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Characterization of porous ceramic pellets from Latvian clays

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Ceramic pellets from four different Latvian clay deposits were produced. Investigated clays have different compositions but the main clay mineral in those is illite. Pellets were shaped from plastic paste and sintered in four different temperatures – 700, 800, 900, and 1 050 °C. For each type of pellets characteristics and properties were studied. Mineral composition of these pellets varies depending on raw clay composition and sintering temperature. Calcareous clay ceramics contain anorthite, diopside, and calcium hydroxide, which elevates pH value of water after immersion of pellets. Non-calcareous clay ceramics contain spinel and hematite. Porosity and specific surface area are highly dependent on sintering temperature. Lower temperature presents higher porosity (15–25%) and specific surface area (up to 30 m^2/g). Addition of sawdust elevates the porosity but diminishes the specific surface area through increasing sintering temperatures. The highest adsorption characteristics for all investigated ceramic pellets are shown towards iodine molecules (12.7 mg/g). Chromate and ammonia ions adsorption rates are much lower than that of iodine.

Key words: porous pellets, illitic clay, porosity, sorption

INTRODUCTION

Porous clay ceramics are low-cost materials with a wide range of applications. Their properties such as porosity, specific surface area, mechanical strength, thermal insulation allow them to be used as sorbents, building materials, insulation materials [1–2]. These properties highly depend on the raw material characteristics and composition, use of additives, shaping technique, thermal treatment [2–5].

In last decades with fast development of industrial manufacturing the produced amount of wastewaters is increasing noticeably. Those waters contain different pollutants such as heavy metals and organic compounds. To insure wastewater reusability it is very important to find effective processes to purify the water. For such purpose many different sorbents are investigated all around the world such as activated carbon, TiO_2, clays [6–8]. Clay ceramics have a potential application for water purification. It is possible to obtain ceramic material with high and active surface. They do not pollute the medium with solid particles in contrary to not sintered clays. Water pH level after immersion of ceramic material influences its adsorption properties, presenting the best results at neutral or low pH levels [9–10].

Ceramic adsorbents in Latvia are being imported from Scandinavia. But it is possible to produce competitive products from local raw materials. Latvia is rich in many clay deposits, which at this moment are not used. This work is conducted with the aim to find new applications for local materials.

In this article the characteristics and properties of ceramic material from different Latvian clay deposits are discussed using X-ray diffraction, mercury porosimetric studies, pH measurements, and adsorption experiments.

EXPERIMENTAL

For preparation of porous ceramic pellets clays with different mineral compositions from 4 deposits are used – Planci, Progress, Laza, and Liepa. Planci and Liepa deposits

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offer Devonian clays but Progress and Laza deposits offer Quaternary clays. From the deposit Planci two different kinds of clay samples are obtained – Planci 1 and Planci 2 with a difference in grain size distribution. Planci 2 samples contain higher amount of sand fraction and are taken from 2.4–3.0 m depth but Planci 1 are taken from 1.5–1.9 m. To observe influence of different additives on the materials porosity and specific surface area sawdust and TiO_2 are added to the clay mixture. The amount of additives in clay mixtures is given in Table 1. Plastic paste for shaping ceramic pellets is obtained with addition of water. Pellets are sintered afterwards at four temperatures – 700, 800, 900 and 1 050 °C. Different sintering temperatures are chosen considering the DTA analysis, from which the temperatures are determined, where the most important mineralogical and structural changes take place [11].

Phase analysis of ceramic pellets is performed by X-ray diffraction (XRD) using a Rigaku Ultima + diffractometer (Cu Kα). Materials are analyzed in a powder form.

Table 1. **Amount of additives**

Clay deposit	Additives, %	
	Sawdust	TiO_2
Laza 1	3	–
Laza 2	3	5
Laza 3	–	–
Liepa 1	3	–
Liepa 2	3	5
Planci 1	3	–
Planci 2	3	–
Progress 1	–	–
Progress 2	3	–
Progress 3	5	–

Mercury porosimetry, used to determine the porosity and surface area of pellets, is performed with a Quantachrome porosimeter PoreMaster.

pH of water immersion of the fired pellets is determined with a pH-meter Mettler Toledo Multi Seven™ using an electrode Mettler Toledo InLab® 415 with an integrated temperature sensor Pt1000.

