

UDK 675.92.027.6: 553.61

The Influence of High Pressure on the Properties of Natural Alumino-silicates

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Abstract: The effect of the application of high-pressure (up to 12 GPa) on natural alumino-silicates has been studied. Chemical and mineral compositions and thermal behaviour have been analyzed of two samples of alumino-silicates. Results obtained indicate that the application of high pressure causes notable changes. A particularly significant one is the formation of amorphous phases on account of crystalline phases. An amorphous layer formed on particle surfaces with its diverse physical, mechanical, chemical, and other properties, especially over a long period of time, can influence the processes provoking or activating land slides or soil settlements. This enables derivation of many new materials with entirely new properties important for use in the ceramic and brick industries.

Keywords: Cold sintering; Natural alumino-silicate; High-pressures; Amorphous phases.

Резюме: В данной работе проведен анализ влияния холодного спекания, т.е. влияния высоких давлений прессования до 12 ГПа на изменение свойств природных алюмосиликатов. Проведено исследование химического и минералогического состава и термического поведения двух образцов природных алюмосиликатов из различных месторождений. Полученные результаты показывают, что под действием высоких давлений происходят изменения, особенно образование аморфных фаз за счет кристаллических. Образованный на поверхности частиц аморфный слой своими физико-механическими, химическими и другими свойствами может через длительный период действия повлиять на процессы возникновения и активирования оползней и оседания почвы. Таким же способом вскрывается возможность получения ряда новых материалов с новыми свойствами важными для керамической и кирпичной промышленности.

Ключевые слова: Холодное спекание; природный алюмосиликат; высокие давления; аморфные фазы.

Садржај: У овом раду анализиран је утицај хладног синтеровања, тј. утицај високих притисака пресовања до 12 GPa на промене својстава природних алумосиликата. Извршено је испитивање хемијског и минеролошког састава и термичко понашање два узорка природних алумосиликата са две различите локације. Резултати показују да деловање високих притисака изазива значајне промене, од којих је од посебног значаја настајање аморфних фаза на рачун кристалних. Формирани аморфни слој на површини честица својим разноврсним физичко-механичким, хемијским и другим својствима, посебно кроз дужи временски период, може да утиче на процесе настајања и активирања клизишта и слегања тла. Такође, на овај начин се отвара

могућност добијања читавог низа нових материјала са сасвим новим својствима од значаја за керамичарску и опекарску индустрију.

Кључне речи: Хладно синтеровање; природни алумосиликати; високи притисци, аморфне фазе.

Introduction

Modern research [1-3] has shown, that high pressures lead to mechanical and chemical processes. The energy released from friction, due to low thermal conductivity of the material, leads not only to a local temperature increase, but also to the formation of a state of mixed ions and electrons, i.e. plasma [4]. Battaglia's tests [5] demonstrate that mechanical and chemical processes on quartz surfaces form a surface layer of amorphous SiO_2 that is detected by a decrease in the reflection intensity of the characteristic X-ray diffraction maxims.

The greatest source for production of various materials is the Earth's crust. Nearly half of the Earth's crust consists of silicate minerals, aluminium silicates in particular, such as kaolinite, montmorillonite, feldspars, etc. Natural alumino-silicates have been mostly studied for their use in ceramic or brick industry, which included testing of temperature variations and the application of low pressure.

Data on the behaviour of silicate materials under high pressure is scanty, and data published is fairly new and mostly refers to testing pure samples synthesized in a laboratory [6]. This work considers the properties of natural alumino-silicate materials subjected to high pressures.

Experimental method

Two samples of natural alumino-silicate materials (natural clays) were tested. The samples were first dried at temperatures up to 105°C and then fractionated on sieves. Size fractions of less than 0.1 mm were used for testing. A spectrographic analysis was performed of the prepared samples.

