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ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA
DIPARTIMENTO DI INGEGNERIA CIVILE, CHIMICA, AMBIENTALE E DEI MATERIALI

CRT glass management: chemical pretreatment for use in cementitious composites

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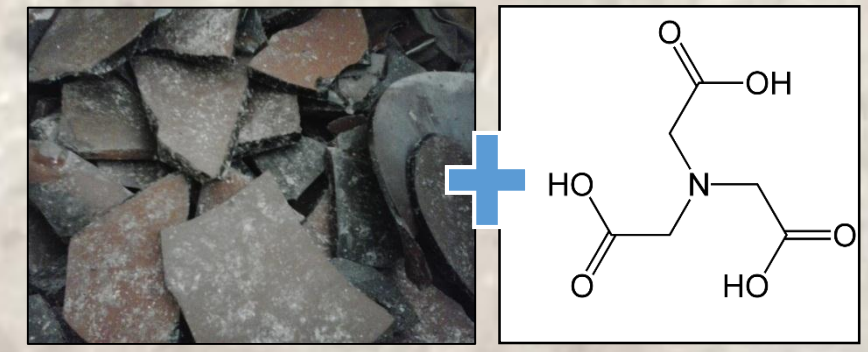
AIM OF THE WORK:

To investigate the effect of a mild chelating agent treatment based on nitrilotriacetic acid (NTA) on the reactivity of funnel glass from waste cathode ray tubes (CRTs) to be used in cement mortars as:

- supplementary cementing material (SCM)

- fine aggregate.

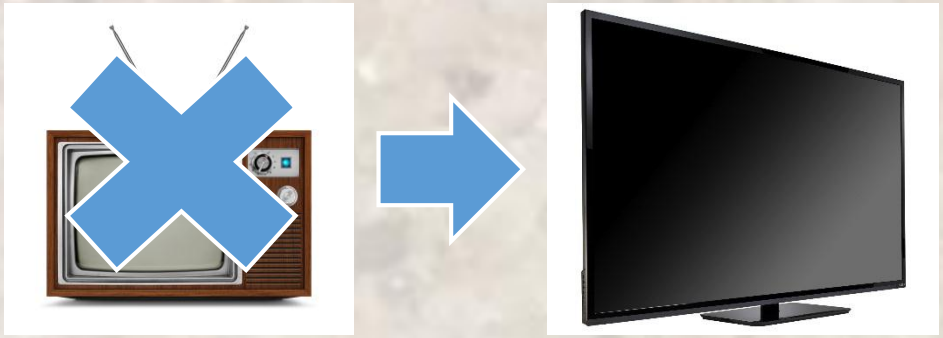


SCM

Treated funnel glass in cement mortar as:

Sand substitute

Waste CRT monitors



- Italy: **peak quantity in collection** between 2011-2013.
- The **return rate** of TVs and PCs is still the highest among WEEE (65.1 kt collected vs 37.4 kt put on market in 2015).

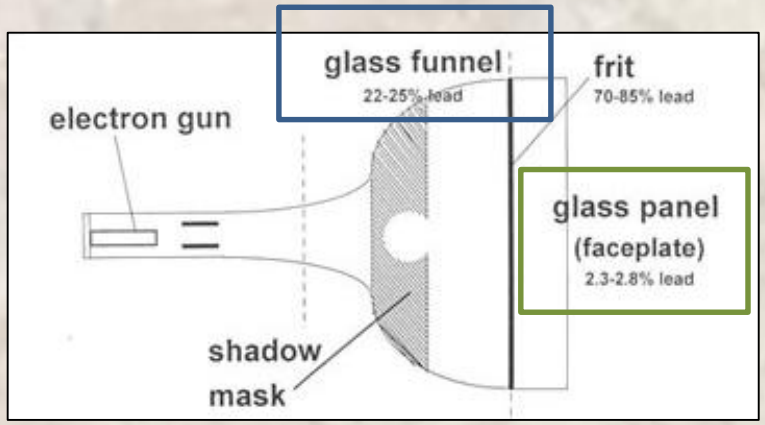
[Centro di Coordinamento RAEE, Annual Report 2015]

- The **global generation** of waste CRTs was around 6.3 Mt in 2014.
- Most of waste CRTs was generated in Asia (2.5 Mt) followed by Europe and America (1.7 Mt).

[Baldé et al., 2015. The Global E-Waste Monitor – 2014. United Nations University, IAS–SCYCLE, Bonn, Germany]

