	51
<2 micron	18	2	7	12	22
<1 micron	7	0.6	3	4.7	10
<0.5 micron	0.20	0.00	0.03	0.07	0.2
BET Specific Surface Area (m^2/g)					
BET SSA	24.57	27.27	26.90	23.53	13.17
Dry Sieving Cumulative Data (% weight)					
60 #	-	54.3	50.2	48.8	Trace
100 #	Trace	67.3	65.8	64.4	0.1
140 #	Trace	73.60	73.0	70.7	0.1
200 #	0.1	79.3	78.7	76.3	0.1
325 #	0.1	86.3	84.9	81.8	0.1
Pan	100	100	100	100	100
TGA Weight Loss (% weight)					
150C	0.547	0.237	0.24	0.112	0.342
150C – 400C	0.301	0.013	0.02	0.024	0.364
400C – 700C	0.51	0.153	0.103	0.047	0.182
1000C	1.484	0.68	0.588	0.378	0.922
Estimated Kaolin	3.92%	1.18%	0.79%	0.36%	1.40%

CC1 and CC5 are the finest and lightest clays. They have similar PSD but markedly different BET SSA: CC5's SSA is about half of CC1's. The other three clays have nearly three times higher density than CCs 1 and 5. The coarsest clay is CC2, followed by CC3 and CC4. Even though CC1 and CC5 are physically similar, Table 2 shows they have markedly different chemical and mineralogical compositions. CC5 is the purest of all five clays, with 95% metakaolin, while CC1's metakaolin content is the lowest of all samples. Mica and quartz impurities in this clay add up to nearly 20%. The other three clays have 90% metakaolin, with mica, anatase and quartz as impurities.

Table 2. Composition of five calcined clays.

	CC1	CC2	CC3	CC4	CC5
Chemical Composition (% weight)					
SiO_2	53.57	51.28	52.58	55.57	51.20
Al_2O_3	39.40	42.00	42.19	39.27	44.32
MgO	0.27	0.17	0.13	0.12	0.12
CaO	0.11	0.43	0.10	0.06	0.06
K2O	1.26	0.16	0.37	0.44	0.18
Na_2O	0.12	0.09	0.09	0.10	0.29
Fe_2O_3	1.95	1.46	1.80	2.11	0.55

TiO_2	1.72	3.22	1.66	1.62	1.69
LOI	2.84	1.08	0.95	0.56	1.81
Estimated Mineralogy (% weight)					
Metakaolin	80	90	90	90	95
Mica	5-10	Trace	<1	<1	<1
Anatase	1-2	3-5	1-2	1-2	1-2
Quartz	10	<2	5	5	<2

The characteristics of the ground limestone are listed in Table 3. A SediGraph III instrument was used to determine PSD of the ground limestone by measuring sedimentation rates of the particles dispersed in a liquid, with X-ray detection used to track concentration changes and calculate sizes via Stokes' law.

Table 3. Characteristics and composition of ground limestone.

Parameter	Measurement
Bulk density loose	60 lb/ft^3
Bulk density packed	85 lb/ft^3
SediGraph PSD (%)	
<20 micron	85
<10 micron	60
<5 micron	39
<2 micron	19
<1 micron	10
<0.5 micron	5
Chemical composition by XRF (%)	
SiO_2	1.18
Al_2O_3	0.04
MgO	0.89
CaO	53.98
K_2O	0.09
Na_2O	0.06
Fe_2O_3	0.14
TiO_2	0.02
LOI	43.2
Estimated mineralogy (%)	
Calcite	95
Acid insolubles	2

The gypsum used in the experiments is a Terra Alba #1 gypsum supplied by USG. It has a BET SSA of 15.9883 m2/g, a density of 2.3219 g/cm3 The PSD of the material determined by laser diffraction is shown in Figure 1. Samples of hemihydrate and two Portland cements (one Type IL and one Type V) have not been characterized.

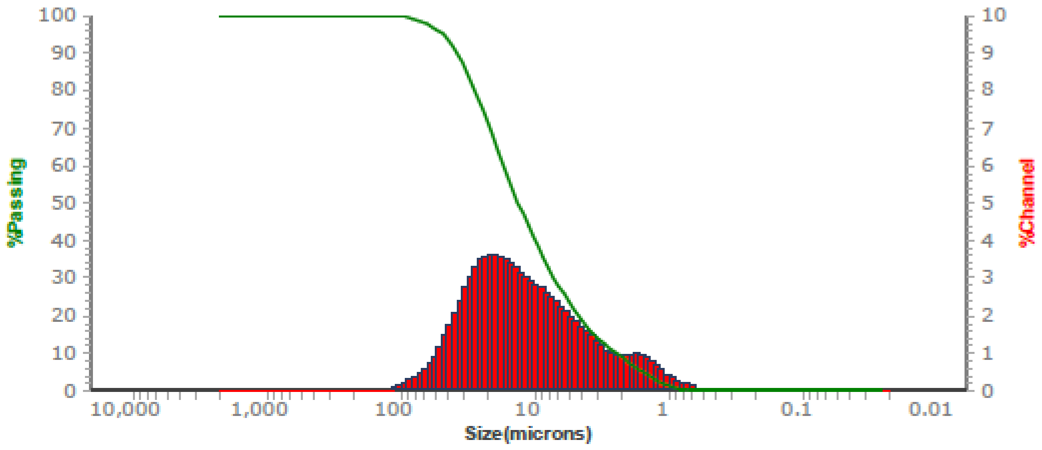

Figure 1. Particle size distribution of the gypsum sample.

2.2 METHODS

2.2.1 Determination of sulfate demand

A source of calcium sulfate, typically gypsum (natural or synthetic) and sometimes natural anhydrite, is added to the Portland cement to control the reactivity of the aluminate phases. Without this external source of sulfate, Portland cement would set very quickly after mixing with water, making it impossible to transport and place concrete into formwork. Sulfate ions “passivate” calcium aluminate reactions, reducing its dissolution rates and associated heat, and forming hydration products that are beneficial for workability. In addition, sulfate balance is critical for achieving optimal mechanical performance and durability of cement-based materials. Optimum sulfate content is typically determined based on compressive strength testing by cement producers. Isothermal calorimetry, which measures the heat flow generated during hydration of cement at a constant temperature, provides additional information to support sulfate optimization, including the time at which gypsum is fully consumed in the system - called sulfate depletion point – and the cumulative heat released after 24 hours of hydration, which correlates to 1 day compressive strengths of systems with a fixed composition[5].

Figure 2 shows a typical heat flow curve of a Portland cement paste subjected to isothermal calorimetry, with the indication of main hydration events that generate heat in the system. Sulfate balance is often assessed by comparing the time elapsed between the silicate hydration peak and the sulfate depletion point (onset of the second aluminate hydration peak) across mixes[6]. A proper sulfate balance for a pure Portland cement paste, for example, is achieved when this time is in the range of 30 and 150 minutes (or 0.5 and 2.5 hours)[7].

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[5] L. Frølich, L. Wadso, ¨ P. Sandberg. (2016) Using isothermal calorimetry to predict one day mortar strengths, Cement and Concrete Research, 88, p.108–113.

[6] Canbek, O., Szeto, C., Washburn, N.R. and Kurtis, K.E. (2023) A quantitative approach to determining sulfate balance for LC3. Cement, 12, p.100063.

[7] Berodier, E., Tregger, N., Cheung, J., Myers, D., Zhang, L., Kazmierczak, D., Roberts, L., Silva, D., Sibbick, R., Thomas, J., Roberts, M., Stoppa, R., Burns, E. (2024) Cement Production. US20240239707A1. Available at: https://patents.google.com/patent/US20240239707A1/.

