

CATALYSIS OF CEMENT HYDRATION BY CHEMICAL ADMIXTURES

Ellis Gartner, August 2005

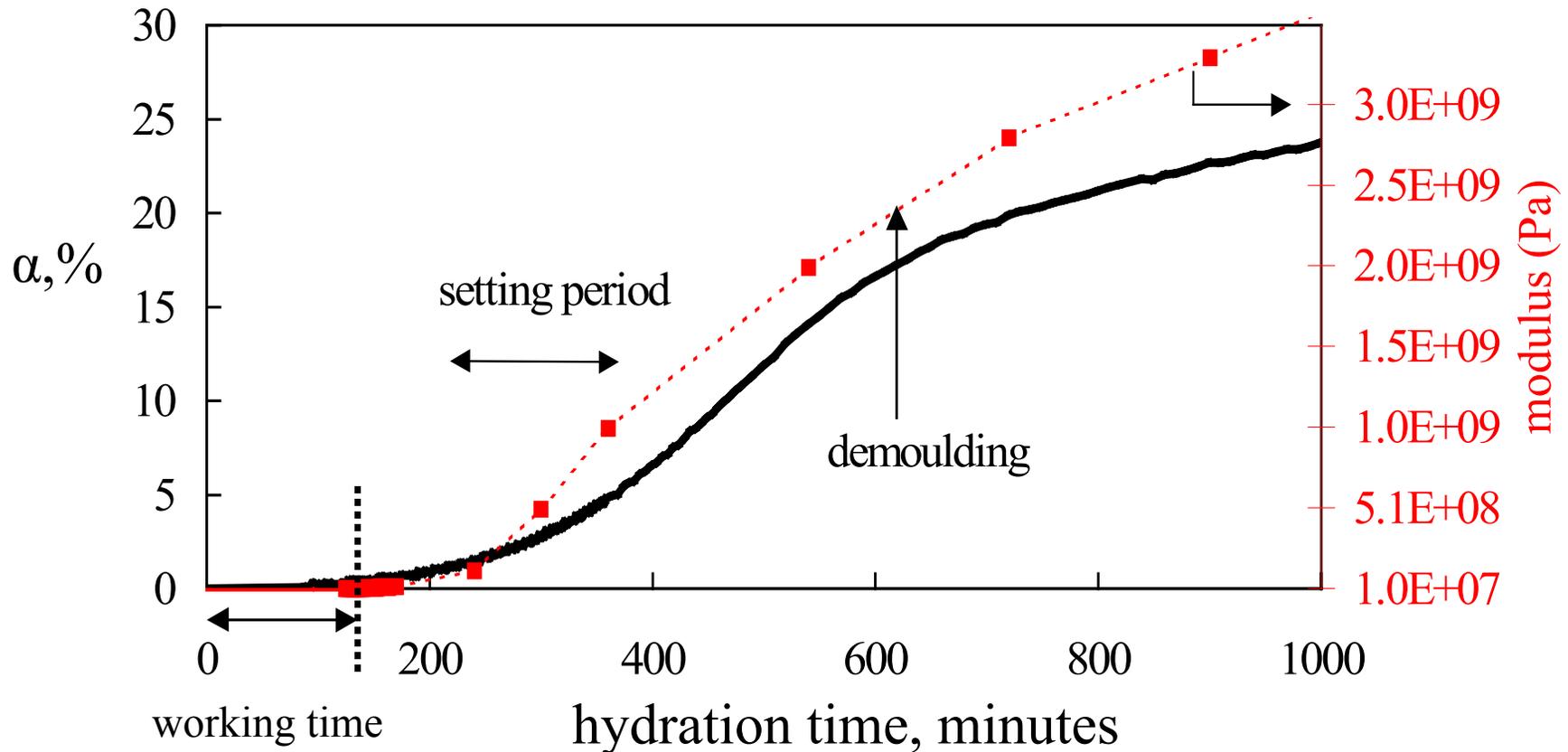
OUTLINE OF LECTURE

1. Introduction
2. Catalysis of alite hydration by calcium salts
3. Catalysis of ferrite-phase hydration by TIPA
4. Industrial applications

Introduction: what is meant by “catalysis”?

- The term catalysis is used here in its classical chemical sense, i.e. the acceleration of a reaction by a substance that is not incorporated into the reactants or the reaction products.
- In this sense, it is more specific than the term “acceleration” that is more often used for the effect of cement accelerators
- The best-understood examples are the two cases chosen here:
 1. The use of calcium chloride to accelerate alite hydration
 2. The use of TIPA to accelerate ferrite phase hydration

Development of mechanical properties



Mechanical strength and Young's modulus both depend mainly on the mean degree of hydration, α , of the cement paste (assuming a constant initial water/cement ratio).

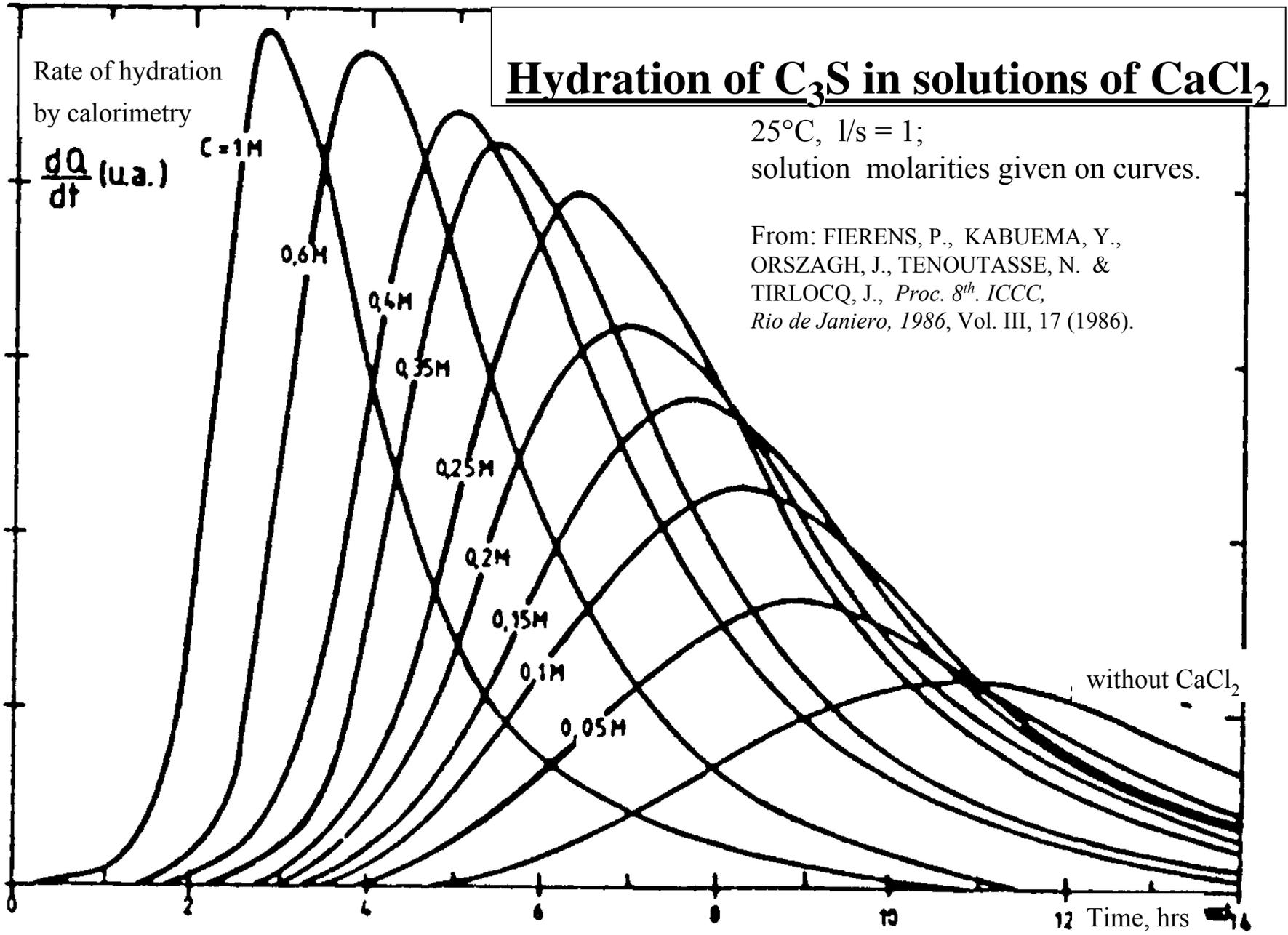
Acceleration of alite hydration by calcium salts

- Calcium chloride has been used for many decades as an accelerator for portland cement hydration in concrete.
- Other soluble calcium salts of monobasic acids (CaX_2) can be used but are usually less cost-effective. Calcium nitrate and nitrite are often used to avoid chloride-catalysed steel corrosion.
- Kantro (1975) used calorimetry to study the effect of a wide range of CaX_2 salts on C_3S hydration and showed that the acceleration mechanism was basically similar for different X^- .
- There is little evidence for any significant uptake of simple monovalent anions such as Cl^- in alite hydration products (C-S-H and CH) at the CaCl_2 concentrations typically used in

Hydration of C_3S in solutions of $CaCl_2$

25°C, $l/s = 1$;
solution molarities given on curves.

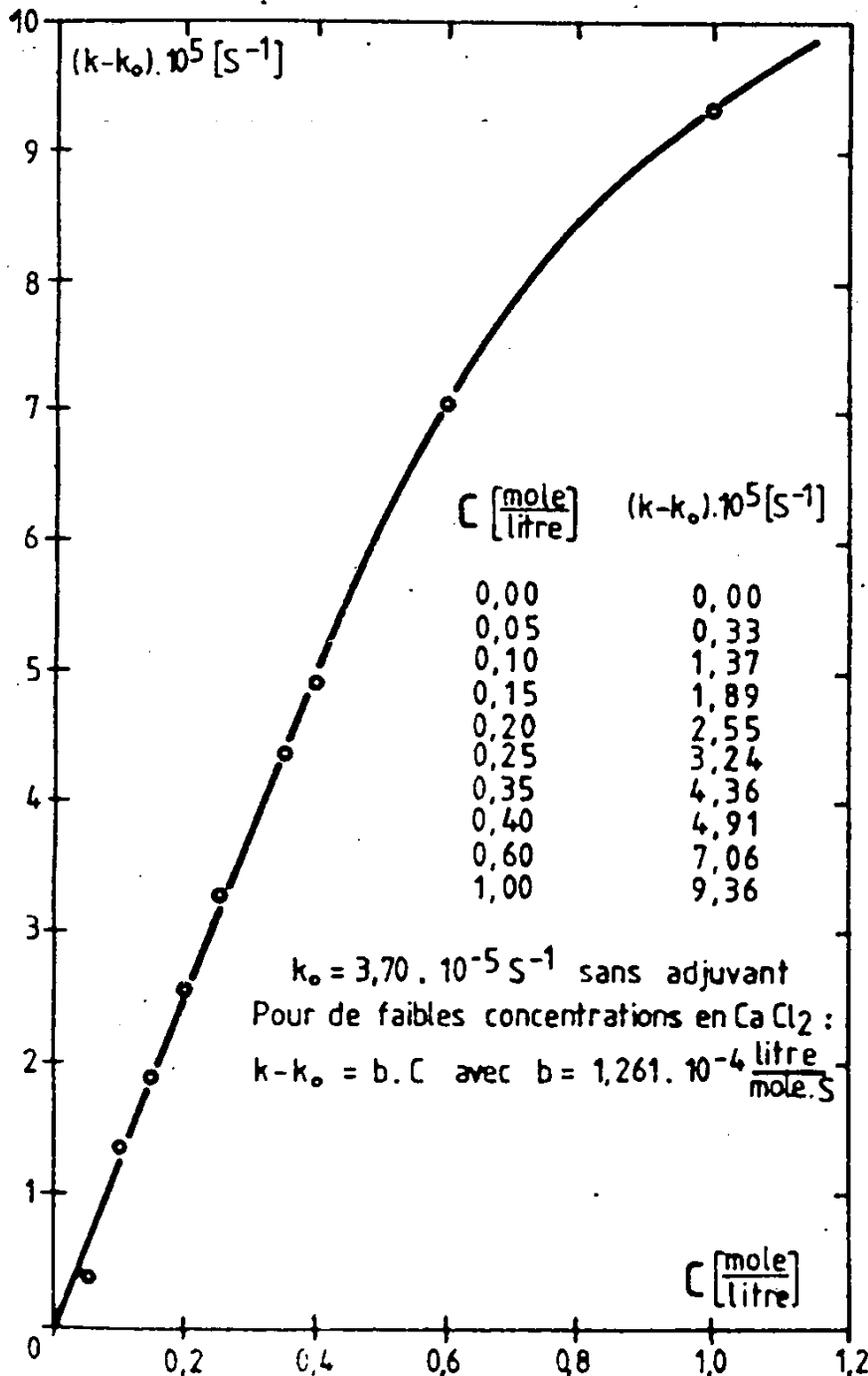
From: FIERENS, P., KABUEMA, Y.,
ORSZAGH, J., TENOUTASSE, N. &
TIRLOCQ, J., *Proc. 8th. ICC*,
Rio de Janeiro, 1986, Vol. III, 17 (1986).



Rate constant for acceleratory period as a function of CaCl_2 concentration.

Equation used: $\alpha = (kt)^3$

This is the Avrami equation with $m=3$, and clearly implies that the rate is controlled by the rate of growth of one of the hydrates. Other evidence indicates that it is the growth of C-S-H which is rate-limiting under these conditions, and implies that CaCl_2 must be acting as a catalyst for growth of C-S-H.