Urgent disposal problem

Funnel glass from waste CRTs



Panel glass

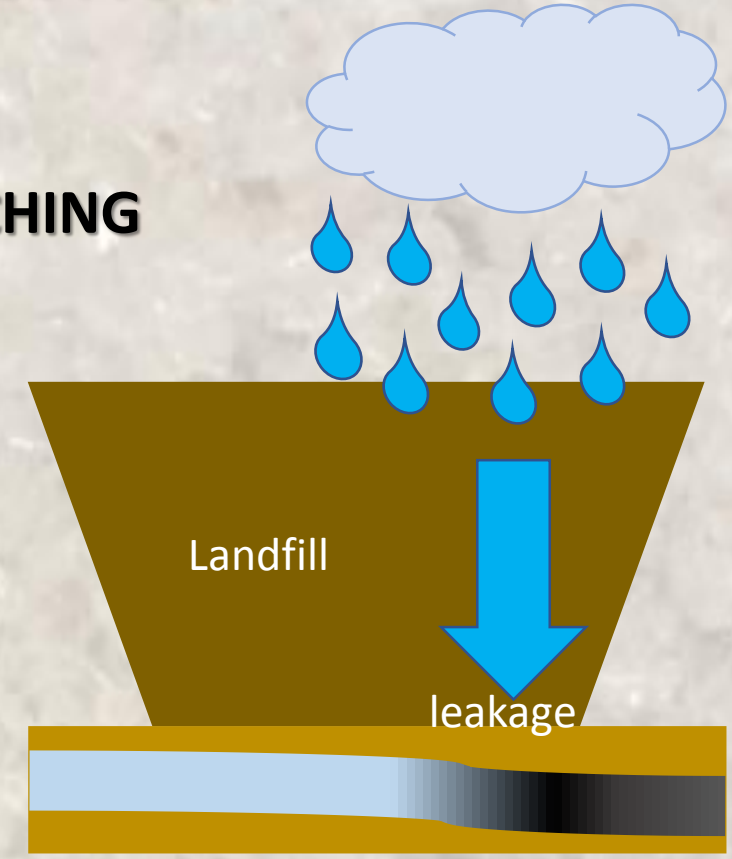
BaO (up to 14wt%)
SrO (up to 12wt%)

Funnel glass

PbO (12 – 25wt%)

radiation shielding

Pb LEACHING



RECYCLING PROCESS

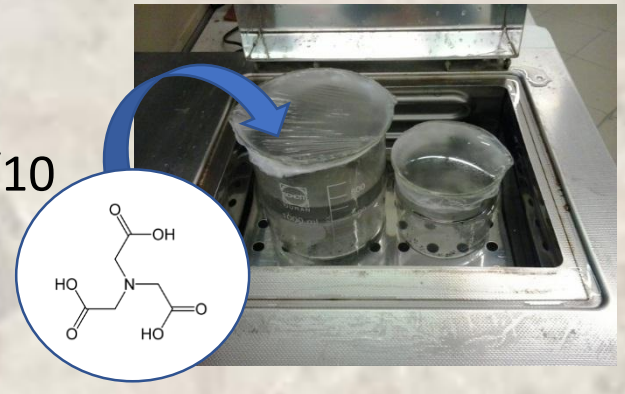
Problematic because of:
- Directive 2002/95/EC (RoHS)
- HIGH ENERGY CONSUMPTION → HIGH COSTS
(Pb is strongly bonded by encapsulation into the glass matrix)

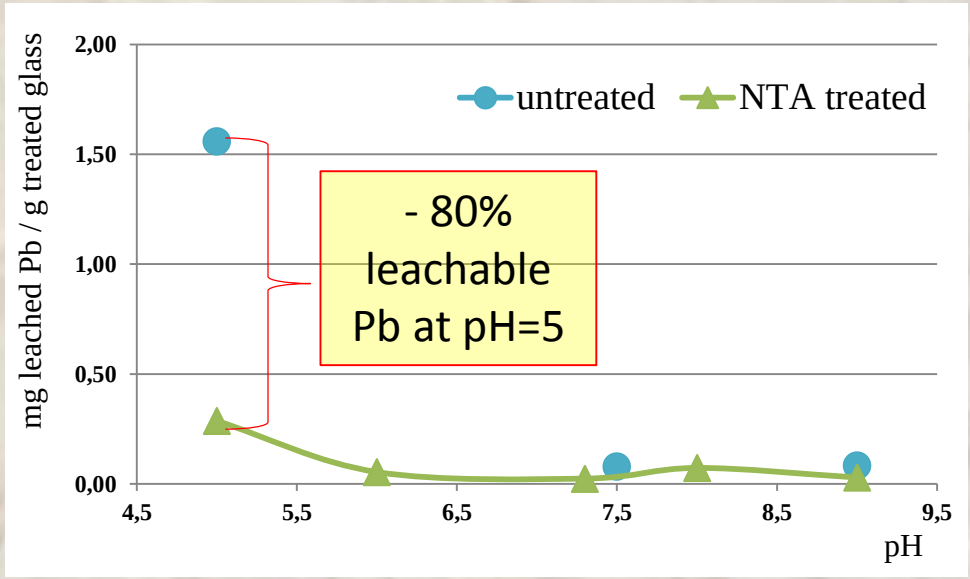
PROPOSED SOLUTION:

mild chelating agent treatment followed by recycling into cement mortar

CONDITIONS:

- NTA concentration = 0.1 M
- solid/liquid weight ratio = 1/10
- pH 10
- T = 80°C
- t = 1h

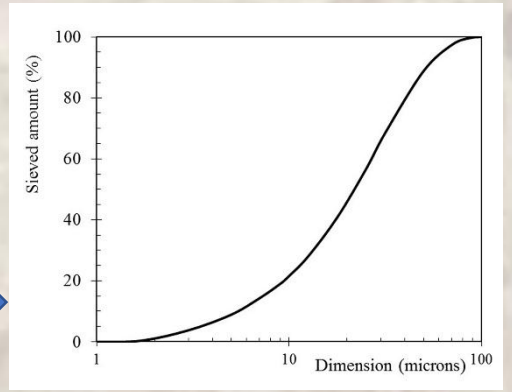




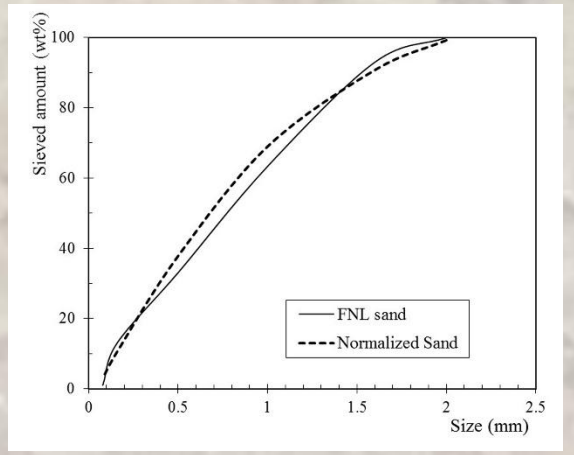
[Bursi et al., 2015. Cathode Ray Tube (CRT) lead glass: lead leaching study after a chelating agent treatment. Environ Eng Manag J]

