Chemical stabilization

of municipal solid waste incineration (MSWI) fly ash

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Introduction

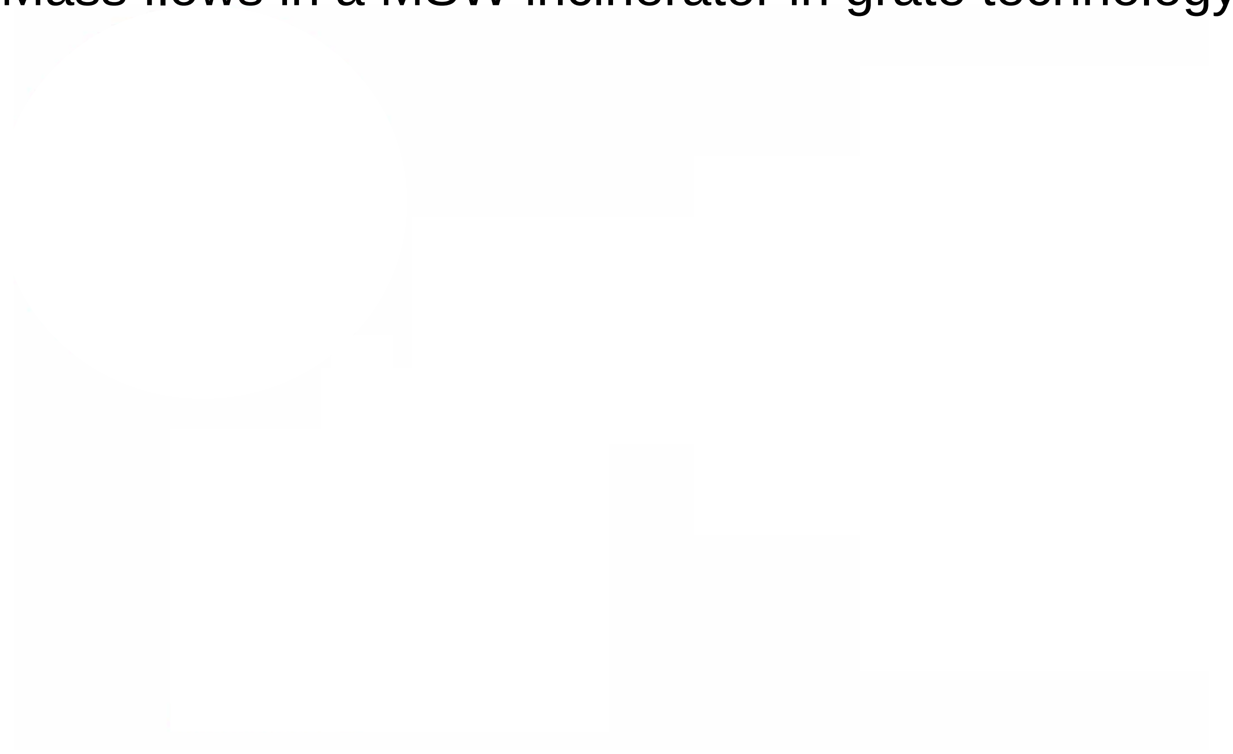
- MSW Incineration Residues – Fly ash
- The problem
- Management
- Treatment Techniques

Our Research on Fly Ash Treatment

- Treatment techniques:
  - Water extraction
  - Chemical stabilization
- Description of lab scale experiments
- Results

Introduction: MSWI Residues

Mass flows in a MSW incinerator in grate technology (values in kg)



WTE Residues	**% by mass of the original waste**
Bottom ash:	15-25%
Heat Recovery System ash:	0.5%
Fly ash:	1-2.5%
Air Pollution Control (APC) residues:	2-5%

APC Residues

The characteristics of APC residues depend mainly on

Waste incinerated	Type of incinerator	Type of APC System

↓

APC residues exist in a number of different varieties

- **DRY AND SEMI-DRY APC SYSTEM RESIDUES**
- **WET APC SYSTEM RESIDUES**

European Waste Catalogue and Hazardous Waste List

APC residues: Hazardous Waste 19 01 07*

The problem with APC residues

The primary environmental concern related to APC residues

is the potential for leaching of salts and heavy metals

when landfilled

Management of APC Residues

Typically, APC residues are disposed of
on special disposal sites

- A large number of combinations of treatment, stabilization, utilization, and landfilling processes exists on an international level
- Overall, three main routes for APC residues exist:
  - **Landfilling**
    (Surface disposal, Subsurface disposal –UK, Germany)
  - **Material recovery**
    (Metals, salts, HCl and gypsum)
  - **Utilization as aggregates**
    (Cement based applications, Asphalt, Neutralization capacity)
- In Europe, either of these options include some degree of treatment and/or stabilization

Treatment techniques

- **Extraction and separation:**
  Extraction and removal of specific components from the residues

- **Chemical stabilization:**
  Binding and immobilization of contaminants by chemical reactions

- **Solidification:**
  Physical binding and encapsulation of residues, and in some cases also chemical stabilization

- **Thermal treatment:**
  Heating of the residues - changes of the physical and chemical characteristics (vitrification, melting, sintering)

Estimated costs of treatment techniques

Process	Estimated cost per ton of residue, €
Cement solidification	25-50
$FeSO_4$ stabilization	65
CO_2 stabilization	80
PO_4 stabilization	25
Acid extraction + thermal integration	100 - 200
Vitrification	100-500
Melting	100-500

(source: ISWA data)

Our research on APC residues

Our research on APC residues: Overview

Sampling from WTE plant

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Untreated Samples

Physicochemical characterization
Leach testing

↓

Treatment

↓

Treated Samples

Physicochemical characterization
Leach testing

↓

Optimization of treatment method

Our research: Treatment techniques

Phosphate stabilization

- Phosphate is a very promising stabilization agent used in the areas of soil restoration, wastewater treatment and fly ash disposal

