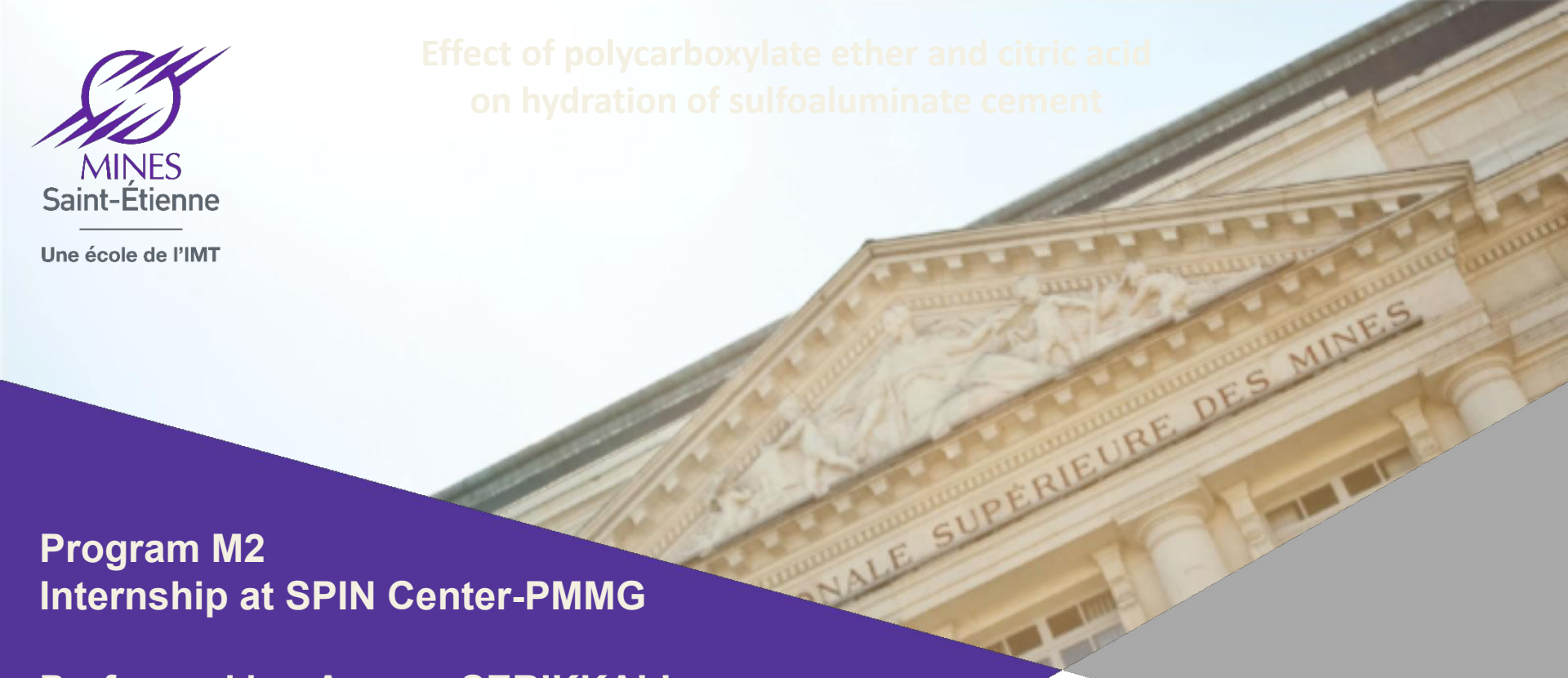
Effect of polycarboxylate ether and citric acid on hydration of sulfoaluminate cement

MINES Saint-Étienne

Une école de l'IMT



Program M2
Internship at SPIN Center-PMMG

Performed by: Angsar SERIKKALI
Supervised by: Alexandre GOVIN

INSPIRING INNOVATION SINCE 1816

SAINT – - ETIENNE 2019

Outline

- General Introduction
- Materials and methods
- Results and Discussion
- Conclusion

Introduction

What is happening in cement production nowadays?
What kind problems cement industry face with?

Portland cement is relatively low embodied energy compared to other building materials [Bing et al. 2014]

Manufacturing of Portland cement consumes approximately 2-3% of global energy [Juenger et al. 2011]

Cement industry contributes 5% of manmade carbon dioxide emissions [Bing et al. 2014]

Introduction

Why calcium sulphoaluminate cement?

CSA have attracted the attention of scientists, as well as of industry [Zajac et al. 2016]

Portland cements are produced from the firing of a calcite at a temperature of about 1450 °C [Bullerjahn. 2018]

CSA cements are produced by burning of clinker at 1250°C [Winnefeld. 2012]

CSA cements are not widely used in Europe and U.S.; its used in China for about 30 years [Winnefeld. 2012]

MINES Saint-Étienne
Une école de l'IMT
INSPIRING INNOVATION SINCE 1816

Introduction

Hydration of CSA cement

The hydration of cement is in simple terms of dissolution/precipitation process [Scrivener et al. 2011]

1. $C_4A_3\bar{S}+18H \rightarrow C_4A\bar{S}H_{12}+2AH_3$
2. $C_4A_3\bar{S}+98H \rightarrow C_6A\bar{S}_3H_{32}+CAH_{10}+2AH_3$
3. $C_4A_3\bar{S}+C\bar{S}+38H \rightarrow C_6A\bar{S}_3H_{32}+2AH_3$
4. $C_4A_3\bar{S}+C\bar{S}+28H \rightarrow 0.5C_6A\bar{S}_3H_{32}+0.5C_4A\bar{S}H_{12}+2AH_3$

The cement notation:

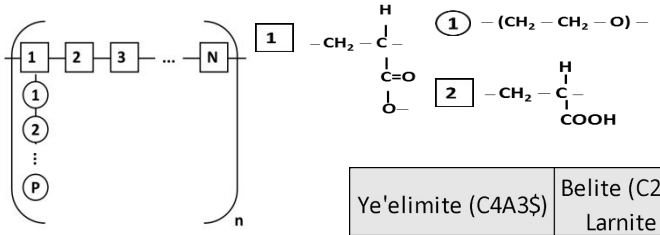
$A=Al_2O_3$, $C=CaO$, $H=H_2O$, $S=SiO_2$, $\bar{S}=SO_3$