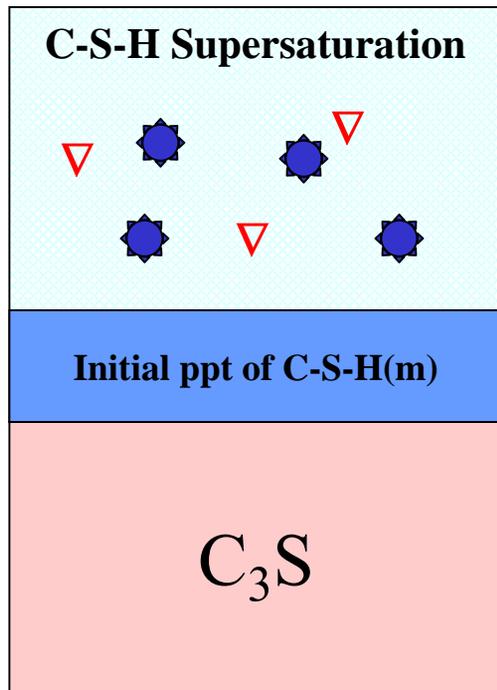


The Gartner-Gaidis model for alite hydration (1989)

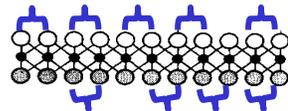
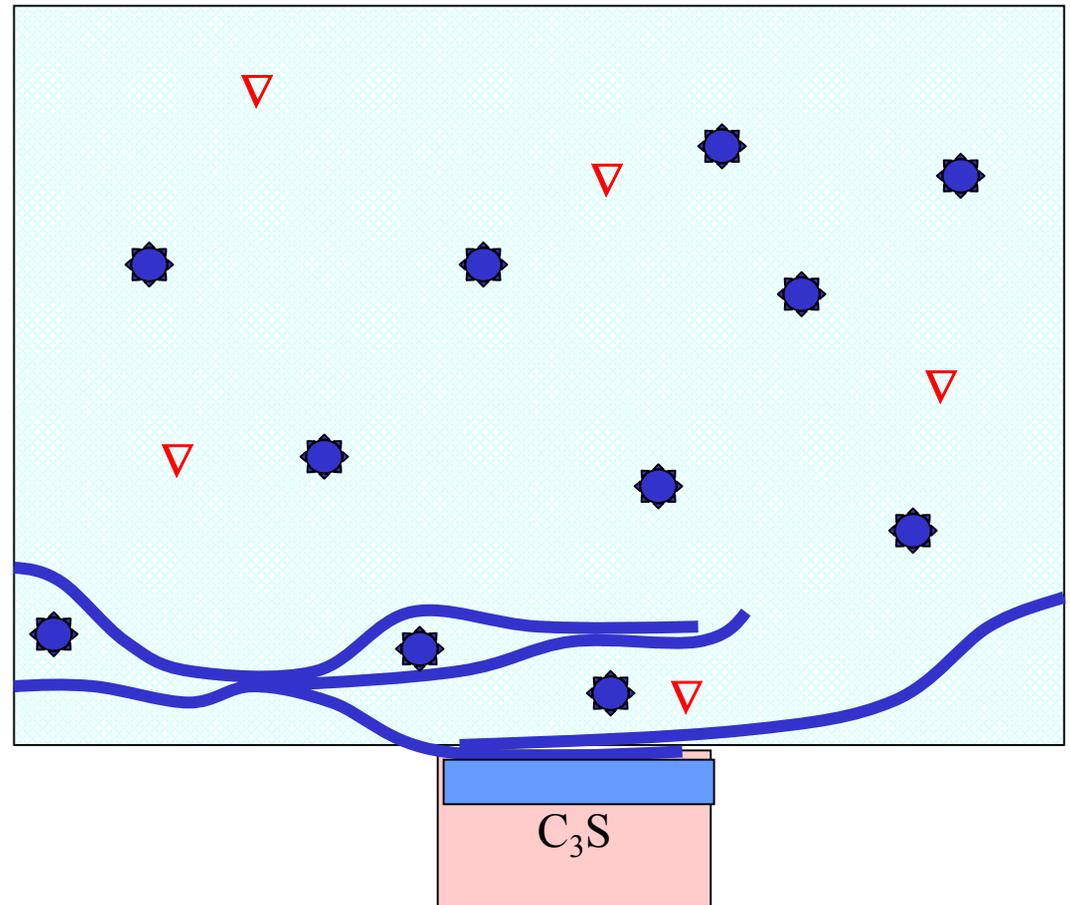
- The initial dissolution of C_3S supersaturates the solution relative to ‘C-S-H(m)’ which precipitates, depositing directly onto the surface of the C_3S forming a barrier (in equilibrium with the solution.) Some may deposit onto other surfaces.
- The amount of this initial product depends on the portlandite saturation and the water/solids ratio; higher w/s results in more of it, and higher [CH] results in less, since the solution supersaturates at much lower silica concentrations.
- ‘C-S-H(m)’ serves as the site for nucleation of a more thermodynamically stable product, ‘C-S-H(s),’ which grows out into the solution (the ‘outer product’)
- The layer of ‘C-S-H(m)’ on the surface of the C_3S dissolves to keep up with the growth of ‘C-S-H(s)’. As it does so, it becomes thinner and the rate is limited by ‘C-S-H(s)’ growth kinetics, which are autocatalytic due to surface growth.
- When the layer of ‘C-S-H(s)’ becomes thick, diffusion (*of what species? – probably silicate ions*) becomes the rate-limiting step.
- This model predicts the acceleratory effect of C-S-H nucleation and the retarding effect of lime-presaturation. **The effect of simple accelerators and retarders is explained principally by their influence on the rate of growth of the product.**

Proposed early hydration model

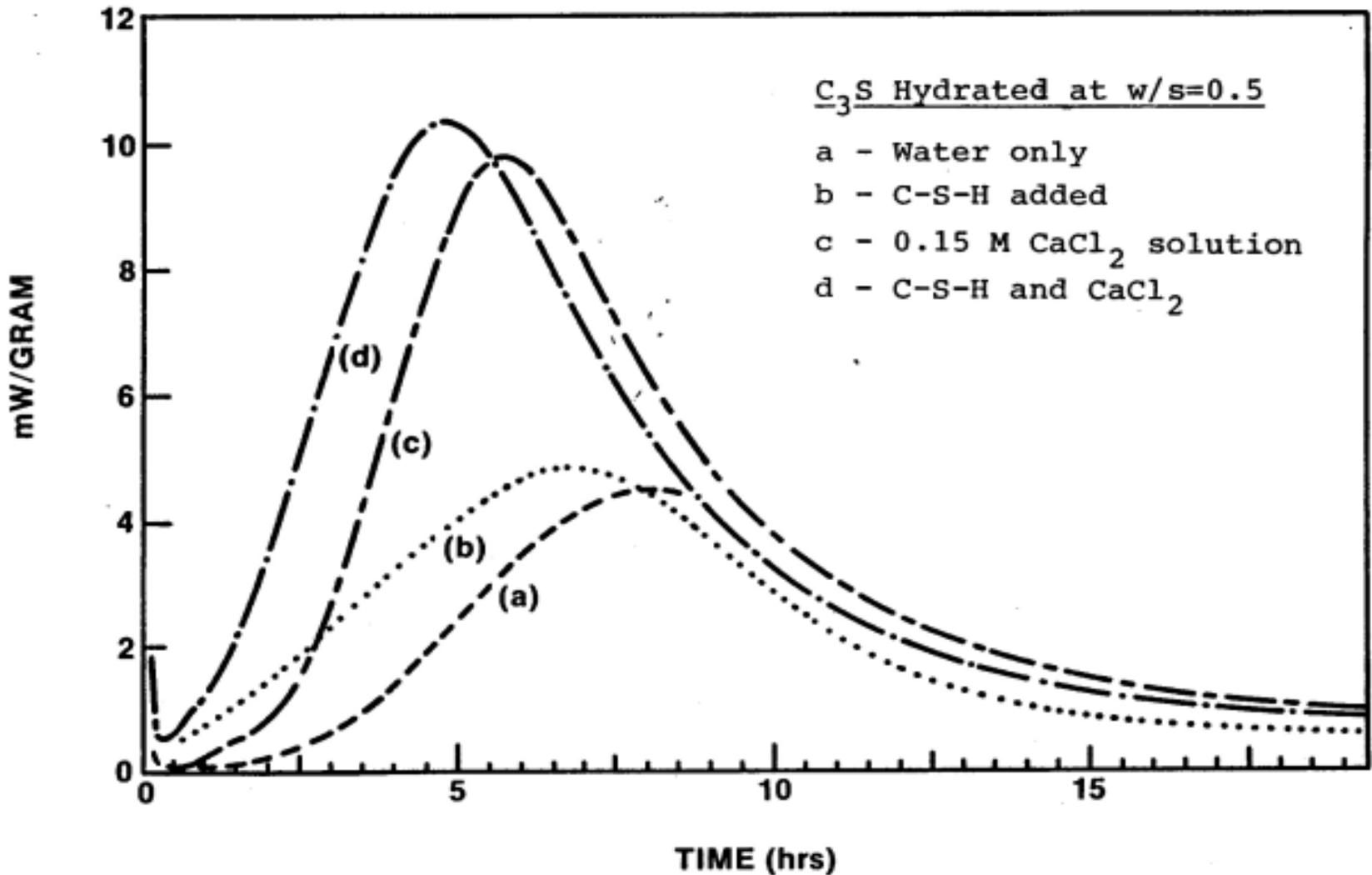
Stage 1



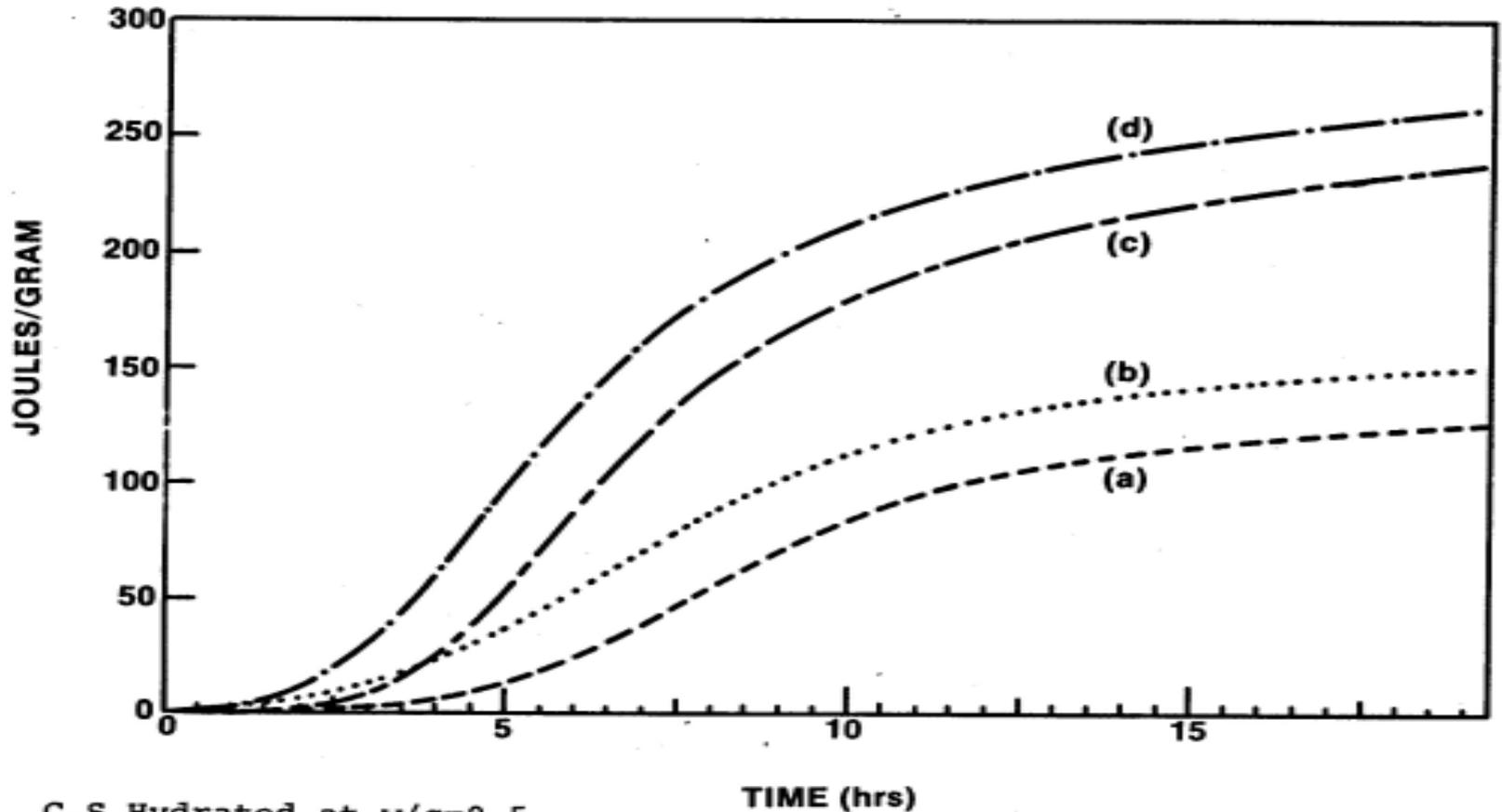
Stage 2



C_3S : rate of hydration vs. time with two types of accelerator:
a nucleating agent (C-S-H) or a catalyst ($CaCl_2$)



C_3S : degree of hydration vs. time with two types of accelerator
(integrated curves from previous figure showing total enthalpy, proportional to α .)