The addition of phosphate to ash reduces the leaching of lead and other metals by converting soluble compounds into more stable and insoluble mineral phases
➔ metals leaching is reduced

Water Washing

- Water washing can remove an important amount of salts from the residues

The wastewater produced has to be properly managed
➔ toxic metals are also removed

Difficult comparison between methods results

- Various leaching tests are used
- Different limits between countries
- Only selected metals measured

Our research: Batch Leaching test

The sample is extracted
with a specific amount of extraction fluid
using a rotary agitation device

↓

Filtration

↓

Leachate analysis

(AAS, ICP-AES, ICP-MS)

↓

The obtained results have to be compared
with specific reference values

EN 12457/2

Extraction fluid: water
L/S = 10 l/kg
pH: not controlled
Max particle size: 4 mm
Agitation for 24h

Limits: Council Decision 2003/33/EC

Novelty of our research

Phosphate Stabilization:
chemical stabilization of metals

Water Extraction:
salts removal

Study the effect of:

- Type of residue
- Phosphate to residue ratio
- Liquid to solid ratio (use of process mixing water)
- Mixing process (time, speed)
- pH
- Sequence of mixing
- Different sources of soluble PO_4^{3-} (H_3PO_4, Na_2HPO_4 etc.)

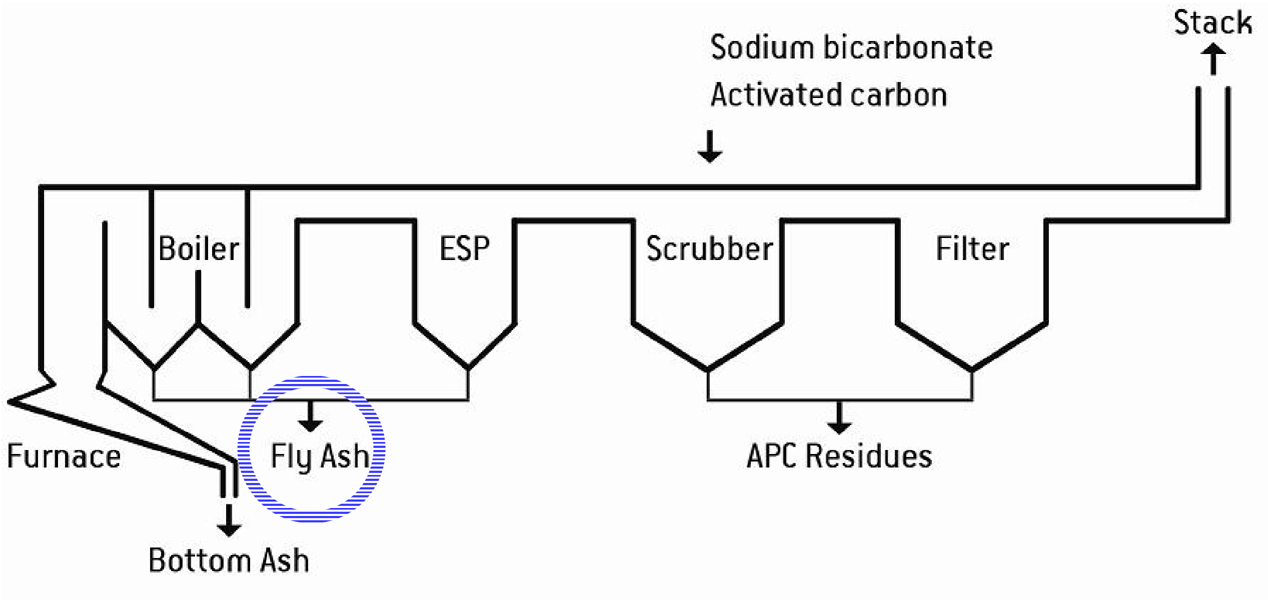
→ Optimization of the process

Leaching properties
of treated ash
(analysis of all metals – 2003/33/EC)

Properties of
Wastewater

RESULTS

Sampling – MSWI plant in France

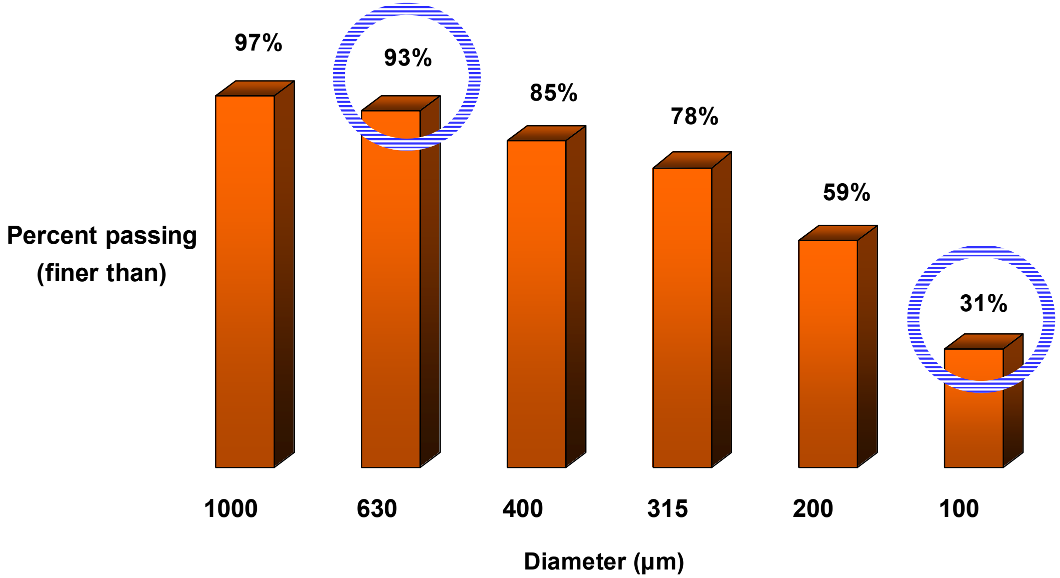


Operational conditions from the incinerator plant

Process:	Incineration by grate furnaces with energy recovery
Nominal capacity:	172 500 tonnes/year 2 furnaces handling 10.8 tonnes/hour
Flue Gas Cleaning:	DRY+ESP+FF
Energy Produced:	Electricity: 80.000 MWh Steam: 10.000 tonnes

