Laboratoire

Matériaux et Durabilité des Constructions

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Zagreb, Croatia, April 3rd 2017

Characterization of sewage sludge ash (SSA) as supplementary cementitious materials

Martin Cyr

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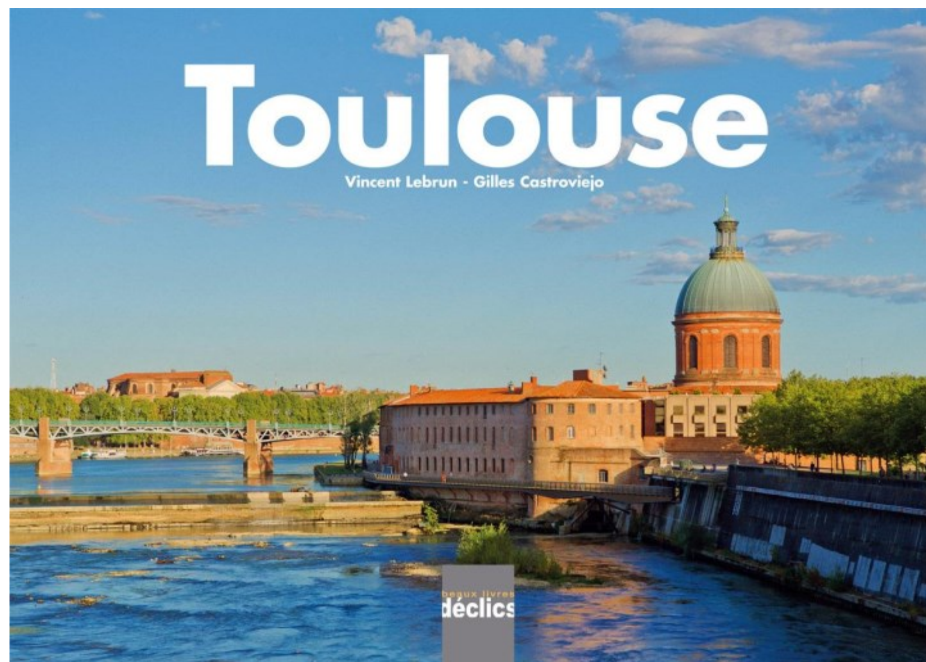
Associate Professor
Sherbrooke University
Canada

University of Toulouse (France)

The University of Toulouse was founded in 1229

- Consortium of French universities and other institutions of higher education and research
- More than 100,000 students



Toulouse (France)

Academic laboratory specialized in civil engineering materials science research

41 researchers

- 16 Professors
- 25 assistant professors

8 technological staff or engineers

~ **50 PhD Students**

~ 8 Post-Doc

~ 20 interns

- 5-8 invited foreign researchers
- 12-15 masters of science

Scientific objectives

To find scientific solutions for **sustainable development** and **eco-management** of building heritage: civil engineering structures and housing.

Research organization and activities

Innovative materials for civil engineering

Prof. Martin CYR

- Eco-materials with low environmental impact
- New materials and new functions
- Material optimization for specific applications

Material and building durability

Prof. Alexandra BERTRON

- Material durability Chemistry
- Mass transfers in cement-based materials
- Sustainable building design methods

Requalification, diagnosis and maintenance

Prof. Jean Paul BALAYSSAC

- Requalification of constructions
- Non-destructive testing methods
- Maintenance, repair and restoration methods

Zagreb, Croatia, April 3rd 2017

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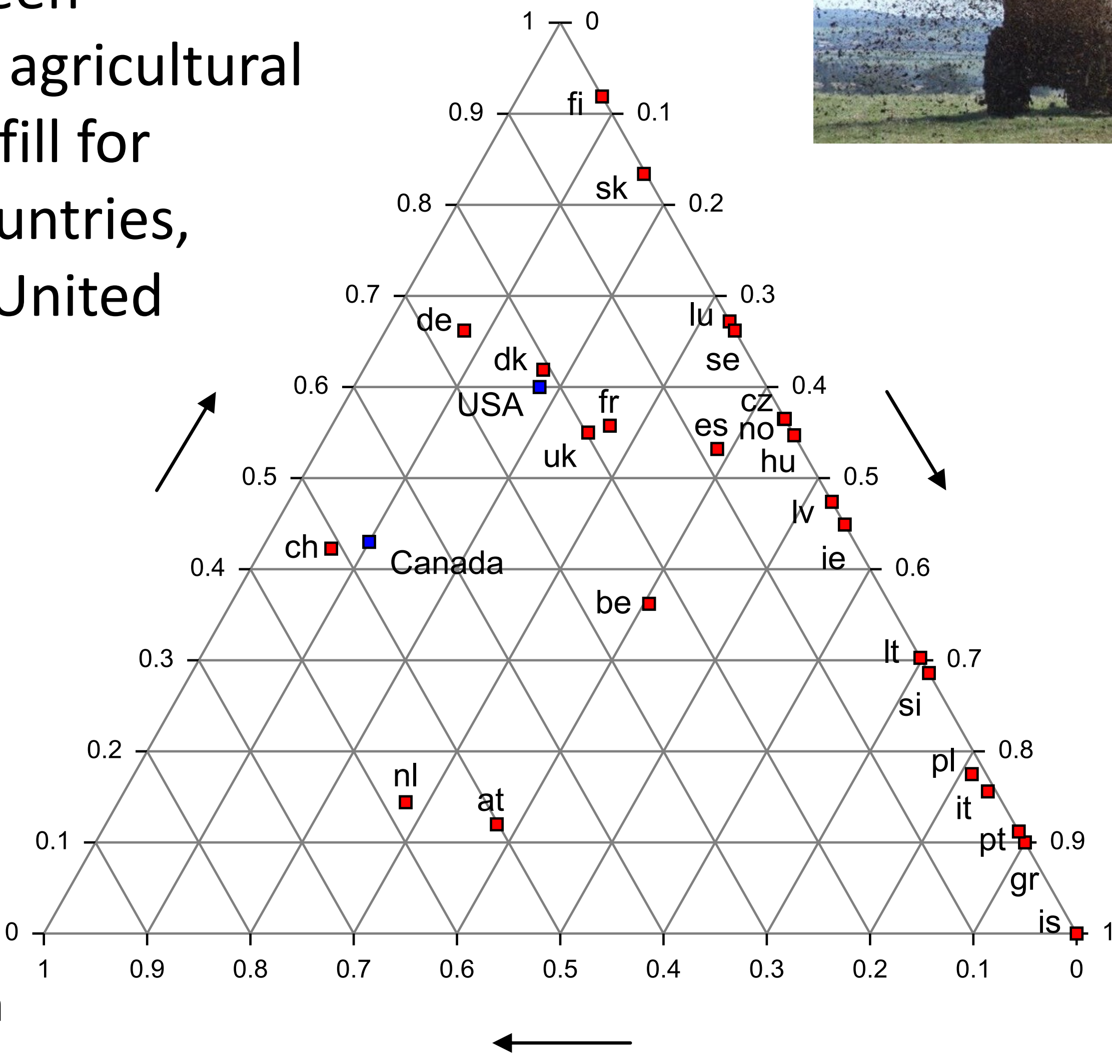
- Treatment of urban wastewater
  → Production of a significant quantity of sewage sludge

- Total production of sewage sludge for USA and countries of the European Union (EU)
  → More than 16 million tons of dry solids per year

Disposal of sewage sludge between incineration, agricultural use and landfill for European countries, Canada and United States



