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*L.R. Harutyunyan*<sup>a</sup>, *L.S. Tangamyanyan*<sup>a</sup>, *H.R. Petrosyan*<sup>b</sup>, *R.K. Adamyan*<sup>b</sup>, *H.H. Sargsyan*<sup>b</sup>,  
*R.S. Harutyunyan*<sup>b</sup>

## DISPOSAL OF SULFUR ANHYDRIDE OF INDUSTRIAL GASEOUS WASTES BY MODIFIED NATURAL ZEOLITES

<sup>a</sup> Armenian National Agrarian University, Yerevan, Armenia

<sup>b</sup> Yerevan State University, Yerevan, Armenia

The effectiveness of sulfur anhydride sorption from roasted molybdenum concentrate gaseous wastes by modified natural zeolites has been studied. Clinoptilolite from Nor Koghb deposit (Noyemberyan, Armenia) has been used as natural zeolite. The modification of zeolite has been done by thermic, acidic and alkaline treatments. It has been established that both thermally and chemically modified zeolites of Nor Koghb deposit are effective sorbents for sorption of sulfur anhydride; moreover, it is determined that the alkaline modified samples of zeolite have the highest sorption ability. Sulfur anhydride has been produced by the three following sources: pure molybdenum disulfate, non-treated molybdenum concentrate from Zangezur Copper Molybdenum Combine (Armenia) and the same molybdenum concentrate after thermal treatment. The highest effectiveness of sulfur anhydride sorption is obtained when pure molybdenum disulfide is used as a sulfur anhydride source. This result is quite predictable because pure molybdenum disulfide practically all turns to sulfur anhydride while additives are present in molybdenum concentrate, which do not produce sulfur anhydride.

**Keywords:** sulfur anhydride disposal, natural zeolite, acidic modified zeolite, alkaline modified zeolite, adsorption from gaseous waste.

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### Introduction

One of the most common contaminants of emitted gases of metallurgical, chemical and energy industries fabrics is sulfur anhydride (SO<sub>2</sub>), which causes great damage to the environment both ecologically and economically. For sorption of SO<sub>2</sub> from gaseous wastes, different methods have been applied, which can be classified in two following groups: wet-scrubbing process and sorption on solids [1]. The most promising are sorption on solids [1]. For sorption of SO<sub>2</sub> from gaseous wastes different sorbents are used: natural [2–6] and synthetic [1,7] zeolites, silica gel and activated carbon [8,9]. Among the solid sorbents, the natural and synthetic zeolites have been known the most promising and effective due to their regeneration possibility [1]. The sorption ability of natural zeolite to SO<sub>2</sub> is determined by different factors: content of clinoptilolite in zeolite

rock, sorption temperature and form of natural zeolite modification. It is known that the sorption ability of natural zeolite to SO<sub>2</sub> is proportional to the content of clinoptilolite in mineral rock [4], the low-silica zeolites better sorb SO<sub>2</sub> from pre-dehydrated systems, while high-silica zeolites better sorb SO<sub>2</sub> from wet environment. It is also established that the ability of modified forms of natural zeolite to adsorb SO<sub>2</sub> is higher than the natural zeolite sorption ability [7].

There are few large deposits of zeolite rock in Armenia, among which the Nor Koghb zeolite (Noyemberyan) is characterized as clinoptilolite (~80% of content) with molar ratio Si/Al=4.92 [10,11], thus, due to high-silica content, Nor Koghb zeolite is quite promising for SO<sub>2</sub> sorption and dry sorption method is preferred.

In this work, the possibility of zeolite from Nor

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*Disposal of sulfur anhydride of industrial gaseous wastes by modified natural zeolites*

Koghb deposit (Noyemberyan, Armenia) for sorption of SO<sub>2</sub> from gaseous wastes has been studied. The use of zeolite has a number of advantages:

– both natural and modified zeolites can be used in cycle multiple times as SO<sub>2</sub> can be desorbed at 350–400°C and then, the desorbed SO<sub>2</sub> can be applied for preparation of sulfur contained products [2];

– zeolites, which adsorbed SO<sub>2</sub>, can be used in production of cement making its quality better [12].

Thus, the application of zeolites as sorbent for disposal of SO<sub>2</sub> from gaseous wastes is an economically cost-effective and environmentally friendly process.

### Experimental

#### Materials

Hydrochloric acid (HCl, ASC reagent, 37%, Sigma-Aldrich, CAS Number 7647-01-0), sodium hydroxide (NaOH, reagent grade, ≥98.0%, pellets (anhydrous), Sigma-Aldrich, CAS Number 1310-73-2), molybdenum disulfide (MoS<sub>2</sub>, nanopowder, 90 nm diameter (ASP), 99% trace metals basis, Sigma-Aldrich, CAS Number 1317-33-5), silver nitrate (AgNO<sub>3</sub>, ASC reagent, ≥99.0%, Sigma-Aldrich, CAS Number 7761-88-8) were used without further purification. All solutions were prepared by double-distilled water.