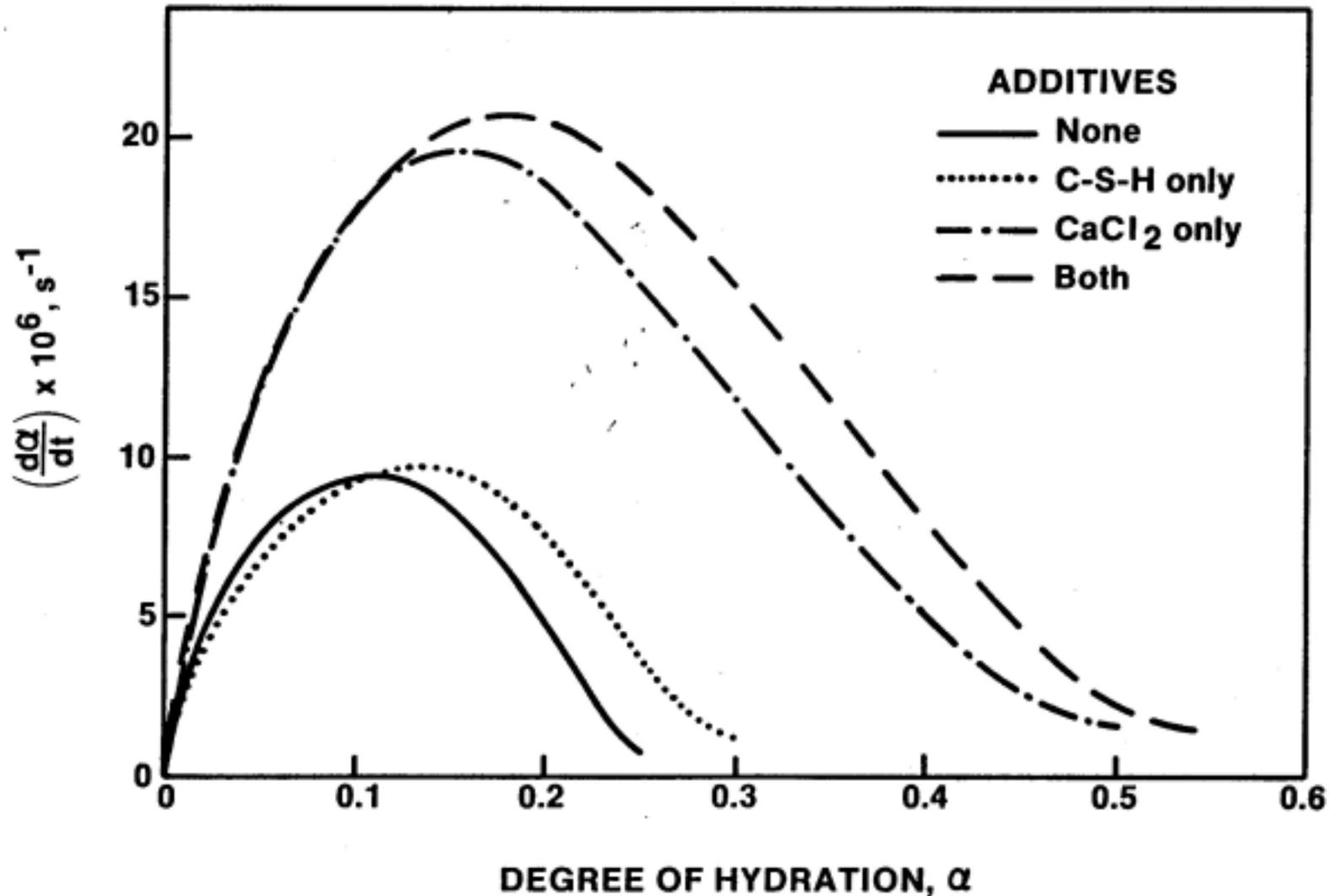


C_3S Hydrated at $w/s=0.5$

- a - Water only
- b - C-S-H added
- c - 0.15 M $CaCl_2$ solution
- d - C-S-H and $CaCl_2$

C₃S: degree of hydration vs. time with two types of accelerator

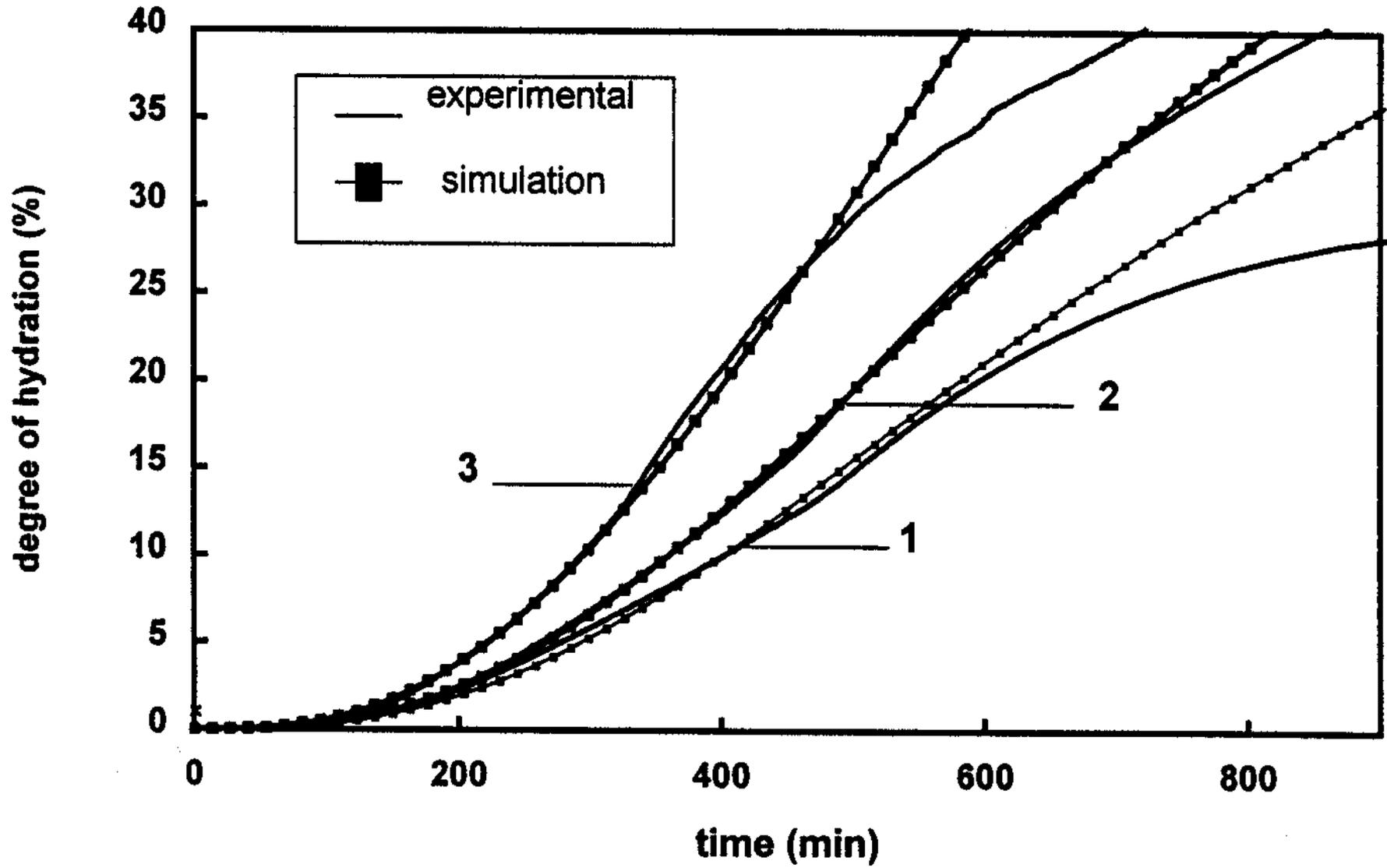
(data from previous figure re-plotted to show rate as a function of α .)



Acceleratory period for C_3S in portlandite-saturated $CaCl_2$ solutions at $25^\circ C$, $w/s = 50$

(Gauffinet, Nachbaur & Nonat, 1997)

1: no $CaCl_2$; 2: $[CaCl_2] = 10mM$; 3: $[CaCl_2] = 50mM$



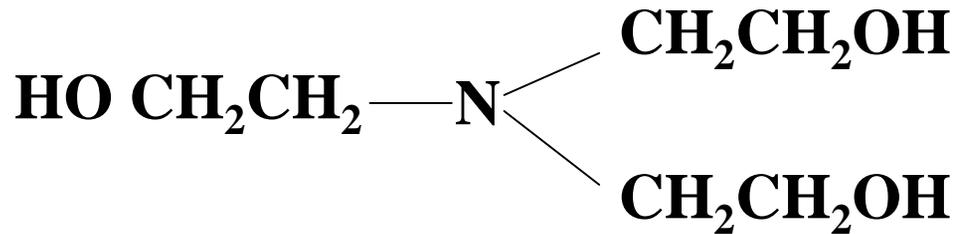
How precisely does CaCl_2 catalyse C_3S hydration?

- Under the usual conditions of temperature and w/c, it is clear that C-S-H growth is rate-determining, so that is presumably the basic reaction step that is catalysed by CaCl_2 .
- How precisely this occurs is not known, because C-S-H growth (on existing C-S-H surfaces) is itself a multi-step process including deposition of Ca^{++} , of OH^- and of H_2SiO_4^- , and dimerization of the silicate anions; and we don't know which step is rate-determining.
- The most effective CaX_2 -type accelerators seem to be those salts that are highly dissociated and also have highly polarizable anions. This suggests that high local $\text{Ca}^{++}(\text{aq.})$ concentrations are necessary to supply this ion rapidly enough to the growth sites and that the polarizability of the (non-reacting) anion may then contribute to stabilization of the transition state involved in Ca^{++} incorporation.

Acceleration of C₄AF hydration by TIPA

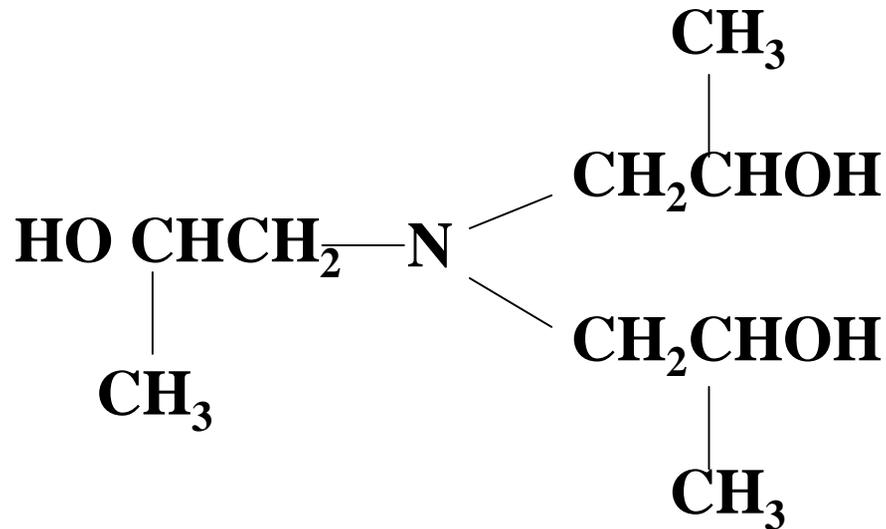
- Discovered and patented by Myers and Gartner at W. R. Grace's Washington Research Center in the late 1980's. [*U.S. patent 4,990,190 "Strength Enhancing Additive for Certain Portland Cements" (Feb. 5, 1991)*]
- Used since early 1990's as a grinding aid and strength enhancer in Grace's "CBA" series of cement additives.
- Principal mechanistic hypotheses published in 1993 [*Gartner, E. M., and Myers, D. F., "Influence of Tertiary Alkanolamines on Portland Cement Hydration", J. Am. Ceram. Soc. 76 (6) 1521-30*]

Triethanolamine ('TEA')



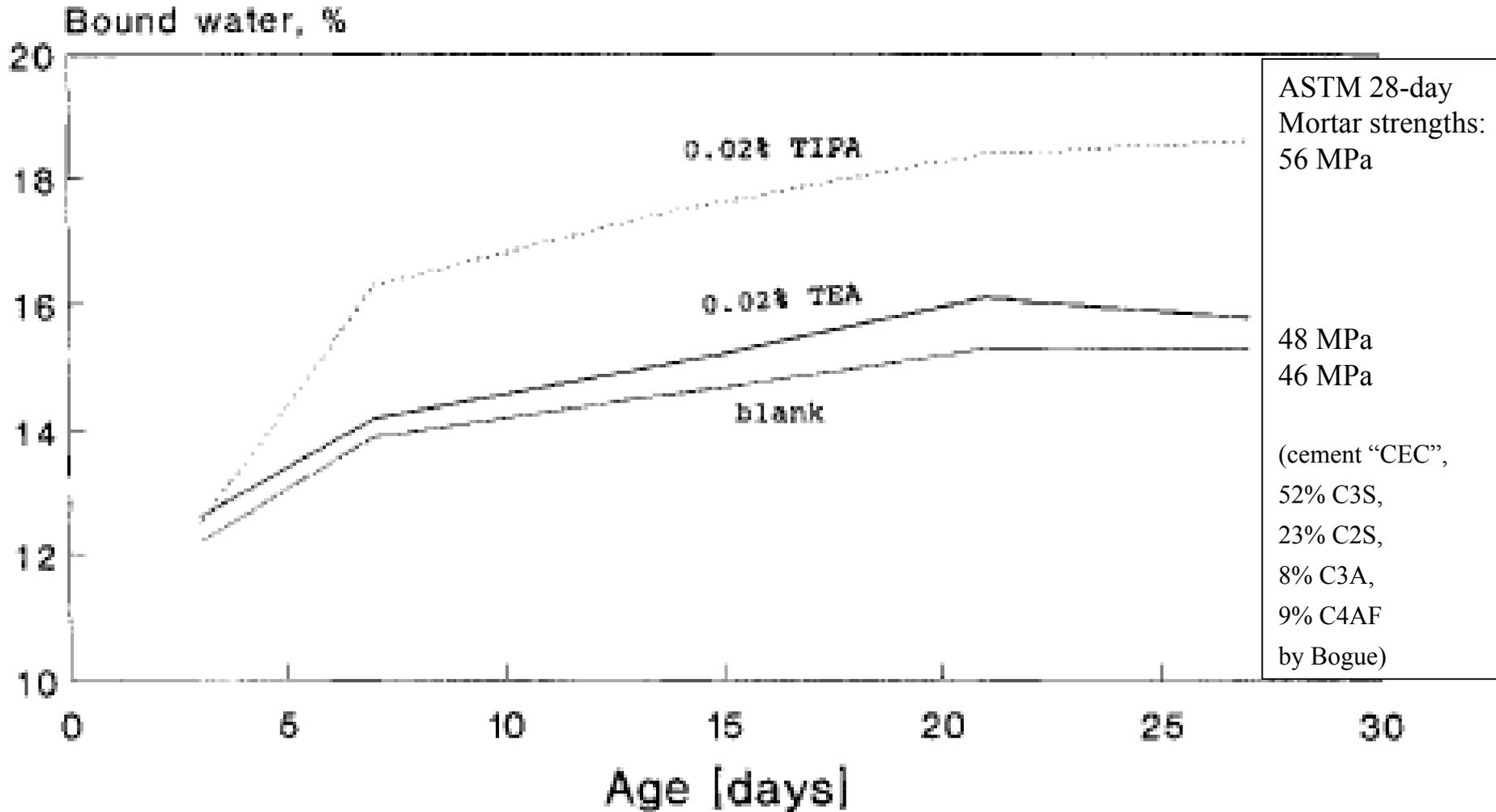
- commonly used as a “grinding aid” in cement manufacture (adsorbs on dry particle surfaces and aids in dry dispersion)
- sometimes has a small accelerating effect (mainly on setting)
- is known to be capable of complexing Fe^{III} at high pH, but usually has little effect on cement hydration or on [Fe] in liquid