Introduction

Between 300 and 400 kg of ashes are produced per ton of dried sludge

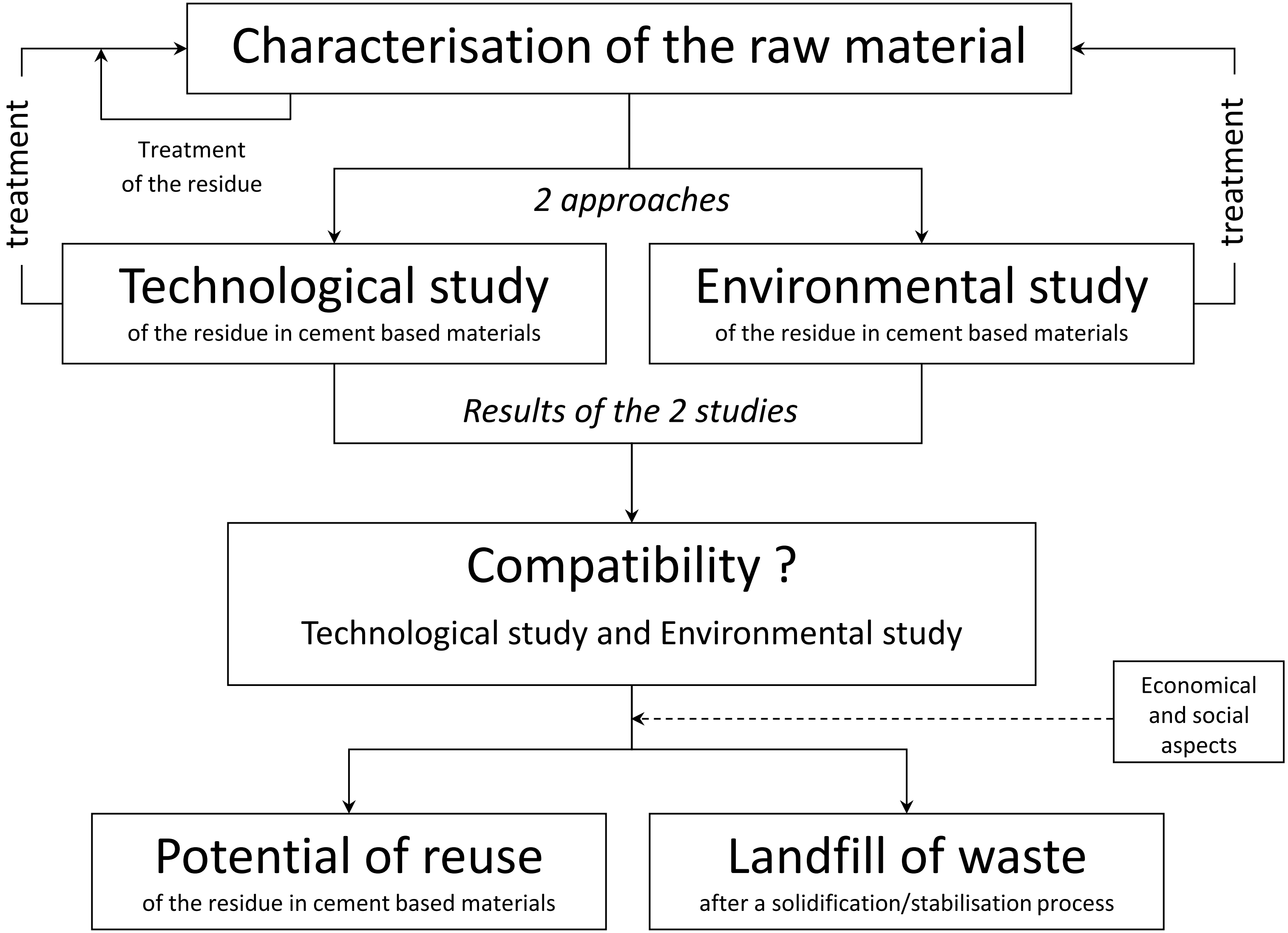
→ More than 1Mt of SSA to manage

Aim of this work

- To provide supplementary knowledge about the characteristics of SSA and its effect on the properties of cement-based materials
- Considering the origin of SSA, its environmental impact was also evaluated

Peer-review journals

- Cyr M., Aubert J.E., Husson B., Clastres P., Management of mineral wastes in cement-based materials, Revue Européenne de Génie Civil, 10 (3) (2006) 323-339.
- Coutand M., Cyr M., Clastres P., Use of sewage sludge ash (SSA) as mineral admixture in cement-based materials, Proceedings of the Institution of Civil Engineers - Construction Materials,159 (4) (2006) 153-162.
- Cyr M., Coutand M., Clastres P., Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials, Cement and Concrete Research, 37 (8) (2007) 1278-1289.
- Mahieux P.-Y., Aubert J.-E., Cyr M., Coutand M., Husson B., Quantitative mineralogical composition of complex mineral wastes - Contribution of the Rietveld method, Waste Management, 30 (3) (2010) 378-388.



Cyr M., Aubert J.E., Husson B., Clastres P., Revue Européenne de Génie Civil (2006)

- Characteristics of SSA

- Effect of SSA on technological properties of mortars
  - ✓Reactivity of SSA
  - ✓Water requirement and mortar consistency
  - ✓Setting time and early hydration
  - ✓Compressive and flexural strength

- Effect of SSA on leaching behavior of mortars

Characterisation of the raw material

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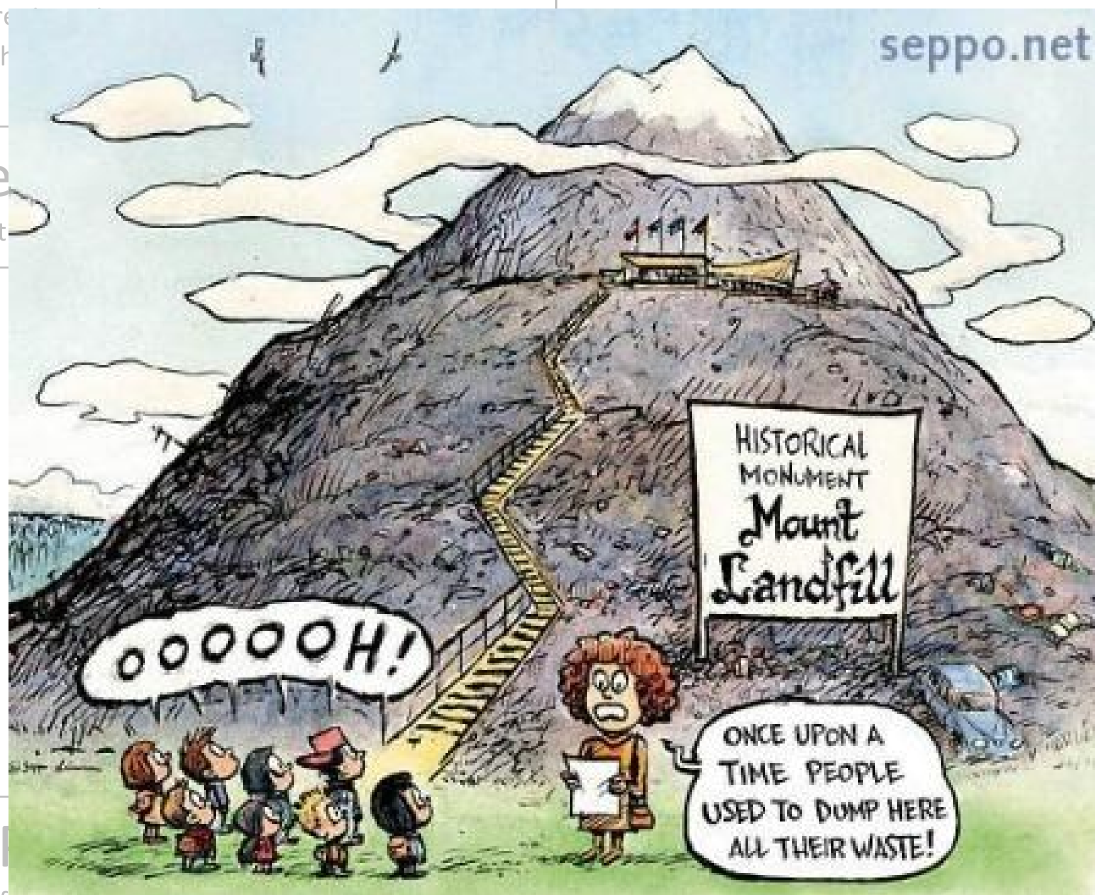


Economical and social aspects

of the residue in cement-based materials

after a solidification/stabilisation process

Sewage sludge ash obtained from the incineration of municipal sewage sludge in a fluidised bed combustor, at a temperature around 850°C

Chemical composition (major)

Chemical composition and trace analysis of SSA compared to other SSA found in literature

Oxide		SiO_2	Al_2O_3	Fe_2O_3	CaO	P_2O_5	SO_3	Na_2O	K_2O
SSA (%)		34.2	12.6	4.7	20.6	14.8	2.8	1.0	1.7
Other SSA [a]	Mean	36.1	14.2	9.2	14.8	11.6	2.8	0.9	1.3
	Min	14.4	4.4	2.1	1.1	0.3	0.01	0.01	0.1
	Max	65.0	34.2	30.0	40.1	26.7	12.4	6.8	3.1
Typical FA	min	38	20	6	1.8	---	0.35	0.8	2.3
	max	52	40	16	10	---	2.5	1.8	4.5

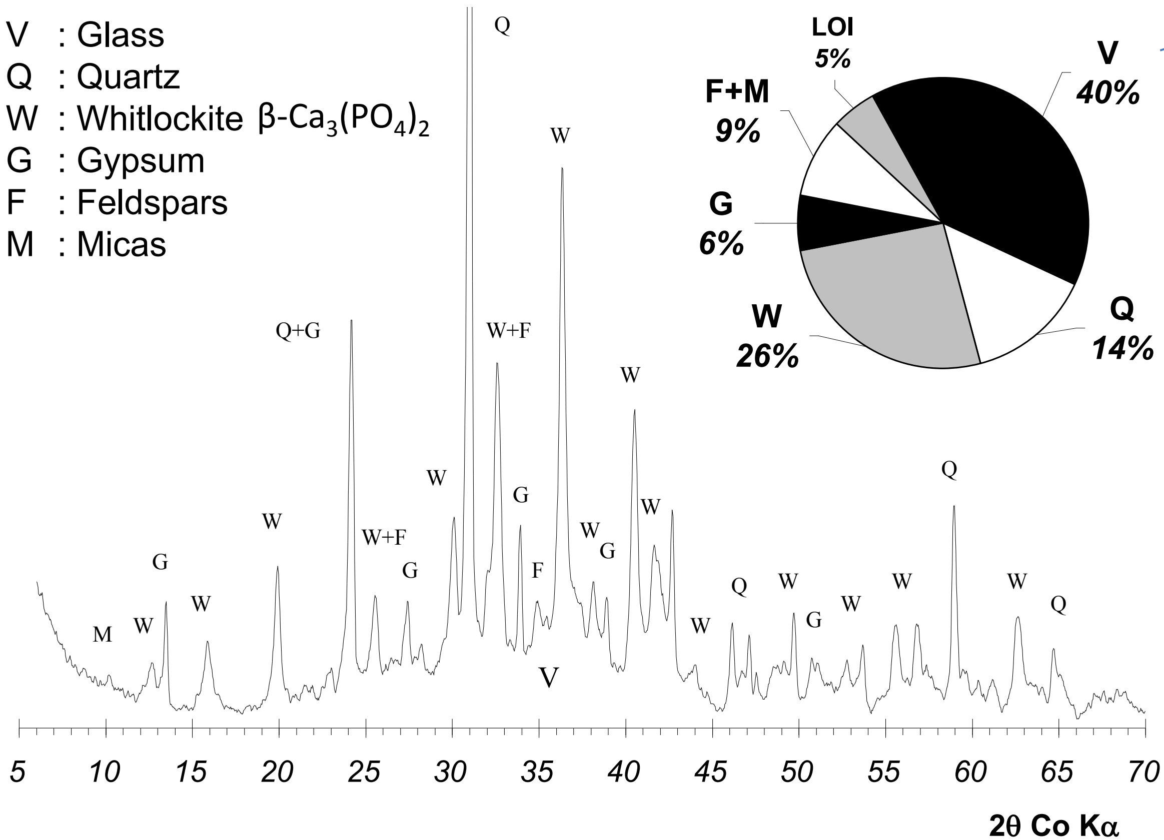
From more than 40 references all over the world

SSA of this study might be considered as representative of other SSAs

The amount of CaO and P_2O_5 is high compared to classical mineral admixtures such as fly ash, silica fume or metakaolin.

