Identification of leaching-controlling process by differential acid neutralization analysis for geochemical modelling – application to metal hydroxide sludge stabilization with coal fly ash.

O. Peyronnard[a] ; D. Blanc[a] ;
M. Benzaazoua[b] and P. Moszkowicz[a]

a. LGCIE – INSA LYON

b. UQAT – Rouyn Noranda - Québec

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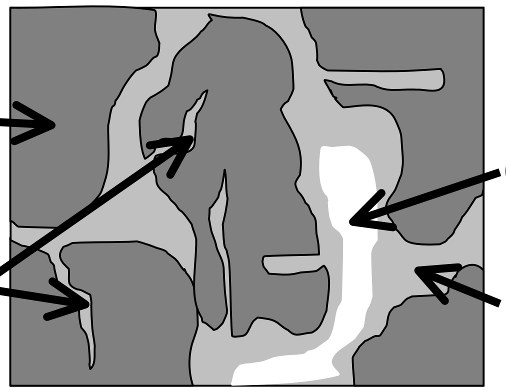
LGCIE Site Carnot

Introduction

- Mineral waste stabilized - solidified by hydraulic binders = solid porous matrix which contains pollutants



- Storage
  - Water infiltration
  - Weathering of the solid matrix
  - Possible release of the pollutants

Introduction

- Evaluation of the risk for environment :
  - Different tests to study the leaching behaviour of the stabilized / solidified waste
    - Acid neutralization capacity
    - Leachable fraction
  - Results of the tests can be extrapolated to the real scenario

➡ Prediction of the pollutants mobilization

Introduction

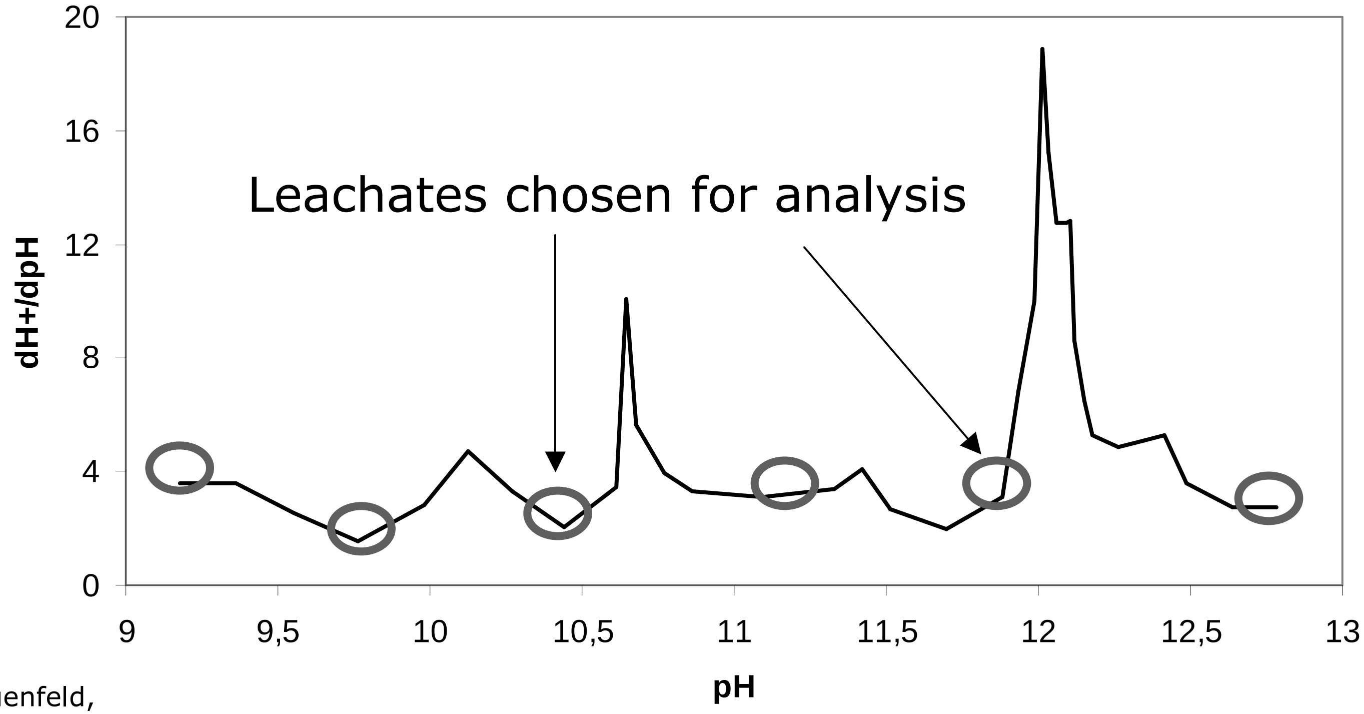
- Prediction with the aid of geochemical model
  - Mineral composition is required. Solid analysis techniques can be used :
    - X-Ray Diffractometry
    - Thermal Analysis
    - Scanning Electronic Microscopy (SEM)
  - But :
    - Amorphous phases are not evaluated
    - Size of hydrated cement phases ≈ SEM resolution