Triisopropanolamine ('TIPA')

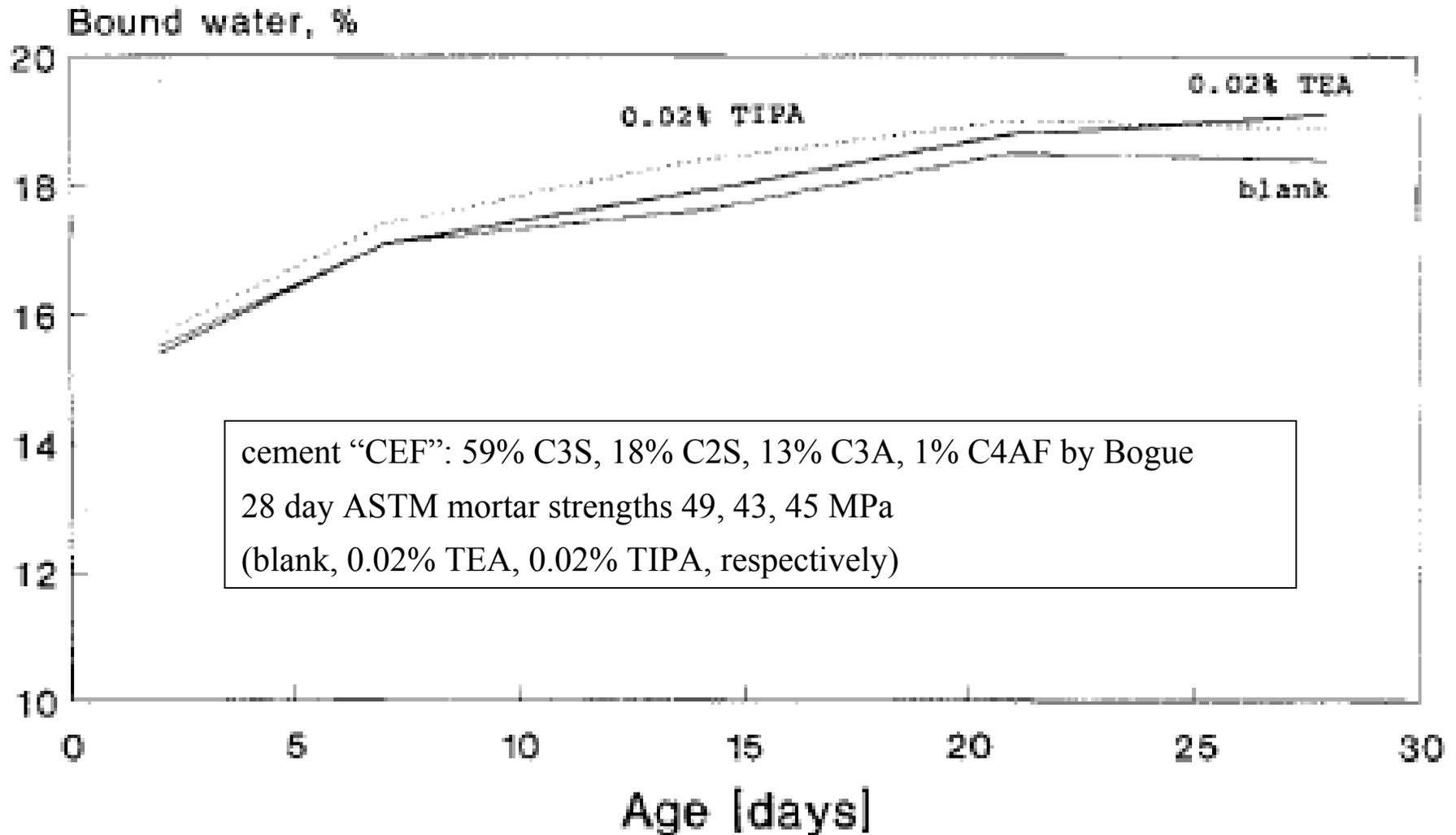


- can also be used as a grinding aid, but more expensive than TEA
- is also known to be capable of complexing Fe^{III} at high pH
- surprisingly, shows large positive influence on strength after about one day of hydration for many grey OPCs: basis of “CBA” patents

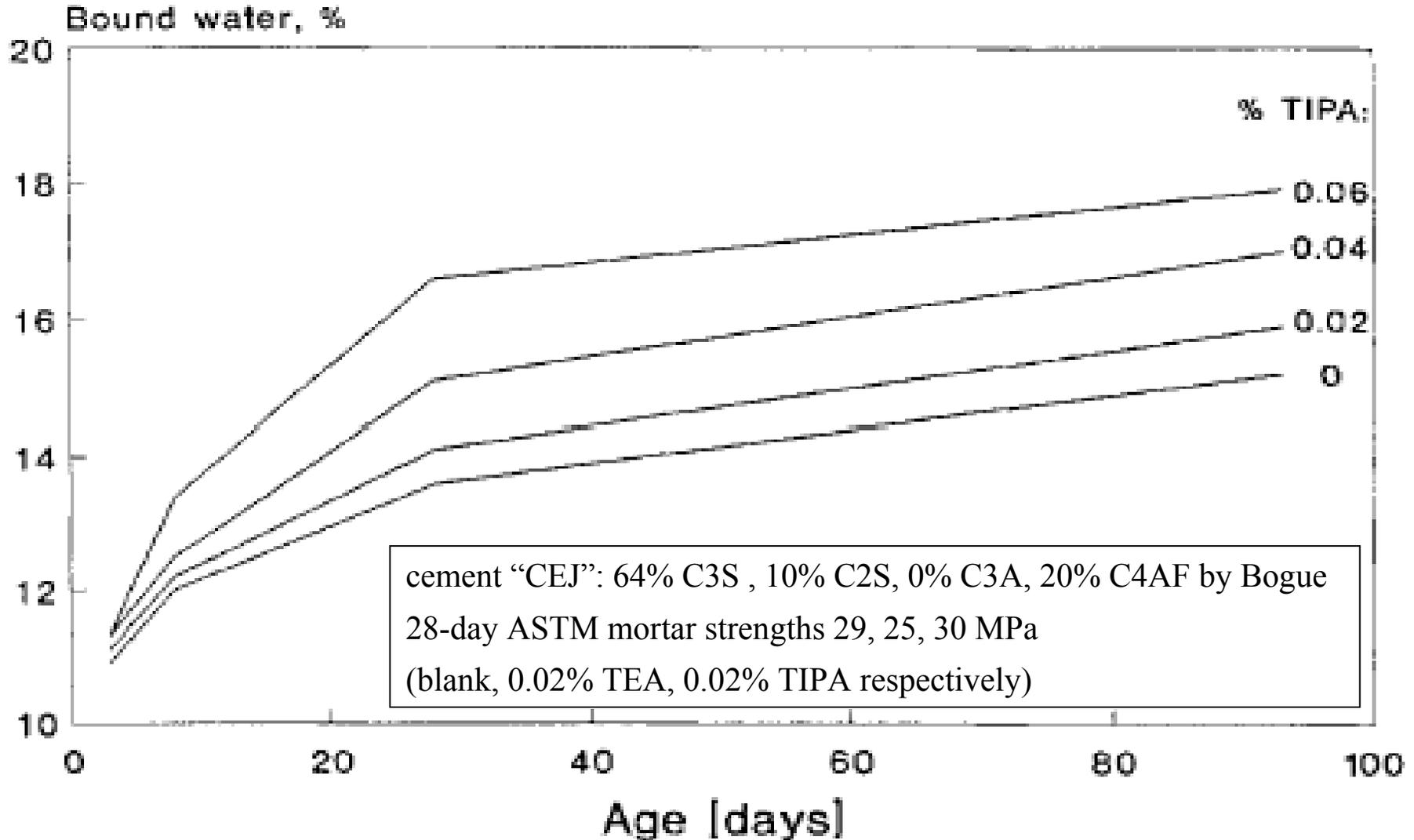
Effects of alkanolamines on a typical grey OPC (*pastes hydrated at $w/c = 0.47$*)



Effect of alkanolamines on a white cement (*pastes hydrated at $w/c = 0.47$*)



Effect of alkanolamines on a zero-C₃A OPC (*pastes hydrated at w/c = 0.47*)

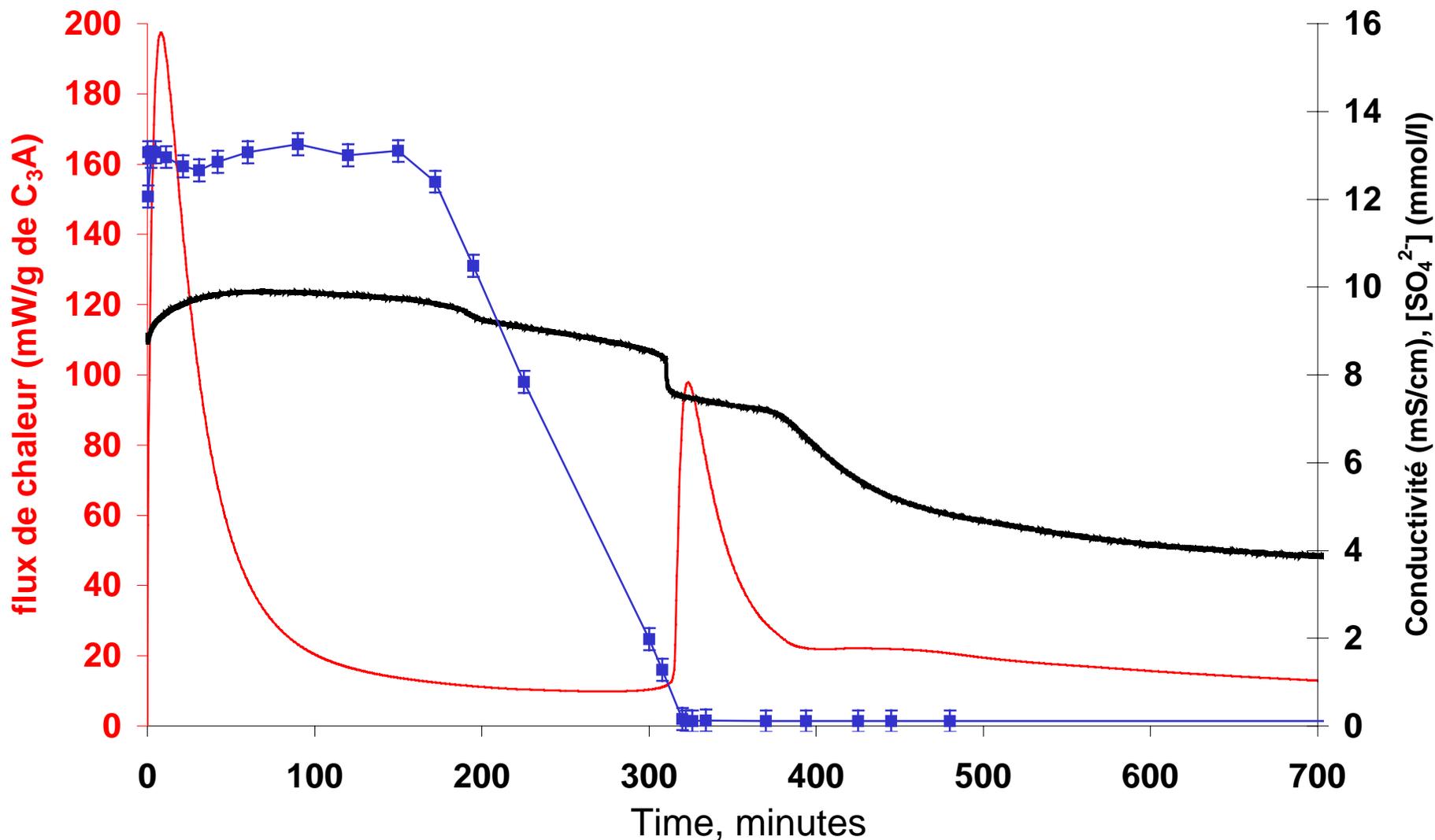


Typical strength enhancements obtained with TIPA in cement pastes and EN 196 mortars (*Sandberg and Doncaster, CCR 34, 973-976, 2004*)