[Bullerjahn 2018]

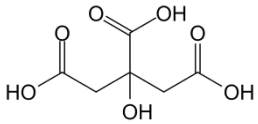
Materials

Polycarboxylate ether

Name	Pure solide mw%	P	N	n (Mp)	Mw
PCE 1	20%	45	5	12	48272
PCE 2	25%	114	5	15	138594
PCE 3	30%	17	2.5	113	118984



Citric acid

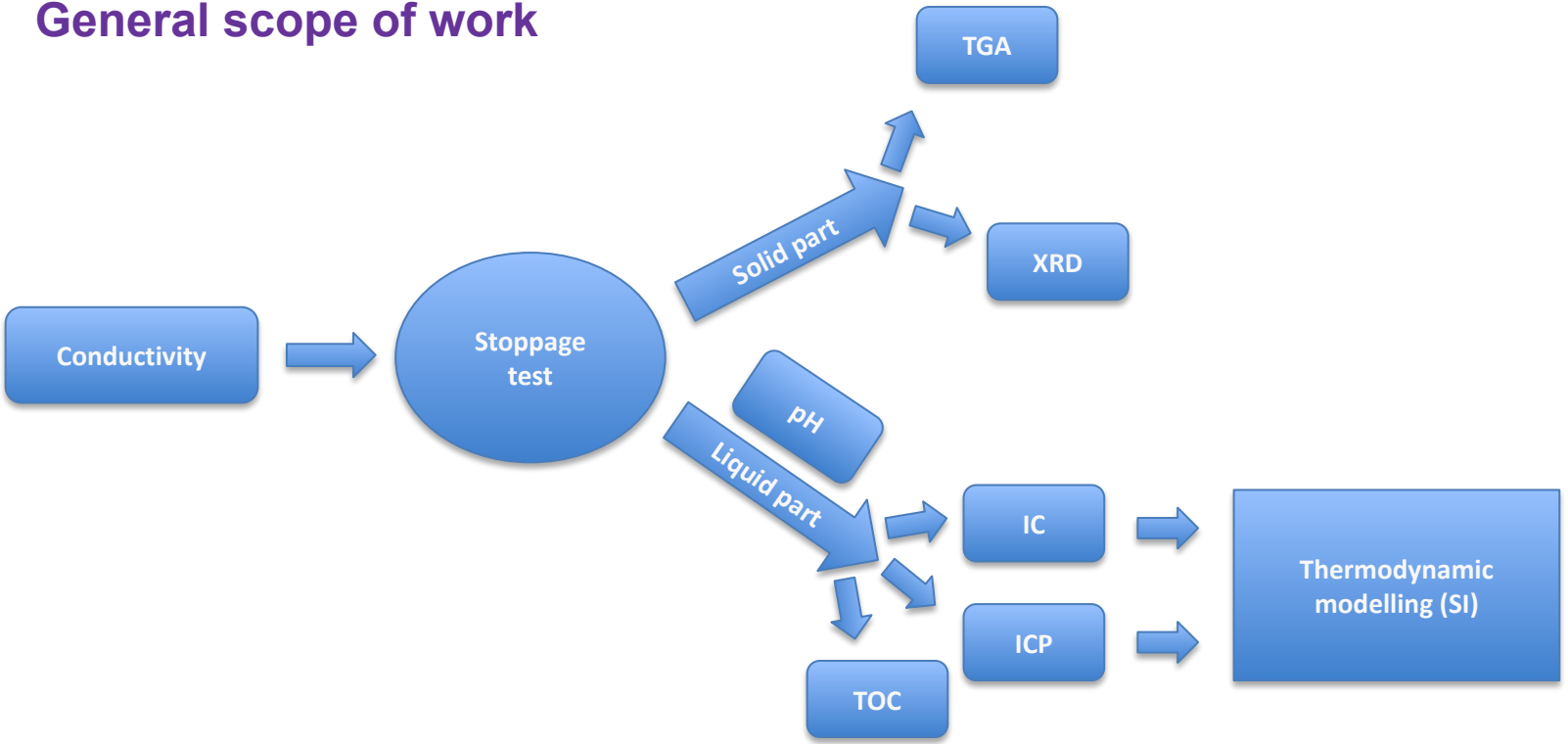


CSA cement

Ye'elimite (C4A3$)	Belite (C2S) Larnite	Anhydrite (C$)	Bredigite (Ca14Mg2(SiO4)4)	Periclase (MgO)	Fluorite (CaF2)	Cacium Iron Oxide (CaFe3O5)
49.44	8	21.9	11.25	4.84	3.13	1.43

Methods

General scope of work



Methods

Overview of the used techniques

Characterisation	Methods	Location	Analyzed by
Hydration reactions and kinetics	pH, conductivity, stoppage test	EMSE (C3-01)	Angsar SERIKKALI
	ICP	EMSE (D3-14)	Frederic GALLICE, Angsar SERIKKALI
	IC	EMSE (D3-14)	Frederic GALLICE, Angsar SERIKKALI
	TOC	EMSE (C2-10)	Angsar SERIKKALI
Saturation indexes	Thermodynamic modelling	EMSE (C3-08)	Angsar SERIKKALI
Mineral composition	XRD	EMSE (D0-16)	Olivie VALFORT, Angsar SERIKKALI
	TGA	EMSE (C2-05)	Angsar SERIKKALI