Physicochemical Characterization

Moisture	0.3 %
Density	2.5 g/cm^3
pH	12.0
Specific surface area	1.897 m^2/g
Pore volume	0.005 cm^3/g
Median pore diameter	105.430 Å

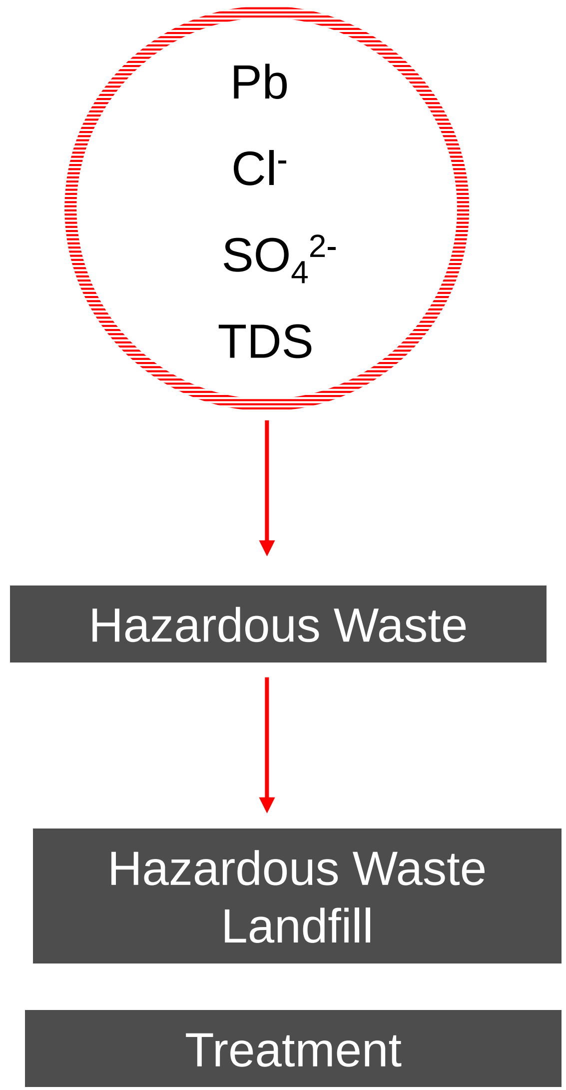


Composition (XRF Analysis)

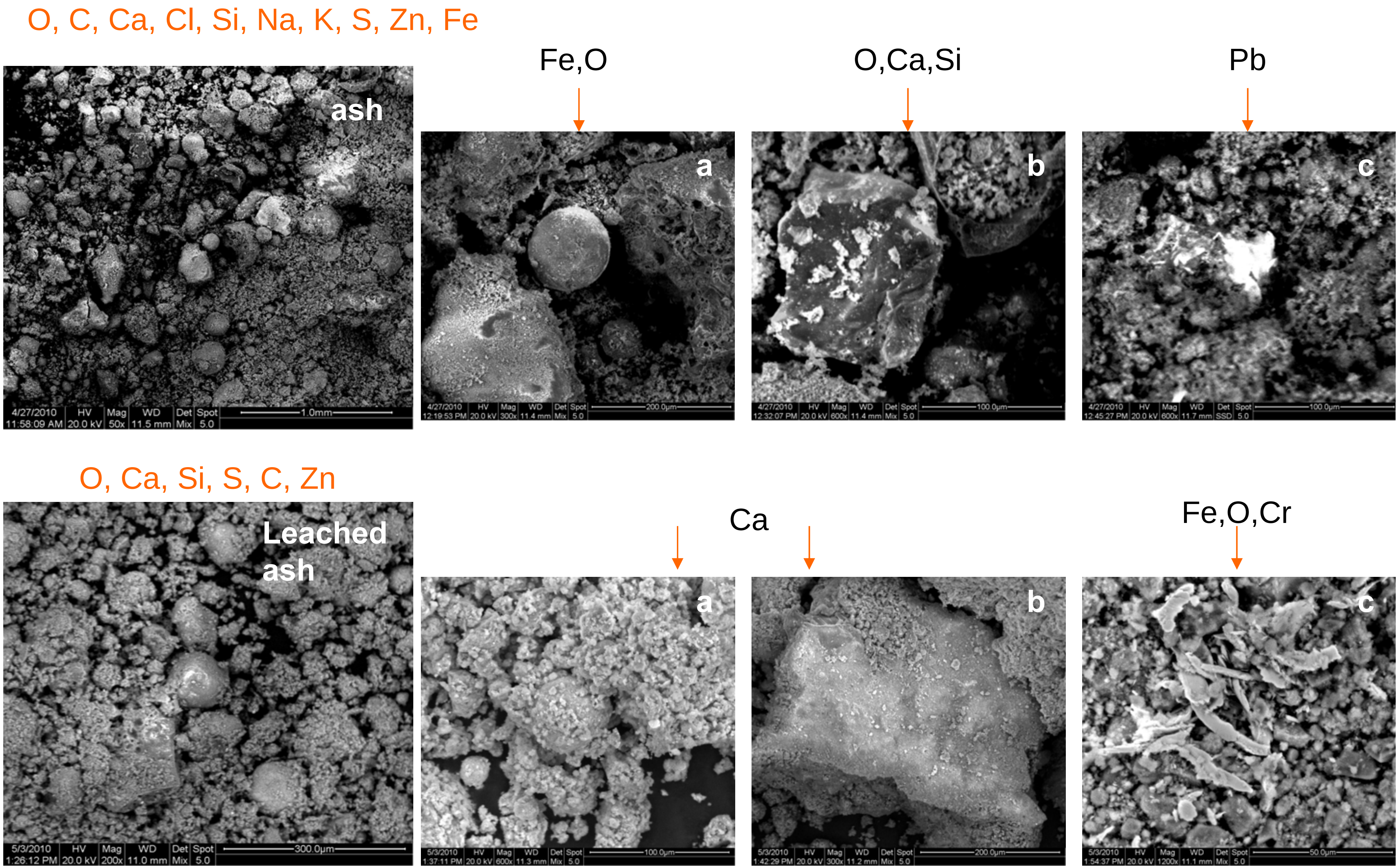
	w/w %		ppm
CaO	29.2	Cr_2O_3	880
SiO_2	15.3	MnO	843
SO_3	10.2	SrO	530
Na_2O	9.6	SnO_2	490
Al_2O_3	7.5	SbO_3	397
K_2O	4.5	ZrO_2	213
Fe_2O_3	3.1	NiO	180
ZnO	2.0	Rb_2O	67
TiO_2	1.9		
MgO	1.7		
P_2O_5	1.7		
PbO	0.5		
BaO	0.2		
CuO	0.2		
LOI (%)	10.01		

