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# THE INFLUENCE OF DIFFERENT WASTE ADDITIONS TO CLAY-PRODUCT MIXTURES

## VPLIV RAZLIČNIH ODPADKOV NA IZHODNO SUROVINO ZA PROIZVODNJO OPEČNIH IZDELKOV

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The potential use of four different wastes in the clay-based industry has been studied. The selected wastes were: stone mud from the stone-processing industry, paper mud, sawdust, and sludge from the polishing process for silicate igneous rocks. Waste, depending on its composition, can be used as i) an opening agent, when it contains a large amount of silica or ii) a pore-forming agent, when it contains combustible materials.

Mixtures of clay and different amounts of selected waste (up to the mass fraction of 50 %) were prepared. The influence of the addition of different wastes on drying and firing shrinkage was determined, as well as the water absorption, bulk density, bending and compressive strengths of fired samples.

We found that the addition of paper mud and sawdust improves the drying process by reinforcing the clay body structure, which counteracts cracking. It also significantly improves the thermal insulation properties. Additions of silica stone mud, as well as granite polishing sludge act as opening agents, which decrease the deformability of green as well as fired specimens.

Using waste in the production of clay-based products could represent a quite significant decrease in costs due to the replacement of basic raw materials with waste, and in some cases also the significant improvement of the quality of the final product.

Key words: industrial waste, paper mud, sawdust, polishing sludge, silica stone mud, clay products

V prispevku so predstavljene možnosti uporabe štirih različnih industrijskih odpadkov v opečni industriji, in sicer kremenov mulj, papirni mulj, žagovina in odpadek, ki nastaja pri poliranju silikatnih magmatskih kamnin. Odpadke glede na sestavo lahko dodajamo kot dodatke, ki povečujejo odprto poroznost, kadar vsebujejo večje količine kremena oziroma kadar vsebujejo organske komponente, ki zgorijo med žganjem, kot dodatke za povečevanje celotne poroznosti.

Pripravili smo mešanice gline in izbranih odpadkov (do masnega deleža 50 %). Določili smo vpliv teh dodatkov na skrčke pri sušenju in žganju ter na vpijanje vode, gostoto, upogibno in tlačno trdnost žganih izdelkov. Ugotovili smo, da dodatek papirnega mulja in žagovine izboljša proces sušenja, saj učvrsti strukturo nežganih proizvodov in tako preprečuje nastanek razpok. Prav tako znatno izboljša toplotno-izolacijske karakteristike opečnega izdelka. Kremenov mulj in odpadek pri poliranju granita sta dodatka, ki povečujeta odprto poroznost in zmanjšujeta skrčke pri sušenju in žganju in s tem možnost nastanka deformacij žganih proizvodov.

Uporaba odpadkov v opekarski industriji lahko pomeni znatno znižanje stroškov zaradi delne zamenjave osnovne surovine z odpadnim materialom; prav tako lahko v določenih primerih odpadki izboljšajo kakovost končnega proizvoda.

Ključne besede: industrijski odpadki, papirni mulj, žagovina, polirni odpadki, kameni mulj, opečni proizvodi

## 1 INTRODUCTION

Different industrial wastes could be quite successfully used in the clay-based industry; some of them have a positive effect on the process and/or on the final properties, others are simply used to replace the basic raw material and lower the cost of the production.

In this investigation four different industrial wastes were checked for their usability in the clay-based industry: silica stone mud from the stone-processing industry, paper mud, sawdust, and granite-like polishing sludge.

The sawdust is a by-product of freshly felled timber and therefore contains no solvents, adhesives or other components. Papermaking sludge is a residue in the paper industry, which mainly consists of paper fibres, kaolin, lime and water. The fibrous structure of both wastes has a favourable influence on the stability of the freshly extruded green ware during drying and so counteracts cracking. Besides a favourable effect on the process parameters, sawdust and paper-making sludge are combustible and they can be used as pore-forming agents. Products with increased porosity have better thermal insulation properties[1-5].

