# SEWAGE-SLUDGE STABILIZATION WITH BIOMASS ASH

## STABILIZIRANJE KOMUNALNEGA MULJA S PEPELOM BIOMASE

#### Primož Pavšič<sup>1</sup>, Danijel Oštir<sup>2</sup>, Ana Mladenovič<sup>3</sup>, Sabina Kramar<sup>3,4</sup>, Matej Dolenec<sup>4</sup>, Peter Bukovec<sup>5</sup>

<sup>1</sup>PMA d.o.o., Tbilisijska 61, 1000 Ljubljana, Slovenia
 <sup>2</sup>VIPAP d.d., Tovarniška 18, 8270 Krško, Slovenia
 <sup>3</sup>Zavod za gradbeništvo Slovenije, Dimičeva 12, 1000 Ljubljana, Slovenia
 <sup>4</sup>Naravoslovnotehniška fakulteta, Aškerčeva 12, 1000 Ljubljana, Slovenia
 <sup>5</sup>Fakulteta za kemijo in kemijsko tehnologijo, Aškerčeva 5, 1000 Ljubljana, Slovenia

Prejem rokopisa – received: 2012-10-01; sprejem za objavo – accepted for publication: 2012-10-23

By mixing the sewage biodegradable sludge and biomass ash a stable composite is formed. A study showed that, in this way, a building material with a compressive strength of about 2 MPa is produced, which can be used mainly for landfill covers, road-shoulder management, road-base stabilization and rehabilitation of degraded areas. An analysis of the chemical composition of the water eluate from the composite showed that the new composite material is inert and, as such, does not pose a threat and does not burden the environment. From the sustainable-development point of view this kind of waste-residue management presents an optimum – a zero waste solution.

Keywords: biodegradable sewage sludge, stabilization, biomass ash, composite construction material

Z mešanjem komunalnega biomulja in pepela biomase se tvori stabilen kompozit. Raziskave so pokazale, da tako pridobljen gradbeni material s tlačno trdnostjo okoli 2 MPa lahko uporabimo na območju deponij komunalnih odpadkov za dnevne in končne prekrivke, za ureditev brežin in bankin, pa tudi kot podlago za gradnjo transportnih poti in sanacijo degradiranih območij. Tudi analiza kemične sestave izlužka iz kompozita je pokazala, da je novi kompozit inerten in kot takšen ne obremenjuje okolja. Z vidika trajnostnega razvoja je takšna rešitev optimalna, saj je rezultat predelave uporaben produkt (predelava "zero waste").

Ključne besede: komunalni biomulj, stabilizacija, pepel biomase, kompozitni gradbeni material

## **1 INTRODUCTION**

In the waste-water treatment process large amounts of biodegradable sewage sludge are produced. Sewage sludge, due to its high organic content, a presence of pathogenic bacteria, heavy metals and organic pollutants,<sup>1</sup> poses a major environmental problem. Up-to-date biodegradable sewage sludge management mainly includes composting and reuse in agriculture, recycling with anaerobic digestion or thermal treatment for energy utilization and landfilling.1 Unfortunately, the reuse of biodegradable sewage sludge in agriculture is often impossible due to the presence of bacteria and heavy metals, while energy utilization and landfilling still burden the environment. In addition, the management of different waste-ash residues is environmentally very demanding. However, some of these products were already successfully applied in the field of construction,<sup>2-5</sup> though this is not true of the ashes from biomass combustion. Alternatively, biodegradable sewage sludge and biomass ash can be treated in the same process.<sup>6</sup> By mixing waste-biomass ash and biodegradable sewage sludge, a composite construction material for specific purposes can be obtained.<sup>7</sup> From the sustainable-development point of view this presents an optimum – a zero waste solution.

### **2 EXPERIMENTAL WORK**

For assessing the mechanical properties of the composite material, cube samples  $(150 \text{ mm} \times 150 \text{ mm} \times 150 \text{ mm})$  were prepared by mixing biodegradable sewage sludge with biomass ash cooled to ambient temperature in the 1 : 1 mass ratio.

