Use of Fly Ash Co-Mingled with Flue Gas Desulfurization Products as Alternative SCM

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ACI Convention, April 2, 2023, San Francisco

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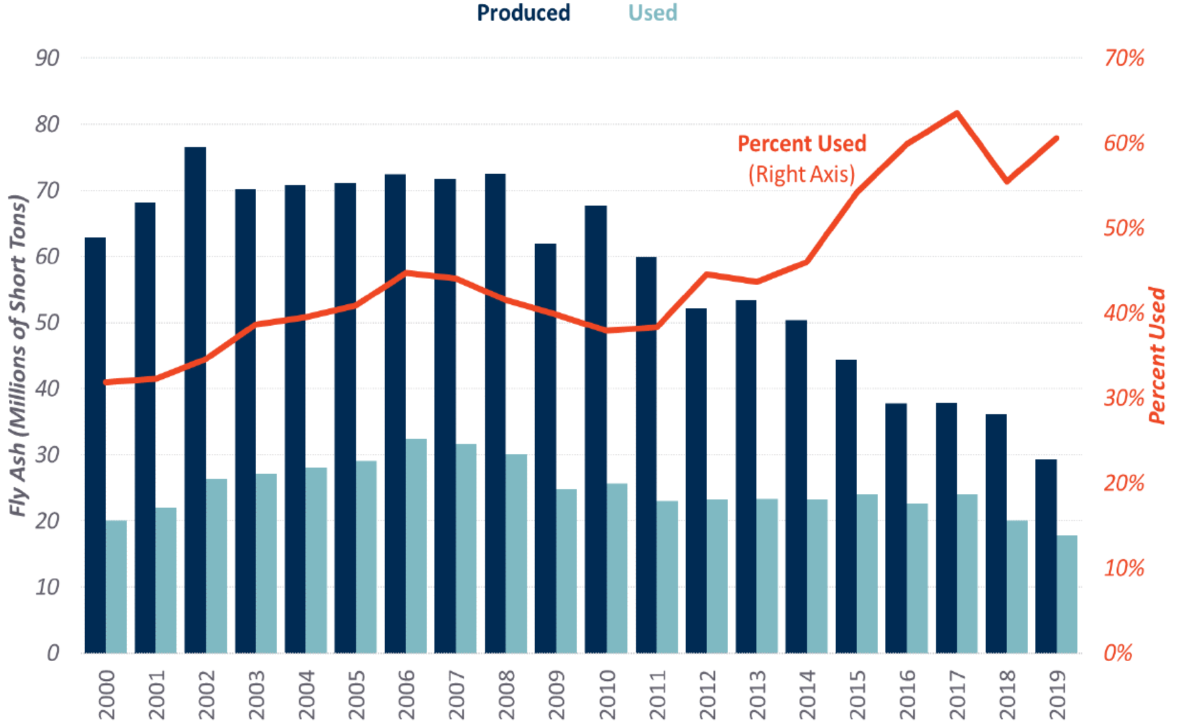
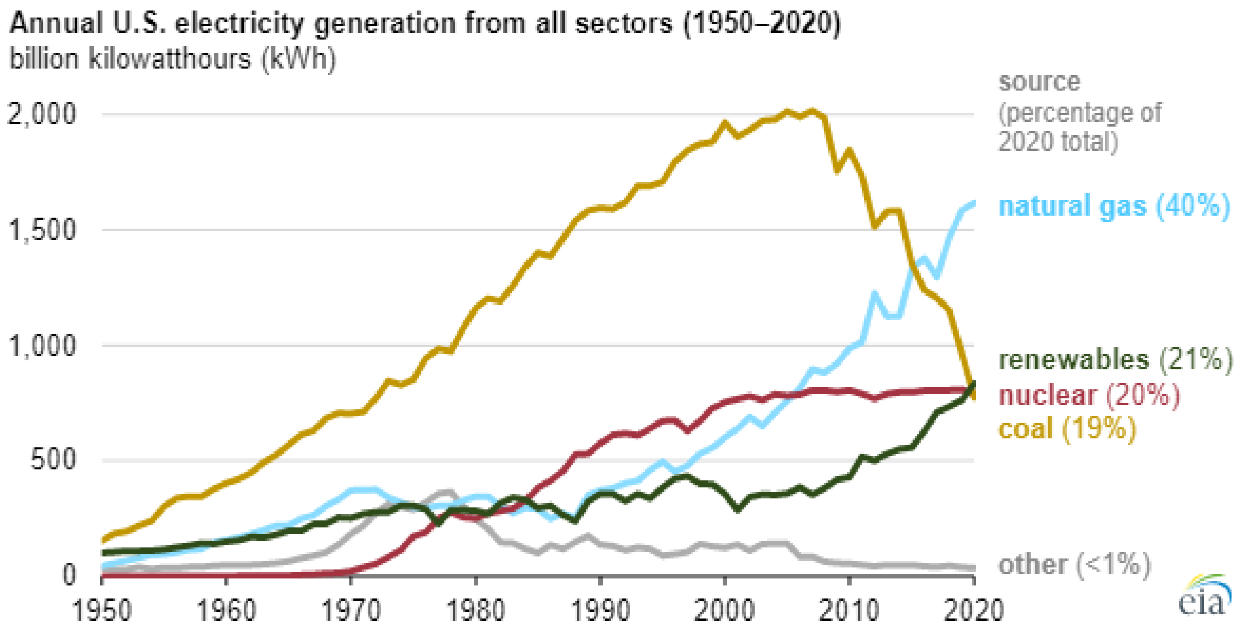
arpa·e U.S. DEPARTMENT OF ENERGY

Motivation: Decline in supply of fly ash necessitates studying and deploying non-traditional pozzolans

Source: ACAA





One new source is high SO_3 coal ash (fresh or harvested)

Currently, ASTM C618 does not allow use of fly ash with SO_3 > 5.0%

Designation: C618 – 22

Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete[1]

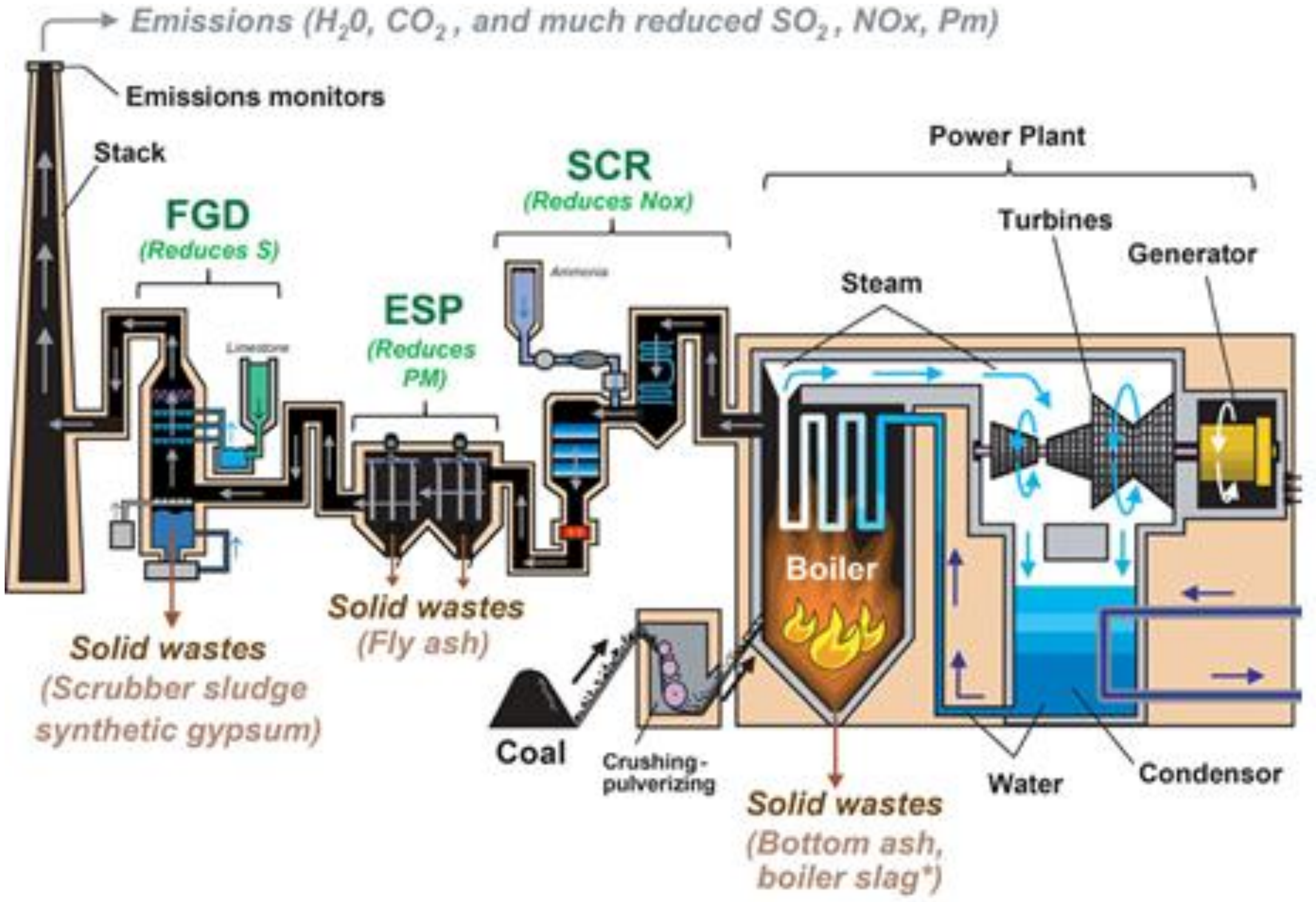
TABLE 1 Chemical Requirements

	Class		
	N	F	C
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70.0	50.0	50.0
Calcium oxide (CaO), %	report only	18.0 max.	>18.0
Sulfur trioxide (SO_3), max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	10.0	6.0[A]	6.0

[A]The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

Where does SO_3 in fly ash come from? What forms of SO_3 may be present in fly ash?

- Pyrite, gypsum, and organic sulfur in coal
- Wet FGD → scrubber sludge ($CaSO_3$)
- Dry FGD → $CaSO_3$ or $NaSO_4$ particles
- FBC boilers → $CaSO_4$ particles
- Sorbent residue may be also present in fly ash: $CaCO_3$, Na_2CO_3, trona

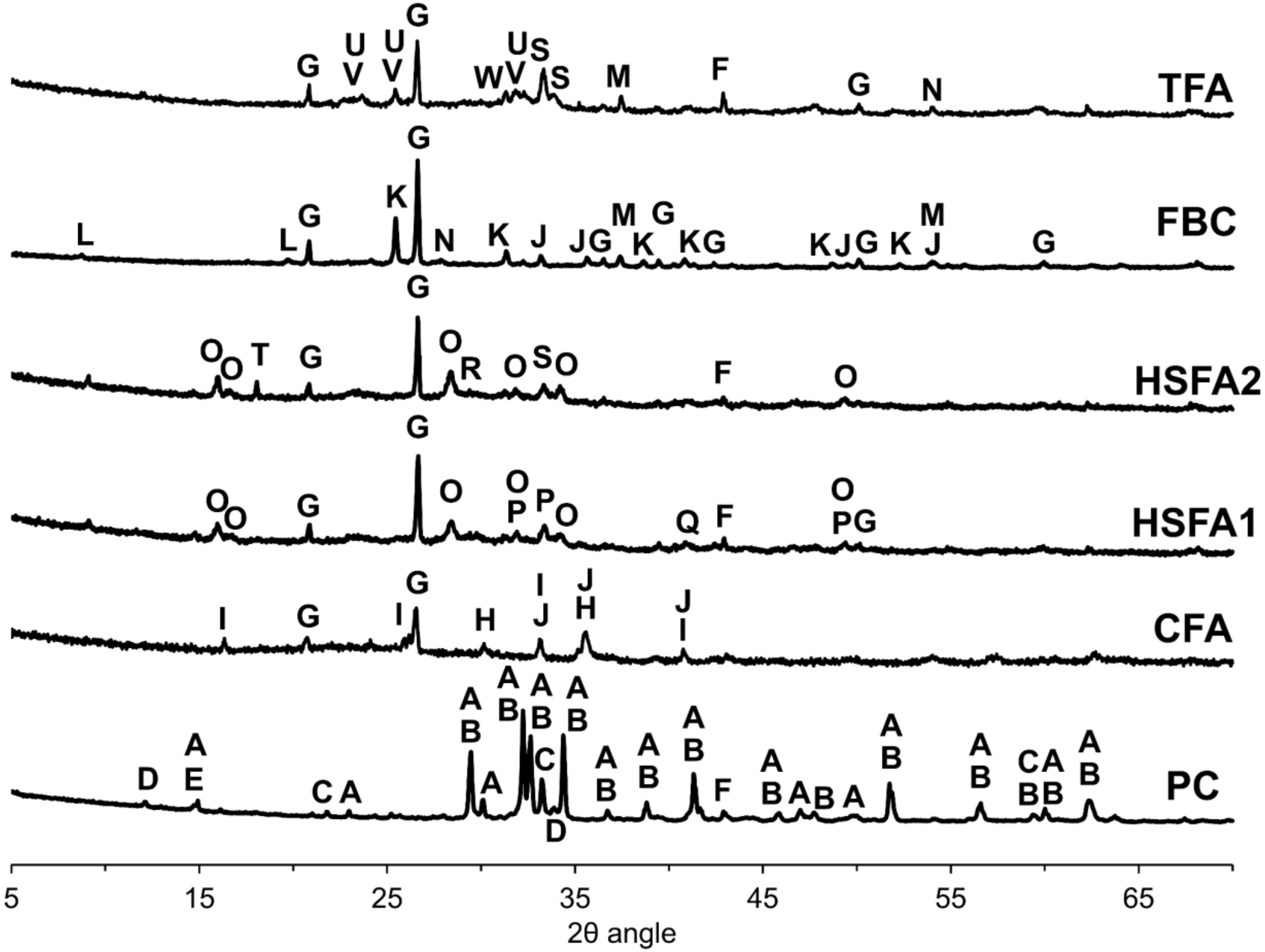


www.uky.edu/KGS/coal/coal-for-combustionbyproducts.php

We tested 4 real high SO_3 fly ashes, plus an in-spec ash doped with various forms of SO_3 up to 11%wt.