The samples were pressed in two stages. Samples in a powder form were pre-pressed under 0.5 GPa to form cylindrical pellets of 1.0 cm in diameter and 1.0 cm high. Two pellets at a time were pressed under 12 GPa.

Thermal testing of samples before and after pressing consisted of differential thermal analysis (DTA). Samples were heated in air atmosphere from room to the temperature of 980°C , using a Du Pont 1090 Thermal Analyzer.

Samples were X-rayed before and after pressing and after heating in an automatic X-ray powder diffractometer (Philips model PW-1710). A fine focus Cu anode, K_α radiation of 1.54060 Å wavelength and a Xe rate counter were used. For measurement of the angles of diffraction maxims and their respective intensities, the basic PW-1877 programme was used.

Results and discussion

The chemical composition of tested samples, obtained by spectrographic analysis, is given in Tab. I. It was used to determine the percentage composition of minerals and is shown in Tab. II.

Tab. I Chemical composition of investigated samples.

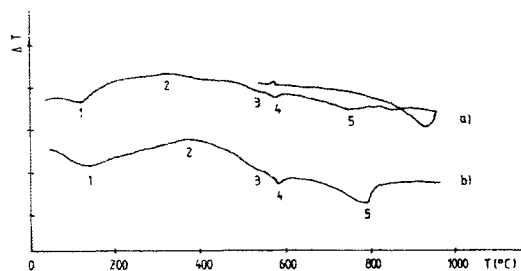
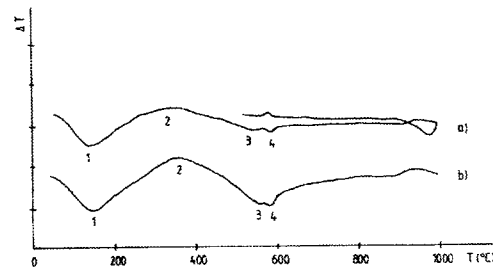
Sample	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	P ₂ O ₅ %	K ₂ O %	Na ₂ O %	CaO %	MgO %	SO ₃ %
1	78.00	11.27	3.65	0.11	1.97	1.37	2.17	1.18	0.15
2	70.34	15.10	5.94	0.14	2.36	0.15	1.13	1.98	0.36

Tab. II Mineral composition of investigated samples.

Sample	Quartz %	Kaolinite %	Na-feldspar %	K-feldspar %	Fe ₂ O ₃ %	CaCO ₃ %	MgCO ₃ %
1	78.00	11.27	3.65	0.11	1.97	2.17	1.18
2	70.34	15.10	5.94	0.14	2.36	1.13	1.98

Differential thermal analyses indicate complex changes in the material caused by high pressures. Endothermic and exothermic changes are particularly visible.

DTA curves (Figs. 1 and 2) of samples 1 and 2 of natural silicate materials (natural clays) before and after pressure application indicate endo- and exo-processes and phase transformations, which are identified on thermographs by numbers from 1 to 5: 1 - endothermal broadly developed minimum that is attributed to moisture and adsorbed water release, 2 - broadly developed exothermal maximum that characterizes the process of oxidation of some components and combustion of the likely present organic matter, 3 - barely noticeable endothermic process of hydration water release, 4 - distinct reverse phase transformation of quartz (β -SiO₂ \leftrightarrow α -SiO₂), 5 - weak endothermic process of CaCO₃ calcite decomposition in sample 1 and absence of this process in sample 2 due to its low content. Consequently, these processes are more or less distinctive, depending on chemical and mineral compositions of the material.

**Fig. 1** DTA thermograph of sample 1 subjected to pressures of 0 and 12 GPa.**Fig. 2** DTA thermograph of sample 2 subjected to pressures of 0 and 12 GPa.