Methods

Conductivity

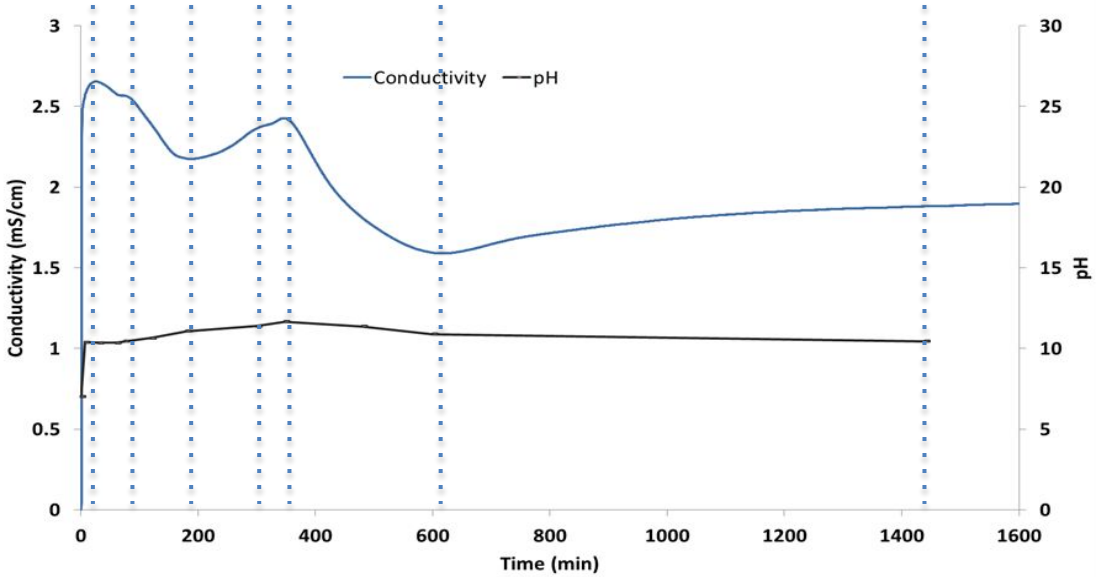
CDM210-MeterLab

- V=1L
- Double walled and water-jacketed reactor
- T=24.6 ℃±0.2
- 270-350 r/min
- Experiment time is around 24 hours
- Water to cement ratio: 20

Calibration: m_{KOH}=2.2365 g and δ=2.097 mS/cm

Methods

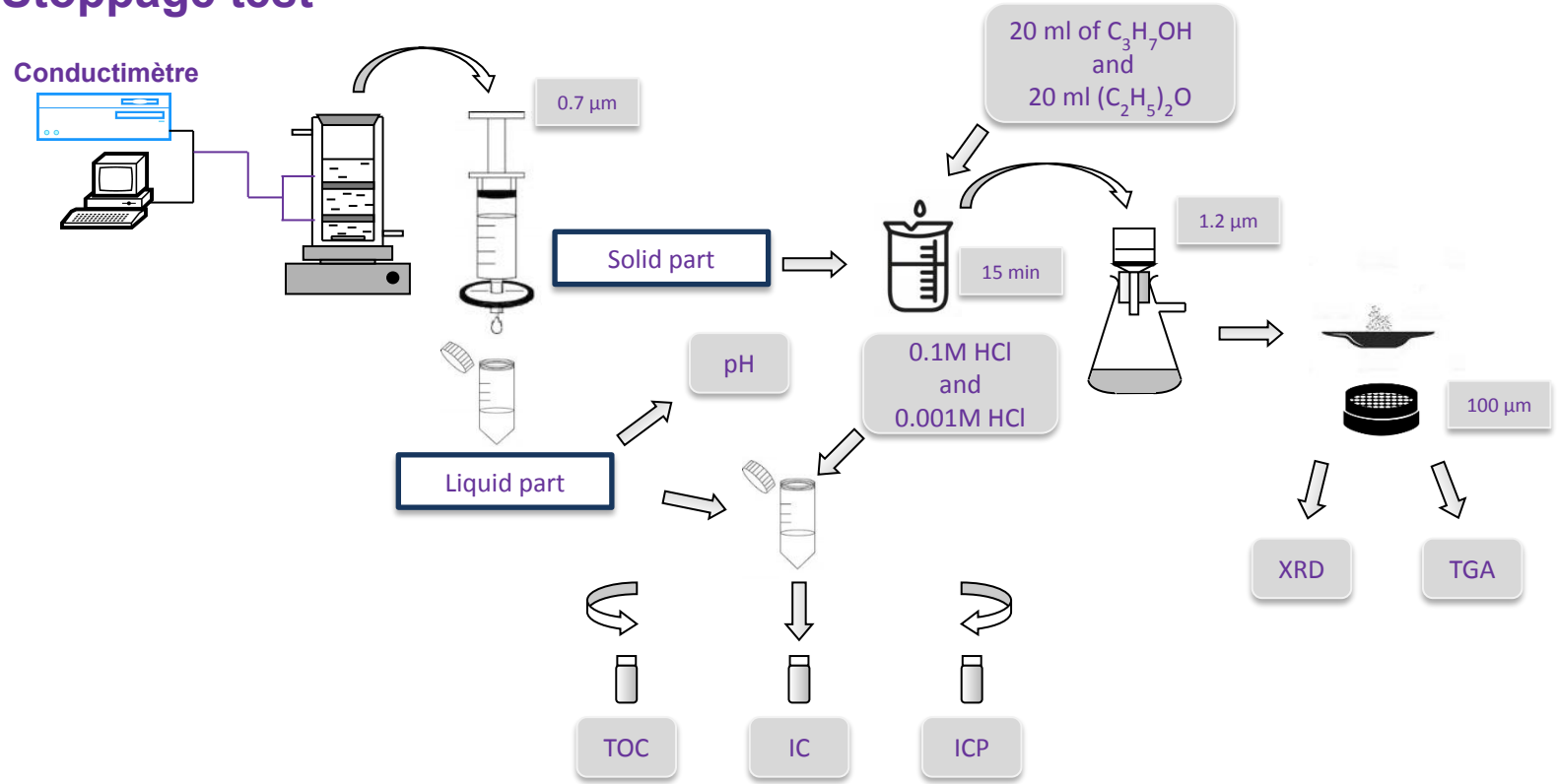
Conductivity



Name of experiments	Water (L)	Cement (g)	Admixture
CSA (Reference)	1	50	-
CSA+PCE 1	1	50	0.1-0.3%* PCE 1
CSA+PCE 2	1	50	0.1-0.3%* PCE 2
CSA+PCE 3	1	50	0.1-0.3%* PCE 3
CSA+CA	1	50	0.2%* CA
CSA+CA	1	50	0.4%* CA
*% is shown regarding to the mass of cement (50 g)			

Methods

Stoppage test



Solid part and liquid part methods

Solid part

X-ray powder diffraction (XRD)

