Influence of Tertiary Alkanolamines on the Hydration of Portland Cement

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GRACE
Construction Products

July 27 – 29, 2009

Outline

- **Review of structures, impact on set and strength performances, mechanisms to explain performances**
  - Triethanolamine (TEA)
  - Triisopropanolamine (TIPA)
- **Conclusion**
- **Knowledge gaps**

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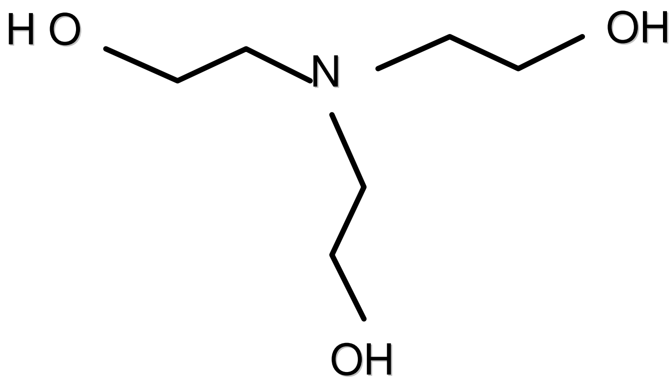
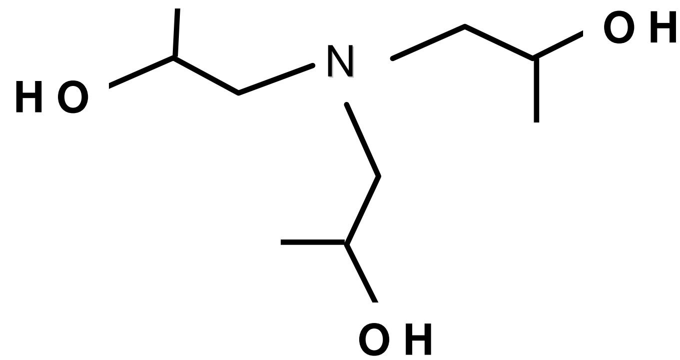
Structures and strength performances of TEA and TIPA



Triethanolamine (TEA)



Triisopropanolamine (TIPA)

En-196 Mortar Strength (% of blank)	1-day	2-day	28-day
Blank	100%	100%	100%
0.02% TEA	116%	106%	97%
0.02% TIPA	100%	110%	110%

- QXRD = 6.9% C4AF, 3.6% *cubic*-C3A, 3.3% *ortho*-C3A, 68.5% alite, 4.4% belite, 5.5% gypsum, 0.7% plaster, 4.4% calcite, 1.6% periclase
- Sol. Alkali (Na_2O eq.) = 0.08%, BSA = 385 m^2/kg

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Effect of set by different dosages of TEA

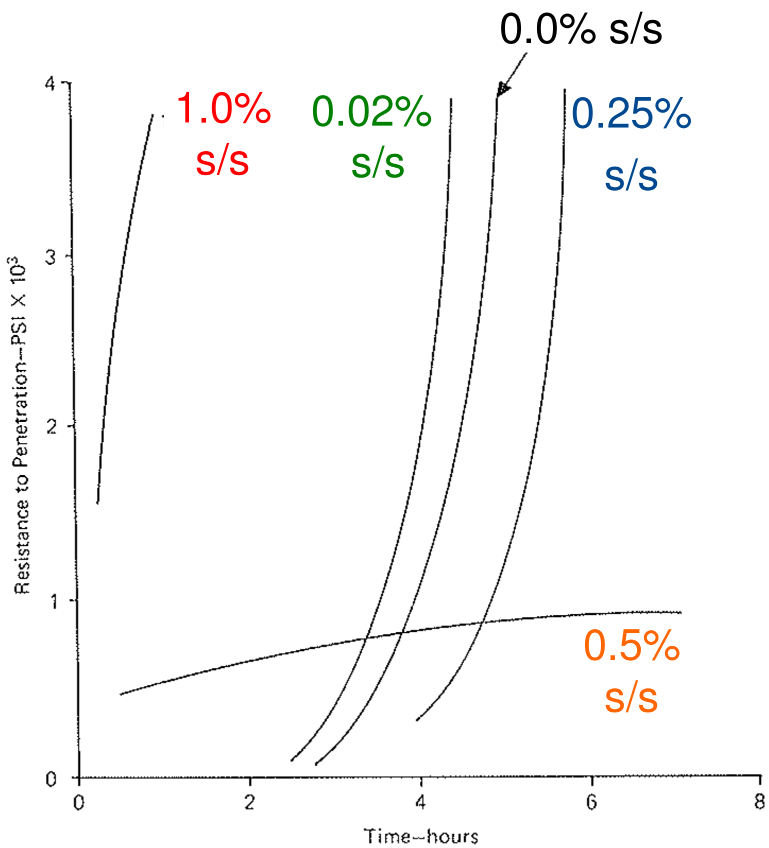


Figure 4-10. Time of setting characteristics of concretes treated with triethanolamine.

For cement tested in this work, cement composition not published

- At 0.02 % by weight of cement (1.3 - 3.4 mM assuming w/c=0.5), typical dosage used in concrete, TEA was an accelerator
- At 0.25% (~34 mM), TEA was a set retarder
- At 0.5% (~68 mM), TEA caused early initial set but did not reach final set
- At 1.0% (~136 mM), TEA led to flash setting

Vance Dodson, Concrete Admixtures, Van Norstrand Reinhold (1990), New York, pg 92-96

Large changes in set performance induced by different dosages of TEA
TEA dosed at ≥0.5% in many publications

Effect of strength by different dosages of TEA

- **Ramachandran (1976***)*

Cement : Bogue = 6.1% C_4AF, 10% C_3A, 54.2% C_3S, 20.7% C_2S, BSA = 310 m²/kg

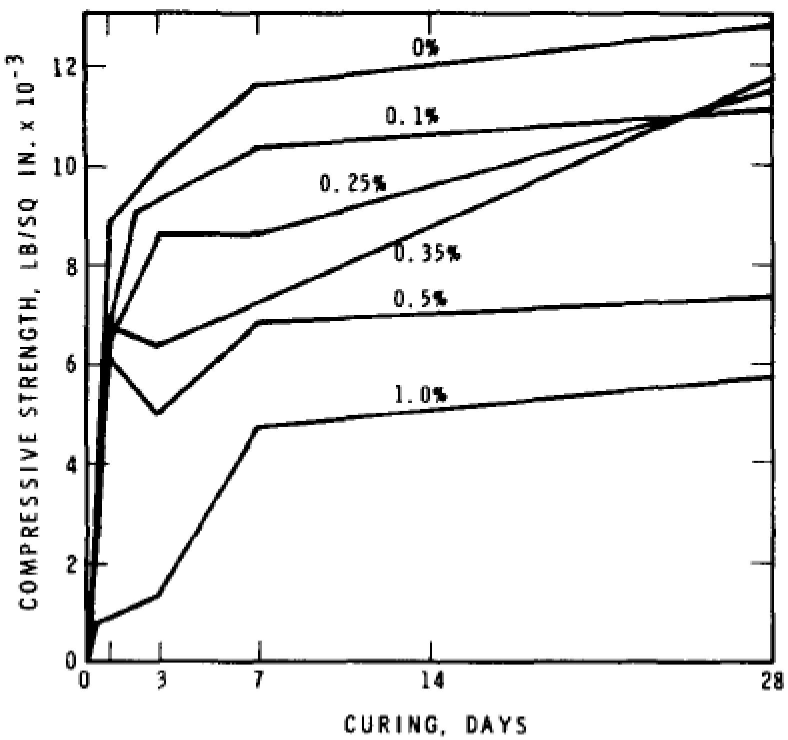
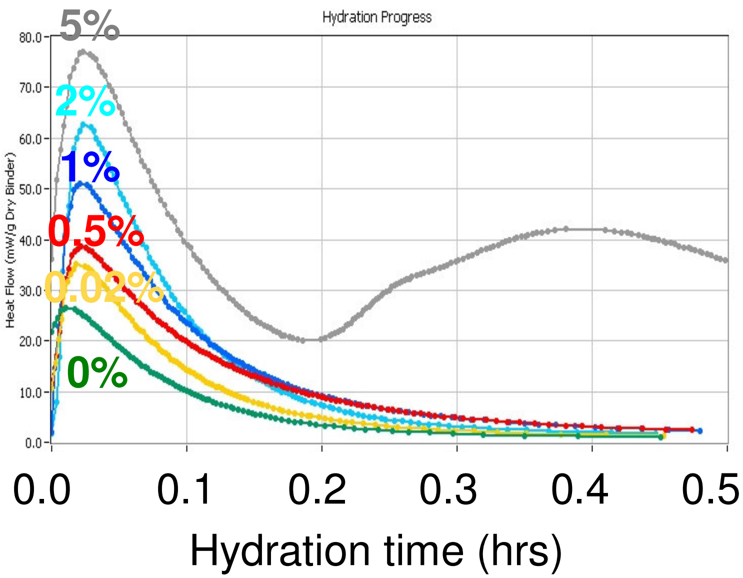