RAW ASH: Leaching test EN 12457/2

	Measured value	Legal Limits
pH	11.94	>6
TDS (mg/kg)	**145404**	60000
Element (mg/l)		
As	<0.02	0.2
Ba	0.48	10
Cd	0.01	0.1
Cr	0.41	1
Cu	0.01	5
Hg	<0.01	0.02
Mo	0.50	1
Ni	<0.01	1
Pb	**34.2**	1
Sb	<0.02	0.07
Se	<0.02	0.05
Zn	0.99	5
Cl^-	**6212**	1500
F^-	0,69	15
SO_4^-	**3060**	2000



SEM Analysis



TREATMENT

Treatment of fly ash (laboratory scale)

Water washing

- Ash + Water
- Mixing
- Filtration → **Washed Ash**
  → **Wastewater**

Chemical Stabilization

- Phosphoric acid + Water
- Ash
- Mixing → **Stabilized ash**

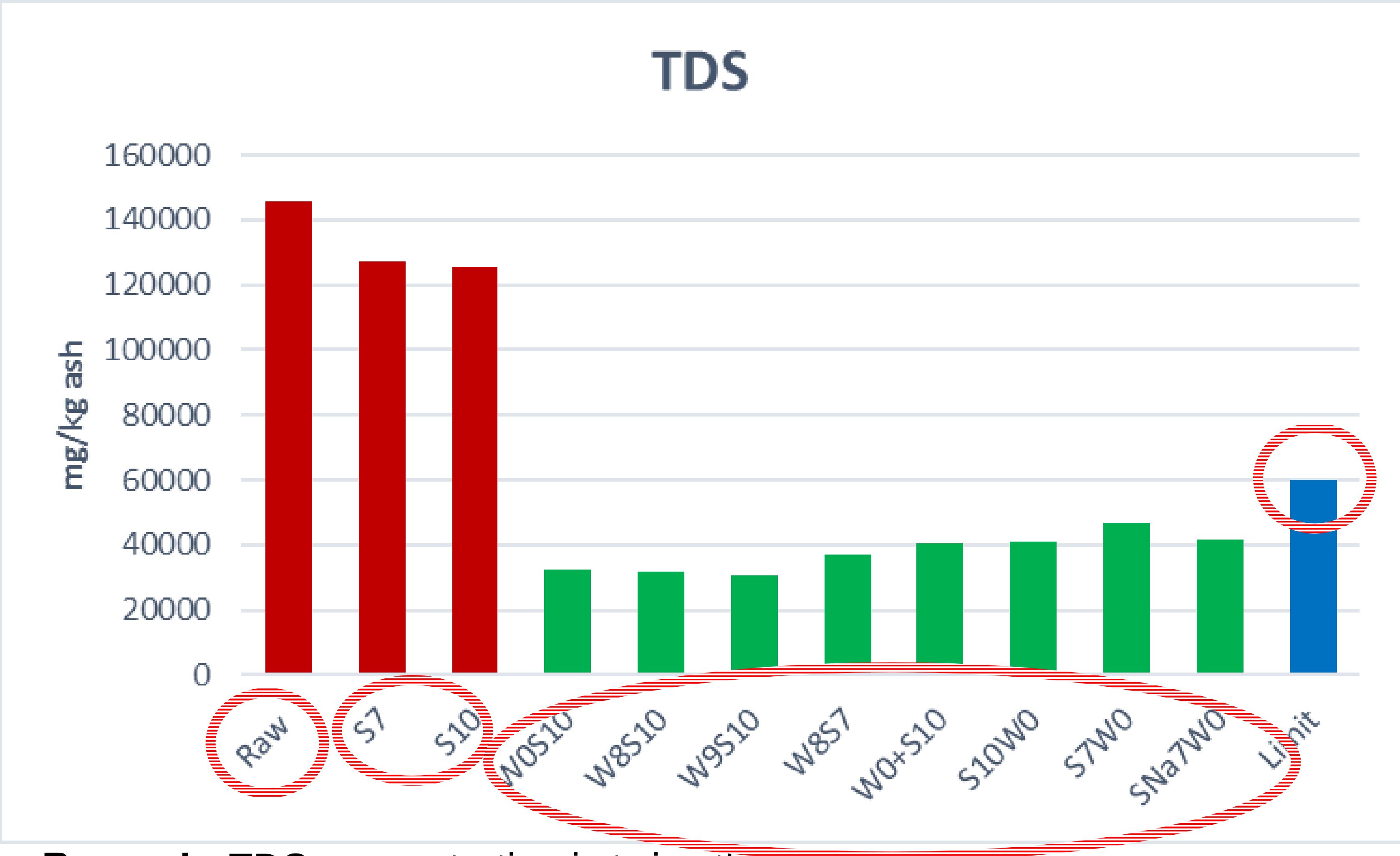
Preliminary results

1. **Water washing** → L/S=2 l/kg, t_{mixing}=15 min
   → 10% of ash is washed (TDS)
   → some heavy metals are also removed through wastewater
   → pH adjustment improves wastewater quality (HNO_3)
2. **Stabilization with Phosphoric acid** → acid to ash ratio =10%
   → L/S=0.7 l/kg
3. **Water extraction & Stabilization**

