MSCA-ETN SULTAN

European Training Network for the Remediation and Reprocessing of Sulfidic Mining Waste Sites

Wienerberger Building Material Solutions

KU LEUVEN

Sustainable use of (cleaned) sulfidic mining waste in ceramics

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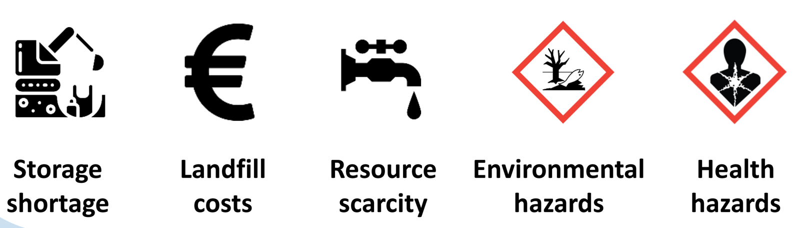
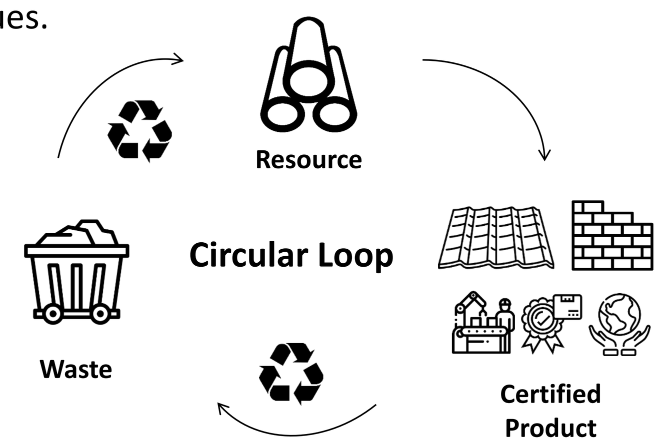
Rationale

According to Eurostat, in 2016, mining and quarrying waste accounted for over 25%, representing around 600 Mt, of all the EU28 waste output. Not only that but also the storage space limitations, landfill costs, resource scarcity (EU 2017 CRMs list), environmental (acid mine drainage) and health hazards (acidic water-rich metals), put this type of waste as one of the key priorities in Europe.



Main goal

To investigate the possibilities to replace primary raw materials for ceramics by (cleaned) sulfidic mine waste residues, taking into account production parameters, product quality and environmental issues.



Milestones

PhD starting month: February 2019 (M6)

- Develop ceramics (roof tiles, blocks, pavers, pipes and bricks) in which primary raw materials, such as clay or sand, are totally/partially replaced by mine waste materials (10-40%), matching technical, aesthetical and chemical criteria (M24).
  - ✓ **Roof tiles:** 5% (initial test) of uncleaned mine waste used by partly replacing local clay and local sand.
  - ✓ **Blocks:** 10% of uncleaned mine waste used by totally replacing local sand and partly red filler.
- Meet environmental legislation (VLAREMA in Flanders) and European product standards (EN1304 for roof tiles, EN1344 for pavers, EN771-1 for bricks and blocks and EN295 for pipes) (M40).
  - ✓ **VLAREMA tests** (metals + organic compounds + column leaching) already done in 3 of the 4 uncleaned mine waste materials.

Deliverables:

- 5 oral/poster presentations (**M14 – CYSC2019**, M19 – 7th MCAA GA, M24 – ICC8, M33 and M46).
- 3 peer-reviewed papers (M25, M37 and M48) – **work in progress** for 1st paper M25.
- 2 secondments (M21+M25 in KU Leuven and M27+M34+M35 in VITO).