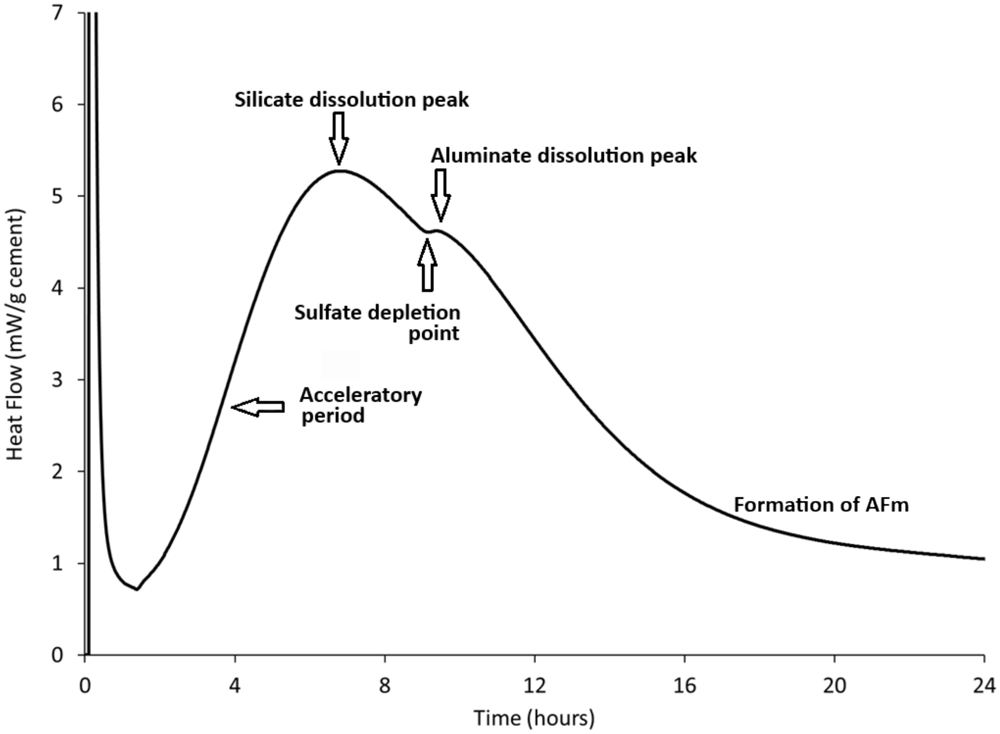

Figure 2. Typical heat flow curve of a hydrating Portland cement.

To determine the necessary amount of calcium sulfate to produce robust CC blends in this investigation, LC3 pastes containing 50% (weight) of Portland cement, 15% ground limestone, and 35% calcined clay with various gypsum contents were submitted to isothermal calorimetry to assess the time elapsed between silicate hydration peak and sulfate depletion point. The pastes were mixed with deionized water and various doses of gypsum using a high shear stirring shaft in an IKA Eurostar 60 Control overhead mixer, as follows: (1) powders weigh up and hand mixing with a spatula for 60 seconds; (2) deionized water weigh up and pouring over powders; (3) overhead mixing at 1,000 rpm for 15 seconds; (4) mixing stopped, stirrer and bottom of container scraped for 15 seconds with a spatula; (5) mixing at 2,000 rpm for 2 minutes. Around 15 grams of each paste were immediately transferred to a Calmetrix Ultra-Cal isothermal calorimeter set at 23^{o}C to measure the heat of cement hydration over time. Heat flow data was acquired for at least 40 hours and up to 168 hours (7 days). Table 4 shows the proportions of materials used in the pastes for each gypsum content, which varied between 2% and 5% (% weight of solids). To maintain the solids concentration unchanged, the content of ground limestone was adjusted as the dose of gypsum varied. All experiments were conducted using 1% of a commercial polycarboxylate (PCE)-based dispersant (% on weight of powders) pre-diluted in the mixing water.

Table 4. Composition of LC3 pastes tested for gypsum demand.

	LC3 Pastes			
Ingredients	**2% Gypsum**	**3% Gypsum**	**4% Gypsum**	**5% Gypsum**
Portland cement (g)	37.5	37.5	37.5	37.5
Calcined clay (g)	22.5	22.5	22.5	22.5
DI water (g)	30.0	30.0	30.0	30.0
PCE-based dispersant (g)	0.75	0.75	0.75	0.75
Ground limestone (g)	**13.5**	**12.75**	**12.0**	**11.25**
Gypsum (g)	**1.5**	**2.25**	**3.0**	**3.75**

2.2.2 Determination of chemical dispersant demand

To determine the demand of LC3 systems for PCE-based dispersant, pastes were prepared as described in 2.2.1 with additional 1 minute rest and 2 minutes at 2,000 r.p.m at the end of the mixing process. A Kantro mini-cone[8] was used to assess the workability of the pastes. The mini-cone was half-filled with paste (scooped for creamier mixes or poured for more fluid ones) and tamped 10 times around the circumference with the spatula's flat side. The second half was then filled and tamped similarly, and the excess leveled with the spatula's straight edge. The cone was then lifted vertically before measuring the spread diameters along the x- and y-axes. Around 7 grams of each paste were also transferred to the isothermal calorimeter set at 23^{o}C to measure the heat of cement hydration over time. Heat flow data was acquired for at least 20 hours. Table 5 shows the proportions of materials used in each paste. All pastes were tested with 2% gypsum (% weight of cement + calcined clay + limestone).

Table 5. Composition of LC3 pastes tested for chemical dispersant demand.

Ingredients	Amounts (g)
Portland cement (g)	37.5
Calcined clay (g)	22.5
Ground limestone (g)	13.5
Gypsum (g)	1.5
DI water (g)	30.0

3. RESULTS AND DISCUSSIONS

3.1 DETERMINATION OF SULFATE DEMAND

Figures 3 and 4 show the heat flow curves of hydrating LC3 pastes containing calcined clay (CC) #1 and cements CEM 1 and CEM 2, respectively, with gypsum content ranging between 2% and 5%. The presence of CC shifts the silicate hydration peak and the sulfate depletion point to earlier times, confirming previous reports[6,9], and steepen the acceleratory period slope, which is evidence of accelerated nucleation of hydrated phases (C-S-H and ettringite) that lead to a faster consumption of sulfate ions. This is the typical 'filler effect' that is due to the introduction of the fine, low-density CCs. Sulfate ions can also adsorb on the surface of CCs, either directly or as calcium-sulfate ion complexes[10,11], accelerating sulfate depletion in Portland cement systems.

Cement CEM 1 shows a clear sulfate depletion point/secondary aluminate reaction onset, as indicated by the red arrow in Figure 3. Conversely, this hydration event is not clearly seen in CEM 2, possibly indicating an excess of calcium sulfate (Figure 4). The addition of CC1 to both CEM 1 and CEM 2 LC3 systems increased the rate of sulfate consumption during cement hydration, evidencing the sulfate depletion point (see black arrows in Figures 3 and 4 as examples). Increasing the content of gypsum from 2% to 5% moves the sulfate depletion point to later times with both CEM 1 and CEM 2. It also increases

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[8] Kantro, D.L. (1980) Influence of water-reducing admixtures on properties of cement paste – a miniature slump test. Cement, Concrete, and Aggregates, CCAGDP, Vol.2, No.2, p. 95-102.

[9] Zunino, F. and Scrivener, K. (2019) The influence of the filler effect on the sulfate requirement of blended cements. Cement and Concrete Research, 126, p.105918.

[10] Maier, S. Scherb, A. Neißer-Deiters, N. Beuntner, K.C. Thienel, Hydration of cubic tricalcium aluminate in the presence of calcined clays, J. Am. Ceram. Soc. 104 (2021) 3619–3631.

[11] , M. Maier, N. Beuntner, K.-.C. Thienel, J. Neubauer, Reaction kinetics during early hydration of calcined phyllosilicates in clinker-free model systems, Cem. Concr. Res. 143 (2021).

the cumulative heat of hydration after around 20 hours of reaction (Figure 5), which implies enhanced performance as the gypsum content increases.

