A novel green method for heavy metals stabilization process based on sewage sludge ash recovery

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Sediment, diffuse pollution and SDG session 8

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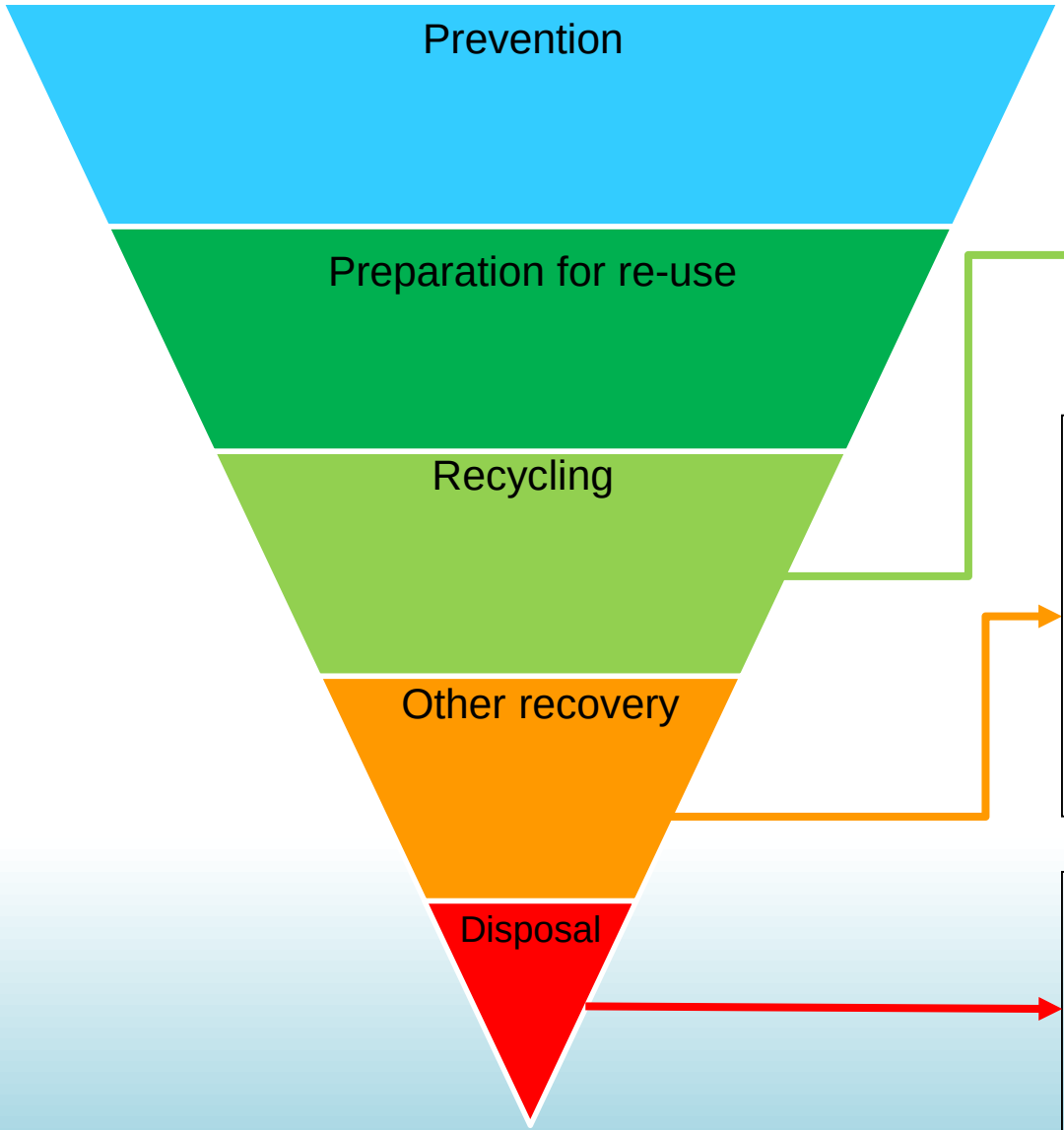
Waste to energy



Communication of 26/01/2017 n. 34
Directive 2008/98/CE

Anaerobic digestion of organic waste if the digestate is recycled as a fertilizer

