Composition-Property Relationships in Low-Energy, Low-CO_2 Calcium Sulfoaluminate-Belite Cement

Irvin A. Chen & Maria C.G. Juenger

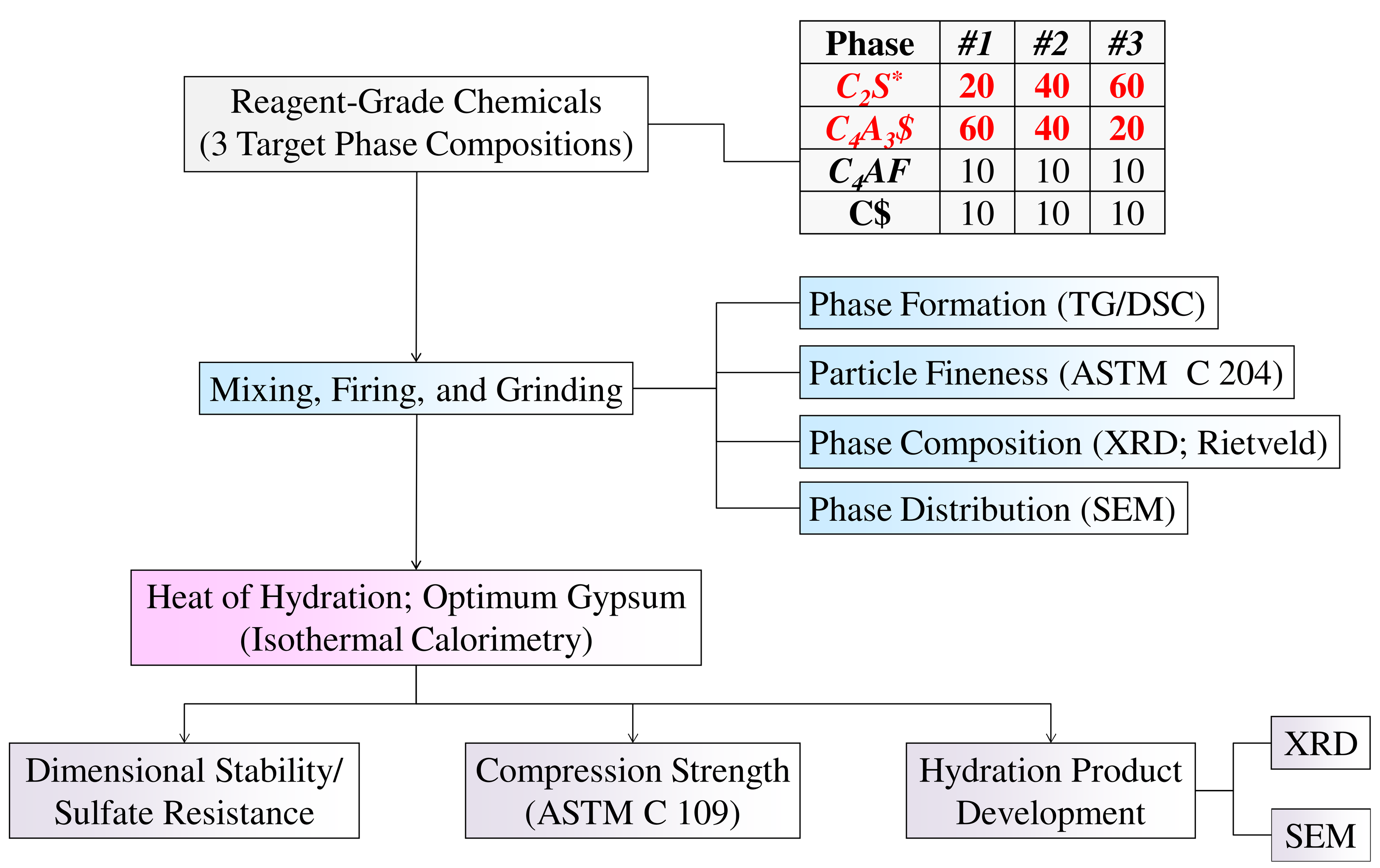
The University of Texas at Austin

Introduction

Portland cement concrete, the most widely used manufactured material in the world, is made primarily from water, mineral aggregates, and portland cement. The production of portland cement is energy intensive and contributes significantly to green house gas emissions. One method of reducing the environmental impact of cement manufacturing is the use and adoption of an alternative environmental friendly binder, calcium sulfoaluminate-belite (CSAB) cement. CSAB cement has a different phase assemblage to portland cement, which requires less lime for its production. The relatively low lime requirement for CSAB cement production reduces energy consumption and carbon dioxide emissions from cement manufacturing. Moreover, CSAB cement can form and is stable approximately 200ºC lower than the temperature used for portland cement production, which further reduces energy consumption and carbon dioxide emissions from cement manufacturing.