Materials, Methods and Results

Physical and Chemical Characterisation of Sulfidic Mine Waste Material

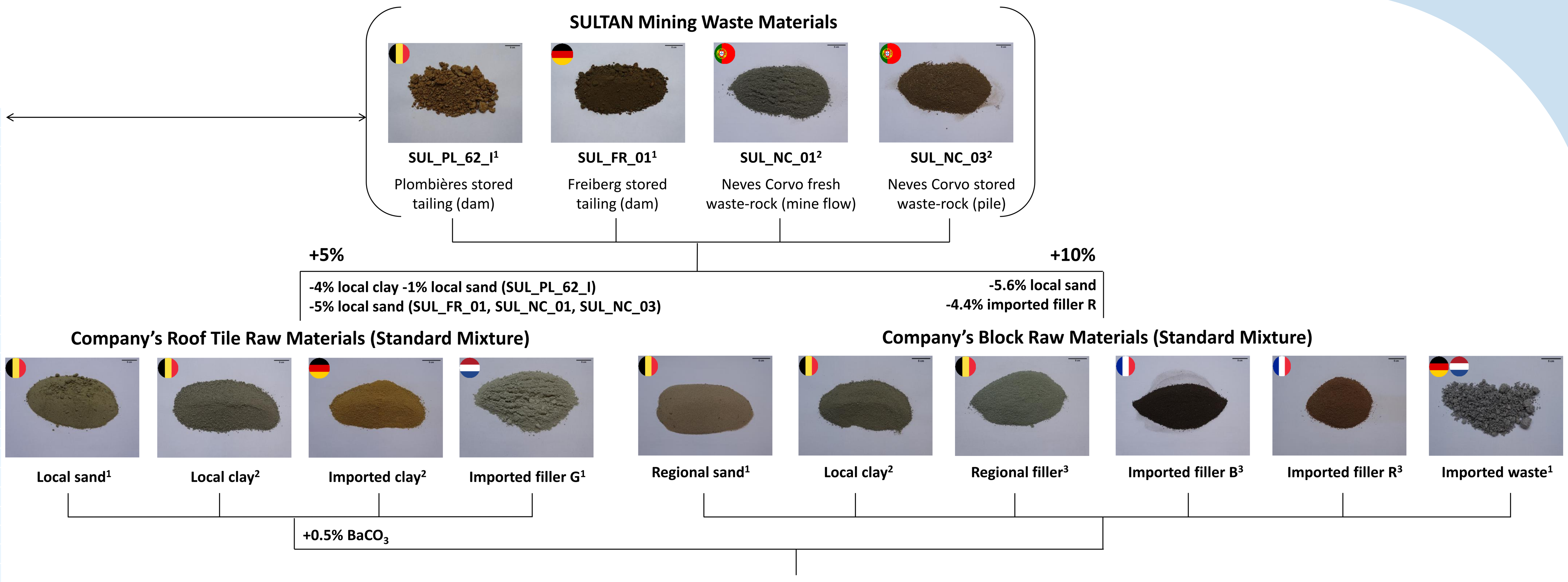
Location	Plombières (Belgium)	Freiberg (Germany)	Neves Corvo (Portugal)	Neves Corvo (Portugal)
Sample code	SUL_PL_62_I[1]	SUL_FR_01[1]	SUL_NC_01[2]	SUL_NC_03[2]
Grain-size distribution	**Mechanical sieve shaker (>50 µm) + Sedigraph (<50 µm)**			
Sample preparation	Dried sieve residue (>50 µm) + 5 g dried sample (sieved 2 mm) with $(NaPO_3)_6$ solution (<50 µm)			
n=1	%	%	%	%
Sand (>50 µm)	14	52	81	66
Silt (50-2 µm)	47	35	9	11
Clay (<2 µm)	39	13	10	23
Classification	Clayey silt	Silty sand	Sand	Sand
Geochemistry (Volatile substances)	**LOI at 1000°C (according to NBN EN 15935 (2012))**			
Sample preparation	0.3 g of dried sample (sieved 250 µm) on a ceramic crucible			
n=1	%	%	%	%
	3.3	14.2	9.3	14.9
Geochemistry (Major elements)	**XRF (Omnian operation mode)**			
Sample preparation	0.2 g of dried sample (sieved 250 µm) for pearl preparation with $C_6H_8O_7$ and LiBr solutions			
n=1	%	%	%	%
SiO_2	74.0	32.1	42.9	39.2
Al_2O_3	12.0	4.4	12.0	10.9
Fe_2O_3	4.3	20.0	17.1	15.8
TiO_2	0.9	0.3	0.6	-
CaO	0.6	1.1	0.5	1.8
MgO	0.9	0.6	1.7	1.4
Na_2O	1.1	-	-	-
K_2O	2.4	1.3	2.1	2.7
MnO	0.2	0.4	0.2	-
SO_3	0.2	22.8	12.3	11.7
P_2O_5	-	0.1	-	0.2
PbO	-	0.5	0.1	-
ZnO	-	1.3	0.5	0.2
CuO	-	-	0.3	1.2
Br	-	-	0.3	-
Geochemistry (Carbon + Sulphur)	**NDIR (firing at 1450°C and flow ± 2.5 lpm, according to ISO 10694-1995 §7.2)**			