Coutand M., Cyr M., Clastres P., Construction Materials (2006)
Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Mineralogical composition



Amorphous phase: effect on the pozzolanic reactivity

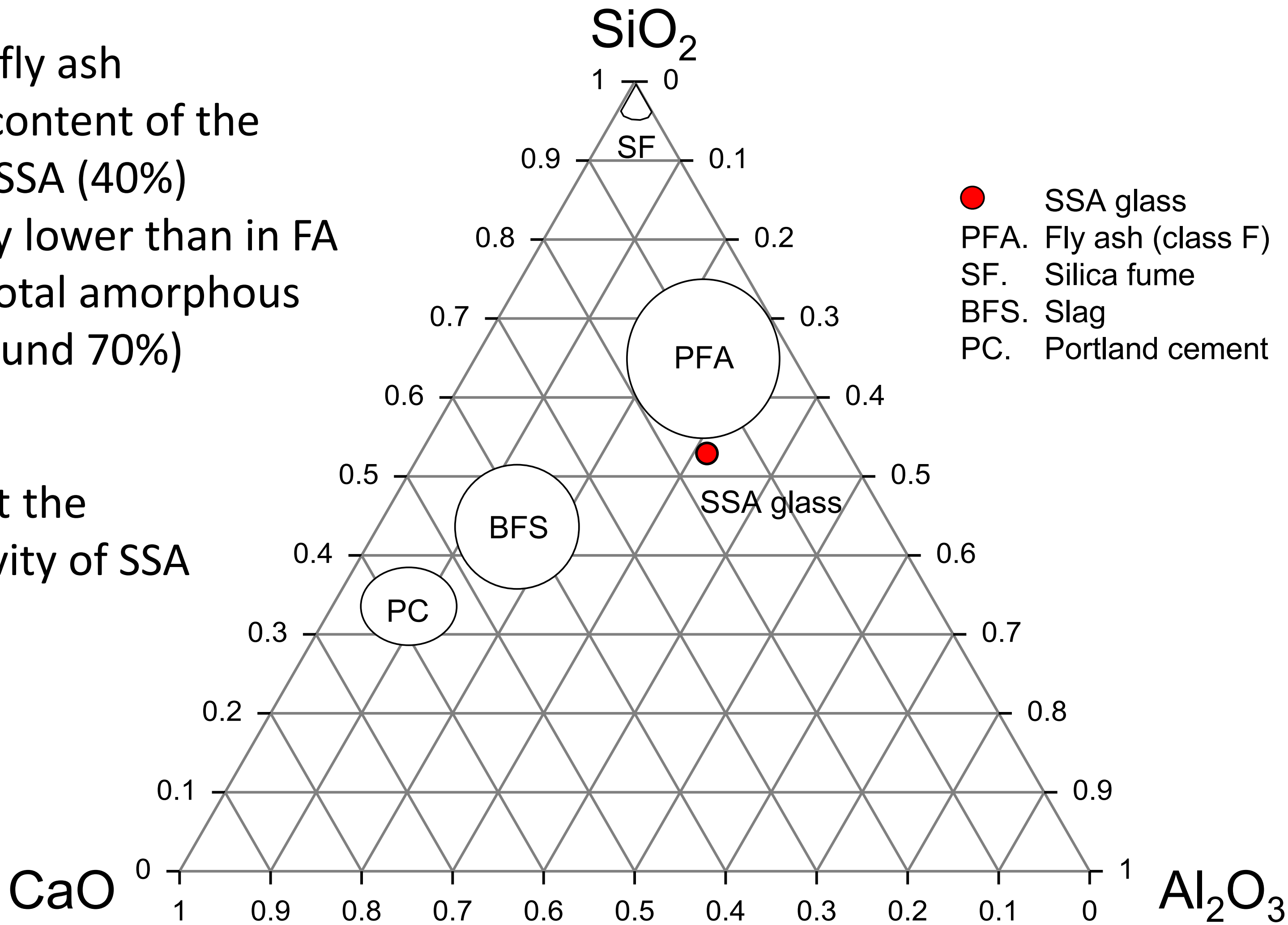
In a soluble form, P can interfere with cement components during cement hydration, and delay its setting

- CaO and P_2O_5 combined to form about 26% of whitlockite, a calcium phosphate mineral weakly soluble in a basic environment
- Sulfates present as gypsum (soluble compound)
- A fraction of SiO_2 and Al_2O_3 in the amorphous phase

Composition of the amorphous phase

- Close to that of fly ash
- However, total content of the glassy phase of SSA (40%)
  → significantly lower than in FA (which has a total amorphous content of around 70%)

- This would limit the pozzolanic activity of SSA



Coutand M., Cyr M., Clastres P., Construction Materials (2006)

Chemical composition (traces)

Elements (mg/kg)		As	Ba	Cd	Co	Cr	Cu	Ni
SSA		23	1430	14	669	2636	2483	621
Other SSA [b]	Mean	87	4142	20	39	452	1962	671
	Min	0.4	90	4	19	16	200	79
	Max	726	14600	94	78	2100	5420	2000

Elements (mg/kg)		Pb	Sb	Sn	Sr	V	Zn
SSA		720	73	283	623	63	7103
Other SSA [b]	Mean	600	35	400	539	35	3512
	Min	93	35	183	539	14	1084
	Max	2055	35	617	539	66	10000

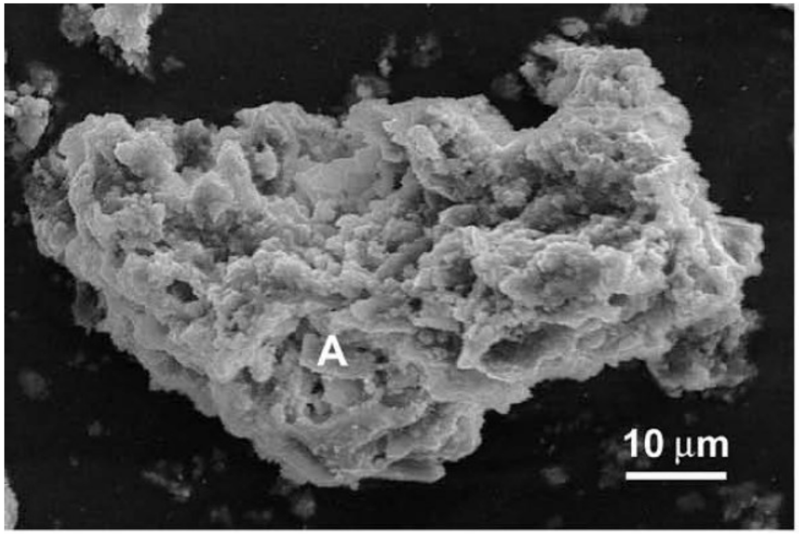
From 16 references all over the world

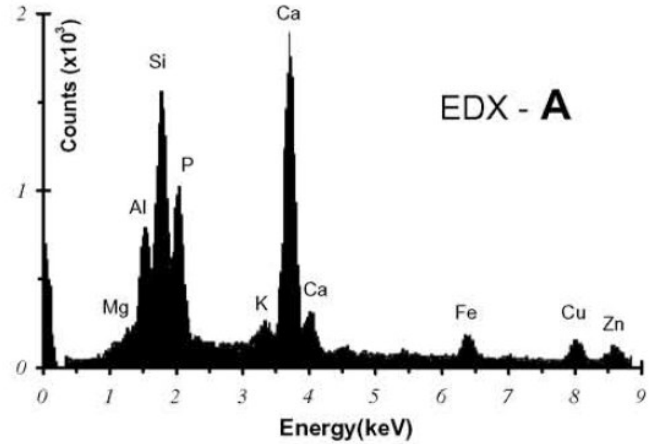
- Some heavy metals: high quantity
- Must be checked regarding leaching
  - ✓ Hydration of cement
  - ✓ Pollution

Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Characteristics of SSA

- Irregular grains
  → aggregation of small particles
- Various compositions





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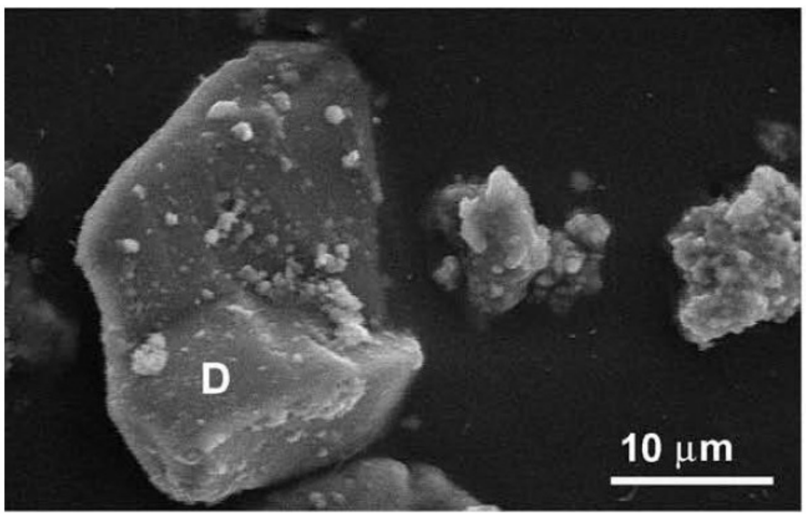
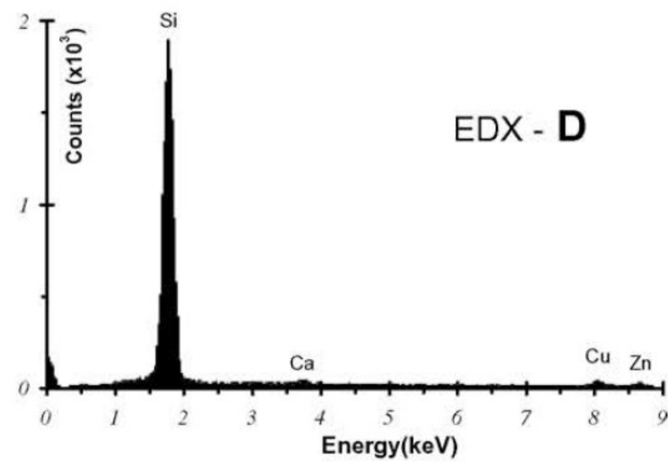
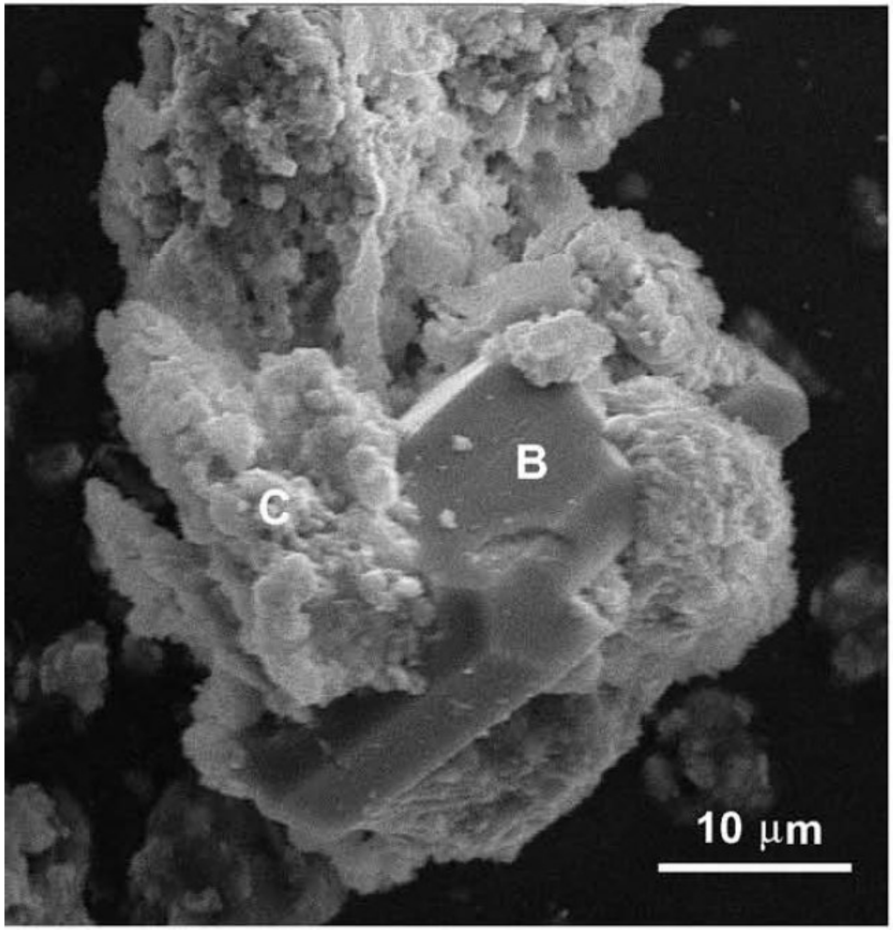
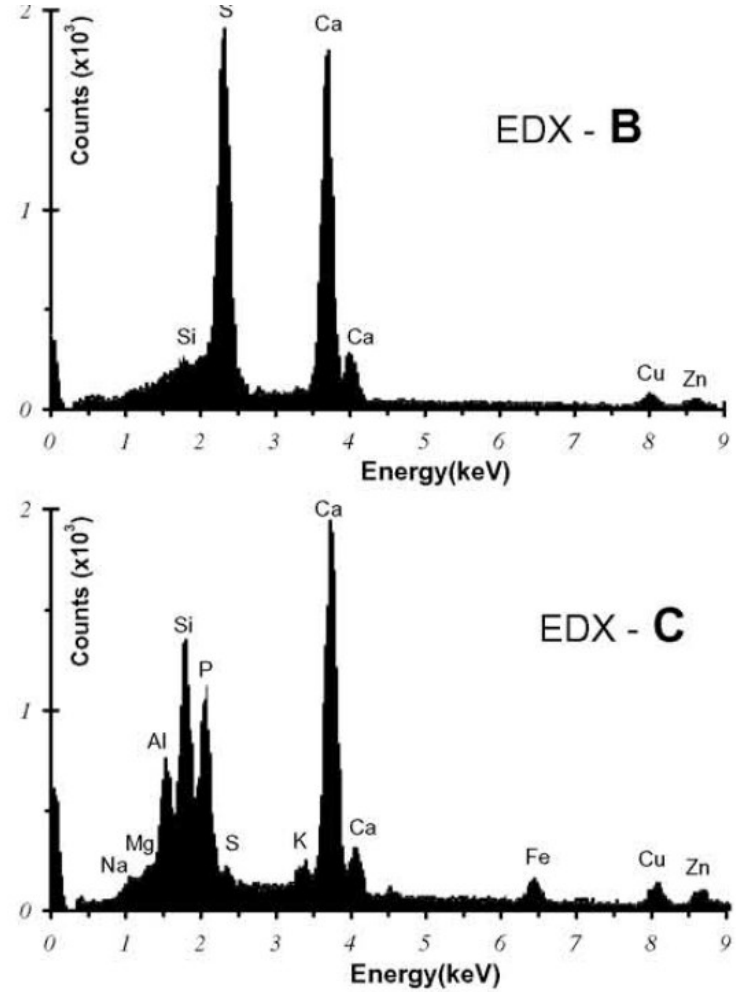




A, C: whitlockite and silico-alumina phase (feldspars and/or amorphous phase)
B: calcium sulfate (gypsum)
D: quartz

Mahieux P.-Y., Aubert J.-E., Cyr M., Coutand M., Husson B., Waste Management (2010)





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Mahieux P.-Y., Aubert J.-E., Cyr M., Coutand M., Husson B., Waste Management (2010)

Physical characteristics

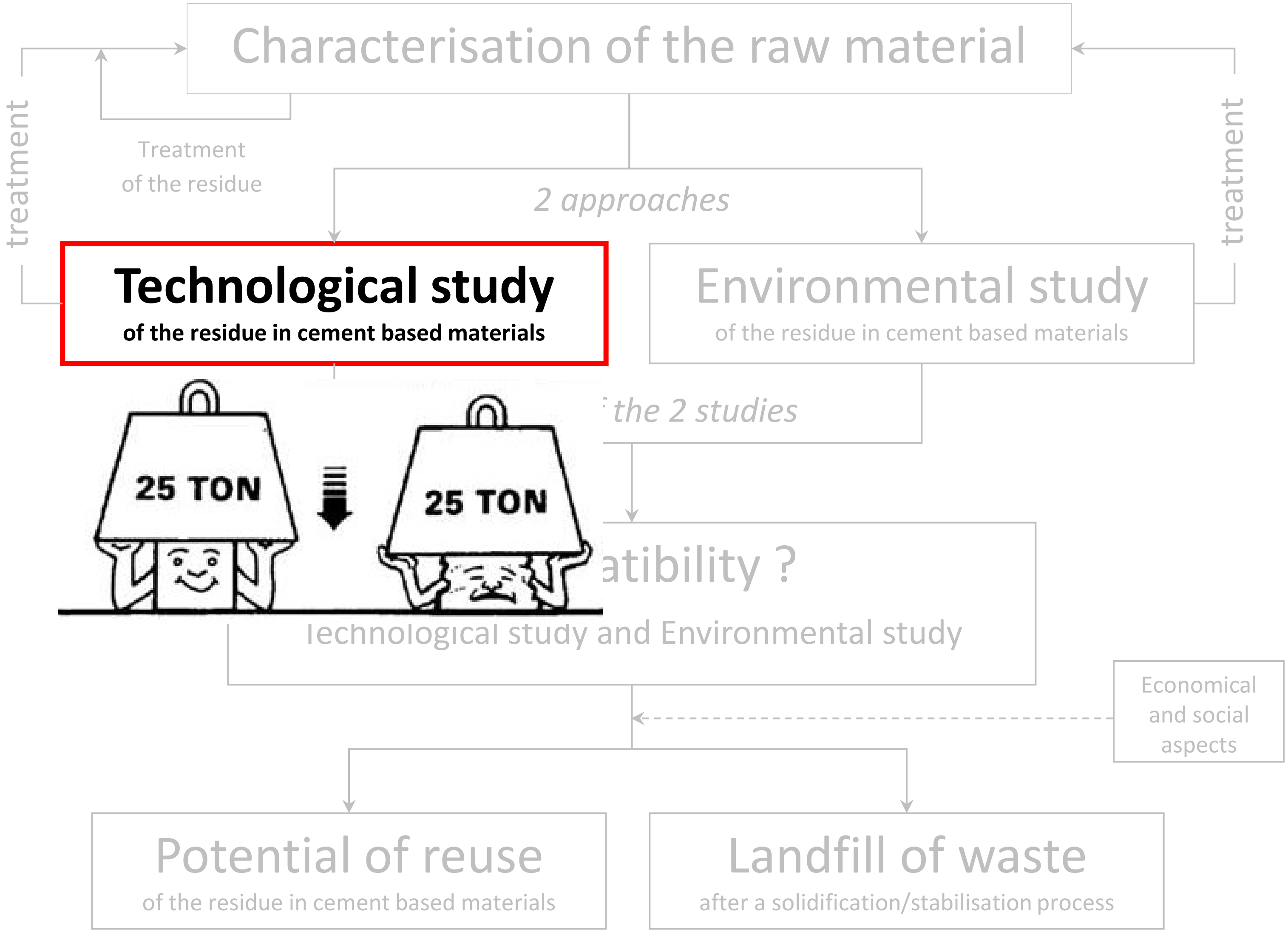
Characteristic	SSA	Fly ash
Density	2640 kg/m^3	2200 kg/m^3
Specific surface area		
Blaine	640 m^2/kg	380 m^2/kg
BET	19 000 m^2/kg	2000 m^2/kg
Particle size distribution (Fig. 2)	1–100 µm	1–100 µm
Mean diameter (d_{50})	26 µm	24 µm
Morphology	Irregular particles (Fig. 1)	Spherical particles
Water demand (pastes of normalised consistency using Vicat apparatus NF EN 196-3)[66]	Water/ash ratio 0·85	Water/ash ratio 0·37