- X-ray diffractometer (BRUKER D8-A25)
- X-ray tube (Cu radiation)
- X-ray detector (Lynxeye XE-T)
- 2θ from ~5° to 90° with rate of diffraction each 0.015°
- Software: DiffracEVA
- Preparation method is backloading
- m=1g; 40% mw ZnO

Thermogravimetric analysis (TGA)

- Instrument : SETARAM 92-16.18
- Gas: He
- Heating: Temperature from 30℃ to 900℃; with rate of heating 10℃/min
- m=100-105 mg
- Data is fitted in the program Fytik

Solid part and liquid part methods

Liquid part

Inducted coupled plasma (ICP)

- **Instrument:**
- **V=8 ml with**
  - x10 dilution by 0.1M HCl
  - x100 dilution by 0.001M HCl
- **Storage T=4°C**
- **Results in ppm for : Al, Ca, Fe, K, Na, S and Si**

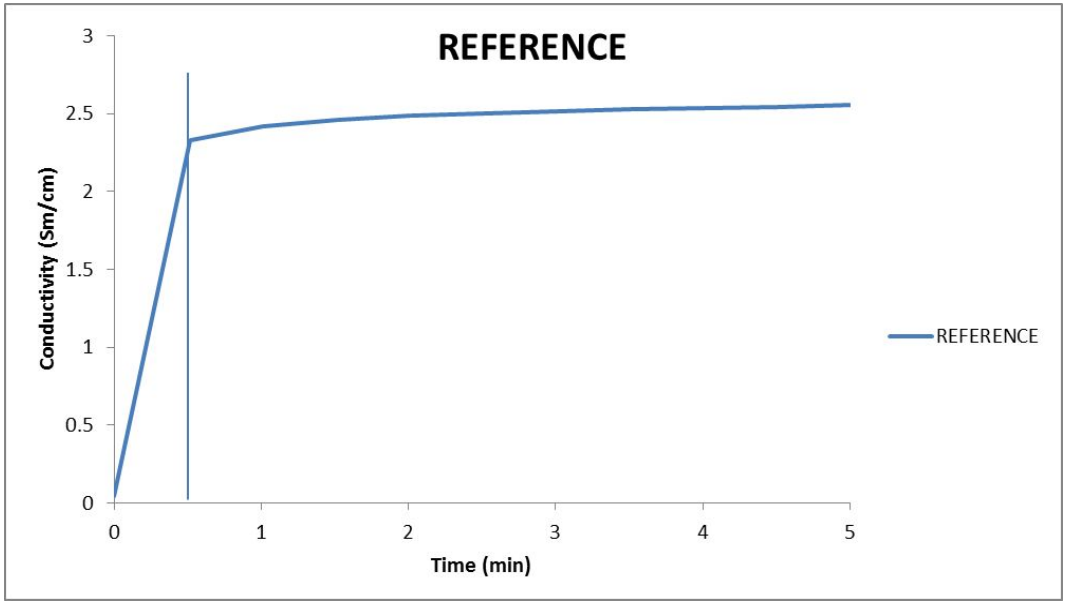
Total organic carbon (TOC)

- **Instrument:**
- **V=8 ml**
- **T=850°C**
- **Gas: O_2**

Ionic chromatography (IC)

- **Instrument:**
- **V=8-10 ml**
  - x100 dilution by 0.1 HCl
  - x1000 dilution by 0.1 HCl
- **T=850°C**
- **Gas: O_2**

Results and discussions



- Pure dissolution period for ye'elimite is 30 seconds

MINES Saint-Étienne
Une école de l'IMT

INSPIRING INNOVATION
SINCE 1816

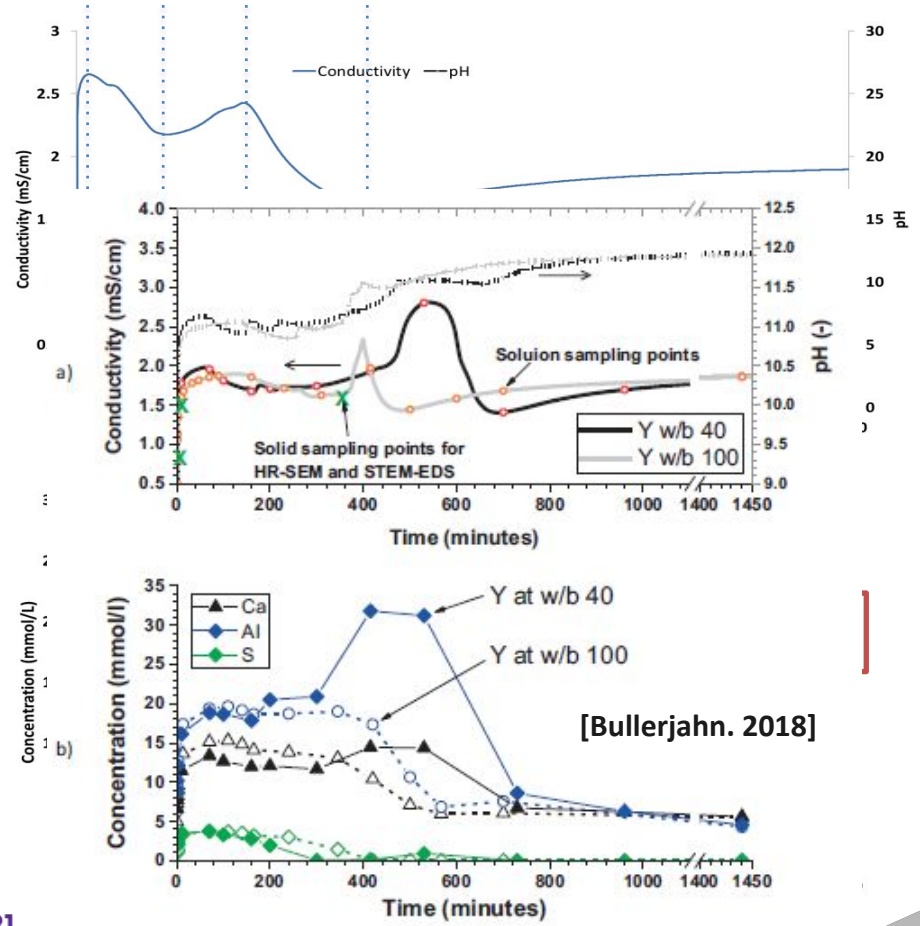
Conductivity & ICP

- ye'elimite dissolves rapidly
- etrringite continues to form slowly
- the highest dissolution/precipitation ratio
- formation of crystalline AH_3