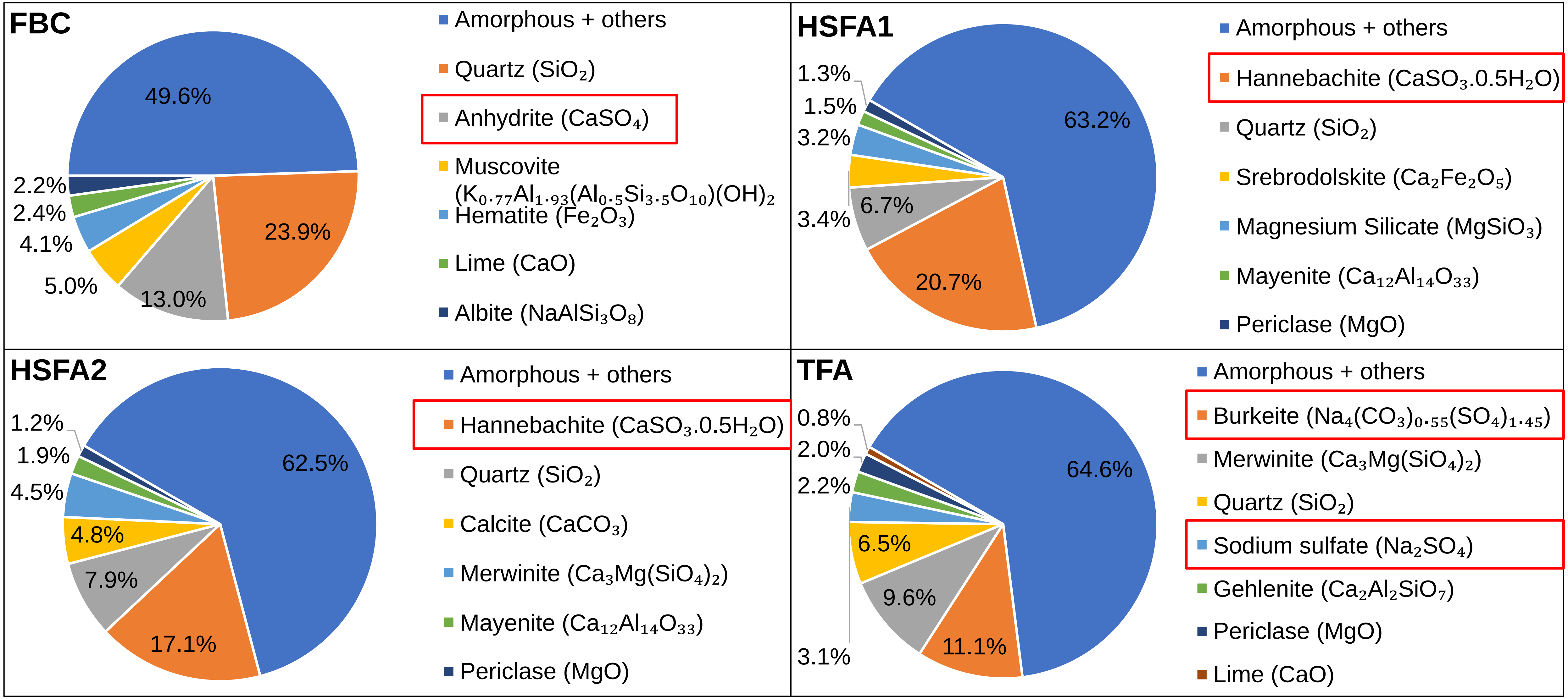
Property	ASTM C618 limits	HSFA1 – $CaSO_3$	HSFA2 – $CaSO_3$	FBC – $CaSO_4$	TFA – Na_2SO_4	Spec. fly ash (CFA)
$SiO_2+Al_2O_3+Fe_2O_3$ (wt%)	Min 50.0%	49.2%	48.3%	68.6%	51.0%	88.0%
CaO (wt%)	F≤18.0%<C	25.5% (C)	27.2% (C)	14.4% (F)	25.4% (C)	3.4% (F)
SO_3 (wt%)	Max 5.0%	13.3%	11.8%	8.0%	6.1%	0.8%
Na_2O_{eq} (wt%)	Max 4.0%	1.4%	1.3%	1.7%	6.5%	1.4%
LOI (wt%)	Max 6.0%	2.6%	2.3%	3.4%	2.6%	2.3%
Fineness (%)	Max 34%	7.5%	9.4%	32.7%	14.8%	23.1%
SAI 7-day	Either one ≥ 75%	96%	85%	86%	75%	75%
SAI 28-day		97%	99%	91%	75%	79%
Water req. (%)	Max 105%	100%	98%	107.4%	100%	100%

QXRD of the four high SO_3 fly ashes

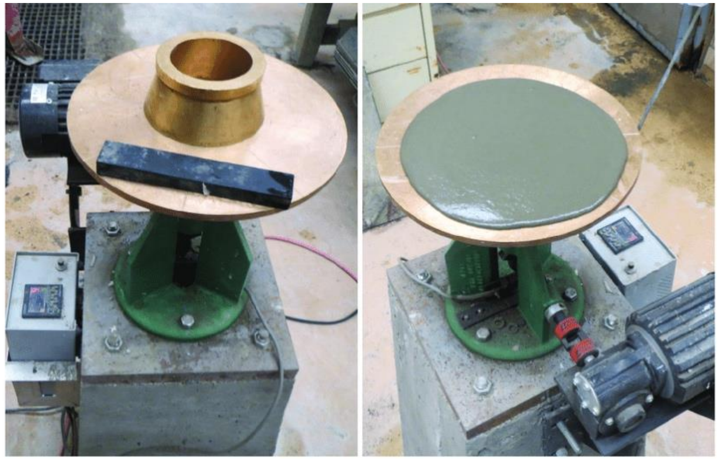


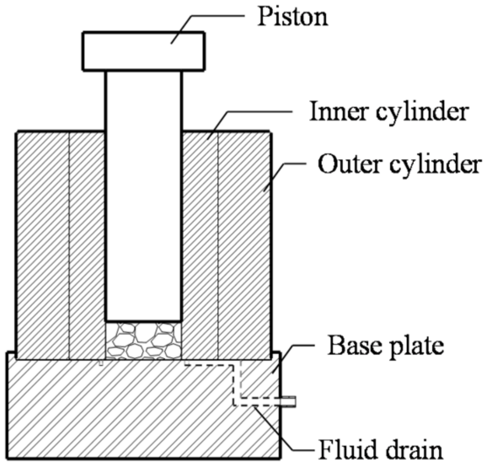
A	Tricalcium silicate	I	Mullite	Q	Magnesium silicate
B	Dicalcium silicate	J	Hematite	R	Calcite
C	Tricalcium aluminate	K	Anhydrite	S	Merwinite
D	Tetracalcium aluminoferrite	L	Muscovite	T	Mayenite
E	Hemihydrate	M	Lime	U	Burkeite
F	Periclase	N	Albite	V	Sodium sulfate
G	Quartz	O	Hannebachite	W	Gehlenite
H	Magnetite	P	Srebrodolskite		

QXRD of the four high SO_3 fly ashes



Next, we evaluated the performance of pastes and mortars with 20% fly ash as OPC repl.





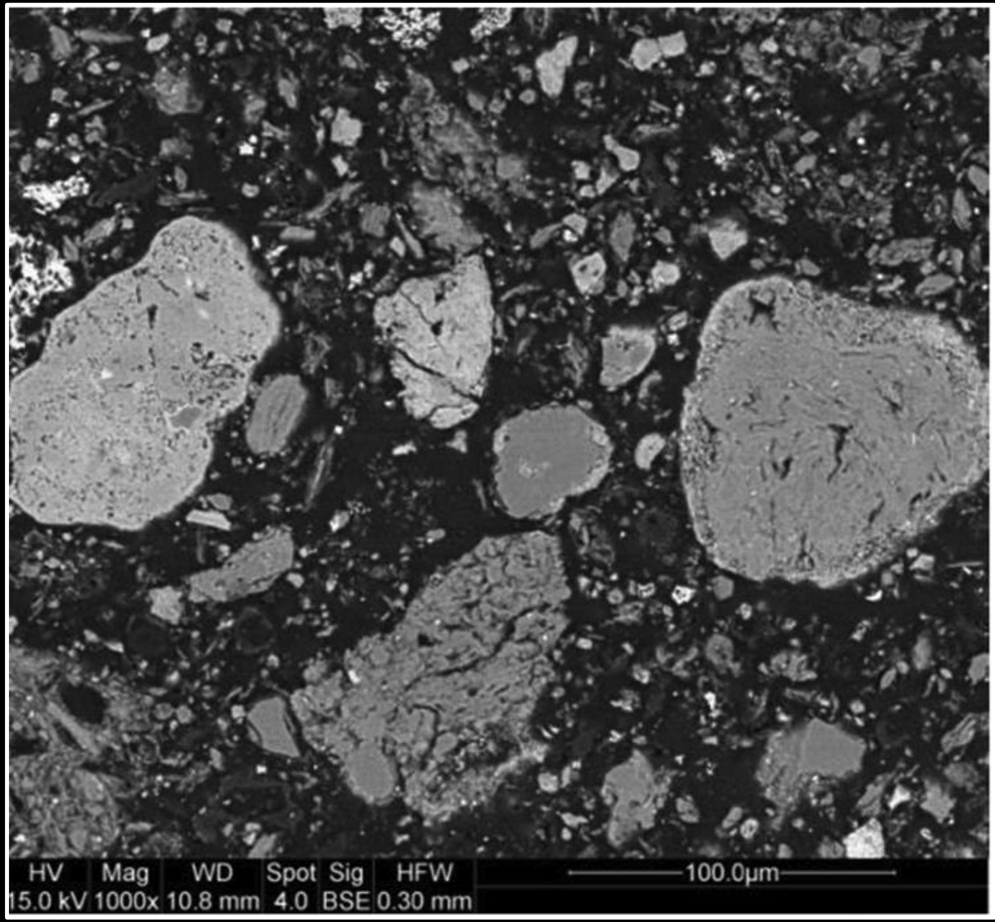
Pore fluid extraction and ICP-AES/titration/C114

Performance of pastes and mortars with 20% fly ash as OPC repl. – Table reports impact vs. Ctr fly ash

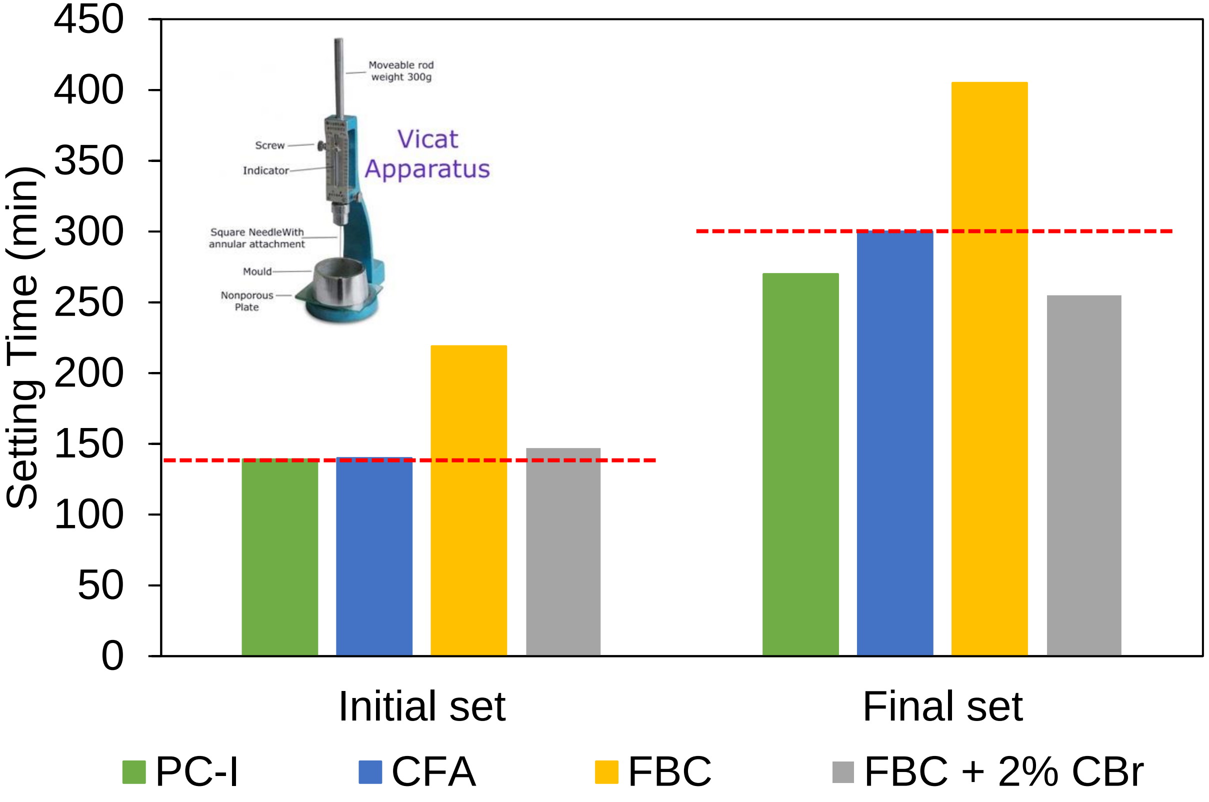
Material	Vicat Setting time	Pore fluid pH	Mortar Flow	Flow retention	Strength (early – 1d)	Strength (later – 91d)	Exp. lime water
Ctr ash doped w/ $CaSO_4$	Minimal	NA	Minimal	Minimal	Slight Reduction	Minimal	High ≥11%SO_3
Ctr ash doped $CaSO_4.2H_2O$	Minimal	NA	Minimal	Minimal	Slight Reduction	Minimal	High ≥11%SO_3
FBC fly ash	Retards (1.5x)	NA	Reduces	Minimal	Minimal	Minimal	Increase but meets limit
Ctr ash doped $CaSO_3.½H_2O$	Slightly retards (SO_3 ≥ 9%)	NA	Minimal	Minimal	Slight Reduction	Minimal	Small increase
HSFA1 & HSFA2	Significant delay (3x)	NA	Minimal	Increases	Slight reduction	Minimal	
Ctr ash doped w/ Na_2SO_4	Accelerates	Significant increase	Minimal	Minimal	Increases	Reduces	Small increase
TFA	Flash setting	Significant increase	Minimal	Rapid loss	Increases	Reduces	