→ Solid analysis techniques are imprecise

Introduction

- Differential analysis of acid neutralization

$$dH^{+}/dpH = f(pH)^{1}$$



Differential analysis spectrum for an ordinary pure cement

1. G. K. Glass and N.R. Buenfeld, Differential acid neutralisation analyses, *Cement and concrete research*, 29, 1999, 1681-1684

Materials and methods

- Materials

Hydroxide sludge : Fe, Zn and Cr (VI)

+

Two binders :

- OPC
- OPC + PFA

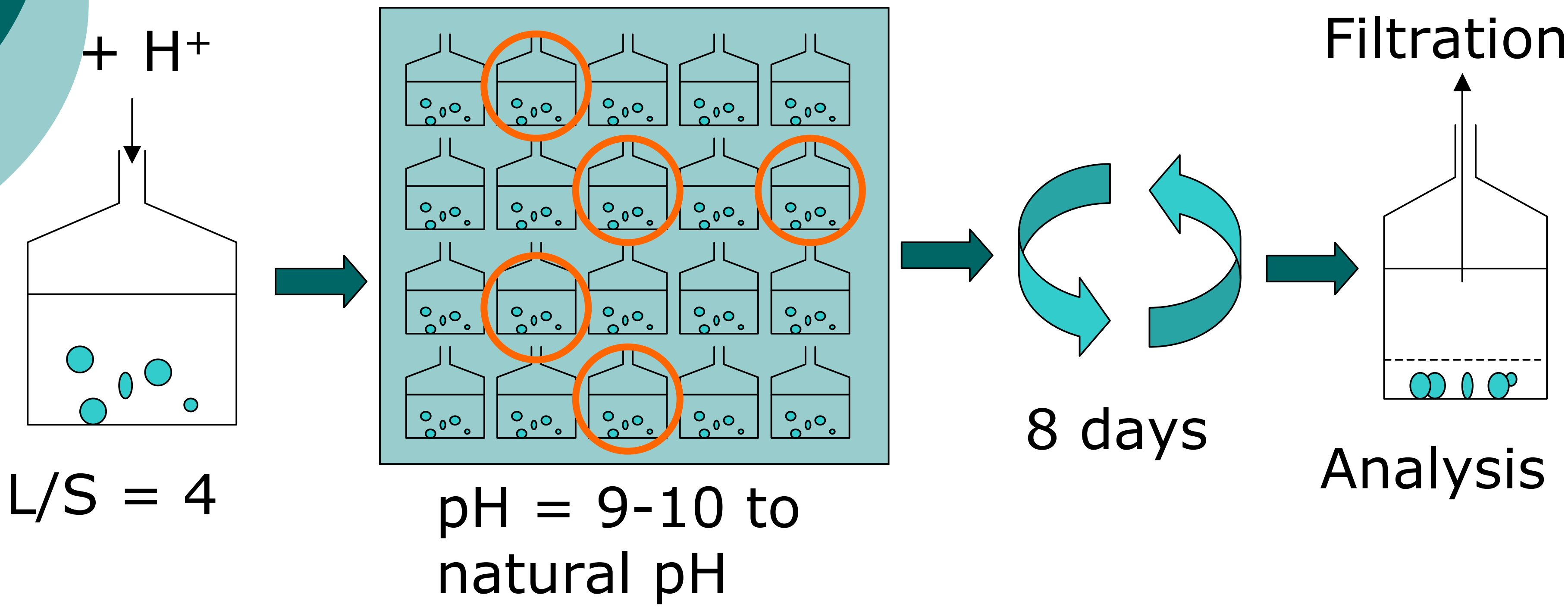
→ 28 days curing

↓ Crushed to particle size < 1 mm

Ref.	OPC (g)	PFA (g)	Dried sludge (g)	Water (mL)
OPC	100	0	0	40
OPC-PFA	50	50	0	40
OPC-S	86.8	0	13.2	46
OPC-PFA-S	43.4	43.4	13.2	48