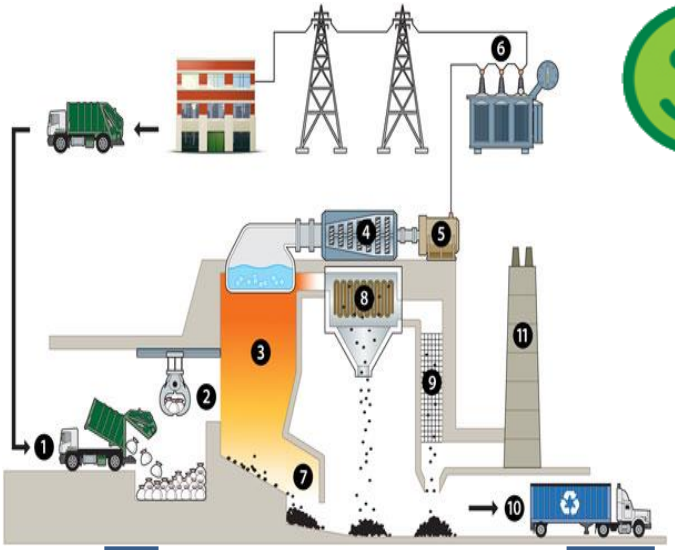
Waste incineration and co-ininération operations with strong energy recovery
Reprocessing of waste materials to be used as solid, liquid or gaseous fuels

Waste incineration and co-incineration with low energy recovery
Use of captured discharge gas

Recovery and waste disposal

Wrong solution: Waste dumps !!!

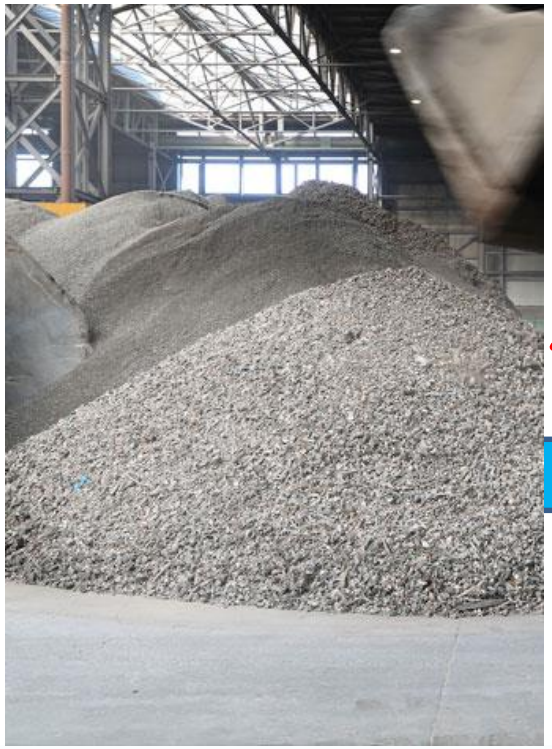
Right and sustainable solution: Incineration plants !!!



Ashes

- Fly ash 1-3% (FA);
- Bottom ash 25-30 % (BA).

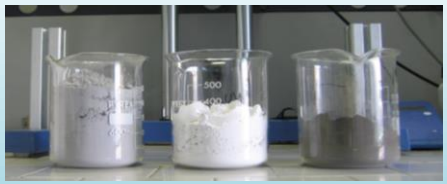
What about Fly Ash (FA)