FBC Fly Ash (contains $CaSO_4$)

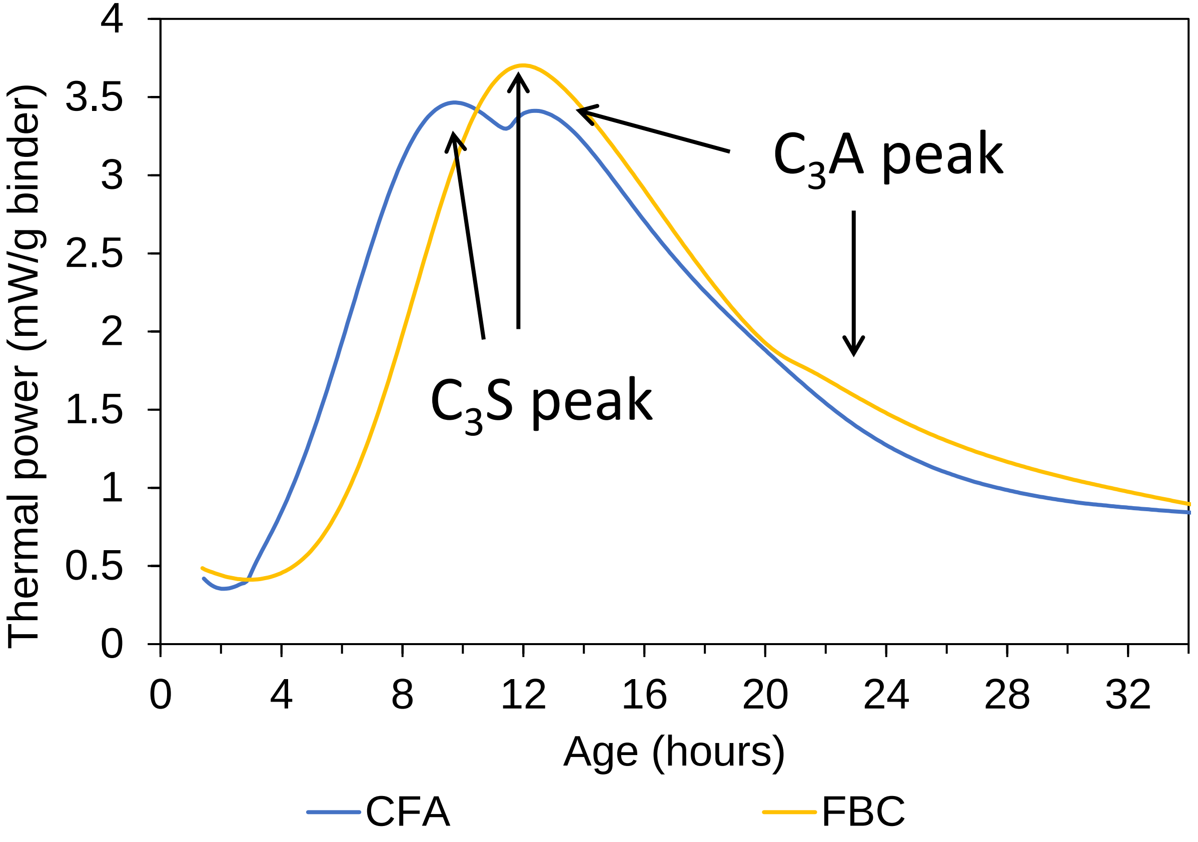
- Note the particle shape and internal porosity of fly ash
- Modestly retards setting
- Causes expansion in hardened mortar (DEF)



Vicat setting time show delay up to 2hrs
Calorimetry: small shift in C_3S and large shift in C_3A peaks

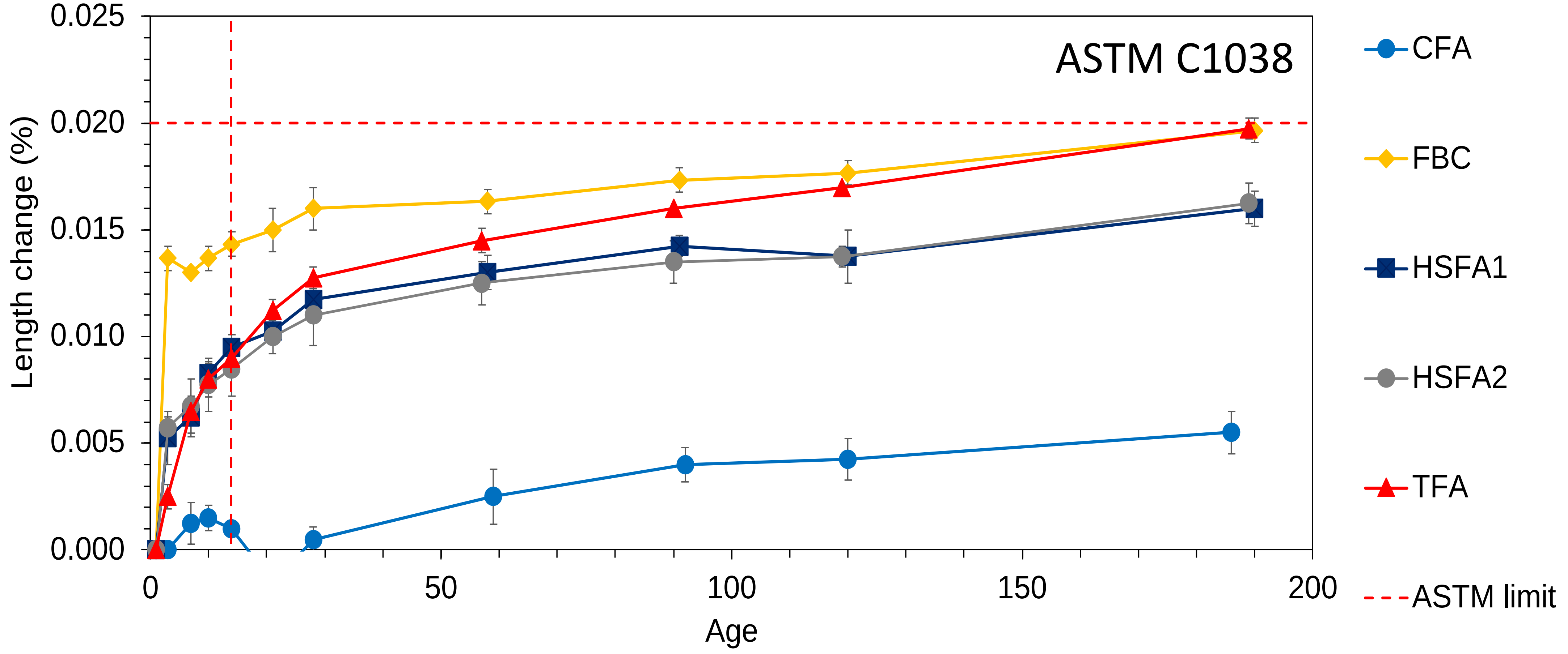


Slight set retardation which is compensated by using $CaBr_2$

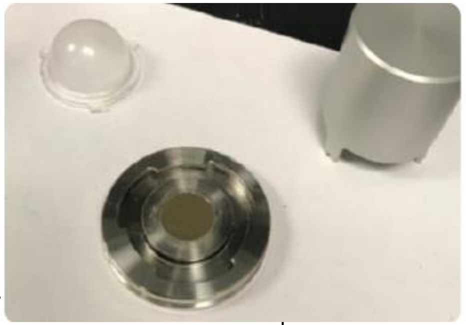


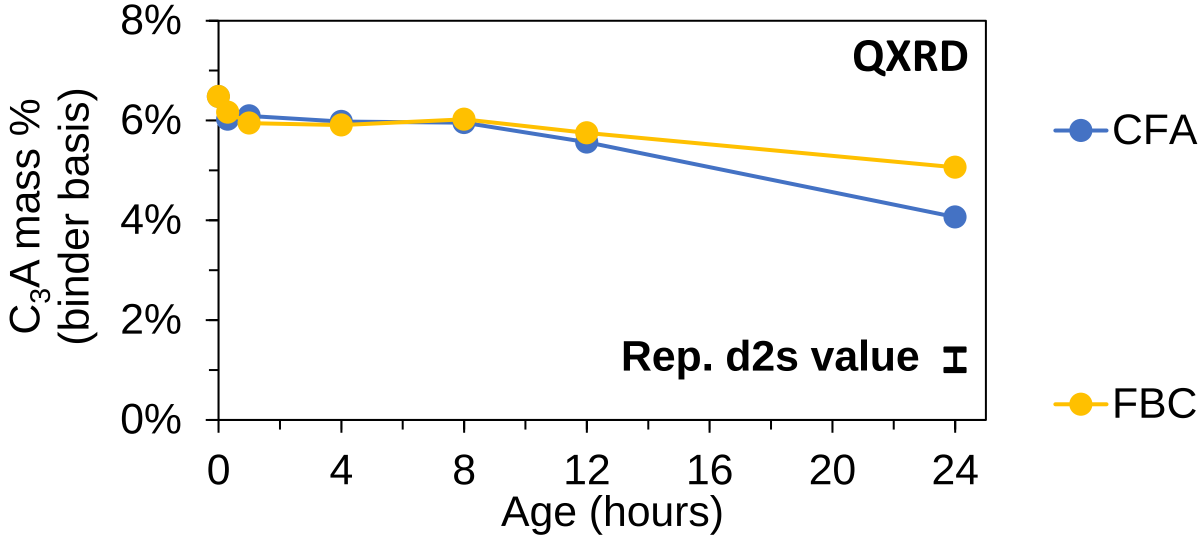
Slight C_3S retardation (2hrs) and large shift in C_3A peak

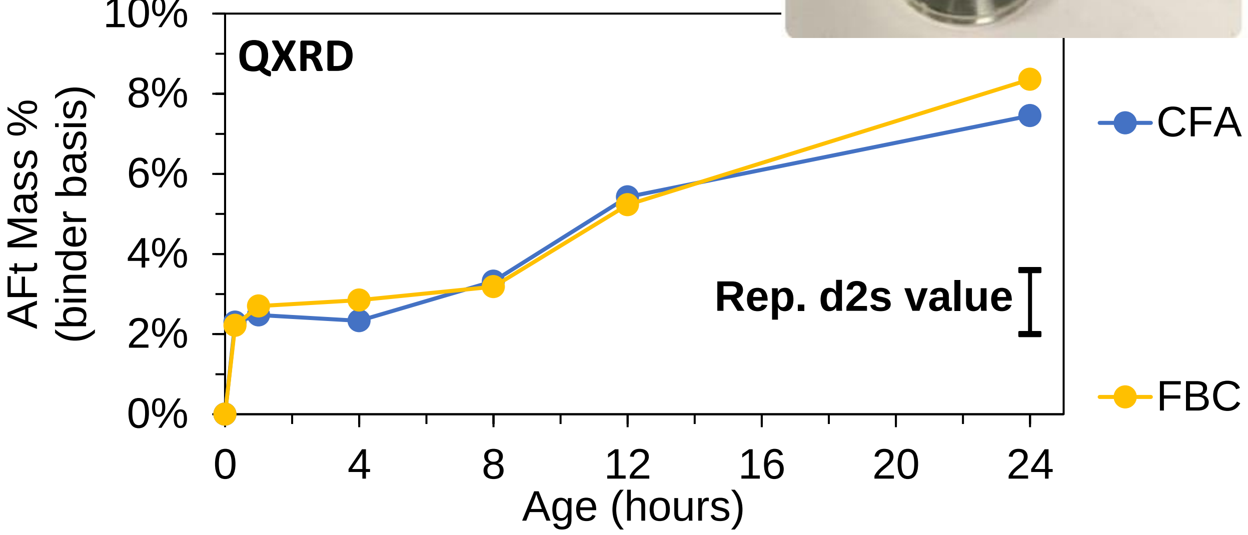
Limewater expansion continues over time (presumably due to ettringite formation)

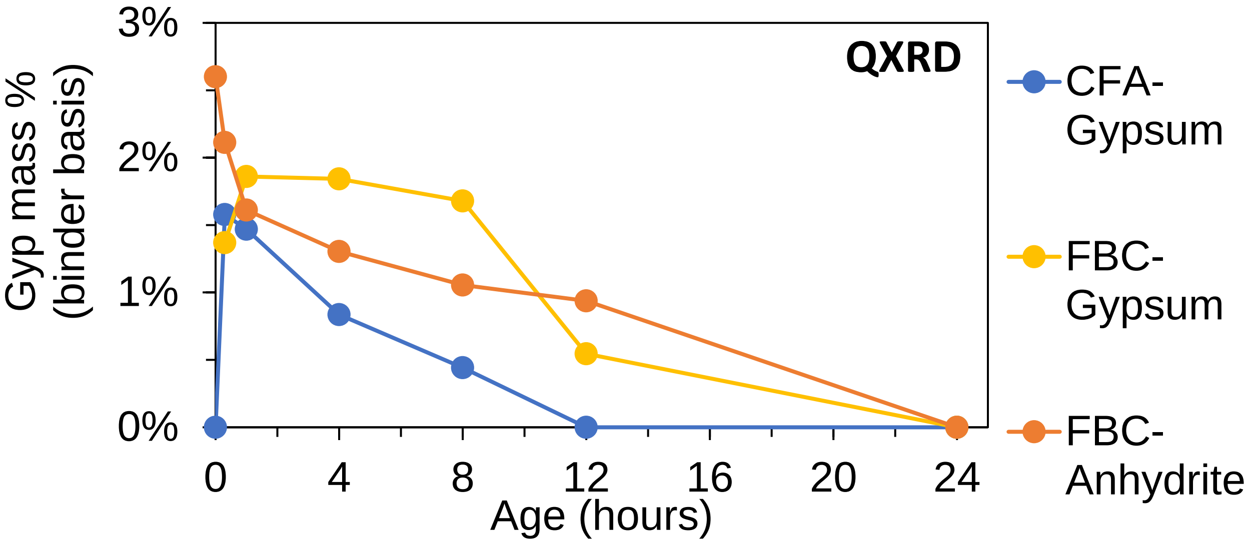


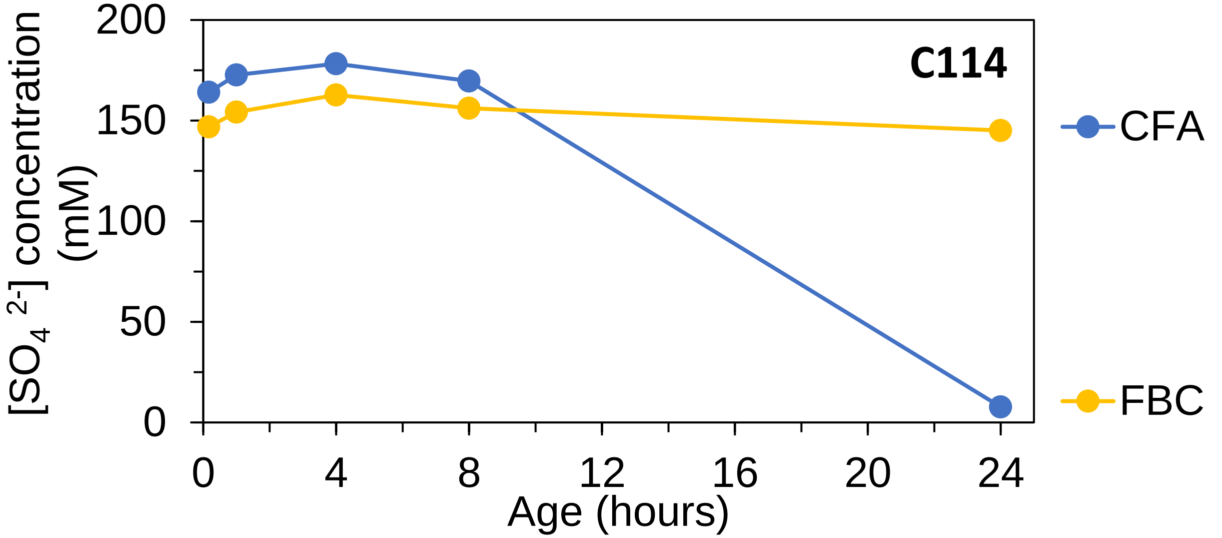
FBC fly ash supplies $CaSO_4$ which delays C_3A hydration and forms ettringite causing expansion