The clinoptilolite tuff from Nor Koghb deposit (Noyemberyan, Armenia) was used as the natural zeolite. Detailed mineralogical and petrographic study of the natural zeolite was given elsewhere [10,11]. Zeolite was air-dried, ground in ball mill and subsequently in pestle and mortar, so as to pass from 123 μm sieves and was stored at room temperature. The chemical composition of natural zeolite is given in Table 1.

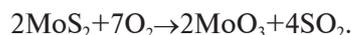
As the sources of SO<sub>2</sub>, (a) pure compound MoS<sub>2</sub> as a model compound; and (b) the molybdenum concentrate from Zangezur Copper Molybdenum Combine (Armenia) were used (their compositions are given in Table 2). Molybdenum concentrate has been used both in non-treated and thermal-treated forms. The thermal-treatment of molybdenum

concentrate has been done at 200°C for removal of humidity.

#### Methods

##### Sulfur anhydride production

The roasting of the molybdenum concentrate and MoS<sub>2</sub> has been done by using the rotary kiln (Laboratory Rotary Kiln 1600C, China) with constant air supply rate. The processes of roasting of molybdenum concentrate and MoS<sub>2</sub> strongly depend on temperature. It is known [13] that at the temperatures lower than 500°C the roasting process goes relatively slow, while at the 600°C the rate of roasting process is very high. At the high rates of roasting, at first, the rate of roasting (rate of SO<sub>2</sub> production) is higher than the rate of SO<sub>2</sub> sorption, and, at the high temperatures, the desorption of SO<sub>2</sub> becomes more intensive. Due to the mentioned processes, the adsorbed amount of SO<sub>2</sub> decreases. Therefore, the roasting process was being done at 500°C with a gradual increase in temperature. The process of MoS<sub>2</sub> oxidation (both chemically pure compound and molybdenum concentrate) is complex and multistep [13], but for quantify the produced gas SO<sub>2</sub> the following reaction completely describes the process:



After roasting the SO<sub>2</sub> sources, air-gaseous mixture went through P<sub>2</sub>O<sub>5</sub> for humidity sorption and then through zeolite.

The rate of air supply to the rotary kiln (Laboratory Rotary Kiln 1600C, China) was kept constant.

##### Natural zeolite modification

Thermal modification: Thermal treatment of zeolite samples consists in calcining prepared (crushed, sieved, washed and dried) samples at 100–700°C. Calcination was carried out in muffle furnace B400/410 (Naberthem, Carl Stuart Group). Zeolite samples were placed in a muffle furnace in heat-resistant round-bottom cups in the amount of 100 g,

Table 1

Chemical composition of natural zeolite [10,11]

constituent	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	TiO <sub>2</sub>	FeO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	H <sub>2</sub> O	other
wt.%	67.80	11.67	4.23	1.67	1.23	0.91	0.72	0.28	0.17	0.13	0.10	3.01	7.58

Table 2

Chemical composition of molybdenum concentrate [13]

constituent	Mo	Cu	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Re	additives
wt.%	51,80	0,44	1,80	35,67	6,90	0,82	0,75	0,025	1,82

subjected to heat treatment under static conditions for 3 h at 100–700°C, then, after a while, these cups were placed in desiccators with calcined CaCl<sub>2</sub> until complete cooling of the heat-treated zeolites.

**Alkaline modification:** the alkaline modified samples were being prepared by treating 10 g natural zeolite with 100 ml 2.0 N NaOH solutions by shaking during 4 h at room temperature. After that, modified samples were dried at 100°C for 3 h.

**Acidic modification:** the acidic modified samples were prepared by treating 10 g of natural zeolite with 100 ml of 2.0 N HCl solutions by shaking at room temperature during 4 h. Then, the modified samples were washed with distilled water until no Cl<sup>-</sup> ions were detected in the washing water by using AgNO<sub>3</sub> solution. After it was modified, samples were dried at 100°C during 3 h.

#### *Characterization of the natural and modified zeolites*

Nitrogen adsorption/desorption isotherms were registered using a NOVAe 2200 (Quantachrom) analyzer. The samples were outgassed under vacuum at 250°C for 5 h. The specific surface area was calculated by the BET method at  $P/P_0 \approx 0.98$  and the size distribution of porous was calculated based on the adsorption and desorption isotherms. Mesoporous surface area and mesoporous volume were calculated by Barrett-Joyner-Halenda (BJH) model. X-ray diffraction (XRD) diagrams were recorded by a diffractometer MiniFlex 600 (Rigaku) with monochromatic CuK<sub>α</sub> operated at 40 kV and 15 mA. Chemical composition of both natural and modified zeolites was obtained by ED XRF method on Thermo Scientific ARL Perform<sup>®</sup>X technique with rhodium tube 3.5 kV.

#### *Adsorption study*

The amount of adsorbed SO<sub>2</sub> was determined by gravimetric method. In each experiment, 5 g of sorbent and 2 g of SO<sub>2</sub> source have been used. Experiments were repeated three times, the average values of measurements were used in further

calculations. Estimated error in mass of adsorbed SO<sub>2</sub> was no more than ±2%.