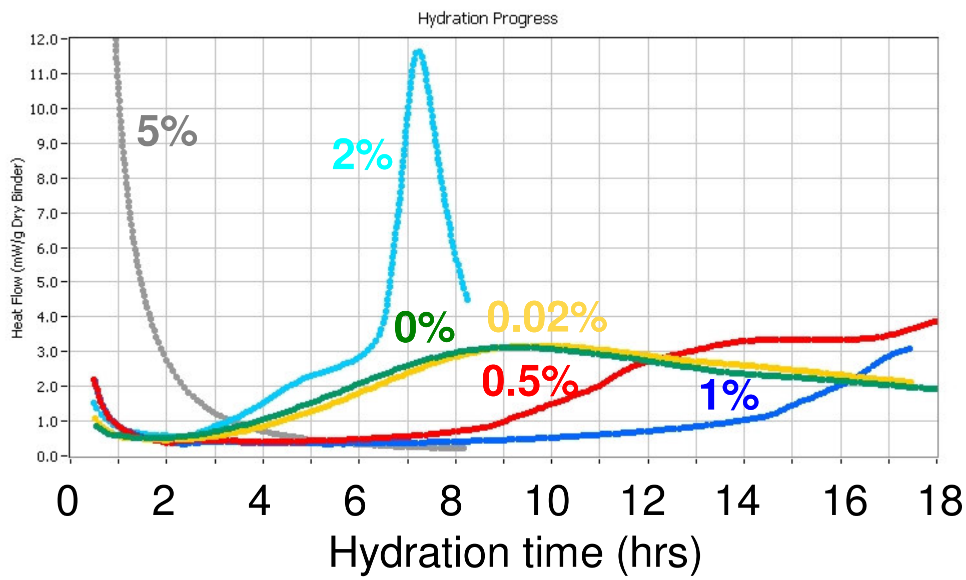
FIG. 6
Compressive strengths of cement pastes containing triethanolamine

- Large strength decrease when TEA is used at 0.1-1%
- Typical dosage used in field = 0.005 – 0.03%
- Strength impact different form typically observed in cement and concrete

Calorimetry of gray cement treated with different doses of TEA

QXRD = 6.9% C4AF, 3.6% *cubic*-C3A, 3.3% *ortho*-C3A, 68.5% alite, 4.4% belite,
Sol. Alkali (Na2O eq.) = 0.08%, BSA = 385 m2/kg,

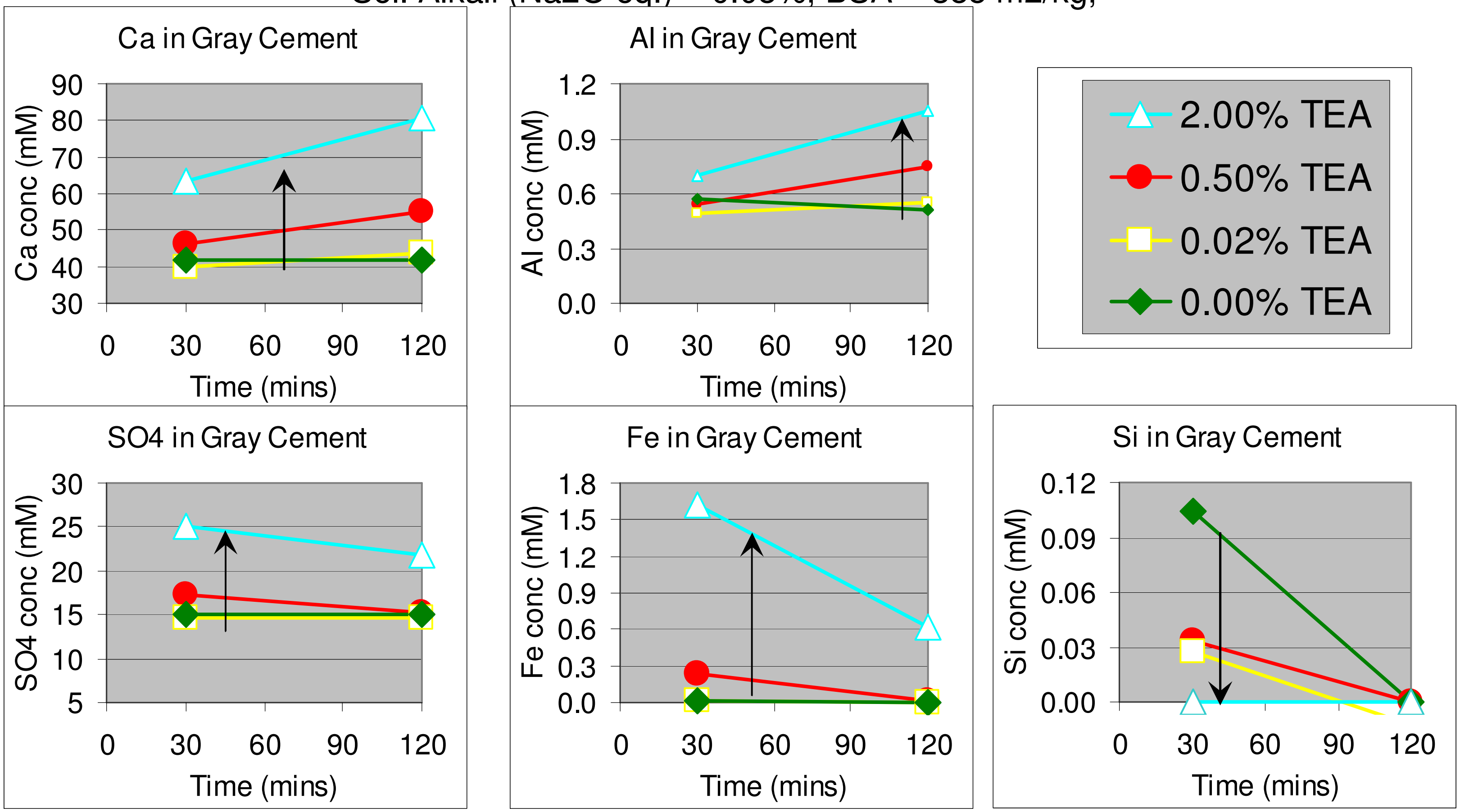




- TEA increases initial exotherm with increasing dosages
- Slight retardation @ 0.02% TEA
- Severe retardation @ 0.5% and 1% TEA
- Abnormal set @ 2% TEA
- Flash set @ 5% TEA
- **Different dosages lead to different set performance on different cements**