Sample preparation	0.2 g of dried sample (sieved 250 µm) on ceramic boats with a protective Ni foil			
n=2	%	%	%	%
C	0.1	0.8	0.7	0.5
S	0.01	9.6	6.8	4.5
Geochemistry (Trace elements)	**ICP-OES ($HNO_3/HClO_4/HF$ digestion according to ISO 14869-1:2001)**			
Sample preparation	0.15 to 0.25 g of dried sample (sieved 250 µm)			
n=1	mg/kg	mg/kg	mg/kg	mg/kg
Ti	3282.9	1435.9	2928.1	2567.9
Fe	32176.5	178866.2	137563.2	122824.3
Ca	3750.1	11776.8	5796.4	13085.1
K	19065.8	11913.6	18631.3	22150.9
Mg	4968.9	6316.5	12073.8	9692.3
Mn	652.4	3259.9	598.5	583.9
Na	4821.0	430.3	1610.8	2598.3
V	78.6	34.3	90.6	91.2
Ba	366.3	157.5	305.6	419.8
Co	19.6	42.0	64.1	46.2
Cr	60.4	33.6	58.8	56.4
Cu	23.1	857.7	2226.2	7039.2
Ni	30.6	68.3	47.1	52.5
Pb	29.8	5142.5	797.5	614.0
Zn	136.8	14685.9	3724.7	1890.0
Geochemistry (Soluble sulphates)	**IC (H_2O_2/Na_2CO_3-$NaHCO_3$ solution according to NBN EN ISO 10304-1 (2009))**			
Sample preparation	Reflux dried sample (sieved 250 µm) with distilled water during 6 hours			
n=1	% (18g/150ml)	% (5g/150ml)	% (1.5g/150ml)	% (1.5g/150ml)
SOx	0.01	3.2	1.1	7.3
Geochemistry (Leachates*)	**ICP-MS (N destruction according to CMA/2/I/B.5, NBN EN ISO 17294-2:2003)**			
Sample preparation	50 ml sample + 0.8 ml H2SO4/l			
n=1	mg/kg	mg/kg	mg/kg	mg/kg
As	0.04	0.46	0.12	0.7
Cd	0.001	29	0.0037	0.99
Cr	0.065	0.02	0.03	0.31
Cu	0.05	<2.6	0.047	1200
Hg	0.0004	0.0004	0.00039	<0.00084
Ni	0.05	5	0.055	8.5
Pb	0.05	2.5	0.046	0.12
Zn	0.18	2600	0.62	530