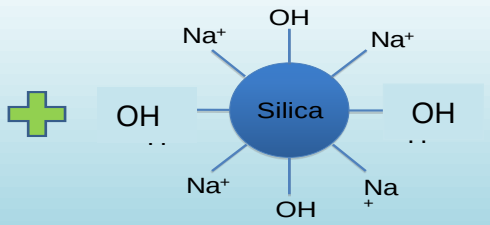


Volatile metals: Zn, Ni, Cu, As, Hg, Cr, Pb and Cd

aste dump

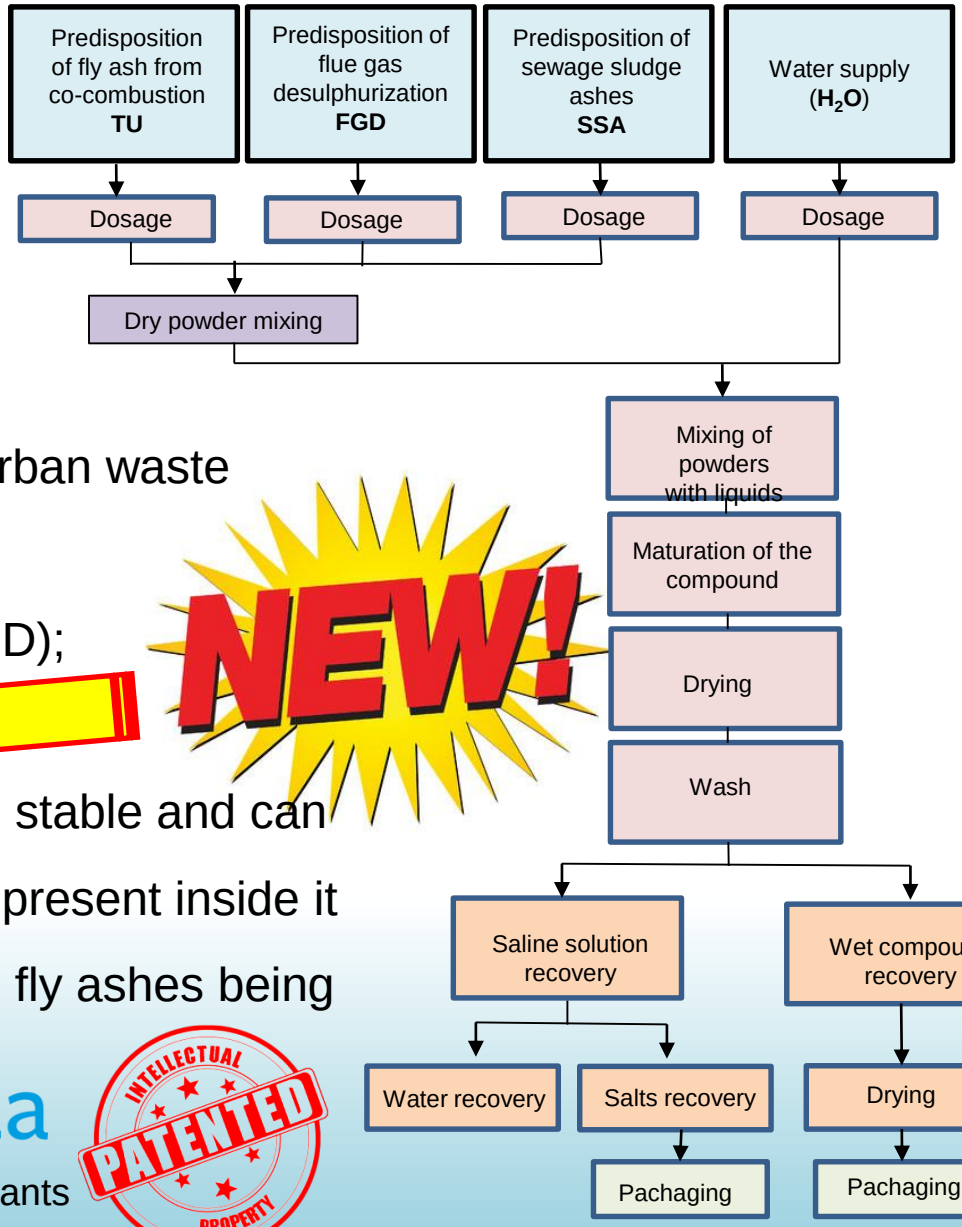
✓ Re-use of the ashes produced by incineration after the stabilization of heavy metals





Fly ash stabilisation process

The process is based on chemical reactions that occur by mixing with and without temperature in appropriate doses of:



- Fly ash from incineration of solid urban waste (MSWI);
- Flue gas desulphurization ash (FGD);
- Sewage sludge ashes

NEW!