#### *Results and discussion*

At the first stage of studies, the sorption capability of natural zeolite to SO<sub>2</sub> was studied. The studies showed that natural zeolite (5 g) adsorbed 0.015–0.025 g SO<sub>2</sub>, the effectiveness of sorption was 0.3–0.5% and it did not have practical importance. Thus, for increasing the effectiveness of SO<sub>2</sub> sorption, the natural zeolite has been modified.

#### *Sorption of SO<sub>2</sub> by thermal-treated zeolites*

The surface characteristics of thermal-treated zeolites are given in Table 3. The rather large surface area of Armenian clinoptilolite (19.4 m<sup>2</sup>/g) undergoes the following changes: it increases after calcination at 200°C, decreases at higher temperatures, but increases again at a temperature slightly below the decomposition point of the crystal structure (Fig. 1).

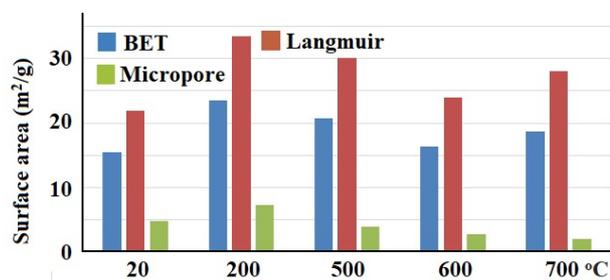


Fig. 1. The BET, Langmuir and micropore surface area of natural and thermal-treated zeolites

The surface area of micropores has a maximum value after calcination at 200°C and decreases monotonically with an increase in the calcination temperature. The clinoptilolite from the Nor Koghb deposit is characterized by a relatively low Si/Al ratio (4.92) and, possibly, such a sample undergoes a transformation into another structure, similar to heulandite-clinoptilolite «intermediates» (Si/Al $\approx$ 4), which decompose into metaheulandites.

The pore diameter of Armenian zeolite decreases with an increase in the thermal-treatment

Table 3

Porosity parameters of zeolite, treated at different temperatures\*

Thermal-treatment temperature (°C)	20	200	500	600	700
Total BET surface area (m <sup>2</sup> /g)	19.4	23.5	20.7	16.3	18.7
Langmuir surface area (m <sup>2</sup> /g)	21.9	33.4	30.0	23.9	28.0
including surface area of micropores (m <sup>2</sup> /g)	4.7	7.2	3.9	2.7	1.9
BJH adsorption volume of pores (cm <sup>3</sup> /g)	0.0744	0.0714	0.0672	0.0557	0.0773
BJH desorption volume of pores (cm <sup>3</sup> /g)	0.0750	0.0749	0.0664	0.0551	0.0767
BJH adsorption average pore diameter (nm)	22.1	17.3	10.5	14.9	15.8
BJH desorption average pore diameter (nm)	11.5	11.3	7.0	9.6	11.2

Note: \* – Estimated error in total BET surface area, Langmuir surface area, BJH adsorption volume of pores, BJH desorption volume of pores, BJH adsorption average pore diameter and BJH desorption average pore diameter are no more than ±2%.

temperature to a minimum value at 500°C, and then increases (Fig. 2).

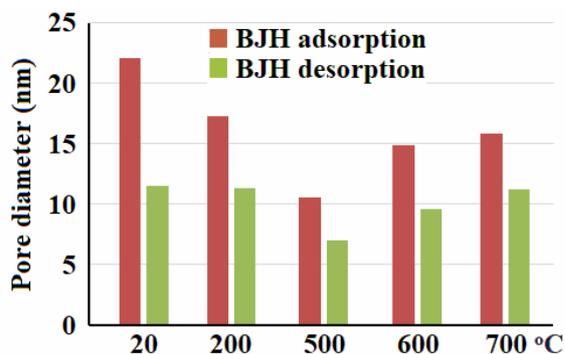


Fig. 2. Diameter of pores in thermal-treated zeolites calculated based on the BJH model

The pore size distribution  $dV/dD$  curves calculated on the basis of the BJH model from desorption isotherms measured on Armenian clinoptilolite show a narrow maximum corresponding to a system of nanometric pores (3–4 nm), as well as another broad maximum of larger pores with a diameter in the range of 15–60 nm; both modes being sensitive to the calcination temperature (Fig. 3). During thermal treatment, the pores of zeolite mainly released from occupied water, which improve the sorption properties of zeolite. It is obvious from the presented data of characteristic parameters of thermal-treated zeolites that the best performance is observed for the samples treated at 200°C, which have been applied for sorption of  $SO_2$ .