FNL glass particle size:

- **SCM**: <100 µm

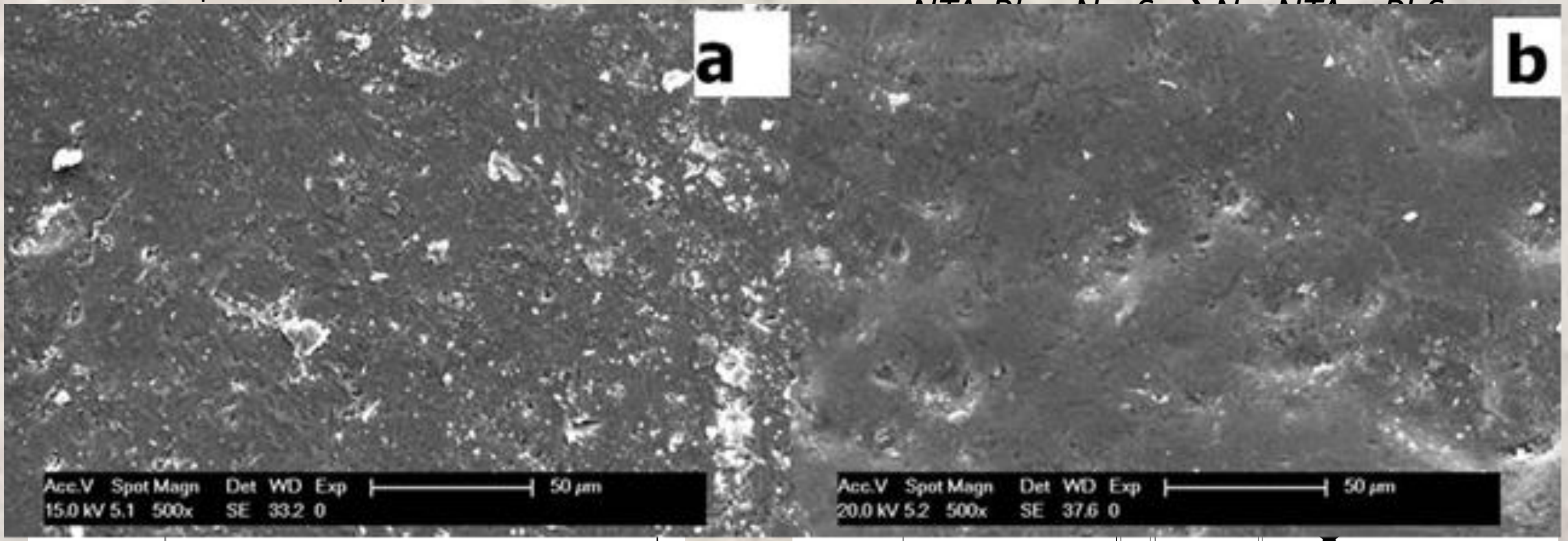


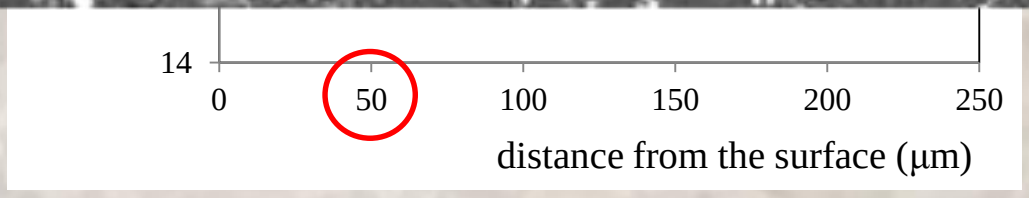
- **Fine aggregate**: 0.075-2.00 mm (distribution close to normalized sand EN 196-1).



Treatment depth analysis

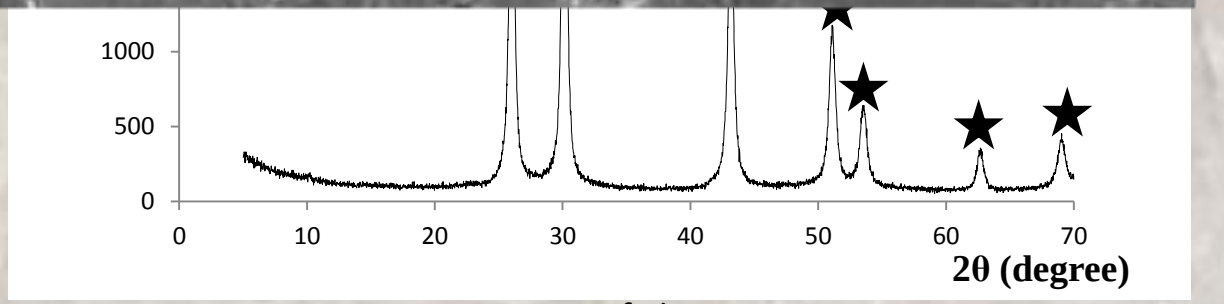
Discoid FNL sample *ad hoc* prepared





Depth of effectiveness < 50µm

Spent chelating agent solution regeneration



XRD spectrum of PbS precipitate

Mortars preparation

BINDER: CEM I 52.5 (Na_2O equivalent of 0.75%)
AGGREGATE: standard siliceous sand (EN 196)