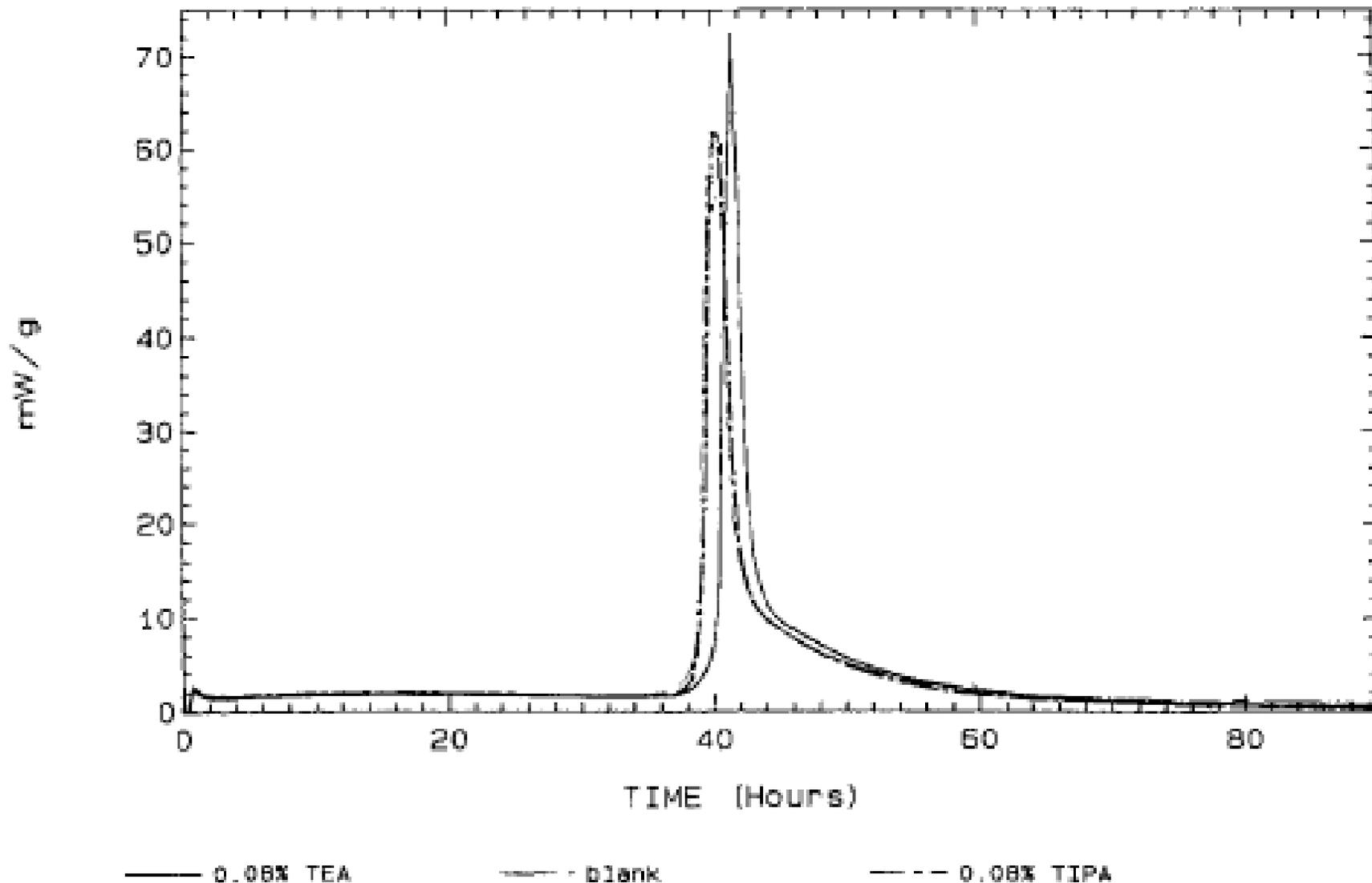
Table 2
Twenty-eight-day compressive strength data on hydrated portland cement paste and EN 196 mortar, Test Series 1

Cement ID	1A		1B		1C		1D		1E		1F	
	Paste	EN 196										
w/c	0.35	0.5	0.35	0.5	0.35	0.5	0.35	0.5	0.35	0.5	0.35	0.5
<i>Blank (no admixture)</i>												
28-Day MPa	85	48	108	60	86	55	62	42	119	67	88	49
S.D. MPa	2.0	1.4	7.8	1.1	3.0	1.5	5.5	0.2	7.4	3.2	3.2	2.3
CV, %	2.3	2.9	7.2	1.8	3.5	2.7	8.8	0.6	6.2	4.8	3.7	4.6
<i>200 ppm TIPA (by weight of cement, added to mix water)</i>												
28-Day MPa	94	54	122	62	104	60	65	44	121	66	97	58
S.D. MPa	5.7	2.1	4.6	1.4	5.7	2.2	5.5	0.9	9.2	2.0	2.9	1.1
CV, %	6.1	4.0	3.8	2.3	5.5	3.7	8.5	2.0	7.6	3.1	3.0	1.8
TIPA % of blank	111	113	113	103	121	109	105	105	102	99	110	118
TIPA effect on air, %	N/A	+0.9	N/A	+2.1	N/A	+2.4	N/A	+0.6	N/A	+1.40	N/A	+0.4
<i>Average</i>												
TIPA % of blank	Paste	EN 196										
	110	108										
TIPA effect on air content, %	N/A	+1.3										

Suspension of C₃A with gypsum and Ca(OH)₂ at w/s = 25;
(40:5:2 by mass) (*heat flux - red; sulfate concentration - blue; conductivity - black*)

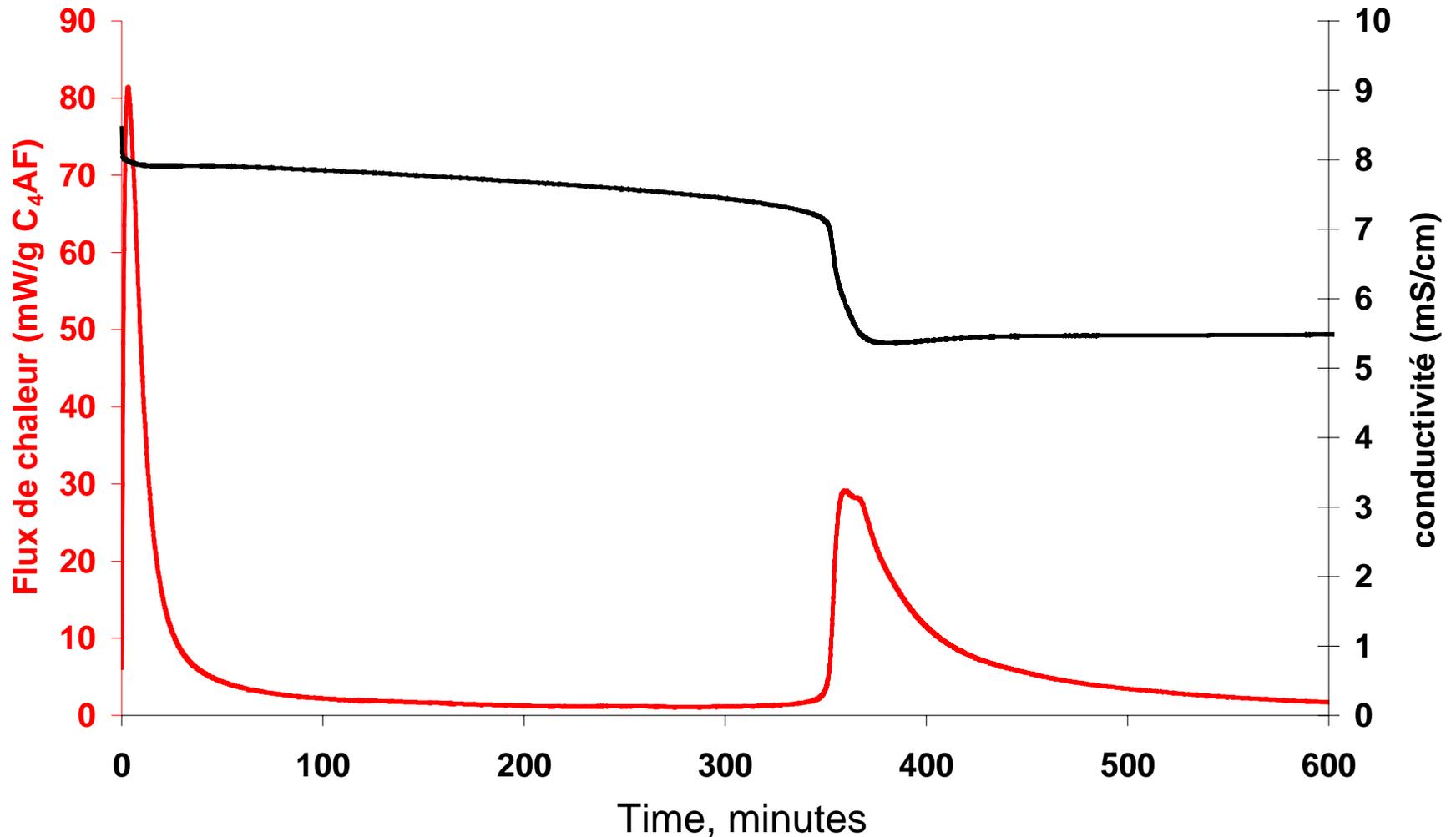


Calorimetry of pastes of $C_3A:CH:C\hat{S}H_2:water:(alkanolamine)$ at $23^\circ C$
[mass ratio = 60:20:20:50:(0.04)]; [ordinate = mW/g C_3A]