In this study, three CSAB cement clinkers with different phase compositions were synthesized. The range of phase compositions was chosen because it allows full evaluation of the phase compatibility and the inter-relationship between phase composition and cement property. The synthetic clinkers were analyzed for phase composition using x-ray diffraction and phase distribution using scanning electron microscopy. The synthetic clinkers were then tested for heat of hydration with isothermal calorimetry to determine their optimum gypsum contents and to study their early-age hydration behavior. The synthetic clinkers were made into cements by adding their optimum gypsum contents and the resulting cements were monitored for hydration product development using x-ray diffraction and scanning electron microscopy to understand property development. Performance of the synthetic cements was characterized through compressive strength, dimensional stability, and sulfate resistance.

Experimental Procedure



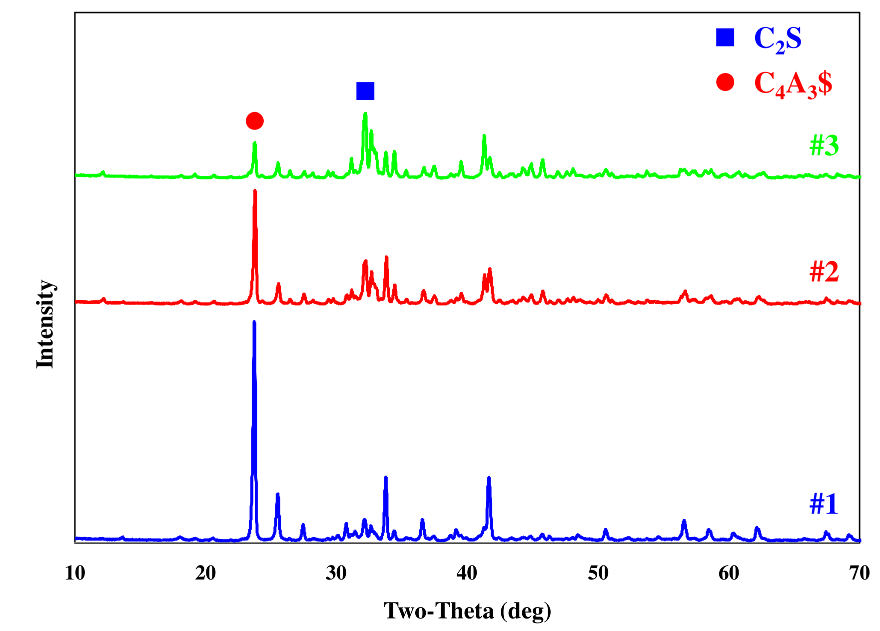
Phase	#1	#2	#3
C_2S*	20	40	60
$C_4A_3\$$	60	40	20
C_4AF	10	10	10
C$	10	10	10

*In cement chemistry notation, oxides are abbreviated by the first capital letter: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, and $=$SO_3$

Acknowledgements

The authors express their thanks to National Science Foundation (Project No. CMMI 0448983) and Portland Cement Association (Project No. F08-07) for financial support.