Pore water analysis & calorimetry of gray cement treated with different doses of TEA (30 min & 2 hr)

QXRD = 6.9% C4AF, 3.6% *cubic*-C3A, 3.3% *ortho*-C3A, 68.5% alite, 4.4% belite,
Sol. Alkali (Na2O eq.) = 0.08%, BSA = 385 m2/kg,



- Significant increase in dissolution of Ca and SO_4 @ 2% TEA – abnormal set

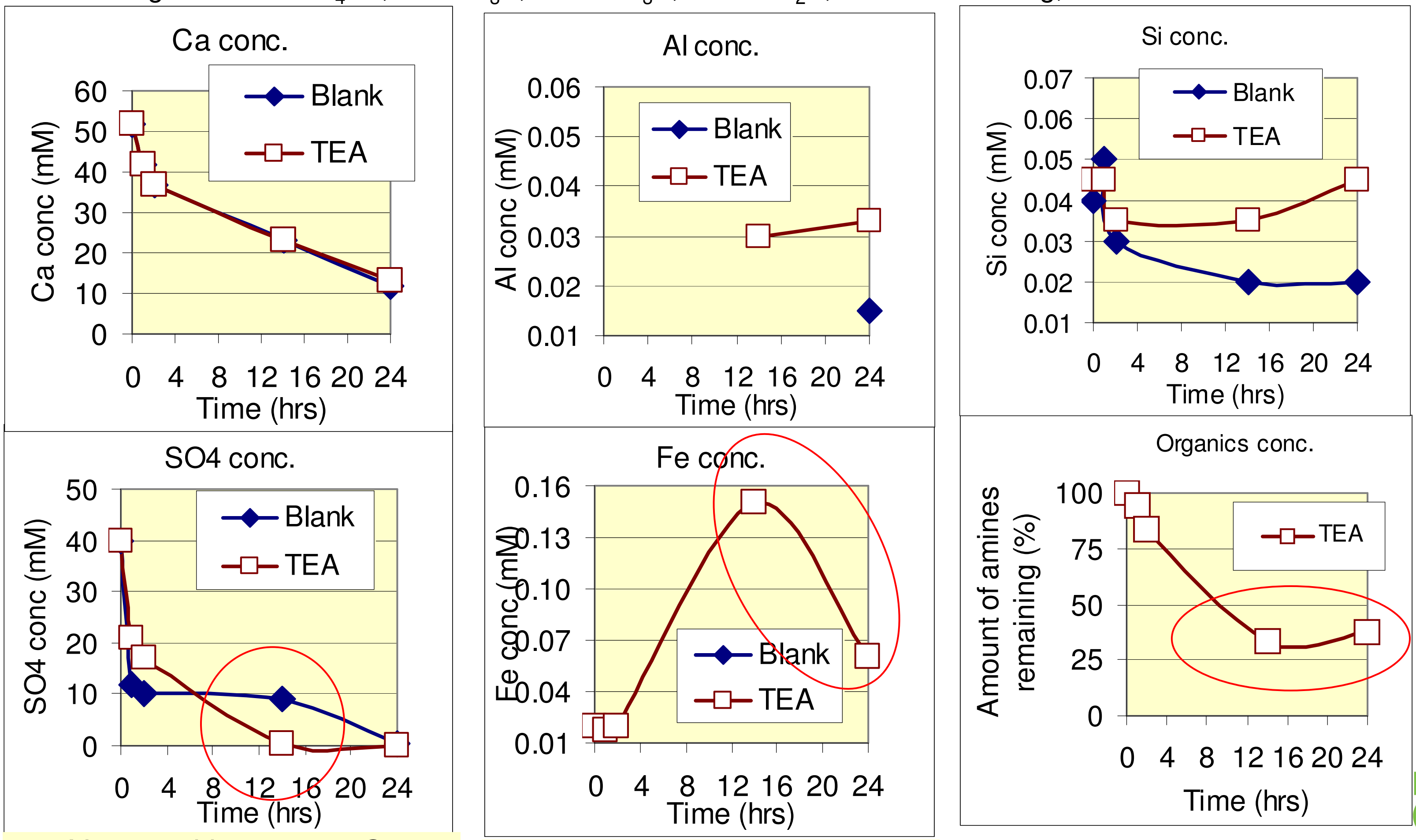
- Increased dissolution of Al and Fe with increasing TEA
- Significant increase in dissolution of Al and Fe with 2% TEA

- Decreased dissolution of Si at 30 min with increasing TEA

Pore solution analysis of cement treated with 0.24% TEA

- *Gartner and Myers (1993)*

Cement : Bogue = 10.1% C_4AF, 5.3% C_3A, 58.9% C_3S, 20.2% C_2S, BSA = 380 m^2/kg, w/c=6

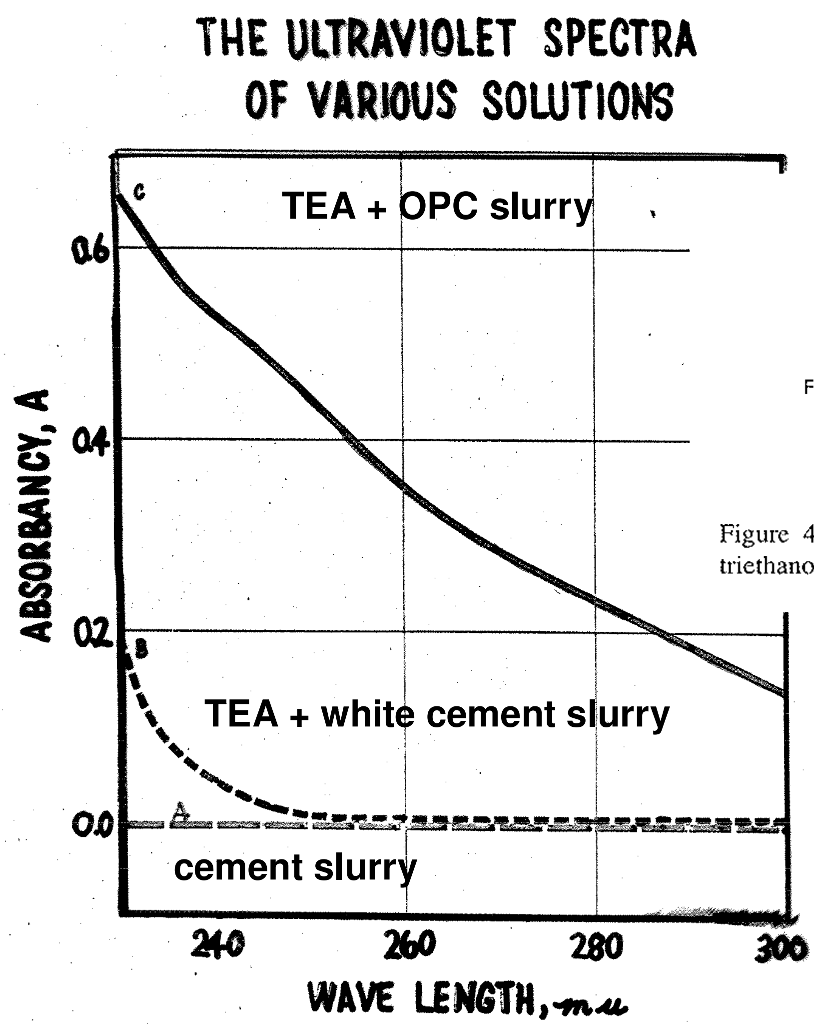


- No noted impact on Ca
- Earlier on-set of sulfate depletion with TEA

- Increased dissolution of Al
- Increased dissolution of Fe coincides with on-set of sulfate depletion