The compressive strength of the composite was determined according to SIST EN 12390-3 after (7, 14, 28, 56 and 90) d of curing the specimens in moist (100 % air moisture) and for some specimens (after 7, 28 and 56 d) also in wet conditions (submerged in water). During the mixing process the changes in the temperature and pH level were monitored. The eluate was obtained from the composite after 28 days of curing the specimens in moist conditions according to SIST EN 1744-3:2002 at the liquid/solid (L/S) ratio of 10 : 1. Inorganic parameters of the composite eluate, biomassash eluate and biodegradable sewage sludge were determined by the inductively coupled plasma mass spectrometry (ICP MS) according to SIST EN ISO 17294-2:2005, ISO 16772:2004-modif. and SIST EN ISO 10304-1:2009, respectively. The effect of stabilization on microbiological quality of the material was assessed with the aerobic mesophilic bacteria count before and after the stabilization according to the internal method of the Pulp and Paper Institute Laboratory. For this purpose samples were kept in aseptic conditions, diluted in a Ringer's solution and spread on a standard plate count agar. After a 2 d incubation period at 37 °C, a colony count was performed. To gather more information on the processes accompanying the stabilization, the mineral compositions of raw materials (sludge, ash) and composites were also determined with the X-ray powder diffraction (XRD) using a Philips PW 3710 diffractometer and Cu K(alfa) radiation. Powdered samples were scanned at a rate of 2°/min, over the range of 2-70°  $(2\Theta)$ . The results were stored on a PC and analysed by the X'Pert HighScore Plus diffraction software. In addition, selected samples were analysed with Fourier transform infrared spectroscopy (FTIR), using a Perkin Elmer Spectrum 100 spectrometer. Sixty-four signalaveraged scans of the samples were acquired. Powder pellets were pressed from the mixtures of the samples with KBr at a ratio of about 1: 200. The FTIR spectra were recorded with a spectral resolution of 4 cm<sup>-1</sup> in the range of 4000-400 cm<sup>-1</sup>.

#### **3 RESULTS AND DISCUSSION**

Biodegradable sewage sludge used in this study originates from an aerobic, biological, waste-water-treatment plant at the company VIPAP d.d., where industrial and municipal waste waters are treated. It represents a fluid component with 0.84 % of dry matter with a pH of 7.1 and conductivity of 318 mS/m. As seen in **Table 1**, concentrations of inorganic substances in the biodegra
 Table 1: Inorganic parameters of biomass-ash and composite eluates, and of biodegradable sewage sludge

 
 Tabela 1: Anorganski parametri izlužkov pepela biomase in kompozita, ter koncentracije preiskovanih parametrov v biomulju

Parameter	Biodegradable sewage sludge	Biomass ash	Composite after 28 days
pH	7.1	12.5	11.9
Conductivity (µS/cm)	3180	7370	18
Inorganic parameters	mg/L	mg/kg <sub>s.s.</sub>	mg/kg <sub>s.s.</sub>
As	0.010	< 0.02	< 0.02
Ba	1.2	59	2.7
Cd	< 0.0005	< 0.005	< 0.005
Total Cr	0.0035	< 0.01	0.016
Cu	0.19	< 0.07	0.08
Hg	< 0.01	< 0.004	< 0.01
Mo	0.0077	< 0.05	< 0.05
Ni	0.0050	0.048	< 0.01
Pb	< 0.005	< 0.05	0.066
2102416 Sb	0.0026	< 0.006	0.018
Se	< 0.001	< 0.01	< 0.002
Zn	0.58	0.12	<0.1
Cl-	44.7	25.3	15.6
F-	<1.0	4.5	<2
SO4 <sup>2-</sup>	50.6	<5	8.6

Note: mg/kgs.s. - milligram per kilogram of dry matter

dable sludge, when compared to the limit values concerning discharge of waste water,<sup>8</sup> are not environmentally problematic. The mineral composition, determined with XRD, showed that the sludge consists of calcite, quartz, dolomite and clinochlore (**Figure 1**).

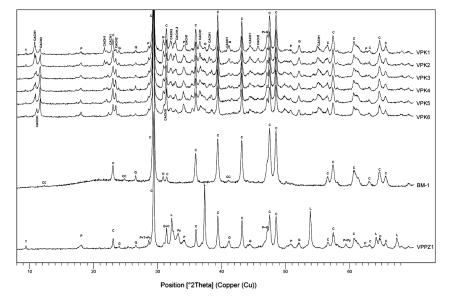


Figure 1: X-ray diffraction pattern of biodegradable sludge (BM), biomass ash (VPPZ1) and the composites after 3, 7, 14, 28, 56 and 90 days (VPK-1 to VPK-6, respectively)

