MECHANIKA
CZASOPISMO TECHNICZNE
TECHNICAL TRANSACTIONS
MECHANICS
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ
5-M/2011
ZESZYT 15
ROK 108
ISSUE 15
YEAR 108

IHOR KOBASA*, JANUSZ MIKUŁA**,
ANATOLIJ WOLOSCHUK*, WALENTINA TSYMBALIUK**

INFLUENCE OF THERMAL TREATMENT ON THE PHYSICAL, MECHANICAL AND SORPTION CHARACTERISTICS OF THE BASALT TUFA

WPŁYW OBRÓBKI CIEPLNEJ NA FIZYCZNE, MECHANICZNE I SORPCYJNE CHARAKTERYSTYKI TUFU BAZALTOWEGO

Abstract

Different methods of classical chemical analysis, flame photometry and atom-absorption spectroscopy were used to check chemical composition of the basalt tufa which is a natural alumosilicate with Si/Al ratio 4.5–4.7. Thermal treatment of the tufa at 105–500°C can activate its sorption capacity of NH_4^+ ions. Thermal treatment of the tufa particles at higher temperatures results in decreasing of the sorption activity, specific surface area and porosity and increase in the wear-off coefficient.

Keywords: basalt tufa, sorption, mechanical characteristics of tufa, thermal treatment of tufa

Streszczenie

Różne metody klasycznej analizy chemicznej, fotometrii płomieniowej i spektroskopii atomowo-absorpcyjnej zostały wykorzystane do stwierdzenia składu chemicznego tufu bazaltowego jako naturalnego glinokrzemiany ze stosunkiem Si/Al, w zakresie 4,5–4,7. Obróbka cieplna tufu w zakresie temperatur od 105 do 500°C może aktywować jego sorpcyjną pojemność w relacji do jonów NH_4^+. Obróbka cieplna cząstek tufu w wysokich temperaturach zmniejsza jego aktywność sorpcyjną, powierzchnie właściwą i porowatość oraz powoduje wzrost współczynnika odporności na ścieranie.

Słowa kluczowe: tuf bazaltowy, sorpcja, właściwości mechaniczne tufu, obróbka cieplna tufu

* Ihor Kobasa, Anatolij Woloschuk, Yu. Fedkovych National University of Chernivtsi, Kotsiubynsky.
** Janusz Mikuła, Walentina Tsymbaliuk, Institute of Materials Engeneering, Cracow University of Technology.

1. Introduction

A problem of water cleaning from various pollutions is ecologically and socially important. That is why research and development of new inexpensive and effective water purification methods remains one of the particulary important scientific and applied problems. In this context, some natural mineral sorbents can be very attractive to resolve this problem since such materials possess high adsorption and ion exchange properties and can be easily reused or utilized. On the other hand, many countries have practically inexhaustible deposits of the mineral sorbents.

Colloid and chemical properties, surface structure and nature of the active centers of the minerals must be determined in order to ensure their effective applying as sorption agents. This issue is under intense investigation in many countries [1]. Results of such investigation projects can be used as a theoretical background for selection of the most effective natural sorbents in the water/polluted water cleaning and treatment technologies.

Basalt tufa is a natural volcanically-originated mineral with the zeolite-like structure. Ukrainian deposits of tufa are estimated to 1 billion tons. There are some incompleted and fragmented investigations of the tufa adsorption and ion exchange properties but even these data evidence good prospects of wider involvement of the tufa into solution of many ecological and technological problems.

2. Experimental

The tufa particles size of 1.5 mm were obtained through the mechanical milling of the natural tufa and used in all experiments. Thermal treatment of the tufa was realised in the air at 105–1000°C during 4 hours. A method of the thermal adsorption of nitrogen (the BET method) with the gas sensor GH-1 was engaged to determine the specific surface area of the tufa particles.

The density of the granules was determined using a pyknometer. Total specific volume of the pores was determined through measuring of capacity of the liquid (twice-distillated water) in the pores. Then porosity of the tufa particles was calculated using total volume of the pores and virtual density of the material.

3. Results and Discussion

It is known that thermal treatment of the minerals can significantly influence on their structural and phase composition that results in changes of their sorption activity [2]. Taking into account this information, we investigated an influence of the temperature of thermal treatment on the weight loss and specific surface area values of the basalt tufa (table 1).