Washing & Stabilization: Treatment Methods

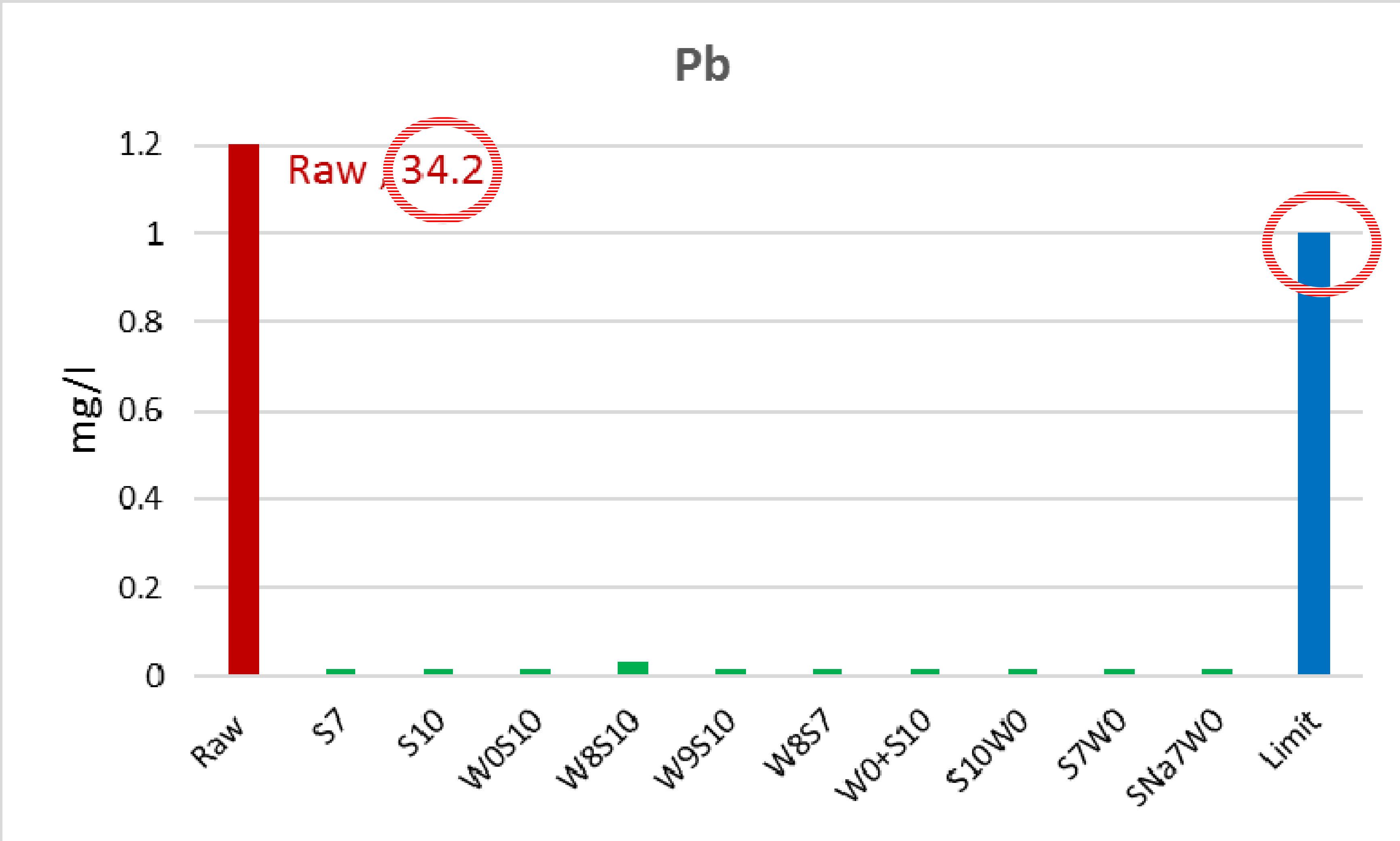
Symbol	Treatment Method description	Parameters
S_x	**Phosphoric Acid Stabilization** x: Phosphoric acid /ash ratio (w/w)	S_7, S_{10}
W_y	**Water Washing** y: ml HNO_3	W_0, W_8, W_9
W_yS_x	Washing **followed by** Stabilization	W_0S_{10}, W_8S_{10}, W_9S_{10}, W_8S_7
W_y+S_x	**Simultaneous** Washing and Stabilization	W_0+S_{10}
S_xW_y	Stabilization **followed by** Washing	S_7W_0, $S_{10}W_0$
$S_{Nax}W_y$	**$NaH_2PO_4.2H_2O$** Stabilization followed by Washing	$S_{Na7}W_0$