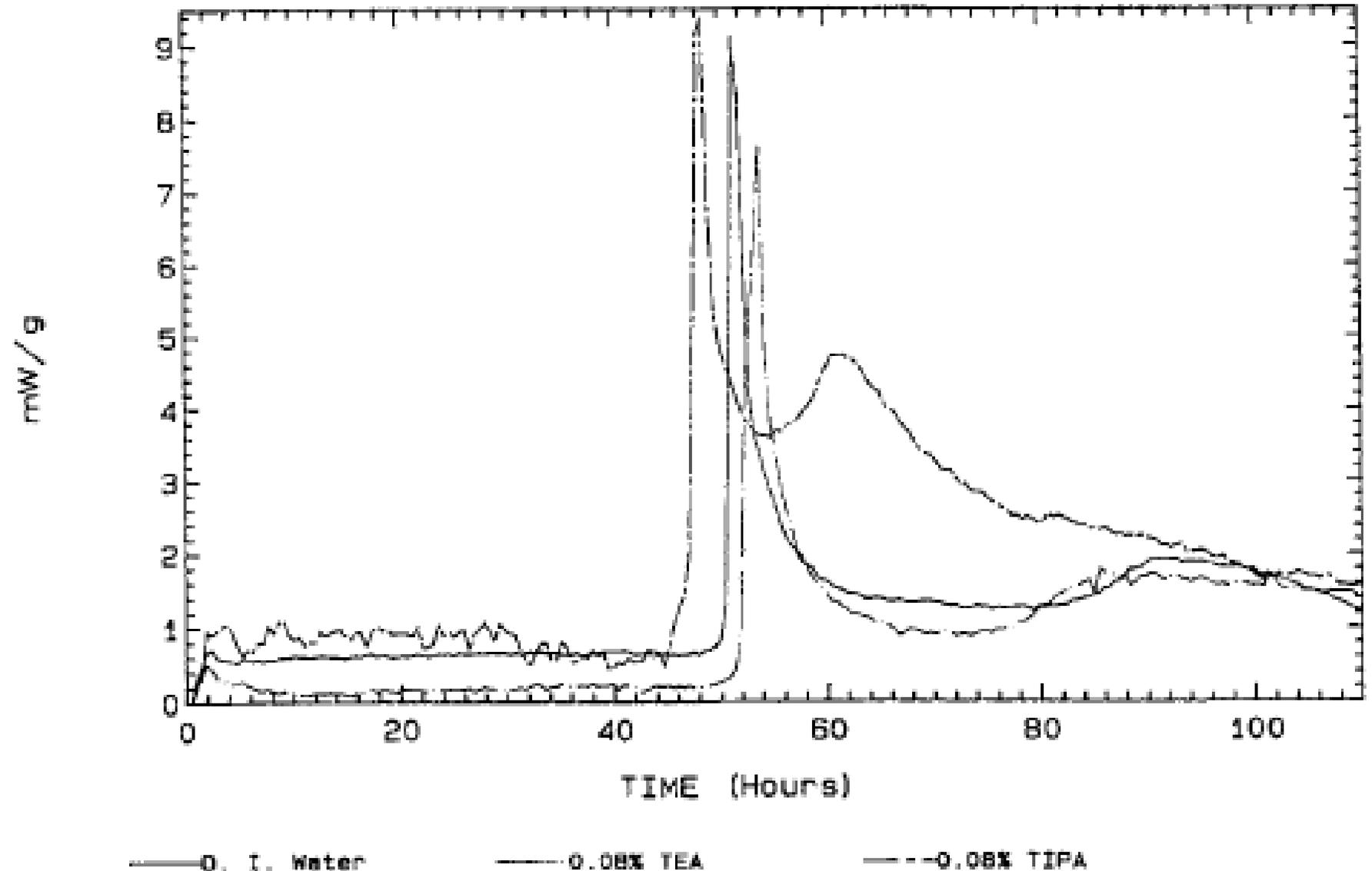


Suspension of C₄AF with gypsum and Ca(OH)₂ at w/s = 25

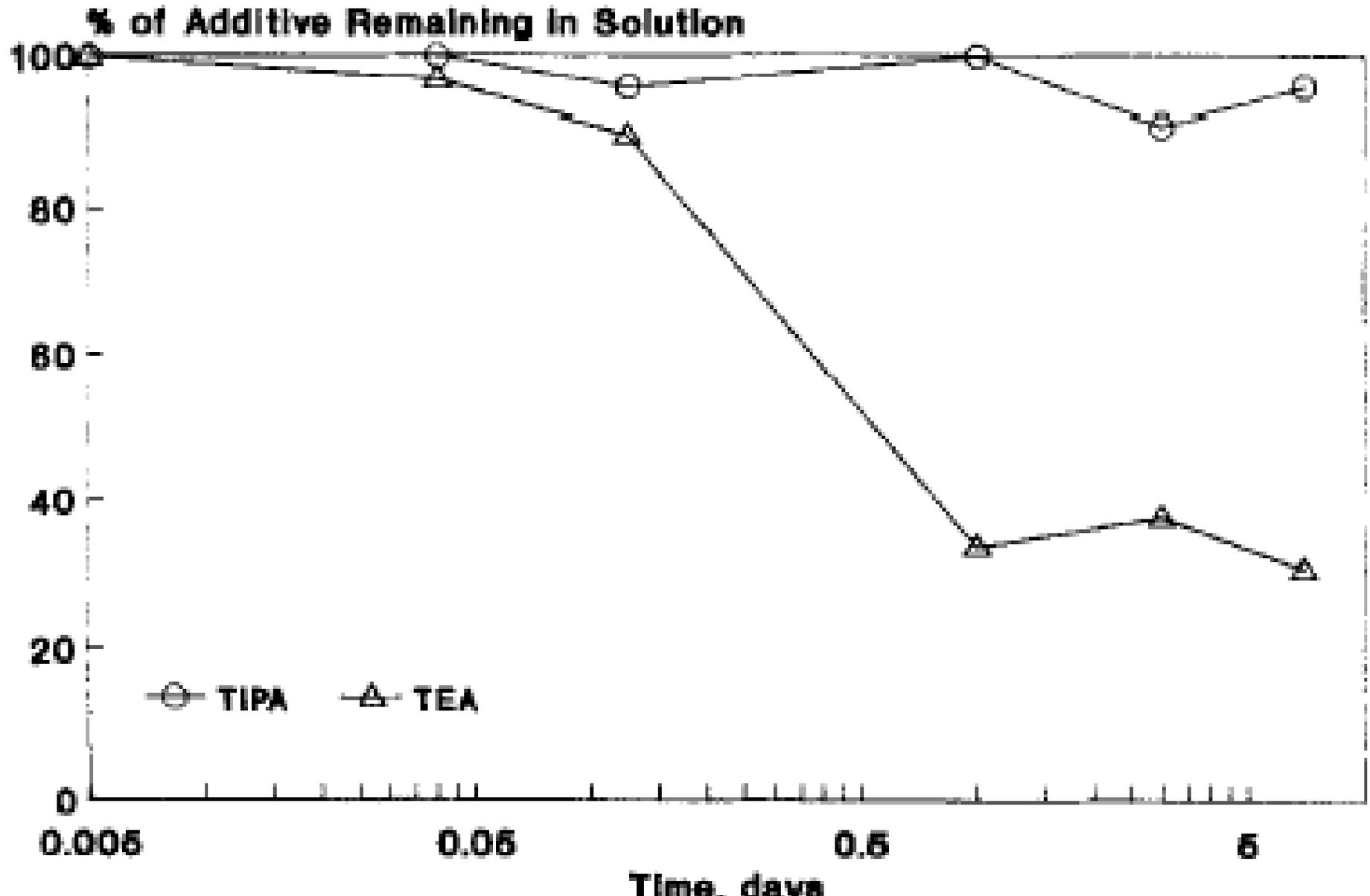
(heat flux - red; conductivity – black)



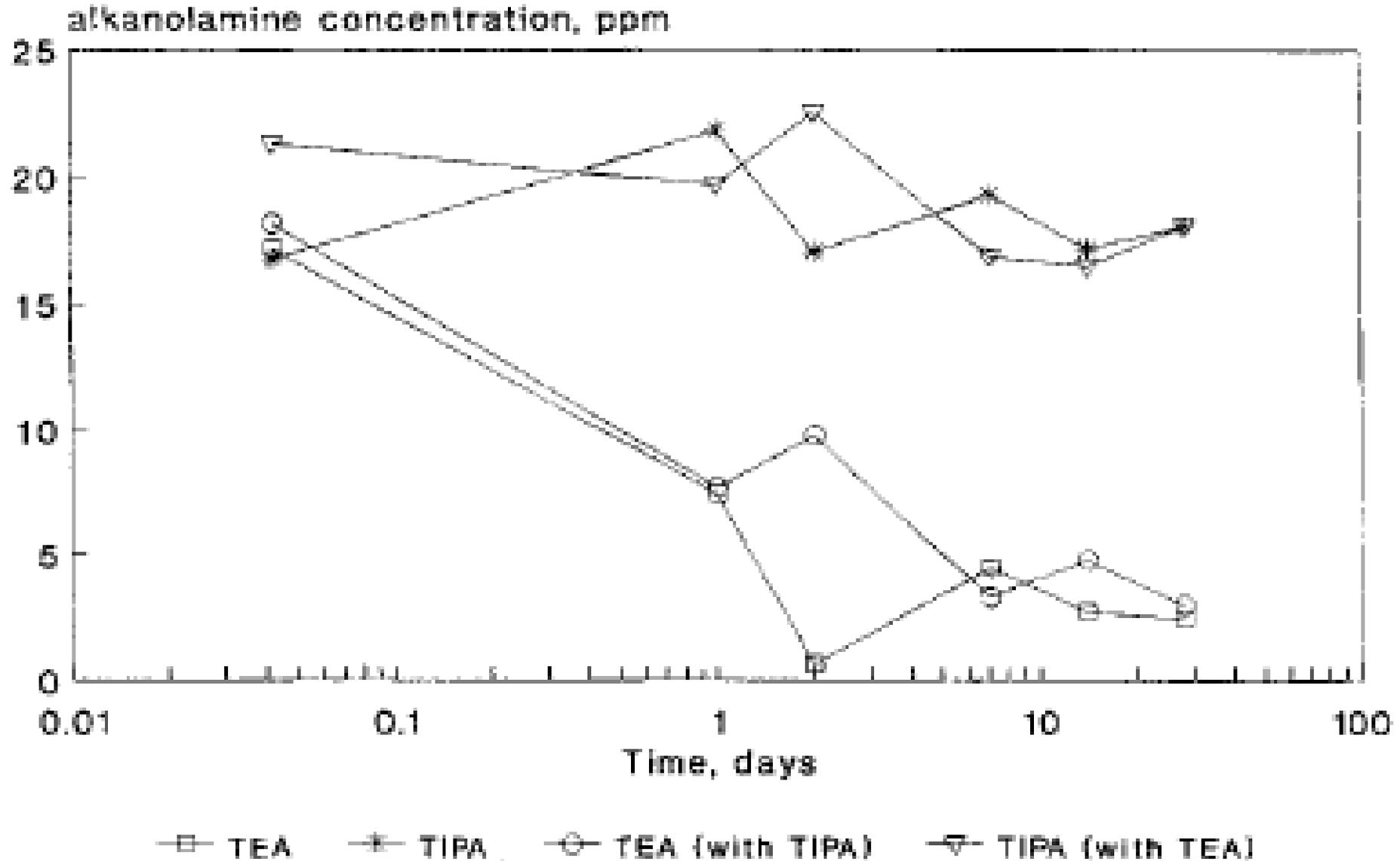
Calorimetry of pastes of $C_4AF:CH:C\hat{S}H_2:water:(alkanolamine)$ at $23^\circ C$
[mass ratio = 58:36:6:50:(0.04)]; [ordinate = mW/g C_4AF]



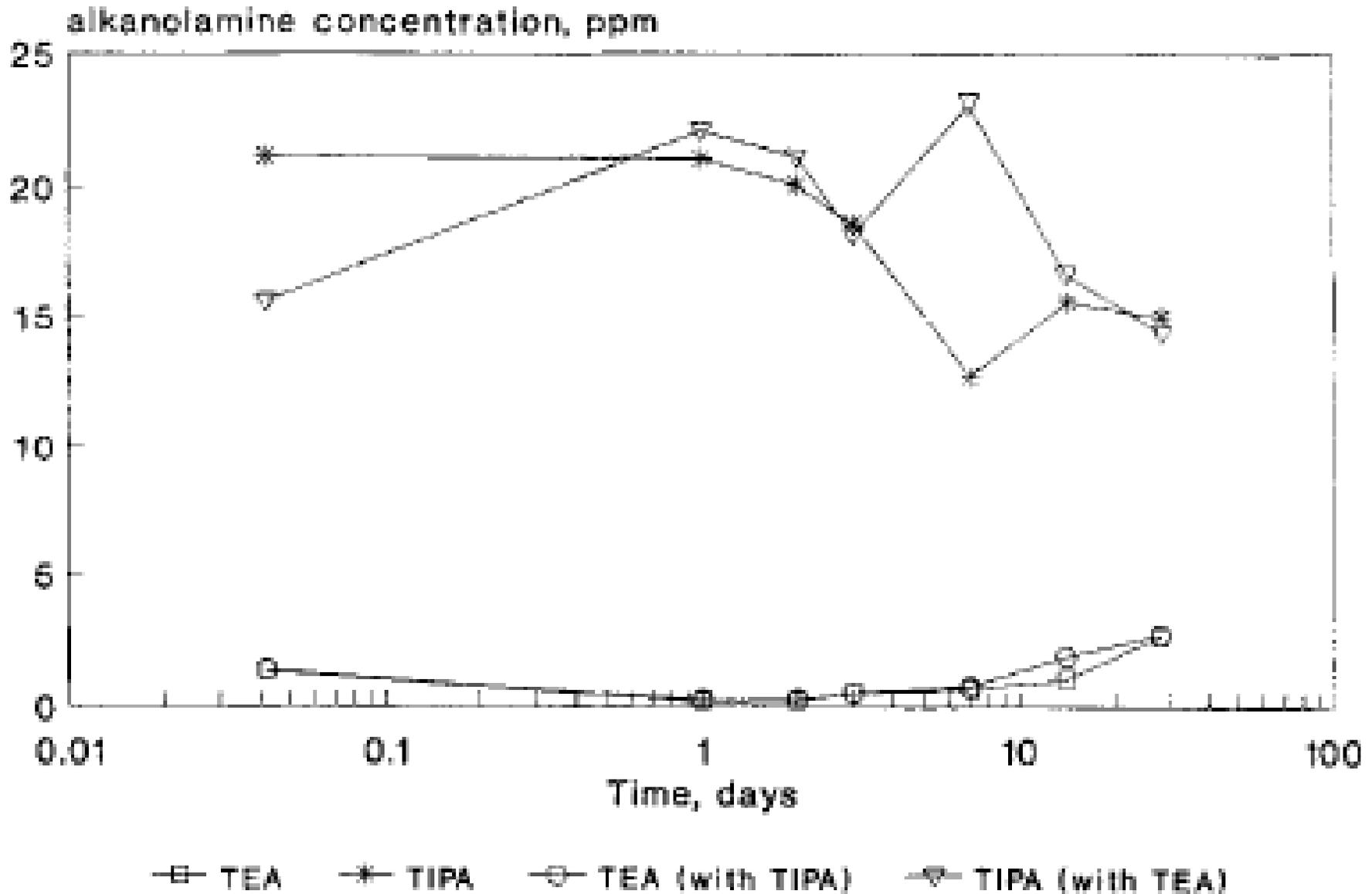
Adsorption of TEA or TIPA by cement "CLFC" at w/c = 6; 23°C
(with initial alkanolamines concentrations of 400ppm in aqueous phase)



Adsorption of TEA and TIPA by cement "CEI" at $w/c = 5$, 23°C
(at initial individual alkanolamine concentrations of 20ppm in the aqueous phase)

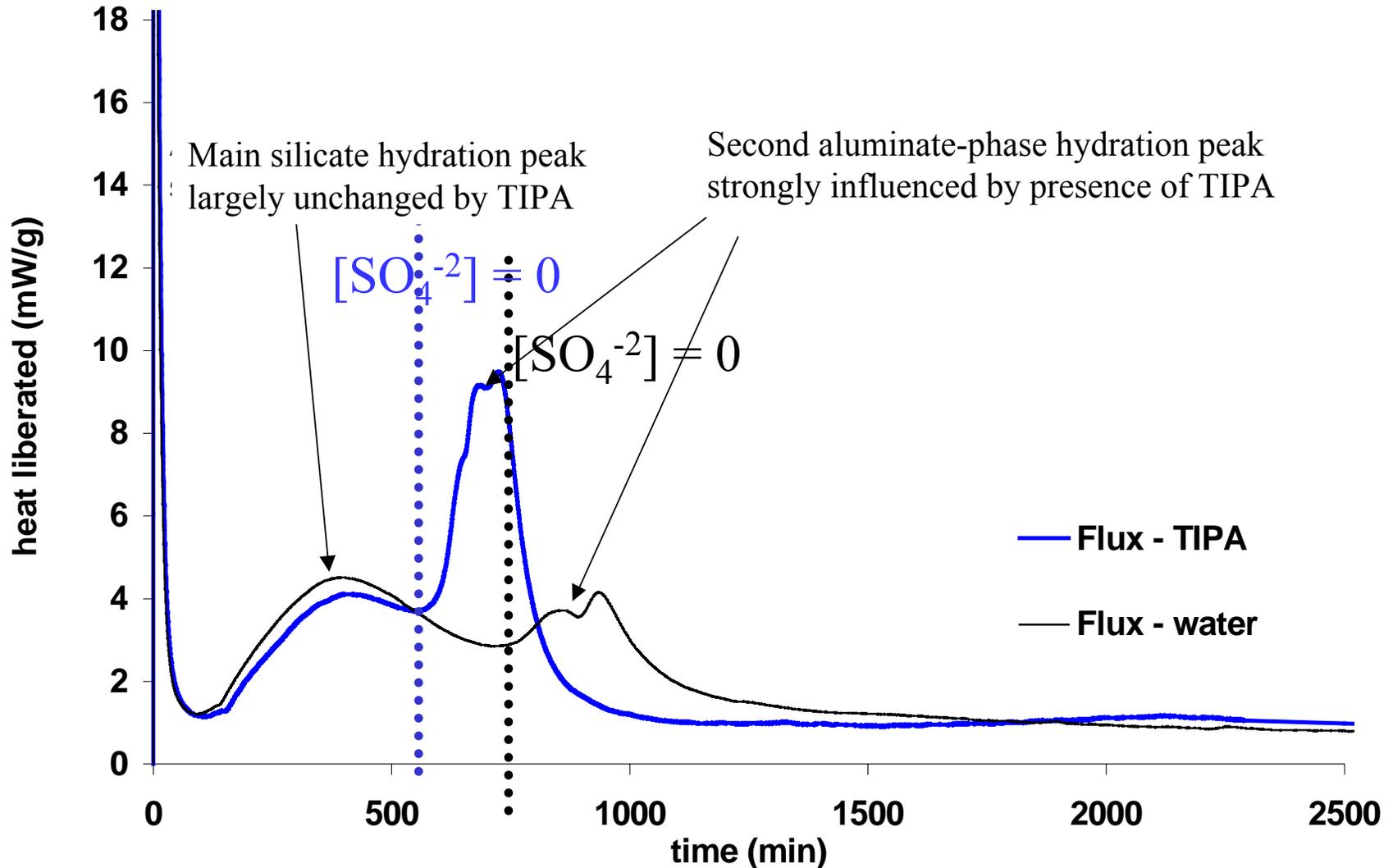


Adsorption of TEA and TIPA by 58:36:6 C₄AF:CH:C \hat{S} H₂ blend at w/s = 5
(at initial individual alkanolamine concentrations of 20ppm in the aqueous phase)