The results of  $SO_2$  adsorption show that at 200°C thermal-treated zeolite samples are better adsorbed  $SO_2$  than natural and the  $SO_2$  sorption efficiency increases. In the case of the use of zeolites thermal-treated at 200°C, the amount of adsorbed  $SO_2$  is higher when thermal-treated molybdenum concentrate is used as a  $SO_2$  source as compared with non-treated molybdenum concentrate (Fig. 4). It also follows from Fig. 4 that when  $MoS_2$  is used as a source of  $SO_2$ , the amount of adsorbed  $SO_2$  is higher than in the case of non-treated molybdenum concentrate source. It can be suggested from the obtained data that in air-gaseous mixture of molybdenum concentrate there are compounds, which to some extent hinder the sorption of  $SO_2$ . 4 h can be chosen as optimal time for  $SO_2$  sorption, because the increase in sorption amount of  $SO_2$  is negligible after 4 h. Based on the data of Fig. 4, the effectiveness of  $SO_2$  sorption has also been calculated. It is obtained that in the case of using  $MoS_2$  as a  $SO_2$  source, the effectiveness of  $SO_2$  sorption on per

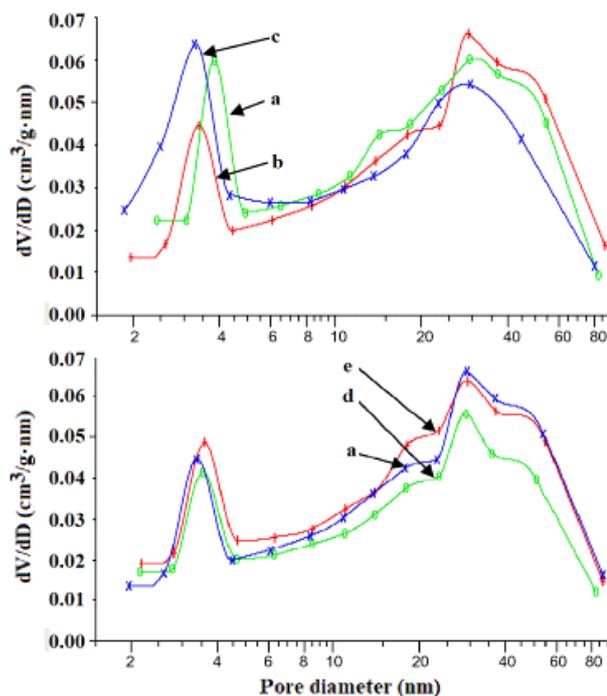


Fig. 3. Pore size distribution  $dV/dD$  curves calculated on the basis of the BJH model from desorption isotherms measured on samples of natural (a) and thermal-treated at 200°C (b), 500°C (c), 600°C (d) and 700°C (e) Nor Koghb zeolite

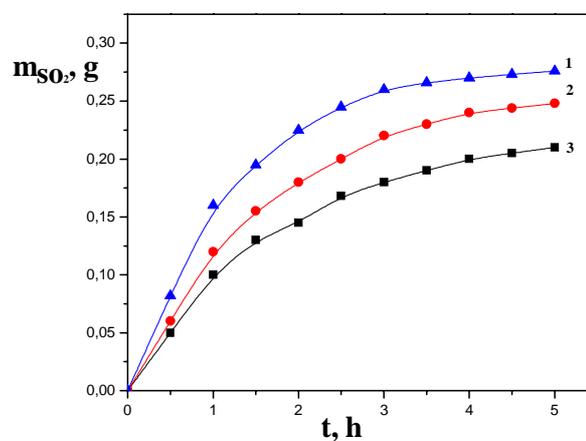


Fig. 4. Kinetic curves of  $SO_2$  sorption on thermal treated zeolite at 200°C. the weight of zeolite is 5 g, and the weight of a  $SO_2$  source is 2 g. 1 – pure molybdenum disulfide; 2 – thermic treated molybdenum concentrate; and 3 – non-treated molybdenum concentrate

gram of sorbent is 6.0%, whereas it is 5.5% and 5.0% in the case of thermal-treated molybdenum concentrate and non-treated concentrate, respectively. These are quite good results.

For the clarification of the possibility of reusing of the at 200°C thermal-treated zeolite samples as sorbent,  $SO_2$  was desorbed from that samples by

heating. The data of SO<sub>2</sub> desorption from the sample of thermal-treated zeolite samples, which has been used for sorption of SO<sub>2</sub> produced by roasting of treated molybdenum concentrate, are given in Table 4.

As expected, the desorbed amount of SO<sub>2</sub> increases when the desorption temperature increases. At heating conditions at 350°C and 4 h, the desorption of SO<sub>2</sub> rises 4.7% and further practically stays constant.

