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INFLUENCE OF THERMAL TREATMENT OF THE BASALT TUFA ON ITS PHASE COMPOSITION AND SORPTION CAPACITY

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Abstract: *The results reflecting influence of thermal treatment of basalt tufa (BT) on its phase composition and capacity of some heavy metal ions (Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) sorption under the static conditions are presented. It has been found that thermal modification of tufa at 400–1000 ^0C results in weight loss of the material from 5,79 % (at 400 ^0C) to 10,18 % (1000 ^0C) caused by changes in the mineral phase composition such as loss of the chemically bound water, decomposition of carbonates and other compounds. It has been shown that the sorption value for the heavy metal ions, being captured on surface of the thermally modified BT samples, is governed by the ion's nature and temperature of its thermal treatment. The negatively charged surface-active adsorption centers were identified for all BT samples since they exhibited the positive suspension effect. Therefore, a competition between adsorption of H^+ and heavy metal ions can take place.*

Keywords: *thermal modification, basalt tufa, phase composition, sorption capacity, suspension effect*

1. Introduction

The sorption technologies for natural water and wastewater cleaning using various mineral adsorbents play an important role for environment protection and contamination prevention. Since natural sorbents such as montmorillonites, diatomites, bentonites are easily available, inexpensive and widely functional [1, 2], they are used extensively in many wastewater treatment and water cleaning solutions.

Zeolites are minerals with some unique properties [3, 4] (ability to ensure high ion exchange capacity, well-ordered lattice with uniform molecule-sized pores, protonic and aprotonic acidity), which are also used widely as effective dryers, gas and liquids cleaning substrates and so on.

Basalt tufa is a volcanogenic mineral having chemical and structural compositions close to zeolites [5]. There are vast deposits of tufa available for mining, but the detailed properties of the mineral are still insufficiently investigated. It should be mentioned that high chemical and thermal durability of tufa facilitates its usability as a raw mineral for various environment protection, agrochemical, technical and biological solutions.

Sorption capacity is one of important characteristics controlling sorption efficiency of any substrate. It was found previously that BT exhibits polyfunctional adsorption, which depends substantially on the conditions of preliminary thermal, chemical and chemo-thermal treatment [6]. In this context, the main aim of this work was to investigate an influence of the thermal treatment temperature on phase composition and sorption capacity of basalt tufa.

2. Experimental

All experiments were done using the basalt tufa obtained from Polytske-2 deposit (Ukraine). The samples were dried in air at 105 ^{0}C and then modified thermally at 400, 600, 800 and 1000 ^{0}C. Sintering was carried out until stable weight of the sample (approx. 3 hours). Then XRD analysis was employed to determine the tufa phase composition. Ion sorption was investigated using the powdered samples (d=80–120 μm) of BT. The well-known low temperature argon adsorption method was employed to determine the specific surface area. Sorption of the heavy metal ions Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} was investigated at the room temperature under static conditions with aqueous solutions of corresponding nitrates ($C_0=2\cdot10^{-4}$ mole/l) keeping 1:100 phase ratio between the solid and liquid components. It took 18–24 hours for the sorbent/sorbate equilibrium to establish. All concentrations of the metal ions were determined by AAS using KAS-120 M1 spectrophotometer operating acetylene/air flame [7]. Suspension effect value (ΔpH), which used to identify negatively or positively charged surface centers [6], was measured by pH-meter and was calculated according to $\Delta pH=pH_1-pH_0$; pH_0 – initial pH value of solution without basalt tufa; pH_1 – pH value of suspension with basalt tufa.

3. Results and Discussion

It is known that both phase composition and structure of BT undergo serious influence after thermal processing of the material [8, 9]. Many processes can occur during this treatment: decomposition of some mineral compounds, sintering and pore formation, which cause various changes in the tufa properties.

An influence of the thermal treatment regime on the samples weight change is shown in Figure 1. As expected, the higher temperatures correspond to greater weight loss. For instance, 5,79 wt % were lost after treatment at 400 ^{0}C while same processing at 1000 ^{0}C results in loss of 10,18 wt %.

These changes can be resulted by evaporation of the crystal water and decomposition of carbonates and some other thermally unstable compounds.

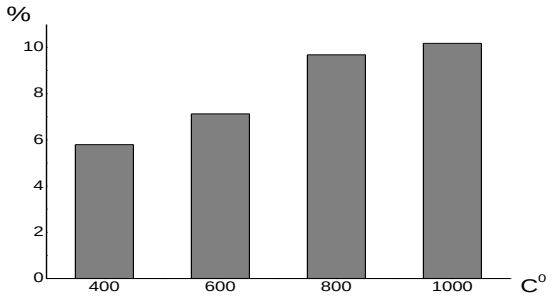


Fig. 1. Influence of thermal treatment temperature on the basalt tufa weight loss

Phase composition of the thermally modified BT samples is represented in Table 1.

Table 1.
Phase composition of the thermally modified BT

Temperature, [^{0}C]	Phase composition
105	$Al_2O_3\cdot54SiO_2$
	SiO_2
	$MgSiO_3$
	Fe_2O_3
400	$Al_2Si_4O_{10}$
	SiO_2
	$MgSiO_3$
	Fe_2O_3
600	$283SiO_2\cdot Al_2O_3$
	SiO_2
	Fe_2O_3
800	Fe_2O_3
	$Al_2O_3\cdot54SiO_2$
	SiO_2
1000	$MgSiO_3$
	Fe_2O_3
	SiO_2

Data of Table 1 prove that phase composition of the samples is substantially dependent on the temperature of their treatment. A 400 ^{0}C treatment results in changes in the aluminosilicate composition: the structure $Al_2O_3\cdot54SiO_2$ transforms into $Al_2Si_4O_{10}$ then the latter compound undergoes transformation into

$283SiO_2 \cdot Al_2O_3$ at 600 ^{0}C. A 1000 ^{0}C treatment results in formation of $MgSiO_3$, Fe_2O_3, SiO_2. This means that a ratio Si/Al in aluminosilicates is being changed with temperature of thermal treatment, which leads to some changes in adsorption capacity of the tufa.