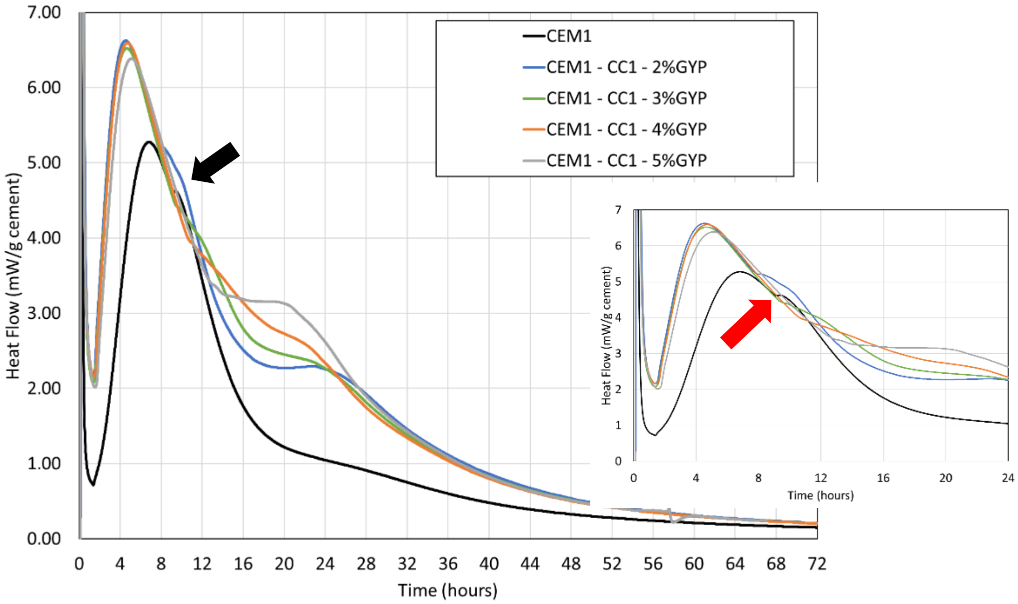


Figure 3. Heat flow curves of LC3 pastes formulated with CEM 1, CC1, and various gypsum contents. The zoom of the first 24 hours of hydration is also shown. The black and red arrows indicate the sulfate depletion points in CEM 1 paste and LC3 pastes, respectively, with 2% gypsum.

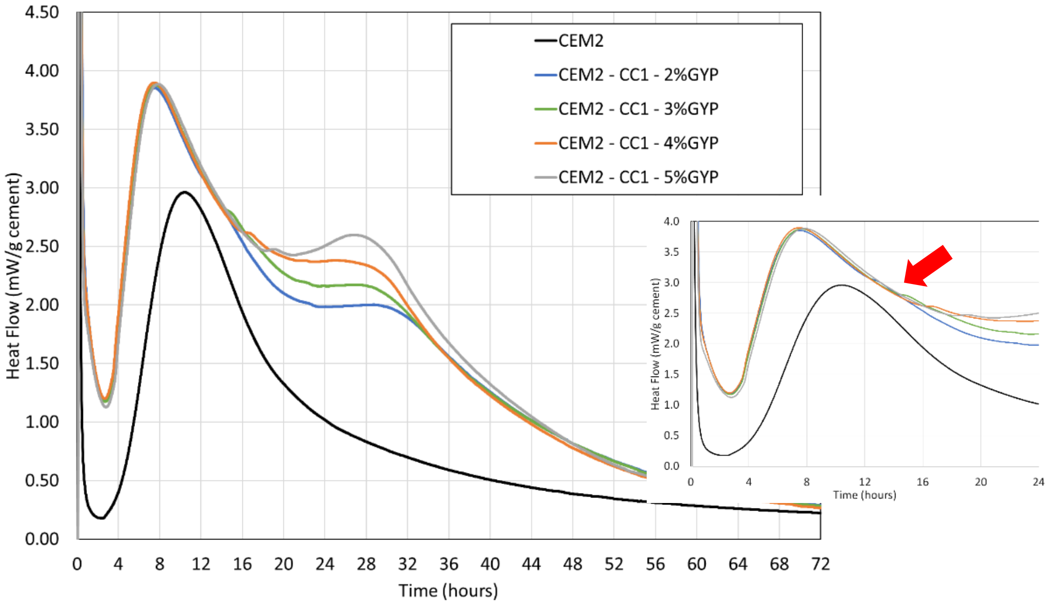
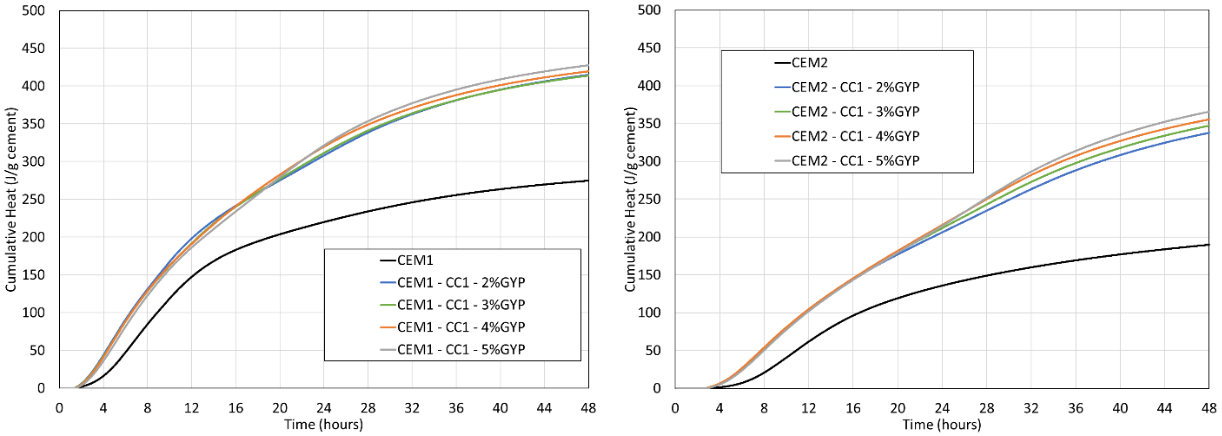


Figure 4. Heat flow curves of LC3 pastes formulated with CEM 2, CC1, and various gypsum contents. The zoom of the first 24 hours of hydration is also shown. The red arrow indicates the sulfate depletion point in LC3 pastes with 2% gypsum. It is not possible to identify the sulfate depletion point in the CEM 2 paste.



(a) (b)

Figure 5. Cumulative heat of (a) CEM1-CC1 and (b) CEM2-CC1 LC3 pastes with increased gypsum contents.

Figures 6 and 7 show the impact of the different CCs on the heat of hydration profile of LC3 pastes with CEM 1 and CEM 2, respectively, in the presence of 2% gypsum and 1% PCE-based admixture. The sulfate depletion point is clearly seen in all CEM 1 systems (Figure 6), except for the paste with CC 2. This paste is less reactive than the others, as evidenced by the longer induction period and lower slope of the acceleratory period compared to the other systems, despite the high metakaolin content and the highest specific surface area of CC 2, suggesting that the filler effect brought up by this clay is less impactful than the others. High internal porosity that does not play a role in particle packing and filler effect may be the responsible for the high SSA of CC 2. Figure 6 also shows that, with CEM 1, the addition of 2% gypsum is sufficient to provide sulfate balance to all LC3 systems.

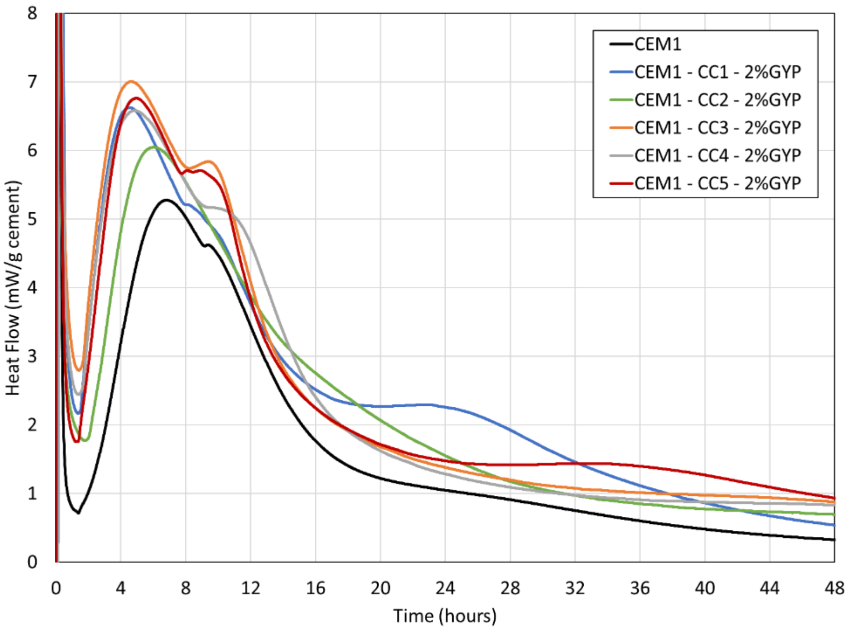


Figure 6. Heat flow of CEM 1 hydrating in the presence of various calcined clays, 2% gypsum, and 1% PCE-based dispersant.