1. $C_4A_3\bar{S}+18H \rightarrow C_4A\bar{S}H_{12}+2AH_3$
2. $C_4A_3\bar{S}+98H \rightarrow C_6A\bar{S}_3H_{32}+CAH_{10}+2AH_3$
3. $C_4A_3\bar{S}+C\bar{S}+38H \rightarrow C_6A\bar{S}_3H_{32}+2AH_3$
4. $C_4A_3\bar{S}+C\bar{S}+28H \rightarrow 0.5C_6A\bar{S}_3H_{32}+0.5C_4A\bar{S}H_{12}+2AH_3$

The cement notation:

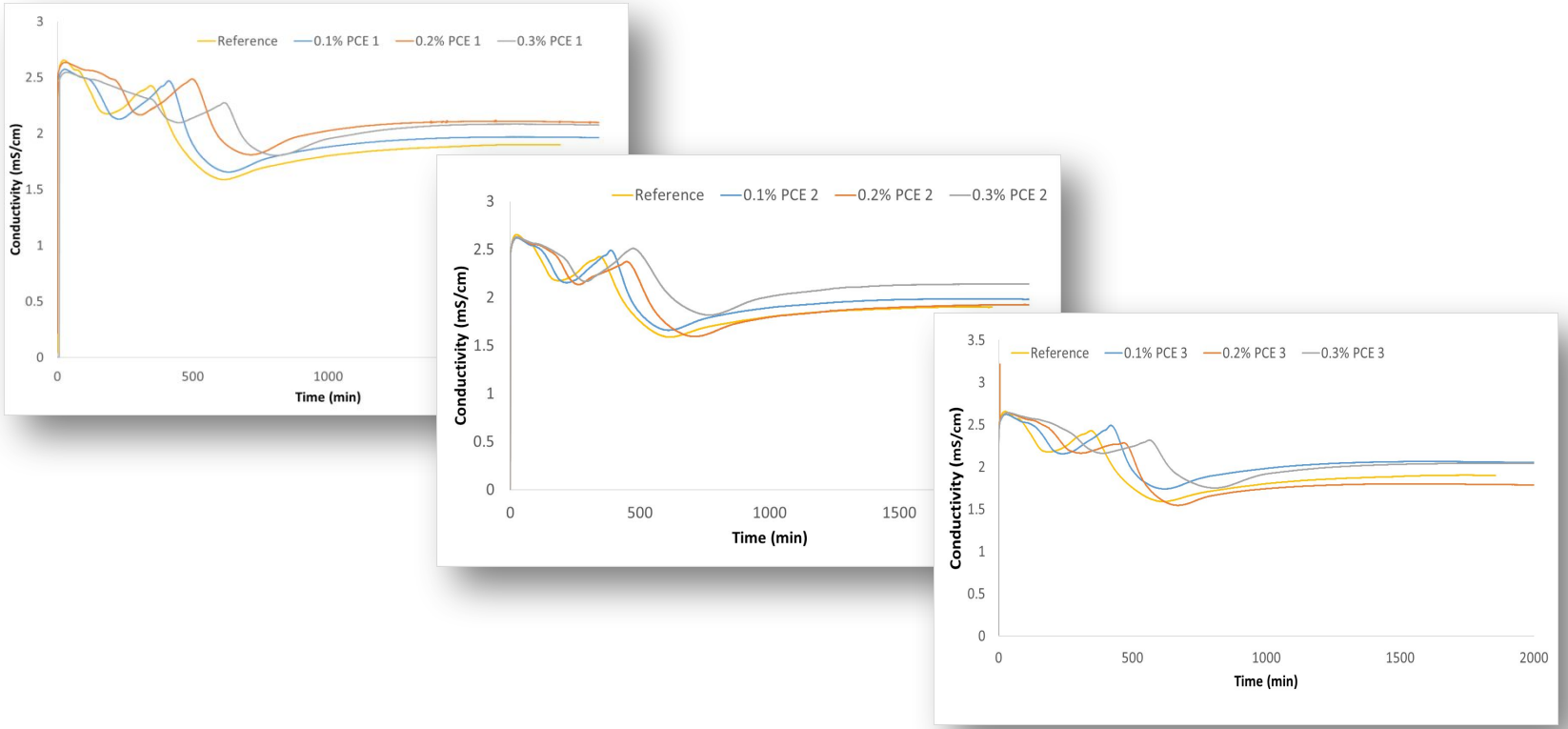
$A=Al_2O_3$, $C=CaO$, $H=H_2O$, $S=SiO_2$, $\bar{S}=SO_3$ [Bullerjahn. 2018]



[Bullerjahn. 2018]

