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Influence of thermal treatment and combustible additives on properties of Latvian clay ceramics pellets[#]

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Abstract

Porous ceramic pellets for possible environmental application were produced from different Latvian clays by sintering at different temperatures. Their characteristics and influence of additives were analysed using X-ray diffraction, mercury porosimetry and BET tests. The obtained ceramic pellets from calcareous clays after immersion in distilled water change its pH value, which affects their capability to adsorb ions or molecules on the surface. The sorption capabilities are dependent on the pH level of water solution, composition of clays, and used adsorbate. Porosity of the produced pellets is mostly within range from 15 to 25 % throughout all sintering temperatures with a slight decrease at 1050 °C. The specific surface area has a wide range up to 30 m^2/g. The highest surface area has pellets sintered at lower temperatures. The adsorption capability of pellets was evaluated using water solutions with different ions. The most promising results were obtained with iodine sorption. For most pellets the sorption capacity was 12.7 mg/g, although for the pellets sintered at 1050 °C it was lower.

***Keywords**: clays, porous materials, sintering, sorption*

I. Introduction

The need for sufficient materials, which can be used for environmental applications, is growing, with increasing manufactured amount of waste water in the world. Many different technologies have been used for water purification - biological, chemical and physical. Among them adsorption on different types of materials, such as activated carbons, modified clays, zeolites, TiO_2, have been investigated all around the world [1–4]. However, still the industry is still searching for new materials.

Porous ceramic materials produced from clays show high porosity and specific surface area [5–7]. These properties are significant for adsorption of ions and can determine whether the ceramic material could be used for water purification or not. Clay-based ceramic materials show good adsorption properties towards volatile organic compounds, organic dyes, heavy metals (such as lead, cadmium and chromium), and also fluoride, phosphorous, nitrogen, ammonia and many other compounds from gaseous and liquid phases [7–10]. These sorbents can be produced both in granular form and as membranes.

II. Experimental

For laboratory scale production of ceramic pellets five clays from four deposits (Liepa, Laza, Planci, and Progress) were used. These clays have different mineral composition and grain size distribution [11]. They have been formed in the Devonian and Quaternary periods and are divided into non-calcareous (Liepa and Planci 2) and calcareous clays (Laza, Progress, Planci 1), respectively.

Sawdust (size < 2 mm) or chopped straw (size 2–5 mm) was added to clays to observe their influence on porosity and surface area of ceramic pellets. The green ceramics pellets were prepared from plastic paste and their compositions are given in Table 1.

To observe the influence of thermal treatment on the microstructure of the obtained ceramic pellets different sintering temperatures were chosen taking into account previously reported differential thermal analysis [12]. The green pellets were sintered at 700, 800, 900

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Table 1. Content of additives in prepared pellets

Ceramic pellets	Sawdust [wt.%]	Straw [wt.%]
Laza 1	3	0
Laza 2	0	3
Laza 3	0	0
Liepa	3	0
Planci 1	3	0
Planci 2	3	0
Progress 1	0	0
Progress 2	3	0
Progress 3	5	0

and 1050 °C. These temperatures describe stages of the most important mineralogical changes in the clay material. Phase analyses for all samples with 3% sawdust addition and each sintering temperature were conducted using powder X-ray diffraction analysis with Rigaku Ultima+ diffractometer (Cu Kα).

The sintered pellets were immersed into distilled water to investigate their influence on change of pH value. Measurement of pH after immersing was conducted using pH-meter Mettler Toledo Multi Seven™ with electrode Mettler Toledo InLab® 415 and integrated temperature sensor Pt1000. These measurements were conducted for all produced ceramic pellets.

Porosity and surface area of the sintered ceramic pellets were evaluated with mercury porosimetry using Quantachrome porosimeter PoreMaster and with Brunauer-Emmett-Teller (BET) tests using Quantachrome Instrument NOVA 1200 e.

To determine environmental applicability of investigated pellets sorption experiments were conducted using three water solutions: 0.01 n I_2, 0.03 n NH_4OH and 1 wt.% $K_2Cr_2O_7$. The test was performed on 20 g of the pellets which were added into 100 ml of the solution and kept in dark for 21 days.