Figure 7 shows that all CCs also increased sulfate consumption in LC3 systems with CEM 2, as evidenced by the sulfate depletion point in the heat flow curves. Similarly to LC3 pastes with CEM 1, the impact of CC 2 was more nuanced than the other clays. From the visual examination of the curves in Figure 7, the addition of 2% gypsum also seems to provide adequate sulfate balance to LC3 pastes with CEM 2.

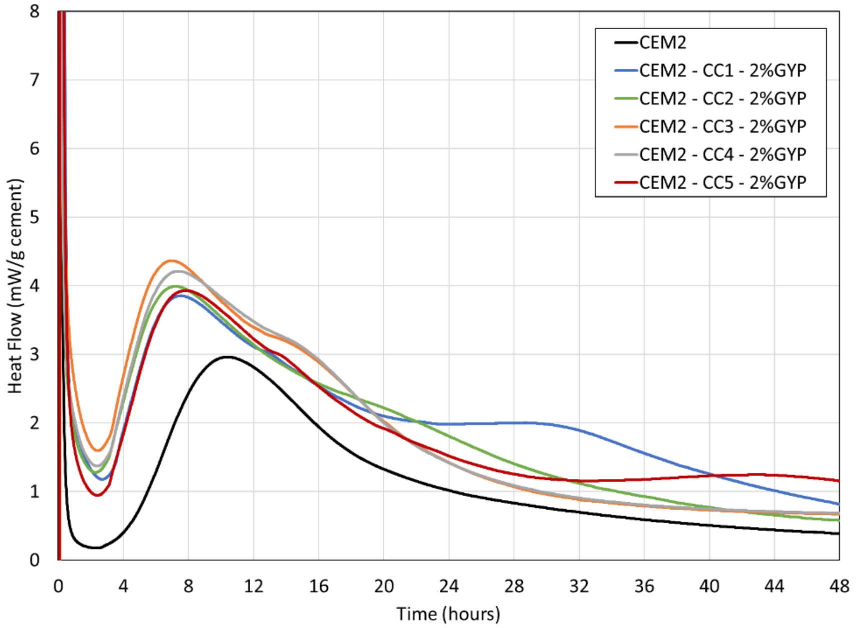


Figure 7. Heat flow of CEM 2 hydrating in the presence of various calcined clays, 2% gypsum, and 1% PCE-based dispersant.

Table 6 lists heat of hydration parameters that are relevant to determine the optimum gypsum content of the LC3 pastes investigated here, and Appendix A shows the scatter plots correlating these values. Regardless of the cement and calcined clay, increasing the amount of gypsum from 2% to up to 5% had the following effects:

- Minor impact on the silicate peak time.
- Increase in time to sulfate depletion point.
- Increase in time difference between silicate peak time and sulfate depletion point.
- Minor to moderate increase in total energy released after 24 hours.

Table 6. Calorimetry parameters of LC3 pastes with various contents of gypsum.

	Silicate peak time (h)	**Sulfate depletion time (h)**	**Difference (min)**	**Cumulative heat after 24 hours (J/g cement)**
CEM 1	6.85	9.30	149.8	219.9
CEM 2	10.48	n/a	n/a	135.7
CEM 1, CC1, 2% GYP	4.55	8.13	214.8	308.0
CEM 1, CC1, 3% GYP	4.67	9.72	303.0	311.4
CEM 1, CC1, 4% GYP	4.75	10.93	370.8	319.6
CEM 1, CC1, 5% GYP	5.13	13.18	483.0	321.3
CEM 2, CC1, 2% GYP	7.57	12.65	304.8	206.2

CEM 2, CC1, 3% GYP	7.68	14.70	421.2	211.8
CEM 2, CC1, 4% GYP	7.40	16.47	634.2	216.0
CEM 2, CC1, 5% GYP	7.52	18.72	672.0	214.7
CEM 1, CC2, 2% GYP	6.10	14.23	487.8	282.5
CEM 1, CC2, 4% GYP	4.82	17.67	771.0	280.8
CEM 2, CC2, 2% GYP	7.22	17.32	606.0	215.9
CEM 2, CC2, 4% GYP	7.37	25.30	1075.8	210.9
CEM 1, CC3, 2% GYP	4.67	8.80	247.8	310.0
CEM 1, CC3, 4% GYP	4.92	13.48	513.6	314.3
CEM 2, CC3, 2% GYP	6.95	13.40	387.0	227.3
CEM 2, CC3, 4% GYP	7.02	17.88	651.6	230.7
CEM 1, CC4, 2% GYP	4.83	9.62	287.4	304.6
CEM 1, CC4, 4% GYP	5.02	15.18	609.6	308.8
CEM 2, CC4, 2% GYP	7.42	13.62	372.0	224.0
CEM 2, CC4, 4% GYP	7.43	n/a	n/a	227.7
CEM 1, CC5, 2% GYP	5.13	8.03	181.2	297.9
CEM 1, CC5, 4% GYP	5.05	11.70	399.0	301.7
CEM 2, CC5, 2% GYP	7.88	13.38	330.0	203.7
CEM 2, CC5, 4% GYP	7.68	18.17	689.4	209.4

Based on the above results, it appears that all LC3 systems prepared with the two different types of cements (IL and V) investigated here would be balanced for sulfate if 2% gypsum were added to the calcined clays.

3.2 DETERMINATION OF CHEMICAL DISPERSANT DEMAND

Figures 8 and 9 show the impact of increased doses of PCE-based dispersant on the average spread diameter of the LC3 pastes using the Kantro mini-cone, for CEM 1 and CEM 2 systems, respectively. The linear correlations between dispersant dose and paste fluidity are strong, as can be seen by the high R^2 values in both graphs. The linear correlations show that the dose range tested did not approach the saturation point of the dispersant in these LC3 systems.

The LC3 pastes with CC2, CC3, and CC4 required less dispersant than the other two clays (CC1 and CC5) to achieve similar fluidity with both CEM 1 and CEM 2. CC1 required the largest dispersant dose, followed by CC5. No strong correlations could be found between the characteristics of the clays, listed in Tables 1 and 2, and the dispersant dose requirement, regardless of the cement type.

There are differences in the responsiveness of the LC3 systems to the dispersant dose, as evidenced by the slope of the linear correlations in Figures 8 and 9. The reasons behind these differences have not been investigated.

LC3 pastes with CEM 2 required less water than those with CEM 1 to achieve similar mini-cone spread: the water/solids ratios in CEM 1 and CEM 2 pastes were 0.40 and 0.35, respectively.

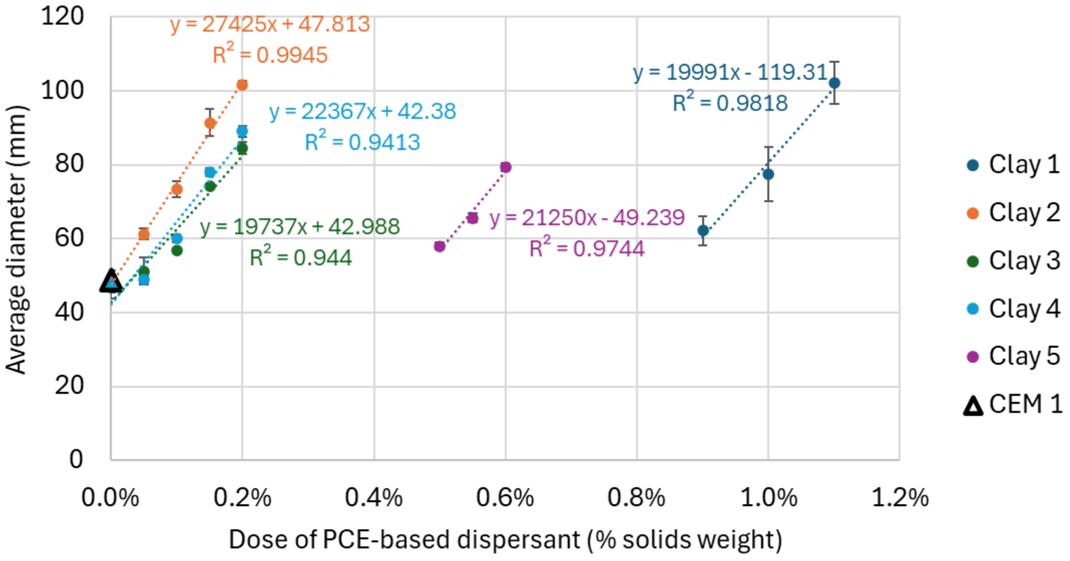


Figure 8. Average spread diameter in Kantro mini-cone test of LC3 pastes with CEM 1 as a function of PCE-based dispersant content. A paste with 100% CEM 1 is also shown. All pastes have a water/solids ratio of 0.4.