- Increased dissolution of Si
- Decrease of TEA coincides with the on-set of sulfate depletion

Chelation of ferric ion by TEA under high pH



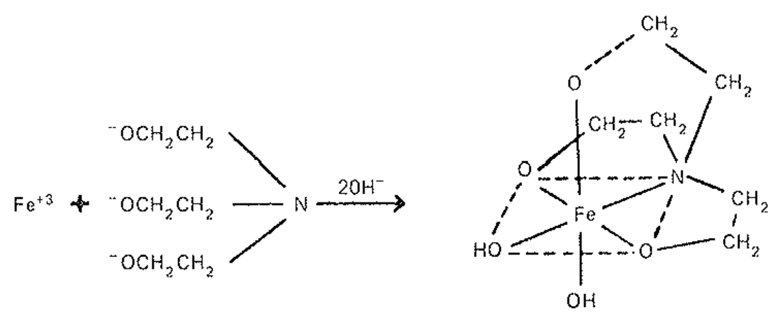


Figure 4-12. Chelation (solubilization) of the ferric ion in Portland Cement by triethanolamine.

S. Chaberek & A. E. Martell, Organic Sequestering Agents, John Wiley & Sons, Inc. New York (1959) pg 325

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Perez (2003)

Bogue of clinker = 12.1% C4AF, 6.5% C3A, 62.7% alite, 18.7% belite

Gypsum added (1.63% SO3) %, BSA = 350 m²/kg

TEA : 17 mmol/l = 0.54% (severely retarding regime)

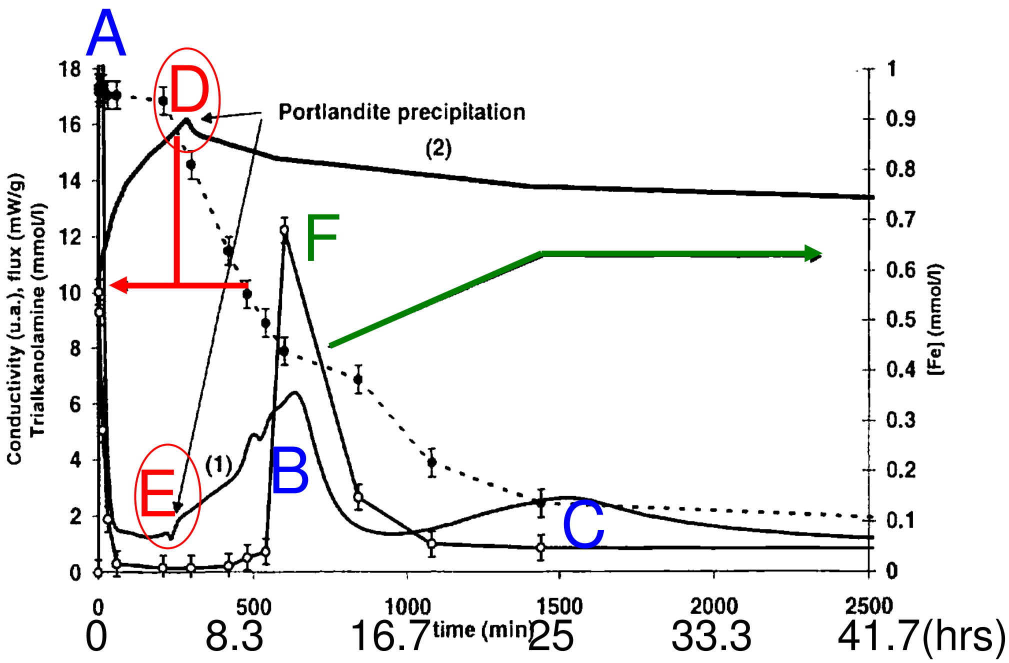

Fig 2.: Evolution at early age of heat liberated (1), conductivity (2), iron (o) and TEA (•) concentration in solution for a cement (4g) hydrated in presence of TEA (17 mmol/l) w/s = 5 at 25°C.

Calorimetry

- **A** = Dissolution of different anhydrous phases followed by precipitation of hydrates (e.g. ettringite and CSH)
- **B** = Acceleration of the silicates
- Sulfate depletion leads to the third peak
- **C** = hydration of aluminates without sulfate,
  ppt. of calcium aluminate hydrates,
  dissolution of ettringite, and
  ppt. of the Ca monosulphoaluminate

Conductivity

- Rise of Ca and OH from C3S dissolution and to CSH precipitation
- **D** = Portlandite precipitates when the solution reaches max. supersaturation
  = drop in TEA
- **E** = Endotherm in calorimetry

Dissolution of Fe

- **F** = Max. dissolution of Fe at 10-14 hr, even though TEA conc is decreasing.

Hydration model for cement treated with TEA

<table>
<tr><th>Dosage</th><th>ICP & calorimetry
by Sandberg (2003) & Cheung</th><th>Observations in Ramachandran (1972, 1973) & Swenson (1971)</th></tr>
<tr><td rowspan="2">0.01 – 0.05 % s/s
Accelerating/ Mildly retarding
*Gartner</td><td>▪ No noted difference in dissolution of Ca, S, Al, Fe, Si. But data not run between 10-14 hours where differences in dissolution of S and Fe were noted at higher addition rates.</td><td>▪ No data found.</td></tr>
<tr><td colspan="2">No additive (Minard 2003)
▪ AFt and hydroaluminates are formed from the beginning of hydration.
▪ Aft -> monosulfate transformation takes several days [in first day]
▪ Proposed that sulfates adsorb onto C3A surfaces and slow its dissolution rate very quickly after wetting
▪ Exhaustion of gypsum causes rapid desorption of sulfates and a reactivation of C3A dissolution to form hydroaluminates
TEA
▪ What causes strength enhancement? Need to run study.</td></tr>
</table>

Hydration model for cement treated with TEA

Dosage	ICP & calorimetry by Gartner (1993) & Perez (2003)	Observations in Ramachandran (1972, 1973) & Swenson (1971)
0.2 – 1 % s/s **Severely retarding** ***Perez** ***Swenson** ***Ramachandran**	▪ Earlier on-set of sulfate depletion ▪ Increase dissolution of Ca, SO4, Al, Fe & Si ▪ TEA adsorbed by portlandite after sulfate depletion	▪ Extension of induction period of C3S and β-C2S phases ▪ Formation of lower calcium-sulfoaluminate phases
	The dissolution of Al, Fe and SO4 by TEA changes the Al-SO4 balance (under-sulfated cement), leading to the formation of lower calcium-sulfoaluminate phases.	
1 - 5 % s/s **Strongly accelerating** **Flash setting** ***Ramachandran**	▪ Cannot extract pore solution without press in flashing setting paste	▪ Extension of induction period of C3S and β-C2S phases ▪ No observation of calcium-sulfoaluminate phases ▪ Formation of cubic calcium aluminates
	TEA rapidly dissolves all ions, creating a severely sulfate deficient system. Only cubic calcium aluminates are formed.	