III. Results and discussion

Main clay mineral in Latvian clays is illite. In addition, all of the investigated clay ceramics contain quartz, which is commonly found in clay samples. In calcareous clays dolomite and calcite is detected. Changes of mineralogical composition and phase tran-

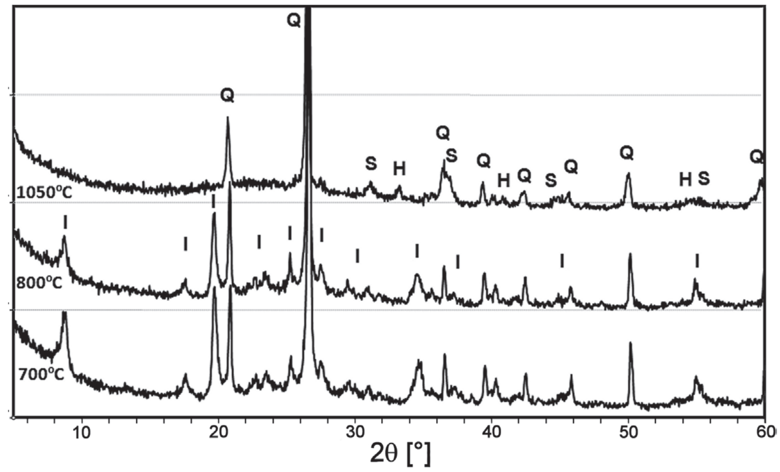


Figure 1. XRD diagram for Liepa ceramic pellets. I – illite, Q – quartz, S – spinel, H – hematite

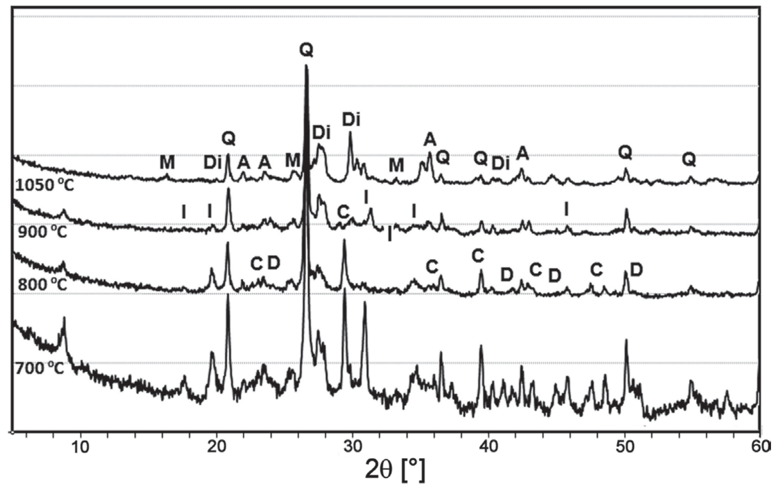
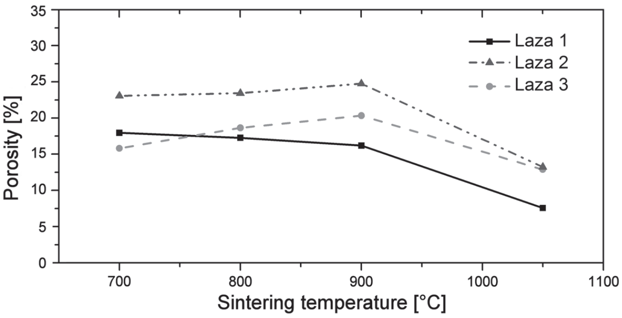


Figure 2. XRD diagram for Progress 1 ceramic pellets. I – illite, C – calcite, D – dolomite, Q – quartz, Di – diopside, A – anorthite, M – mullite

sitions of the Liepa and Progress clays can be seen in Figs. 1 and 2, respectively. XRD patterns of the clays Laza and Planci 1 are similar to the pattern of the clay Progress, whereas the Planci 2 has similar composition like the clay Liepa. At 800 °C decomposition of calcite and dolomite starts to take place and CO_2 gas is released. This process ends at 900 °C. As a product of this decomposition CaO is formed, which is bounded afterwards into structures of new crystalline phases. In the presence of calcareous minerals at 900 °C and higher temperature anorthite and diopside are formed (Fig. 2). In the case of the non-calcareous clays this transformation leads to formation of spinel (Fig. 1). At 1050 °C traces of mullite are also detected. Hematite gives the specific red colour of the non-calcareous clay ceramics.



