

# THE PURPOSE OF THE WORK

To investigate the secondary Al slag (SAS) technical and environmental properties in correlation with its Portland cement matrix compatibility.

The estimation of SAS valorization potential as secondary raw material (SRM) for low mechanical strength cement matrix composites, as construction products.

## EXPERIMENTAL PRINCIPLE

**The SAS valorization in concrete must fulfill the technical and environmental requirements, both SRM and construction products.**

The Portland cement - SAS compatibility can be featured as following:

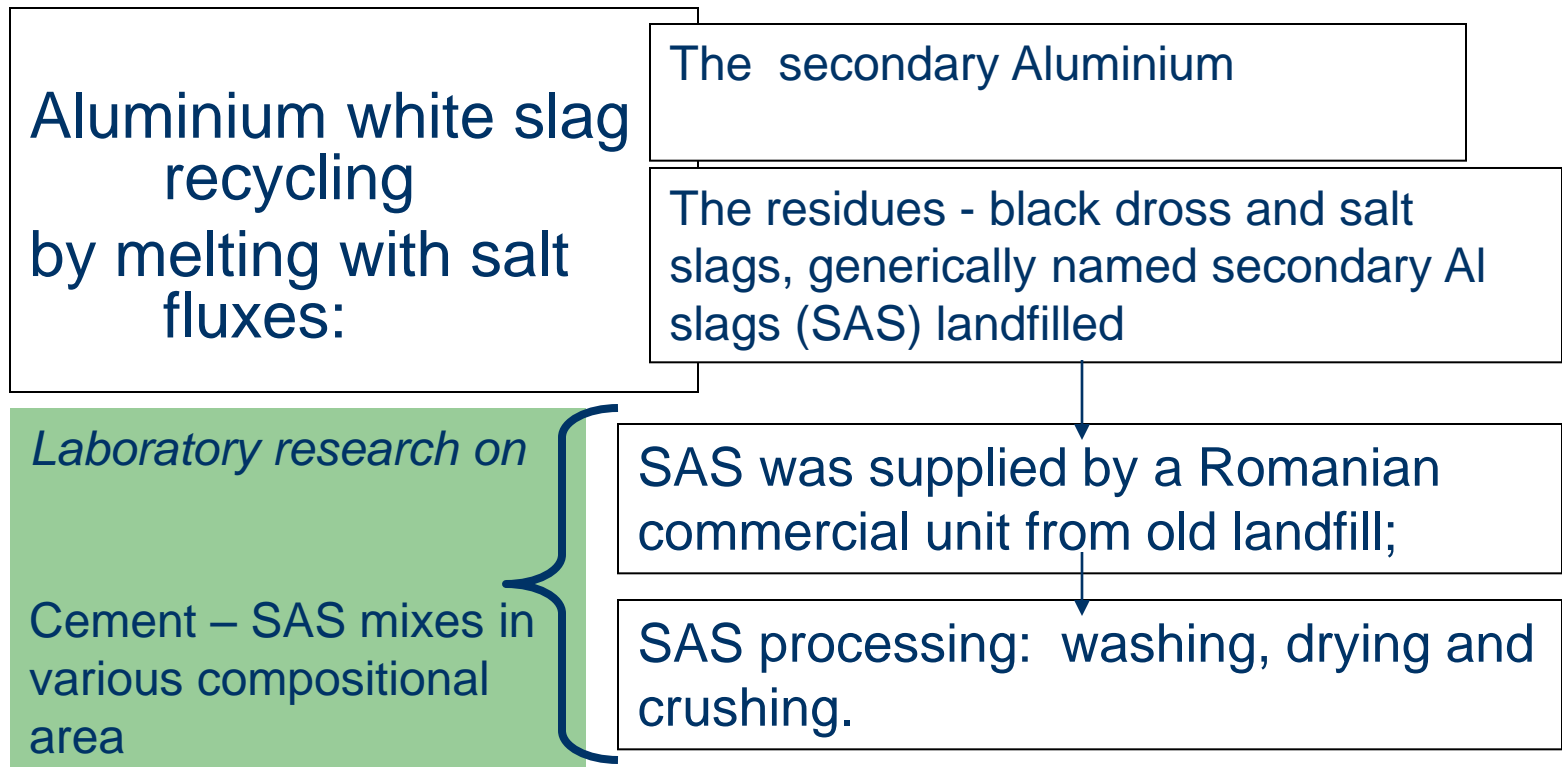
- SAS don't hide cement paste hardening structure development;
- CEMENT most stabilize the SAS potential hazardous by chemical and physical process (e.g. very low soluble precipitates of hydrosilicate and hydroaluminatesulfate, solid solution, adsorption).