The material obtained once solidified is stable and can be washed to remove the soluble salts present inside it without the heavy metals in the starting fly ashes being leached.

a2a

National company that operates incineration plants

INTELLECTUAL PROPERTY PATENTED

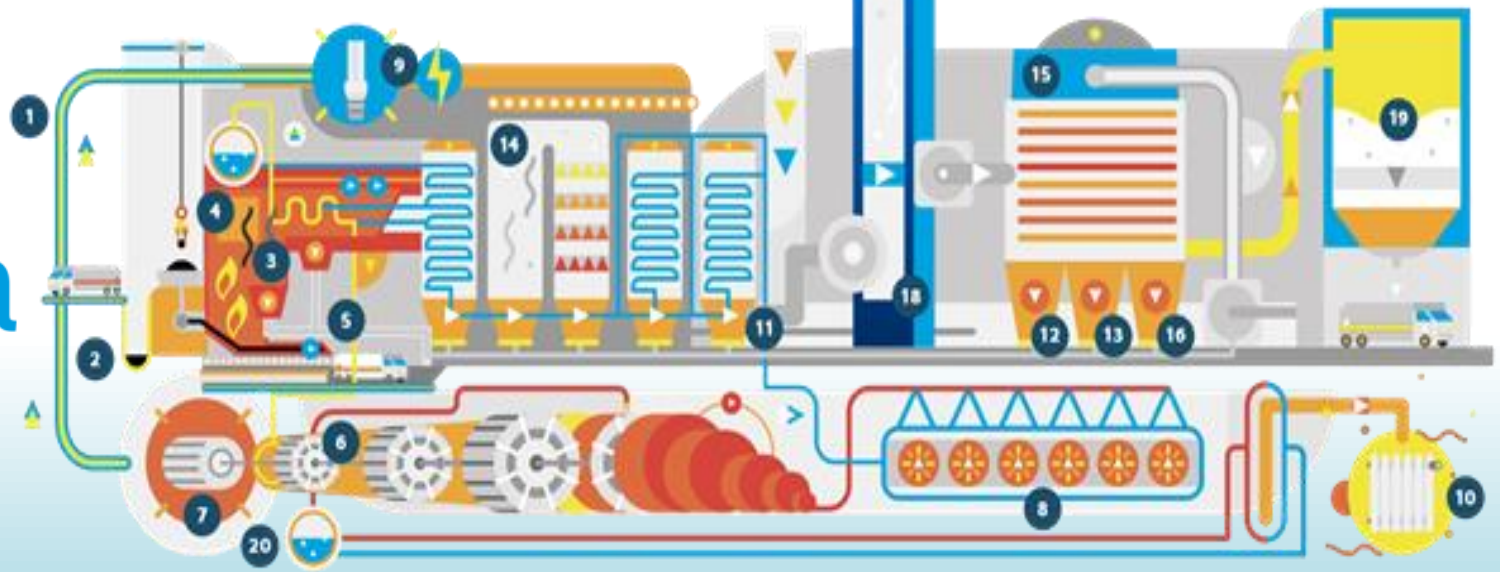
Incineration plant of Brescia

1. Control and conferment
2. Waste tank
3. Combustion chamber
4. Boiler
5. Bottom ash disharge
6. Steam turbine
7. Electricity generator
8. Steam discharge condenser
9. Electrical energy
10. Heat for district heating
11. Boiler ash discharge
12. Active carbons
13. Hydrated lime
14. Catalyze No_X abatement
15. Bag filter
16. Fly ash discharge
17. Chimney
18. Emission control
19. Silos for the storage and discharge of fly ash
20. Heat exchanger