DTA of sample 1, before and after pressing to 12 GPa, indicates that the temperature of the adsorbed water release process (peak 1), oxidation process (peak 2), and CaCO₃ decomposition (peak 5) increases (peak 1 from T = 127 to 143°C, peak 2 from T = 325 to 400°C, peak 5 from T = 765 to 790°C). This phenomenon can be explained by a better particle sorting in the sample subjected to pressures up to 12 GPa than in the un-pressed sample. Unlike this phenomenon, the temperature needed for the hydration water release process (peak 3) decreases with growing pressure from T = 550 to 525°C. The temperature of reverse quartz-SiO₂ phase transformation (peak 4) is unchanged under high pressures, T = 586°C, indicating a stable process-phase transformation.

The described occurrences are documented by DTA thermographs for sample 2. The temperature of the adsorbed water release process (peak 1) and the oxidation process (peak 2) increases with rising pressure (peak 1 from $T = 139$ to 154°C ; peak 2 from $T = 335$ to 355°C), and the temperature needed for hydration water release (peak 3) decreases from $T = 550$ to 540°C . The temperature of the quartz-SiO₂ phase transformation (peak 4), like in sample 1, remains unchanged, $T = 586^{\circ}\text{C}$.

Besides the temperature deflections of endo- and exo-processes, with the rising pressure both samples demonstrate more prominent peaks of these processes than before pressing.

X-ray analysis was performed to determine structures and mineral compositions of the samples. The diffractograms obtained are given in Figs. 3 and 4, which show reflection maxims of the components (numbered 1 to 16) and respective angles of reflection, 2θ : 1 - Montmorillonite 6° ; 2 - Mica 9° ; 3 - Kaolinite $12-13^{\circ}$; 4 - Feldspar 14° ; 5 - Mica 18° ; 6 - Quartz 21° ; 7 - Quartz 27° ; 8 - Feldspar $27-28^{\circ}$; 9 - Feldspar 28° ; 10 - Quartz $29-30^{\circ}$; 11 - Mica and Kaolinite 35° ; 12 - Quartz $36-37^{\circ}$.

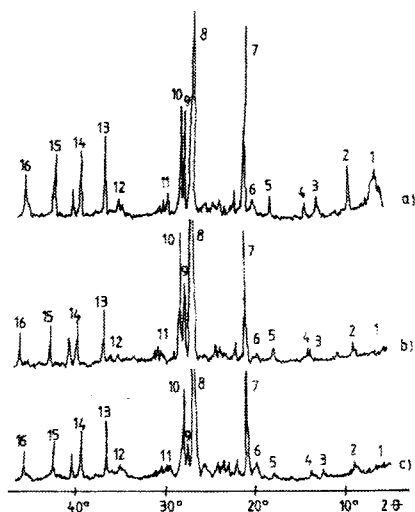


Fig. 3 X-ray diffractogram of sample 1: a) under pressure of 0 GPa; b) after firing at 980°C ; c) under pressure of 12 GPa.

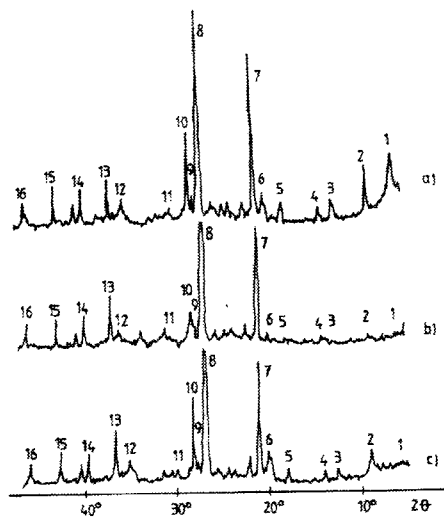


Fig. 4 X-ray diffractogram of sample 2: a) under pressure of 0 GPa; b) after firing at 980°C ; c) under pressure of 12 GPa.

A comparison of diffractograms of samples 1 and 2 for their states before pressing, after pressing under 12 GPa, and after firing at 980° show notable effects of high pressures and firing on the quantitative content of certain components, and consequently the quality.