Materials and methods

- Differential acid neutralization data



•pH
•Spectrum representation : choice of analysed batches
•Elements concentrations : ICP-AES and ionic chromatography

Materials and methods

- Modelling (1)
  - Based on the calculation of the pH of dissolution of various hydrated phases.
  - Comparison between calculated and experimental pH

Identification of the hydrates

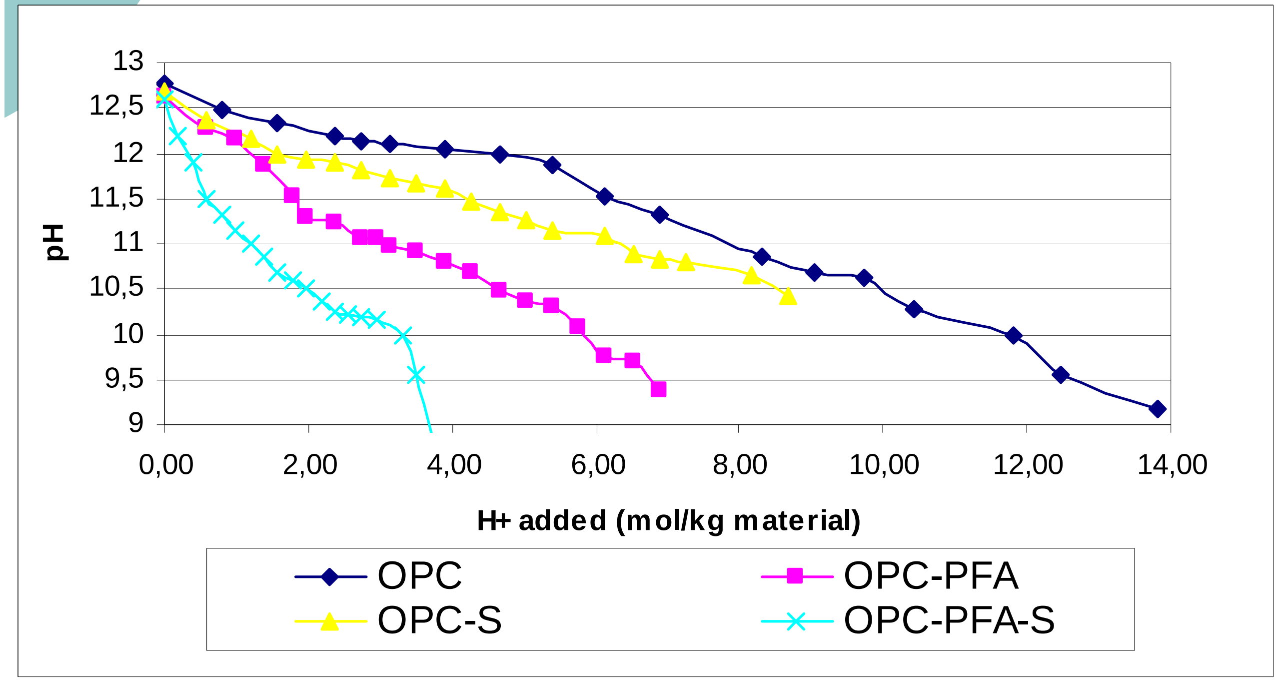
→ Mineral assemblages representing materials are determined

Materials and methods

- Hypothesis of simulation
  - Use of USGS's software PHREEQC.
  - Hypothesis of equilibrium between solid and liquid, no gas.
  - Cementitious phases = pure phases or ideal solid solutions. No sorption mechanisms.
  - Amorphous CSH = 3 CSH with different Ca/Si ratio (1.8, 1.1 and 0.8).