# METHODOLOGY - EXPERIMENTAL SCENARIO

- The chemical, mineralogical and leaching properties of secondary Al slag (SAS);
- The study of cement - SAS - water systems hydrolise-hydration process;
- The carrying out some Cement –SAS relevant composites as mortar type;
- Leaching test and time-compression strengths testing of Cement –SAS mortars.

# MATERIALS (1)

## Secondary Al slag (SAS)



# MATERIALS (2)

## CEMENTS with granulated blast slag (GBS) addition

- CEM II/A-S with 20% granulated blast slag - GBS, addition;
- CEM III/A with 40% GBS addition.

(SR EN 197-1:2002);

# MATERIALS (3)

## CEMENT –SAS MORTARS:

with different sand /waste ratios (as weight parts)

Mortar code	Cement	SAS <sub>nw</sub> *	SAS <sub>w</sub> **	Sand		W/C Ratio
				0/2 mm	2/4mm	
REM – control	1			3		0.52
MNn05	1	0.5			2.5	0.6
MNs05	1		0.5		2.5	0.6
MNn1	1	1			2	0.8
MNs1	1		1		2	0.86
MNn2	1	2			2	1.34
MNs2	1		2		2	1.34

\*SAS<sub>nw</sub> - unwashed slag; \*\*SAS<sub>w</sub> slag processed by washing, drying and grinding

# METHODS (1)

## *The XRD phase analyse investigation*

- Mineralogical characterisation of the SAS as initial state from landfill;
- Evolution of hydration process of cement:SAS pastes after various time periods of 15 min., 45 min., 2 days and 28 days.

## *Leaching test*

- **Materials:** SAS and 28 days hardened mortar samples with 40% SAS content, grounded samples (<1 mm), demineralised water.
- **Experimental conditions:** own natural pH of material; shacking for 24 hours; four sequences- L/S 10, L/S30, L/S 50, and L/S 100.
- **Results:** The pH and electric conductivity values and the leached contaminants concentrations values.

# METHODS (3)

## The released $\text{Ca}^{2+}$ of cement hydrolyse measuring by titrimetric analyse of solution with EDTA

- **Suspensions:**

- *cement-water suspensions;*
- *(1:0.5) cement-SAS ratio at water/solid (L/S) of 100*

- **Experimental conditions:**

The soluble  $\text{Ca}^{2+}$  ions concentration measuring after time periods of one hour, 2, 24 and 48 hours from suspension preparation.

- **Results** as the  $\text{Ca}^{2+}$  ions leached concentration values in time.

# METHODS (4)

## Sampling. The mortar compression strengths evolution

- Mortar samples full testing period cured at 100% R.H.;
- Compression strengths testing at 2, 7, 28, 90, 180 and 360 days.

# OBTAINED RESULTS (1)

## Chemical composition of Secondary Aluminium Slag, SAS, %

Waste	<i>Al</i>	<i>K</i>	<i>Na</i>	<i>Cu</i>	<i>Zn</i>	<i>Ca</i>	<i>Si</i>	
SAS <sub>w</sub>	31,3	0,44	0,12	1,41	0,9	1,00	2,90	
SAS <sub>nw</sub>	46,8	2,04	2,71	1,155	0,839	1,02	2,78	
Waste	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Cr</i>	<i>Sn</i>	<i>SO<sub>4</sub></i>	<i>Cl</i>
SAS <sub>w</sub>	5,10	0,17	0,18	0,71	0,043	0,17	1,08	0,036
SAS <sub>nw</sub>	2,53	0,155	0,142	0,808	0,029	0,191	0,3	0,192