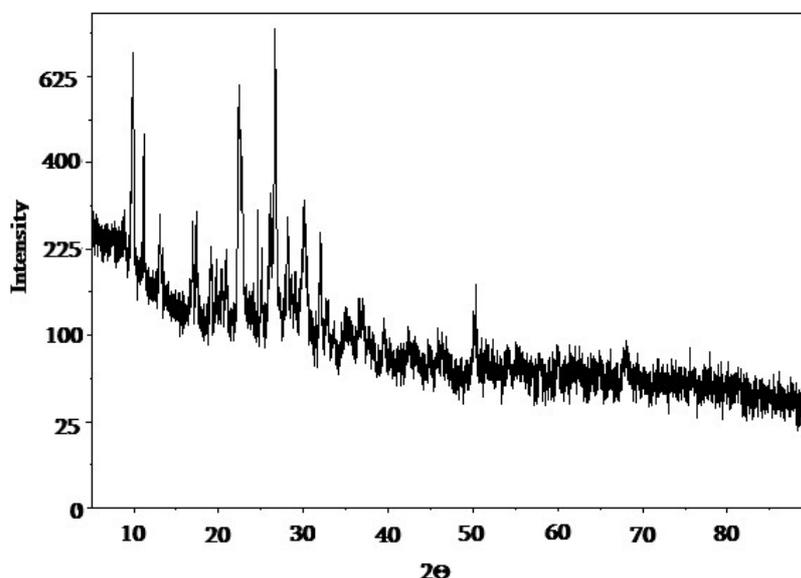


Fig. 5. XRD of natural zeolite from Nor Koghb deposit

Table 4

Data of SO<sub>2</sub> desorption from thermal-treated zeolite\*

Desorption temperature, °C (duration of treatment is 4 h)	Desorbed mass of SO <sub>2</sub> , g	Mass of desorbed SO <sub>2</sub> on initial mass of sorbent sample, %
150	0.09	1.8
250	0.160	3.2
300	0.205	4.4
350	0.222	4.7
400	0.226	4.73
500	0.228	4.74

Note: \* – Estimated error in mass of desorbed sulfur anhydride is no more than ±2%.

Table 5

Chemical composition of natural, acidic (2.0 N HCl) and alkaline (2.0 N NaOH) modified zeolites

Constituent	Content, wt.%		
	natural zeolite	acidic modified zeolite	alkaline modified zeolite
O	63.70	63.11	61.52
Mg	0.76	0.80	2.81
Na	0.64	0.69	0.96
Al	5.32	4.49	5.17
Si	16.16	28.43	25.27
K	1.20	1.15	1.20
Ca	1.58	0.77	2.17
Fe	0.63	1.36	0.90
Si/Al	4.92	6.33	4.89