880 tons/day of MSW

+

Sewage sludge



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RENDERING project

RENDERING project
2018-2021

Financed by: MINISTRY OF THE ENVIRONMENT AND THE PROTECTION OF THE TERRITORY AND THE SEA

3 Mt/year in Italy

New proposal

Current treatment

Destination to be eliminate

Sewage sludge

Thickening

Stabilisation

Disinfection

Compost

Dehydration

Dump

0,45 Mt/year in Italy

Co-incineration

Stabilisation

Agriculture

REUSE

Filler

Preparation of stabilized sample

RENDERING

50 % **MSWI**

27 % **FGD**

23 % **SSA**

SSA_N - SSA_G

COSMOS

50 % **MSWI**

27 % **FGD**

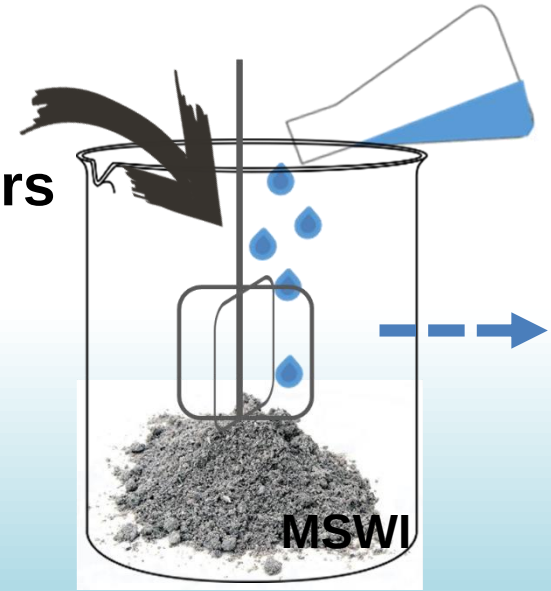
23 % **Silica fume**

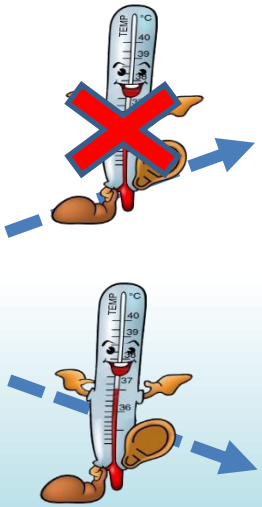
Blank sample

65 % **MSWI**

35 % **FGD**

Powders





Room temperature

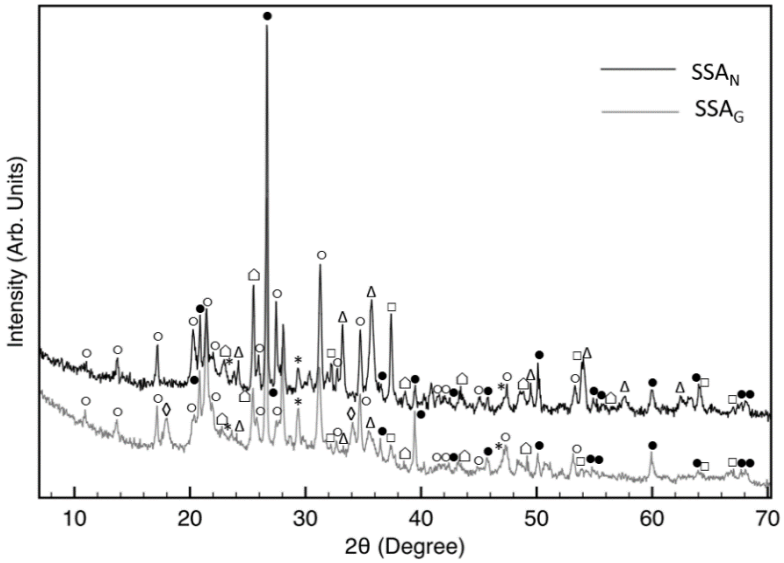
$t_{stabilization}$ = 2 month

Thermal treatment

T (120 °C) 6h

Characterization of SSA

XRD analysis



* Calcium Carbonate ($CaCO_3$);
○ Calcium Magnesium Phosphate ($Ca_7Mg_2P_6O_{24}$);
● Quartz (SiO_2);
Δ Burnt ochre (Fe_2O_3);
□ Calcium Oxide (CaO);
⌂ Anhydrite ($CaSO_4$);
◊ Calcium Hydroxide [$Ca(OH)_2$]

ICP MS analysis

- Si, P, **Al**, Ca, **Fe**.

SSA_N rich of Fe
SSA_G rich of Al
} Precipitation methods (Salts of Al or Fe)

- Heavy metals: As, Cd, Cr, Ni, e Zn.