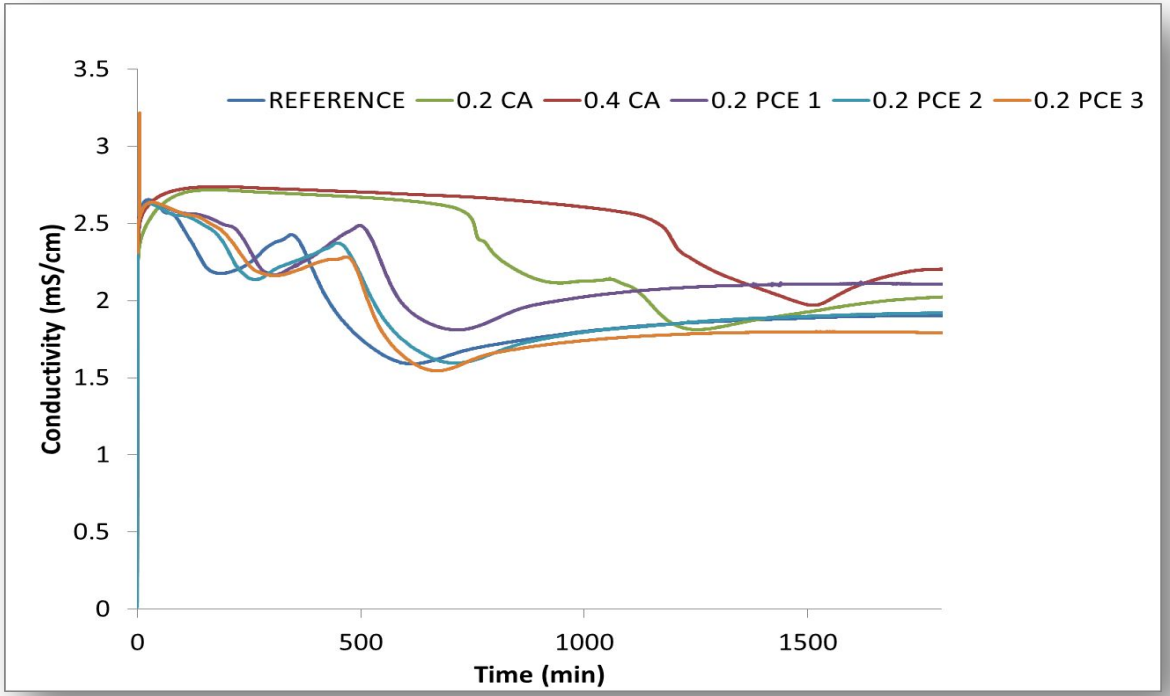
Results and discussions

Conductivity of superplasticizers

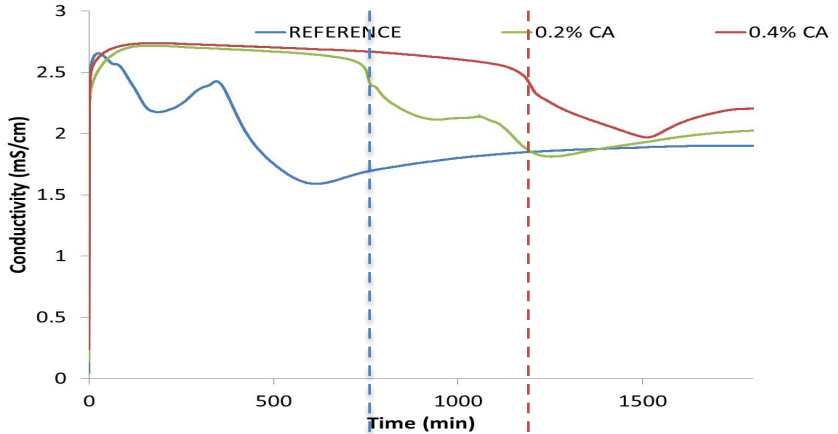


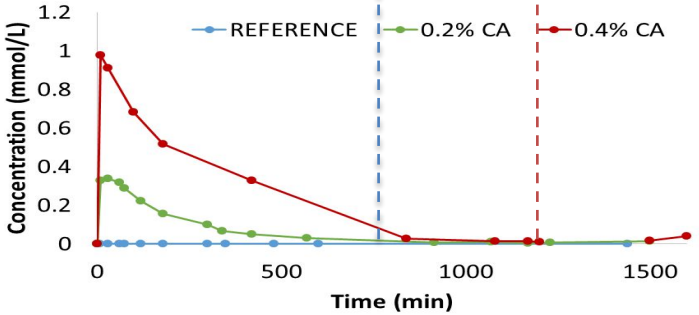
Results and discussions

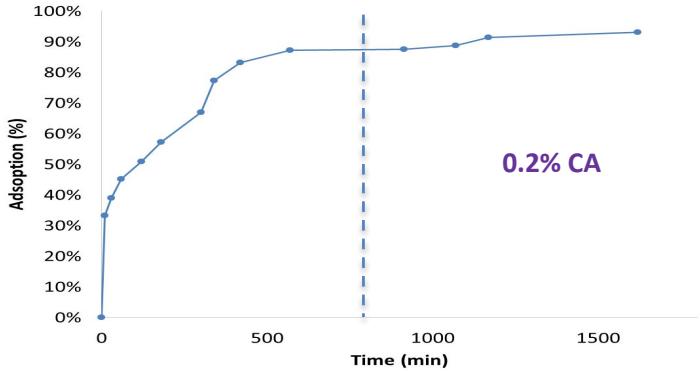
Conductivity of reference, superplasticizers and citric acid