The sorption experiments for all pellets are done during a three-week period to estimate sorption characteristics and their changes over time. The sorption properties are determined by a titrimetric method. For these experiments different water solutions are prepared – 0.005 mol/l I_2, 0.03 mol/l NH_4OH and 1 wt% $K_2Cr_2O_7$. 20 g of ceramic pellets are immersed in 100 ml of solution. The flasks are held in the dark and solution samples are periodically taken for analysis.

RESULTS AND DISCUSSION

From the XRD phase analysis it is concluded that all investigated clays contain quartz and the main clay mineral is illite, which is a characteristic feature for Latvian clay deposits. In some cases microcline is also detected. Quaternary clays from Progress and Laza deposits contain calcite and traces of dolomite. Devonian clays from Liepa and Planci 2 are non-calcareous. Meanwhile samples Planci 1 contain dolomite.

The XRD analysis shows that during sintering new crystalline phases are formed. Illite transforms into anorthite in the case of calcareous clays and into spinel in the case of non-calcareous clays (Figs. 1, 2). At 800 °C in calcareous clays decomposition of calcite and dolomite occurs. Both ceramic pellets from Progress and Laza deposits contain diopside,

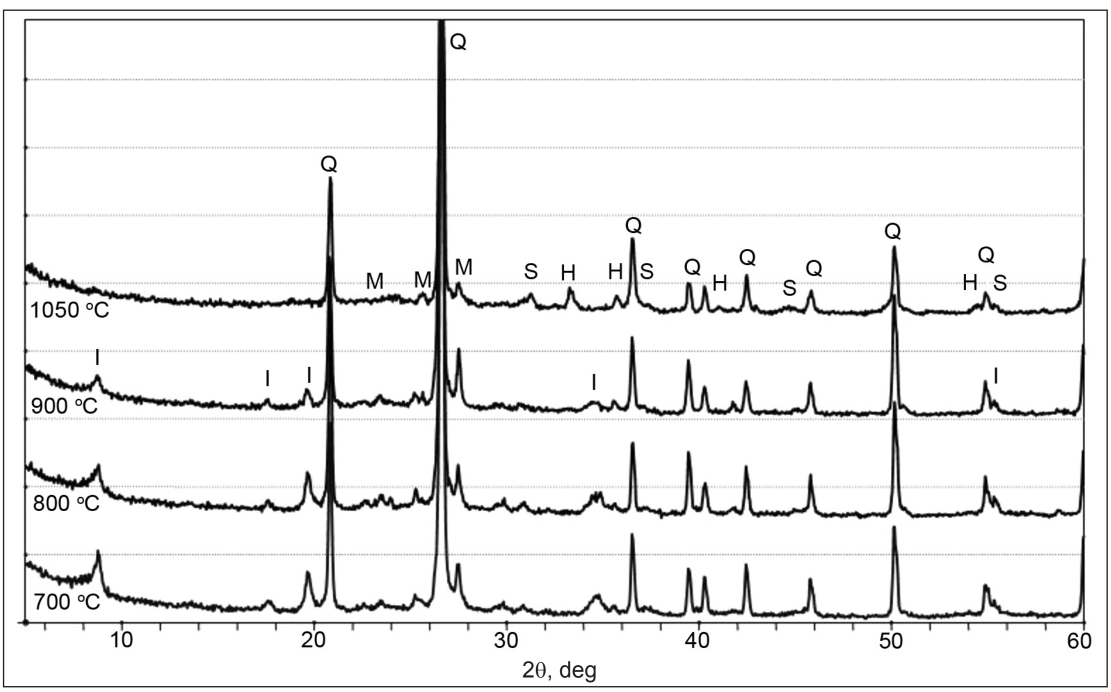

Fig. 1. XRD pattern for ceramic pellets from the Planci 2 deposit. I – illite, M – microcline, Q – quartz, S – spinel, H – hematite