In collaboration with BAM Federal Institute

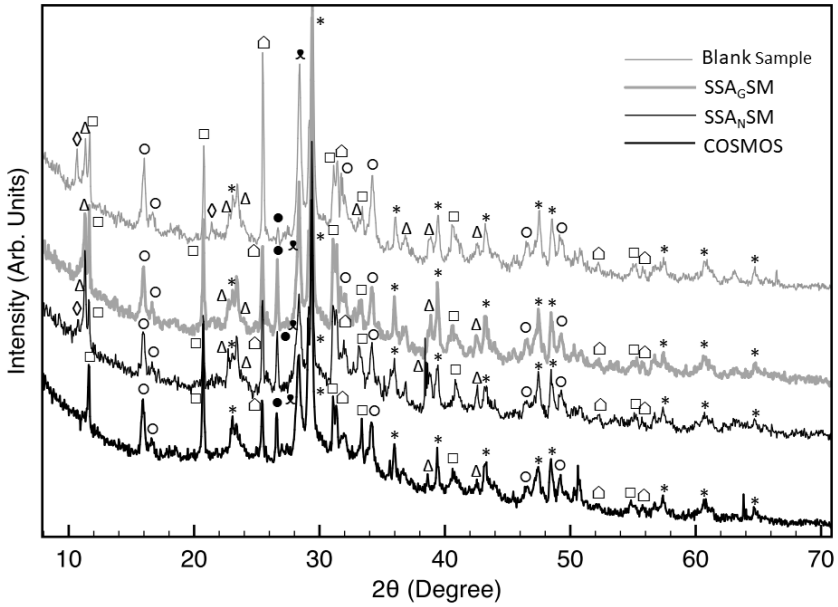
✓ Amorphous phases: Al_2O_3 and SiO_2

✓ Crystalline phases: CaO, $CaCO_3$,$Ca(OH)_2$, Calcium Magnesium Phosphate

✓ SSA_N → Fe
✓ SSA_G → Al

Characterization of stabilized samples

XRD analysis after 2 months



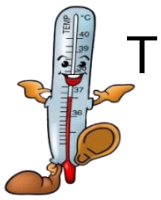
* Calcium Carbonate ($CaCO_3$);
○ Hannebachite ($CaSO_3 \cdot 0.5H_2O$);
● Quartz (SiO_2);
Δ Calcium Aluminum Hydroxide Chloride Hydrate [$Ca_2Al(OH)_6Cl \cdot 2H_2O$];
□ Gypsum ($CaSO_4 \cdot 2H_2O$);
⌂ Anhydrite ($CaSO_4$);
◊ Calcium Hydroxide [Calcium Aluminum Silicate Hydrate $CaAl_2Si7O_{18} \cdot 1.7H_2O$];
ᵡ Sylvite (KCl)

- ~~CaO and $Ca(OH)_2$~~
- Chloro-complex Friedel's salt

Pozzolanic reactions

Stabilization of heavy metals

Leaching test

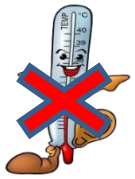


Thermal treatment
T (120 °C) 6h

pH	pH 13.5	pH 12.5	pH 12.5	pH 10	pH 12.5
			mg/L		
Element	**MSWI**	**SSA_NSM**	**SSA_GSM**	**COSMOS**	**Blank Sample**
S	1 ± 1	162 ± 11	143 ± 4	229 ± 60	153 ± 28
Cl	10948 ± 1081	3110 ± 306	4076 ± 174	3058 ± 587	4897 ± 297
K	2597 ± 337	787 ± 98	974 ± 73	569 ± 183	1235 ± 91
Ca	6668 ± 540	2814 ± 255	2821 ± 125	2530 ± 91	3909 ± 186
Mn	1 ± 0.2	0.13 ± 0.03	0.22 ± 0.05	0.09 ± 0.04	0.28 ± 0.06
Fe	4 ± 1	2 ± 1	1.6 ± 0.9	1.4 ± 0.6	3 ± 1
Cu	1.2 ± 0.2	0.03 ± 0.01	0.07 ± 0.03	0.06 ± 0.04	0.04 ± 0.01
Zn	13 ± 1	1.4 ± 0.4	1 ± 0.4	1.12 ± 0.03	4 ± 2
Se	LLD	LLD	LLD	0.01 ± 0.01	LLD
Br	160 ± 11	44 ± 4	61 ± 1	70 ± 6	65 ± 3
Rb	8 ± 1	2.1 ± 0.2	3.17 ± 0.04	3.9 ± 0.4	3.5 ± 0.2
Sr	5.9 ± 0.3	3.9 ± 0.3	6.1 ± 0.2	6.3 ± 0.5	5.5 ± 0.2
Ba	15 ± 2	1.69 ± 0.06	2.5 ± 0.4	1.7 ± 0.3	3.5 ± 0.4
Pb	86 ± 3	1.11 ± 0.08	0.4 ± 0.1	LLD	8.7 ± 0.4

- ✓ Heavy metals stabilization with SSA;
- ✓ COSMOS best performance, pH reduction;
- ✓ No stabilization with only FGD.