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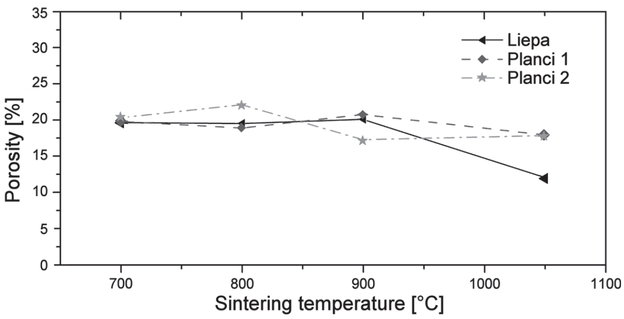
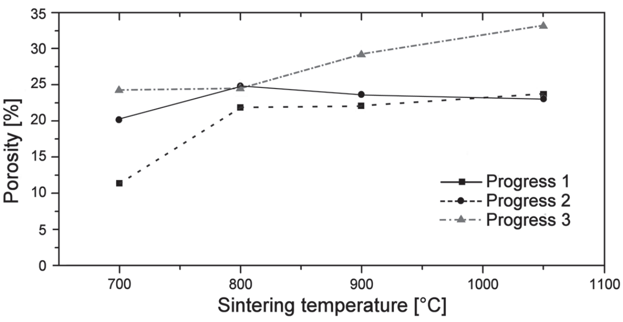


b)

Figure 3. Porosity of ceramic pellets prepared from clays: a) Laza and b) Liepa and Planci



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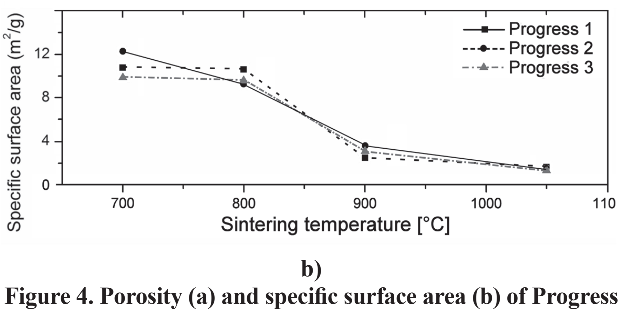

b)

Figure 4. Porosity (a) and specific surface area (b) of Progress ceramic pellets with different amount of sawdust

The sintered pellets were immersed into distilled water and the change of the pH value was measured. From the pH measurement it can be concluded that part of the investigated pellets shown increased pH level in water. These ceramic pellets are produced from the calcareous clays from the Laza and Progress deposits. Higher pH value is also observed for the Planci 1 clay ceramic pellets. Although Planci 1 are the Devonian clays, they contain traces of calcite and dolomite (<7%). Calcareous minerals and CaO, which are formed during decomposition of calcite and dolomite, are responsible for such increased pH. CaO is not completely bounded in new crystalline phases till sintering temperature is raised up to 1050 °C and in the presence of moisture and water it forms $Ca(OH)_2$. pH values for the Laza and Progress ceramic pellets sintered at 700–900 °C are in range from 9.8 to 10.7 but for the pellets sintered at 1050 °C it drops to neutral level, because no carbonates or CaO are left unbounded. At the same time ceramic pellets from the non-calcareous Liepa and Planci 2 clays show neural pH level at all sintering temperatures and range from 6.2 to 7.5.

Using either sawdust or straw as pore forming additives and altering added amount of saw dust different results were obtained. Porosity results from mercury porosimetry show that for the most of the investigated ceramic pellets they are in range of 15 to 25% (see Fig. 3). A decrease of the values at 1050 °C is easily explainable with densification of ceramic material. The Progress 3 pellets with 5 wt.% of sawdust show increased porosity over 30% as a combined result of decomposition of calcareous minerals and combustion of organic additives.