As it was shown in table 1, weight loss coefficient increases from 2.12 to 3.62% while the temperature increase from 105 to 1000°C. This small weight loss can be caused by emission of the hygroscopic and constitutional water. So it can be concluded that the basalt tufa samples are thermally quite stable and there is no components of the tufa which can decompose in the temperatures range of 105–1000°C.

Table 1

Influence of the temperature of preliminary thermal treatment of the basalt tufa particles on the weight loss coefficient and specific surface area

Temperature, [°C]	105	250	400	500	750	850	1000
Specific surface area, [m^2/g]	7.25	7.81	7.65	7.58	4.54	3.47	1.82
Weight loss coefficient, [%]	2.12	2.48	2.62	3.05	3.45	3.58	3.62

A small increase in the specific surface area has been determined for the temperatures range of 105–500°C and it can also be caused by evaporation of the crystallized water, which results in formation of new micropores in the material. Further decrease in the specific surface area after 500°C can be caused by agglomeration of the material. Sintering of the tufa has been determined at the temperatures > 750°C. Further heating of the tufa to 1050–1100°C results in its melting.

It is known [3] that a character of the sorption and ion-exchange processes in the systems "Me_xO_y–H_2O" depends mainly on the dissociation ratio of the surface-located hydroxyl groups of the oxides. Two ways of the dissociation are possible

$$(\equiv Si–OH)(s) \rightleftarrows (\equiv Si^+)(s) + OH^-(v) \quad (1)$$

$$(\equiv Si–OH)(s) \rightleftarrows (\equiv SiO^-)(s) + H^+(v) \quad (2)$$

Charged active centers can also be formed on the surface of alumosilicates as a result of adsorption of H^+ and OH^- from the aqueous solution

$$(\equiv Si–OH)(s) + OH^-(v) \rightleftarrows (\equiv Si(OH)_2)^-(s) \quad (3)$$

$$(\equiv Si–OH)(s) + H^+(v) \rightleftarrows (\equiv SiOH_2^+)(s) \quad (4)$$

Potentiometric investigation of aqueous suspensions of the basalt tufa proved [4] increase of positive suspension effect after thermal treatment. This result can be caused by formation of the negatively charged adsorption centers due to dissociation of OH-groups according to equation (2) and adsorption of OH^- ions according to (3).

"Soft" thermal treatment of the natural alumosilicates at 200–500°C results in additional activation of their sorption and catalytic properties [5]. This effect can be caused by gradual emission of the constitutional water and increasing in the specific surface area value. Constitutional water in the form of surface and structural hydroxyl groups is usually present in the natural alumosilicates. Thermal treatment results in decomposition of the hydroxyl layer [3] and this process causes release of the 'old' active centers and formation of the new ones according to

$$(\text{–O–}\overset{\displaystyle OH}{\overset{|}{Si}}\text{–O–}\overset{\displaystyle OH}{\overset{|}{Al}}\text{–O})_S \xrightarrow{t\,°C} (\text{–O–}\overset{\displaystyle +}{Si}\text{–O–}\overset{\displaystyle O^-}{\overset{|}{Al}}\text{–O})_S + H_2O$$

Therefore, thermal treatment of the natural mineral sorbents leads to significant changes in the nature and quantity of the adsorption centers.

Surface concentration of the structural complexes =Al–OH and =Fe−OH rises if water contacts with the thermo-treated mineral particles. Hydrogen atoms in the above complexes can be substituted with other cations through ion exchange reactions.

Taking into account results of the potentiometric titration of aqueous suspensions of the basalt tufa and possible processes of formation of the negatively charged active centers, the authors investigated dynamic sorption of ammonium ions on the natural and thermotreated samples of the basalt tufa.

Results of this investigation are shown in table 2. A 210-mm adsorption column filled with 114 g of the tufa was engaged for this investigation. Initial concentration of aqueous solution of NH_4Cl was 1.087 g/dm^3 (366 mg/dm^3 for NH_4^+) and filtration rate was 5 m/h. Concentration of NH_4^+ determined using photometrical method.