Silica stone mud is a secondary material that remains after the screening of stone aggregate in quarries. It contains a large amount of very fine silica sand, feldspar and clay. Waste granite-like mud is a residue material of polishing operations in the natural stone industry. It contains very fine particles of silicate igneous rocks and a residue of the grinding abrasives. Both wastes could be used as a filler (opening agent) in the clay-based industry due to the large amount of very fine silica sand, which decreases the plasticity of the clay and reduces its shrinkage on drying and firing[6-10].

In order to study the influence of selected waste materials on the production and final properties of clay bricks, different mixtures of clay and waste were prepared (see **Tables 1, 2, and 3** for the composition of the individual mixtures).

## 2 EXPERIMENTAL

### *2.1 Raw materials and test mixtures*

#### 2.1.1 Brick-making clay A

Clay taken from the production of masonry bricks from the eastern part of Slovenia was used. The clay can be classified as the chlorite-illitic type, with traces of montmorillonite and around the mass fraction $w$ = 38 % of quartz. The grain size distribution is as follows (in mass fractions): 18.1 % > 20 μm; 36.0 % 2–20 μm, and 45.8 % < 2 μm.

#### 2.1.2 Brick-making clay B

Clay taken from the production of masonry bricks from the southern part of Slovenia was used. The clay can be classified as chlorite-illitic type, with around $w$ = 23 % of quartz. The grain size distribution is as follows (in mass fractions): 22.5 % > 20 μm, 40.0 % 2–20 μm, and 37.5 % < 2 μm.

#### 2.1.3 Papermaking sludge

The papermaking sludge used was in the form of filter cake, with a water content of approximately $w$ = 52 %. It consists of the following inorganic components: calcite, kaolinite and illite. The loss on ignition at 500 °C is $w$ = 24 % and at 900 °C it is $w$ = 48 %.

#### 2.1.4 Sawdust

The sawdust was chopped to pieces of around 1 mm: 11.7 % of the particles were ≥ 1 mm, 76.7 % of the particles were between 1 mm and 0.2 mm, and 11.6 % of the particles were < 0.2 mm. The water content was 19.7 %. Sawdust consists of 99 % combustible substances. The loss on ignition at 500 °C was 98 % and at 900 °C it was 98.6 %.

#### 2.1.5 Silica stone mud

The waste silica mud contained about 35 % of quartz, the rest is clay and feldspar. It had the following grain size distribution in mass percent: 16.5 % > 20 μm, 34.9 % 2–20 μm, and 48.6 % < 2 μm. Silica stone mud also contains the swelling mineral montmorillonit.

#### 2.1.6 Granite-like polishing mud

The waste granite polishing mud contained about 30 % quartz; the rest is clay, feldspars, carbonates and a residue of SiC polishing tools. It had the following grain size distribution in weight percentage: 8.4 % > 20 μm, 75.3 % 2–20 μm, and 16.3 % < 2 μm.

### *2.2 Shaping, drying and firing of the test specimens*

The test specimens were shaped in a laboratory de-airing extruder at a vacuum of about 80 %, i. e., 20 kPa. During extrusion, a proper amount of water was added to the mixtures to avoid surface cracks on the test

**Table 1:** Mixtures of clay, papermaking sludge and sawdust and the average properties of laboratory-made test specimens
**Tabela 1:** Mešanice gline, papirnega mulja in žagovine ter pripadajoče lastnosti laboratorijsko pripravljenih vzorcev

| MIXTURE | A1 | A2 | A3 | A4 | A5 | A6 | A7 |
|---|---|---|---|---|---|---|---|
| Clay content – clay A ($\varphi$/%) | 100 | 90 | 80 | 70 | 70 | 70 | 80 |
| Sawdust ($\varphi$/%) | | 10 | 20 | 30 | | 10 | 15 |
| Papermaking sludge ($\varphi$/%) | | | | | 30 | 20 | 5 |
| Shaping | | | | | | | |
| Water content based on dry mass ($w$/%) | 26.9 | 28.4 | 29.3 | 34.7 | 34.5 | 33.8 | 30.2 |
| Water content based on wet mass ($w$/%) | 21.2 | 22.1 | 22.6 | 25.7 | 25.7 | 25.2 | 23.2 |
| Shrinkage after drying (%) | | | | | | | |
| Measured along the prism length | 7.7 | 6.8 | 6.5 | 7.2 | 8.6 | / | 7.1 |
| Measured across the prism width | 6.4 | 6.5 | 6.4 | 7.5 | 9.6 | / | 6.7 |
| Firing temperature (°C) (±15) | 850 | 850 | 920 | 920 | 920 | 910 | 920 |
| Body density after firing (kg/dm$^3$) | 1.81 *1.85 | 1.69 | 1.65 | 1.44 | 1.59 | 1.58 | 1.63 |
| Water absorption (%) | 16.7 | 19.6 | 21.5 | 30.5 | 24.9 | 25.3 | 22.2 |
| Compressive strength (MPa) | | | | | | | |
| Prisms | 23.9 | 17.4 | 19.0 | 10.7 | 29.3 | 23.0** | 23.4 |