\*SAS<sub>nw</sub> - unwashed slag;

\*\*SAS<sub>w</sub> slag processed by washing, drying and grounding

# OBTAINED RESULTS (2)

## XRay Diffraction analyse of the of SASnw

Phase identification	% estimate
Al	<u>1</u> p.
Si	1 p.
<b>SiO<sub>2</sub> – <math>\alpha</math> Quartz</b>	<b><u>p.</u> z.p.</b>
$M^{+2}O \cdot (Al, M^{+3})_2O_3$ – solids solutions of spinels ( $M^{2+}$ = Cu <sup>2+</sup> , Mg <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>2+</sup> etc.	p.
<b>AlO(OH) – Boehmite</b>	<b>Z.P.</b>
<b>Al(OH)<sub>3</sub> – Nordstrandite</b>	<b>p. z.p.</b>
KCl – Silvite	p.
NaCl – Halite	p.

SASnw with particle size  $d < 1$  mm

# OBTAINED RESULTS (3)

## Leaching test of SAS

*Cummuled released quantities  
(at L/S 100 ratio)*

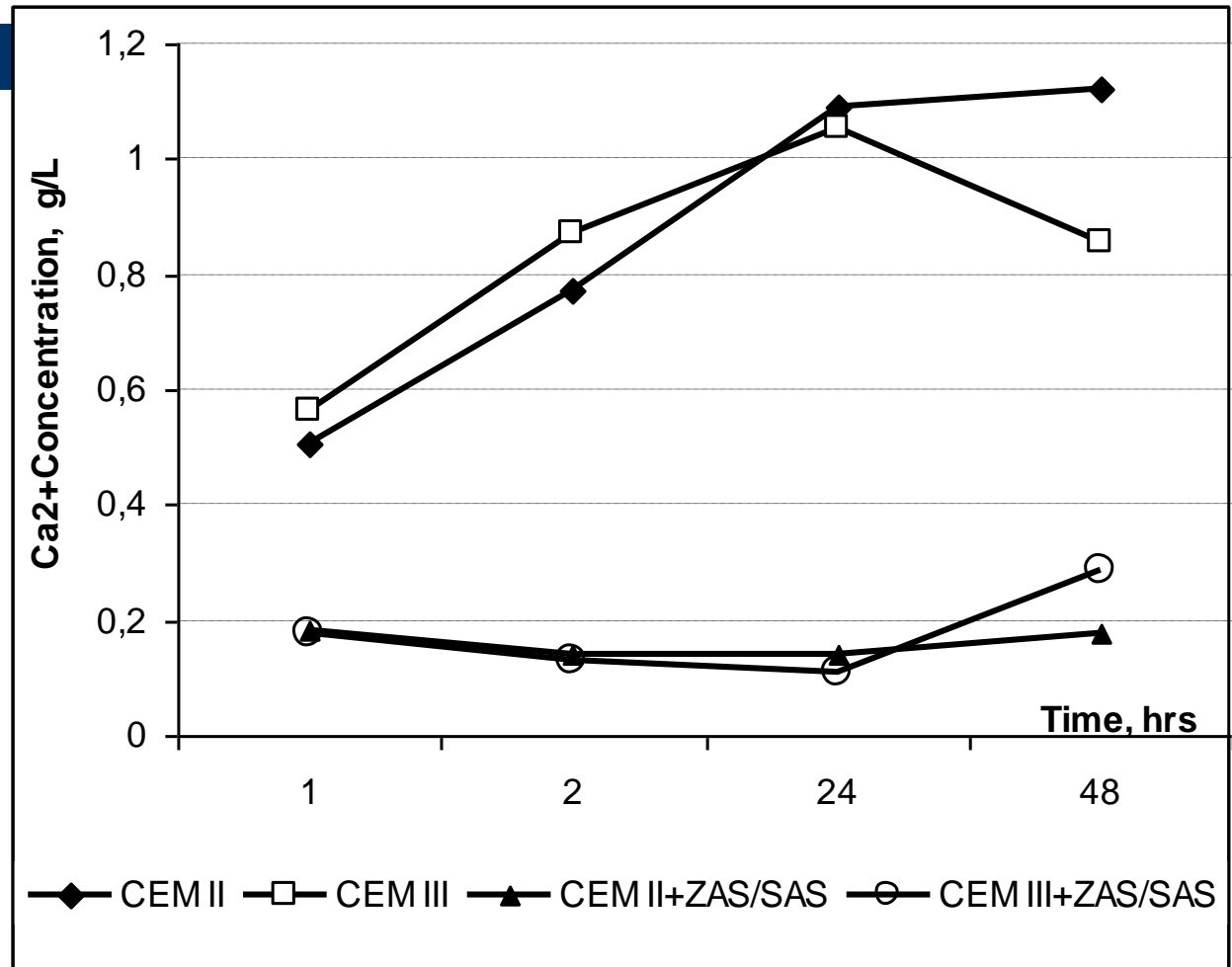
- The pH values - own of materials in the neutral limits of 6,3 ...7,3;
- The electric conductivity decreased according as releasing of the soluble ions, from 5840  $\mu\text{S/cm}$  (sequence 1) to 94  $\mu\text{S/cm}$  (sequence 4).
- *The 0/1 mm particle size river sand as reference material was considered.*
- *The leaching test of the washed sand in the same experimental conditions.*