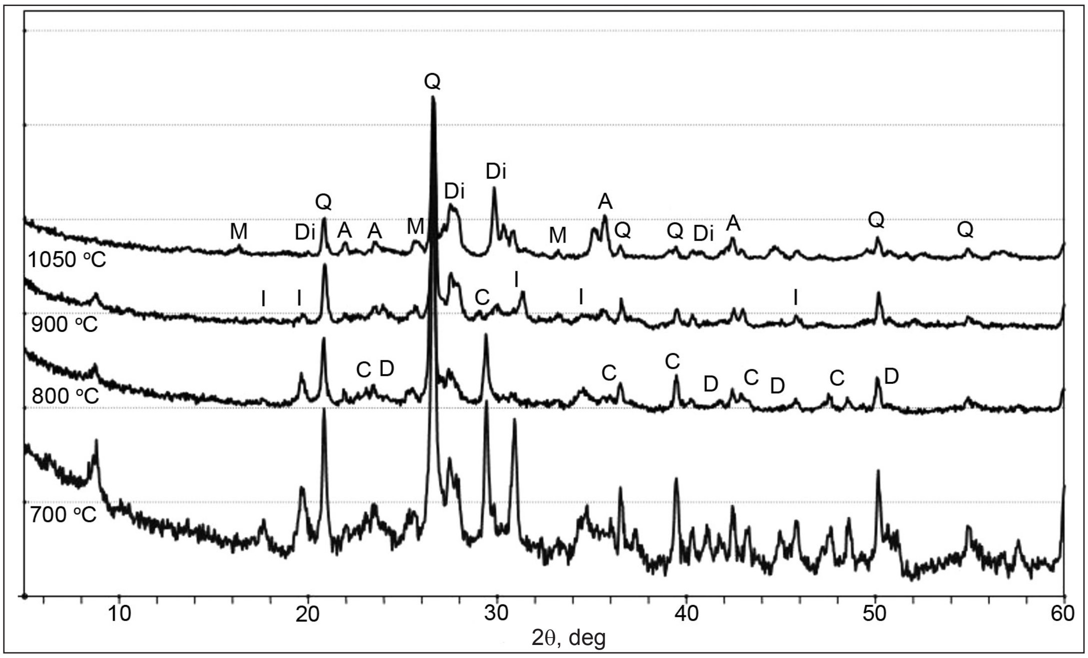

Fig. 2. XRD pattern for ceramic pellets from the Progress deposit. I – illite, Q – quartz, C – calcite, D – dolomite, A – anorthite, Di – diopside, M – mullite

which forms during the decomposition of dolomite, however, the amount of diopside in Laza clay ceramics is much lower than that in Progress clay ceramics. In fact, dolomite in Laza deposit clay is found in the dust fraction and its content is lower than in the case of Progress clay. In the case of ceramic pellets from Progress deposit mullite can be also observed in the XRD pattern. The specific red colour of ceramic pellets from Planci 2 and Liepa deposits is given by hematite. Also ceramic pellets from Progress and Laza deposits contain Fe_2O_3 but it is in an X-ray amorphous state. In the case of pellets with addition of TiO_2, the XRD pattern shows that it is a stable phase and does not go through modification changes during sintering. The phase of TiO_2 identified in these ceramic pellets is anatase.

Release of CO_2 gas as a result of combustion of organic additives and decomposition of calcite and dolomite as well as densification of ceramic pellets during the sintering process affect the value of porosity and specific surface area [2].

Figures 3 and 4 offer an observation that porosity is mostly in range from 15 to 25% throughout all temperatures with a decrease at 1 050 °C for most ceramic pellets. The highest porosity is shown by calcareous clay ceramic pellets. Formation of gas phase helps to increase a pore size and amount and shape them in ceramic material. Decrease at 1 050 °C is linked to the presence of a liquid phase in the material as a result of intensified sintering process.

Porosity results for Planci 1 and 2 are quite close. The difference is only 0.5–1.5% in all sintering temperatures. At