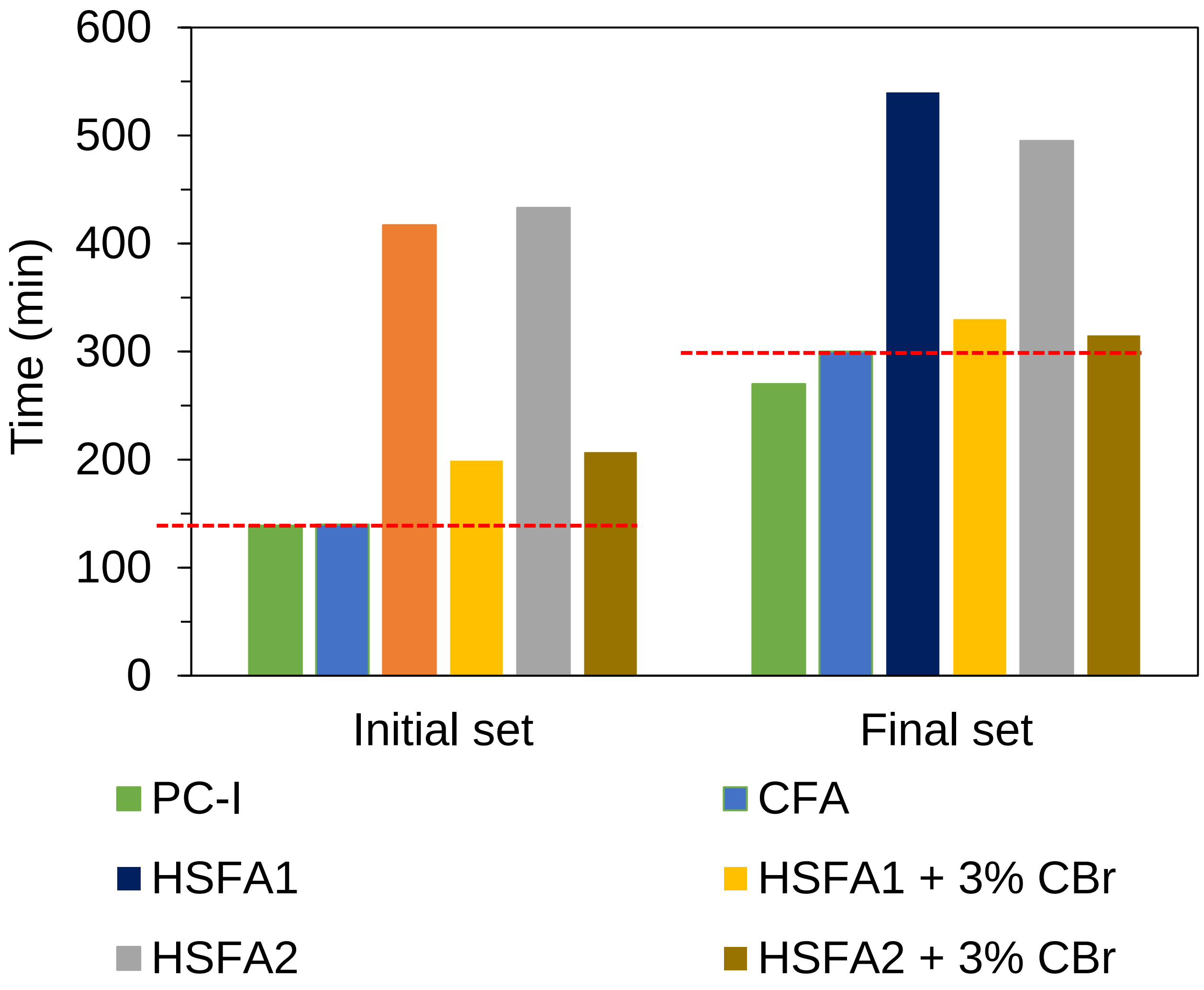




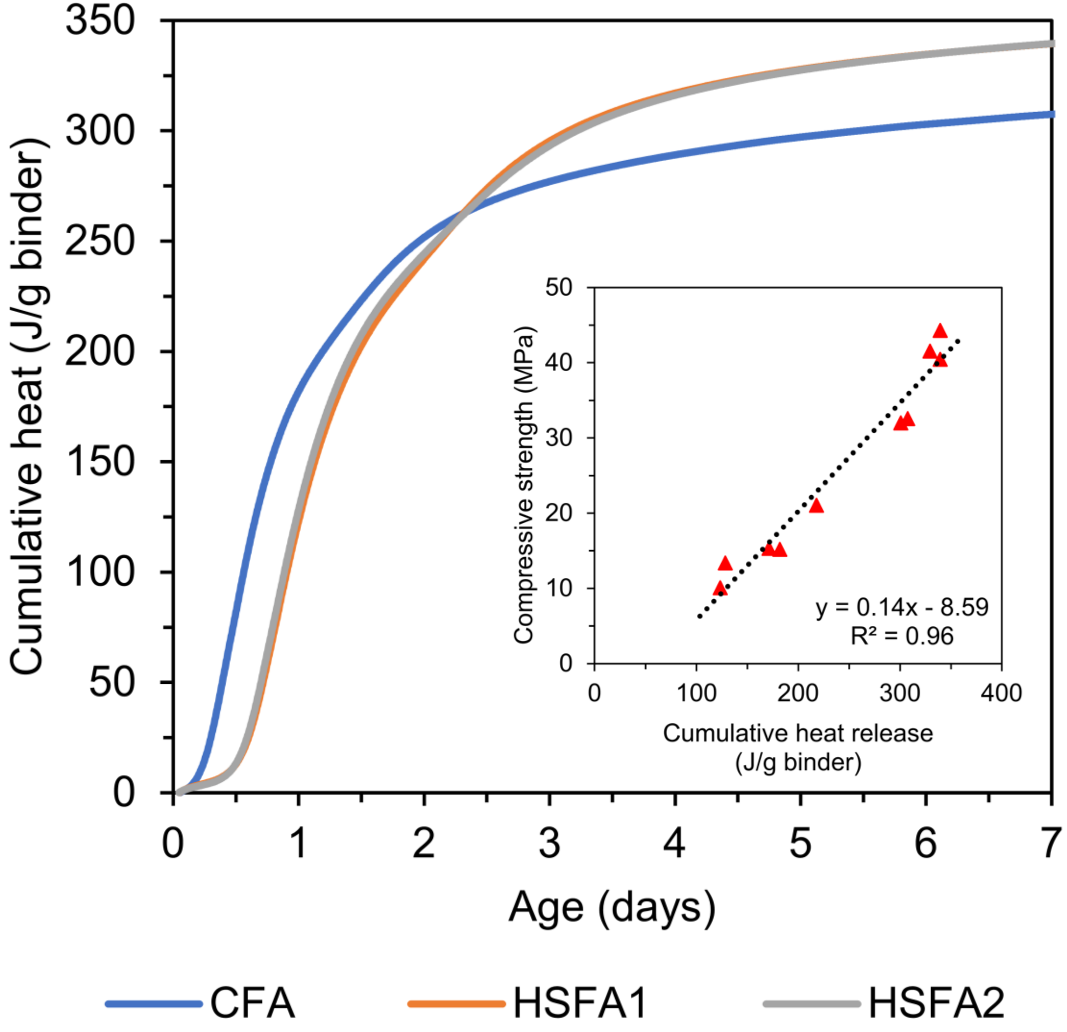
Fly ash containing $CaSO_3$

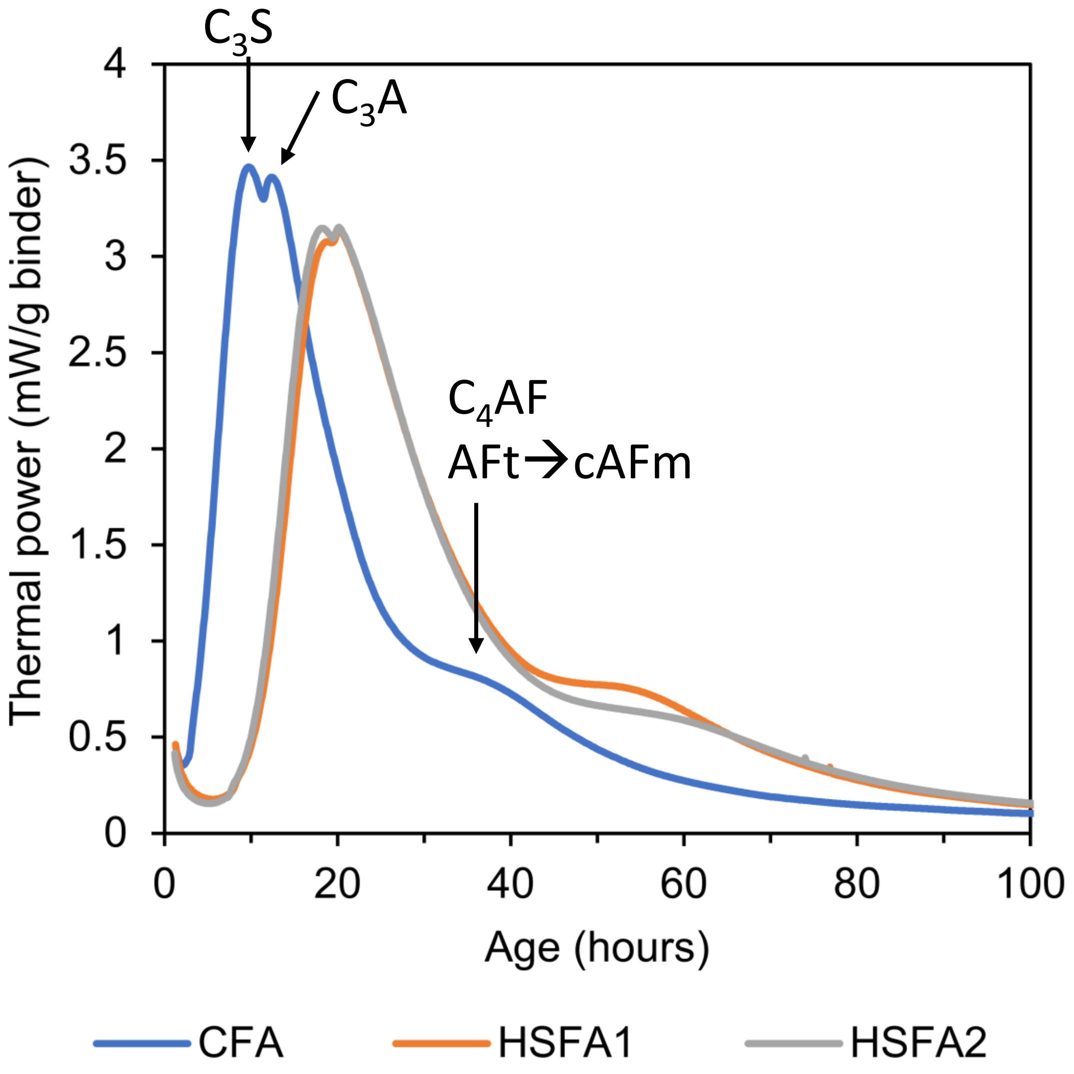
Material	Vicat Setting time	Pore fluid pH	Flow	Flow retention	Strength (early – 1d)	Strength (later – 91d)	Exp. lime water
Ctr ash doped $CaSO_3.½H_2O$	Slightly retards ($SO_3 \geq 9\%$)	NA	Minimal	Minimal	Slight Reduction	Minimal	Small increase
HSFA1 & HSFA2	Significant delay (3x)	NA	Minimal	Increases	Slight reduction	Minimal	

$CaSO_3$ initial and final setting by >4hrs. Accelerators can help.