Table 4. Physical characteristics of SSA and FA

High BET value related to the morphological irregularities of the grains

→ increase of water demand

Coutand M., Cyr M., Clastres P., Construction Materials (2006)


Characterisation of the raw material
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Treatment
of the residue
2 approaches
treatment
Technological study
of the residue in cement based materials
Environmental study
of the residue in cement based materials
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the 2 studies
atibility ?
Technological study and Environmental study
Economical
and social
aspects
Potential of reuse
of the residue in cement based materials
Landfill of waste
after a solidification/stabilisation process

Reactivity of SSA

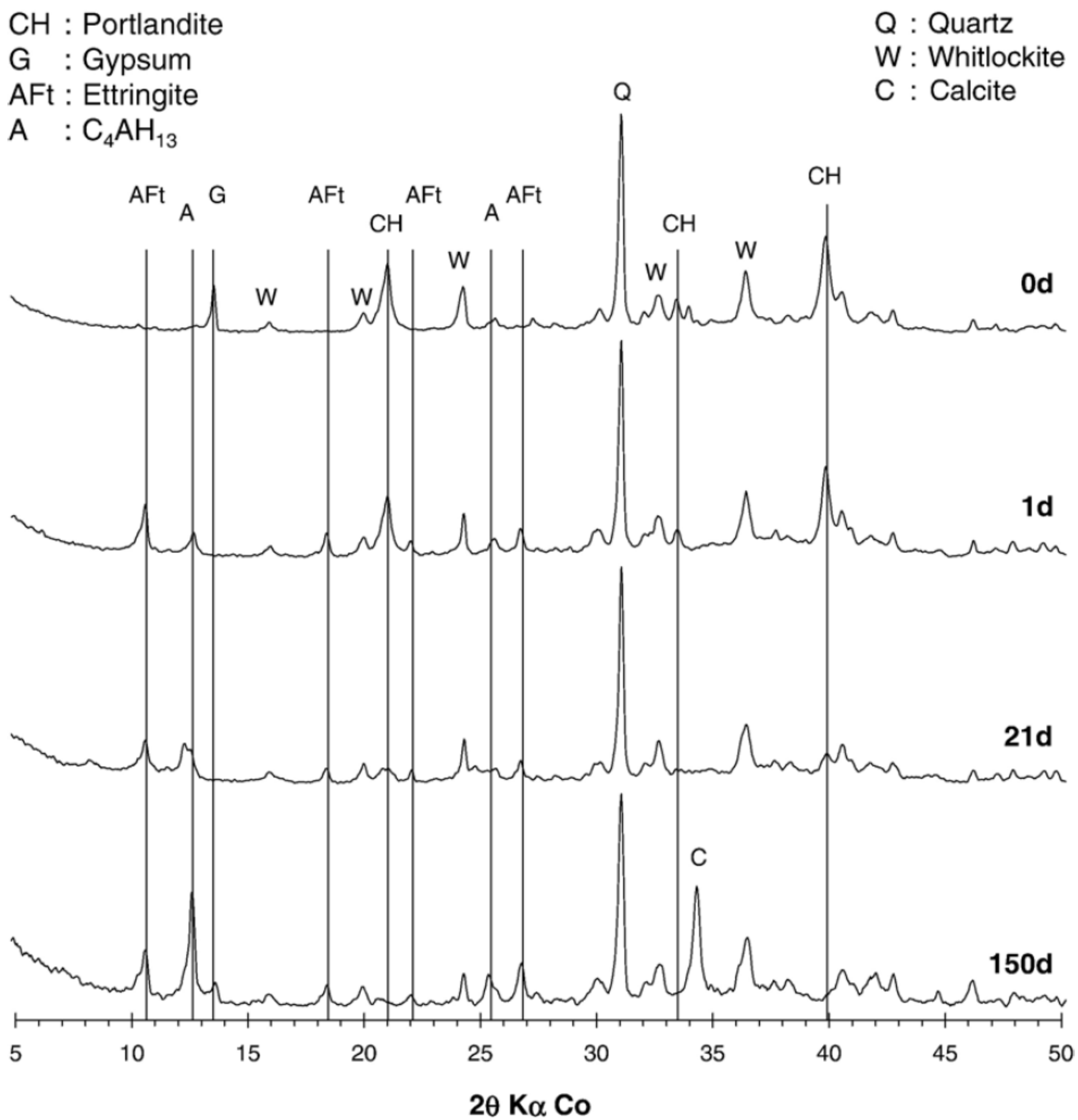
- Hydraulic:
  SSA with water →
- Pozzolanic: SSA with lime and water

XRD evolution of phase changes →

- ✓ Gypsum totally dissolved at 1 day
- ✓ Sulfates combined with Ca, Al and water to form ettringite
- ✓ Consumption of lime → new hydrates

↓

strengthening of the paste

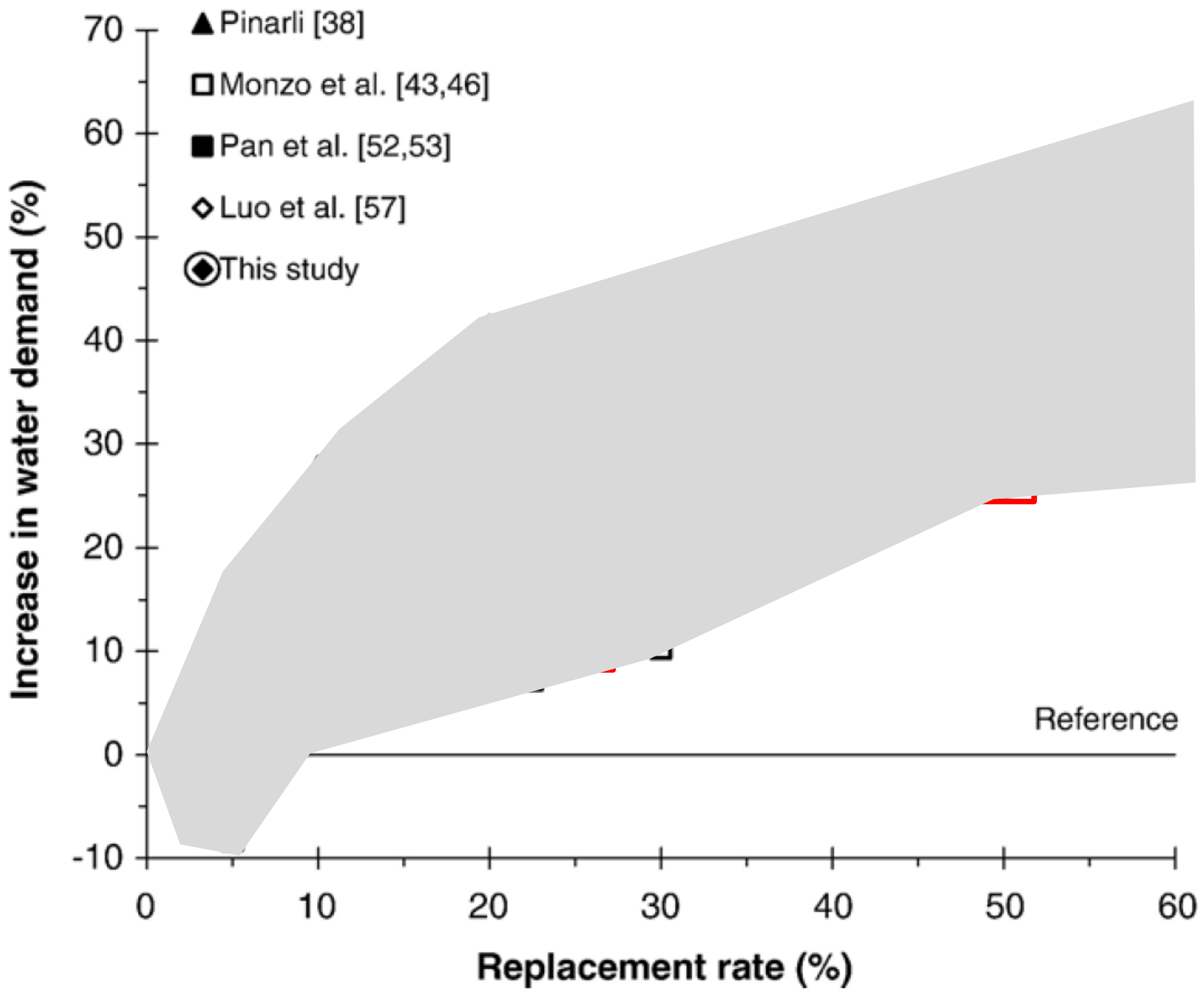


Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Water requirement and mortar consistency

- **Increase** of water demand of mortars and pastes containing SSA as a cement replacement

- Related to the high specific surface area of the grains, which are mainly composed of small sintered particles