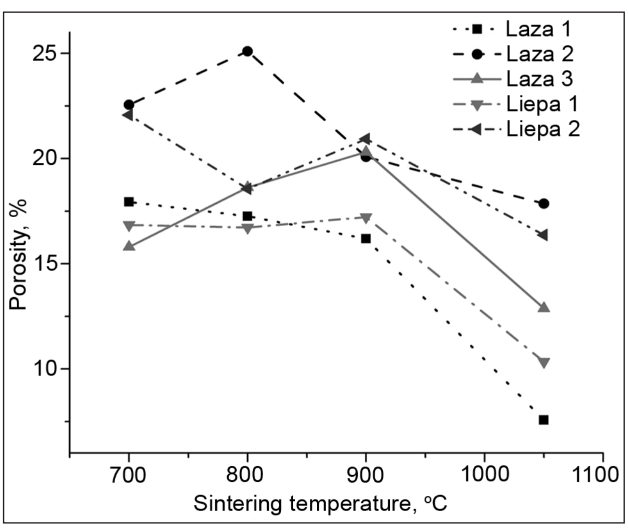

Fig. 3. Porosity of Liepa and Laza ceramic pellets

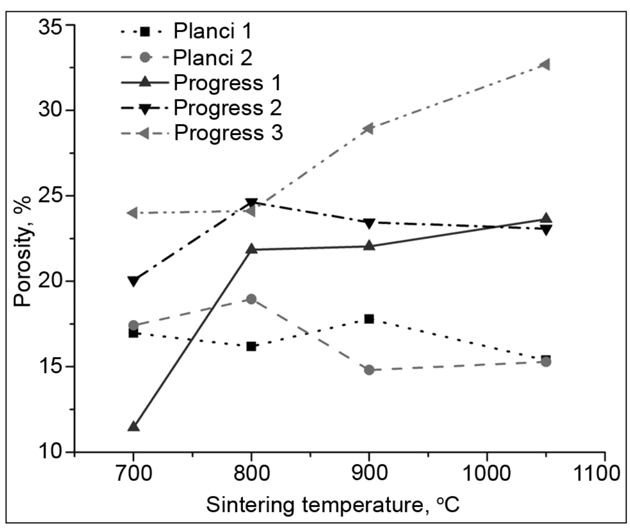

Fig. 4. Porosity of Planci and Progress ceramic pellets

700 and 800 °C Planci 1 ceramic pellets show higher porosity than Planci 2 but at 900 and 1 050 °C it is the opposite.

Comparing results for Progress ceramic pellets a general effect of slightly increased porosity by raising the added amount of sawdust from 0 to 5 wt% can be concluded (Fig. 5). Such result is reasonable considering that during the combustion of organic compounds the gas phase releases increasing the pore size. At the same time some discrepancies can be seen. Adding just 3 wt% of sawdust does not cause distinct influence on porosity.

At 700 °C pellets Progress 1 show a comparatively low porosity. Mercury porosimetry cannot determine the closed porosity. At 800 °C the decomposition of carbonates starts and in such a way it increases the open porosity of the material.

Unexpected results are shown by pellets Laza 3 without additives. They have higher porosity than pellets Laza 1 with sawdust in all temperatures except 700 °C. In samples with sawdust the temperature gradient during sintering might be more evenly distributed through the material. In this case burning process takes place not only on the outside of the pellets but combustion of sawdust increases the temperature inside the pellets as well. This effect might provide more even pore formation due to easier gas escape from the inside of material. If there is no sawdust in the material, the temperature on the surface is higher than inside. Consequently, gases get stuck inside the pellets in the case without sawdust and increase the pore size in the material.

Addition of TiO_2 increases the porosity of ceramic pellets from Laza and Liepa deposits. TiO_2 activated the pore shaping process during the decomposition on calcite at 800 °C.

The obtained data for the specific surface area show a decrease of its value with increasing sintering temperature as expected. At lower temperatures (700 and 800 °C) the specific surface area is higher. The value varies in a wide range from 9.5 to 30 m^2/g depending on clay composition and additives. At higher temperatures a sharp decrease is observed and the shown specific surface area for all pellets drops below 4 m^2/g at 1 050 °C (Fig. 6). Such results are easily explainable with the intensification of sintering process, fusion of small pores at high temperatures still keeping high porosity but reducing the specific surface area.

In the case of calcareous clay ceramic at 900 °C decomposition of calcite and dolomite is completed. As a result, large pores are formed sharply decreasing the specific surface area. The following densification at 1 050 °C for these ceramic pellets shows slower further reduction of this value.

The specific surface area of both Planci 1 and 2 differs noticeably. The obtained results for Planci 1 at 700 and 800 °C demonstrate high specific surface area which is even higher than that of calcareous Progress 1 and 2 ceramic pellets, but Planci 2 pellets have the lowest specific area values of all investigated samples.