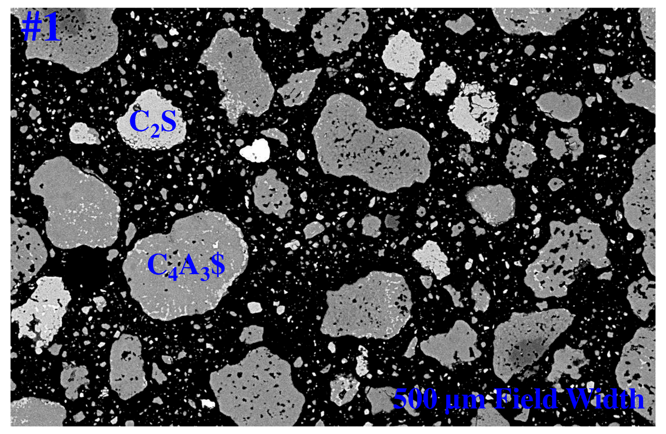
Phase Composition & Microstructure

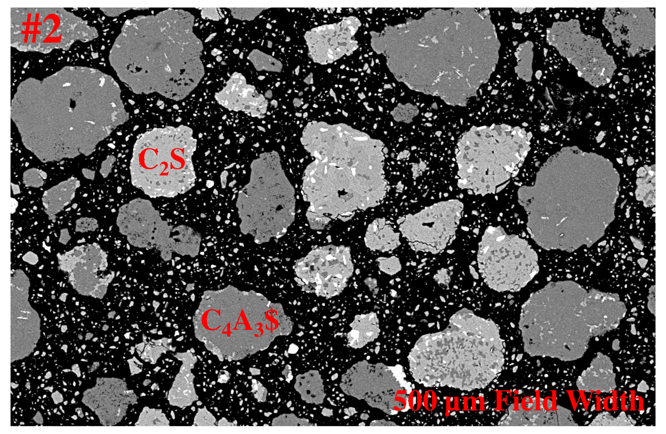


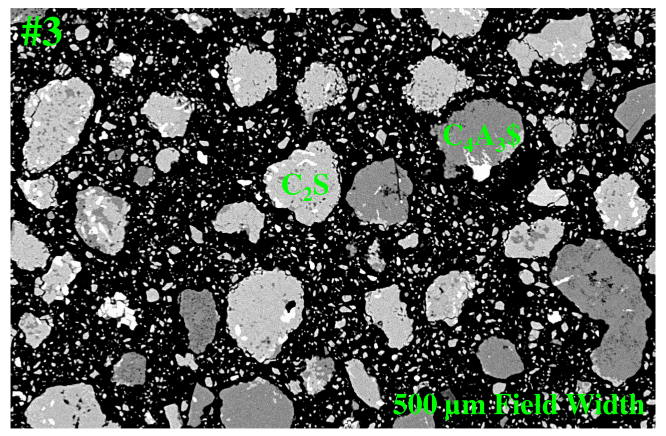
Phase	Synthetic Clinkers Phase Composition (weight %)					
	#1		#2		#3	
	TG[†]	R	TG	R	TG	R
C_2S	20	22.36	40	44.94	60	70.82
$C_4A_3\$$	60	65.34	40	41.96	20	15.38
C_4AF	10	3.20	10	6.11	10	7.21
C$	10	8.89	10	6.83	10	6.57
Lime	0	0.21	0	0.16	0	0.02

[†]TG: target phase composition; R: actual phase composition obtained through Rietveld analysis

- Quantitative x-ray diffraction results show that the CSAB cement clinkers were successfully synthesized
- Their phase compositions were reasonably close to their target phase compositions
- All the CSAB cement clinkers had low free lime contents indicating that the 1250ºC synthesis temperature was high enough for the raw materials to completely react