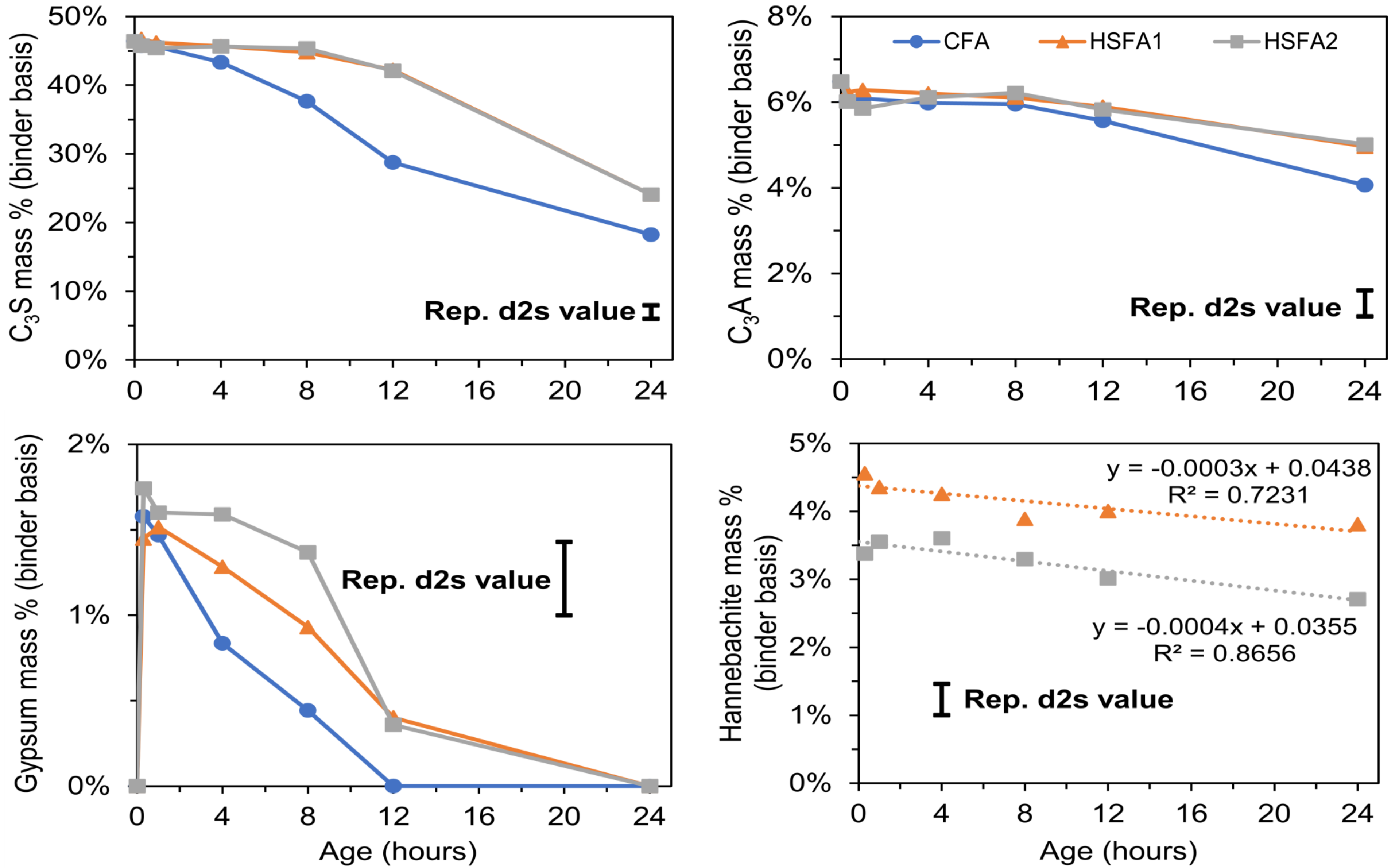


$CaSO_3$ delays both C_3S and C_3A hydration. Cumulative heat (and strength) cross over at ~3 days.

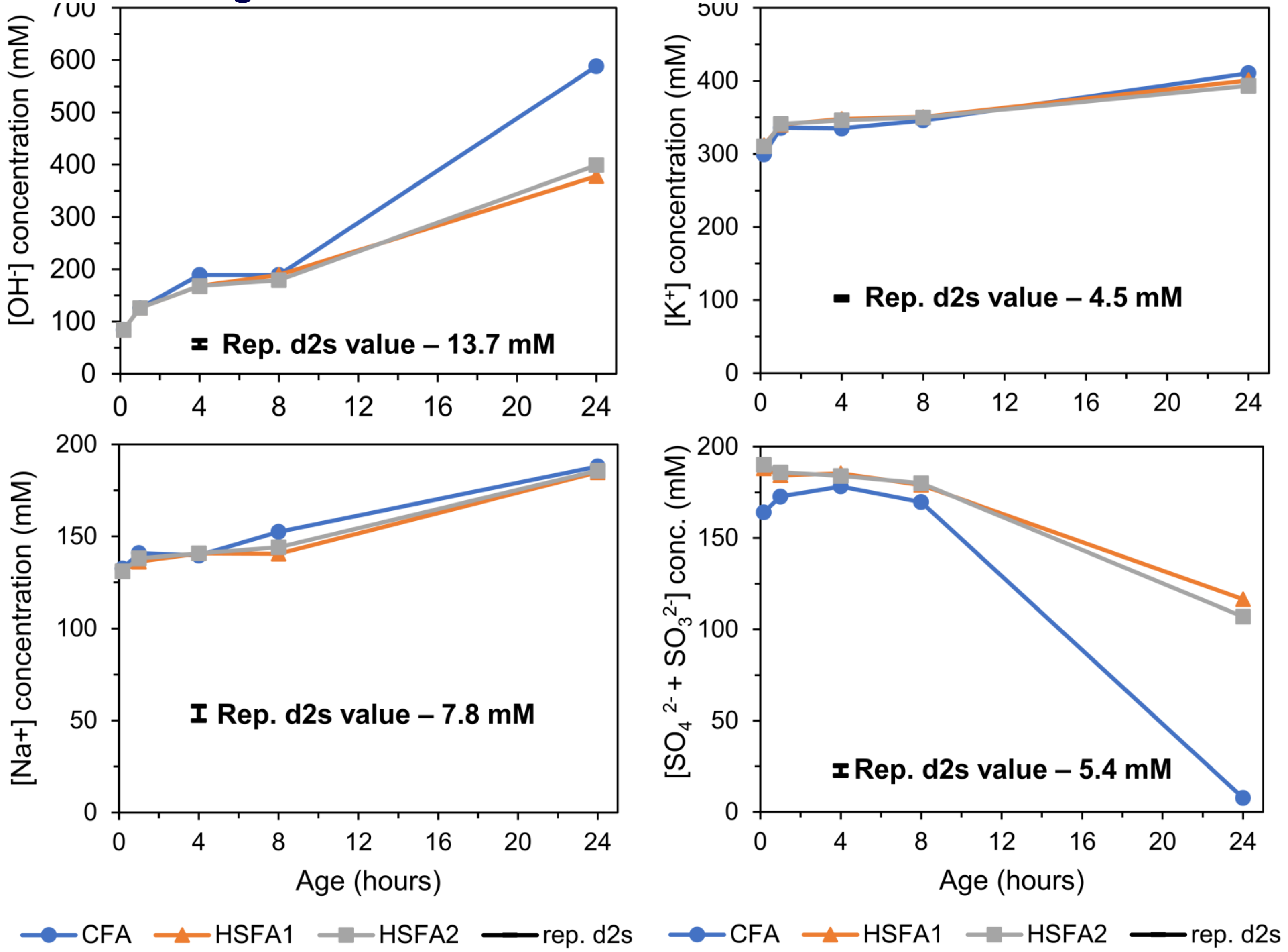




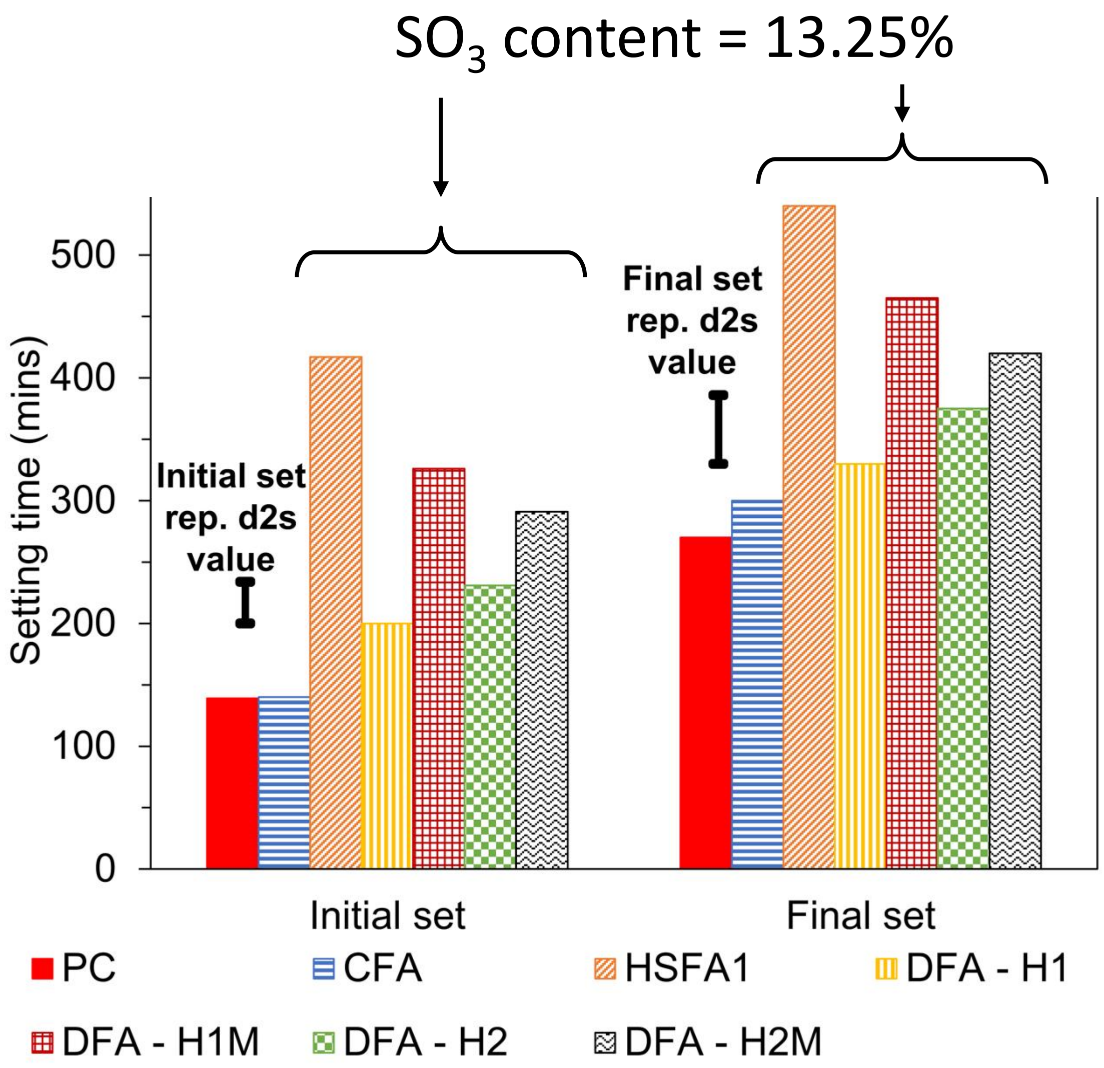
QXRD: $CaSO_3$ retards rxn of C_3S, C_3A, Gyp w/in the first 24h. $CaSO_3$ is only slowly consumed.



ICP: $CaSO_3$ lowers [OH], maintains higher [SOx]
(due to reduced C_3S hydration and C-S-H availability as [SOx] sink)



$CaSO_3$ solubility is low (2mM), so its particle size matters! (finer $CaSO_3$ leads to further setting delay)



Material	Particle size (µm)		
	D10	D50	D90
Han-1	8.8	58.8	214.4
Han-1 milled	**3.0**	**24.7**	74.7
Han-2	8.4	14.8	24.8
Han-2 milled	**2.1**	**9.3**	18.5
HSFA1	**1.4**	5.9	35.0
HSFA2	**1.7**	12.2	43.8

Beneficiation options:

1. Accelerators (chemical or fine LS powder)
2. Acid washing (generates SO_2 gas)
3. Discard fine fraction of fly ash (<3um)

Conclusions

- Both the form and content of SO_3 in fly ash matter.
- The 5.0% SO_3 limit of ASTM C618 maybe too conservative.
- Instead, we recommend performance testing for flow, set time, strength, and expansion of mortar.
- $CaSO_4$ (in FBC fly ash) leads to ettringite formation and risk of expansion only when $SO_3 \geq 11\%$.
- $CaSO_3$ (and SO_3 ions) retard C_3S hydration → delay C_3A and Gyp consumption.
- More work needed in understanding long-term hydration, durability, and methods to offset setting delays.

Thank you very much!