Table 2

Influence of the preliminary thermotreatment of the tufa on characteristics of ammonium ions sorption

Thermotreatment temperature, [°C]	105	250	500	750	1000
Sorption ratio, [%]	33,0	38,8	43,2	30,7	16,1
Dynamic sorption capacity, [mg/g]	13,1	15,4	16,8	12,2	6,4

As it was shown in table 2, quantitative characteristics of NH_4^+ sorption on the tufa depend on the temperature of preliminary annealing. Annealing of the tufa at 105–500°C causes activation of the sorption, which can be resulted by increase in the specific surface area and porosity of the particles.

Hence, it can be concluded that thermotreatment of the tufa provides significant influence on its physico-chemical and adsorption properties.

As seen in fig. 1 and 2, the specific surface area and porosity of the basalt tufa particles ($1.0 < d < 2.0$ mm) depend on the annealing temperature. Dependencies of the both parameters are similar and reach the highest values for the samples treated at 200–400°C. Treatment at higher temperatures results in a stable decrease in the specific surface area and porosity.

Extreme values of the both parameters can be caused by active emission of the hygroscopic and zeolite water, which was previously reported in this temperatures range [4].

It is known that non-saturated coordination atoms of silicon in the groups =SiOH and $=Si(OH)_2$ can act as active adsorption centers on the surface of alumosilicates [6]. If the temperature of annealing is higher, the more intense dehydroxylation of the surface occurs. Spectroscopic investigations and quantum mechanics calculations proved that the dehydroxylation is caused by dissociation of the zwiter-ion structures $\mathbf{=Si^+–O–Si–O^-}$ into two electrically neutral groups **Si=O**. A surface concentration of the negatively charged centers decreases, which results in drop of the tufa sorption activity related to NH_4^+ ions.

Mechanical durability is an important parameter for the mineral sorbents intended for dynamic cleaning of technological gases and polluted water [7].

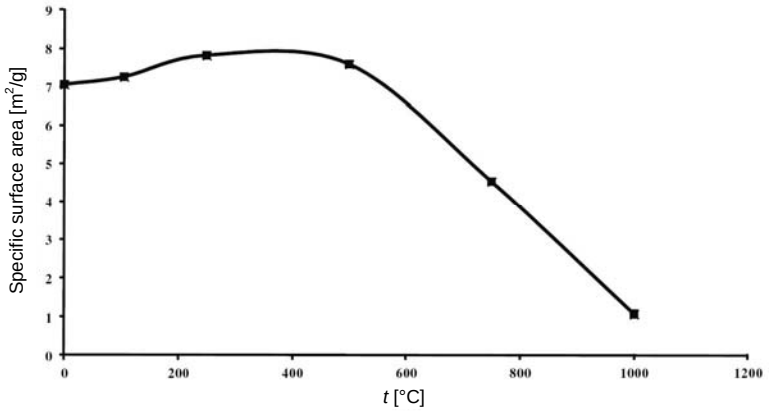

Fig. 1. Influence of the annealing temperature on specific surface area of the tufa (treatment time – 4 hours)

Rys. 1. Wpływ temperatury wyżarzania na powierzchnię właściwą tufu (czas obróbki – 4 godziny)

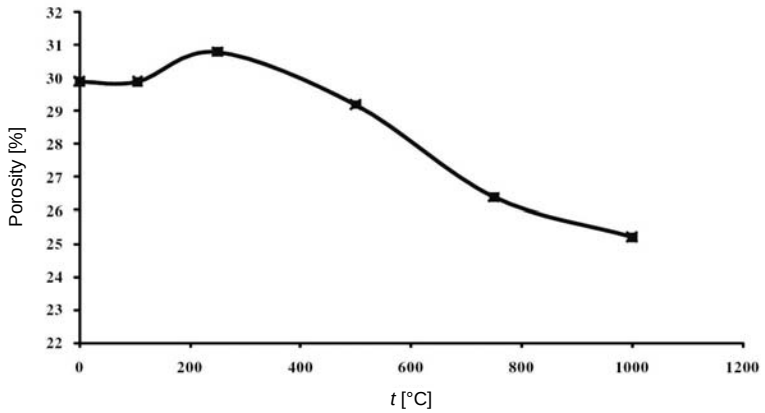

Fig. 2. Influence of the annealing temperature on porosity the tufa (treatment time – 4 hours)

Rys. 2. Wpływ temperatury wyżarzania na porowatość tufu (czas obróbki – 4 godziny)

As seen from fig. 3, mechanical durability of the granules is linearly increasing with increase in the caking temperature. X-ray phase analysis proved [8] that no new phases were formed for tufa caking at 105–1000°C. Therefore, increase in the tufa samples durability can be caused by additional structurization of the material after emission of the constitution water. This assumption can also be proved by an experimentally registered stability of the fill-up weight, true and virtual densities of the tufa granules and increasing of their wearing-off durability (see table 3).