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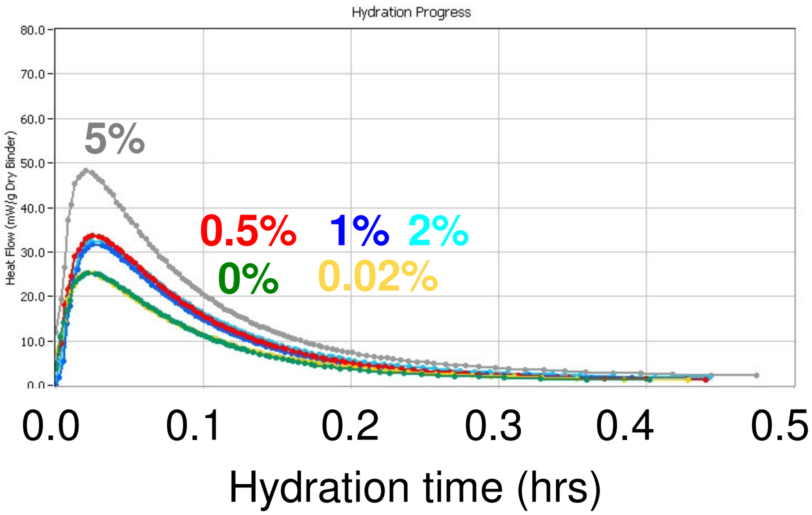
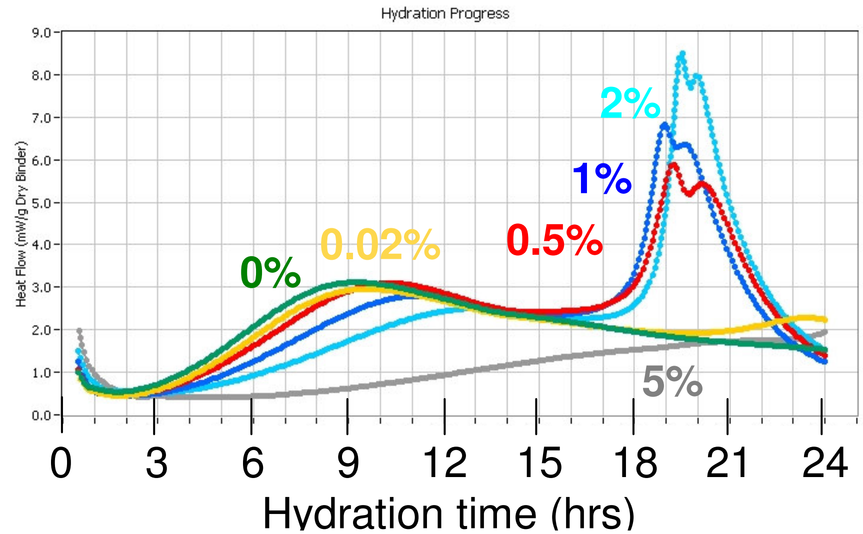
Calorimetry of gray cement treated with different doses of TIPA

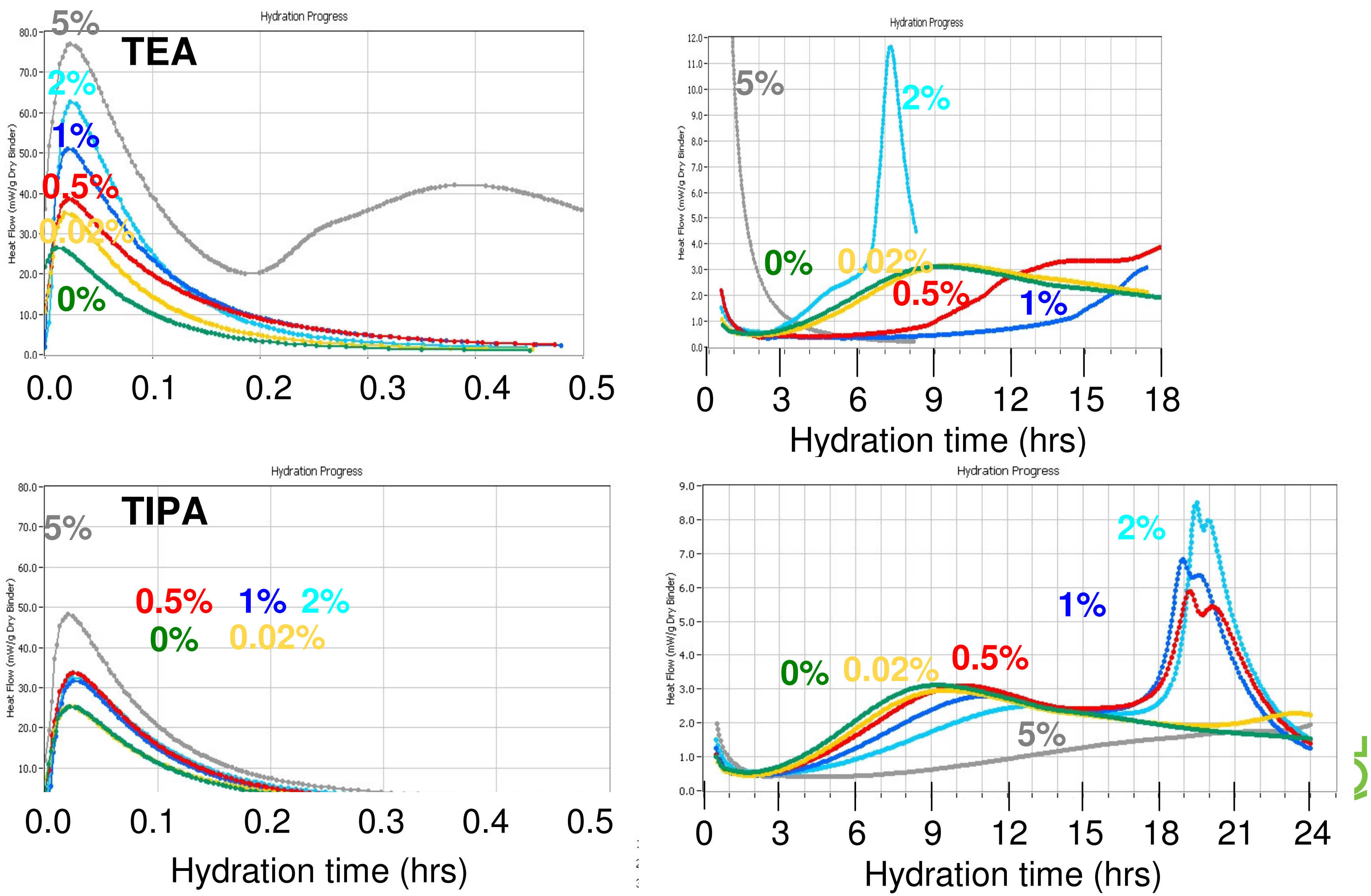
QXRD = 6.9% C4AF, 3.6% *cubic*-C3A, 3.3% *ortho*-C3A, 68.5% alite, 4.4% belite,
Sol. Alkali (Na2O eq.) = 0.08%, BSA = 385 m2/kg,





- **Initial exotherm less impacted by TIPA in comparison to TEA**
  - Slight retardation @ 0.02%, 0.5% TIPA
  - More retardation @ 1%, 2% TIPA
  - Severe retardation @ 5% TIPA
- **Earlier rise of third aluminate peaks** observed @ 0.5%, 1%, and 2%% TIPA
- **No early nor flash set noted with TIPA**

