



Univerza *v Ljubljani* Fakulteta za kemijo in kemijsko tehnologijo

The main goals of the project are: (i) successful development of a new procedure for removal of heavy metals

from sediment and (ii) successful development of new building materials (bricks and alkali-activated materials

Investigation of the distribution and mobilization of heavy metals, regarding to particle size fractionated sediment in area of eight hydropower plants and Ptuj accumulation lake.

Design a multistep procedure for heavy metal contaminated sediment cleaning based combined sieving and

Determination of bricks and alkali activated materials process parameters and preparation of bricks with desired



# **REACTIVITY OF CALCINED RIVER SEDIMENTS**

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vashing process

**XRD ANALYSIS** 

and 950 °C, respectively).

Fig. 1:

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#### INTRODUCTION

er sediment within hydro power plant systems affect the safety of dams, and reduce energy production, storage and discharge capacity and can effect river flow, consequently meaning that they must be regularly dredged Depending on the chemical and mineralogical compositions of such dredged materials, as well as their particle size, they may be suitable to be used in the building sector as precursors for geopolymers (alkali activated materials) [1], the production of cement clinker [2], bricks [3], lightweight aggregates [4], and concrete [5], or for other purposes. If dredged sediments are calcined and then rapidly cooled, the materials become more reactive due to an increase in the content of amorphous phase.

The aim of the present study was to evaluate the reactivity of two sediments from the Drava River following calcination at various temperatures, and to evaluate the materials obtained for further use as supplementary cementitious materials (SCM) and/ or alkali activated precursors.

### METHODS

Two sediments, designated as V-429/20 and V-430/20, were subjected to thermal exposure using a Protherm furnace fired to 700, 750, 800, 850, 900 and 950 °C at a heating rate of 600 °C/h, using a dwelling time of 20 min at each selected temperature. Following the temperature exposure the sediments were quickly cooled in order to obtain the greatest possible amorphous phase content. Three different methods were applied to assess the reactivity of the calcined material: i) quantitative XRD analysis, ii) pozzolanic activity determined by lime consumption, and iii) determination of the strength activity index (SAI).

Amorphous phase was determined by XRD analysis, via Rietveld refinement using X'Pert High Score Plus diffraction software. Pozzolanic activity was determined following the procedure described in [6], where Ca(OH), consumption software rozzoal method with was determined bolowing the processing description of  $M_{12}^{-1}$  constants and  $M_{12}^{-1}$  constants of  $M_{12}^{-1}$  constants and  $M_$ coment with the calcined sediment studied. Further, also microstructural analysis of the sediment powders before and after exposure to 900 °C was performed by a JEOL JSM-IT500 LV (back-scattered electrons image mode) SEM in a high vacuum. Quantitative analysis was performed using energy dispersive spectroscopy (EDX, Oxford instruments, using Aztec software platform). Prior SEM scanning, the samples were vacuum-dried and sputter-coated with gold. The chemical composition of the sediments was determined using a Wavelength Dispersive X-ray Fluorescence (WD XRF) analyser (Thermo Scientific ARL Perform X).

V-429/20

## SEM/EDS AND CHEMICAL ANALYSIS

To provide further insight into the microstructural and chemical composition of the river sediments, SEM/EDS and XRF analysis was utilised to attain powder micrographs of the unexposed sediments (designated as R.T.) as well as the sediments exposed to 900  $^\circ\text{C}$ (designated as 900 °C) and chemical composition of selected powders. SEM micrographs reveals, that in both river sediment types (specimen V-429/20 and V-430/20) particles are similar - they are of random shape and the particle size is in the range between few microns to approximately 100  $\mu m$ . Interestingly, also after the temperature exposure, the particle size distribution as well as particle shape has not change significantly. Chemical composition of sediments is evident from **Tab. 2** and **Tab. 3**. It can be seen, that both used methods give comparable results (with only exception being  $Al_2O_3,$  where deviation in results is slightly higher). Over 50 % of chemical composition represents  $SiO_2$  and  $Al_2O_3$ , which is crucial for the alkali activation process. The chemical composition, however, has not changed significantly also after high temperature exposure.