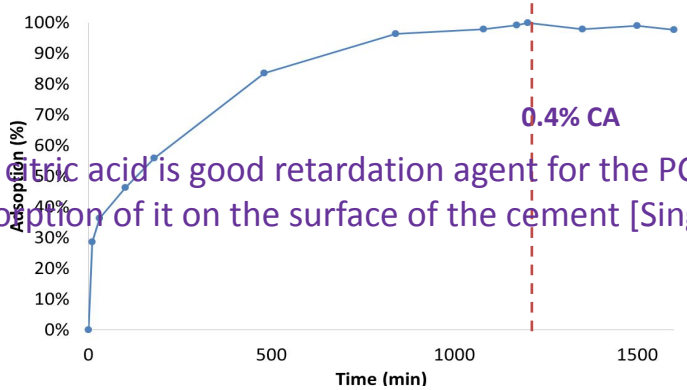


Results and discussions





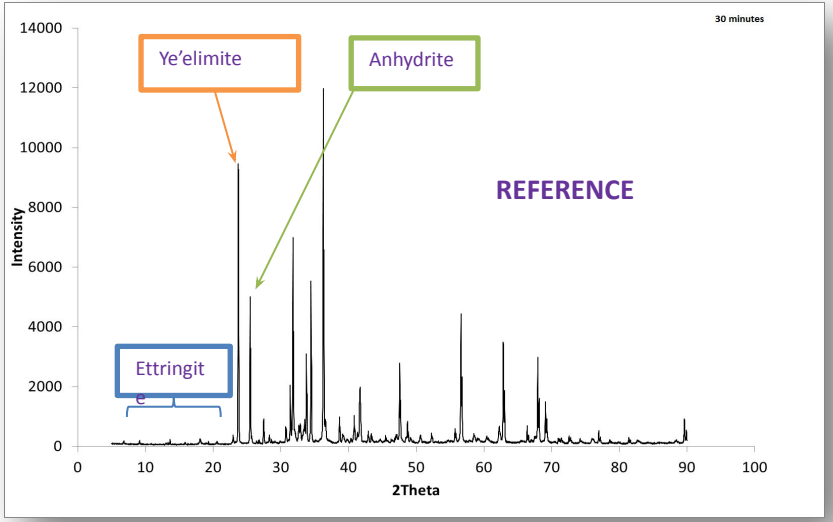


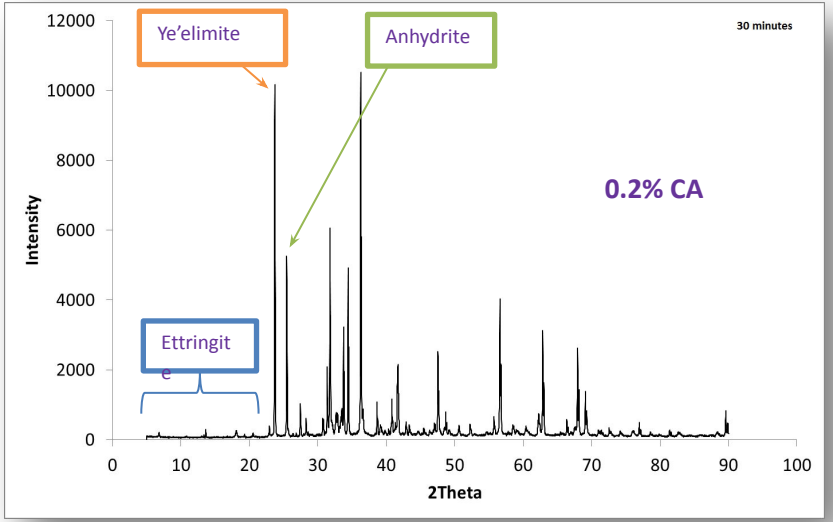


The citric acid is good retardation agent for the PC, due to the absorption of it on the surface of the cement [Singh et al. 1986]

Results and discussions

XRD results



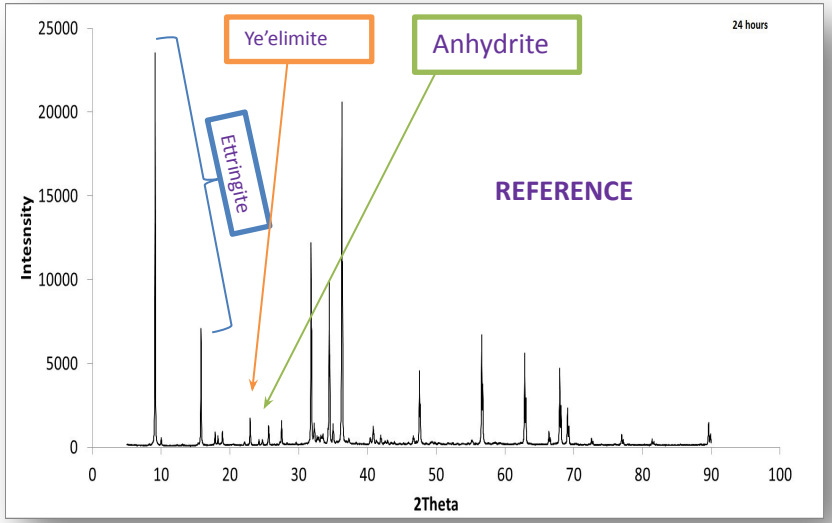


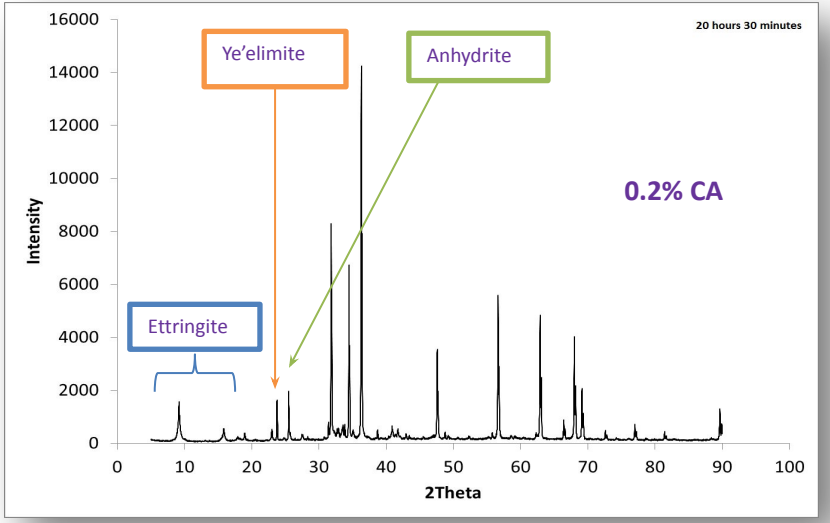
Results and discussions

XRD results

There is only qualitative analyses, not quantitative!