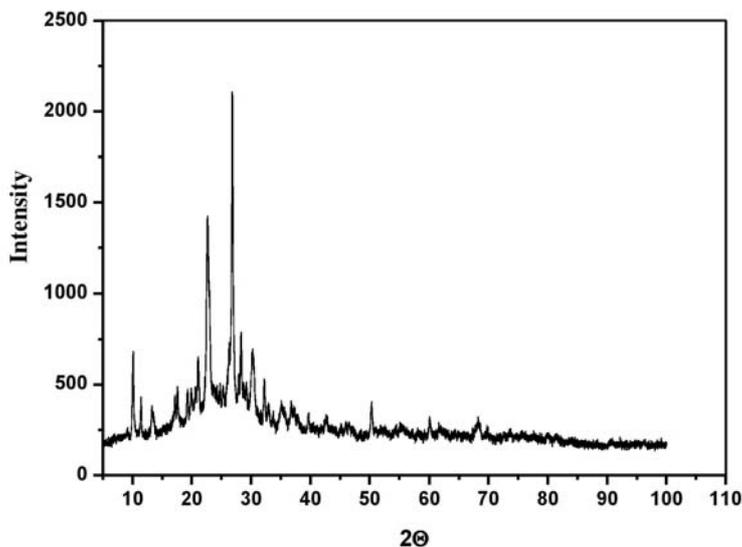


Fig. 6. XRD of zeolite modified by 2.0 N HCl

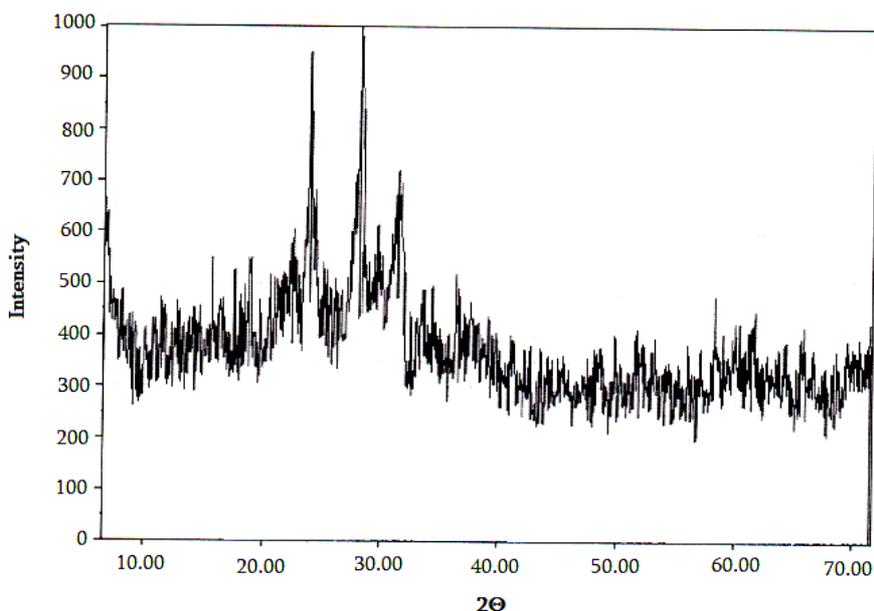


Fig. 7. XRD of zeolite modified by 2.0 N NaOH

The same sorbent sample was reused for sorption of  $\text{SO}_2$  from roasting of treated molybdenum concentrate and the effectiveness of  $\text{SO}_2$  resorption was 4.5 %. Comparison of  $\text{SO}_2$  sorption data on primary (5.0%) and repeated (4.5%) use of the thermal-treated zeolite sample allows us to suggest that not all sorption sites are released due to desorption. It can be suggested that it is the result of the presence of different impurities in the produced air-gaseous mixture due to roasting of treated molybdenum concentrate.

#### *SO<sub>2</sub> sorption by chemically modified zeolites*

The data of chemical composition of both acidic and alkaline modified zeolites are given in Table 5.

The obtained data indicate that natural zeolite undergo significant dealumination. In zeolite, due to both the acidic and alkaline modification, decationization is insignificant (5–8%); the contents of sodium and, in particular, potassium increase due to a decrease in the calcium content; and the magnesium content remains unchanged. The relative intensity of the peaks in the powder X-ray diffraction patterns of chemically modified zeolites (Figs. 5, 6 and 7) does not practically change, which is quite explained by the insignificant degree of decationization during chemical treatment.

Table 6  
**Changes of adsorption parameters (specific surface of mesopores  $A_{BJHads}$  and  $A_{BJHdes}$ , the outer surface  $A_{ext}$ , specific surfaces of BET  $A_{BET}$  and Langmuir  $A_L$ , surface of micropores  $A_{micro}$ , total volume of pores  $V_{sp ads}$  and  $V_{sp des}$ , pore diameter  $D_{sp ads}$  and  $D_{sp des}$ , volume  $V_{BJH ads}$ ,  $V_{BJH des}$  and diameter of mesopore  $D_{BJH ads}$ ,  $D_{BJH des}$ ) of zeolite modified by 2.0 N HCl and 2.0 N NaOH, calculated based on the nitrogen low-temperature adsorption-desorption static data**

Adsorption parameter	Zeolite samples		
	natural zeolite	2.0 N HCl modified sample	2.0 N NaOH modified sample
$A_{sp}$ , m <sup>2</sup> /g	19.4	44.6	42.8
$A_{BET}$ , m <sup>2</sup> /g	19.4	41.3	41.7
$A_L$ , m <sup>2</sup> /g	21.9	39.2	43.8
$A_{micro}$ , m <sup>2</sup> /g	3.7	17.0	15.0
$A_{ext}$ , m <sup>2</sup> /g	16.2	27.6	22.8
$A_{BJHads}$ , m <sup>2</sup> /g	13.5	14.9	16.2
$A_{BJHdes}$ , m <sup>2</sup> /g	26.0	42.2	38.4
$V_{sp ads}$ , cm <sup>3</sup> /g	5.47	17.7	18.0
$V_{sp des}$ , cm <sup>3</sup> /g	5.61	18.0	15.6
$V_{BJH ads}$ , cm <sup>3</sup> /g	1.44	8.3	6.8
$V_{BJH des}$ , cm <sup>3</sup> /g	1.50	8.0	7.1
$D_{sp ads}$ , nm	12.4	23.8	25.2
$D_{sp des}$ , nm	16.0	25.9	26.8
$D_{BJH ads}$ , nm	22.1	39.9	42.4
$D_{BJH des}$ , nm	11.5	26.6	23.3

Note: \* – Estimated error in adsorption parameters is no more than  $\pm 2\%$ .

Thus, it has been found that the modification both with HCl and NaOH does not cause the destruction of the crystal microporous structure of the zeolite, it retains compensating ions, losing mainly calcium, as evidenced not only by EDS analysis data, but also by XRD. The data given in Table 6 show that the surface of samples, as also the surface of micropores, increase due to modification, which means that the sorption capability of the modified samples also increases.

The data of SO<sub>2</sub> sorption on acidic and alkaline modified zeolites are given in Tables 7 and 8. Comparison of data on SO<sub>2</sub> sorption given in Tables 7 and 8 indicates that the effectiveness of sorption depends on both the SO<sub>2</sub> source and the form of modified zeolites. In the case of MoS<sub>2</sub>, the mass of adsorbed SO<sub>2</sub> is higher than when the molybdenum concentrate is used as the SO<sub>2</sub> source. Perhaps, the greater amount of SO<sub>2</sub> is produced due to roasting MoS<sub>2</sub> than due to roasting of molybdenum concentrate. It can be suggested that in molybdenum concentrate besides MoS<sub>2</sub>, other sulfur-contained compounds can be present and not all sulfur-contained compounds in molybdenum concentrate are turned to SO<sub>2</sub> due to roasting process.