The obtained values of specific surface area from mercury porosimetry and BET tests differ (Table 2) due to the fact that BET tests take into account pores which have smaller size, whereas mercury porosimetry can detect pores with larger diameters. Still both of these methods portray the same tendency with increasing sintering temperature, specific surface area decreases. The lowest specific surface area for all investigated pellets is obtained for the pellets sintered at 1050 °C in the presence of liquid phase. It decreases even below 4 m^2/g.

The influence of adding the sawdust to change the porosity properties and specific surface area can be seen on the samples made from the Progress clays (see Fig. 4). With increased content of sawdust at the same sintering temperature porosity is raising and specific surface area is decreasing. Combustion of sawdust occurs at around 400 °C and it gives the primary porosi-

Table 2. Specific surface area (SSA) of ceramic pellets

Ceramic pellets	Sintering temperature [°C]	Mercury porosimetry SSA [m²/g]	BET SSA [m²/g]
Liepa	700	17.8	26.94
	800	20.21	20.69
	900	14.18	2.09
	1050	3.01	0.35
Planci 2	700	9.61	15.80
	800	9.2	13.94
	900	2.49	1.73
	1050	0.22	0.06
Laza 1	700	30.89	24.74
	800	16.21	7.23
	900	6.07	1.48
	1050	2.67	0.05
Progress 2	700	12.29	0.49
	800	9.32	4.82
	900	3.63	1.22
	1050	1.56	0.69

ty. At 700 °C clear correlation between the amount of sawdust and porosity can be seen. For these pellets porosity is influenced only by amount of sawdust. When the decomposition of calcite and dolomite set in, the difference between these three pellets is almost nonexistent. At 900 °C porosity for the pellets with 5 wt.% sawdust addition raises above 30% due to fusion of smaller pores, but specific surface area stays almost the same for all three pellets. With regards to the specific surface area it can be seen that the highest values are shown by pellets sintered at 700–800 °C. This means that at higher sintering temperatures porosity

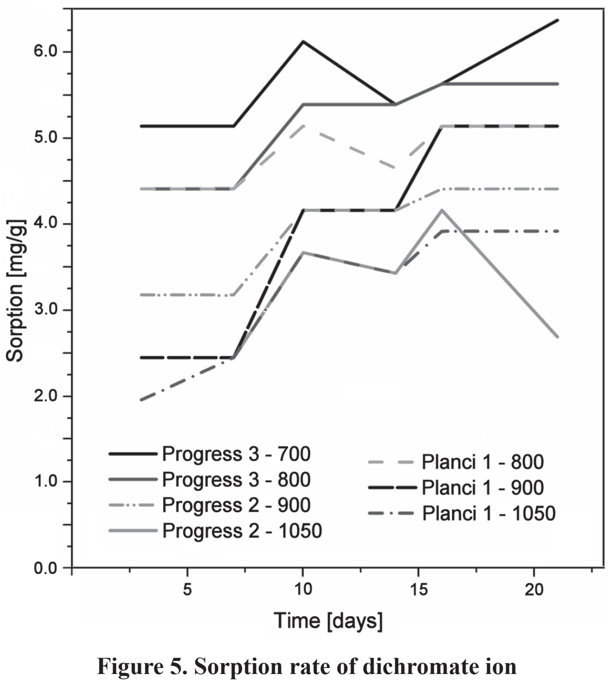

Figure 5. Sorption rate of dichromate ion

increases due to the growth of pore size while it happens due to released gas phase. At the same time this growth noticeably decreases the specific surface area.

With addition of straw, larger pellets were produced due to the size of straw chips. In this case porosity is mostly affected by combustion of straw and rather than decomposition of carbonates as it is in case of sawdust addition. The obtained data from mercury porosimetry show that porosity for these pellets is for about 6–8% higher throughout all sintering temperatures comparing with data for the pellets with sawdust.