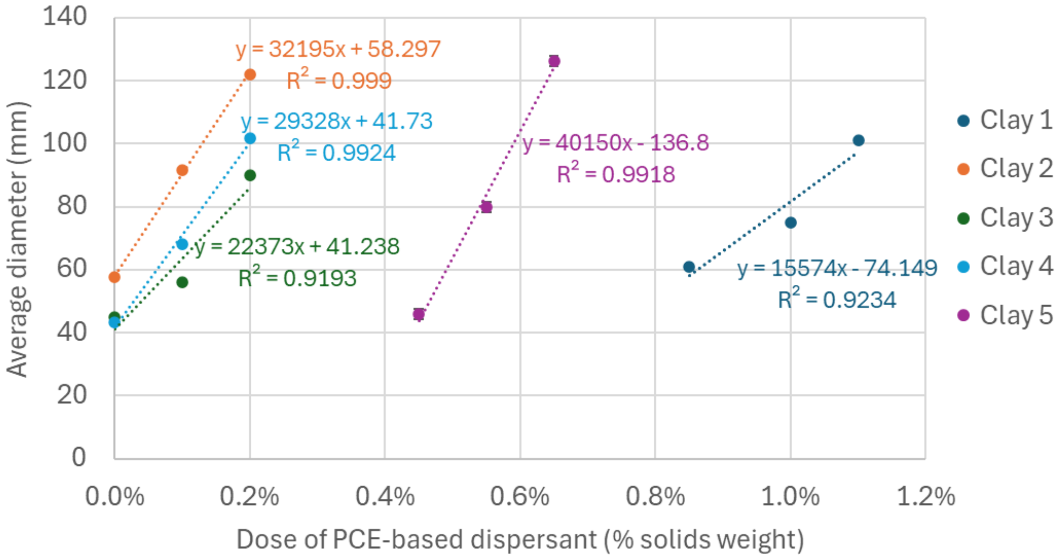
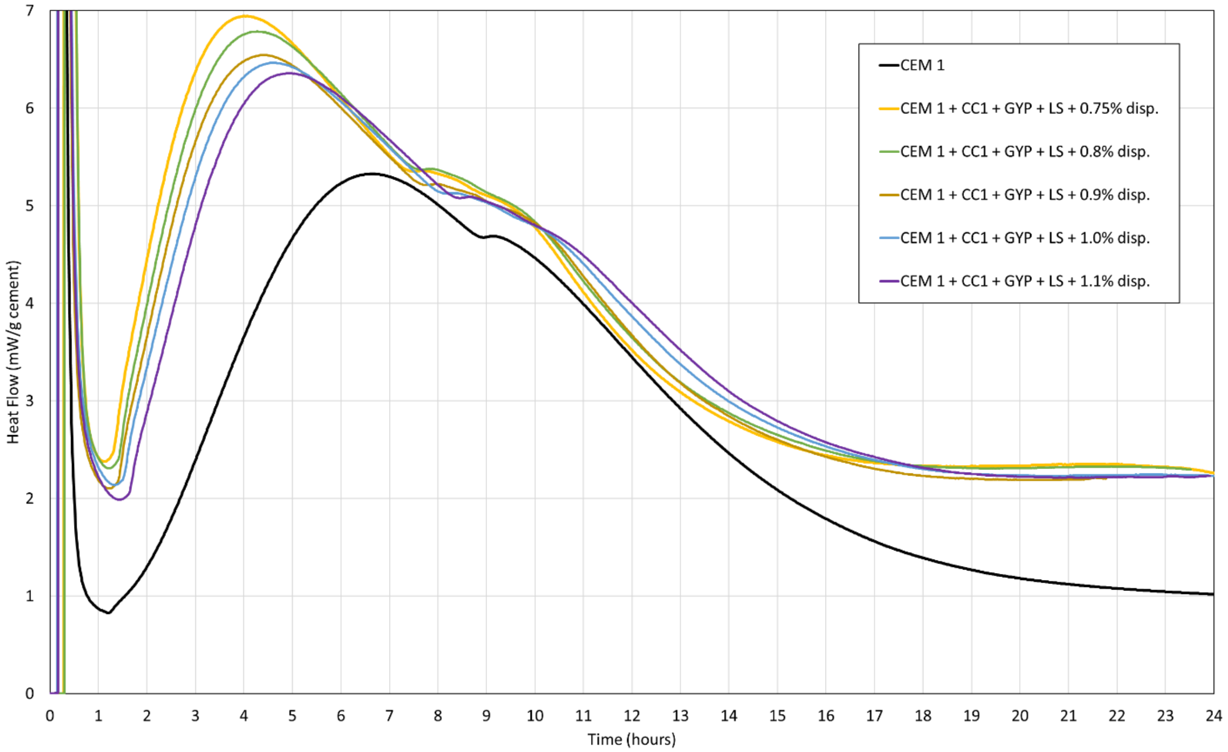


Figure 9. Average spread diameter of LC3 pastes with CEM 2 as a function of PCE-based dispersant content. All pastes have a water/solids ratio of 0.35.

Figure 10a shows the heat flow curves of LC3 pastes with CEM 1 + CC 1 and various doses of dispersant. From a simple visual examination of these curves, the retarding effect of increased doses of dispersant is clearly seen. Initial and final setting times can be estimated from isothermal calorimetry[12,13]. In this investigation, setting times were estimated as the time elapsed from the preparation of the pastes through half time between the onset of the acceleratory period and the silicate hydration peak. An increase in dispersant content from 0.75% to 1.1% (% solids weight), for example, increased setting time by nearly 50 minutes. Figure 10b plots the first derivative of the heat flow curves as a function of time. The analysis of the first derivative helps quantify the slope of the acceleratory period as well as the time to sulfate depletion point.



(a)

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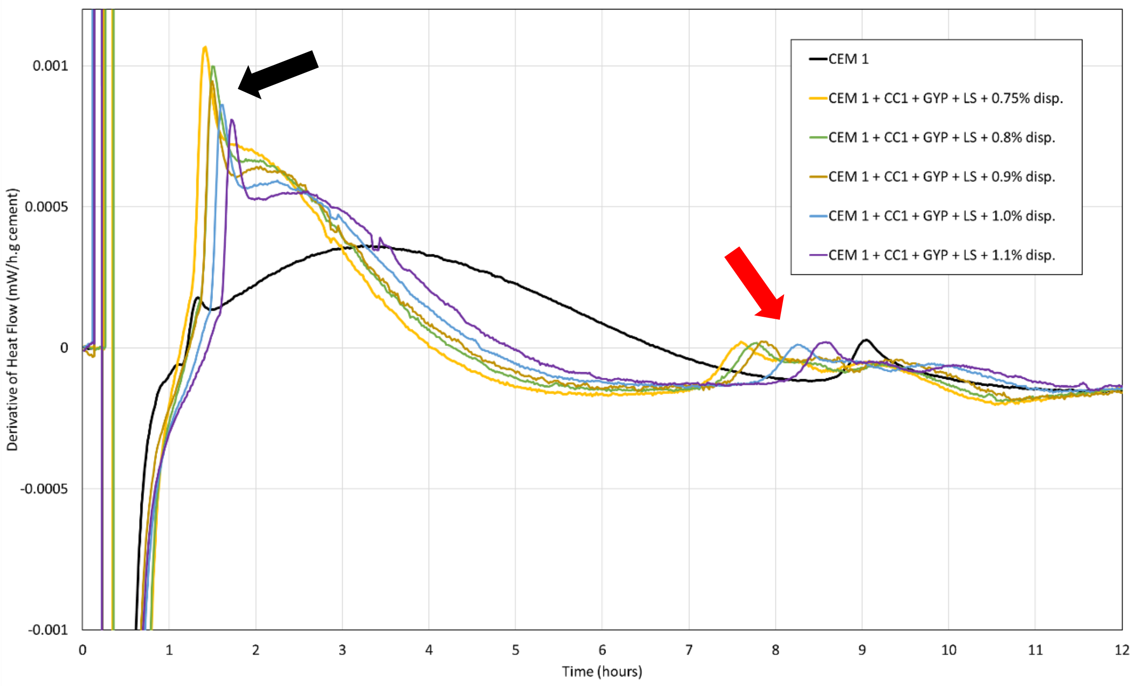
[12] Bentz, D.P. & Ferraris, C.F. (2001). Isothermal calorimetry and setting time correlations in cement pastes. Cement and Concrete Research, 31(5), 701–709.