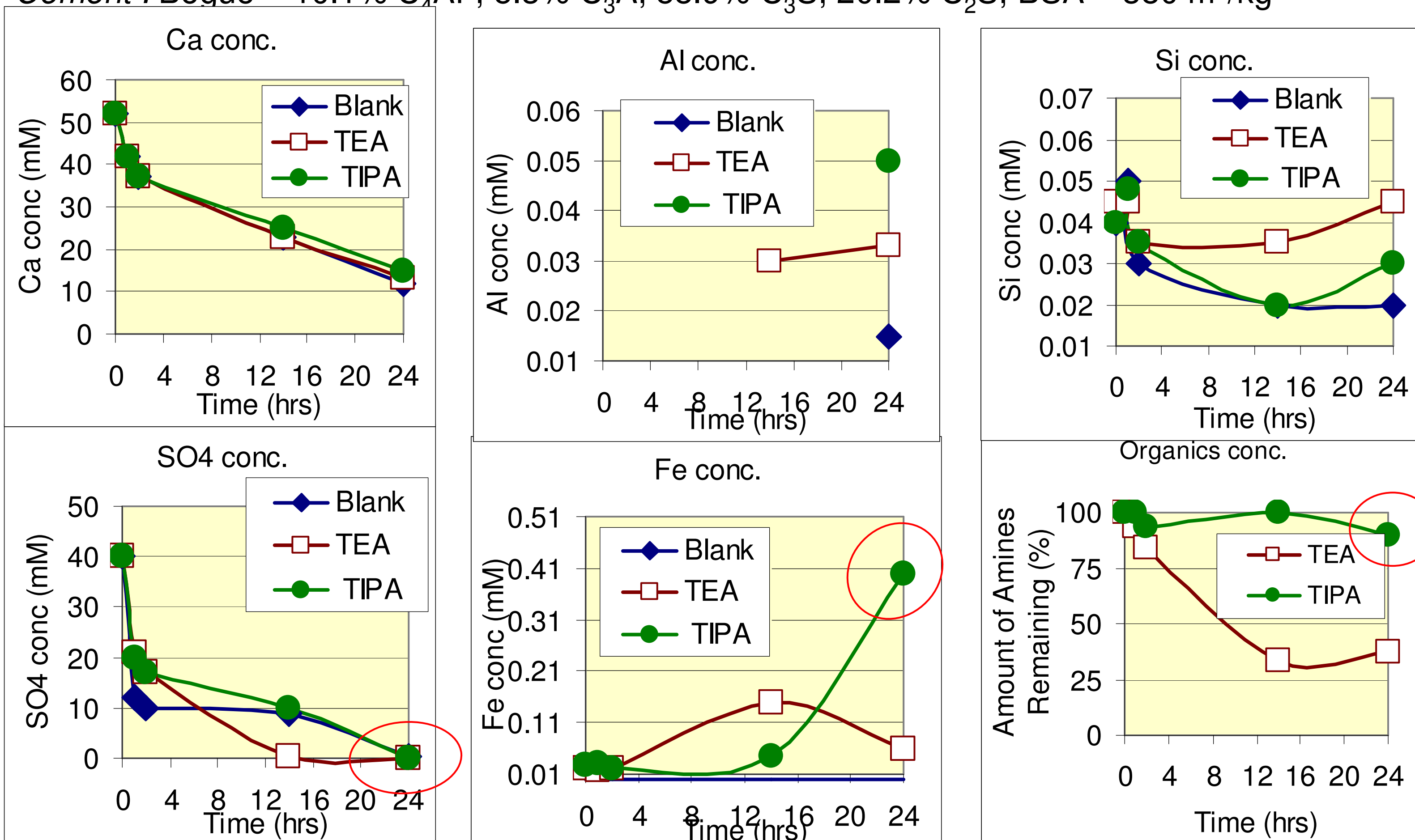
Calorimetry of TEA vs. TIPA (0.02%– 5%)



Pore solution analysis of cement treated with 0.24% TIPA

** Gartner and Myers (1993)*

Cement : Bogue = 10.1% C_4AF, 5.3% C_3A, 58.9% C_3S, 20.2% C_2S, BSA = 380 m^2/kg



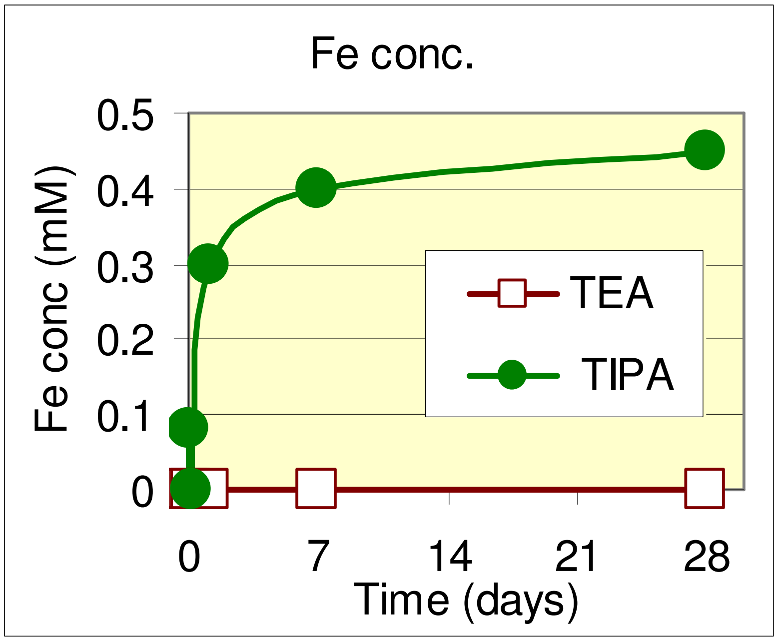
- No noted impact on Ca
- No noted impact on sulfate depletion form blank

- Increased dissolution of Al and Fe coincides with sulfate depletion

- No impact on Si from blank
- TIPA remains in solution even after depletion of sulfate

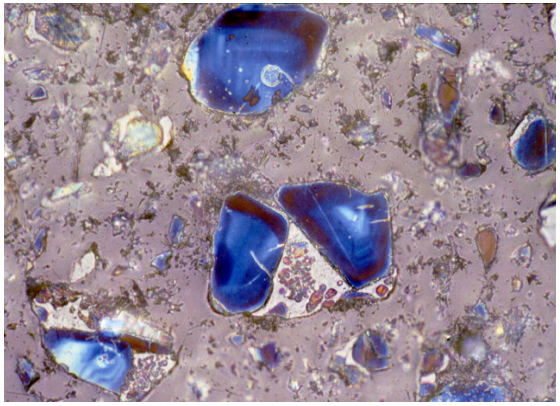
Fe Solubilization by 0.02% TIPA & 0.02% TEA (Sandberg, 2003)

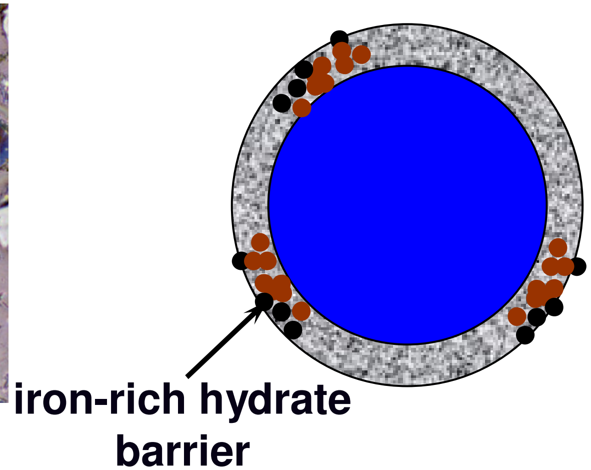
QXRD = 15% C4AF, 6% C3A, 51% alite, 27% belite w/c=0.5