Leaching Results



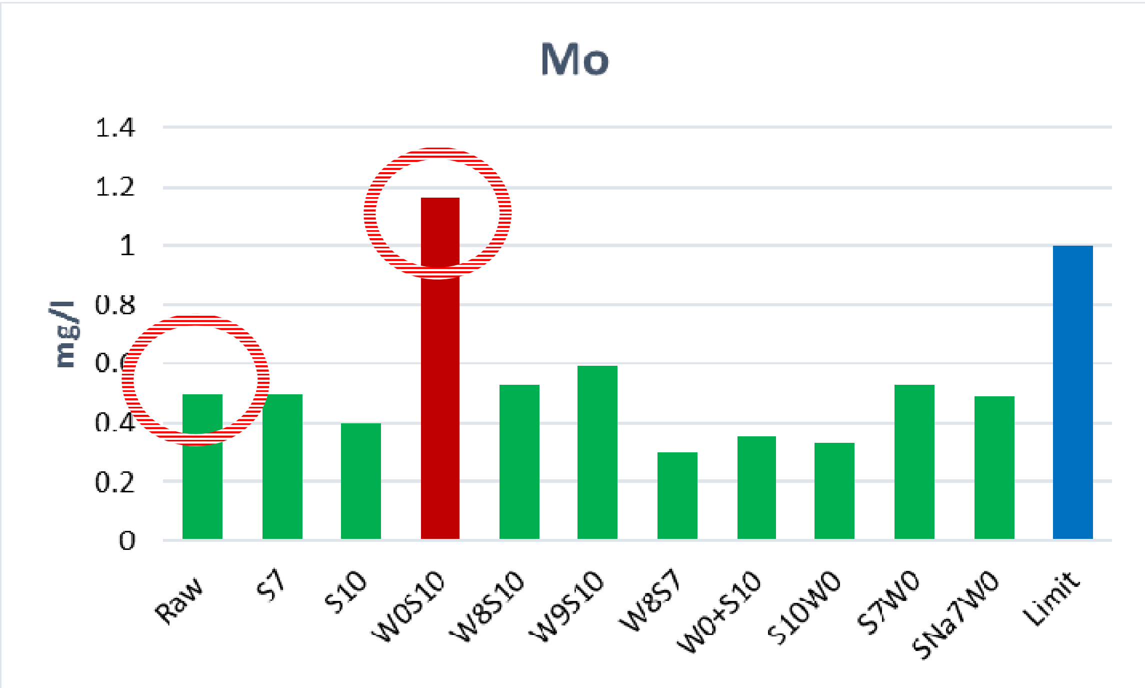
- **Raw ash:** TDS concentration is twice the limit
- **Stabilization process:** slightly reduces TDS but not enough
- **Washing process combined with stabilization:** successfully reduces TDS for all methods

Leaching Results



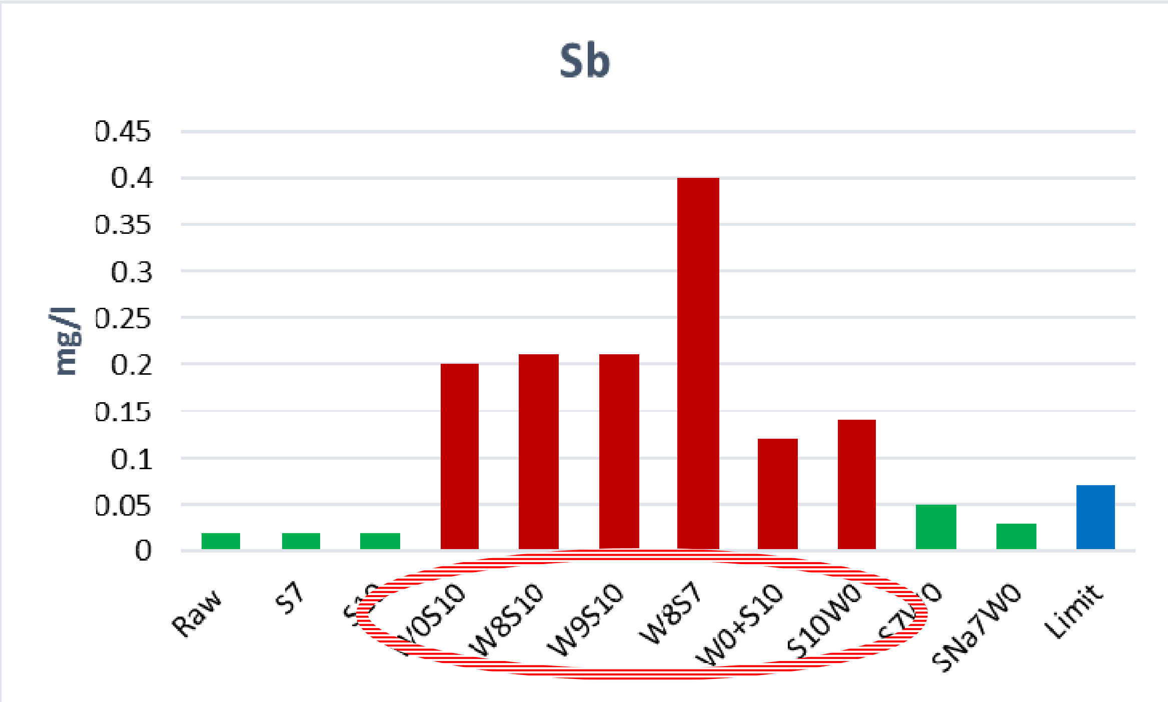
- All methods highly reduce Pb leaching
- Over a wide range of pH between methods examined (pH: 7.3–10.8)