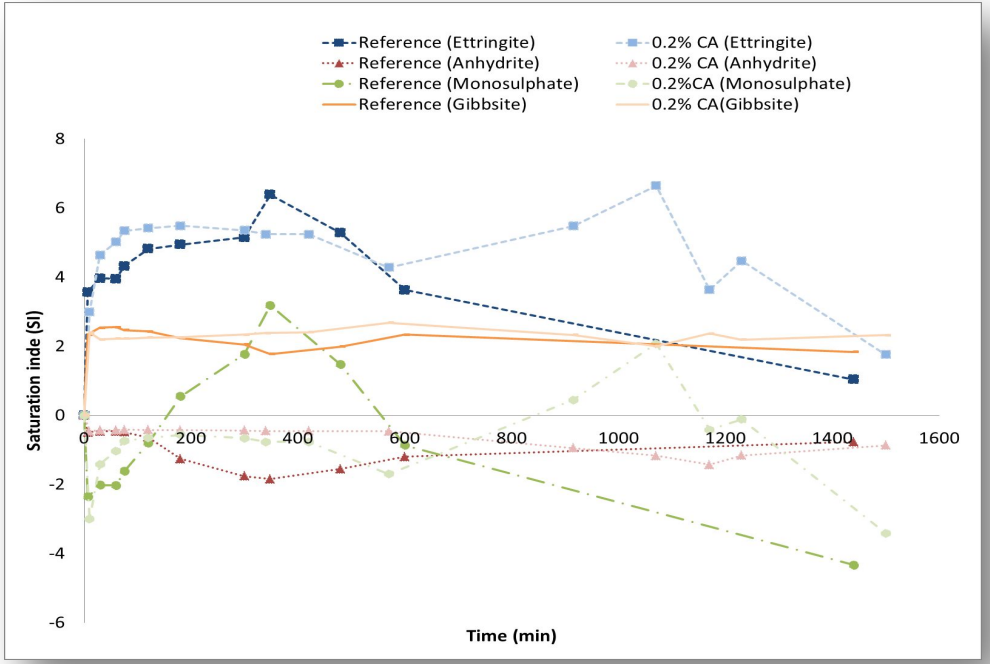
Why? 2





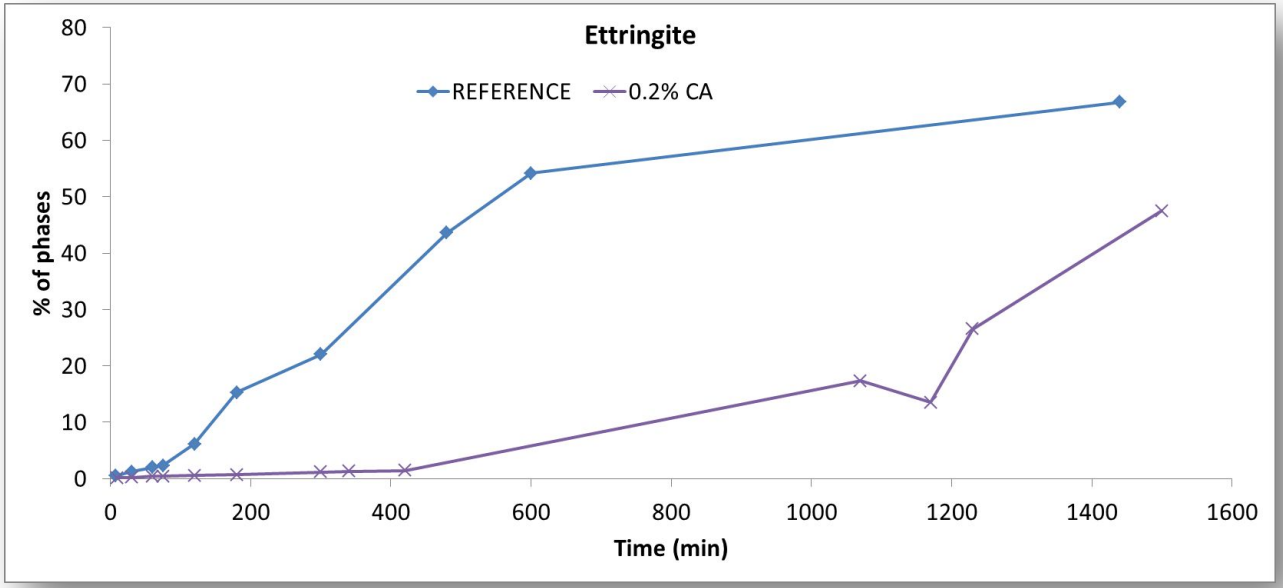
Results and discussions

Thermodynamic modelling (SI) results



Results and discussions

TGA results



Conclusion

Conductivity analyses
- Reference
- 0.1-0.3% PCE 1
- 0.1-0.3% PCE 2
- 0.1-0.3% PCE 3
- 0.2% and 0.4% CA

IC ,ICP and TOC analyses
- Reference
- 0.2% PCE 1
- 0.2% PCE 2
- 0.2% PCE 3
- 0.2% and 0.4% CA

Thermodynamic modelling (SI)
- Reference
- 0.2% PCE 1
- 0.2% PCE 2
- 0.2% PCE 3
- 0.2% and 0.4% CA

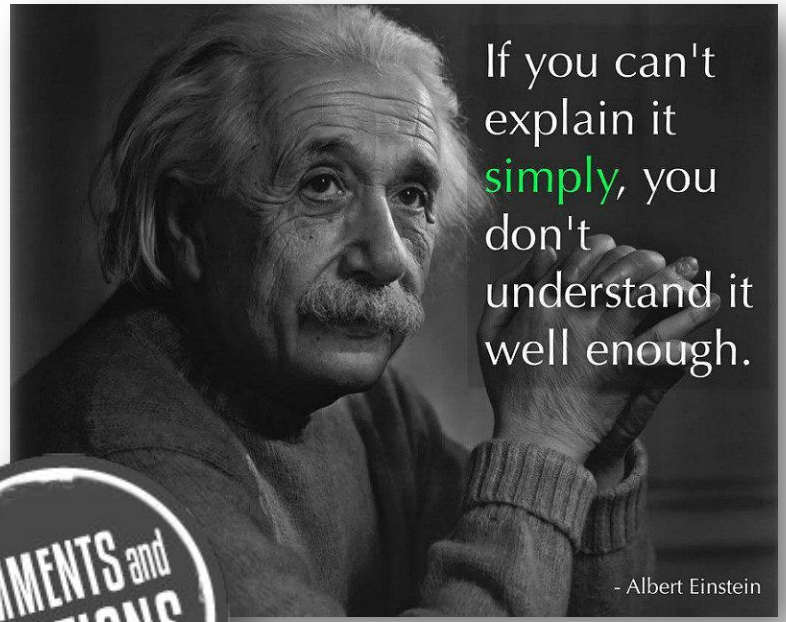
TGA analyses
- Reference
- 0.2% PCE 1
- 0.2% PCE 2
- 0.2% PCE 3
- 0.2% and 0.4% CA

XRD analyses
- Reference
- 0.2% PCE 1
- 0.2% PCE 2
- 0.2% PCE 3
- 0.2% CA

Conclusion

1 **Sulfur** ⬆

2 **Ye'elimite** ✖



MINES
Saint-Étienne
Une école de l'IMT
Institut Mines-Télécom
Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE
MINISTÈRE DE L'ÉCONOMIE ET DES FINANCES