In the case of Progress pellets without additives there are no changes visible to the specific surface area between 700 and 800 °C (Fig. 7). Formation of larger pores and

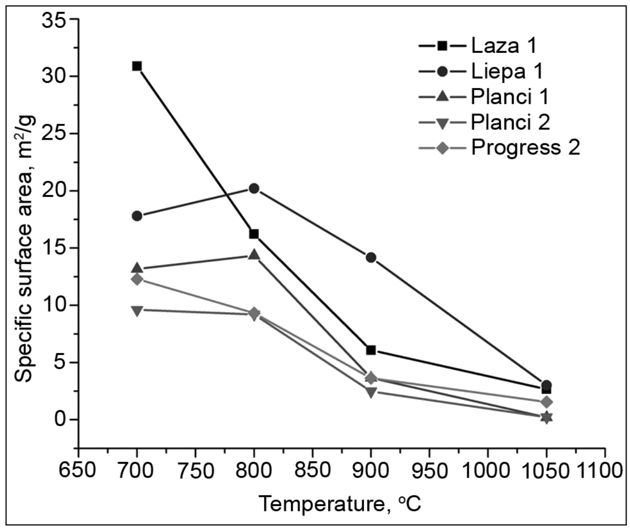

Fig. 6. Specific surface area for pellets with 3 wt%. Influence of sintering temperature

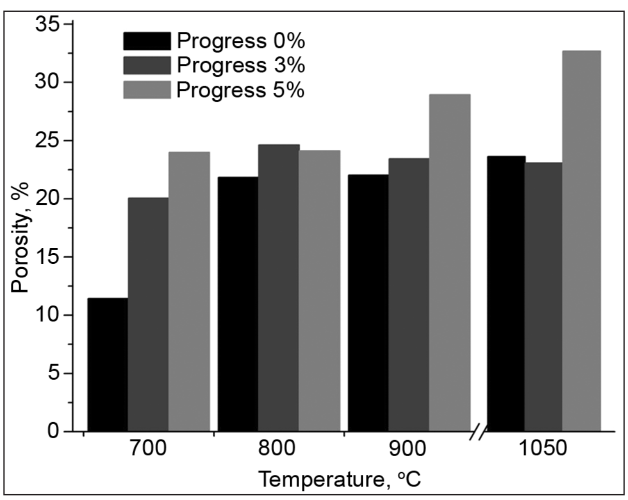

Fig. 5. Porosity comparison for Progress ceramic pellets. Influence of the amount of sawdust (0, 3, and 5 wt%)

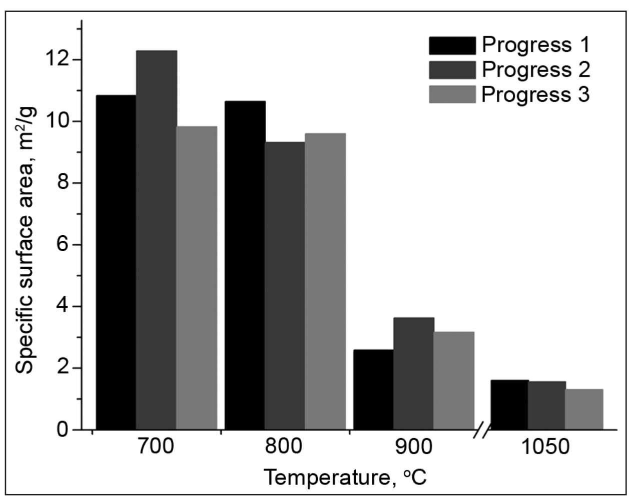

Fig. 7. Specific surface area for Progress ceramic pellets. Influence of the amount of sawdust (0, 3, and 5 wt%)

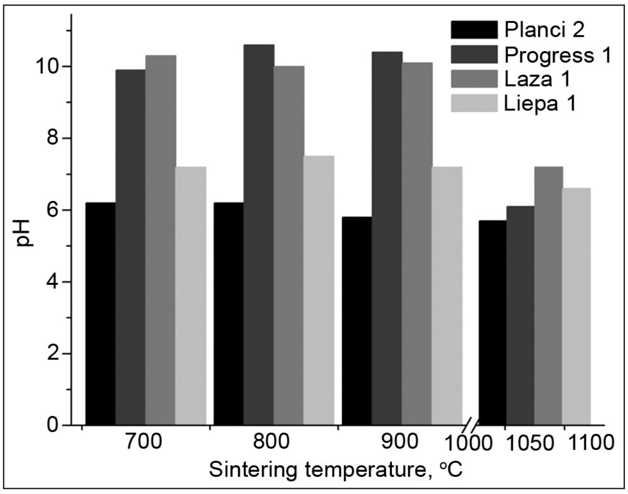

Fig. 8. Water pH after immersion of ceramic pellets

simultaneous opening of closed pores keep this value practically unchanged.

TiO_2 influence on the specific surface area is compatible with the porosity results. Increase of porosity is a result of the increase of pore size in the presence of TiO_2 particles which decreases the specific surface area.