*Leachates from column leaching test according to method CMA/2/II/A.9.1, NEN 7373 (2004) with L/S_{cum}= 10 (7 fractions)

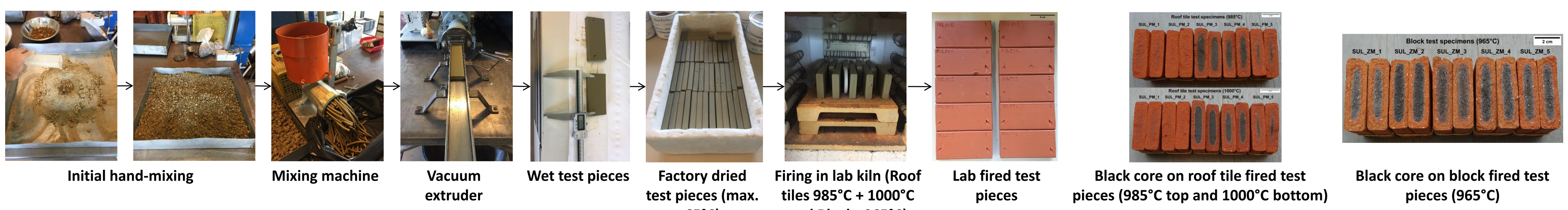
n= number of samples

Values above VLAREMA guidance values for metal concentration (mg/kg): As (250), Cd (10), Cr (1250), Cu (375), Hg (5), Ni (250), Pb (1250) and Zn (1250)

Values above VLAREMA limit values for leachates (mg/kg): As (0.8), Cd (0.03), Cr (0.5), Cu (0.5), Hg (0.02), Ni (0.75), Pb (1.3) and Zn (2.8)



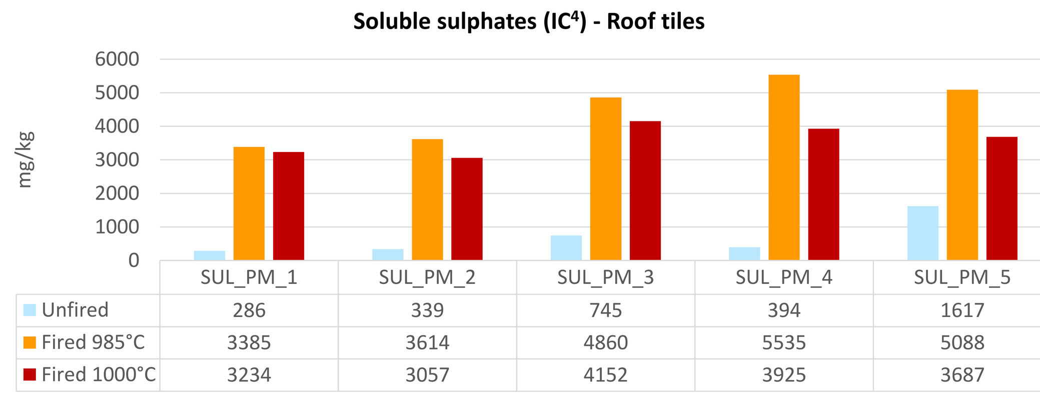
Laboratory Test Pieces (Preparation, Drying and Firing)



