# New clay ceramic materials

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Clays are one of important rocks on our planet and one of most widely used raw material for production of varied ceramic articles. Ceramic production history is well known since the beginning of human development. Diversity of ceramic articles and products is established by variety of clays and clay minerals in these rocks.

1:1 clay mineral kaolinite containing clays are used for production of refractory materials in the thermal treatment kilns and some other heat-resistant productsare used as well. In the structure of kaolinite neither tetrahedral neither octahedral sites have isomorphic substitution of $Si^{4+}$ or $Al^{3+}$ ions respectively and properties of obtained materials has been influenced only by various admixture in kaolin. However, some isomorphic substitution of $Mg^{2+}$, $Fe^{3+}$, $Ti^{4+}$ and $V^{3+}$ for $Al^{3+}$ can occur in octahedral site. In the oil cracking technology kaolin as catalyst is used.

The more complicated is the question about hydromicas. Hydromicas such as hydrobiotite and hydromuscovite have large amount of various substitution both in the tetrahedral and octahedral sites that influences not only structure and properties of same minerals but also properties of ceramic materials produced from hydromica containing clays. The identification of hydromicas phases by use of XRD phase analysis is problematic. Wide variety of ceramic materials have been produced from hydromica containing clays. The deciding factor by use of clay in ceramic technology is not only type and structure of same hydromica, but also presence of various admixtures in the natural clays. The sintering temperature of clay is the most important practical property in the ceramic technology that determine real firing temperature and properties of articles. A sintering temperature depends on substitutions in the structure of minerals and admixture type. The 2:1 clay mineral structure and admixture in the natural clay are influenced by geological conditions, it means, the age of clay sediments.

In Latvia there are two clay types: the oldest Devonian (age ~495 million years) and the youngest Quaternary clay (age about 70000 years). Illite has been the main clay mineral in these clays but they contain also 5–15 % of kaolinite. Amount and type of admixtures is the general difference between these clays. Devonian clays are called lime less clay and the main admixture is a quartz sand and 5-9 % of very small iron (III) oxide in form of thin layer on the clay or sand particles. Red, light or purple color is the characteristic sight of this clay and ceramic articles after sintering are colored red. Quaternary clays differ from the Devonian with admixture of alkaline earth metal carbonates in the amount up to 20 %. The amount of clay fraction (particle diameter $< 0.005$ mm) in average $\geq 70$ % is the second important difference between Latvia's clay types. A content of iron oxide in the Quaternary clays is lower and $Fe^{3+}$ ions mainly are bounded in the octahedral site of illite. It determines color of Quaternary clays – brownish, but color of articles after sintering depends on the sintering temperature and amount of carbonates in the raw clays. A color of ceramic articles depends also on the environment in the sintering kiln. Creation of reducing environment on the end stage of sintering leads to formation of dark colored surface.

Despite the fact that history of ceramic is very ancient, possibility to create ceramic materials with new properties and for other uses is very urgent today. Porous ceramic materials for environmental technology are used in a variety of ways such as filters, sorbents or catalyst. Lightweight material pellets of expanded clay are well known thermal insulating filler in the technology of concrete. Technology of production is multi-stage and energy-intensive. A new one-stage production technology has been developed by enlarging traditional basis of raw illite clay materials and reducing of production time [1]. The possibility to produce expanded clay pellets with variable properties and various use has come around. There are pellets with apparent density 0.53 $g/cm^3$ that can float on the surface of water a long time and serves to collect contaminants on the surface of water reservoirs. A new type of ceramic sorbent has been developed on the basis of new expanded clay technology. The raw materials are iron oxide containing illite clays and additive of large amount of crushed wood. Material has been produced by very fast thermal treatment of dried pellets. The structure of porous pellets is formed from two parts - porous ceramic shell and black core that contains predominantly carbon. Thermal treatment temperature is lower that temperature that characterize full dehydroxilation of illite. A change of crystalline phases has been determined by XRD analysis and some shift of diffraction lines that characterize the basal plates of dioctahedral illite have been detected. Obtained material combine two types of sorbents: activated carbon with large specific surface area and characteristic physical sorption and porous ceramic with a smaller specific surface area but physical and possible chemical sorption. Obtained materials characterize large specific surface area and BET analyses shows presence of nanosize pores (Fig.1). Pyrolysis of wood particles in the presence of clay minerals in the hydrothermal condition inside pellets is a driving force for the obtaining such sorbent and catalytic influences of illite on this process. A sorption ability and speed depends on the type of raw illite clay.

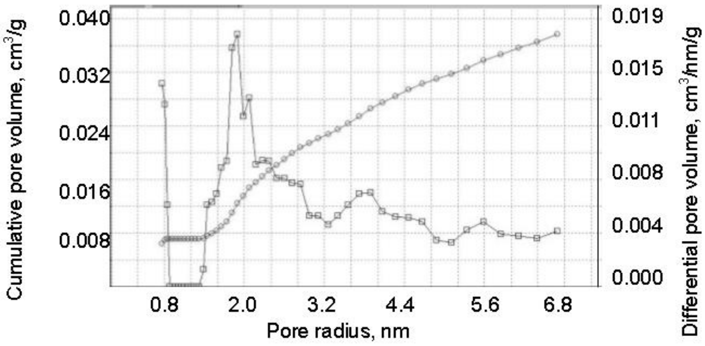


Fig.1. Pore size distribution in the Devonian clay ceramic containing activated carbon

Catalytic influence of 1:1 clay mineral kaolinite has been detected in the ceramic processing. Highly porous oxide ceramic has been obtained by casting concentrated suspension of metal oxides and kaolin by additive of small amount of aluminum powder. Pore formation in the suspension and during thickening and solidification has been happened as a result of chemical reaction between aluminum powder and water with elimination of hydrogen [2]. The cause of the reaction is contact between charged kaolinite particles (zeta potential -19,8 mV) and aluminum particles with following corrosion of metal. In the dried samples XRD analysis confirmed presence of kaolinite without any changes. Similar process has been detected in the concentrated suspensions of illite clay by additive of kaolin. Obtaining of highly porous clay ceramic by this method was influenced by type of illite clay. Quaternary illite clays with admixture of carbonates are not valid for the production of highly porous ceramic in such way. Presence of carbonates in clays influences a viscosity of suspension, whereas the presence of $Ca^{2+}$ ions thicken the suspension and delays formation of homogeneous pore structure in the material.

*Aknowledgement*
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