 $\label{eq:legend: C-calcite, T-talc, P-portlandite, Q-quartz, L-lime, G-gehlenite, CC-clinochlor, D-dolomite, Py-pyrite; CACH1: Ca_8Al_4O_{14}CO_2*24H_2O, CACH2: Ca_4Al_2O_{14}CO_9*11H_2O, CaCh1H: Ca_4Al_2O_6Cl_2*10H_2O$ 

Slika 1: Difraktogram komunalnega biomulja (BM), pepela biomase (VPPZ1) in kompozitov po 3, 7, 14, 28, 56 in 90 dneh (VPK-1 do VPK-6) Legenda: C-kalcit, T-lojevec, P-portlandit, L-apno, G-gehlenit, CC-klinoklor, D-dolomit, Py-pirit, CACH1: Ca<sub>8</sub>Al<sub>4</sub>O<sub>14</sub>CO<sub>2</sub>\*24H<sub>2</sub>O, CACH2: Ca<sub>4</sub>Al<sub>2</sub>O<sub>14</sub>CO<sub>9</sub>\*11H<sub>2</sub>O, CaCh1H: Ca<sub>4</sub>Al<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>\*10H<sub>2</sub>O

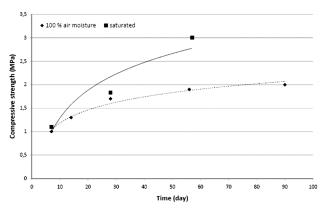
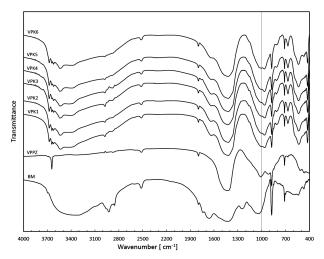


Figure 2: Compressive strength of the composite vs. the curing time Slika 2: Odvisnost tlačne trdnosti kompozita od časa negovanja

Biomass ash is a residue from a steam boiler K5 at VIPAP d.d. According to the inorganic parameters of the eluate (**Table 1**) this material is classified as a non-hazar-dous waste.<sup>9</sup>

The ash consists of free lime (CaO), portlandite  $(Ca(OH)_2)$ , gehlenite, calcite, quartz, pyrite, talc, and an amorphous phase.

In the process of mixing the biodegradable sludge and biomass ash a stable matrix is formed. As recognized experimentally, the optimum mass ratio of biodegradable sludge (liquid component) and biomass ash is 1 : 1. This ratio ensures an adequate hardening time (starting at 285 min, ending at 1140 min) and workability of the produced material. During mixing, the temperature is elevated up to about 45 °C and the pH value exceeds 12. This reduced the mesophilic bacteria count from 2.6  $\times$  10<sup>11</sup> CFU/g a. s. to 2.2  $\times$  10<sup>5</sup> CFU/g a. s., thus, the microbial activity was effectively inhibited and the obtained composite product does not pose a



**Figure 3:** FTIR spectra of biodegradable sludge (BM), biomass ash (VPPZ) and the composites after 3, 7, 14, 28, 56 and 90 days (VPK-1 to VPK-6, respectively)

Slika 3: FTIR-spekter komunalnega biomulja (BM), pepela biomase (VPPZ) in kompozitov po 3, 7, 14, 28, 56 in 90 dneh (VPK-1 do VPK-6)

Materiali in tehnologije / Materials and technology 47 (2013) 3, 349-352

health threat<sup>10</sup> when used for the intended purpose. Furthermore, analyses of the eluate from a cube sample of the composite after 28 days of moist curing (Table 1) showed, that the new composite material is inert<sup>9</sup> and, as such, environmentally acceptable. Mechanical properties, assessed with the compressive-strength determination, are time dependent (Figure 2). The compressive strength after 28 d ranged from 1.7 MPa (moist curing) to 1.8 MPa (wet curing - saturated). As seen from the compressive-strength evolution, the process of hydration was not yet completed after 28 d. The compressive strength after 57 d increased up to about 2 MPa or even up to 3 MPa (saturated). Although the qualitative mineralogical composition of the composites (Figure 1) consisted of talc, dolomite, portlandite, calcite, gehlenite and quartz, and did not change with time, we can observe that the amounts of free lime and portlandite are reduced, but the amount of calcite is increased. During the curing period new hydration products were also observed, namely, calcium carboaluminate (chloride) (CACH1), hydrates  $Ca_8Al_4O_{14}CO_2$ ×  $24H_2O$  $Ca_4Al_2O_{14}CO_9 \times 11H_2O$  (CACH2) and  $Ca_4Al_2O_6Cl_2 \times 10^{-1}$ 10H<sub>2</sub>O (CAChlH), where the CACH1/CACH<sub>2</sub> ratio is changing with the curing time. The formation of new products during the curing was also confirmed with FTIR spectra (Figure 3) that show an obvious difference when comparing the initial materials and the composites. This is especially indicated by the shift of bands in the range of 1015-1075 cm<sup>-1</sup> towards the lower wavenumbers after the stabilisation of the composite, and by the appearance of three additional bands at around  $(3675, 3621 \text{ and } 3530) \text{ cm}^{-1}$  ascribed to the newly formed hydrates.