The obtained results for pH levels of water after immersion of ceramic pellets can be relatively divided in two ranges – neutral and alkaline (Fig. 8). Calcareous clay ceramic pellets show high pH level due to traces of $Ca(OH)_2$, which is weakly soluble in water. The pH levels for all samples of Progress and Laza clay ceramics are in the range 9.8–10.7 for the sintering temperatures 700–900 °C. Increasing sintering temperature to 1 050 °C pH values drops to the neutral level: 5.8–7.2 due to the fact that CaO is now bounded in the structure of new crystalline phases such as anorthite and diopside.

pH for non-calcareous Liepa ceramic pellets is 6.2–7.5 for all sintering temperatures. In fact, the pH level at 1 050 °C is slightly lower than at other temperatures. Such tendency can be linked to formation of a new crystalline phase – spinel. At the same time non-calcareous Planci ceramic pellets cannot be divided in such neutral group. In this case Planci 2 show the neutral pH value for all temperatures 5.7–6.2 as expected but Planci 1 gives more alkaline pH of 9.5–10.8 at 700–900 °C and 8.2 at 1 050 °C. Such alkalinity is explainable with $Ca(OH)_2$ presence in them due to decomposition of dolomite.

Addition of TiO_2 in all investigated cases increases the pH values for about 0.7–1.0 pH points at 700–900 °C and decreases it for about 0.1–0.4 pH points at 1 050 °C.

Sorption characteristics for these three solutions are considerably different. For example, in half of the cases ammonia solutions concentration changes were difficult to determine due to the elevated pH level of water after the immersion of ceramic pellets.

The highest sorption activity is shown by all samples towards iodine molecules. The majority of samples sintered at 700–900 °C have 100% (12.7 mg/g) adsorption already after one week's time (Table 2).

Complete adsorption of iodine is shown by ceramic pellets with TiO_2 addition as well but only at one sintering temperature for each case – Laza 2 at 800 °C and Liepa 2 at 900 °C. Lower sorption activity is shown by pellets sintered at the highest temperature and range from 9.78 to 11.43 mg/g in all cases. Such results are obtained after longer contact time mostly from 14 to 21 days but are still high considering the percentage values 77–90%.

The iodine adsorption tendency matches the results from porosimetry. Since iodine adsorption is a physical process it