Experimental results

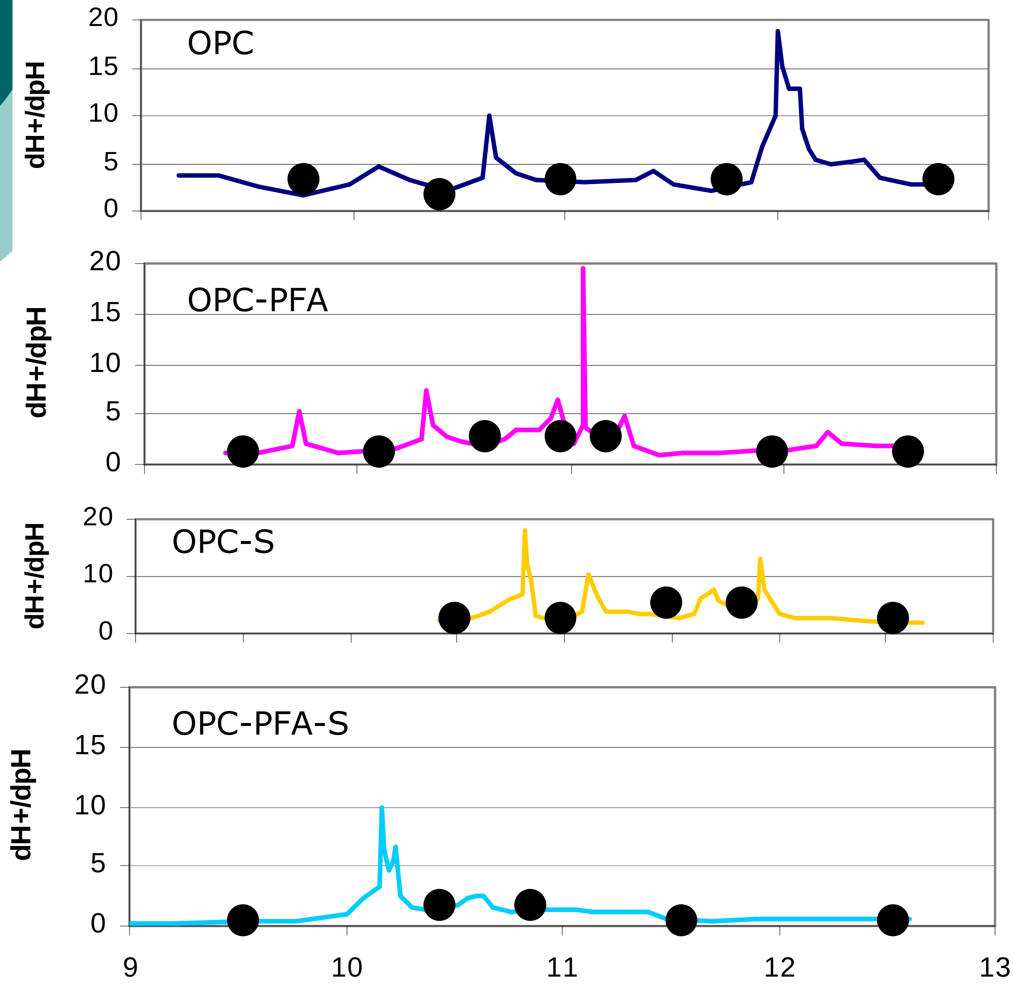
- Titration curves of the four studied materials



- Loss of neutralisation capacity with fly ash or sludge :
  - OPC-S : Dilution of OPC in the binder.
  - OPC-PFA and OPC-PFA-S : pouzzolanic reaction.

Experimental results

- Differential acid neutralization analysis



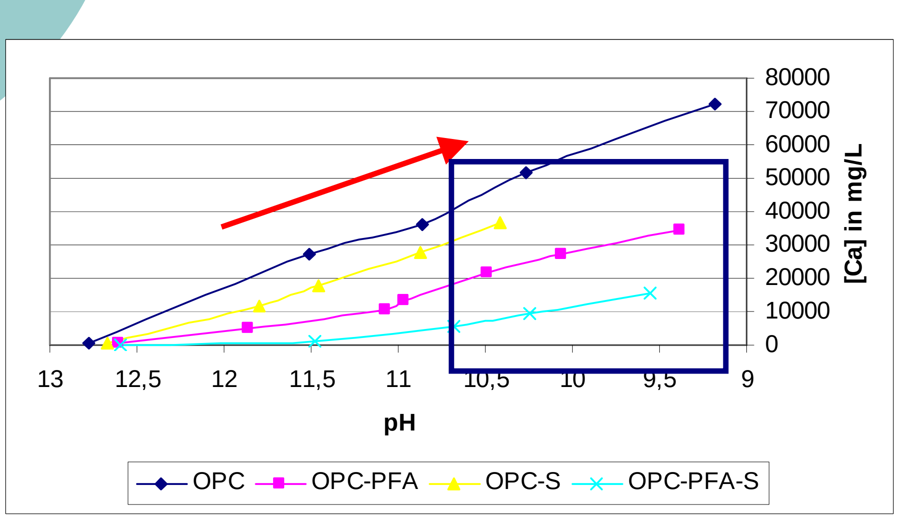
- •OPC : 5 peaks
- •Other materials : more than 5 peaks
- •3 main differences :
  - •Peak intensity : quantity of phase
  - •pH dissolution different
  - •Apparition of new peaks