Technical properties – Roof tiles and Blocks

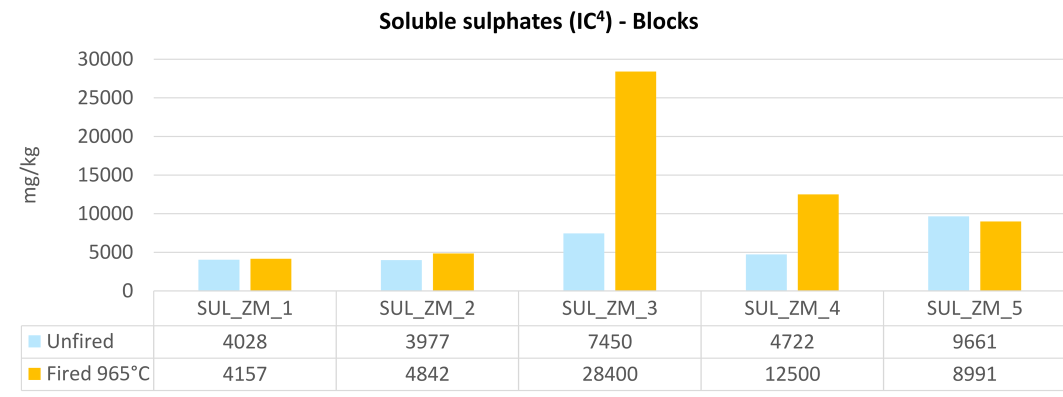
Ceramic mixture	Test piece code	Plasticity (Pfefferkorn) imprint (mm)	Drying shrinkage %	Firing / Total shrinkage %		Water absorption %		Saturation level ($E_{prog}/E_{fullvac}$) %		E-modulus GPa	
Roof tile mixture	**Roof tile test piece code**	**Unfired mix**	**Industrial dryer**	**Lab 985°C**	**Lab 1000°C**	**E_{prog} 985°C**	**E_{prog} 1000°C**	**Lab 985°C**	**Lab 1000°C**	**Lab 985°C**	**Lab 1000°C**
Reference (standard)	SUL_PM_1	7.3	6.4	1.5 / 7.8	1.9 / 8.3	7.3	6.3	72	65	17.6	19.6
Ref. (-4% local clay -1% local sand) + 5% SUL_PL_62_I	SUL_PM_2	8.0	6.2	1.5 / 7.7	2.0 / 8.2	7.7	6.9	73	69	16.5	18.5
Ref. (-5% local sand) + 5% SUL_FR_01	SUL_PM_3	7.0	6.1	1.7 / 7.9	2.4 / 8.6	6.6	5.1	68	57	20.9	22.8
Ref. (-5% local sand) + 5% SUL_NC_01	SUL_PM_4	6.7	6.0	1.6 / 7.6	2.1 / 8.1	6.7	5.3	70	60	20.0	22.2
Ref. (-5% local sand) + 5% SUL_NC_03	SUL_PM_5	6.1	6.0	1.8 / 7.7	2.3 / 8.3	7.1	5.8	72	65	19.7	22.8
Block mixture	**Block test piece code**	**Unfired mix**	**Industrial dryer**	**Lab 965°C**		**E_{24h} 965°C**		**Lab 965°C**		**Lab 965°C**	
Reference (standard)	SUL_ZM_1	7.3	5.4	0.8 / 6.2		11.4		Not Applicable		14.0	
Ref. (-5.6% regional sand -4.4% imported filler R) + 10% SUL_PL_62_I	SUL_ZM_2	6.0	5.3	0.7 / 6.0		10.1		Not Applicable		18.2	
Ref. (-5.6% regional sand -4.4% imported filler R) + 10% SUL_FR_01	SUL_ZM_3	6.3	5.6	0.7 / 6.3		11.0		Not Applicable		17.6	
Ref. (-5.6% regional sand -4.4% imported filler R) + 10% SUL_NC_01	SUL_ZM_4	6.3	5.4	0.6 / 6.0		11.2		Not Applicable		16.4	
Ref. (-5.6% regional sand -4.4% imported filler R) + 10% SUL_NC_03	SUL_ZM_5	5.0	5.4	1.1 / 6.4		11.4		Not Applicable		17.4	

Soluble sulphates (IC[4]) - Roof tiles



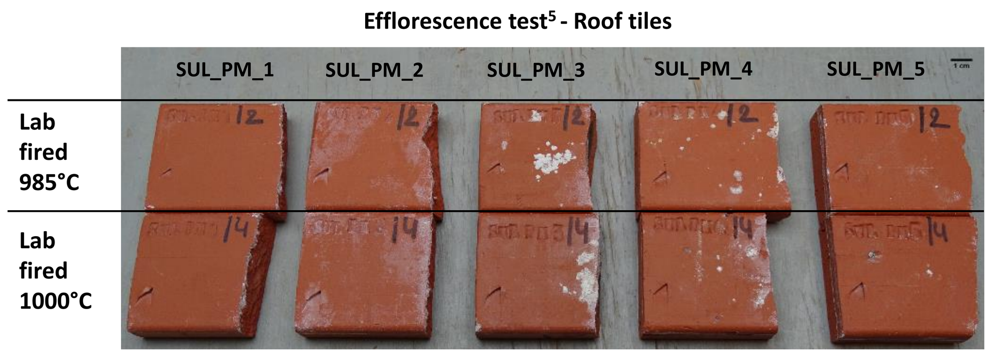
	SUL_PM_1	SUL_PM_2	SUL_PM_3	SUL_PM_4	SUL_PM_5
Unfired	286	339	745	394	1617
Fired 985°C	3385	3614	4860	5535	5088
Fired 1000°C	3234	3057	4152	3925	3687