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References

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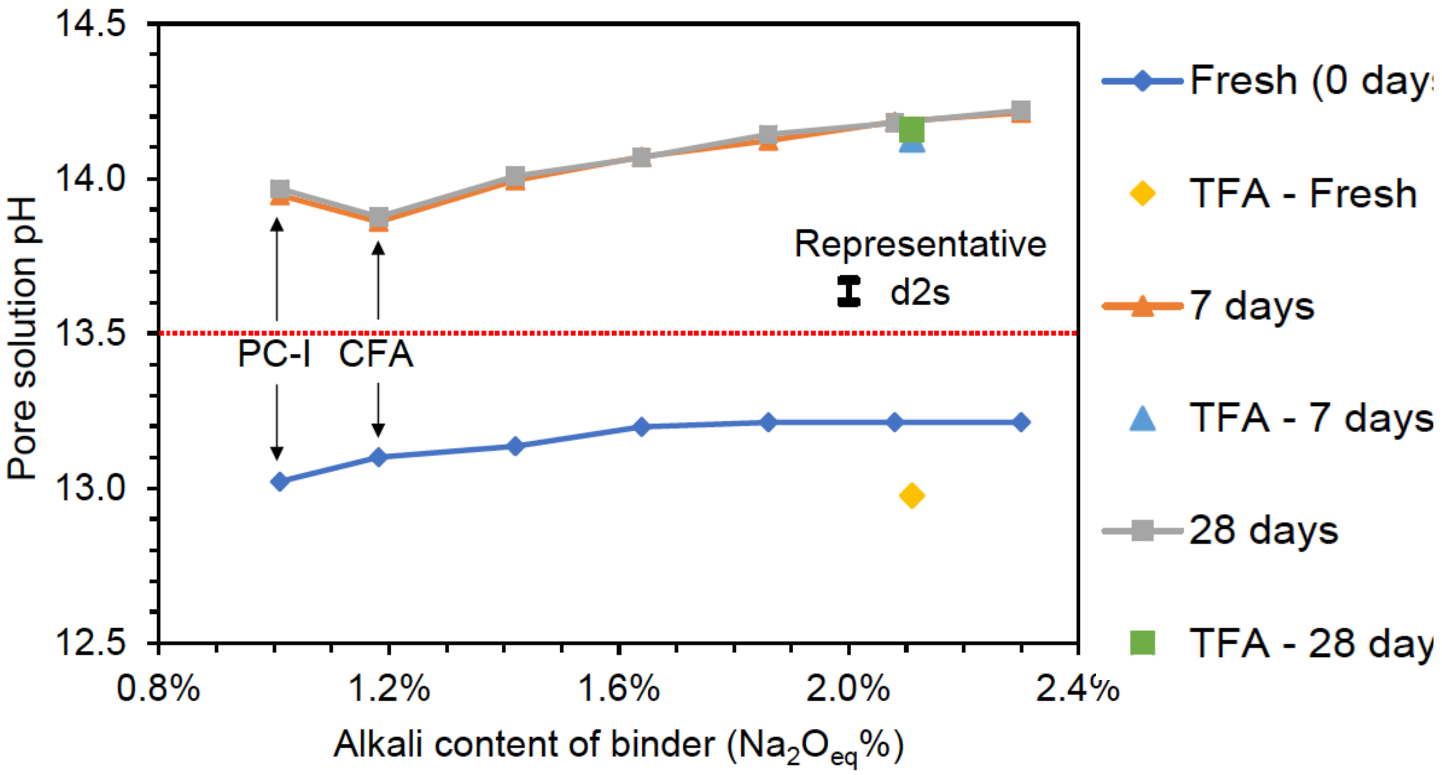
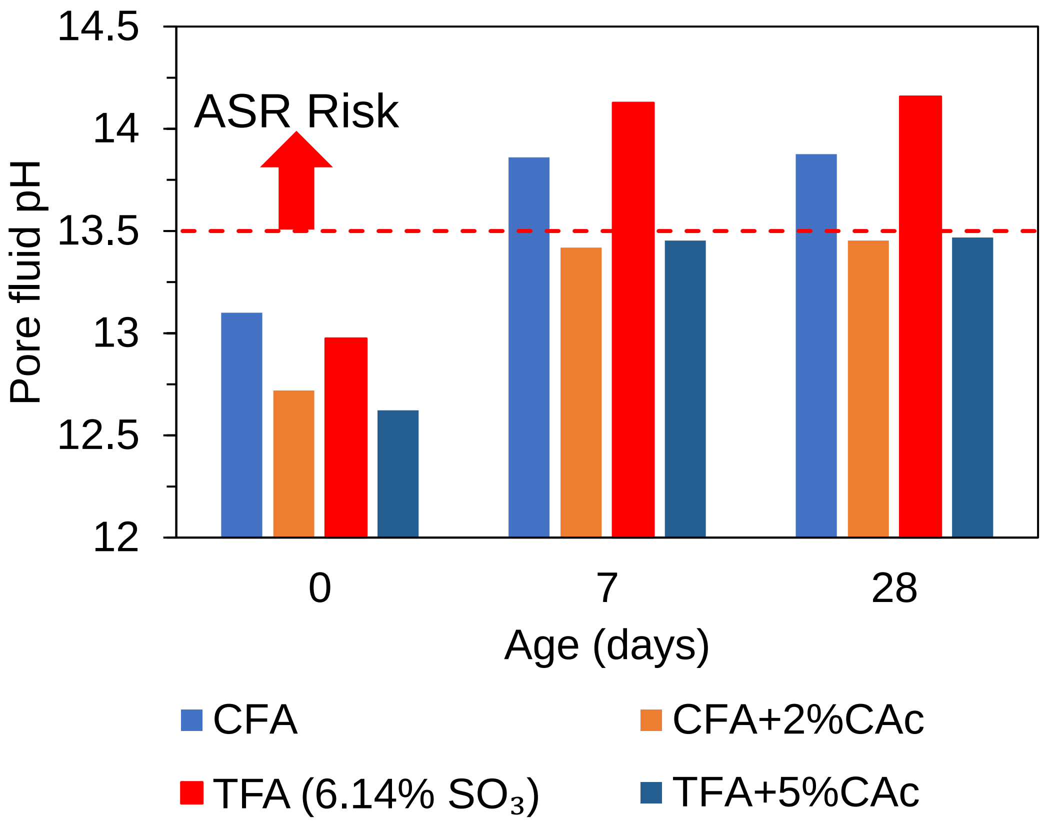
- M. Zahedi, K. Jafari, F. Rajabipour, Properties and durability of concrete containing fluidized bed combustion (FBC) fly ash, Construction and Building Materials, 258 (2020); https://doi.org/10.1016/j.conbuildmat.2020.119663
- G. Kaladharan, F. Rajabipour, Evaluation and beneficiation of high sulfur and high alkali fly ashes for use as supplementary cementitious materials in concrete, Construction and Building Materials, 339 (2022); https://doi.org/10.1016/j.conbuildmat.2022.127672
- G. Kaladharan, RM. Ghantous, F. Rajabipour, Early age hydration behavior of Portland cement-based binders incorporating fly ash contaminated with flue gas desulfurization products, Cement and Concrete Composites, in review

Fly ash containing Na_2SO_4 (e.g., trona contaminated ash)

Material	Vicat Setting time	Pore fluid pH	Flow	Flow retention	Strength (early – 1d)	Strength (later – 91d)	Exp. lime water
Ctr ash doped w/ Na_2SO_4	Accelerates	Significant increase	Minimal	Minimal	Increases	Reduces	Small increase
TFA	Flash setting	Significant increase	Minimal	Rapid loss	Increases	Reduces	

Higher Na_2SO_4 in fly ash leads to higher pore solution pH; Good news: pH-regulating admixtures work

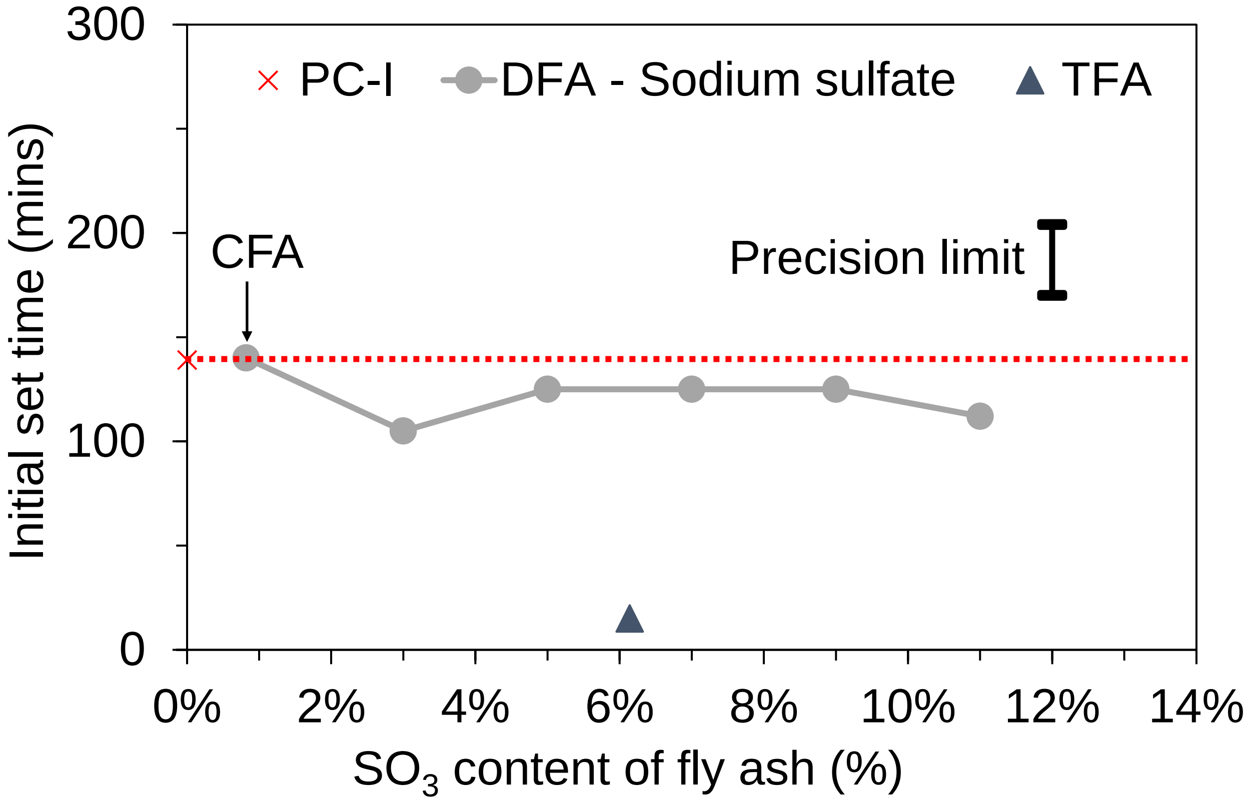




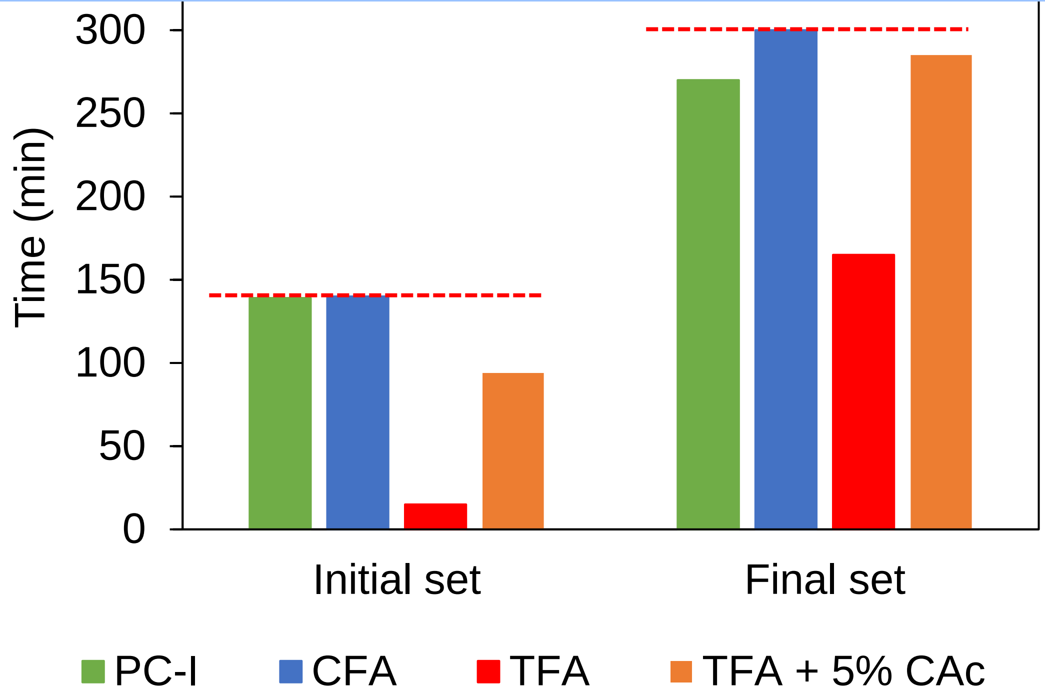
$$Na_2SO_4 + Ca(OH)_2 \rightarrow 2\ NaOH + CaSO_4$$

$$Ca(CH_3COO)_2 + 2\ NaOH \rightarrow 2\ Na(CH_3COO) + Ca(OH)_2$$

Doping Na_2SO_4 in fly ash slightly accelerates setting, but trona fly ash flash sets, why?