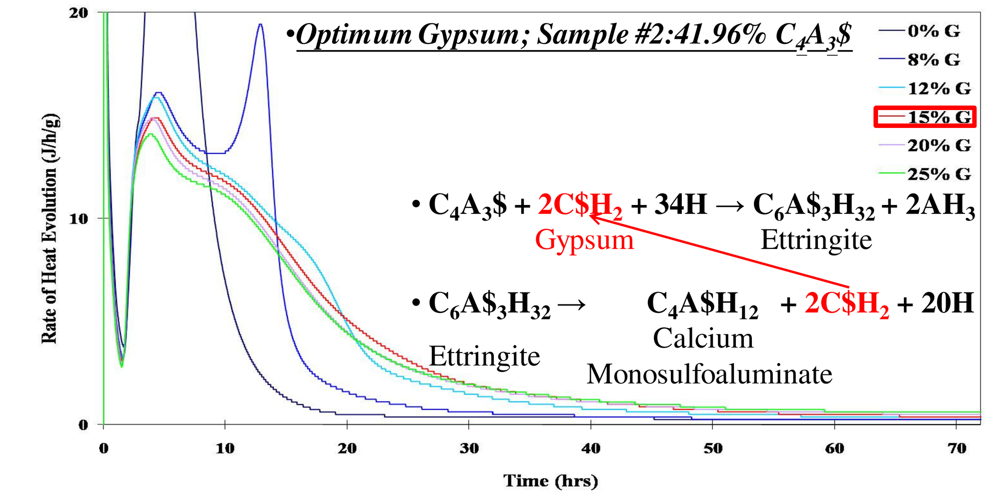




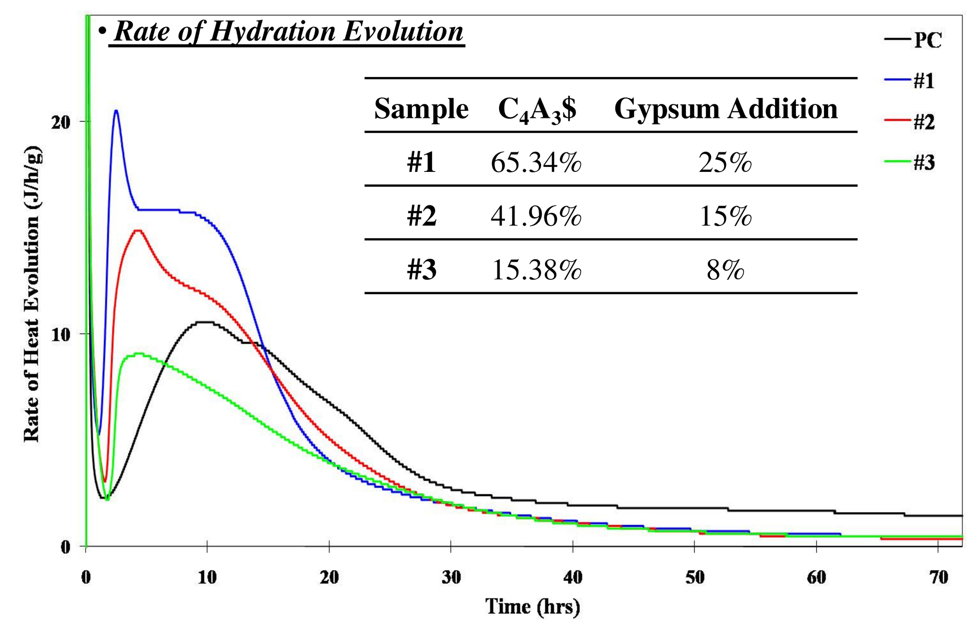


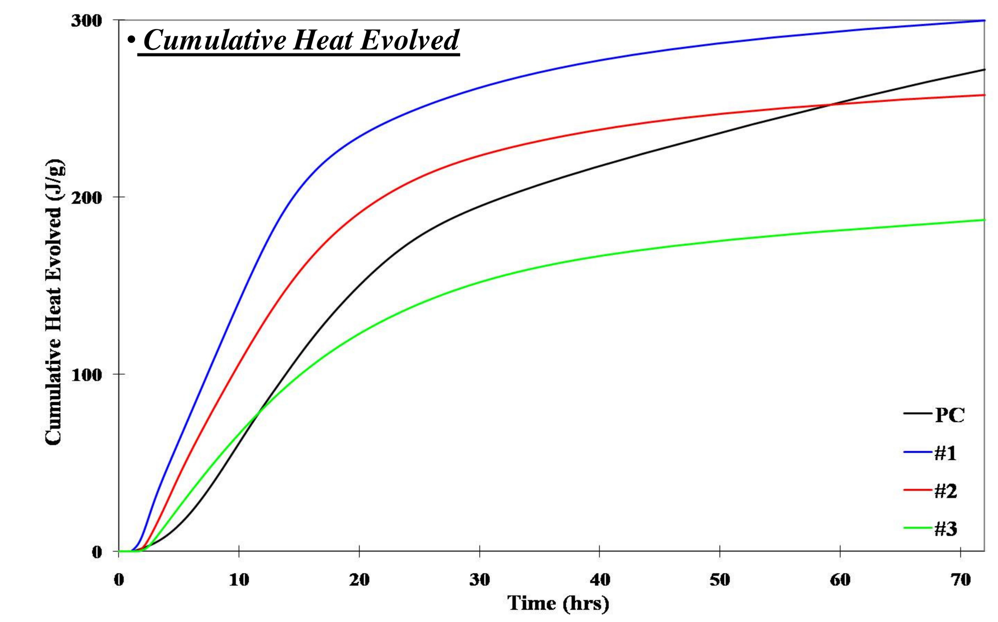
- The CSAB cement clinkers were ground to a fineness comparable to commercial portland cement
- Backscattered electron images clearly show phase contrast; dark gray areas in these images represent $C_4A_3\$$ while light gray areas represent C_2S