CASTING ACCORDING TO EN 196-1
a/b = 3/1
w/b = 0.50

AMOUNT OF SUBSTITUTED CEMENT OR SAND = 25wt%.
(both NTA-treated and untreated FNL glass were used)

CURING → 24 h; 100 % R.H.; 25°C

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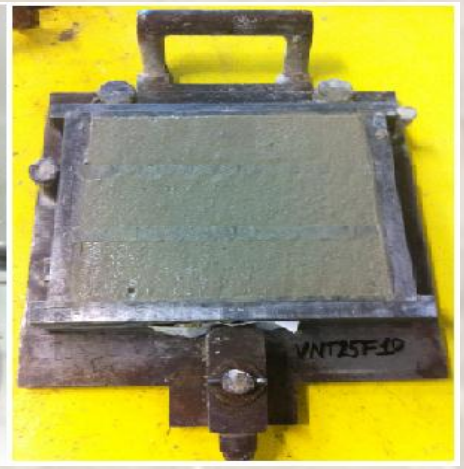
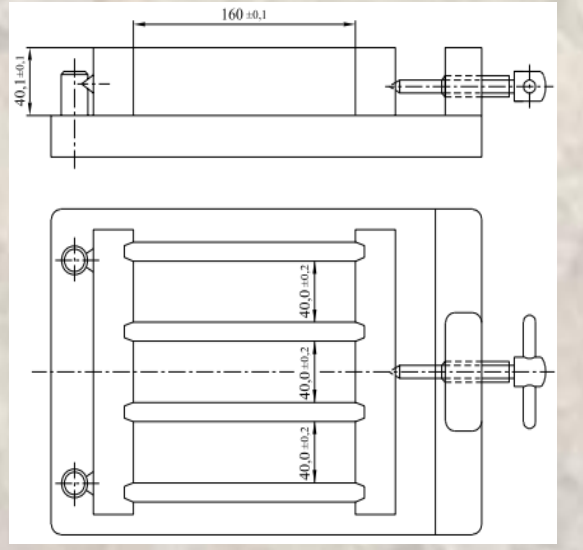
Glass addiction (both as SCM and sand) slightly increased mortars workability → 10% higher slump (EN 196)

Mortars mixing



Mortars' mould



Mould geometry

UNTREATED FNL (XRF)

Oxide	wt%
SiO_2	55.15
PbO*	17.98
K_2O	5.84
Na_2O	9.13
Al_2O_3	2.96
CaO	2.51
BaO	2.16
MgO	1.82
SrO	1.02
Br	0.39
Sb_2O_3	0.17
ZnO	0.14
ZrO_2	0.15
Cr_2O_3	0.01
Fe_2O_3	0.09
TiO_2	0.08
NiO	0.13

Experimental test

Glass solubility test:

- Alkaline attack (pH=12) with NaOH+$Ca(OH)_2$ solution, l/s=60, 80°C, 28 h
- Analysis by EDS

Glass and mortars leaching test (EN 12457-2):

- Sample ground and sieved under 4 mm
- Leaching in distilled water, l/s=10, T room, 24 h, under stirring
- Analysis by ICP-OES

Mechanical test:

1) Compression on mortars (EN 196-1)

- Curing → 25°C, R.H. 100%
- Testing machine: 100 KN Wolpert, speed test 50 mm/min

2) Activity Index (EN 450-1)