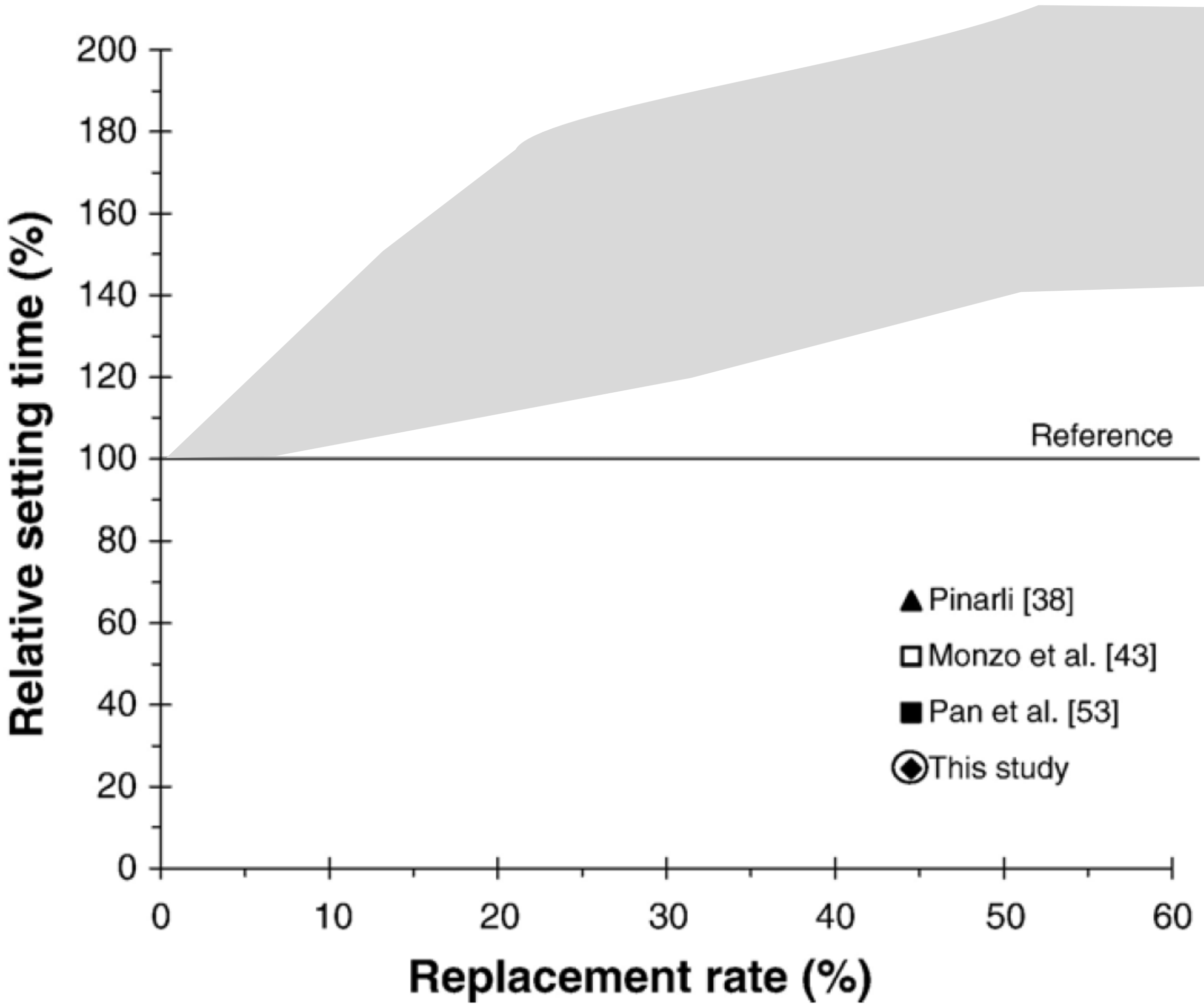


Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Setting time and early hydration

- Increasing fractions of SSA induced **higher** setting delays compared to a control mortar

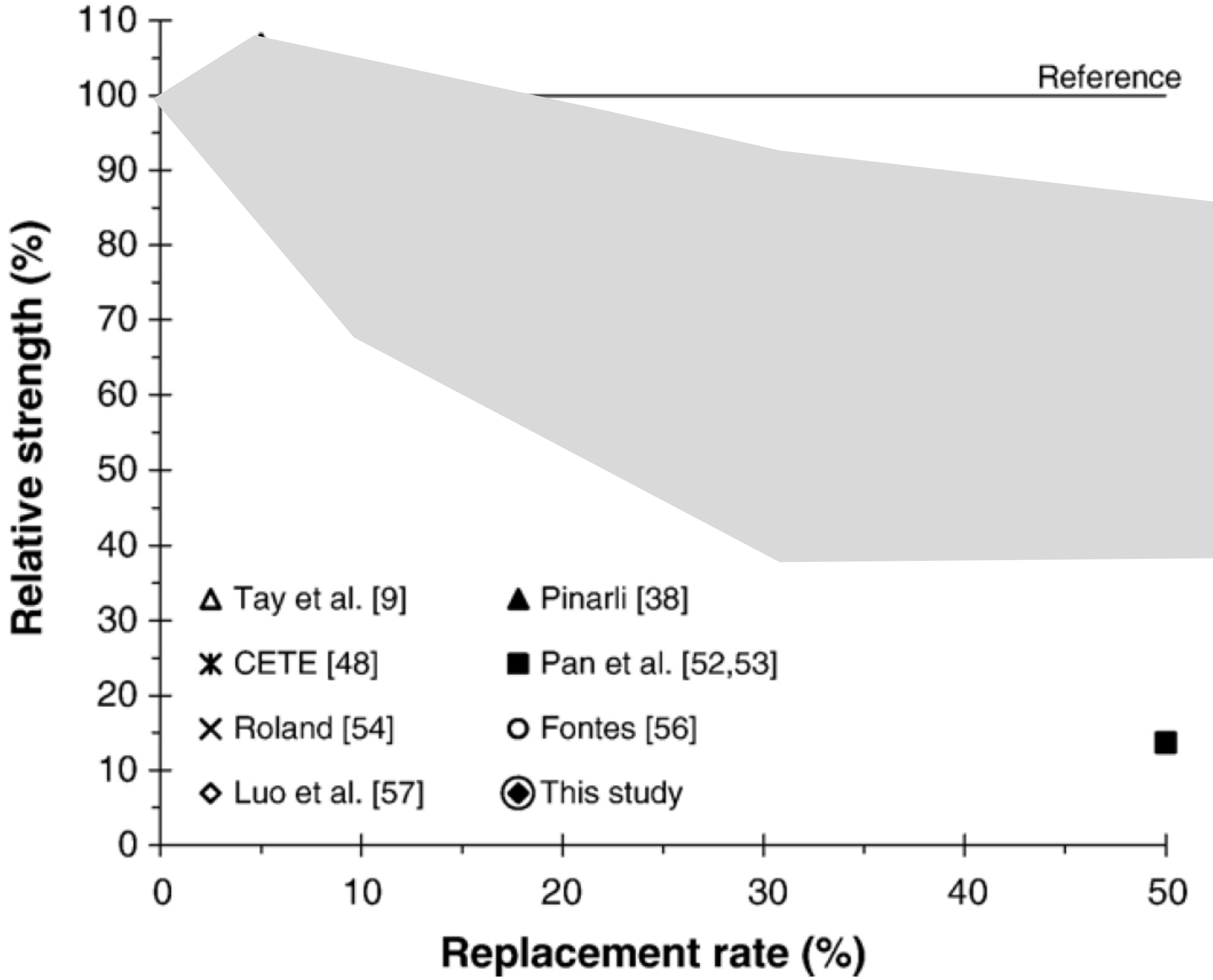
✓ dilution of cement
✓ minor elements in SSA



Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Compressive strength

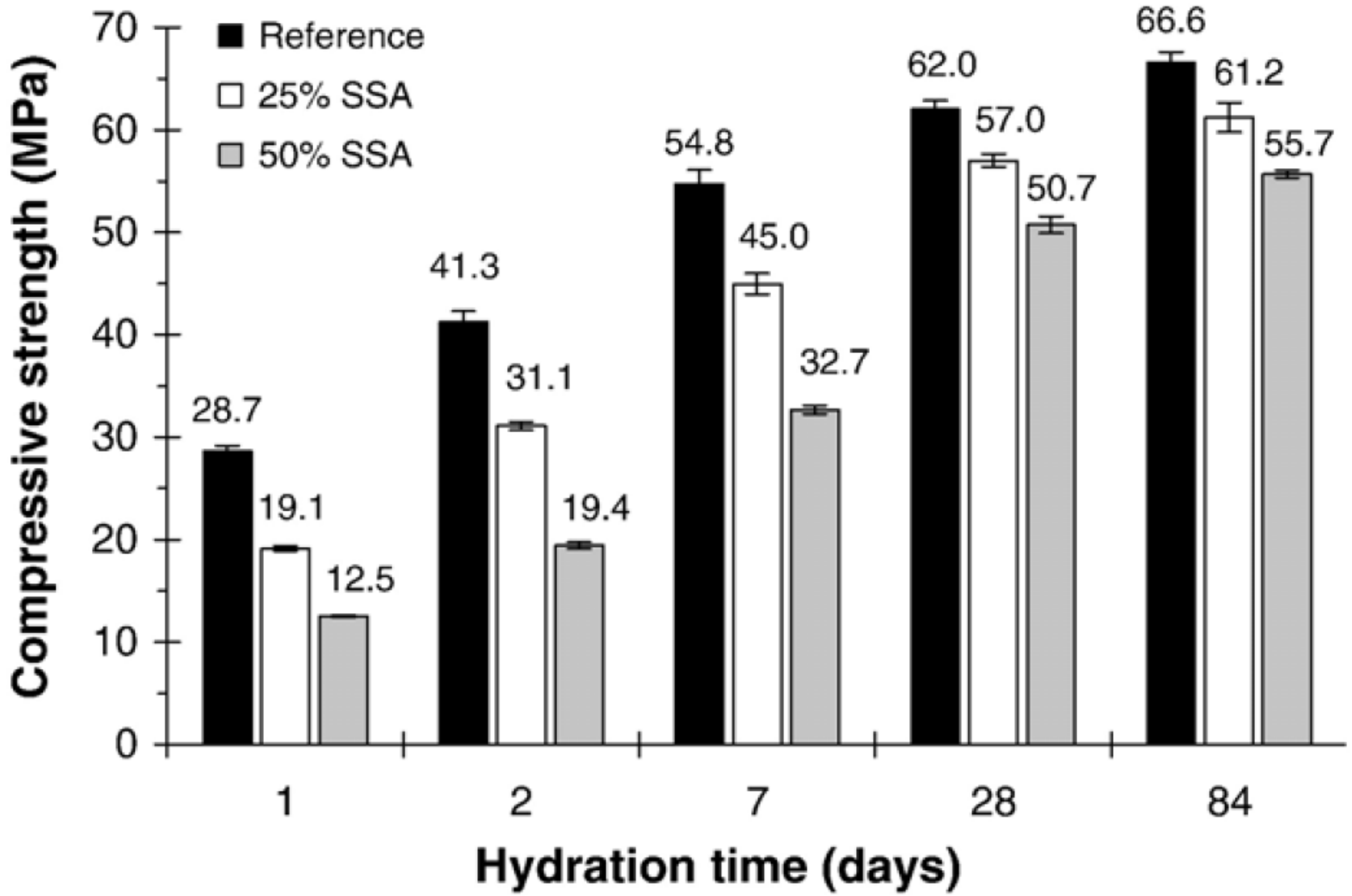
- Decrease in compressive strength when SSA used in mortars
- In accordance with results found in the literature



Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Compressive strength

- But the gap decreased over time → pozzolanic reaction



Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

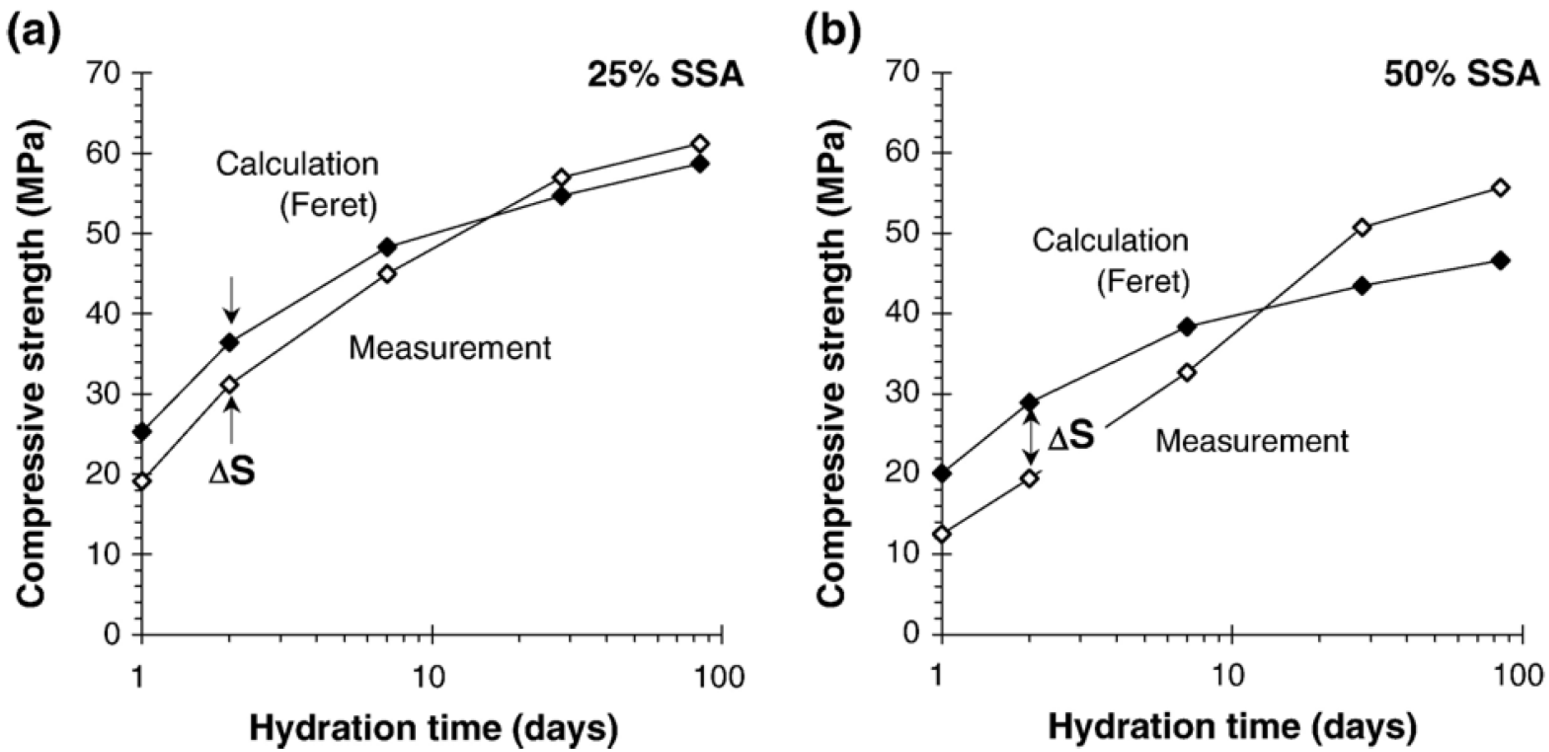
Compressive strength

- But the gap decreased over time → pozzolanic reaction

Feret's law

$$S = F\left(\frac{c/\rho_c}{c/\rho_c + w_e/\rho_w}\right)^2$$

where c and we are the masses of cement and water respectively, ρ_c and ρ_w are the density of cement and water respectively, and F is a variable parameter



Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Characterisation of the raw material

treatment

Treatment
of the residue

2 approaches

treatment

Technological study
of the residue in cement based materials

Environmental study
of the residue in cement based materials

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Potential of reuse
of the residue in cement based materials

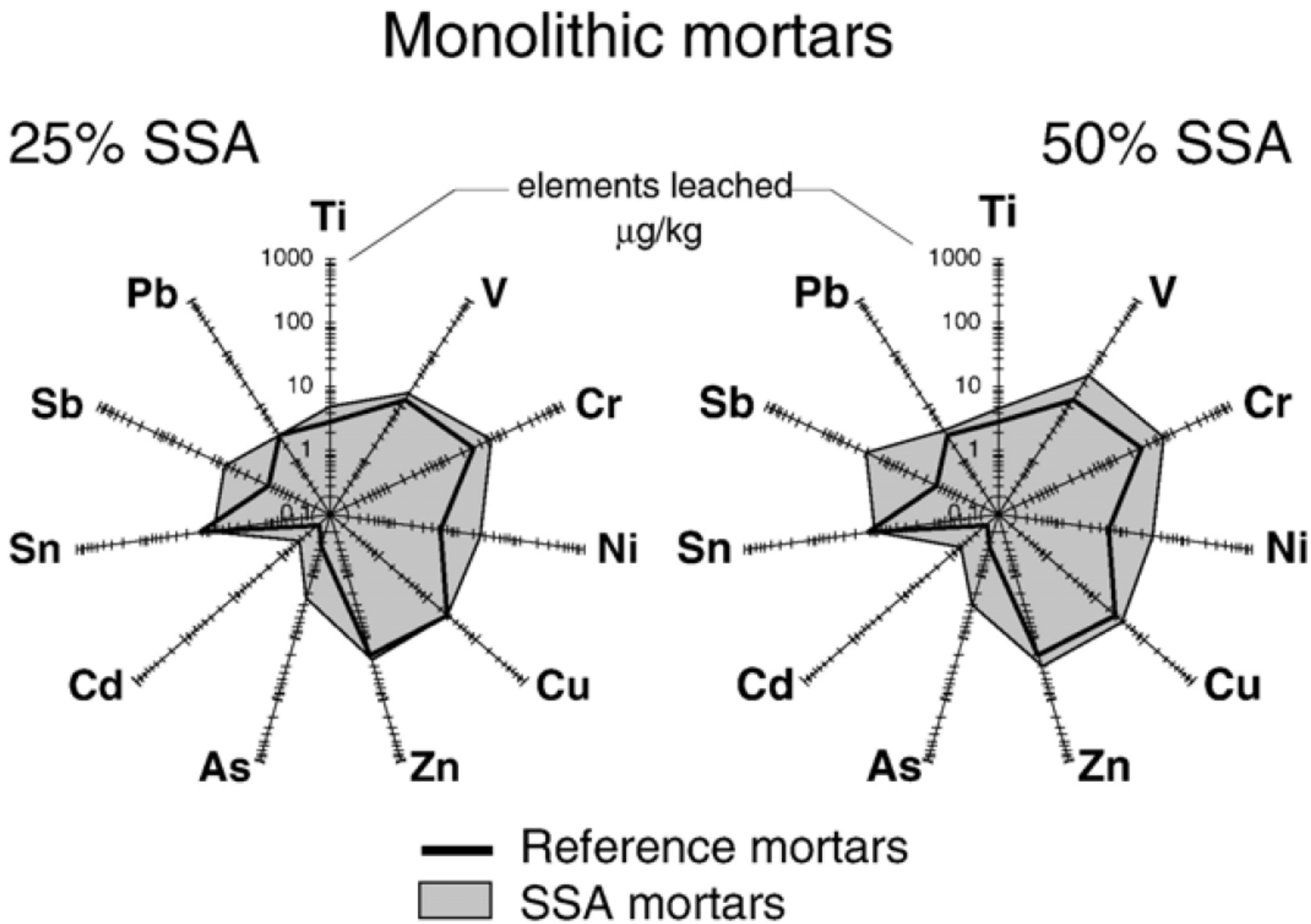
Concentrations of leached minor components (in µg/kg of mortar), total soluble fraction and pH at L/S=10 of **monolithic** and **crushed** mortars containing 0, 25 and 50% SSA

	NF XP 31-211 (3×3×8 cm pieces)			NF EN 12457-2 (fragments finer than 4 mm)		
	Monolithic mortars			Crushed mortars		
	Ref	25% SSA	50% SSA	Ref	25% SSA	50% SSA
Total, 11 elements (µg/kg)	115.7	177.2	243.0	608.2	642.5	919.3
Soluble fraction (g/kg)	5.0	4.0	3.3	31.9	30.2	21.5
pH	11.6	11.6	11.4	12.6	12.5	12.3

(Arrows under the Total row: + → ; arrows under the Soluble fraction row: - →)