* fired at 920 °C, ** measured on cylinder / not determined

**Table 2:** Mixtures of clay and silica stone mud and average properties of laboratory-made test specimens
**Tabela 2:** Mešanice gline in kremenovega mulja ter pripadajoče lastnosti laboratorijsko pripravljenih vzorcev

| MIXTURE | B1 | B2 | B3 | B4 |
|---|---|---|---|---|
| Clay content – clay B ($w$/%) | 100 | 70 | 50 | 0 |
| Silica stone mud ($w$/%) | 0 | 30 | 50 | 100 |
| Shaping | | | | |
| Water content based on dry mass ($w$/%) | 25.1 | 31.6 | 30.0 | 52.9 |
| Water content based on wet mass ($wt$/%) | 20.0 | 23.1 | 23.1 | 34.6 |
| Shrinkage after drying (%) | | | | |
| Measured along the prism length | 8.4 | 10.5 | 11.6 | 15.4 |
| Measured across the prism width | 7.3 | 8.8 | 11.2 | 15.6 |
| Firing at temperature (°C) (±15) | 900 | 900 | 900 | 900 |
| Shrinkage after firing (%) | | | | |
| Measured along the prism length | 1.4 | 0.9 | 1.2 | 1.6 |
| Measured across the prism width | 1.2 | 1.1 | 1.4 | 1.4 |
| Body density after firing (kg/dm$^3$) | 1.96 | 1.90 | 1.86 | 1.79 |
| Water absorption (%) | 9.2 | 10.6 | 12.5 | 16.8 |
| Clinker point | | | | |
| Temp. of firing where water absorption amounts to $w$ = 6 % | 1017 | 1029 | 1042 | 1095 |
| Bending strength (MPa) | | | | |
| Measured on prisms | 22.0 | 20.7 | 20.0 | 6.3* |
| Compressive strength (MPa) | | | | |
| Measured on prisms | 62.5 | 52.5 | 50.7 | /* |

*cracks visible before testing

**Table 3:** Mixtures of clay and granite stone mud and average properties of laboratory-made test specimens

**Table 3:** Mešanice gline in odpadka od poliranja granite ter pripadajoče lastnosti laboratorijsko pripravljenih vzorcev

| MIXTURE | C1 | C2 | C3 | C4 | C5 |
|---|---|---|---|---|---|
| Clay content – clay B (*w*/%) | 100 | 95 | 90 | 80 | 70 |
| Granite like stone mud (*w*/%) | 0 | 5 | 10 | 20 | 30 |
| Shaping | | | | | |
| Water content based on dry mass (*w*/%) | 26.1 | 27.0 | 28.3 | 32.6 | 34.6 |
| Water content based on wet mass (*w*/%) | 20.7 | 21.3 | 22.1 | 24.6 | 25.7 |
| Shrinkage after drying (%) | | | | | |
| Measured along the prism length | 8.7 | 8.5 | 9.5 | 9.8 | 9.3 |
| Measured across the prism width | 7.5 | 6.6 | 7.6 | 8.7 | 7.8 |
| Firing at temperature (°C) (±15) | 915 | 915 | 915 | 915 | 915 |
| Body density after drying (g/cm$^3$) | 2.05 | 2.02 | 1.98 | 1.88 | 1.80 |
| Shrinkage after firing (%) | | | | | |
| Measured along the prism length | 1.0 | 1.5 | 1.4 | 1.5 | 1.3 |
| Measured across the prism width | 1.1 | 1.5 | 1.4 | 1.7 | 1.4 |
| Body density after firing (g/cm$^3$) | | | | | |
| Measured on prisms | 2.00 | 1.96 | 1.92 | 1.84 | 1.76 |
| Water absorption after firing (%) | | | | | |
| Measured on prisms | 8.8 | 9.6 | 10.7 | 12.8 | 16.6 |
| Clinker point | | | | | |
| Temp. of firing where water absorption amounts to $w$ = 6 % | 1008 | 1022 | 1037 | 1045 | 1052 |
| Bending strength (MPa) | | | | | |
| Measured on prisms | 16.1 | 15.6 | 16.7 | 13.5 | 10.4 |
| Compressive strength (MPa) | | | | | |
| Measured on prisms | 86.2 | 77.6 | 78.5 | 71.7 | 62.4 |