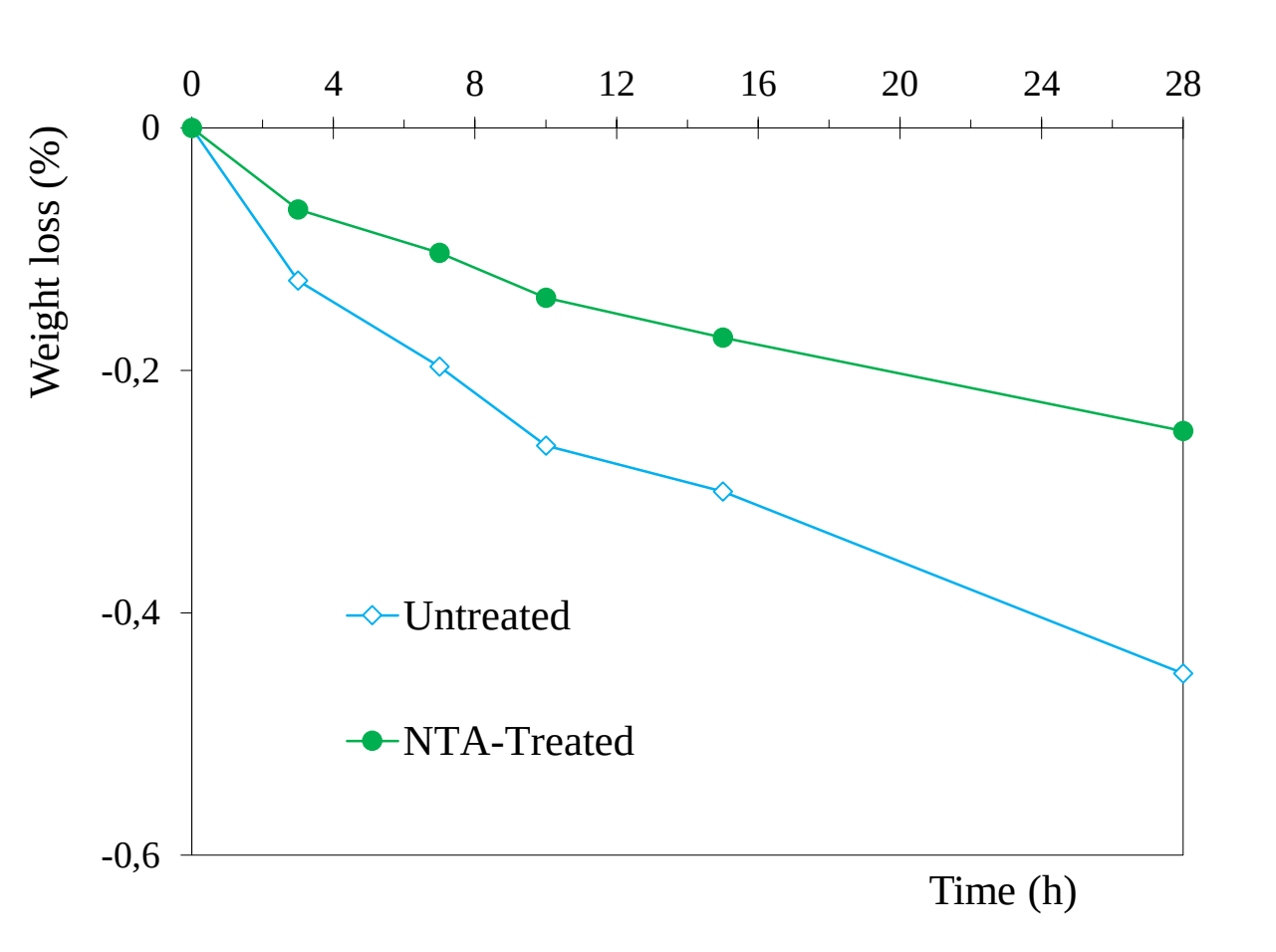
Expansion test ASR (ASTM C1260 and ASTM C227):

- a/b= 2.25/1
- Curing → 80°C, NaOH solution (mortars)
- Analysis by mechanical comparator

compression test

Solubility test

(alkaline attack (pH=12) with NaOH+$Ca(OH)_2$ solution, l/s=60, 80°C, 28 h)



WEIGHT LOSS:

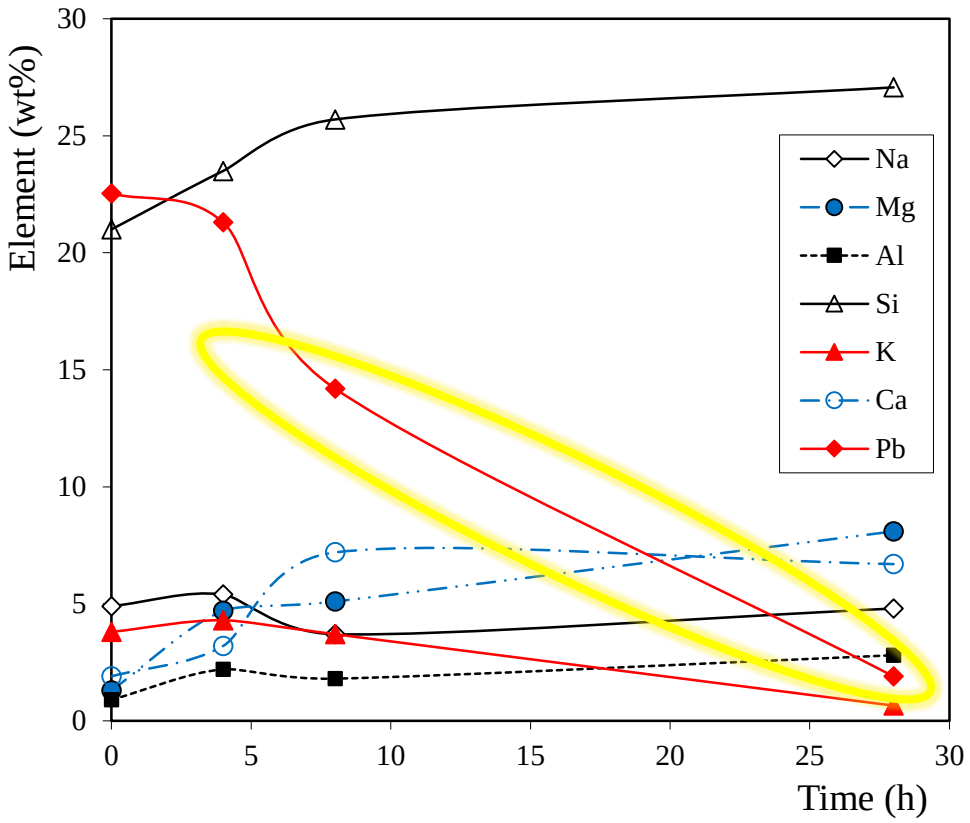
By decreasing Pb amount on the outer surface, FNL glass becomes less soluble.