● Batch chosen for analysis

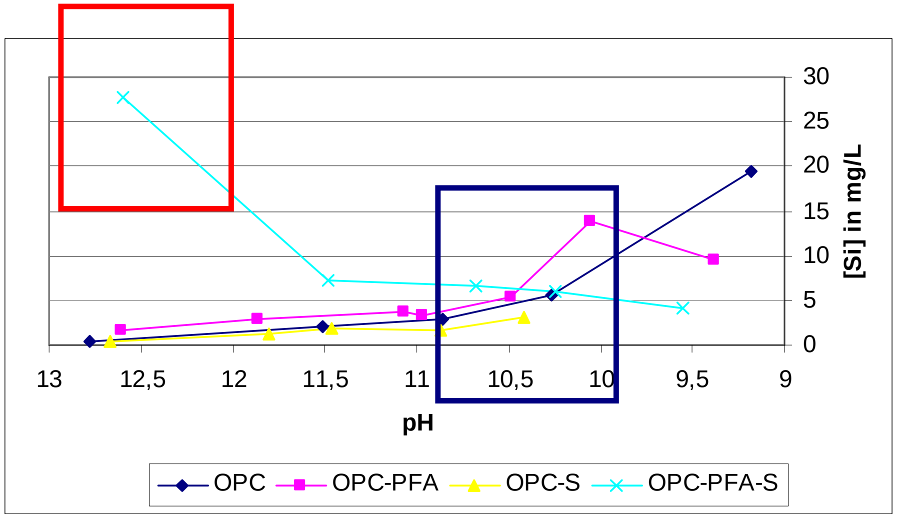
Experimental results

- Release of elements

Calcium



Silicon



→ Increase with pH decrease

→ Less release for material containing sludge.

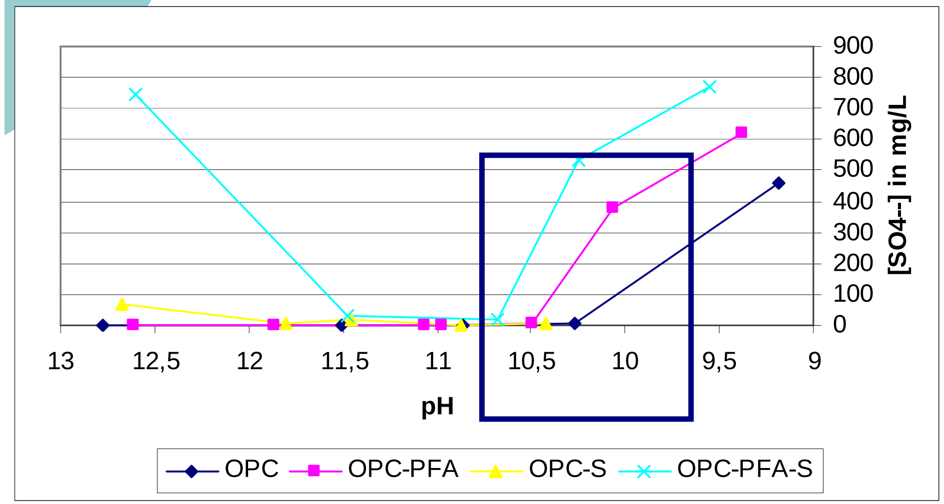
→ Dissolution of CSH.

→ OPC-PFA-S : remaining of non hydrated cement.