specimens and to maintain a Pff number of 1.4 (±0.1) – see **Tables 1, 2, and 3**.

The test specimens were dried for 7 d in ambient room conditions, followed by 24 h at 60 °C and 8 h at 100 °C in a dryer. The dried samples were then fired for 4 h in a laboratory kiln at selected temperatures using heating rates of 80 °C/h up to 400 °C, and 50 °C/h between 400 °C and the final temperature. These firing conditions are similar to those generally applied in the brick-making industry.

## 2.3 Test methods

The particle size distribution of the tested clays was determined by sieving it down to 90 μm. Below 90 μm, the sedimentation method was applied using a Quantachrome Microscan II apparatus. The Quantachrome Microscan II apparatus was also used to determine the particle size distribution of the silica stone mud and the granite polishing mud.

The mineral components of both clays and both stone wastes were determined by X-ray diffractometry using a Phillips Norelco apparatus.

The linear shrinkage, ceramic body density, water absorption (by boiling test specimens in water for 2 h), and compressive strength were determined on fired samples of (160 × 50 × 25) mm prisms.

The pore size and the pore size distribution were measured using Hg porosimetry. The maximum pressure when filling was 206,843 kPa, $\theta$ 130° and $\gamma$ 485 · 10$^{-5}$ N/cm.

## 3 RESULTS AND DISCUSSION

### *3.1 The addition of sawdust and papermaking sludge*

The properties related to shaping, drying and firing are listed in **Table 1**. The shaping parameter (i.e., the water content) shows that with the additions of pore-forming agents, more water should also be added to mixtures to avoid surface cracks during shaping. The shrinkage after drying is reduced with the addition of sawdust; most significantly for the specimen with the volume fraction of 20 % of sawdust, where the shrinkage after drying is 6.5 % in comparison to pure clay, where the shrinkage is 7.7 % (specimen A1). In contrast, the shrinkage after drying with the addition of papermaking sludge is increased to 8.6 % when the volume fraction of 30 % of the papermaking sludge is added. The decrease in the drying shrinkage is favourable because it reduces the danger of cracking during drying.

In **Figure 1** the firing analysis from the gradient kiln is presented for pure clay and the mixture A5 containing the mass fraction of 30 % of paper-making sludge. It is clear that the sludge addition increases the water absorption of the specimen, which is to be expected due to its pore-forming action. The shrinkage after firing is lower for the specimen with the sludge, which is a favourable effect since it contributes to the dimensional stability during firing.

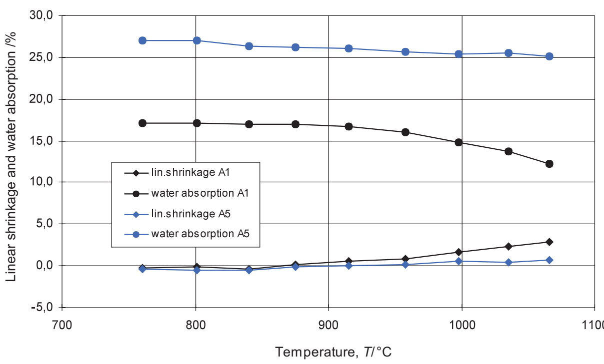


**Figure 1:** Determination of the effect of firing temperature on the linear shrinkage and water absorption by firing in a gradient kiln for samples A1 and A5