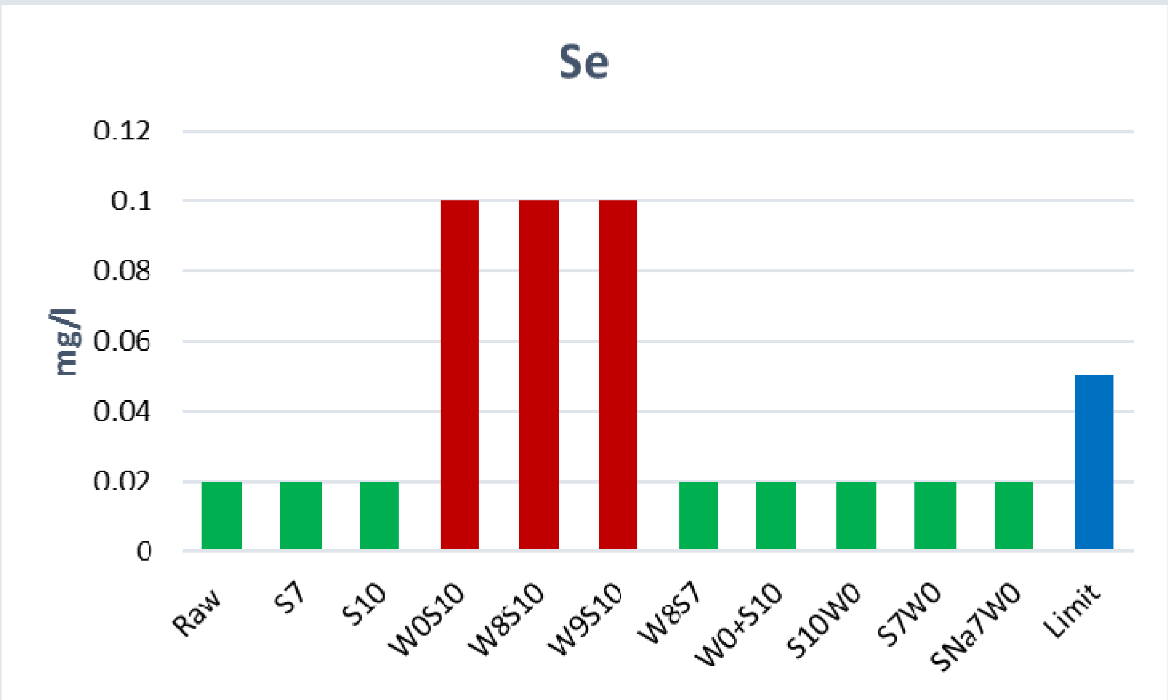
Leaching Results



Cr and Mo showed
low concentration for raw ash

but they were mobilized
after the treatment
with some methods





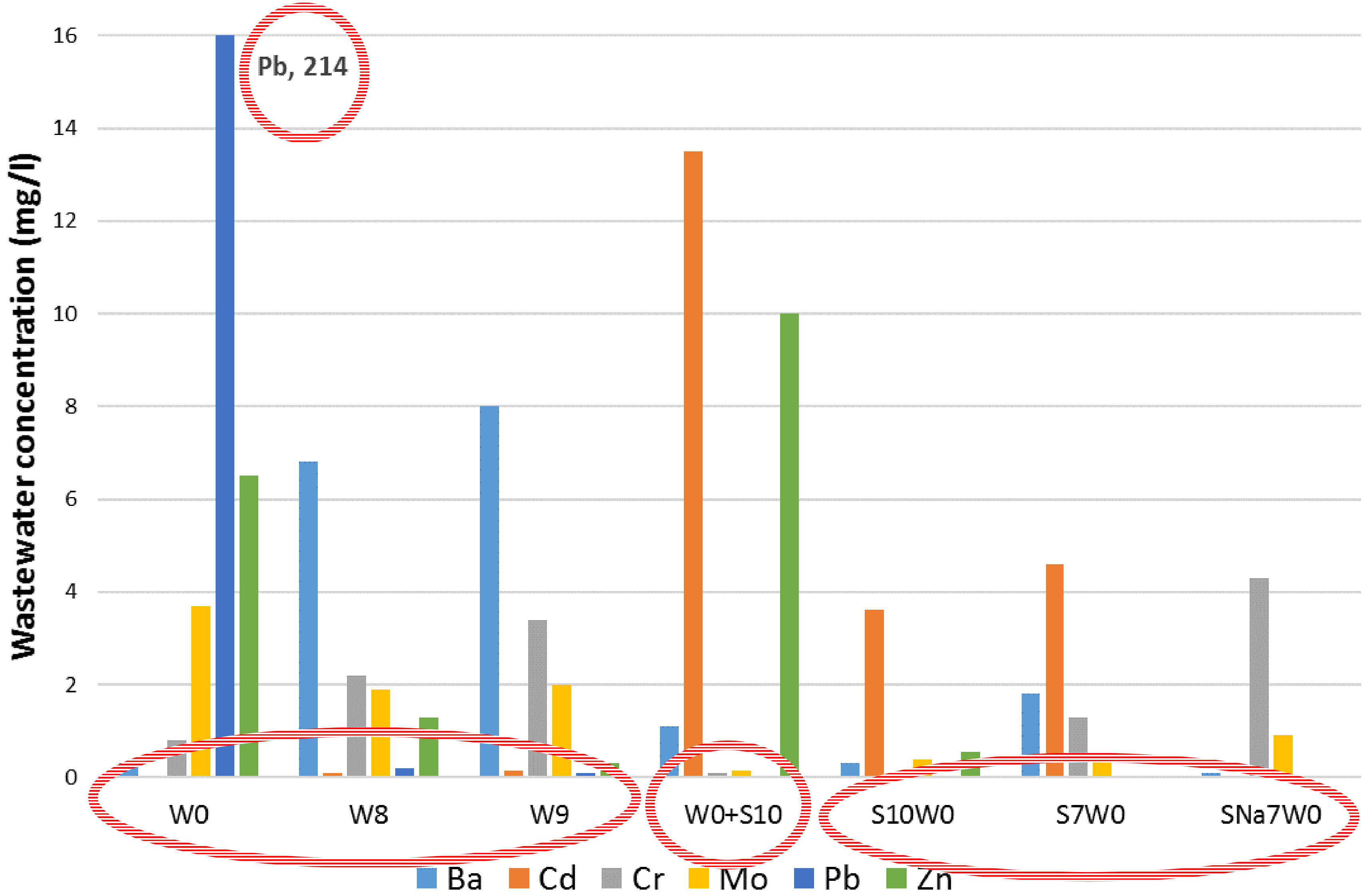
Sb :

- ✓ Problematic mobilization
- ✓ Usually is not measured
- ✓ No limit value for other tests
- ✓ Low limit for EN 12457 test

Leaching results for all treatment methods: Overview

- Water washing, with and without pH adjustment, followed by phosphoric acid stabilization failed to stabilize the fly ash → metals mobilization.
- Simultaneous washing and phosphoric acid stabilization reduces concentrations of all metals in the leachate, except from Sb that exceeds the legal limit.
- A successful combination was found by a simple change in the sequence of the two techniques: phosphoric acid stabilization followed by water washing, using an optimum acid to ash ratio of 7 % w/w.
- Finally, regarding Cr leaching, the use of sodium dihydrogen phosphate dehydrate gives worse results than phosphoric acid.