from XRF analysis (R.T. = no exposure).				
Oxide (%)	V-429 /20 R.T.	V-430/20 R.T.		
Na <sub>z</sub> O	1.4	1.4		
MgO	4.6	4.9		
Al <sub>2</sub> O <sub>3</sub>	13.8	13.8		
SIO2	48.5	45.4		
P <sub>2</sub> O <sub>5</sub>	0.2	0.2		
SO3	0.7	0.9		
K <sub>2</sub> O	2.4	2.4		
CaO	7.0	7.9		
TIO2	0.9	0.9		
Cr <sub>2</sub> O <sub>3</sub>	/	/		
MnO	0.1	0.1		
FeO	6.0	6.1		
LOI	14.7	15.8		

V-430/20

Tab. 3: Chemical composition obtained from EDS analysis (R.T. = no exposure; 900 °C =

exposure to soor ej.				
Oxide (%)	V-429/20 R.T.	V-430/20 R.T.	V-429/20 900 °C	V-430/20 900 °C
Na <sub>2</sub> O	1.6	1.4	2.2	2.0
MgO	5.9	6.9	6.3	6.5
$Al_2O_3$	21.8	22.7	21.7	20.4
SiO <sub>2</sub>	48.8	46.0	49.1	46.5
$P_2O_5$	0.4	0.4	0.3	0.5
SO3	0.8	0.7	1.1	2.1
K <sub>2</sub> O	3.8	4.0	3.5	3.1
CaO	7.0	8.3	7.6	8.6
TiO <sub>2</sub>	0.9	1.0	0.8	1.0
$Cr_2O_3$	0.1	/	0.1	/
MnO	/	0.1	0.1	0.3
FeO	8.9	8.5	7.4	9.1
Total	99.9	99.9	100	99.9

## **CONCLUSIONS**

- Both river sediments' (specimen V-429/20 and V-430/20) particles are similar they are of random shape and the particle size is in the range between few microns to approximately 100 µm.
- Also chemical composition is similar for both sediments, with no obvious changes after firing. All three applied methods showed that reactivity depends on the calcination temperature.
- Results also confirmed that increased reactivity after calcination, particularly evident after calcination above 850 °C, should open up the possibility of using calcined sediments such as these for SCM and/ or as precursors for alkali
- activated materials Further analysis in this direction will be performed.

# REFERENCES

 Lirer et al. (2017) J Environ Manage 191:1–7; [2] Anger et al. (2017) Eur J Environ Civ Eng 23:957-970;
Slimanou et al. (2020) J Build Eng 28:101085; [4] Wang et al. (2017) Mar Georesour Geotec 35:472-480; [5] Junakova & Junak (2017) Sustainability 9:852; [6] Tironi et al. (2013) Cement Concrete Comp de agent Circuit and Concentration and Concenter Comp 37:319-327; [7] EN 196-3.

#### MORE ...

about READY4USE project on webpage http://www.zag.si/si/projekti-zag/I7-2629

#### N [count] 700 °C 40000 -950 °C 30000 20000 10000 25 45 65

20 [°]

y diffractograms of sediment V-429/20 fired at 700 and 950  $^{\circ}$ C (A = albite; C = calcite D = dolomite; H = hematite; I = ilite; P = periclase; Q = quartz; Z = zeolite).

In Fig 1. X-Ray diffractograms of specimen V-429/20 fired at two different

phases are quartz and albite, which are present at both temperatures. It is

also evident, that some phases (calcite, dolonite, zeolite) disappear after firing to 950 °C, and Rietveld analysis also reveals that the amount of

phous phase is higher (9 and 31 % for sediment samples fired at 700

temperatures (700 and 950 °C) are presented. Two of the main prese

**READY4USE – PROJECT OBJECTIVES** 

(AAMs) by using sediment raw material). This will be achieved by: • Identification of heavy metals and their distribution in sediments.

properties on pilot scale by using sediment as raw material.