Soluble sulphates (IC[4]) - Blocks

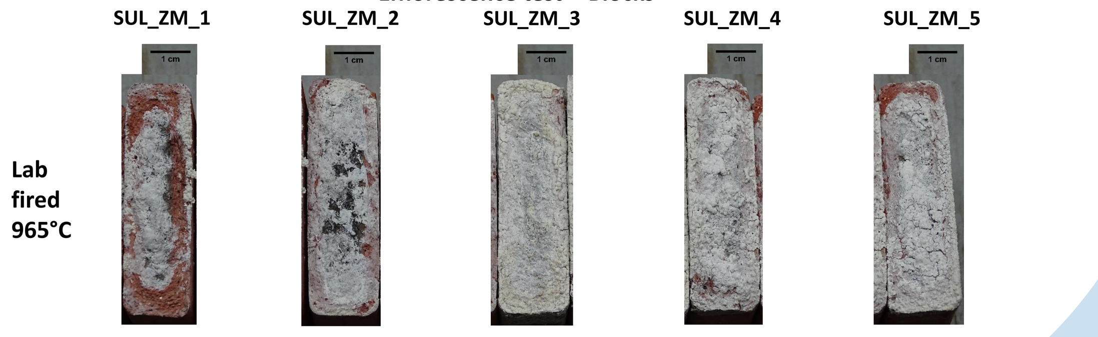


	SUL_ZM_1	SUL_ZM_2	SUL_ZM_3	SUL_ZM_4	SUL_ZM_5
Unfired	4028	3977	7450	4722	9661
Fired 965°C	4157	4842	28400	12500	8991

Efflorescence test[5] - Roof tiles



Efflorescence test[5] - Blocks



[1] Dried 105°C. [2] Dried 105°C + Shredded. [3] Dried 105°C + Grinded (jaw breaker).
[4] Ion Chromatography (IC): for unfired raw materials sample preparation includes refluxing dried sample (sieved 250 µm) with distilled water during 6 hours + for fired products includes shaking dried sample (sieved 250 µm) with distilled water (L/S) 200ml/20g at 120 strokes/min during 1 hour.
[5] Efflorescence: 3x cycles of partly immersion of fired test pieces in water during 3 days + 1 night 50°C drying stove. Finishing the 3 cycles, dry again the fired test pieces but this time at 105°C in a drying stove (Roof tiles pieces tested in horizontal position and Blocks pieces tested in vertical position).

Conclusions

- Roof tiles and blocks test pieces present general positive results on technical properties. Aesthetical aspects with no dry efflorescence but efflorescence after firing was visible in all the test pieces (on the block test pieces including the reference). Chemically, apart from Plombières tailing material, all the other test pieces presented higher values of soluble sulphates when compared to the reference.
- Therefore, Plombières tailing material (SUL_PL_62_I) can be considered the best fit when partly replacing local clay (4%) and local sand (1%) on the standard roof tile mixture and when totally replacing local sand (5.6%) and partly replacing filler R (4.4%) on the standard block mixture. Nevertheless, Plombières test pieces presents small, but visible, efflorescence stains after firing on roof tiles test pieces and evident efflorescence on the block test pieces most probably due to which increase the percentage of finer material in the mixture (finer porosity → more sulphates trapped during sintering → more efflorescence).

Next steps

- Produce new sample mix with two Plombières tailing residues (SUL_PL_62_I + SUL_PL_55_J).
- VLAREMA tests (metals + organic compounds + column leaching) on new Plombières mix sample.
- Test new Plombières mine waste using the same (5% for roof tiles and 10% for blocks) and higher amounts (up to 20% in roof tiles and blocks).
- Column and tank leaching test once we have all the fired ceramic roof tiles and blocks test pieces using different amounts of mine waste (VITO secondment).
- Start testing other proposed ceramic products, firstly pavers and pipes (higher firing temperatures), and finally facing bricks.
- Verify compliance with European product standards (EN1304, EN1344, EN771-1 and EN295).

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This project has received funding from the European Union's EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No 812580.