#### **4 CONCLUSIONS**

The study showed that the stabilization process of biodegradable sewage sludge with biomass ash in a mass ratio of 1:1 effectively inhibits further microbial activity and the associated degradation. In the process a stable composite is formed with a 28 d compressive strength of about 1.7 MPa. In the process of hydration the amounts of free lime and portlandite were reduced, whereas the amount of calcite increased due to the carbonation of the composite. During this period, hydration products were generated - namely, the calcium carboaluminate hydrates. An analysis of the chemical composition of the water eluate from the composite showed that the new composite material is inert and, as such, does not pose a threat for the environment. This kind of composite can be used as a construction material mainly for landfill covers, road-shoulder management and road-base stabilization, as well as rehabilitation of degraded areas. In view of sustainable development the described wasteresidue management presents an optimum - a zero waste solution.

P. PAVŠIČ et al.: SEWAGE-SLUDGE STABILIZATION WITH BIOMASS ASH

#### **5 REFERENCES**

- <sup>1</sup> V. Grilc, G. D. Zupančič, M. Roš, Alternativni načini sodobnega ravnanja z odvečnim blatom iz bioloških čistilnih naprav, Zbornik referatov / [Simpozij z mednarodno udeležbo] Vodni dnevi, Portorož, 2006, 99–109
- <sup>2</sup> H. K. Lam, J. P. Barford, G. McKay, Utilization of incineration waste ash residues as Portland cement clinker, Chemical Engineering Transactions, 21 (2010), 757–762
- <sup>3</sup> M. A. Daous, Utilization of Cement Kiln Dust and Fly Ash in Cement Blends in Saudi Arabia, JKAU: Eng. Sci., 15 (**2004**) 1, 33–45
- <sup>4</sup> M. M. Al Bakri, H. Mohammed, H. Kamarudin, I. Khairul Niza, Y. Zarina, Review on fly ash-based geopolymer concrete without Portland Cement, Journal of Engineering and Technology Research, 3 (2011) 1, 1–4
- <sup>5</sup> D. J. White, Fly Ash Soil Stabilization for Non-Uniform Subgrade Soils, Volume I: Engineering Properties and Construction, Guidelines (IHRB Project TR-461, FHWA Project 4), Iowa Highway Research Board, Federal Highway Administration, 2005

- <sup>6</sup> F. Černec, J. Zule, Stability properties of biosludge-wood ash composites, International Conference Waste Management, Environmental Geotechnology and Global Sustainable Development (ICWMEGGSD'07 - GzO'07), Ljubljana, 2007
- Available from World Wide Web: http://www.srdit.si/gzo07/papers/ 97FCernec\_FinalPaperGzO07.pdf
- <sup>7</sup> P. Pavšič, Poročilo o rezultatih raziskav biomulja stabiliziranega z ostanki gorenja kotla K5 v družbi VIPAP, PMA d.o.o., 2011
- <sup>8</sup> Uredba o emisiji snovi in toplote pri odvajanju odpadnih voda v vode in javno kanalizacijo, Uradni list RS, 2007, 45
- <sup>9</sup> Uredba o odlaganju odpadkov na odlagališčih, Uradni list RS, 2011, 61
- <sup>10</sup> T. Rupel, T. Pavlica, P. Planina, J. Vidrih, S. Glas, T. Car, L. Kobola, M. Lušicky, D. Bošnjak, D. Sabotin, Smernice za mikrobiološko varnost živil, ki so namenjena končnemu potrošniku, IVZ RS, 2005 Available from World Wide Web: http://www.mz.gov.si/fileadmin/ mz.gov.si/pageuploads/mz\_dokumenti/zakonodaja/varnost\_hrane/pes ticidi/smernice\_za\_mikrobiolo\_ko\_varnost\_\_ivil.pdf