#### Conclusions

It was established that the modification of natural zeolite increases the sorption effectiveness of sulfur anhydride due to an increase in the specific surface area and micropores volume. The chemically modified samples of zeolite are more efficient sorbents than thermal-modified samples. Among chemically modified samples, the alkaline modified samples of zeolite have higher sorption capability to

Table 7

**Data on SO<sub>2</sub> sorption by acidic modified zeolite (by 2.0 N HCl)\***

SO <sub>2</sub> source	Mass of adsorbed SO <sub>2</sub> on initial mass of sorbent sample, %				
	Sorption duration, h				
	1	2	3	4	5
thermal-treated molybdenum concentrate	3.02	3.83	4.91	5.50	5.52
pure MoS <sub>2</sub>	3.20	4.00	5.40	5.90	5.93

Note: \* – Estimated error in mass of adsorbed sulfur anhydride is no more than  $\pm 2\%$ .

Table 8

**Data on SO<sub>2</sub> sorption by alkaline modified zeolites (by 2.0 N NaOH)\***

SO <sub>2</sub> source	Mass of adsorbed SO <sub>2</sub> on initial mass of sorbent sample, %				
	Sorption duration, h				
	1	2	3	4	5
thermal-treated molybdenum concentrate	4.81	5.60	5.80	6.00	6.05
pure MoS <sub>2</sub>	5.40	6.60	7.00	7.40	7.42

Note: \* – Estimated error in mass of adsorbed sulfur anhydride is no more than  $\pm 2\%$ .

sulfur anhydride than acidic modified samples. In view of potential practical application, it is important that the sorption of sulfur anhydride is more efficient when it is produced by roasting of thermal-treated molybdenum concentrate of Zangezour Copper Molybdenum Combine (Armenia) as compared with non-treated molybdenum concentrate. The maximum adsorption of sulfur anhydride is reached after 4 h of process beginning; the highest effectiveness of sulfur anhydride sorption is 6%.

## REFERENCES

1. *Marcu I.C., Sndulescu I.* Study of sulfur dioxide adsorption on Y zeolite // *J. Serbian Chem. Soc.* – 2004. – Vol.69. – No. 7. – P.563-569.
2. *Modeling and simulation of the sulfur dioxide adsorption process in natural zeolites / Sfechis S., Abrudean M., Sas D.M., Ungursan M.L., Clitan I., Muresan V.* // *Appl. Mech. Mater.* – 2015. – Vol.811. – P.35-42.
3. *Physicochemical properties of the solid component of welding aerosol. I. Phase composition / Rakitskaya T.L., Truba A.S., Ennan A.A., Oprya M.V.* // *Odesa Natl. Univ. Her. Chem.* – 2015. – Vol.19. – P.6-13.
4. *Grigoryan F.A.* Issledovanie adsorbtsii oksida sery prirodnyim tseolitom Armenii // *Chem. J. Armenia.* – 2010. – Vol.63. – No. 2. – P.214-219.
5. *Mahmoodi Meimand M., Javid N., Malakootian M.* Adsorption of sulfur dioxide on clinoptilolite/nano iron oxide and natural clinoptilolite // *Health Scope.* – 2019. – Vol.8. – No. 2. – Art. No. e69158.
6. *Simultaneous sulfur dioxide and mercury removal during low-rank coal combustion by natural zeolite / Gani A., Wattimena Y., Erdiwansyah, Mahidin, Muhibbuddin, Riza M.* // *Heliyon.* – 2021. – Vol.7. – Art. No. e07052.
7. *Allen S.J., Ivanova E., Koumanova B.* Adsorption of sulfur dioxide on chemically modified natural clinoptilolite. Acid modification // *Chem. Eng. J.* – 2009. – Vol.152. – P.389-395.
8. *Lee K.T., Bhatia S., Mohamed A.R.* Removal of sulfur dioxide using absorbent synthesized from coal fly ash: role of oxygen and nitrogen oxide in the desulfurization reaction // *Chem. Eng. Sci.* – 2005. – Vol.60. – P.3419-3423.
9. *The performance of natural sorbents in the sulfur dioxide adsorption / Rakyts'ka T.L., Kiose T.O., Kameneva A.V., Mykhaylova O.V.* // *Odesa Natl. Univ. Her. Chem.* – 2015. – Vol.16. – No. 13. – P.24-33.
10. *Petrosov I.H., Jrbashyan R.T., Mnatsakanyan A.H.* Glavneishie mestorozhdeniya tseolitov Armenii. – Yerevan: Armenian NAS Publisher, 1999.
11. *Characterization of Georgian, Kazakh and Armenian natural heulandite-clinoptilolite / Tsitsishvili V., Panayotova M., Miyamoto M., Dolaberidze N., Mirdzveli N., Nijaradze M., et al.* // *Bull. Georgian Natl. Acad. Sci.* – 2022. – Vol.16. – No. 4. – P.39-46.
12. *Natural zeolite and its application in concrete composite production / Tran Y.T., Lee J., Kumar P., Kim K.H., Lee S.S.* // *Compos. B Eng.* – 2019. – Vol.165. – P.354-364.
13. *Optimum parameter research and definition of Kajaran molybdenite concentrate annealing process / Aghbalyan S.G., Hovsepyan A.H., Zakaryan F.H., Zurnachyan M.Gh.* // *Proc. NAS RA and SEUA Tech. Sci.* – 2004. – Vol.57. – No. 3. – P.388-392.