[13] Schöler, A., Lothenbach, B., Winnefeld, F., & Zajac, M. (2017). Hydration of Portland cement with calcium aluminate cement and calcium sulfoaluminate cement. Cement and Concrete Research, 95, 288–302.



(b)

Figure 10. (a) Heat flow curves of LC3 pastes with CEM 1 and CC1 with various doses of PCE-based dispersant. (b) First derivative of heat flow as a function of time of the same systems. The peaks identified with a black arrow represent the slope of the acceleratory phase of the heat flow peak associated with silicate hydration. The peaks identified with a red arrow represent the sulfate depletion point. All pastes have a water/solids ratio of 0.40.

Figure 10 is shown as an example. The curves for all LC3 pastes tested with CEM 1 and CEM 2 and the five calcined clays are not included in this report, but Tables 7 and 8 list the heat of hydration parameters obtained from these curves as explained below. These parameters are relevant to determine the impact of different doses of the PCE-based dispersant on the different LC3 pastes studied here, and Appendix B shows the scatter plots correlating these values. Regardless of the cement and calcined clay, increasing the amount of PCE-based dispersant in the LC3 pastes had the following effects:

- Retardation of cement hydration kinetics, leading to lengthening of setting times and delay in silicate hydration peak.
- Slope decrease of the acceleratory phase of the silicate hydration peak, suggesting a negative impact on the nucleation of hydrates.

It is interesting to note that the much larger dose of dispersant necessary to ensure workability to LC3 pastes prepared with CC1 and CC5 did not result in significantly different impact on cement hydration kinetics of these systems compared to those with the other three clays. Based on the knowledge that higher doses of PCE-based dispersants retard cement hydration kinetics in a linear fashion (the higher the dose, the higher the retardation)[14], it is reasonable to conclude that calcined clays CC1 and CC5 are

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[14] Silva, D.A.; Pileggi, R.G.; Rebmann, A.J.; Aldykiewicz Jr.; A.; Hemrick, J.G.; Tsai, W.Y. (2023). Application of interparticle spacing model to maximize filler content in cementitious pastes. 16th ICCC Proceedings, Bangkok, Vol. 1, pp. 457-460

removing part of the dispersant from the solution. The reasons behind this effect have not been investigated at the time of this report.

The graphs in Appendix B also show that the impact of the dispersant dose on the time for sulfate depletion and on the difference between this event and the time of the silicate hydration peak is not consistent across all CCs and CEMs.

Table 7. Calorimetry parameters of LC3 pastes with CEM 1 and various doses of chemical dispersant.

	Estimated setting time (h)	**Slope of acceleratory period (mW/g_{cem}.h)**	**Silicate peak time (h)**	**Sulfate depletion time (h)**	**Difference (min)**
CEM 1	3.93	1.78E^{-4}	6.62	9.07	147.0
CEM 1, CC 1, % DISP					
0.75%	2.58	10.63E^{-4}	4.05	7.62	214.2
0.80%	2.75	9.99E^{-4}	4.25	7.80	213.0
0.90%	2.83	9.34E^{-4}	4.43	7.87	206.4
1.00%	2.98	8.60E^{-4}	4.58	8.25	220.2
1.10%	3.23	8.10E^{-4}	4.97	8.58	216.6
CEM 1, CC 2, % DISP					
0.00%	3.03	7.27E^{-4}	4.77	12.75	478.8
0.05%	3.17	6.23E^{-4}	4.93	13.13	492.0
0.10%	3.32	6.05E^{-4}	5.23	13.13	474.0
0.15%	3.36	5.90E^{-4}	5.28	13.03	465.0
0.20%	3.40	6.15E^{-4}	5.32	12.95	457.8
0.50%	3.87	5.29E^{-4}	5.88	15.40	591.2
0.80%	4.80	4.32E^{-4}	7.37	16.05	520.8
CEM 1, CC 3, % DISP					
0.00%	2.81	N/A	4.33	8.50	250.2
0.05%	2.97	9.32E^{-4}	4.60	8.90	258.0
0.10%	3.04	8.91E^{-4}	4.70	9.03	259.8
0.15%	3.09	7.99E^{-4}	5.00	9.23	253.8
0.20%	3.20	7.63E^{-4}	4.97	9.23	255.6
CEM 1, CC 4, % DISP					
0.00%	2.95	8.70E^{-4}	4.65	9.67	301.2
0.05%	3.00	8.29E^{-4}	4.72	9.58	291.6
0.10%	3.14	7.81E^{-4}	4.95	9.92	298.2
0.15%	3.20	7.73E^{-4}	5.02	10.03	300.6
0.20%	3.31	7.17E^{-4}	5.18	10.02	290.4
CEM 1, CC 5, % DISP					
0.50%	2.86	8.31E^{-4}	4.53	7.78	195.0
0.55%	2.91	7.86E^{-4}	4.60	7.73	187.8
0.60%	2.94	7.60E^{-4}	4.62	7.68	183.60

Table 8. Calorimetry parameters of LC3 pastes with CEM 2 and various doses of chemical dispersant.

	Estimated setting time (h)	Slope of acceleratory period ($mW/g_{cem}.h$)	Silicate peak time (h)	Sulfate depletion time (h)	Difference (min)
CEM 2, CC 1, % DISP					
0.85%	4.11	$4.03E^{-4}$	6.18	9.37	197.4
1.00%	4.48	$3.74E^{-4}$	6.63	10.15	211.2
1.10%	4.77	$3.47E^{-4}$	7.10	10.60	210.0
CEM 2, CC 2, % DISP					
0.00%	4.64	$2.75E^{-4}$	7.05	17.70	639.0
0.10%	5.01	$2.44E^{-4}$	7.77	17.70	595.8
0.20%	5.19	$2.45E^{-4}$	7.93	17.83	594.0
CEM 2, CC 3, % DISP					
0.00%	4.14	$3.76E^{-4}$	6.30	12.73	385.8
0.10%	4.54	$3.32E^{-4}$	6.83	12.95	367.2
0.20%	4.84	$3.01E^{-4}$	7.25	12.80	333.0
CEM 2, CC 4, % DISP					
0.00%	4.21	$3.57E^{-4}$	6.40	12.73	379.8
0.10%	4.71	$3.09E^{-4}$	7.18	13.53	381.0
0.20%	4.89	$3.06E^{-4}$	7.40	13.13	343.8
CEM 2, CC 5, % DISP					
0.45%	3.80	$3.93E^{-4}$	5.98	10.33	261.0
0.55%	4.20	$3.59E^{-4}$	6.57	10.83	255.6
0.65%	4.55	$3.26E^{-4}$	7.07	11.37	277.8

4. CONCLUSIONS

The results shown in this report indicate that robust blends of calcined clay and calcium sulfate can be obtained for use in LC3 concrete by adding 6.7% of gypsum (% of calcined clay weight) to the clay. However, the effects of these blends on LC3 concrete workability will depend on the calcined clay. In the investigation reported here, the dose of PCE-based dispersant to achieve a given flow with each clay varied by 10-fold. Hence, concrete producers will need to adjust the dose of chemical admixtures depending on the source of clay.