The results from sorption experiments vary considerably depending on the solution used. The most promising results were obtained from iodine adsorption experiments. The initial amount of iodine in the solution was 12.7 mg/g. Complete adsorption was achieved by most of the investigated ceramic pellets already after one week. Such results were shown by all Progress, all Laza, and Planci 1 pellets sintered at 700–900 °C. It is significant to note that these pellets have higher porosity and specific surface area. The Liepa and Planci 2 ceramic pellets and ceramic pellets sintered at 1050 °C showed lower adsorption capacity ranging from 9.78 to 12.38 mg/g and was reached in longer time period 14–21 days. However, these results are still higher than 77%.

In experiments with adsorption of other solutions, the obtained results were noticeably inferior in comparison to the iodine adsorption. The sorption capacity of dichromate ions ranges from 0.98 to 6.37 mg/g (Fig. 5). In this case ceramic pellets reached limit of only 14.5% of the initial amount of dichromate ions in the solution. The investigated pellets can be again divid-

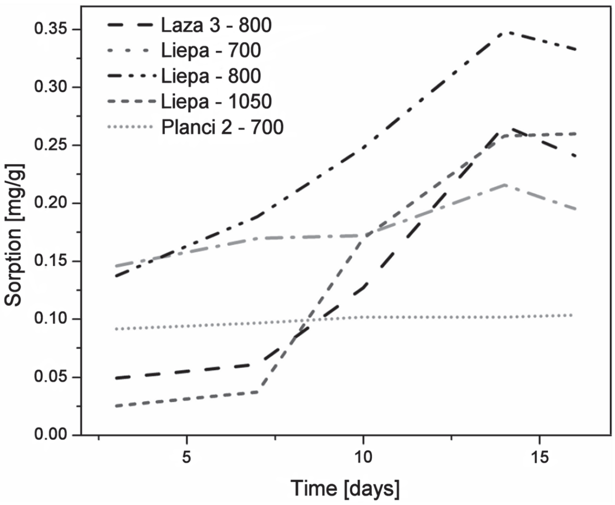

Figure 6. Sorption rate of ammonia ion

ed into two groups regarding time period after which the maximum adsorption rate was reached. In the case of all Progress and both Planci ceramic pellets their adsorption limit was reached after 16–21 days. These pellets also adsorbed higher amount of dichromate ion than others, i.e. over 3.18 mg/g. 4–7 days were required for the Liepa and Laza ceramic pellets to reach their maximum, which was below 4.32 mg/g. The best results in all cases were again obtained for the pellets sintered at 700–900 °C.

In the case of ammonia solution the results were even lower reaching maximum of only 7.5%, which corresponds to 0.35 mg/g (see Fig. 6). Best results were obtained using the Planci 2 and Liepa ceramic pellets, which after immersion do not change pH value of the water significantly. pH of solution has a significant influence on adsorption of different ions including ammonia ion because it determines interaction between the adsorbent and ions [13]. For pellets with the elevated pH levels it was not possible to obtain results using the acid-base titrimetric analysis.

IV. Conclusions

Porous ceramic pellets for possible environmental application were produced from different Latvian clays by sintering at different temperatures. Porosity and pore size of investigated ceramic pellets are affected by particle size of used combustible additives, presence or absence of carbonates in clays, and sintering temperature. By adding straw porosity is higher than in case of sawdust. The highest specific surface area is shown by pellets sintered at 700–800 °C, which also have the best adsorption results. After immersing sintered pellets into distilled water, pH measurements showed that calcareous clay ceramic pellets caused an increase on pH (up to 9.8–10.7) due to the content of carbonates in clays and formation of $Ca(OH)_2$ in water. Other pellets had neutral water pH levels after immersion.

The investigated pellets have great sorption capability towards iodine molecules showing complete adsorption (100% of initial amount of iodine in the solution). Neither different specific surface area nor pH differences seem to affect this process. The highest results regarding dichromate ion adsorption (14.5%) were obtained using ceramic pellets with the largest porosity. In this case no effect of pellet on water pH is observed. Contrary to the case of ammonia ion adsorption pH of the solution has a great effect on this process and the highest results (7.5%) are obtained using the pellets which keeps pH of water at neutral level.

The research results showed that produced ceramic pellets can be selectively applicable for environmental technologies.

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