**Slika 1:** Vpliv temperature žganja na skrček in vpijanje vode (žganje v gradientni peči) vzorcev A1 in A5

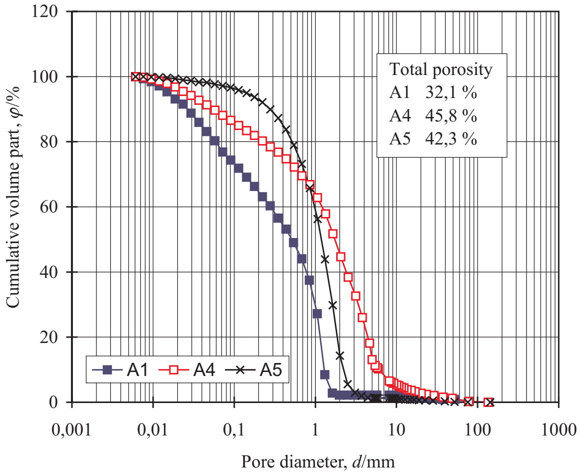


**Figure 2:** Pore size distribution for samples A1, A4, and A5
**Slika 2:** Porazdelitev velikosti por vzorcev A1, A4 in A5

After firing the body density is significantly reduced with the addition of pore-forming agents, especially when sawdust is added. The density of sample A4 with 30 % of added sawdust is 1.44 kg/dm$^3$, whereas the density of the clay without additives is 1.85 kg/dm$^3$. The distribution of the porosity for samples A1, A4, and A5 is presented in **Figure 2**. In the case of clay without additives (mixture A1) the pore size distribution is uniform. The total porosity in the volume fraction is 32.1 % and over 95 % of the pores are smaller than 3 μm. The addition of sawdust (A4) creates larger pores, where 35 % of the pores are larger than 3 μm and the total porosity is 45.8 %. The addition of papermaking sludge (A5) influences the formation of finer pores, where with a total porosity of 42.3 % over 95 % of the pores are smaller than 3 μm.

The reduction in density also influences the compressive strength: from 23.9 MPa for pure clay (fired at 850 °C) to 10.7 for the specimen with 30 % of sawdust. From comparisons of the compressive strengths for specimens A4 and A5 (30 % of sawdust and 30 % of papermaking sludge, respectively), as well as A6 and A7, both with the addition of pore-forming agents, it is clear that with the addition of papermaking sludge, an increase in the compressive strength is observed. This was ascribed to the presence of calcite in the papermaking sludge, as already described in the literature, where it was observed that the addition of 15 % of calcite increases the compressive strength of the clay body by up to 40 %, and at the same time it practically doubles the bending-tensile strength[11].

As previously described[4], the optimal results regarding shrinkage, compressive strengths and body density after firing are obtained with a combination of both pore-forming agents.

### 3.2 The addition of silica stone mud

The properties of the clay mixture with silica stone mud are presented in **Table 2**. Mixtures with silica stone

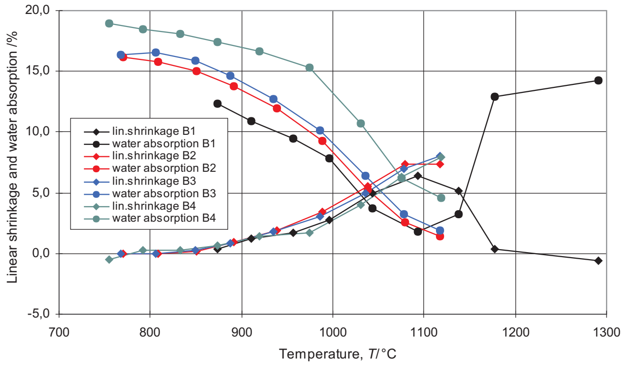


**Figure 3:** Determination of the effect of firing temperature on the linear shrinkage and water absorption by firing in a gradient kiln for samples of series B
**Slika 3:** Vpliv temperature žganja na skrček in vpijanje vode (žganje v gradientni peči) vzorcev serije B

mud that contain swelling minerals required quite a large content of water for proper shaping. The requirement for a larger amount of water is generally discouraging because this water should be removed in the drying process and this consequently increases the shrinkage after drying: from 8.4 % for pure clay to 15.4 % for pure silica stone mud. A high shrinkage introduces cracks into the green body, which was observed in specimen B4. This sample was prepared from pure silica stone mud, and the water content required for the extrusion amounted to 52.9 %.