This behaviour confirms:

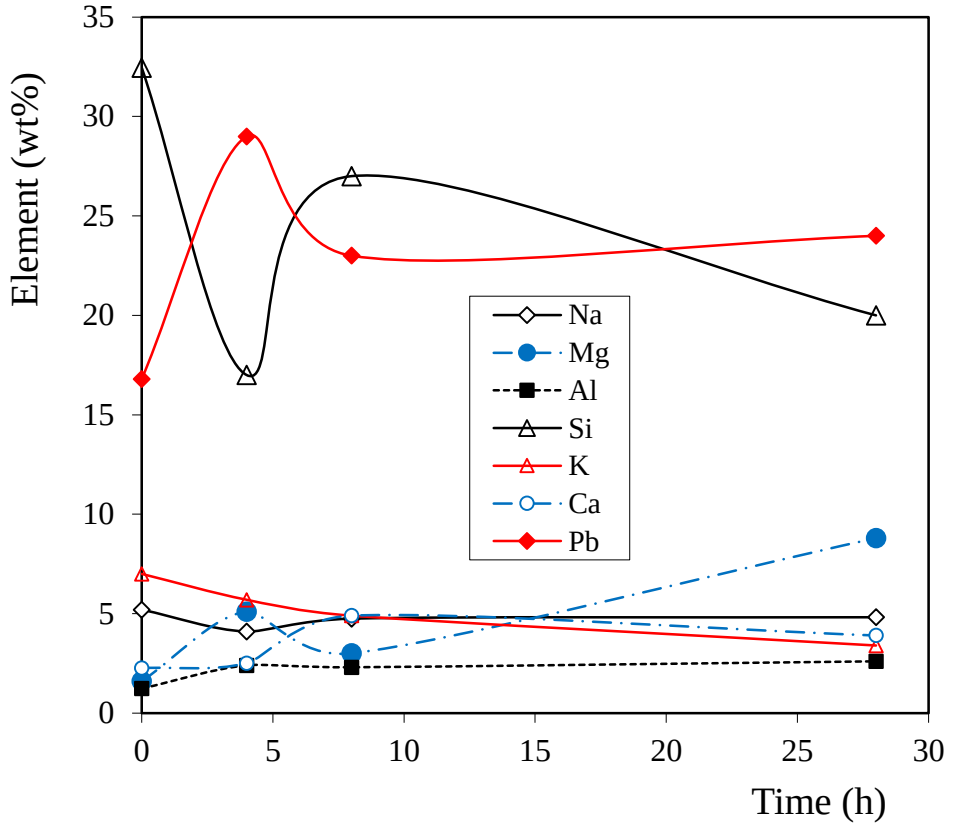
- the relatively poor resistance of Pb glass to alkaline solutions (Volf, 1984);
- that Pb behaves as a NETWORK MODIFIER when <50wt%. (Schultz-Münzenberg et al., 1998)

Solubility test

UNTREATED



NTA-TREATED



- A steady and progressive dissolution of Pb and K (soluble cations, **network modifiers**) takes place.
- Ca and Mg (**stabilizing oxides** in glassy network) are almost costant.

- Smaller variation of elemental composition takes place (less solubility of NTA-treated glass).

Leaching test

(EN 12457-2)

	NTA-FNL SCM	FNL SCM	NTA-FNL aggregate	FNL aggregate	NTA-FNL glass	FNL glass
Pb (mg/L)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

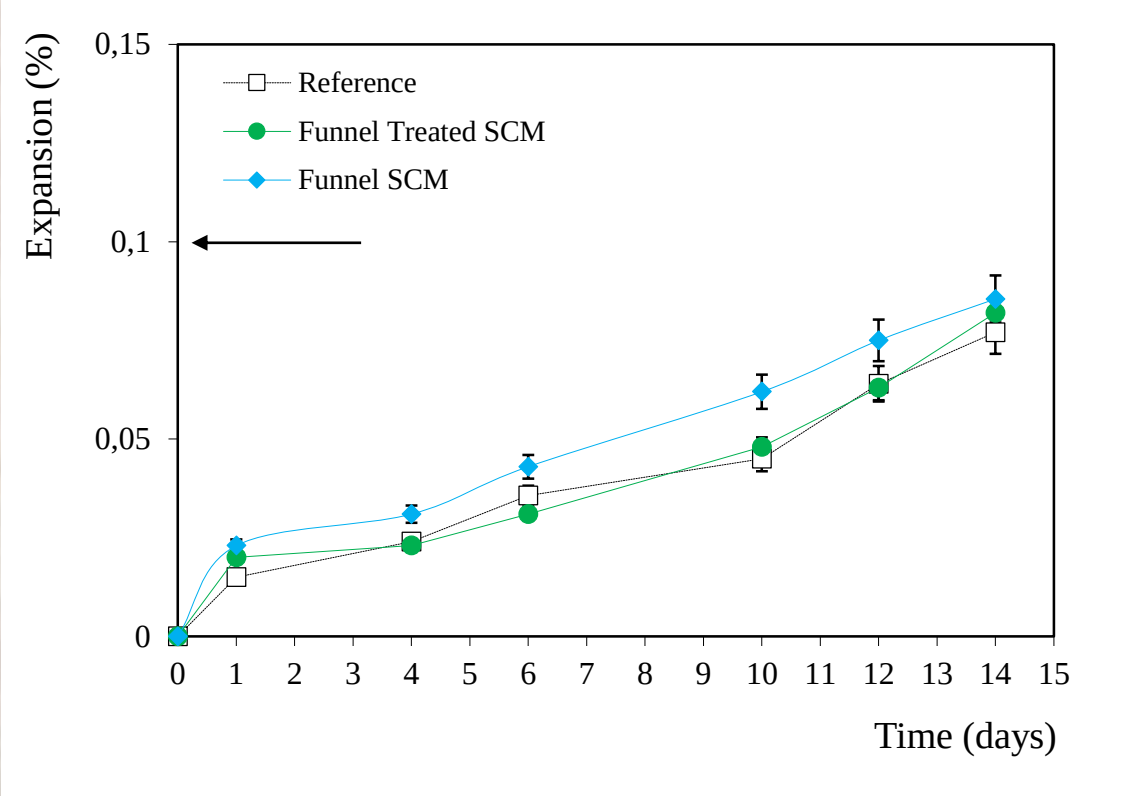
In all the samples the Pb concentration resulted to be ten times **under the limit** for acceptance in landfills for non-hazardous waste, namely 1 mg/L (EU Landfill Directive 1999/31/EC)