Adsorption of the heavy metal ions was found depending on the ion nature and temperature of the tufa treatment (see figure 2).

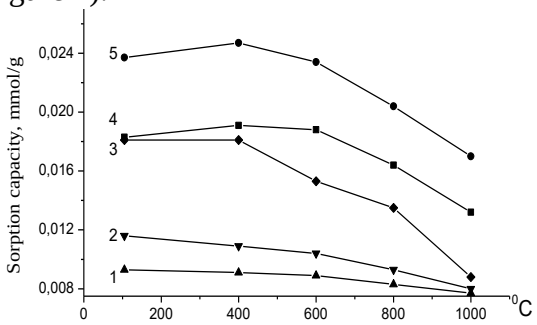


Fig. 2. Influence of the tufa thermal treatment temperature on its adsorption capacity in regard to some heavy metal ions: 1 – Ni^{2+}, 2 – Pb^{2+}, 3 – Zn^{2+}, 4 – Cu^{2+}, 5 – Mn^{2+}

As seen from Fig. 2, the ions adsorption value grows in the row: $Ni^{2+} < Pb^{2+} < Zn^{2+} < Cu^{2+} < Mn^{2+}$. A 400 ^{0}C treatment of the samples causes some rise in the adsorption value followed by further decrease at the higher temperature treatment. A comparison between adsorption value and specific surface area proves that both parameters change similarly (see Table 2) as it is typical for the fine-dispersed adsorbents.

Table 2.

Area of specific surface for the thermally modified BT

T,[°C]	105	400	600	800	1000
S_{BET}, [m^2/g]	7.25	7.81	7.65	4.54	1.82

According to [8], following groups: ≡Si–OH and ≡Al–OH play role of the aluminosilicate surface active centers. Thermal treatment causes their partial dissociation according to the mechanism that depends on the treatment temperature. A mechanism of dissociation has been identified using IR-spectroscopy, which proved [10] that the dissociation runs through removal of H^+ ion at the temperature under 400 ^{0}C and formation of of the negatively charged surface centers (≡S–O^- and =Al–O^-). Alternatively, this process may run through removal of OH^- groups resulting in formation of the positively charged surface centers (≡Si^+ and =Al^+). This explanation is based on the results of pH-measuring carried out with aqueous aluminosilicate suspensions (Table 3).

As seen from Table 3, all the systems under investigation has revealed the positive suspension effect that means that the charge of the surface active centers is negative and a competing adsorption of H^+ and Mn^{2+} is possible. This is also proved by another experiments were ΔpH for the suspensions containing Cu^{2+} is decreasing for all modified BT samples.

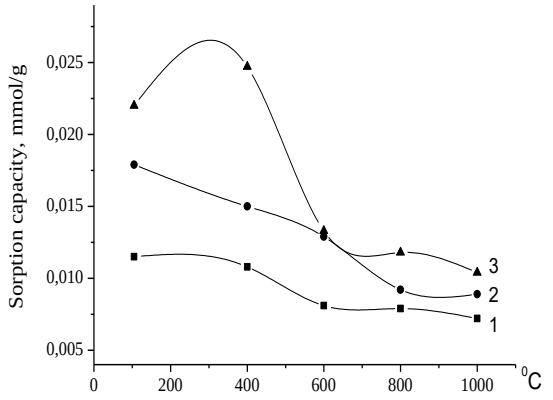
Another experiment has been carried out for the grains (d=1-2 mm) of BT similarly to the powdered samples. Results of this investigation are shown in figure 3. It can be seen that the sorption value of the heave metal ions is growing within the sequence $Pb^{2+} < Zn^{2+} < Mn^{2+}$, which is similar to the one obtained for the powdered samples. Again, a thermal treatment at 400 ^{0}C results in some increase in the adsorption values while any

Table 3.

Influence of the basalt tufa thermal processing temperature on the suspension effect value

Suspension medium	Suspension effect value for the samples modified at the temperature, [^{0}C]				
	105	400	600	800	1000
Distilled water, pH	2.005	2.743	4.108	3.382	2.748
Solution of $Cu(NO_3)_2$, pH	1.916	1.947	3.843	3.228	2.582

higher temperature of the treatment causes temperature of the treatment causes decrease in the heavy metal ions adsorption. A comparison between the granule and powder samples adsorption values shows that the former is somewhat higher than the latter because of a higher specific surface area of the powdered samples.



Fig, 3. An influence of the BT thermal treatment temperature on adsorption of some heavy metal ions: 1 – Pb^{2+}, 2 – Zn^{2+}, 3 – Mn^{2+}

4. Conclusion

It has been found that thermal treatment of basalt tufa results in significant changes in its phase composition, which depends greatly on the temperature regime of sintering. Weight loss during thermal treatment is ranged from 5,79 % (at 400 ^{0}C) to 10,18 % (1000 ^{0}C). Adsorption of the heavy metal ions on the powdered tufa samples decreases for the sequence: Ni^{2+} < Pb^{2+} < Zn^{2+} < Cu^{2+} < Mn^{2+}. When the sample undergoes thermal treatment, its adsorption capacity increases while further increase in the thermal treatment temperature results in decrease in this value because of drop in the specific surface area of the samples.

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