APPENDIX A. SULFATE BALANCE GRAPHS

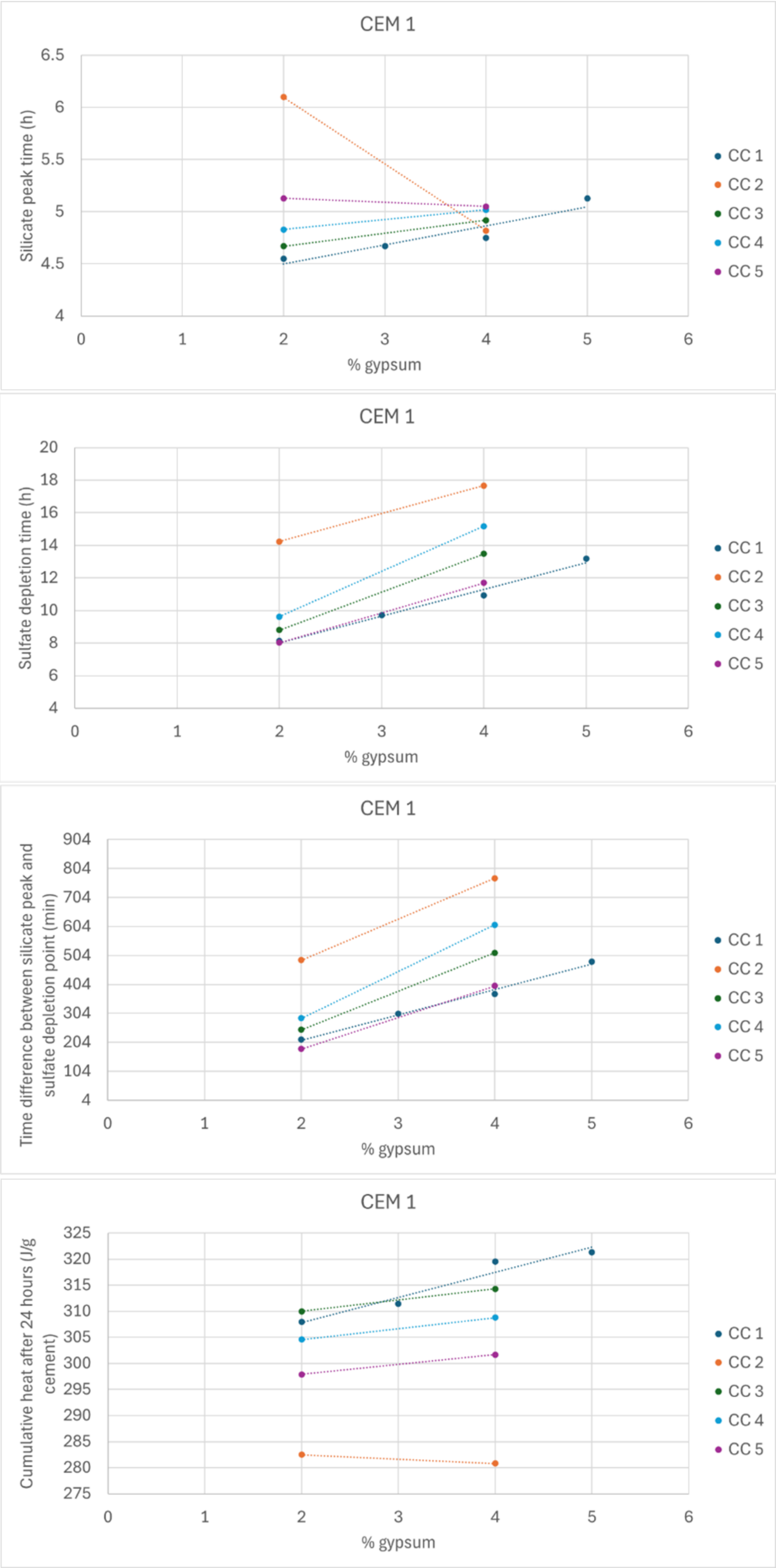

Figure A1. Impact of gypsum on heat of hydration parameters of LC3 systems with CEM 1 and 1% PCE-based dispersant.

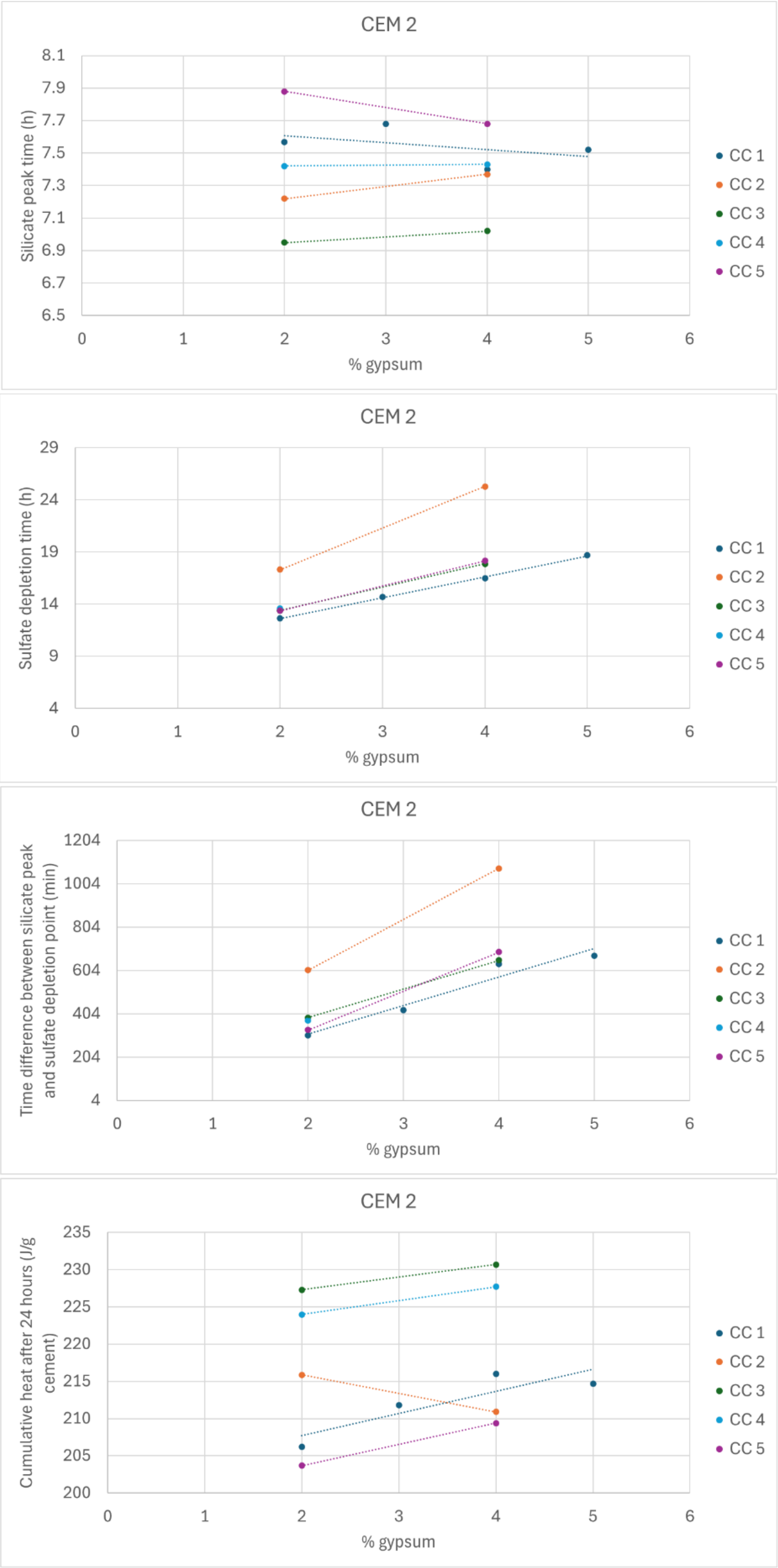

Figure A2. Impact of gypsum on heat of hydration parameters of LC3 systems with CEM 1 and 1% PCE-based dispersant.