Material	mg/kg				
	Zn	Cu	Pb	Ni	Cl-
SASnw	1.085	1.786	1.745	1.531	305250
SASw	1.256	2.125	2.384	2.651	8320
Natural sand	1.059	0.857	1.06	0.774	157.6

# OBTAINED RESULTS (4)

*The evolution of  $\text{Ca}^{2+}$  ions into cement-water and cement-SAS-water suspensions*

- ✓ The  $\text{Ca}^{2+}$  concentration time changing;
- ✓ SAS contribution at the early hardening, by its capacity to  $\text{Ca}(\text{OH})_2$  bounding.



## Pozzolanic activity of SAS

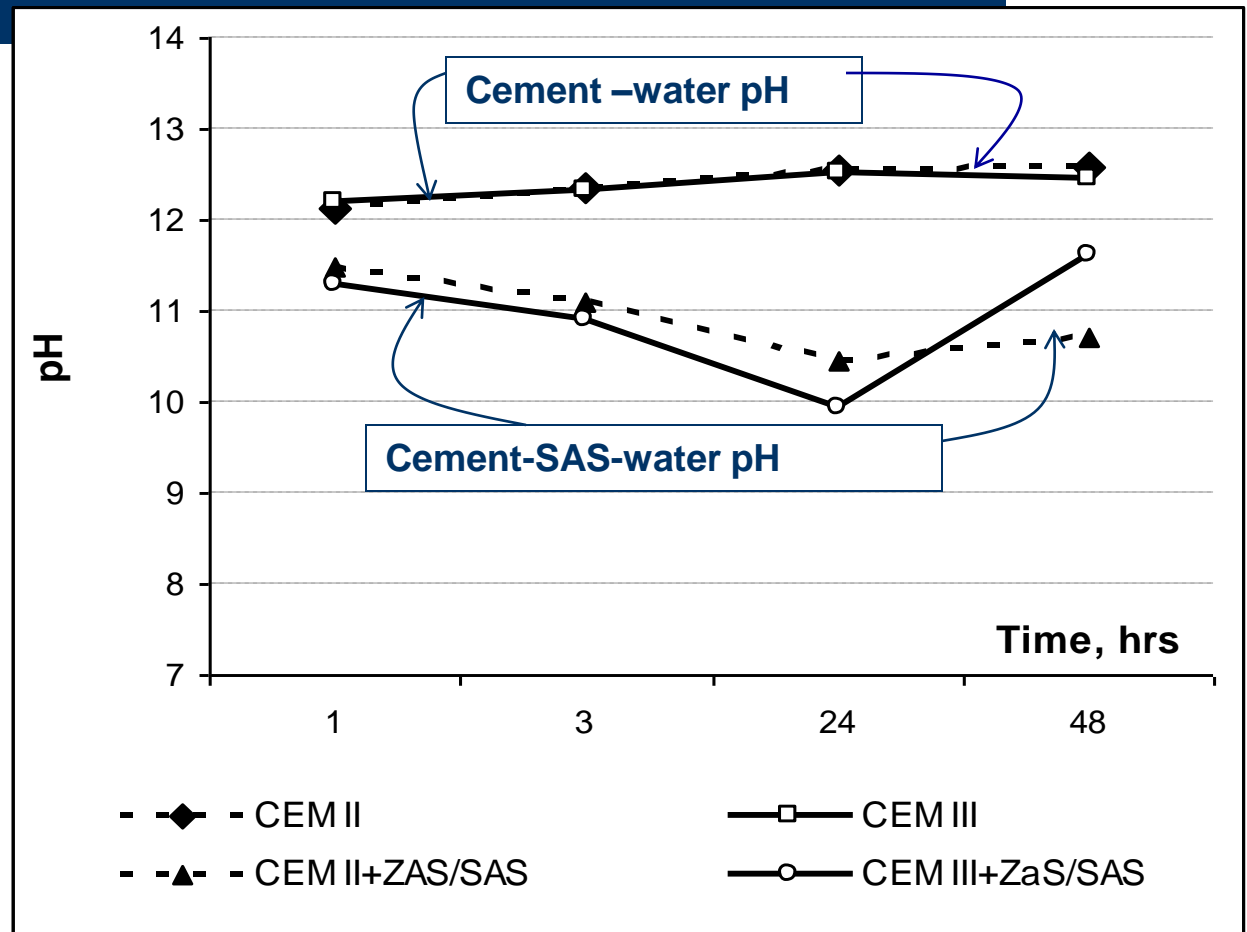
- The  $\text{Ca}^{2+}$  concentration of the CEM-SAS –water suspension is less than of the CEM suspension,
- The partial substitution of the cement with SAS blocking of  $\text{Ca}^{2+}$  from cement hydrolyze as calcium hydroaluminates products
- $\text{Ca}^{2+}$  is blocked as hydroaluminates products by the reactive  $\text{HAlO}_2$  –boehmite, of SAS.

# OBTAINED RESULTS (5)

*The evolution of pH into cement-SAS-water suspensions*

✓The pH change of the cement-water and of the cement-SAS-water systems is close correlated with the calcium ions evolution.

✓The pH decreasing in the first 24 hours due probably, of  $\text{Ca}^{2+}$  precipitation as calciumhydroaluminate by reaction with  $\text{AlO}(\text{OH})$  from SAS.



# OBTAINED RESULTS (6)

## THE HYDRATION PROCESS EVOLUTION IN THE CEMENT-SAS- SYSTEMS

*Phase compounds of SAS and developed of cement-SAS-water pastes  
Investigated by X-Ray diffraction*