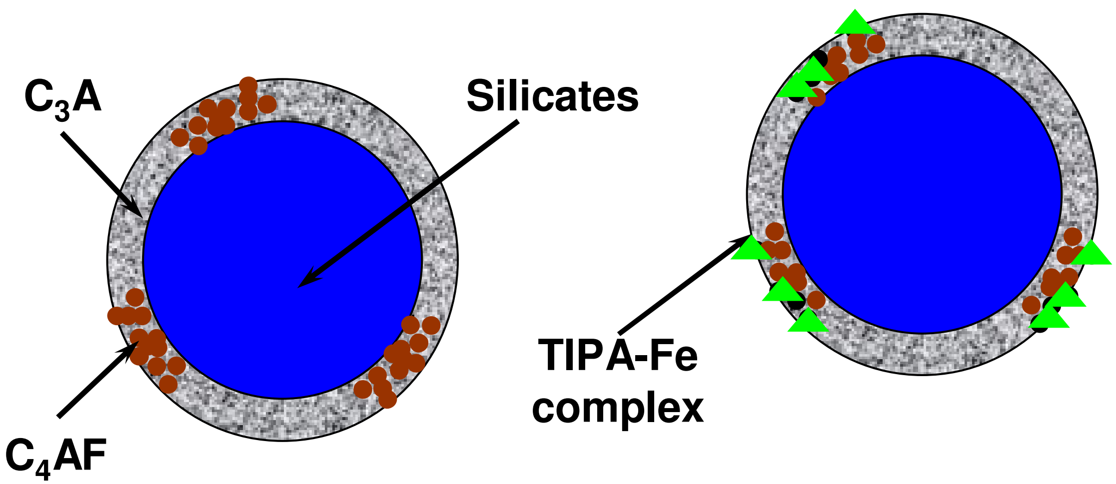


- More dissolution of iron seen with 0.02% TIPA, particularly at later ages
- Otherwise pore solution compositions were similar
- 0.02% TIPA = 2.1mM
- Sol. Fe at 7 and 28 days = 0.4-0.5 mM
- Total Fe from cement = 1235 mM

Schematic model of facilitated iron transport (Gartner 1993)





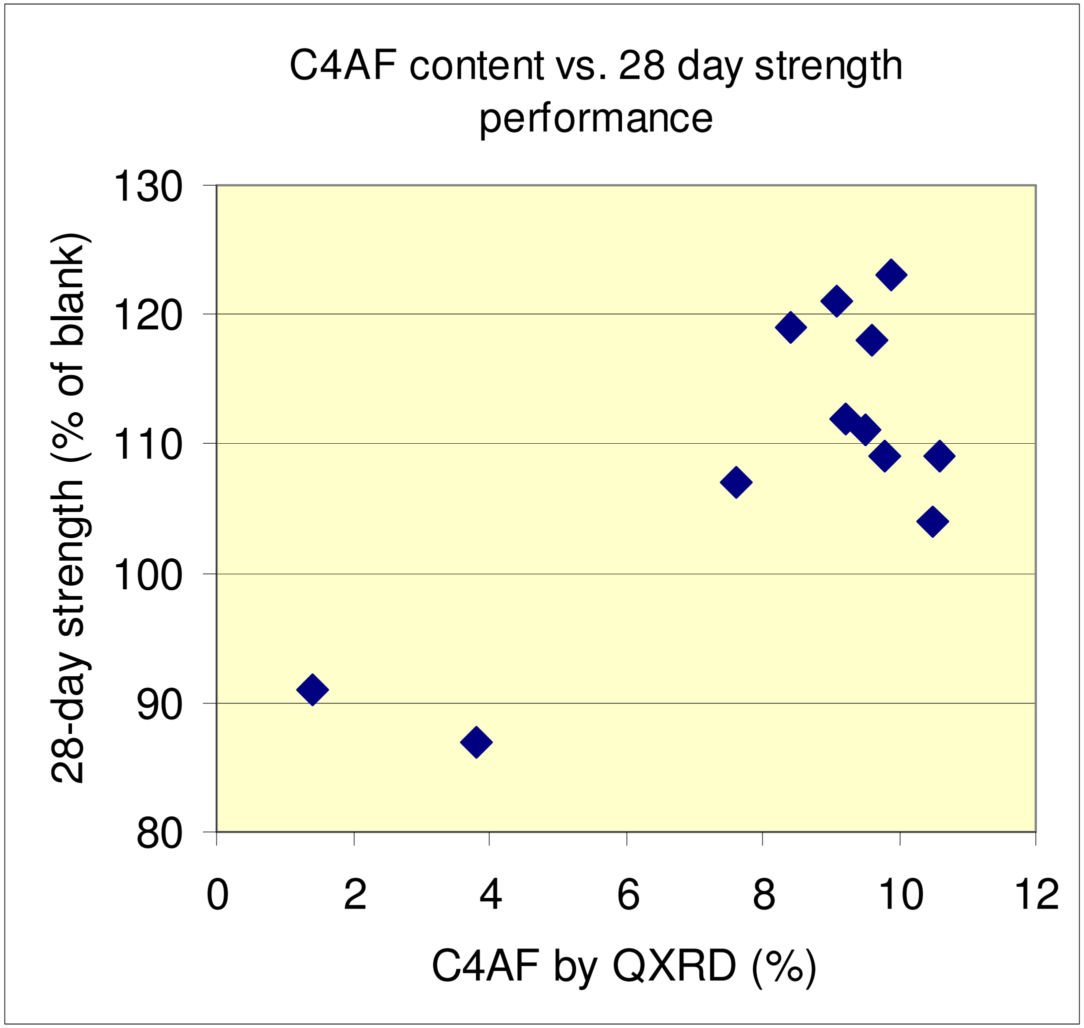


No TIPA - silicate phase blocked by iron hydroxide

TIPA solubilizes Fe beyond sulfate depletion. removing hydrate barriers, opening up more paths for silicate hydration

<u>Anhydrous</u>   <u>Hydration</u>

Correlation of C_4AF content and 28 strength enhancement



Gartner (1993)

- No results reported for 4 - 7.6% C4AF
- > 7.6% region, enhanced strength seen, but correlation between C4AF content and strength enhancement levels is not noted, suggesting there are other influencing factors
  - cement fineness
  - thickness and distribution of barriers

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Effect of fineness on performance of TIPA-ground cements

Blaine SSA (m2/kg)	Number of Tests	Compressive Strength (% over Blank)			
		1 day	2/3 days	7 days	28 days
< 350	10	102	104	105	111
351-375	21	100	101	105	111
376-400	16	98	101	104	108
401-425	13	98	97	101	105