Sediment preparation:

- exposure until desired T fast cooling
- milling and sieving under
- d < 63 µm XRD and XRF analysis
- Rietveld analysis

# Tab. 1: The proportion of the amorphous

phase in both samples. (R.I. = no calcination).				
Calcination T (°C)	V-429-20	V-430-20		
R.T.	17.1	25.6		
700	15.9	8.8		
750	15.0	21.6		
800	26.8	20.4		
850	32.5	34.8		
900	39.2	33.6		
950	44.2	36.8		

Composition for strength measurements

calcinated sediment : CEM I = 25 % : 75 %

calcinated sediment : CEM I = 25 % : 75 % Further, also the consistence of fresh morta determination test by flow table was executed according to SIST EN 1015-3 and is presented in Tab. 4. As can be concluded, the sediments show less consistence in comparison standard material, probably due to more fine

225 g of binder

125 g of water

Sample age: 28 and 90 days Composition for determination of

consistence of fresh mortar:

169 g of CEM I 56 g of calcinated sediment

v/c = 0.5Ratio

structure of the powder.

Ca(OH)<sub>2</sub> (at 40 +/- 1 °C) filtration

concentration of Ca(OH)<sub>2</sub>

(saturated) solution

Procedure for lime consumption determination (Ca(OH)2):

preparation of saturated solution of

25 mL of saturated solution + 2,5 g of

nvestigated sample (calcinated sediment) suspensions are fed at 40 +/- 1 °C

measurements after 1, 7, 14 and 28 days the suspension is then filtered and titrated

with 0.02 M HCl, to determine the

result is given as [Ca(OH)<sub>2</sub>]/[Ca(OH)<sub>2</sub>]

where [Ca(OH)<sub>2</sub>], is concentration in initial

675 g of sand Standard – CEM I

(SAI):

Ratio:

# Chemical analysis confirmed that the sample fired at 850 °C

exhibited the highest consumption of lime (Fig. 2, Tab. 5). Similarly, the SAI test (Tab. 4) also revealed that the drop in compressive strength after 28 days was the lowest (compared to the reference sample CEM I) following calcination at 850  $^\circ\text{C}.$ 

SAI INDEX AND LIME CONSUMPTION

Tab. 4: SAI index and consistence determination for sample V-429/20.				
	V-429/20			
Calcination T (°C)	SAI (28 days)	SAI (90 days)	Consistence (mm	
Standard	/	/	179	
700	72.1 %	77.3 %	137	
850	72.7 %	64.8 %	130	
950	65.4 %	66.7 %	137	

Tab. 5: Lime consumption test results for sample V-340/20

	Ratio: calcinated sediment/blank				
Cal	cinated T (°C)	1 day in Ca(OH)₂ at 40°C	7 days in Ca(OH) <sub>2</sub> at 40°C	14 days in Ca(OH) <sub>2</sub> at 40°C	28 days in Ca(OH) <sub>2</sub> at 40°
	700	0.59	0.37	0.23	0.24
	750	0.85	0.46	0.27	0.28
	800	1.00	0.38	0.29	0.33
	850	2.21	0.85	0.70	0.64
	900	1.95	0.75	0.47	0.48
	950	1.77	0.51	0.34	0.36
	2.5 -				→-700 °C
/ [Ca(OH) <sub>2</sub> ]。	2.0 -	~			← 750 °C → 800 °C
		$\langle \rangle$			<del></del> 850 °C
	1.5 -				900 °C
					<u></u> 950 °C



1 dav 7 days 14 days 28 davs ne consumption test results for sample V-340/20 Fig. 2: Graph

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Ca(OH),]

0.5