Wastewater Results

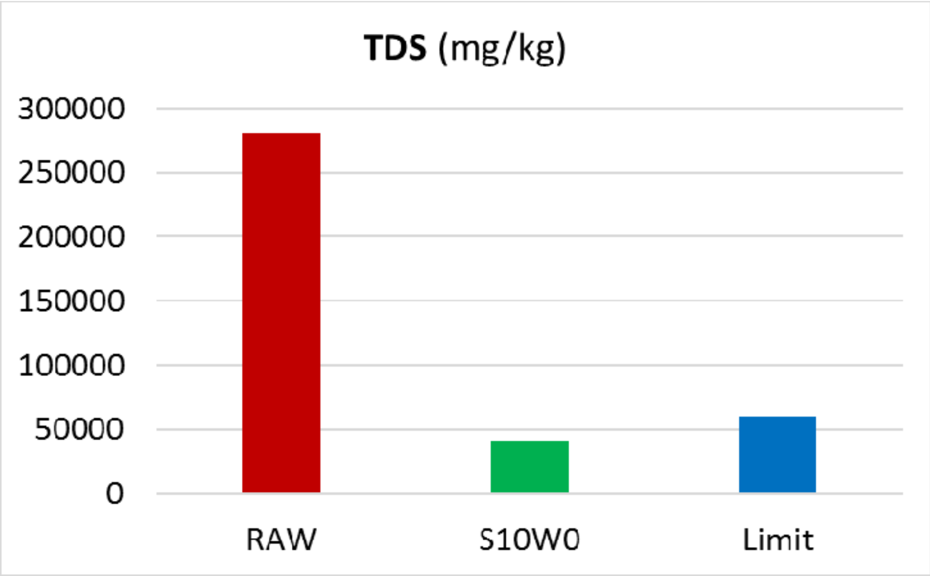


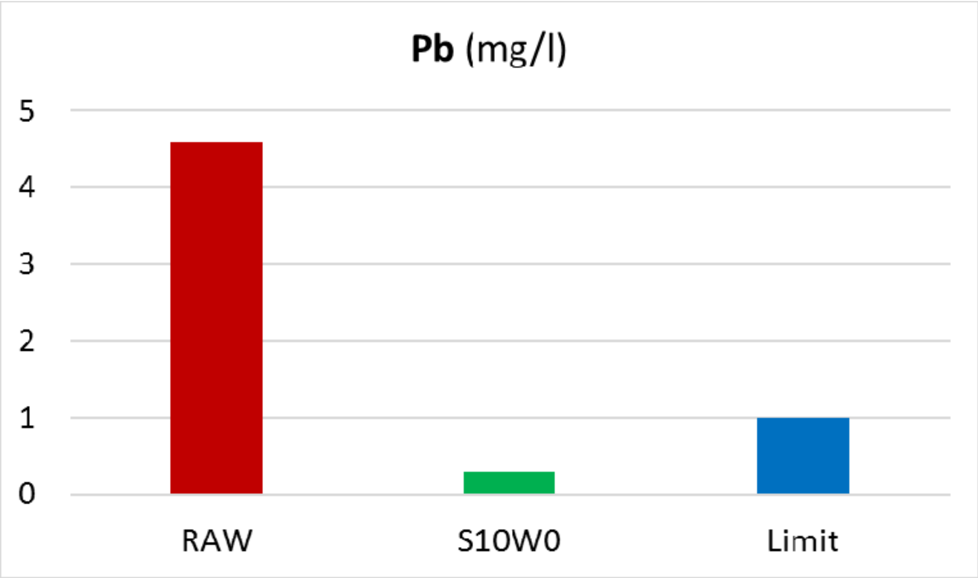
The successful method produces also a cleaner wastewater.

Medical Waste Incineration Fly Ash:
Treatment Method results

- Finally, we used this method for the stabilization of another type of fly ash
- Sampling: Medical Waste incinerator in Athens
- Similar properties with MSWI fly ash (finer, higher amount of Ca)
- Leaching test: TDS and Pb exceed the limits as well → hazardous waste

Method application → Successful stabilization → Non-hazardous waste





Conclusions

- APC Residues management →Open issue for incineration plants
  → Various treatment techniques and management practices
- Fly Ash → Hazardous Waste (leaching of Pb and salts)
- Water extraction → Effectively removes salts
  → Wastewater properties – heavy metals – pH effect
- Phosphoric acid Stabilization→Reduces the leaching of Pb and other metals
  →Low cost, relatively simple technique
- Washing & Stabilization → Very complicated balance between fly ash successful stabilization and wastewater quality
  → Strongly affected by pH and many parameters
  → Water washing followed by phosphoric acid stabilization failed to stabilize the fly ash
  → Metals mobilization
  → Successful stabilization & cleaner wastewater: phosphoric acid stabilization followed by washing

"Waste is better utilized through **incineration** than through **landfills** but **recycling** is an even better option.
Of course, the best option is **prevention** of waste production altogether, which often requires **direct reuse**.
The less waste, the better - it's as simple as that."

"Copenhagen Waste Solution, City of Copenhagen (2008)