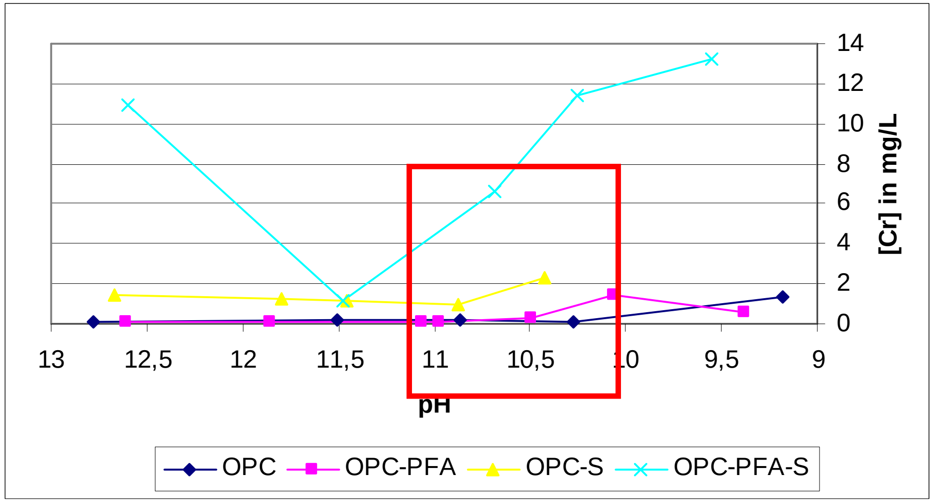
Experimental results

- Release of elements

Sulfate



Chromium



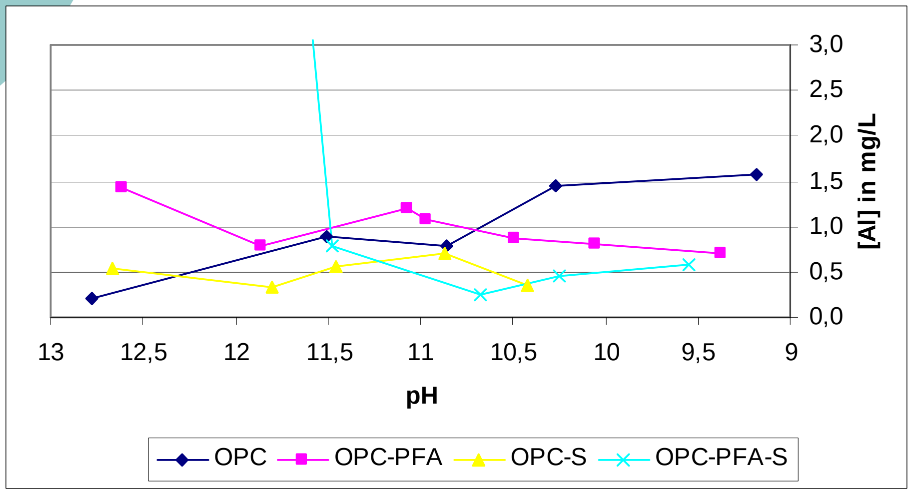
→ Dissolution of ettringite or Al-monosulfate or Fe-monosulfate.

→ Linked at the sulfate release : substitution of sulfate by chromate in AFt or AFm phases.

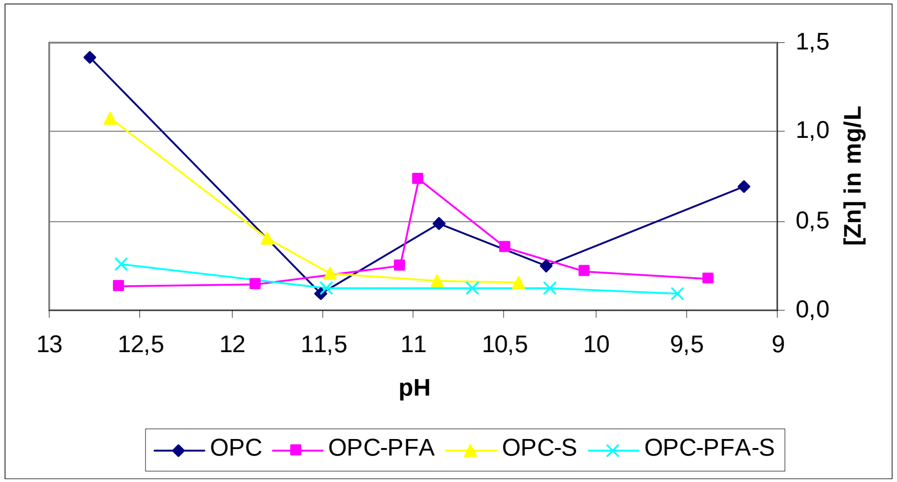
Experimental results

- Release of elements

Aluminium



Zinc



Release of Al relatively low.