X-ray analysis of unfired and fired to 980°C samples 1 and 2 shows thermal instability of some components. In addition to the known decomposition of calcite-CaCO₃ and other carbonates at about 800°C , some crystal structures also decompose while new amorphous components are formed. Samples fired to 980°C reveal an essential change in the crystal composition: montmorillonite (peak 1), mica (peaks 2, 5), kaolinite (peaks 3, 12), feldspar (peaks 4, 9, 10) and calcite (peak 11) have almost disappeared (Figs. 3 and 4).

The changes noted in X-ray diffractograms of samples 1 and 2, before and after the high-pressure effect, are similar to those resulting from firing. Some components (minerals) get transformed under high pressures from a crystalline to amorphous state. Tab. III gives relative intensities of some mineral reflections in relation to the applied pressure for each sample separately.

Tab. III Sample 1 - Relative peak heights for the following reflection angles 2 θ : 1 - Montmorillonite 6°; 2 - Mica 9°; 3 - Kaolinite 12-13°; 4 - Feldspar 14°; 5 - Mica 18°; 6 - Mica and Kaolinite 20°; 7 - Quartz 21°; 8 - Quartz 27°; 9 - Feldspar 27-28°; 10 - Feldspar 28°; 11 - Calcite 29-30°; 12 - Mica and Kaolinite 35°; 13 - Quartz 36-37°; 14 - Quartz 39-40°; 15 - Quartz 42-43°; 16 - Quartz 46° and pressure, P.

P (GPa)	Relative peak height (mm)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	27	46	24	16	23	15	240	310	108	112	20	15	86	74	70	47
12	0	11	6	8	5	14	220	310	20	70	7	7	58	52	40	30

Tab. IV Sample 2 - Relative peak heights for the following reflection angles 2 θ : 1 - Montmorillonite 6°; 2 - Mica 9°; 3 - Kaolinite 12-13°; 4 - Feldspar 14°; 5 - Mica 18°; 6 - Mica and Kaolinite 20°; 7 - Quartz 21°; 8 - Quartz 27°; 9 - Feldspar 27-28°; 10 - Feldspar 28°; 11 - Calcite 29-30°; 12 - Mica and Kaolinite 35°; 13 - Quartz 36-37°; 14 - Quartz 39-40°; 15 - Quartz 42-43°; 16 - Quartz 46° and pressure, P.

P (GPa)	Relative peak height (mm)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	45	46	21	13	17	24	170	280	14	83	0	21	43	35	41	23
12	0	23	11	10	12	28	121	280	10	80	0	9	50	32	34	21

The obtained test results indicate, that for natural alumino-silicate materials (natural clays) under the influence of high pressure, a number of components change structurally. This allows derivation of many new materials that will have new properties usable in (ceramic, brick, etc.) industries. The rising pressure level leads to an increased layer of the amorphous phase on particle surfaces, and this further to a growth of the water-sorption capacity. A higher amount of sorption water in the amorphous phase renders, by its various chemical, physical and mechanical and other properties, the given material less viscous, or more fluid and liquid. Some of the data suggest that under natural conditions of not so high pressures, but over a long period of time, the amorphous phase increases a lot in certain soil layers and the increased water-sorption causes greater or smaller soil mobility (sliding or settling).

Conclusion

Differential thermal analysis (DTA) and the X-ray analysis data obtained indicate, that mechanical and chemical processes occur in the tested natural alumino-silicates under the influence of high pressures.

The DTA method reveals complex changes, including deflection of the phase transformation temperature, in tested samples before and after pressure application within the temperature range from room temperature to 980°.

X-ray analysis shows that pressure levels up to 12 GPa provoke great changes: alter the mineral composition, form new alumino-silicate phases, of which amorphous phases on account of crystalline phases are particularly important. The growing quantity of the amorphous phases increases the sorption capacity for water and other fluids, thus making the material less viscous, or more mobile.

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