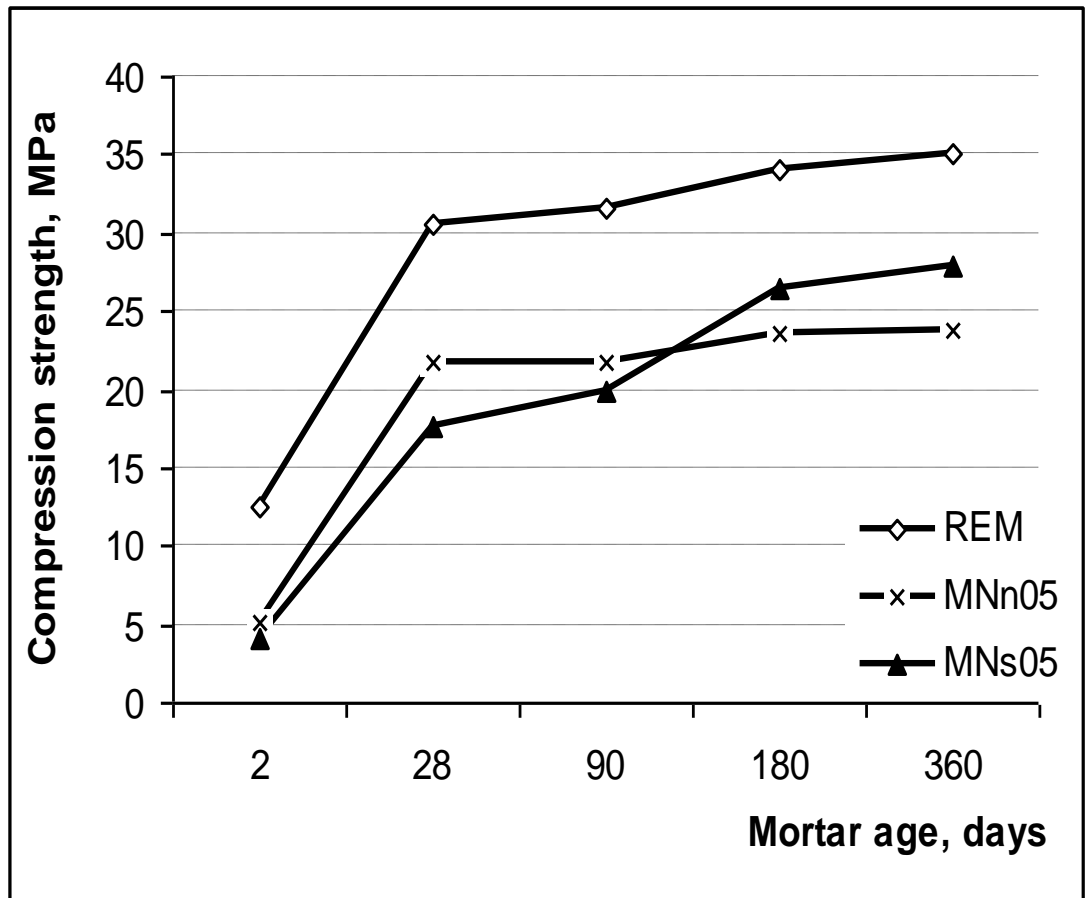
Sample code*	SiO <sub>2</sub> (d=3,33)	AlO(OH) (d=3,33)	Ca(OH) <sub>2</sub> (d=1,92)	C <sub>3</sub> AΣ <sub>3</sub> H <sub>32</sub> ettringite (d=5,61)	C-S-H tobermorite (d=2,97)	C <sub>4</sub> AH <sub>13</sub> (d=2,86)
SAS washed/ dried powder	104	<b>176</b>				
AS <sub>0.5</sub> paste after 45 min	22	<b>5</b>	20	11	0	11
AS0.5 paste after 2 days	9	<b>3</b>	16	14	0	7
AS0.5 paste after 28days		<b>0</b>	<b>26</b>	<b>22</b>	<b>12</b>	<b>0</b>
BS0.5 paste after 45 min.			27	0	0	0
BS0.5 paste after 2days	17	<b>6</b>	25	0	0	7
BS0.5 paste after 28days		<b>0</b>	<b>25</b>	<b>10</b>	<b>19</b>	<b>33</b>

AS0.5-pastes with cement type CEM IIA-S/slag ratio of 1/0.5; \*\* BS0.5- pastes with cement CEM III A /slag ratio of 1/0.5

# OBTAINED RESULTS (7)

## COMPRESSION STRENGTH OF THE MORTARS (MPa)

- ✓ The decreasing 28 days-compression strength of SAS admixture mortars ;
- ✓ A strength continuous positive evolution of 12.5 and 25% washed SAS addition only;
- ✓ The 360 days -testing period is enough short and recommendation of SAS valorization as SRM in concrete is unrealistic.