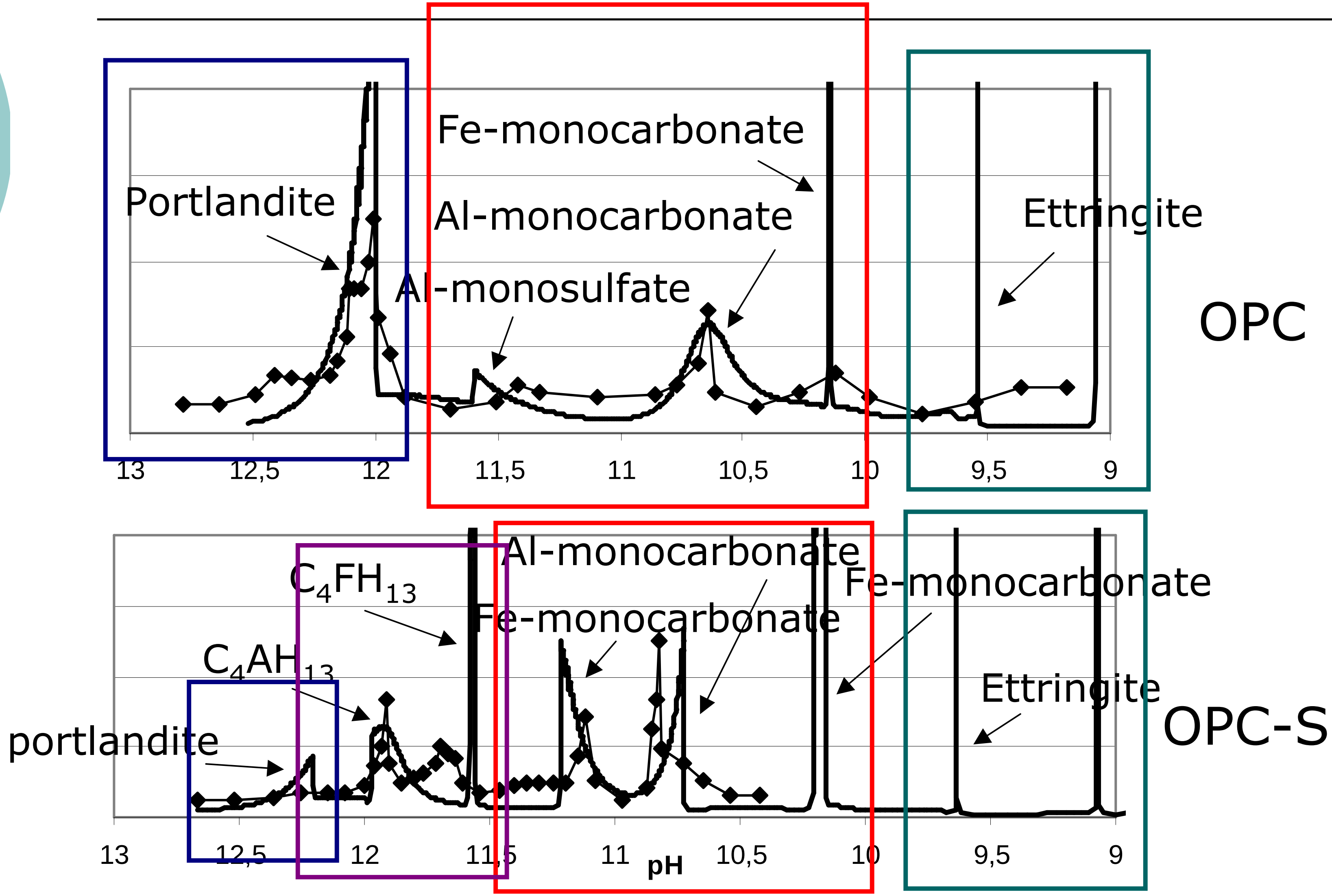
Dissolution of aluminates phases.

Release of Zn depends on the binder, and on the presence of sludge.