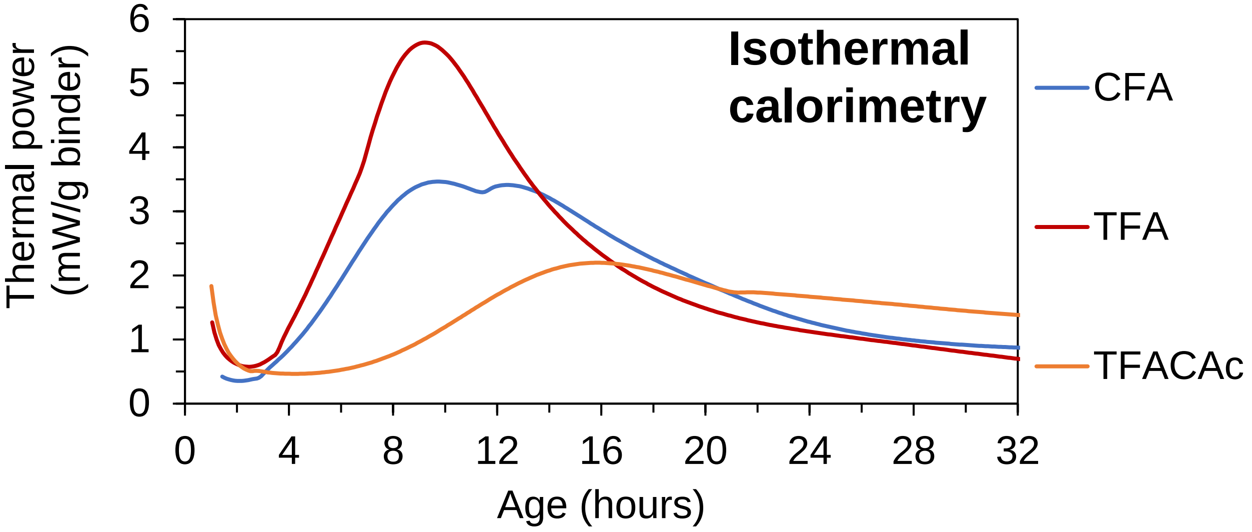


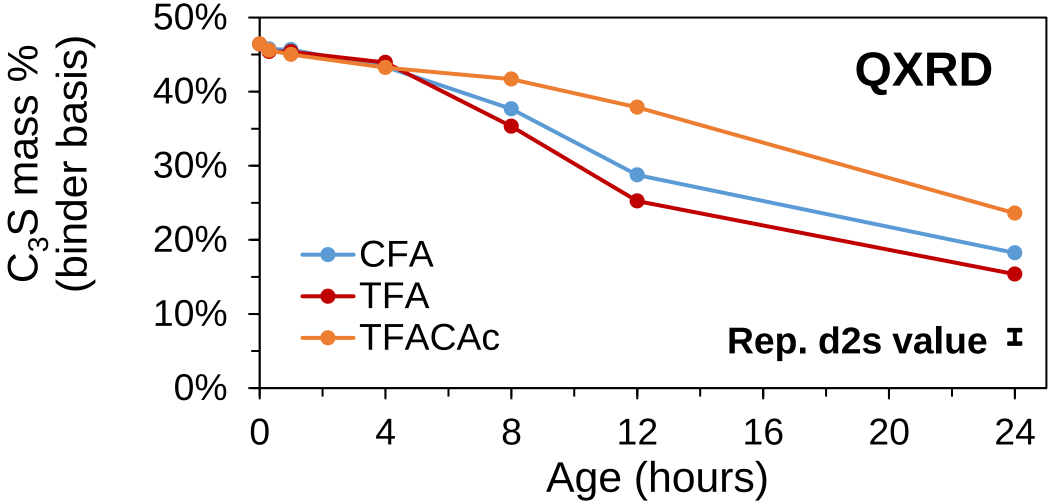
Na_2CO_3 accelerates C_3A hydration

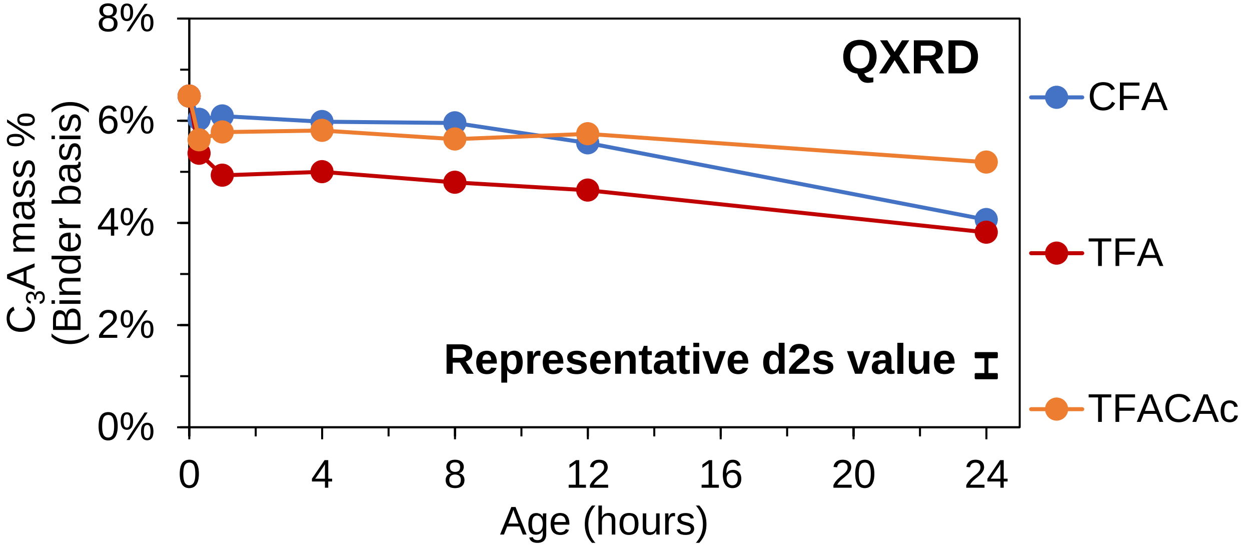


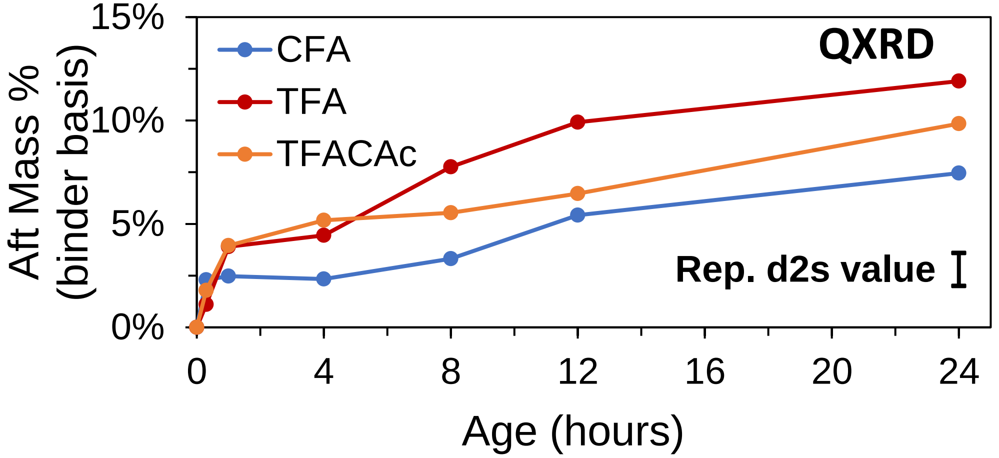
$$Ca(CH_3COO)_2 + (Na_2CO_3/Na_2SO_4) \rightarrow 2\ Na(CH_3COO) + (CaCO_3/CaSO_4)$$

Na_2CO_3 accelerates C_3A and C_3S hydration; CAc retards both C_3A and C_3S

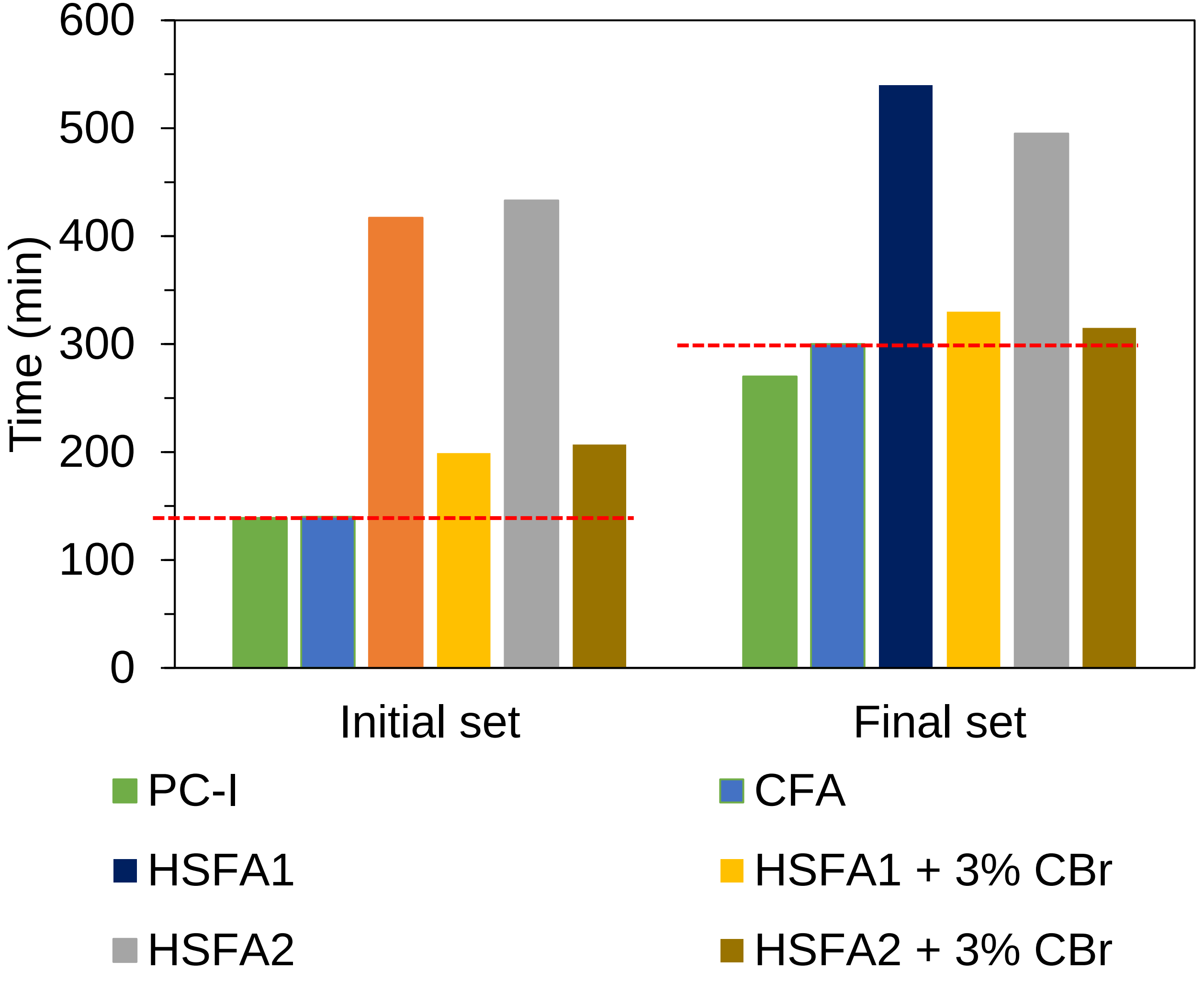


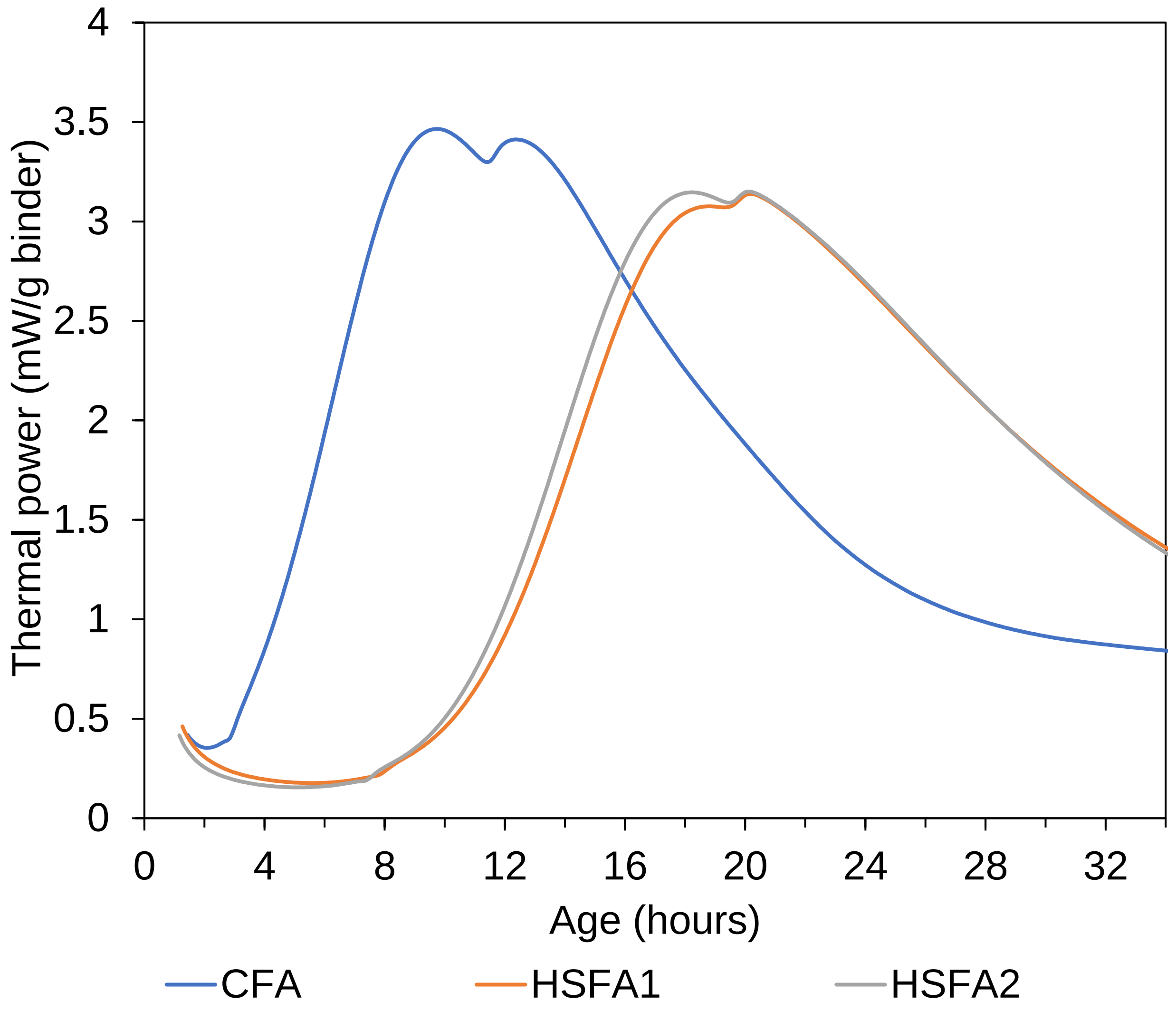






$CaSO_3$ delays both C_3S and C_3A hydration
Accelerators can help





Existing standards limit SO_3 and alkali content in fly ash; validity of limits tested using doped and real systems