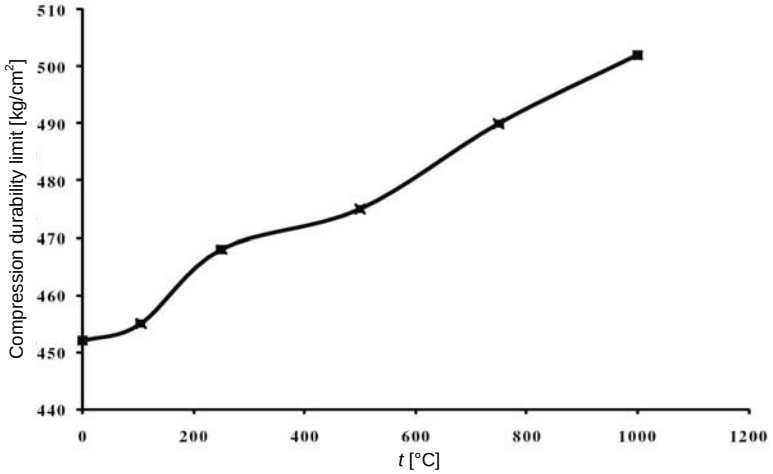

Fig. 3. Influence of the tufa particles after heat treatment vs. compression durability limit (4 hours of heat treatment)

Rys. 3. Wpływ wyżarzania na wytrzymałość na ściskanie (czas obróbki – 4 godziny)

Table 3

Influence of the thermal treatment on some physico-chemical parameters of the tufa particles

Thermal treatment temperature, [°C]	Fill-up weight, [g/cm^3]	Specific density, [g/cm^3]		Wearing-off coefficient, [%]
		true	virtual	
105	1,09	2,75	1,95	74,6
250	1,11	2,88	1,95	76,2
500	1,20	2,90	2,12	80,5
750	1,25	2,95	2,18	84,4
1000	1,25	2,98	2,30	86,2

4. Conclusions

Therefore, experimental results proved that thermal treatment can provide significant influence on some physico-chemical parameters of the basalt tufa and its technological sorption activity.

References

[1] Davila-Rengel J.I., Solace-Rios M., *Sorption of cobalt by two Mexican clinoptiloliterich tuffs zeolitic rocks and kaolinite*, J. Radional. and Nucl. Chem. **270**, 465 (2006).

[2] Yu. I. Tarasevich, *Natural sorbents in the water treatment processes*, Kiev, Naukowa Dumka, (1981) (in Russian).

[3] Ailer R.K., *Chemistry of Silica: Solubility, polymerization, colloid and surface properties, biochemistry*, Moscow, Mir, (1982) (in Russian).

[4] Shvets O.M., Woloschuk A.G., *Influence of thermal treatment on chemical composition, structure and adsorption parameters of the basalt tufa*, Bul. Odessa Univ., Chemical series, **9**, 138 (2004) (in Russian).

[5] Ababi V., Bilba N., Onu P., *Structural and adsorption characteristics of activated tufa*, Bul. Inst. Politechn. Iasi, **26**, 51 (1980).

[6] *Surface chemistry of silica. Surface structure, active centers, sorption mechanism*, Kiev, Naukowa Dumka, (1990) (in Russian).

[7] *Natural sorbents of USSR*, ed., Distanov A.S., Moscow, Nedra, (1990) (in Russian).

[8] Rakitskaya T.L., Kiose T.A., Reznik L.I., Ennan A.A., *X-ray phase investigation of a catalyst fixed on the basalt tufa*, Bul. Odessa Univ., Chemical series, **12**, 87 (2007) (in Russian).