Early-Age Hydration Behavior & Property Development

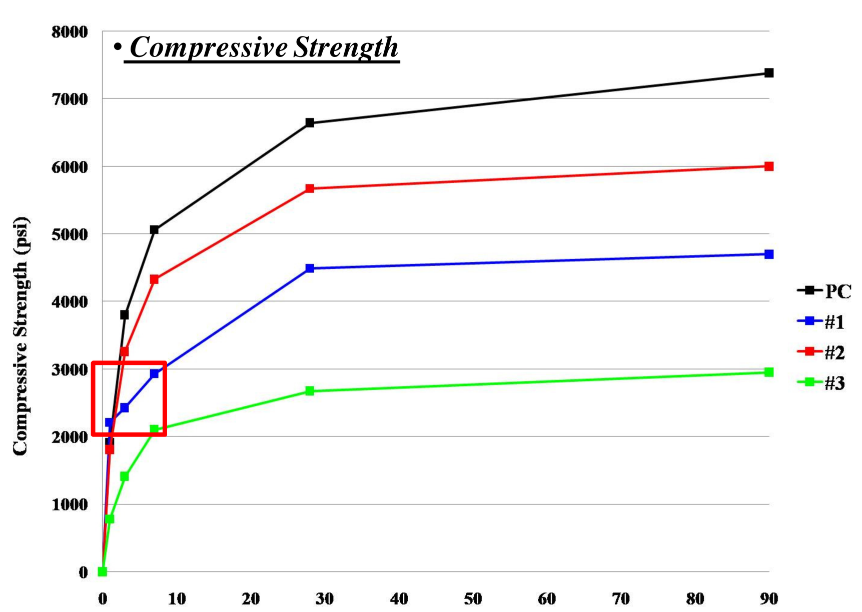


- Optimum gypsum contents for the CSAB cement clinkers were determined by the lowest amount of gypsum addition that resulted in only one main hydration peak from the reaction of $C_4A_3\$$ with gypsum and water to form ettringite; the shape of the peak no long changes with gypsum addition higher than the optimal amount
- The additional hydration peak generally indicates the formation of calcium monosulfoaluminate from ettringite due to the lack of gypsum in the system; calcium monosulfoaluminate is subject to transform back to ettringite in the presence of environmental sulfate, causing cracking