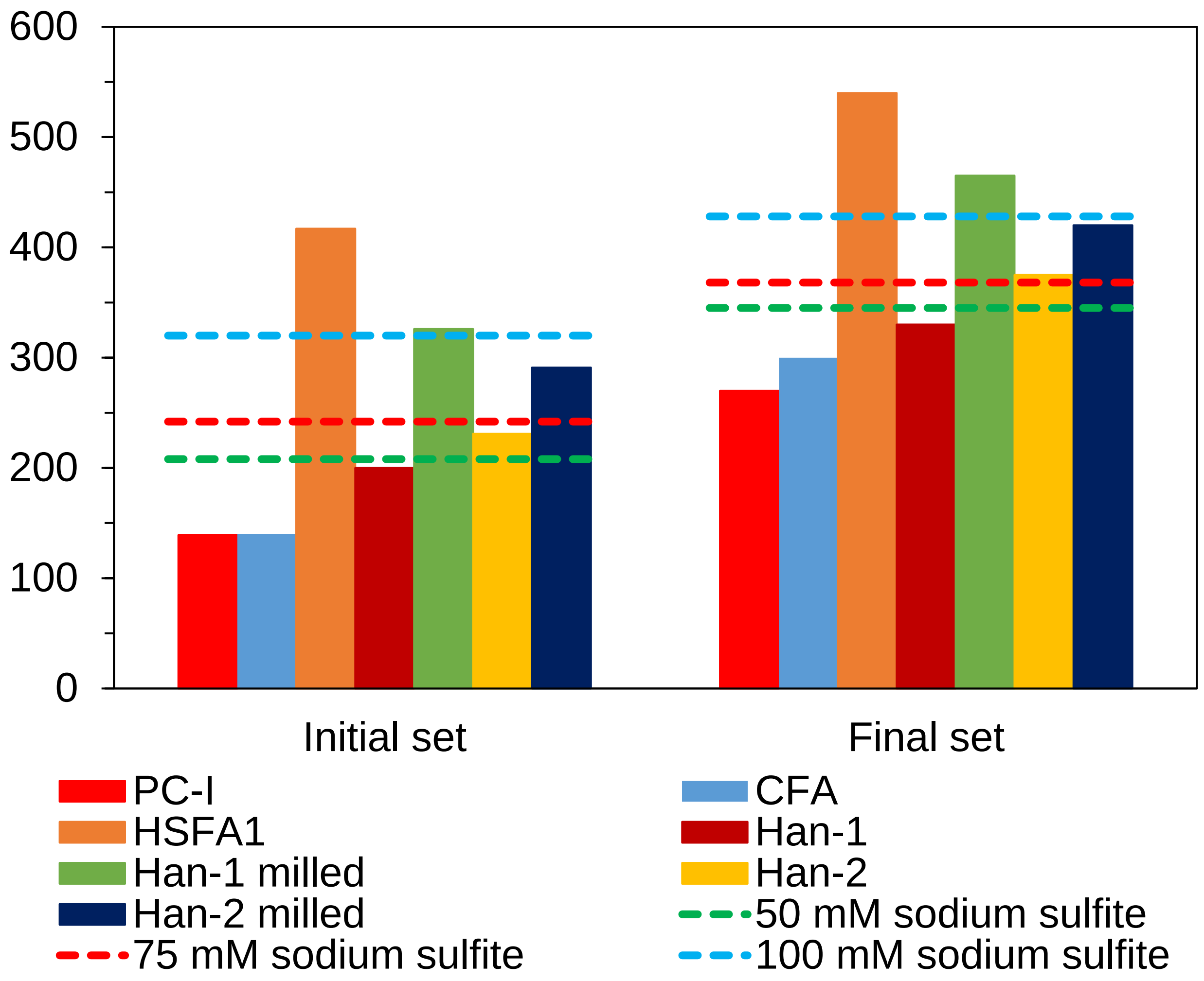
Standard	SO_3 limit	Na_2O_{eq} limit	Remarks
ASTM C618	Max 5.0%	Report	Based on OPC performance?
ASTM C595	Max 4.0% (IP)	Report	Higher SO_3 allowed – C1038 expansion limit
ASTM C1778	None	Max 4.0%; <3.0% pref.	Low pH for ASR mitigation

- Testing doped systems allows wide range and variety
- SO_3 levels chosen based on:
  - HSFA/HSAFA observed in literature and those obtained for testing
  - Represents values below & above ASTM limits

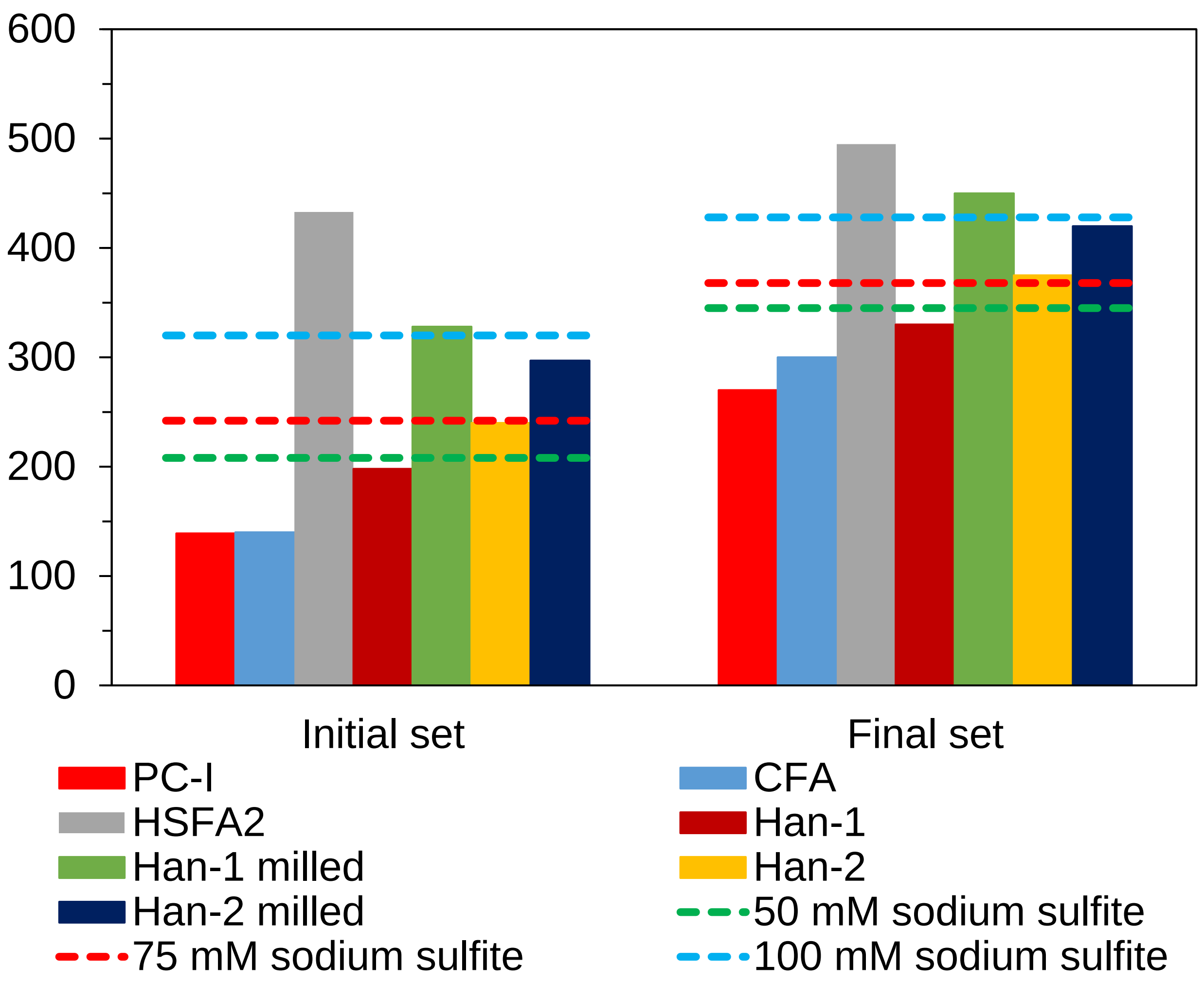
Doped fly ash (DFA) SO_3 content	3%	5%	7%	9%	11%
Binder SO_3 content	3.75%	4.15%	4.55%	4.95%	5.35%

- PC replacement level fixed at 20% by mass

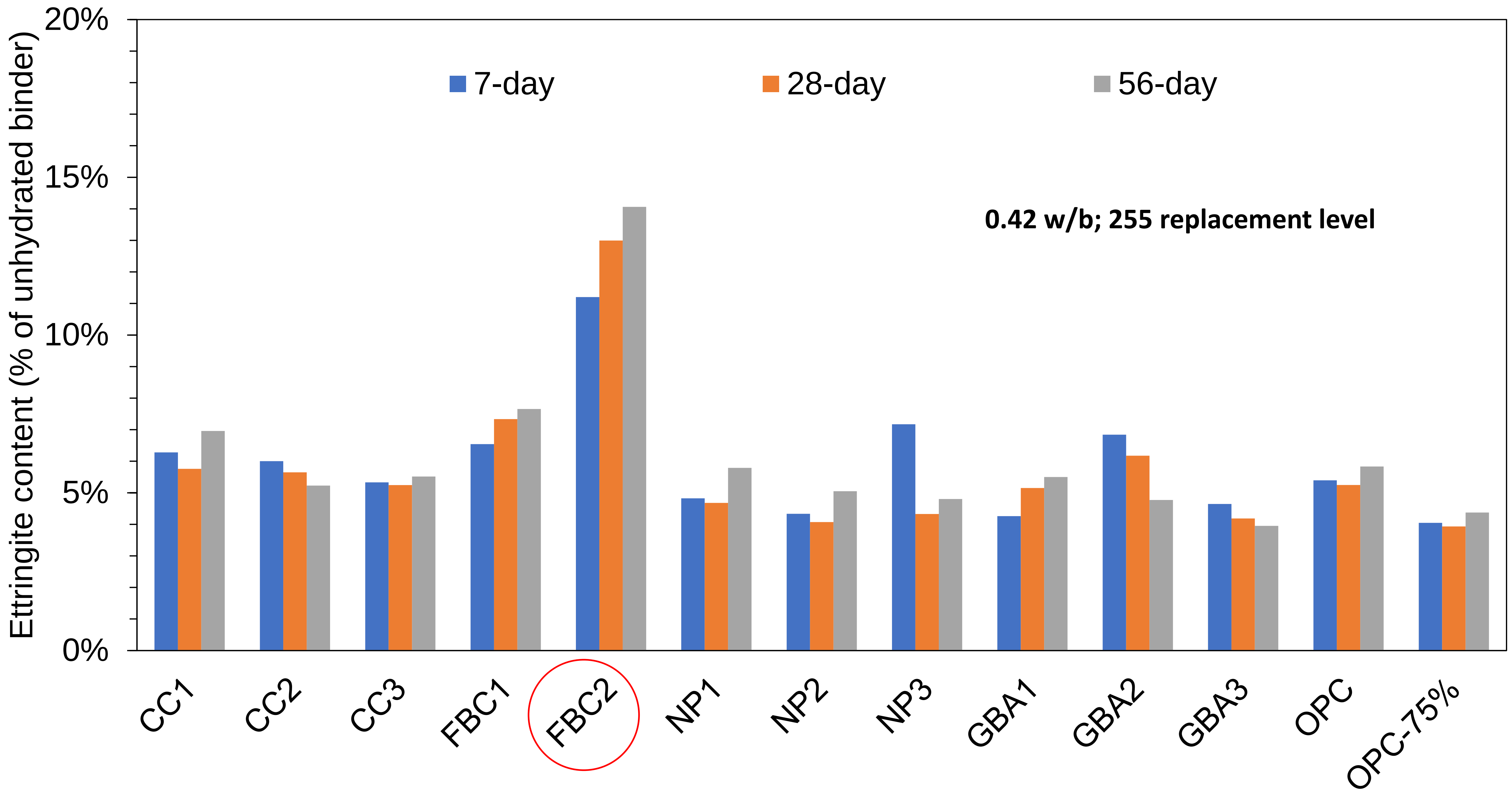
Fine hannebachite and sodium sulfite both showed significant setting delay – effect of sulfite ion



HSFA1 – 13.3% SO_3

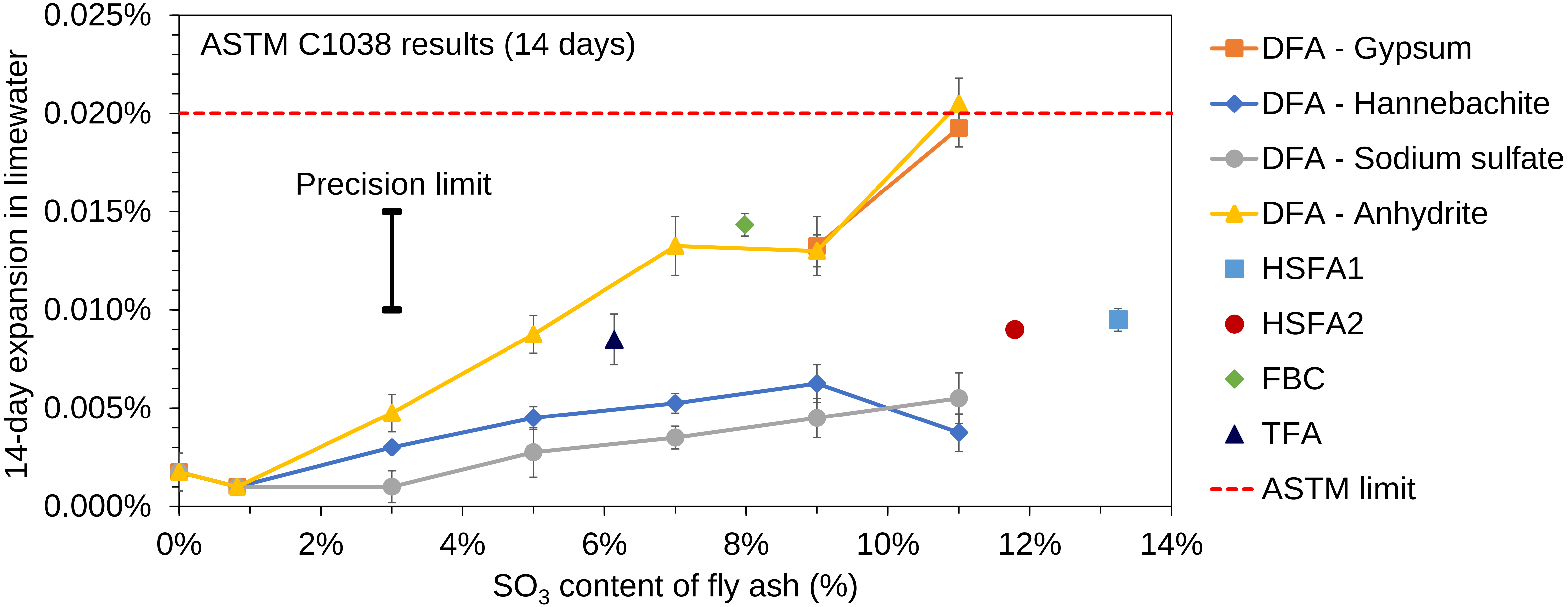


HSFA2 – 11.8% SO_3



Etringite content (% of unhydrated binder)
20%
15%
10%
5%
0%
7-day
28-day
56-day
0.42 w/b; 255 replacement level
CC1
CC2
CC3
FBC1
FBC2
NP1
NP2
NP3
GBA1
GBA2
GBA3
OPC
OPC-75%

All SO_3 forms result in expansion of hardened mortar but only $CaSO_4$ at $SO_3 \geqslant 11.0\%$ exceeds the limit



Acknowledgements

Project Title: Thermodynamic and kinetic simulations and testing procedures to screen for enhanced durability of concrete containing industrial waste