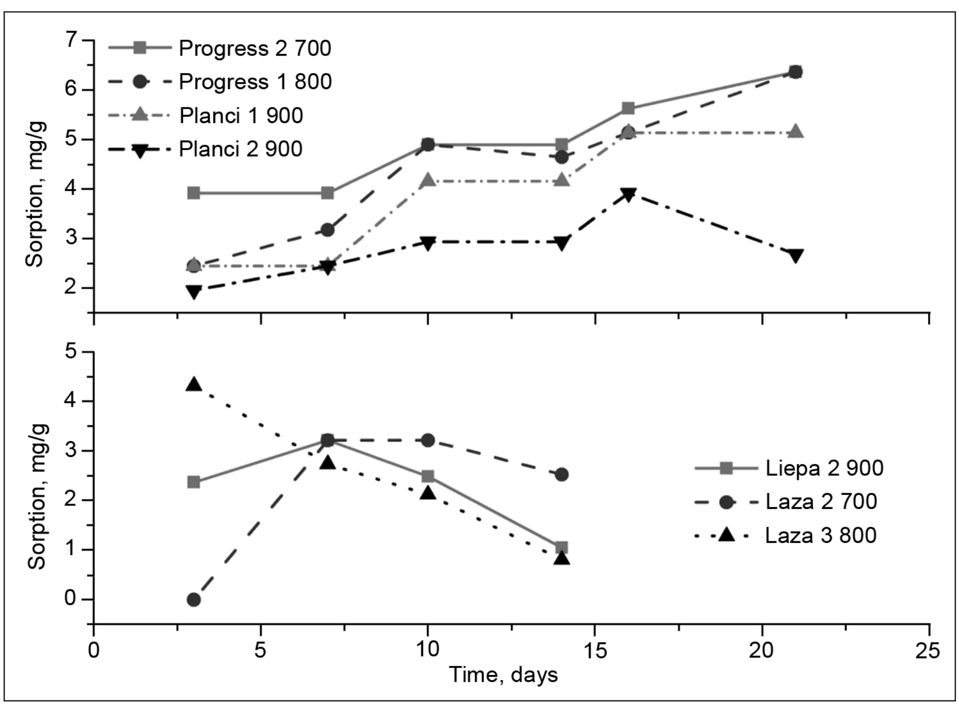

Fig. 9. Sorption of dichromate ion

Table 2. **Adsorbed amount of iodine, mg/g**

		Days					
		3	7	10	14	16	21
Progress 1	700	12.19	12.7	12.7	12.7	12.7	12.7
	800	11.94	12.7	12.7	12.7	12.7	12.7
	900	12.07	12.7	12.7	12.7	12.7	12.7
	1050	9.27	9.4	9.53	9.65	9.65	9.78
Progress 2	700	12.19	12.7	12.7	12.7	12.7	12.7
	800	12.19	12.7	12.7	12.7	12.7	12.7
	900	12.45	12.7	12.7	12.7	12.7	12.7
	1050	9.53	10.1	10.16	10.16	10.16	10.29
Progress 3	700	12.19	12.7	12.7	12.7	12.7	12.7
	800	12.38	12.7	12.7	12.7	12.7	12.7
	900	12.45	12.7	12.7	12.7	12.7	12.7
	1050	8.89	9.21	9.21	9.4	9.78	9.78
Planci 1	700	10.29	11.94	12.13	12.38	12.7	12.7
	800	11.49	12.7	12.7	12.7	12.7	12.7
	900	12.06	12.7	12.7	12.7	12.7	12.7
	1050	9.91	12.38	12.46	12.7	12.7	12.7
Planci 2	700	8.38	9.02	9.65	9.91	10.41	10.79
	800	8.76	9.27	9.4	10.1	10.35	10.79
	900	8.89	9.84	10.35	10.35	10.67	11.3
	1050	8.64	9.91	9.97	10.03	10.6	10.92
Liepa 2	700	9.84	9.84	9.84	9.84	9.84	9.84
	800	8.89	9.21	9.52	10.79	10.48	10.48
	900	11.43	12.38	12.7	12.7	12.7	12.7
	1050	9.52	9.52	9.52	10.48	10.48	10.48
Liepa 1	700	11.43	12.07	12.07	12.07	12.07	12.07
	800	11.75	12.07	12.38	12.38	12.38	12.38
	900	9.4	9.5	9.9	10.54	10.54	10.54
	1050	9.84	10.16	10.16	10.16	10.16	10.16
Laza 2	700	8.89	9.21	9.52	10.79	10.48	10.48
	800	11.43	12.7	12.7	12.7	12.7	12.7
	900	8.89	9.21	9.84	10.79	10.79	10.79
	1050	8.25	8.89	9.21	11.43	11.11	11.11
Laza 1	700	12.07	12.38	12.7	12.7	12.7	12.7
	800	12.19	12.7	12.7	12.7	12.7	12.7
	900	11.94	12.19	12.7	12.7	12.7	12.7
	1050	10.8	11.11	11.11	11.11	11.11	11.11

highly depends on materials specific surface area. The greater specific surface area, the more physical space is there for iodine molecules to get attached to.

The adsorption activity towards chromate anion is lower than towards iodine. Results are spread in a wide range and differ from 0.98 to 6.37 mg/g. Such sorption levels are below 14.5% of the initial amount of chromate ions in the solution.

A distinct tendency can be seen in Fig. 9 that the investigated pellets can be divided in two groups regarding the time when the highest point of the adsorbed amount of chromate is reached. Ceramic pellets from Laza and Liepa clays reach their sorption maximum after 4 to 7 days and the adsorbed amount varies from 0.98 to 4.32 mg/g. The highest sorption properties in this group are shown by Laza 3 ceramic pellets sintered at 800 °C. Meanwhile, ceramic pellets from Progress and Planci reach their sorption maximum after 16 to 21 days. These pellets also show higher sorption properties – from 3.18 to 6.37 mg/g. In the case of Progress clay ceramic pellets with and without sawdust the highest sorption properties are shown at 700–900 °C. For pellets Planci 1 and 2 the best properties are shown by ceramic pellets sintered at 900 °C.

The values of adsorbed chromate fluctuate during the experiment time. That could be linked with elution of ions out of pores because of the weak bind with the surface or chemical changes (reduction of dichromate ion) in the solution which gives inconsistent results.