# OBTAINED RESULTS (8)

Leaching properties of mortars with SAS addition

***The heavy metals leach concentrations released from Mns2 mortar (with 40 % SAS addition)***

L/S ratio	Leach Concentration, mg/L						
	Zn	Ni	Pb	Sn	Cu	Mn	Cd
10	<0,02	<0,02	<0,02	<0,05	<0,02	0,04	<0,02
30	<0,02	<0,02	<0,02	<0,05	<0,02	0,05	<0,02
50	<0,02	<0,02	<0,02	<0,05	<0,02	0,08	<0,02
100	<0,02	<0,02	<0,02	<0,05	<0,02	0,06	<0,02

# Comments

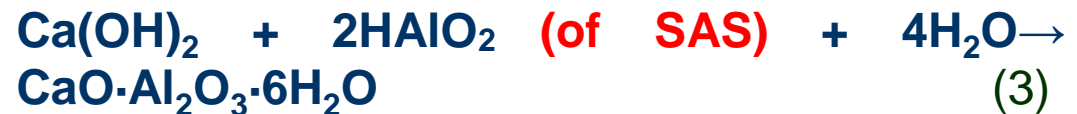
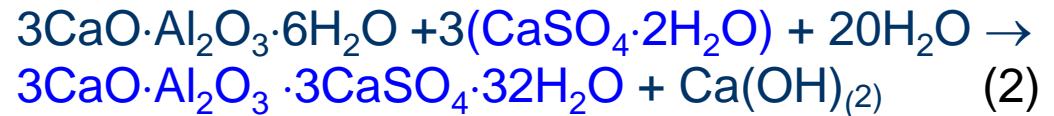
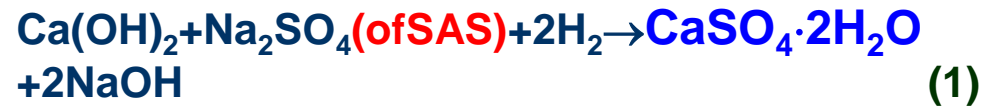
Free Ca (OH)<sub>2</sub> from cement hydrolyse is involving into two concurrent reactions as following :

I) Available for pozzolanic reaction with GBS silicates:



**Me<sub>2</sub>O · nSiO<sub>2</sub> · xH<sub>2</sub>O (of GBS)**  
**CaO · nSiO<sub>2</sub> · xH<sub>2</sub>O**-structural compound of *cement-SAS* composite matrix

II) Available for reactive aluminium compounds with precipitation of expansive compounds:



**CaSO<sub>4</sub> · 2H<sub>2</sub>O (dihydrate)** and **3CaO · Al<sub>2</sub>O<sub>3</sub> · 3CaSO<sub>4</sub> · 32H<sub>2</sub>O (etringite)** expansively compounds of matrix

# Comments

The heavy metal immobilisation,

Immobilisation of Cu by new **CaO·nSiO<sub>2</sub>·xH<sub>2</sub>O**- (very reactive, as product of pozzolana reaction), by precipitation of copper hydrosilicate as following:



## CONCLUSIONS (1)

### Cement type influence of hydration products balance in the CEM-SAS systems

- The more amount of granulated furnace slag (GBFS) in CEM III/A is favorable of the calcium hydrosilicates, C-S-H, precipitation;
- The less content of GBFS of CEM II/A-S seems to be favorable to hydroaluminates phase's precipitation.

# CONCLUSIONS (2)

## Heavy metal immobilisation

- The heavy metals - Zn, Cu and Pb, released from cement matrix of mortars was insignificant - below spectrometer detection limit.
- The beneficial role of Portland cement matrix to immobilize heavy metals from secondary aluminium slag (SAS).

# CONCLUSIONS (3)

## Compression strengths

- The positive evolution of 360 days- compression strengths were showed by mortars with 12.5 and 25% SAS addition;
- The 360 days -testing period can be considered enough short and, consequently, predictions on mortar /concrete mechanical strengths evolution appears to be unrealistic.

# Acknowledgements

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## ISCOWA

„Sustainable Management of Waste and Recycled Materials in Construction”

*Thank you!*



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