From **Figure 3**, which presents the firing analysis in a gradient kiln, it is clear that the addition of mud significantly influences the water absorption's dependence on firing temperature, but only slightly influences the shrinkage after firing. The compressive strength of the fired specimen decreases with the silica stone mud additions, from 62.5 MPa for pure clay to 50.7 MPa when 50 % of silica stone mud is added.

### 3.3 The addition of granite-like stone mud

The properties of the clay mixtures with granite-like polishing waste are presented in **Table 3**. Mixtures with

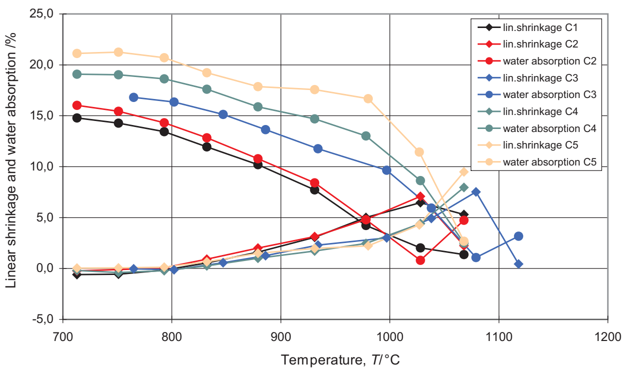


**Figure 4:** Determination of the effect of firing temperature on the linear shrinkage and water absorption by firing in a gradient kiln for samples of series C
**Slika 4:** Vpliv temperature žganja na skrček in vpijanje vode (žganje v gradientni peči) vzorcev serije C

waste additions require more water for proper shaping and consequently the linear shrinkage after drying increases from 8.7 % for the mixture without granite-like stone mud to 9.3 % for the mixture containing the mass fraction of 30 % mud. The effect is not pronounced for mixtures with up to 10 % of mud addition.

The firing analysis in a gradient kiln showed that the addition of mud significantly increased the water absorption and that it reduced the shrinkage of the basic clay (**Figure 4**). The addition of mud increased the water absorption of the test specimens and decreased their body density and compressive strength after firing. The decrease in mechanical properties is more significant with a larger amount of mud, when for samples containing up to 10 % of mud addition only a slight decrease in mechanical properties can be observed.

## 4 CONCLUSIONS

Many wastes, depending on their properties and the type of clay, can be successfully used in the brick-making industry. The clay designated as A contains traces of the swelling mineral montmorillonite, which contributes to the sensitivity to cracking of the products on drying. The addition of sawdust and papermaking sludge to brick-making clay favourably influences the process of shaping and drying due to the fibrous structure, which strengthens the green body and prevents the final products from cracking on drying. The addition of sawdust greatly increases the porosity of the fired body and therefore also significantly reduces the compressive strength. Papermaking sludge additions slightly increase the porosity and at the same time introduce finer pores, whose distribution is more homogeneous, thus lowering the compressive strength only slightly. At the same time, if paper sludge contains calcite, which is the case here, it contributes to an improvement in the mechanical properties of the fired clay products. With the optimal combination of paper-making sludge and sawdust (the amount of both wastes in the volume fraction is up to 30 % ) porous clay products can be achieved with almost the same mechanical properties as for the basic brick-making clay.

The addition of silica stone mud that contains the swelling mineral montmorillonite requires a larger amount of water for shaping than the basic clay, and this amount of water will evaporate during the process of drying, which can introduce cracks into the green product. The use of such a stone mud is therefore limited. If silica stone mud was used in the clay-based industry anyway, great attention should be paid to the drying phase in order to avoid cracks.

Granite-like polishing waste facilitates shaping, but it also makes the basic clay more sensitive to drying, especially when a larger amount is added. It also decreases the mechanical properties of the products. Both effects are not so pronounced when up to the mass fraction of 10 % of mud is added.

The use of different wastes in the clay-based industry can have, in some cases, a positive impact on the final properties of clay products. In other cases it can be used as a substitute for basic raw materials, which can contribute to a significant saving in natural resources, and at the same time to a reduction in the amount of landfill

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