APPENDIX B. DISPERSANT DOSE GRAPHS

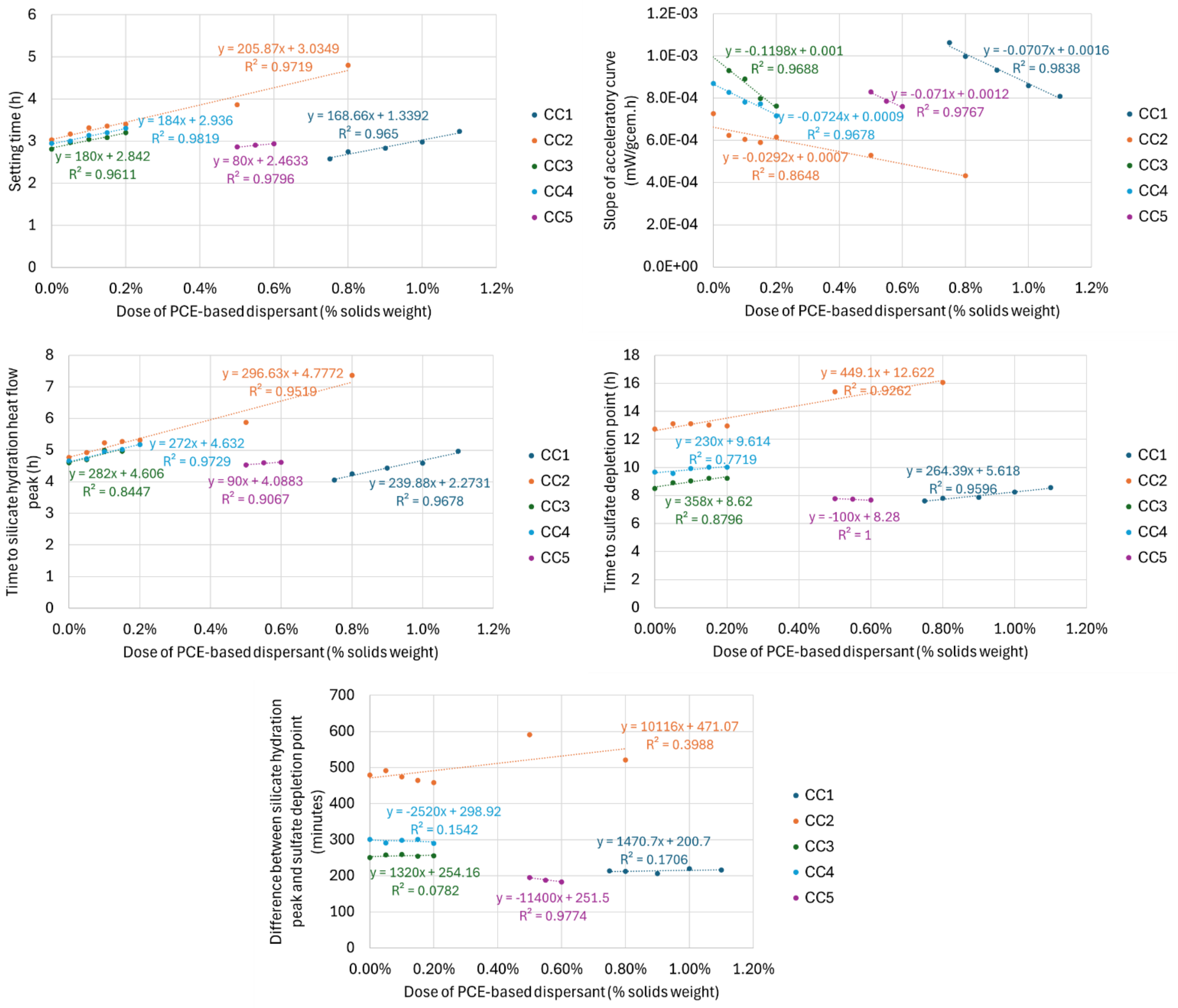

Figure B1. Impact of dose of PCE-based dispersant on heat of hydration parameters of LC3 systems with CEM 1 and 2% gypsum.

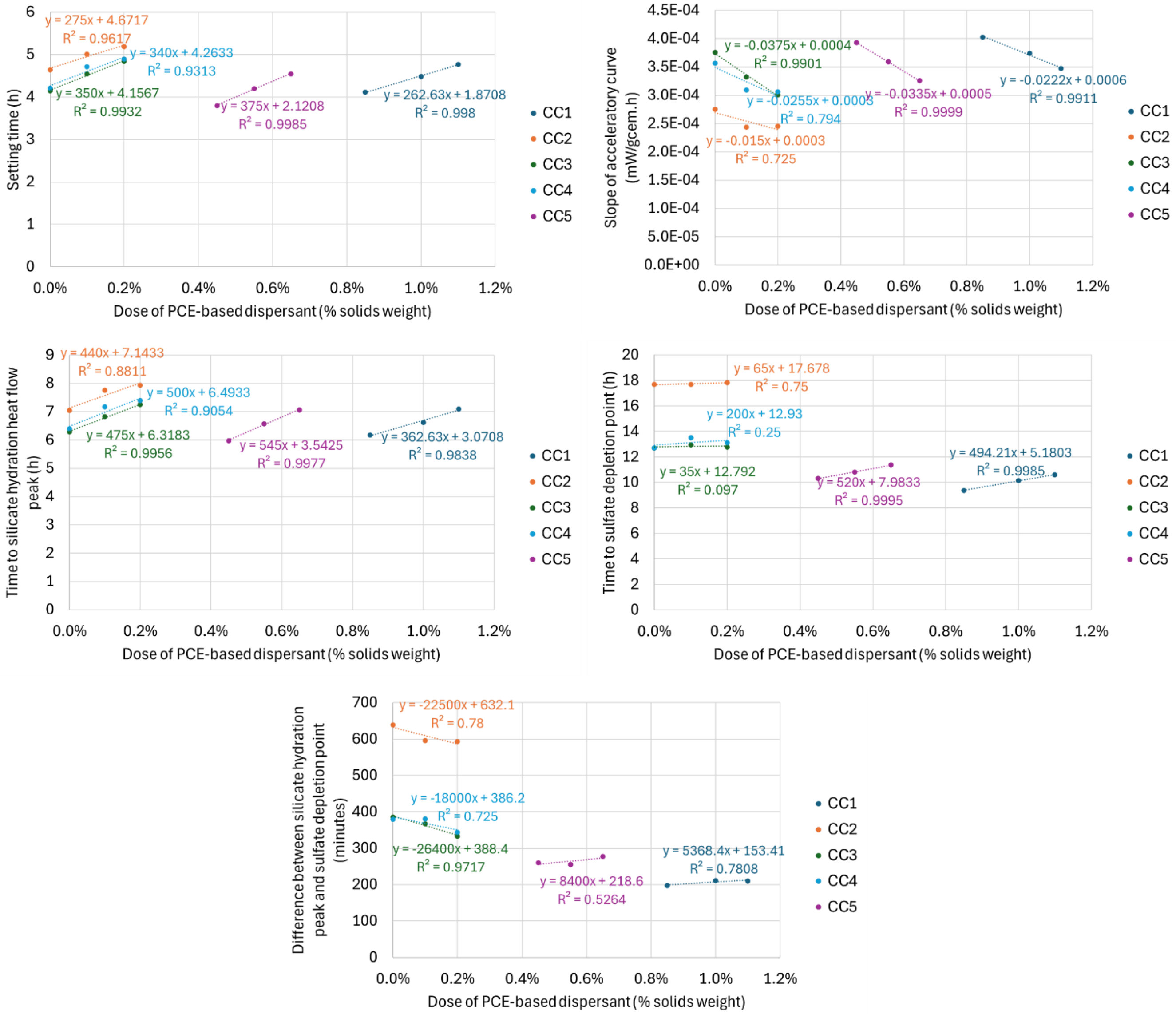

Figure B2. Impact of dose of PCE-based dispersant on heat of hydration parameters of LC3 systems with CEM 2 and 2% gypsum.