Leaching test



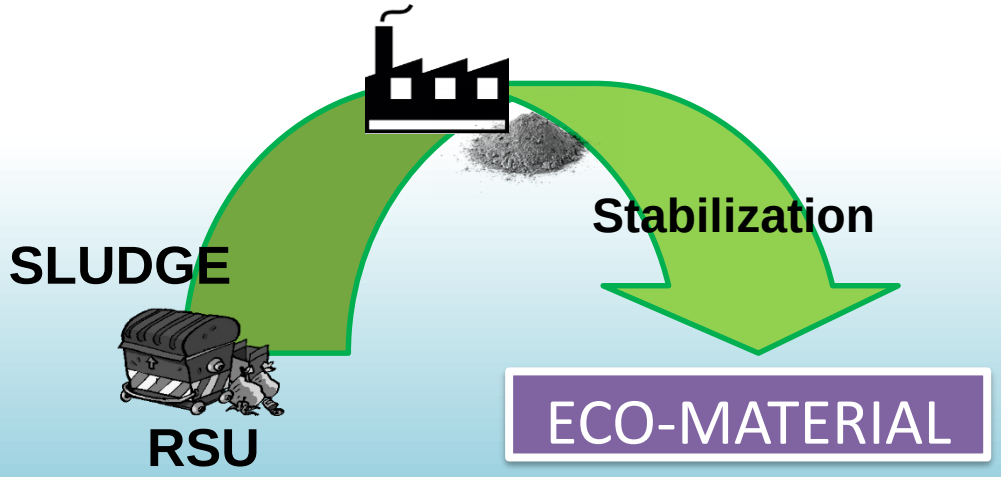
Room temperature
$t_{stabilization}$ = 2 month

pH	pH 13.5	pH 9.5	pH 9.5	pH 9.5	pH 12
			mg/L		
Element	**MSWI**	**SSA_NSM**	**SSA_GSM**	**COSMOS**	**Blank Sample**
S	1 ± 1	108 ± 33	151 ± 30	201 ± 87	142 ± 15
Cl	10948 ± 1081	1835 ± 423	2274 ± 1000	2485 ± 194	4451 ± 1024
K	2597 ± 337	373 ± 110	490 ± 267	541 ± 44	1056 ± 296
Ca	6668 ± 540	1198 ± 112	1524 ± 376	1794 ± 24	2628 ± 578
Mn	1 ± 0.2	0.06 ± 0.05	0.07 ± 0.07	0.08 ± 0.03	0.27 ± 0.08
Fe	4 ± 1	0.27 ± 0.09	0.3 ± 0.2	0.3 ± 0.1	1 ± 0.22
Cu	1.2 ± 0.2	0.03 ± 0.003	0.02 ± 0.02	0.02 ± 0.02	0.02 ± 0.02
Zn	13 ± 1	0.08 ± 0.01	0.09 ± 0.04	0.07 ± 0.03	0.14 ± 0.02
Se	LLD	LLD	LLD	0.02 ± 0.01	LLD
Br	160 ± 11	38 ± 4	44 ± 14	47 ± 1	62 ± 12
Rb	8 ± 1	1.9 ± 0.3	2.2 ± 0.7	2.09 ± 0.04	3.1 ± 0.6
Sr	5.9 ± 0.3	3.1 ± 0.1	5.1 ± 0.6	3.8 ± 0.7	4.9 ± 0.8
Ba	15 ± 2	0.9 ± 0.1	1 ± 0.5	0.9 ± 0.2	2.1 ± 0.5
Pb	86 ± 3	LLD	LLD	LLD	LLD

- ✓ COSMOS and SSASM results comparable;
- ✓ Friedel's salt reduction of Cl and Ca;
- ✓ pH reduction carbonation reactions.

Conclusions

- ✓ Use of a waste material (SSA) for the immobilization of leachable heavy metals contained in MSWI fly ashes;
- ✓ Leaching tests highlight that heavy metals concentrations (mainly Pb and Zn) are reduced;
- ✓ The mix of wastes and by-products used in the new procedure allows to promote synergic stabilization mechanisms such as pozzolanic reactions and phosphate precipitation;
- ✓ Carbonation reaction occurs, reducing the pH from 13.5 to 9.5.



Chemistry for technologies laboratory

THANKS FOR THE ATTENTION,

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