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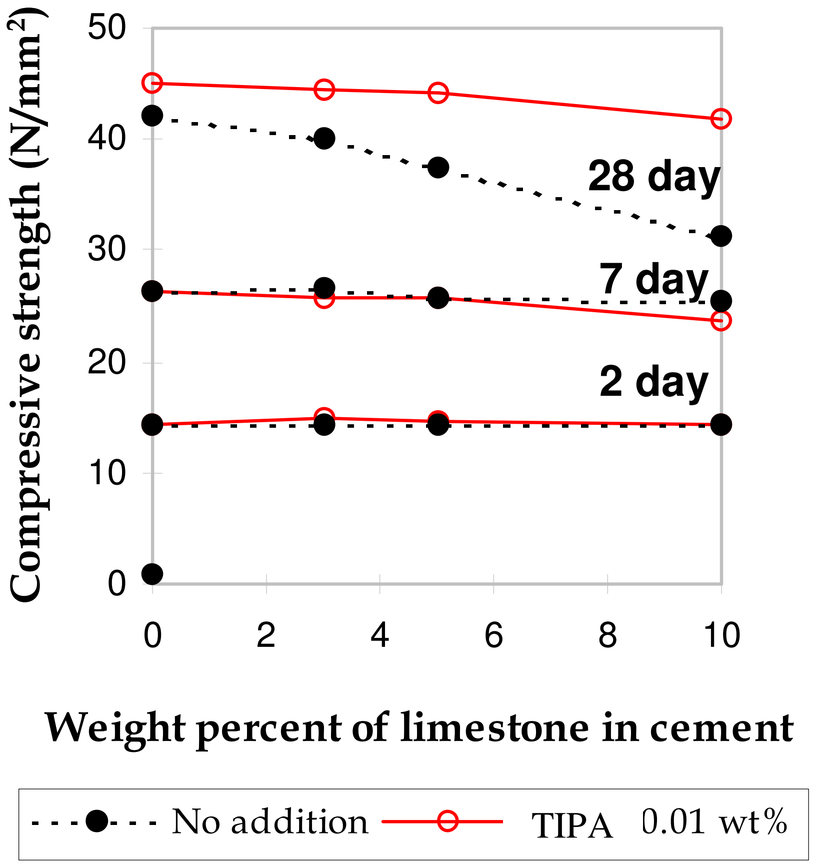
Compressive strength of 0.02% TIPA with limestone cements



From Ichikawa, et al., Proceedings of the 10th International Congress on the Chemistry of Cement; Gothenburg, Sweden, June 1997.

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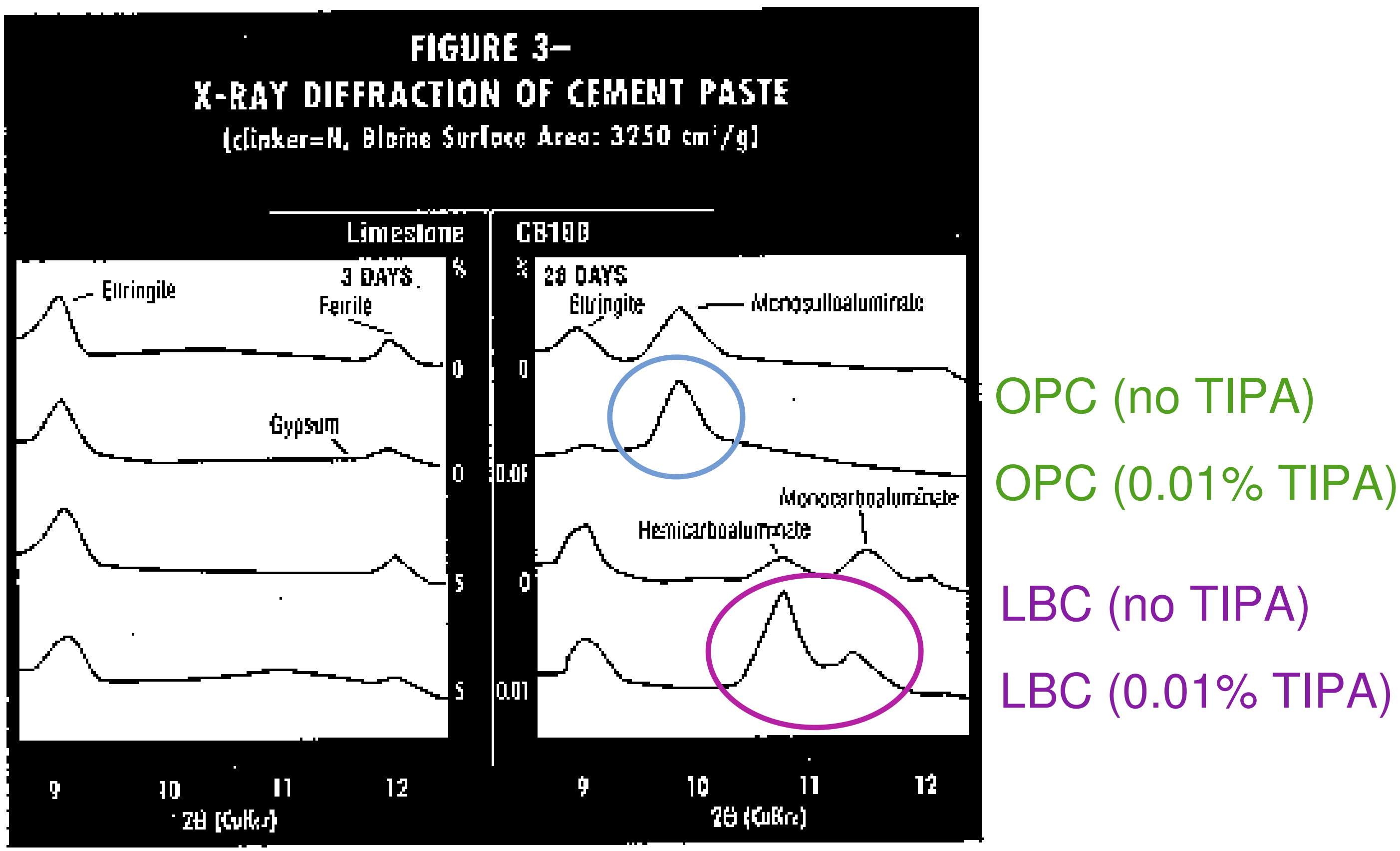
XRD pattern of Ordinary Portland Cement (OPC) and Limestone Blended Cement (LBC) with 5% limestone



From Ichikawa, et al., Proceedings of the 10th International Congress on the Chemistry of Cement; Gothenburg, Sweden, June 1997.

OPC vs. LBC

Cement Type	Number of Tests	Compressive Strength, % of Control			
		1 Day	2/3 Days	7 Days	28 Days
OPC	43	98	97	101	106
Limestone filled	19	99	102	106	109
Weighted mean	62	99	99	103	107

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Conclusion

- At 0.02%
  - TIPA solubilizes iron even after sulfate depletion
  - Presence of the three bulky methyl groups in TIPA provides steric hindrance that minimizes adsorption of TIPA on the hydration products. This allows the facilitated iron transport to continue beyond the sulfate depletion point.
  - More strength gain at late ages for cements with more than 4% C4AF
  - More strength gain with coarser cements
- At > 0.2%,
  - both TEA and TIPA chelate Fe and Al under high pH
  - TEA is adsorbed by hydration product (portlandite) after sulfate depletion

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Knowledge Gaps

- Little published results found
  - Cement analysis (composition and PSD) not published with data
  - Work done at non-representative dosage rates – need data at realistic dosage rates
- Questions
  - How do chemicals impact Al-SO4 balance?
  - Which model can simulate undersulfated cement hydration? Can the models also simulate or predict impact of admixtures?
  - What is the impact of dosage rates?
  - What is the impact of chemicals on cement with finenesses?
  - What is the impact of chemicals on the different cement phases
    - ortho-C3A vs. cubic-C3A
    - different alite phases (monoclinic vs. triclinic and others)
  - What is the impact of interstitial phase hydration, including the ferrite phases, affect the silicate phase hydration?
- More complexities when chemicals are used. Hope to use models to simulate and help gain understanding of the underlying mechanisms.

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