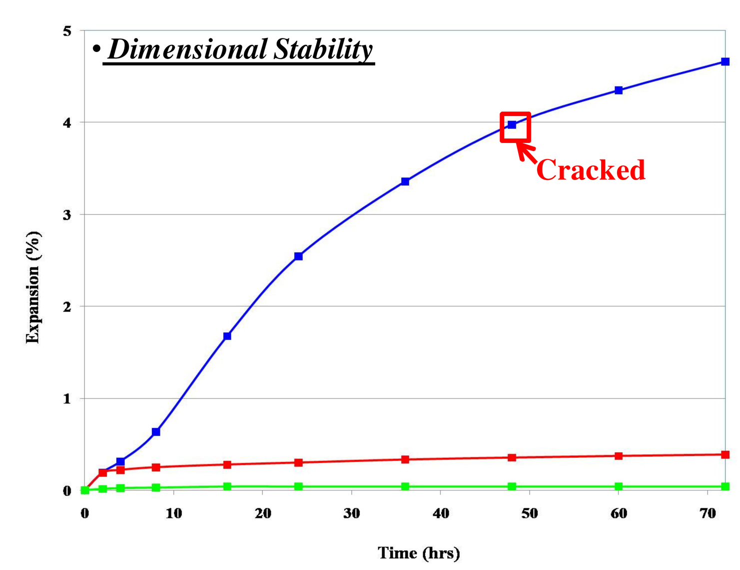


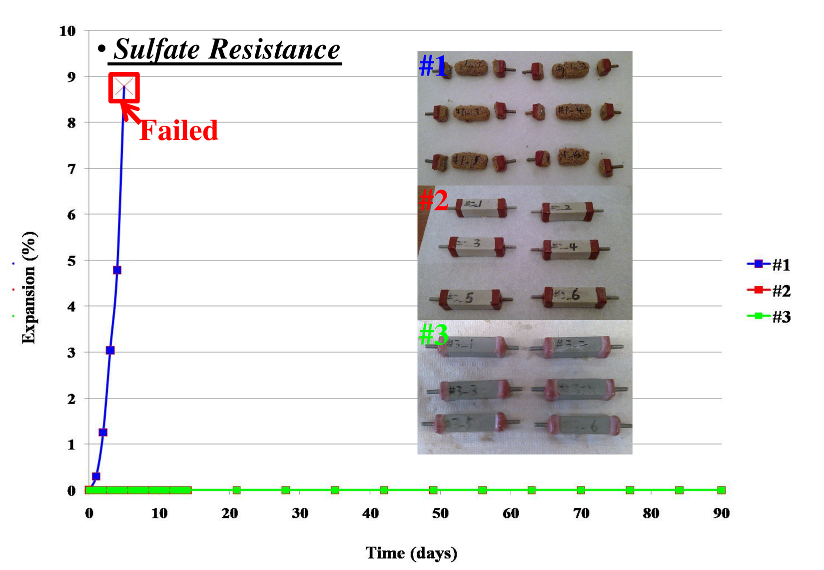
- The CSAB cement clinkers were made into cements by adding their optimum gypsum contents
- Heat of hydration results show that the synthetic cements with higher $C_4A_3\$$ contents had higher maximum heat evolution rates and cumulative heat than the synthetic cements with lower $C_4A_3\$$ contents
- Commercial portland cement (PC) reacted differently to the synthetic cements. The differences can be attributed to the different hydration mechanisms between C_3S in portland cement and $C_4A_3\$$ in CSAB cement, which both are responsible for the early-age property development



Sample	C_2S	$C_4A_3\$$	C_4AF	C$	Lime	Gypsum	Ettringite	Amorphous	Calcite
	Hydrated Synthetic Cements Phase Composition (weight %)								
#1_1Day	12.02	14.59	1.04	1.40	0.03	33.19	**26.78**	10.95	N/A
#1_3Day	11.98	8.16	0.93	1.11	0.01	14.95	**40.54**	22.32	N/A
#1_7Day	10.56	3.93	0.82	1.05	0.03	9.84	**49.71**	24.06	N/A
#1_28Day	9.12	2.61	0.54	0.80	0.03	4.53	51.72	30.65	N/A
#1_90Day	8.18	2.01	0.71	0.87	0.04	1.93	60.36	23.97	1.93
#2_1Day	24.59	10.13	2.88	2.18	0.06	6.28	24.47	29.41	N/A
#2_3Day	24.51	4.82	3.02	1.18	0.04	2.71	34.63	29.06	N/A
#2_7Day	25.19	3.12	2.61	1.03	0.07	1.89	38.54	27.55	N/A
#2_28Day	23.33	3.52	2.26	1.18	0.05	2.33	40.03	27.30	N/A
#2_90Day	20.67	3.87	2.61	1.27	0.04	2.10	40.86	26.85	1.73
#3_1Day	55.33	4.91	4.16	2.76	0.05	2.99	17.59	12.21	N/A
#3_3Day	55.76	1.76	4.00	1.68	0.10	1.92	21.11	13.67	N/A
#3_7Day	53.53	1.79	4.01	0.85	0.12	1.30	23.80	14.60	N/A
#3_28Day	52.47	1.89	4.09	0.51	0.13	1.39	24.46	15.06	N/A
#3_90Day	47.62	1.25	4.48	0.42	0.12	0.76	32.61	12.74	N/A

- The #1 CSAB cement (blue line) developed high 1 day strength due to its high fast-reacting $C_4A_3\$$ content; however, no significant strength gain was shown from 1-7 days because of the large amount of ettringite formed after cement hardened, which might cause expansion and affect compressive strength development (highlighted in red)
- The #3 CSAB cement (green line) showed sluggish strength development due to its low fast-reacting $C_4A_3\$$ and high slow-reacting C_2S content; C_2S remained mostly unhydrated after 90 days in all the synthetic cements
- The #2 CSAB (red line) cement that contained medium $C_4A_3\$$ and C_2S contents showed similar compressive strength development to commercial portland cement (PC)





- The #1 CSAB cement (blue line) expanded and cracked in the dimensional stability test, which explains the low strength gain from 1-7 days in the compressive strength test
- The #1 CSAB cement expanded severely and failed in the sulfate resistance test; sodium sulfate solution accelerated the reaction rate of unhydrated $C_4A_3\$$ and gypsum to form ettringite and caused expansion
- The #2 and #3 CSAB cements (red and green line, respectively) showed limited expansion in both the dimensional stability test and the sulfate resistance test
- **The #2 CSAB cement that contained medium $C_4A_3\$$ and C_2S contents showed good compressive strength, dimensional stability, and sulfate resistance and was considered the optimum phase composition for CSAB cement**