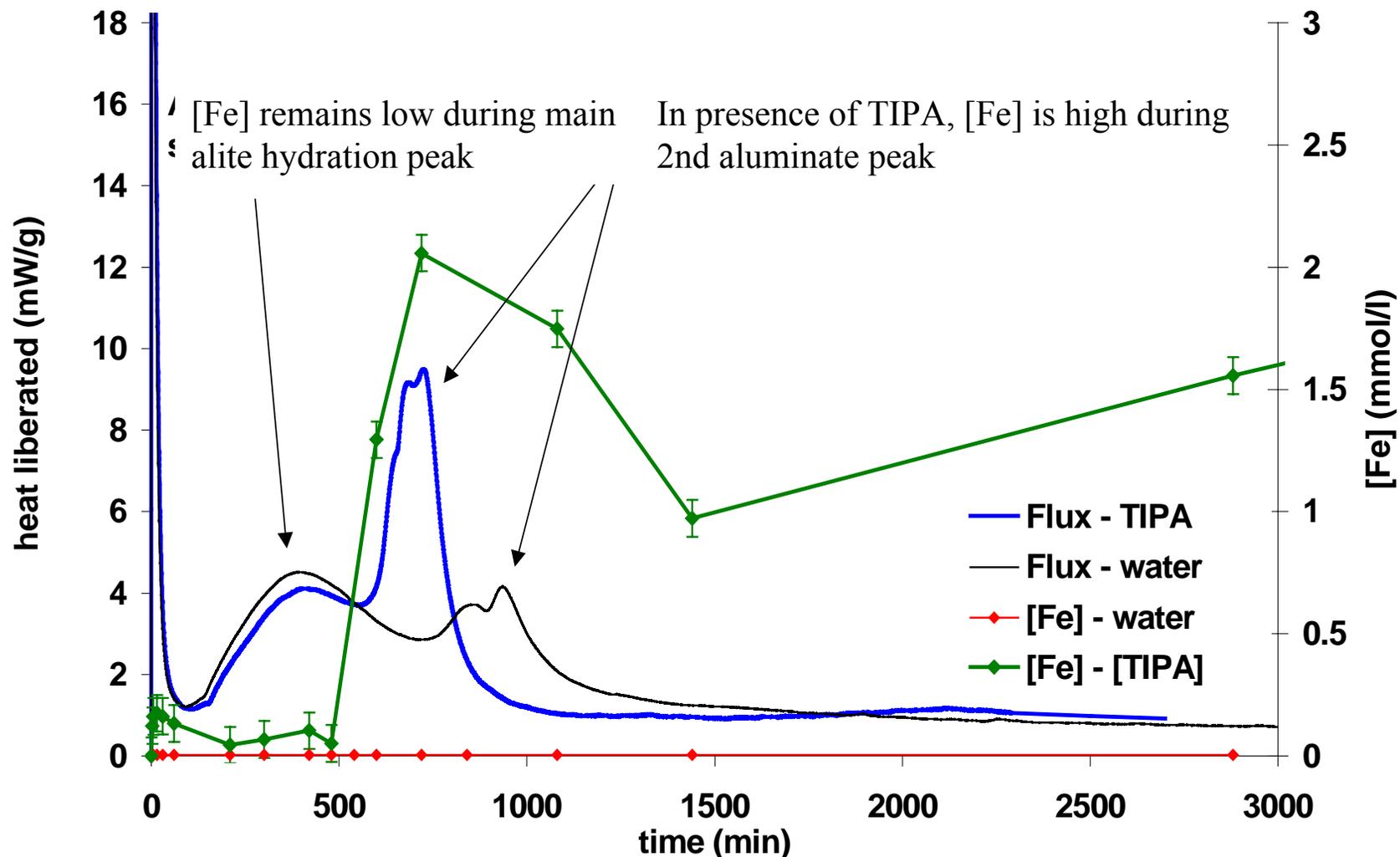
Cement hydration with or without TIPA

Slurry, w/s = 5, in either D.I. water or TIPA solution (3.2 g/l)



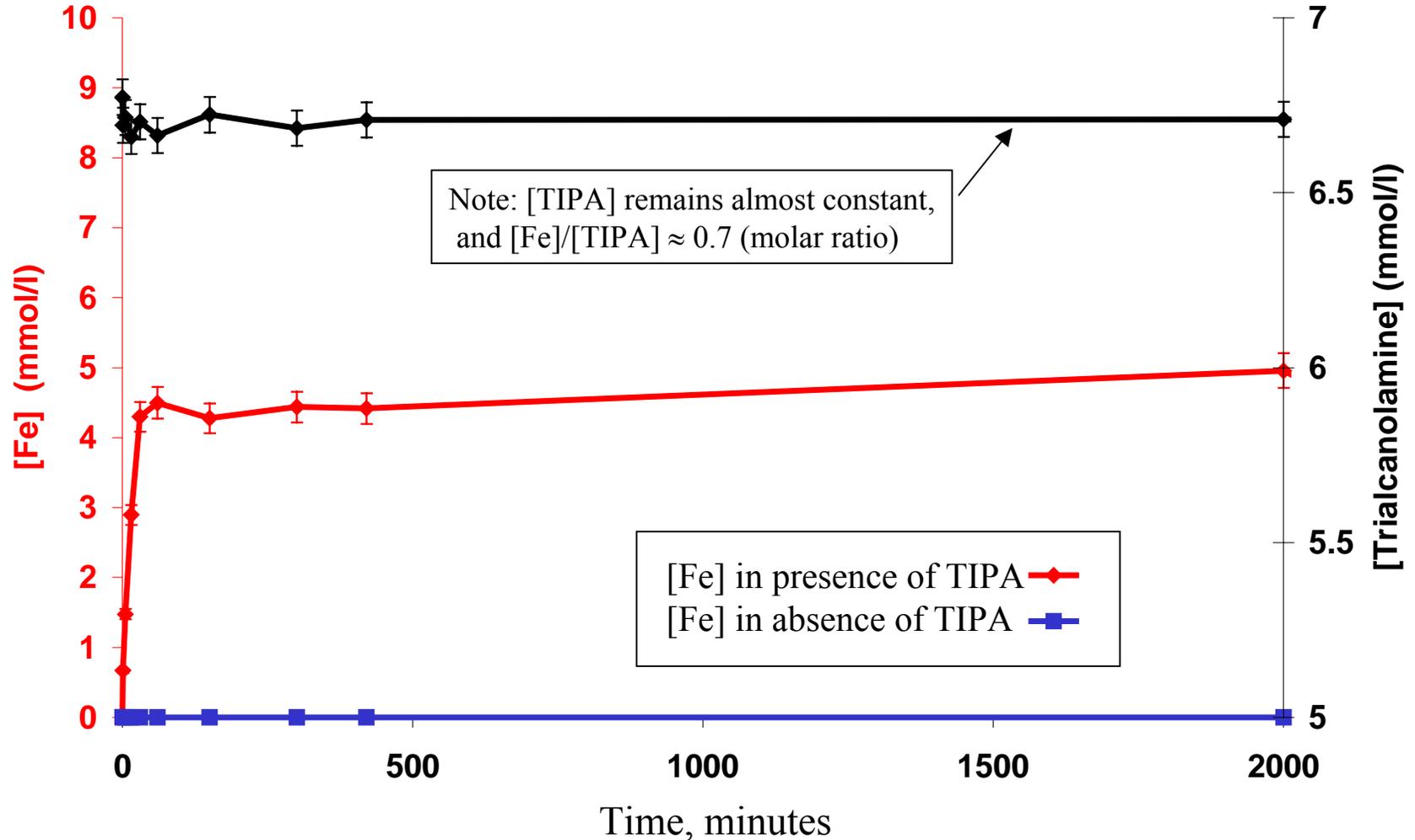
Influence of TIPA on dissolved iron concentration

Cement slurry, w/s = 5, in either D.I. water or TIPA solution (3.2 g/l)

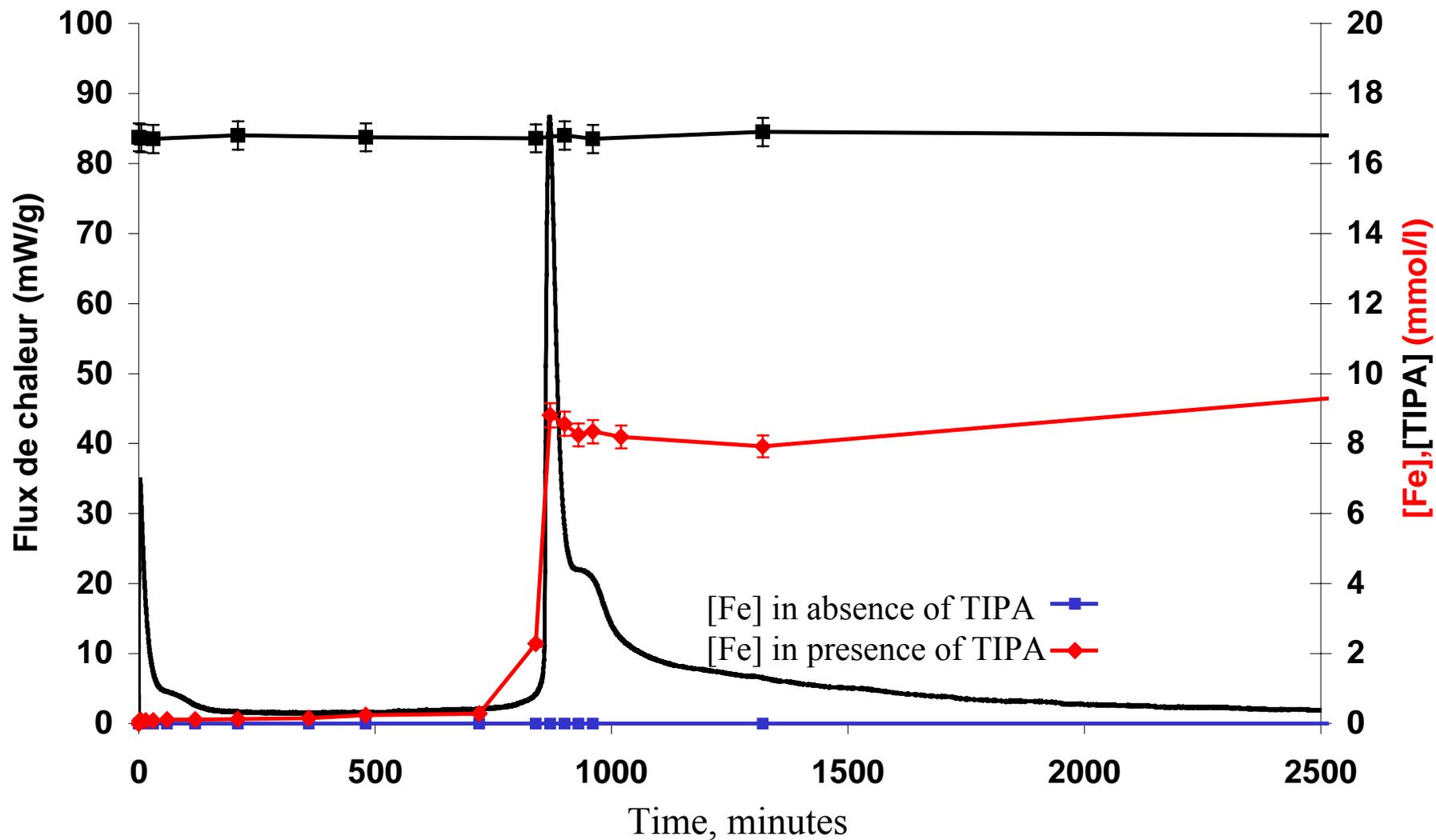


Big increase in dissolved Fe is evidence for complexation by TIPA.

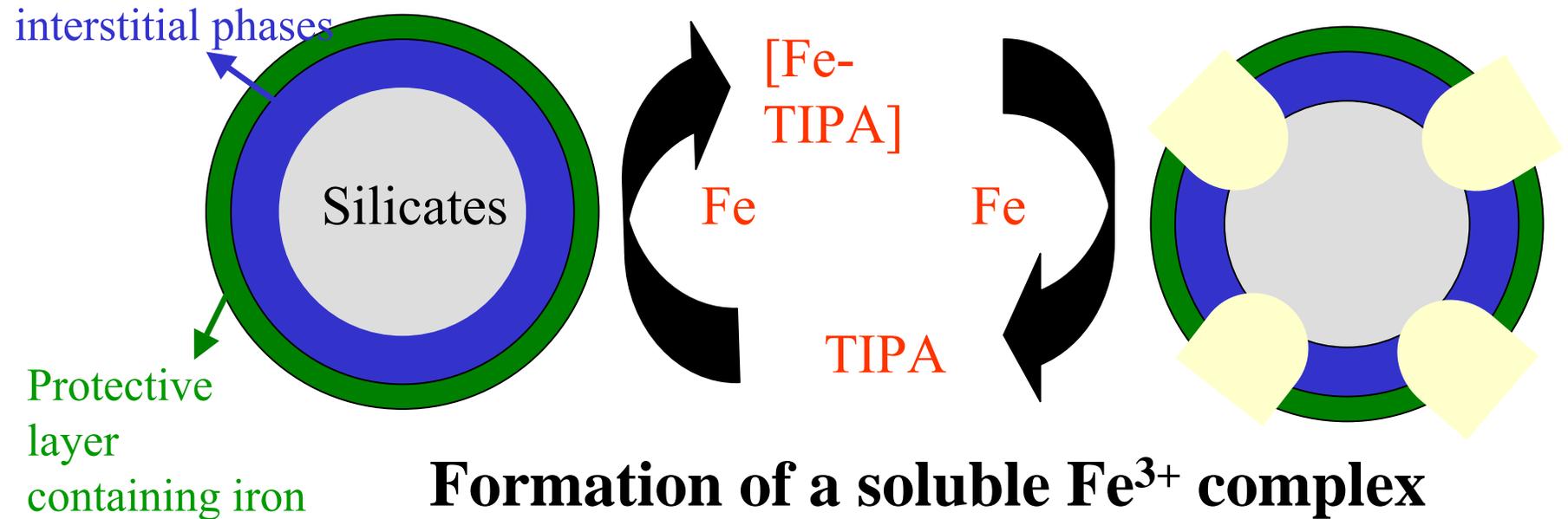
Suspension of C_4AF with excess $Ca(OH)_2$ at $w/s = 50$ (aqueous concentrations in presence or absence of added TIPA)



Suspension of $C_3A + C_4AF$ (1:1 molar) + gypsum + $Ca(OH)_2$ at $w/s=50$
(Heat flux and TIPA concentrations in black; Fe concentrations in blue or red)



Catalytic mechanism proposed by Gartner and Myers



Disruption of an Fe^{III} -rich protective layer by facilitated Fe^{3+} transport. In large polyphasic clinker grains the retardation of ferrite hydration can also block all of the other clinker phases.