The lowest sorption ability for all investigated ceramic pellets is detected towards the ammonia ion. In all cases the adsorbed amount is under 0.35 mg/g which accords to 7.5% of the initial amount of ions in the solution (Fig. 10). In most cases it is even lower – under 0.2 mg/g.

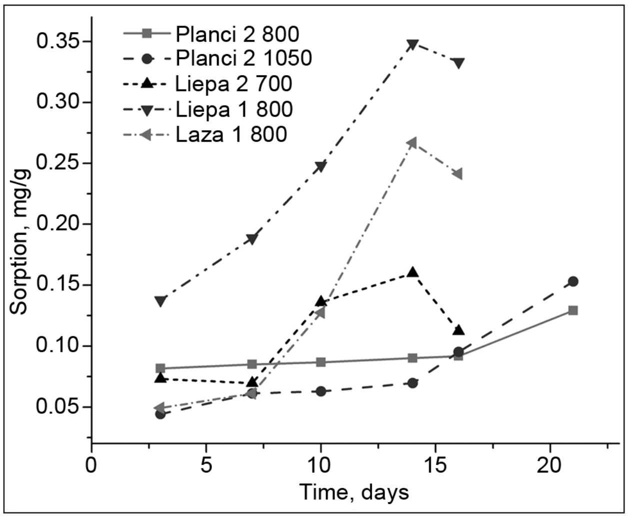

Fig. 10. Sorption of ammonia ion

In some cases the ceramic pellets do not show any sorption tendency. Such observation is obtained with Laza 2 pellets sintered at 700 and 800 °C, Progress 2 and 3 both sintered at 800 °C. These results are linked to the elevated pH levels. Liepa 1 pellets sintered at 800 °C after two weeks time show the highest absorbed amount of chromate ions between all investigated pellets. A bit lower results are shown by Laza 1 at all temperatures, Liepa 1 at 700, 900 and 1 050 °C, Liepa 2 at 700 °C after two weeks time. These results vary between 0.11 and 0.27 mg/g. Planci 2 pellets sintered at all temperatures fit to this range but it takes three weeks to get such an adsorption amount.

The highly elevated pH level for most ceramic pellets present difficulties to obtain results as the titration is performed according to the acid-base principle. Another effect which explains low adsorption characteristics towards the ammonia ion is the fact that ammonia ions have hydratation shell, which increases the size of ions and affinity to be adsorbed.

CONCLUSIONS

Presence of calcite and dolomite in clay material increases the porosity and specific surface area of ceramic pellets during the sintering process at 700 and 800 °C due to the decomposition of these minerals and gas phase release. At higher sintering temperatures the porosity raises but the specific surface area drops due to pore association. Addition of sawdust increases the porosity but decreases the specific surface area through all sintering temperatures. Sawdust particles form greater pores leading to lower total surface area. TiO_2 addition has the same effect on the porosity and specific surface area. For future investigations BET (Brunauer-Emmett-Teller) experiments for these ceramic pellets are advisable.

Water pH levels after immersion of the ceramic pellets can be divided in two groups – neutral and alkaline. Mostly alkaline pH levels are shown by calcareous clay ceramics because at this temperature CaO is not yet bonded in compounds. TiO_2 addition increases pH levels for the pellets sintered at 700–900 °C.

The highest adsorption characteristics for all investigated ceramic pellets are shown towards iodine molecules and reach 100% adsorption in the majority of cases already after one week's time. Adsorption rates of chromate and ammonia ions are much lower than that of iodine, respectively 14.5% and 7.5%. In the case of chromate the best results are reached after 14–21 days by Progress and Planci ceramic pellets. Regarding ammonia, 7.5% degree is reached only by one sample – Liepa 1 sintered at 800 °C with the pH level at 7.5.

The produced ceramic pellets show good characteristics which are compatible with environmental applications. They can be used both in batch and flow-through methods for cleaning water. These pellets have a stable structure and do not pollute the medium with solid particles. As these ceramic pellets are produced from local raw materials they are cheaper than competing sorbents which are being imported.

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KERAMINIŲ RUTULĖLIŲ IŠ LATVIJOS MOLIO CHARAKTERIZAVIMAS

Santrauka

Pagaminti keraminiai rutulėliai iš įvairių Latvijos molių. Rutulėliai buvo kaitinami skirtingoje temperatūroje – 700, 800, 900 ir 1 050 °C. Pateikiamos visų tirtų pavyzdžių charakteristikos ir savybės.