Geochemical modelling : phases

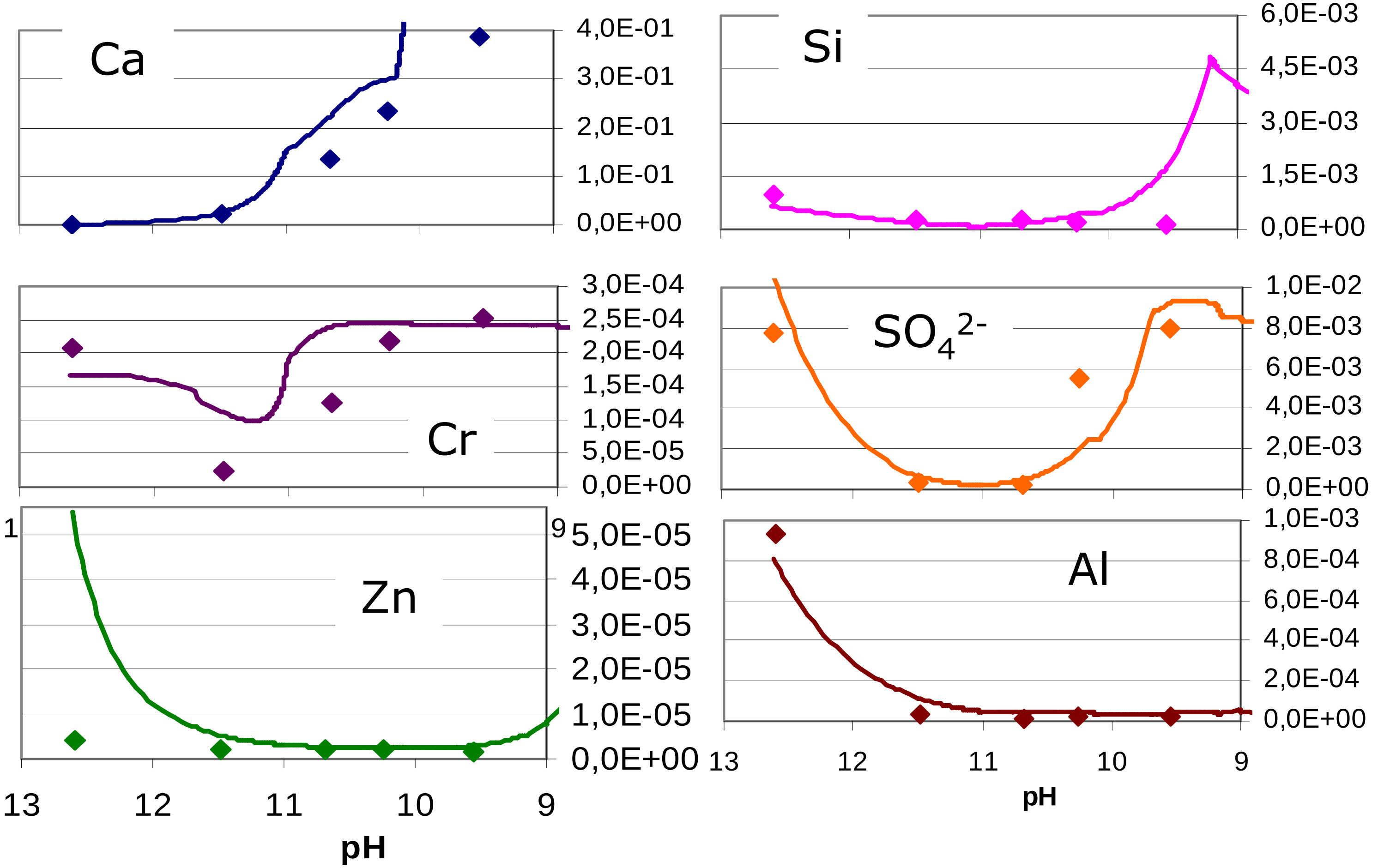
	Phases (mol/L)	OPC	OPC-PFA	OPC-S	OPC-PFA-S
	Portlandite	**0.55**	**0.2**	**0.1**	**0.02**
	Brucite	**0.02**	**0.035**	**0.015**	**0.03**
	$Zn(OH)_2$	**8.10^{-5}**	**0**	**0**	
	Ca-Hydroxyzincate		**1.10^{-5}**	**$7.5.10^{-6}$**	**$7.5.10^{-3}$**
	C_2ASH_8	**0**	**0**	**0**	**0.045**
	CSH1.8	**0.5**	**0.05**	**0.2**	**0.06**
CSH	**CSH1.1**	**0.25**	**0.5**	**0.2**	**0.3**
	CSH0.8	**0**	**0**	**0**	**0**
	Al-Monosulfate	**0.03**	**0.04**		
	Fe-Monosulfate	**0.01**	**0.04**	**0.07**	**0.025**
AFm	**Cr-Monophase**	**9.10^{-5}**	**3.10^{-5}**	**0**	**0**
	Al-Monocarbonate	**0.18**	**0.06**	**0.08**	**0.01**
	Fe-Monocarbonate	**0.08**	**0.03**	**0.1**	**0.02**
	Friedel's Salt			**0.015**	
	Ettringite	**0.04**	**0.01**	**0.01**	**0.005**
	Fe-Ettringite	**0.02**			
AFt	**Cr-Ettringite**	**0**	**0**	**2.10^{-5}**	**0**
	Al-Tricarbonate	**0**	**0.01**	**0.01**	**0.04**
	C_4AH_{13}			**0.06**	
	C_4FH_{13}			**0.06**	

Geochemical modelling : spectra



Geochemical modelling : elements

- Release of elements for OPC-PFA-S



Conclusion

- Test of the use of differential analysis of acid neutralization.
- Efficient aid-tool for the identification of phases governing the leaching behaviour of synthetic hydroxide sludge stabilized/solidified by an hydraulic binder.
- Number of analysis limited by the choice of pertinent batches.