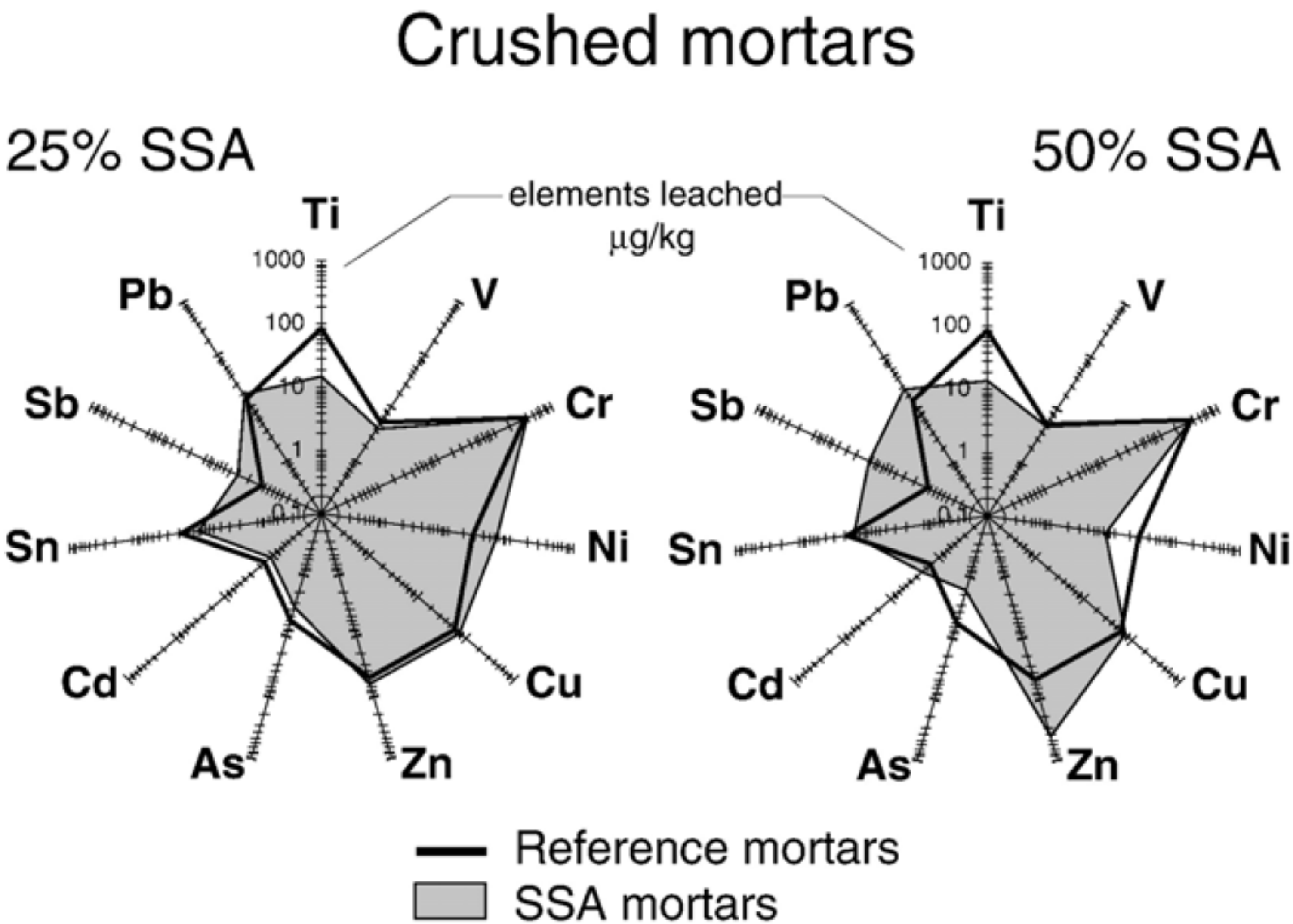
- Lower soluble fractions (less cement)
- More heavy metals

Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)



Slightly higher heavy metal release, higher porosity of SSA

Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)



similar order of magnitude for all mortars

Cyr M., Coutand M., Clastres P., Cement and Concrete Research (2007)

Leaching impact of SSA

	Ref	25% SSA	Limits[77,78]
Ti: µg/l	0·3	0·5	n.m.*
V: µg/l	1·4	1·9	n.m.
Cr: µg/l	3·1	6·5	50
Ni: µg/l	0·5	2·5	20
Cu: µg/l	2·6	2·6	2000
Zn: µg/l	2·0	2·4	3000[77]/n.m.[78]
As: µg/l	0·04	0·25	10
Cd: µg/l	0·02	0·05	3[77]/5[78]
Sn: µg/l	1·1	0·7	n.m
Sb: µg/l	0·1	0·7	20[77]/5[78]
Pb: µg/l	0·3	0·3	10
SF†: g/l	0·53	0·45	n.m.
pH	11·6	11·6	6·5 < pH < 9·5

*n.m.: not mentioned.
†Total soluble fraction of mortars (g) per litre (l) of leaching solution.

Table 6. Leaching (liquid–solid ratio of 10) of minor components in monolithic mortars; comparison with limits for drinking-water quality

→ World Health Organisation and European standards for drinking-water quality

- Leaching concentrations within the Limits
- Only the pH values exceed the guideline values

Coutand M., Cyr M., Clastres P., Construction Materials (2006)

Characterisation of the raw material

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Compatibility ?

Technological study and Environmental study

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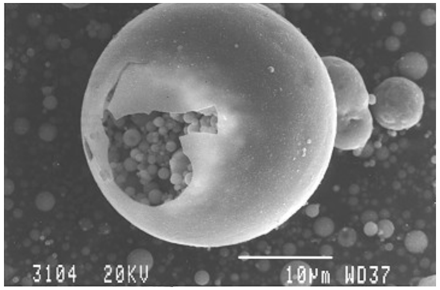
after a solidification/stabilisation process

Sewage sludge ash vs. Coal fly ash

- Fly ash from pulverised coal thermal power stations is the main mineral admixture coming from a thermal process that is widely used in the concrete industry
- Morphologies, specific surface areas, and mineralogical and elemental compositions are quite different



Sewage sludge ash vs. Coal fly ash

	SSA	ASTM C618 Specifications	Standard requirement	NF EN 450 Specifications	Standard requirement
Chemical requirements					
Reactive SiO_2	16% in glass [a]	---	---	$SiO_2 \geq 25\%$	N
Total ($SiO_2 + Al_2O_3 + Fe_2O_3$)	51.5%	≥ 70% Class F ≥ 50% Class C	N Y	---	---
CaO (free)	0.09%	---	---	≤ 1.0% (2.5%)	Y
CaO (total)	20.6%	≤ 10% Class F > 10% Class C	N Y [b]	---	---
Cl^-	tr	---	---	≤ 0.10%	Y
SO_3	2.8%	≤ 5.0%	Y	≤ 3.0%	Y
LOI	5.5%	≤ 6.0%	Y	≤ 5.0% (7.0%)	Y

[a] evaluated using combined results of chemical analysis, selective dissolution and QXRD; the total glass content is around 40%.

[b] Class C fly ash generally presents cementitious properties, which was not the case for SSA.

Sewage sludge ash vs. Coal fly ash

	SSA	ASTM C618 Specifications	Standard requirement	NF EN 450 Specifications	Standard requirement
Physical requirements					
Free moisture	18%	≤ 3.0%	N	---	---
fraction > 45 µm	21%	≤ 34%	Y	≤ 40%	Y
Activity in mortars					
Strength Activity Index Percentage of control (see Figure 6)	25% ash [c] 7d : 82% 28d : 92% 84d : 92%	20% ash 7d : 75% 28d : 75%	---	25% ash 28d : 75% 90d : 85%	Y
Water requirement Percentage of control	25% ash 110-122%	20% ash 105%	N	---	---
Stability (only if free CaO > 1%)	---	---	---	≤ 10mm	---

[c] mixtures with superplasticizer.

Conclusion

(a) SSA has physical, chemical and mineralogical characteristics quantitatively **different** from those of fly ash

(b) SSA is formed of irregular particles, which have a high specific surface area, thus leading to a **high water demand** when used in mortars.

(c) SSA is composed mainly of calcium phosphates, quartz, and glass. However, **the silica content in the glass is low**, which probably limits the pozzolanic activity of SSA.

(d) The strength activity index of SSA reaches **more than 90%** after 28 days when superplasticiser is used.

(e) The leaching behaviour of mortars containing SSA is of **the same order of magnitude** as that of reference mortar without the SSA residue.

SSA could at least be used as a lower-grade pozzolan and/or a good quality filler for concrete applications

References

Peer-review journals

- Cyr M., Aubert J.E., Husson B., Clastres P., Management of mineral wastes in cement-based materials, Revue Européenne de Génie Civil, 10 (3) (2006) 323-339.
- Coutand M., Cyr M., Clastres P., Use of sewage sludge ash (SSA) as mineral admixture in cement-based materials, Proceedings of the Institution of Civil Engineers - Construction Materials,159 (4) (2006) 153-162.
- Cyr M., Coutand M., Clastres P., Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials, Cement and Concrete Research, 37 (8) (2007) 1278-1289.
- Mahieux P.-Y., Aubert J.-E., Cyr M., Coutand M., Husson B., Quantitative mineralogical composition of complex mineral wastes - Contribution of the Rietveld method, Waste Management, 30 (3) (2010) 378-388.
- Cyr M., Idir R., Escadeillas G., Use of metakaolin to stabilize sewage sludge ash and municipal solid waste incineration fly ash in cement-based materials, Journal of Hazardous Materials, 243 (2012) 193-203.

International congresses

- Cyr M., Klysz G., Julien S., Clastres P., Can sewage sludge ashes be used in cementitious materials?, in: The Future of Waste Management in Europe, Strasbourg (France), October 7-8, 2002, pp.353-356.
- Cyr M., Clastres P., Sewage sludge ashes in cementitious materials, in: Waste Materials in Construction (Wascon 2003), San Sebastian (Spain), June 4-6, 2003, pp.917-920.
- Cyr M., Aubert J.E., Husson B., Clastres P., Recycling waste in cement-based materials: a studying method, in: International Conference on the Use of Recycled Materials in Building and Structures - RILEM proceedings PRO 40, Topic 3: General Approach to Reuse and Recycling in Construction, Barcelona (Spain), November 9-11, 2004, pp.306-315.
- Cyr M., Idir R., Escadeillas G., Julien S., Menchon N., Stabilization of industrial by-products in mortars containing metakaolin, in: 9th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Warsaw (Poland), May 20-25, 2007, pp. 51-61.