No preferential channel for Pb release were opened by NTA treatment

FNL glass as SCM

EXPANSION TEST

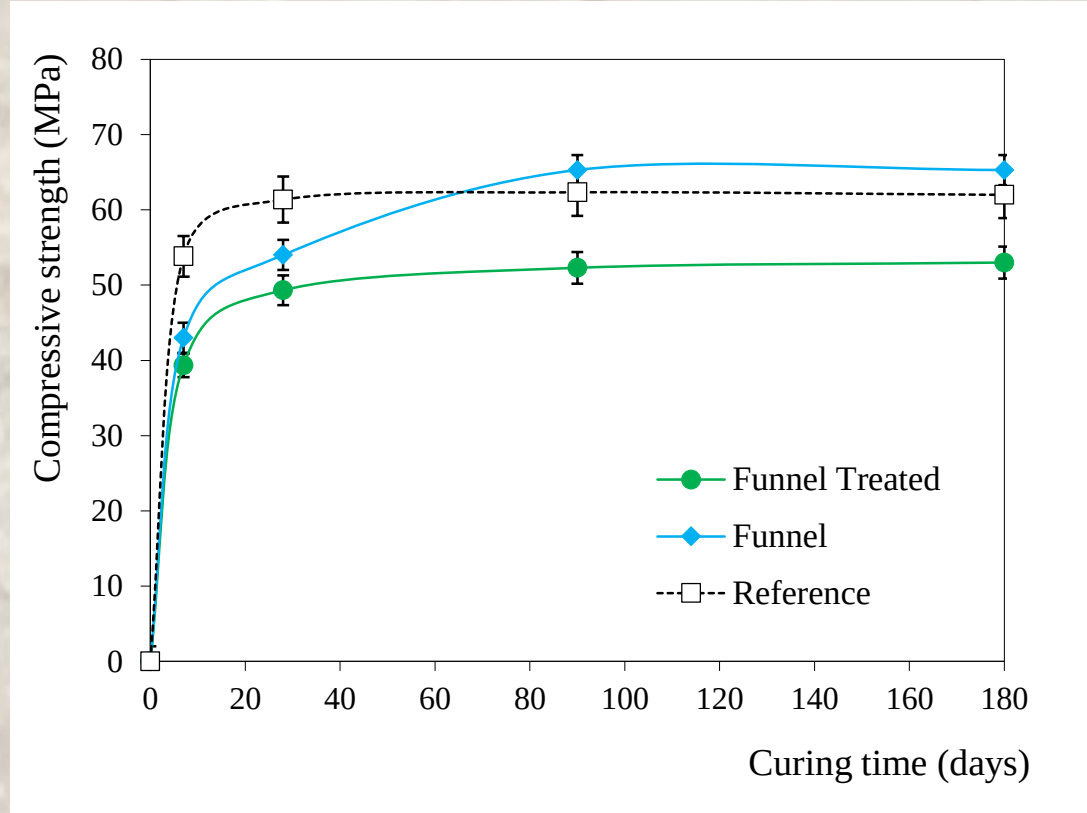
(ASTM C1260 and ASTM C227)



The expansion of the samples is below the safety limit (0.1%) defined by the standards

MECHANICAL TEST

(EN 196--1)