Degree of hydration of all clinker phases is increased.

Mechanical strength enhancement

Further supporting evidence for this model

- Ichikawa *et al.** confirmed by X-ray diffractometry that small additions of TIPA increased the degree of hydration at 28 days of both the ferrite phase and of the alite in grey OPC pastes.
- The strength-enhancing effect of TIPA was greater in more coarsely-ground cements and those with higher alite contents, but was not observed in a white cement.
- TIPA also enhanced the reaction of a limestone filler.

* [paper 3iii005 in “*Proceedings of the 10th International Congress on the Chemistry of Cement,*” Gothenburg, Sweden, (1997).]

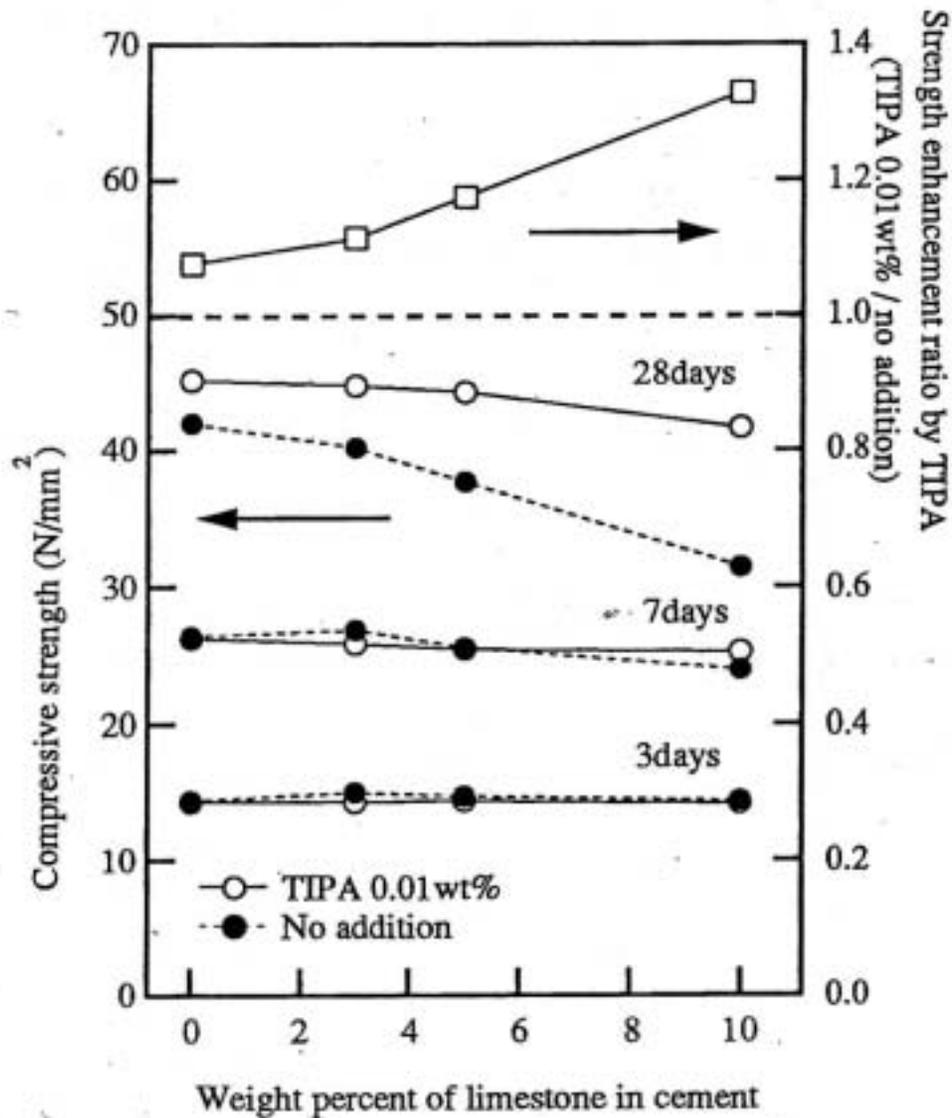
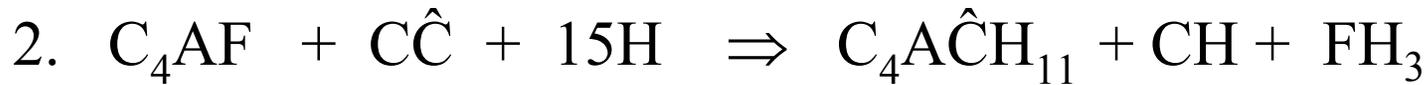
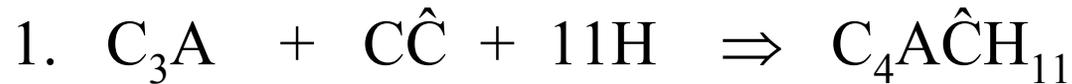


Fig. 3 Relationship between the limestone content in cement and the strength enhancement of mortar by TIPA. (Clinker: N, Blaine specific surface area: 325m²/kg, SO₃: 2.0%)

From: Ichikawa, M., Kanaya, M. and Sano, S. "Effect of triisopropanolamine on hydration and strength development of cements with different character", paper 3iii005 in "Proceedings of the 10th International Congress on the Chemistry of Cement," Gothenburg, Sweden, 1997.

Enhanced reaction with limestone fillers

After complete consumption of the readily soluble sulfate, the aluminates phases continue to hydrate to give AFm phases. If limestone ($C\hat{C}$) fines are present, the following reactions can occur:



Results of Ichikawa *et al* (1997) and of Gartner *et al* (1998)§ confirm that TIPA catalyses reaction (2) but do not show clearly whether or not it also catalyses reaction (3). Either reaction will increase the amount of bound water and thus the hydrate volume per unit cement.

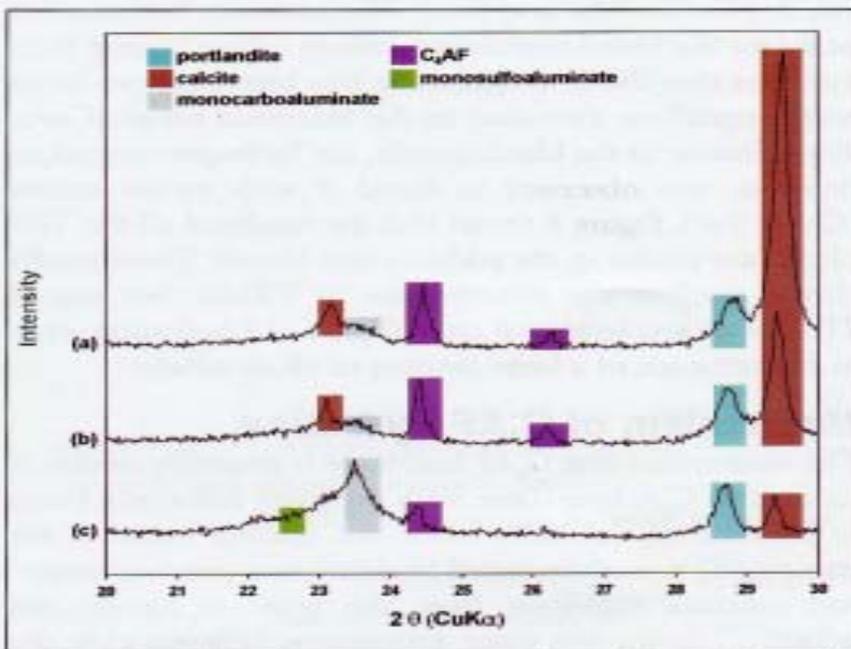


Figure 4. X-ray Diffraction Patterns at 40-56 hours after t_1 with no additives of (a) Blend 8, (b) Blend 6, and (c) Blend 7.

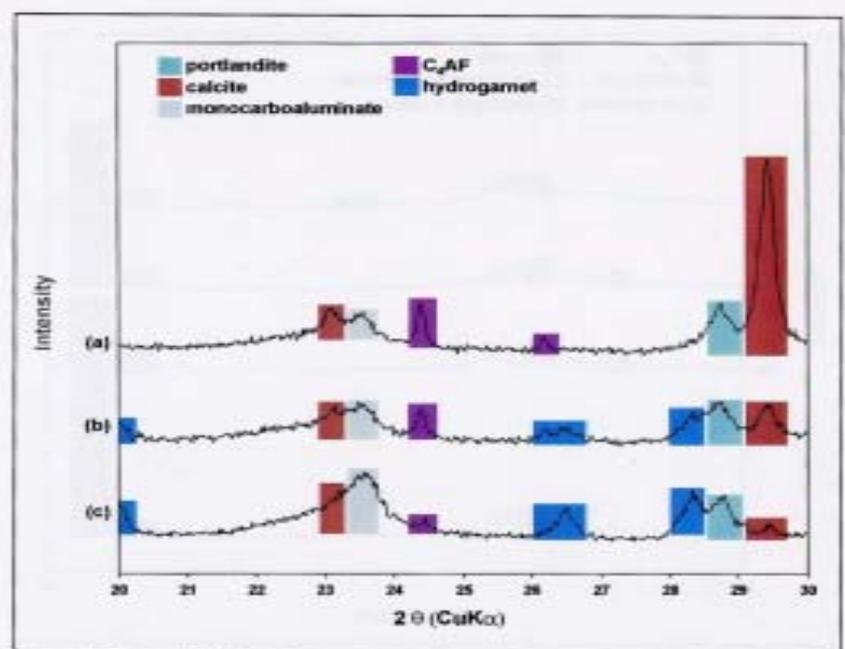


Figure 5. X-ray Diffraction Patterns at 40-56 hours after t_1 with CB100 of (a) Blend 8, (b) Blend 6, and (c) Blend 7.

Note: CB100 = TIPA!

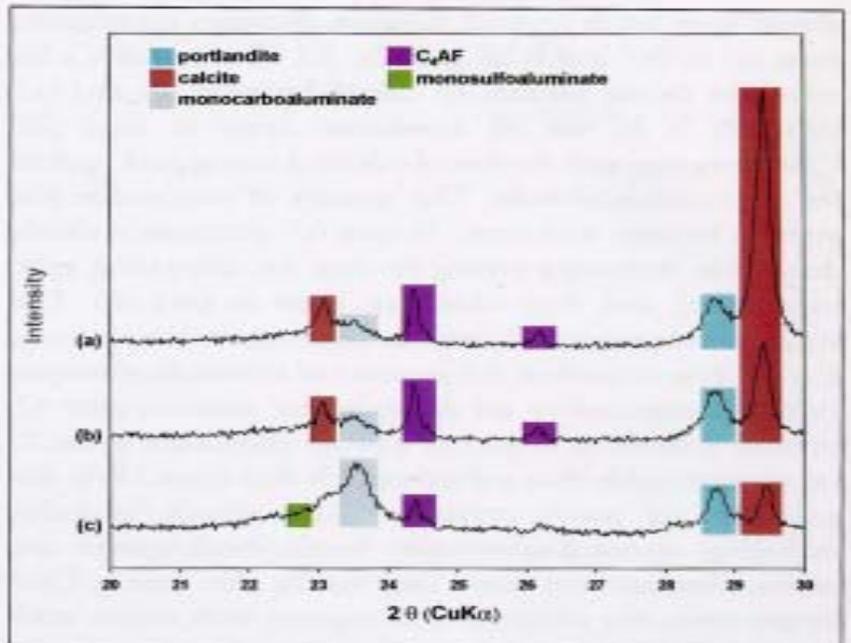


Figure 6. X-ray Diffraction Patterns at 40-56 hours after t_1 with TEA of (a) Blend 8, (b) Blend 6, and (c) Blend 7.

From: Gartner, E. M., Hu, R., and Cheung, J. H., "Influence of Tertiary Alkanolamines on Rates of Reaction of C_3A and C_4AF with Calcite Under Conditions Typical of Portland Cement Hydration in Concrete," World Cement, Research and Development, pp. 2-6, (June 1998)

Mass and (approximate) volume balances



$$270 + 100 + 198 \Rightarrow 568 \text{ (g)}$$

$$89 + 37 + 198 \Rightarrow 262 \text{ (ml)}$$



$$486 + 100 + 270 \Rightarrow 568 + 214 + 74 \text{ (g)}$$

$$130 + 38 + 270 \Rightarrow 262 + 57 + 33 \text{ (ml)}$$

For a typical OPC with 8% C_3A and 10% C_4AF , 3% (by mass of cement) of limestone can react with the C_3A and at least 2% (up to 4% if reaction (3) occurs) can react with the C_4AF and water to generate new hydrates.

Value of TIPA for enhanced cement performance

- It allows a greater volume of hydrates to be produced per unit clinker content (after 28 days curing), thereby reducing specific energy consumption and CO₂ emissions per unit of cement.
- It can also permit more effective use of reactive limestone fillers, further saving on energy use, especially for finish grinding.

But there are some important unanswered questions:

- Why doesn't TIPA work well in every grey cement?
- Does the improved performance observed at 28 days in standard tests persist even after many years in actual service?
- What is the long term effect on concrete durability, especially if it is used as a means of reducing clinker content/concrete volume.
- Is the carboaluminate hydrate phase good for durability?
- Does TIPA increase the Fe/Al ratio of the AFt or AFm phases?