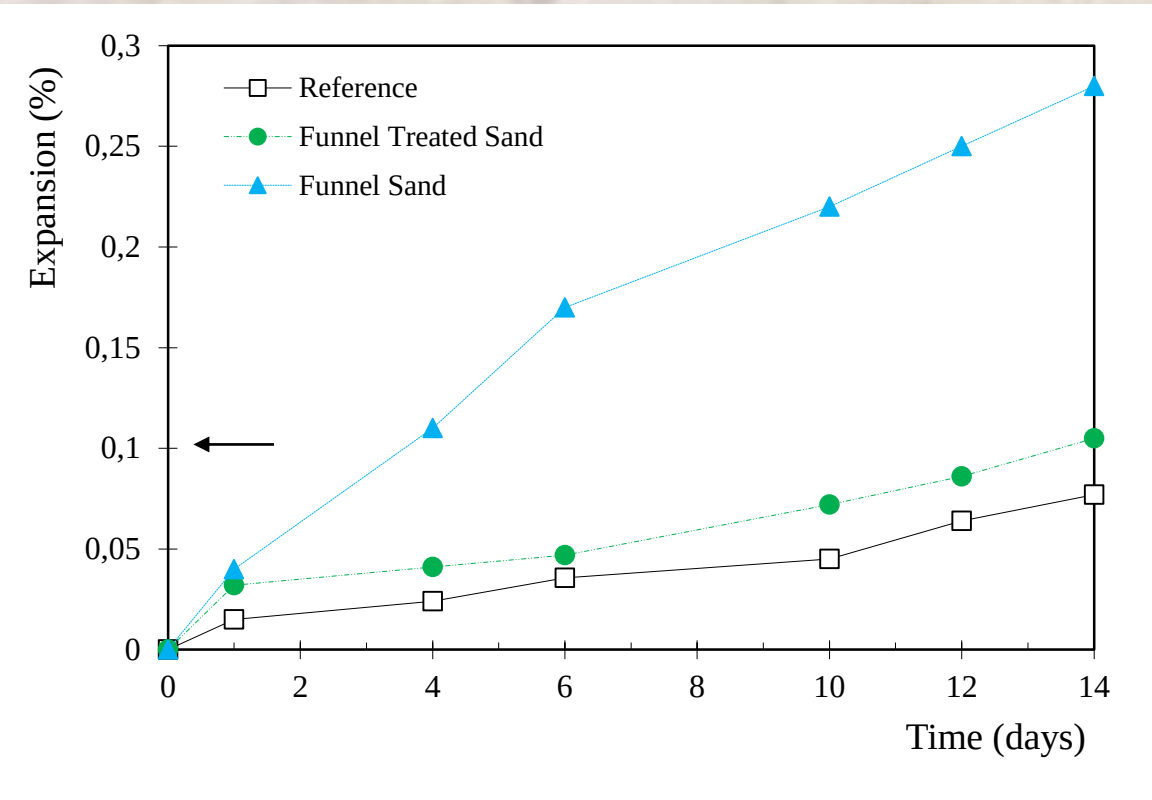


- Untreated funnel glass behaves as an efficient pozzolanic material
- Treated funnel glass instead behaves as a poorly reactive material: the activity index (EN 450-1) is 80 at 28 d and 85 at 90 d (limits for SCM: ≥ 75 at 28 d and ≥ 85 at 90 d)

FNL glass as fine aggregate

EXPANSION TEST

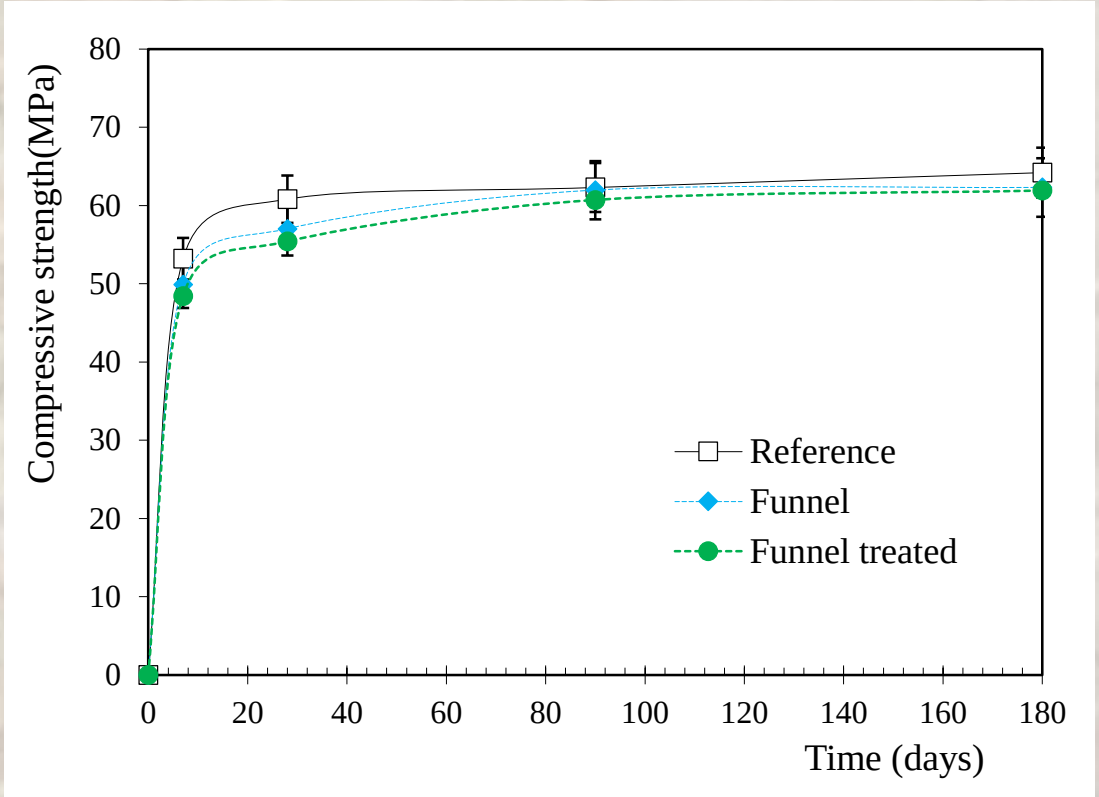
(ASTM C1260 and ASTM C227)



- FNL sand exceeds the limit of 0.1% expansion at 4 days of curing
- Treated FNL shows an expansion comparable to that of the unreactive control sand

MECHANICAL TEST

(EN 196--1)



- Treated and untreated FNL cause a small reduction of mechanical strength for short curing times (smoother surface of the glass compared to that of natural sand)
- At long curing times the mechanical strength of mortars containing FNL is comparable to the standard

Conclusions

→ A mild, environmentally sustainable treatment based on NTA has been performed on CRT glass to be used in cement mortars.

→ NTA treated glass becomes less soluble because of Pb depletion that should reduce the risk of pollution from leaching.

→ NTA treatment decreases the pozzolanic activity of the glass, making it a filler material rather than SCM.

→ NTA treatment allows its use as fine aggregate in substitution of natural sand suppressing ASR reactions.

THIS APPLICATION IS ENVIRONMENTALLY PREFERRED SINCE IT REDUCES THE ENERGETIC COSTS AVOIDING STRONG MILLING PROCESS

Thank you for your kind attention!

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