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## ВИДАЛЕННЯ СІРКОВОГО АНГІДРИДУ З ВІДХОДІВ ПРОМИСЛОВИХ ГАЗОВИХ ЗА ДОПОМОГОЮ МОДИФІКОВАНИХ ПРИРОДНИХ ЦЕОЛІТІВ

*Л. Р. Арутюнян, Л.С. Тангамян, Г.Р. Петросян, Р.К. Адамян, Г.Г. Саргсян, Р.С. Арутюнян*

Досліджено ефективність сорбції сіркової ангідриду з відходів випаленого молібденового концентрату за допомогою модифікованих природних цеолітів. Як природні цеоліти було використано кліноптилоліт з родовища Нор Кохб (Нойемберян, Вірменія). Модифікування цеоліту проводили термічним, кислотним і лужним методами. Встановлено, що як термічно, так і хімічно модифіковані цеоліти родовища Нор Кохб є ефективними сорбентами для сорбції сіркового ангідриду; більше того, було визначено, що лужно-модифіковані зразки цеоліту мають найвищу здатність до сорбції. Сірковий ангідрид було одержано з трьох джерел: чистого дисульфиду молібдену, необробленого молібденового концентрату з Мідно-молібденового Комбінату (Зангезур, Вірменія) та того самого молібденового концентрату після термічної обробки. Найвища ефективність сорбції сіркового ангідриду досягається, коли чистий дисульфід молібдену використовується як джерело сіркового ангідриду. Цей результат є досить передбачуваним, оскільки практично весь чистий дисульфід молібдену перетворюється на сірковий ангідрид, тоді як домішки, присутні в молібденовому концентраті, не утворюють сірковий ангідрид.

**Ключові слова:** видалення сіркового ангідриду, природний цеоліт, кислотно-модифікований цеоліт, лужно-модифікований цеоліт, адсорбція з газових відходів.

## DISPOSAL OF SULFUR ANHYDRIDE OF INDUSTRIAL GASEOUS WASTES BY MODIFIED NATURAL ZEOLITES

*L.R. Harutyunyan<sup>a,\*</sup>, L.S. Tangamyanyan<sup>a</sup>, H.R. Petrosyan<sup>b</sup>, R.K. Adamyan<sup>b</sup>, H.H. Sargsyan<sup>b</sup>, R.S. Harutyunyan<sup>b</sup>*

<sup>a</sup> *Armenian National Agrarian University, Yerevan, Armenia*

<sup>b</sup> *Yerevan State University, Yerevan, Armenia*

\* e-mail: [l.harutyunyan@anau.am](mailto:l.harutyunyan@anau.am)

The effectiveness of sulfur anhydride sorption from roasted molybdenum concentrate gaseous wastes by modified natural zeolites has been studied. Clinoptilolite from Nor Koghob deposit (Noyemberyan, Armenia) has been used as natural zeolite. The modification of zeolite has been done by thermic, acidic and alkaline treatments. It has been established that both thermally and chemically modified zeolites of Nor Koghob deposit are effective sorbents for sorption of sulfur anhydride; moreover, it is determined that the alkaline modified samples of zeolite have the highest sorption ability. Sulfur anhydride has been produced by the three following sources: pure molybdenum disulfate, non-treated molybdenum concentrate from Zangezour Copper

Molybdenum Combine (Armenia) and the same molybdenum concentrate after thermal treatment. The highest effectiveness of sulfur anhydride sorption is obtained when pure molybdenum disulfide is used as a sulfur anhydride source. This result is quite predictable because pure molybdenum disulfide practically all turns to sulfur anhydride while additives are present in molybdenum concentrate, which do not produce sulfur anhydride.

**Keywords:** sulfur anhydride disposal; natural zeolite; acidic modified zeolite; alkaline modified zeolite; adsorption from gaseous waste.

#### REFERENCES

1. Marcu IC, Sdndulescu I. Study of sulfur dioxide adsorption on Y zeolite. *J Serbian Chem Soc.* 2004; 69(7): 563-569. doi: 10.2298/JSC0407563M.
2. Sfechis S, Abrudean M, Sas DM, Ungursan ML, Clitan I, Muresan V. Modeling and simulation of the sulfur dioxide adsorption process in natural zeolites. *Appl Mech Mater.* 2015; 811: 35-42. doi: 10.4028/www.scientific.net/amm.811.35.
3. Rakitskaya TL, Truba AS, Ennan AA, Oprya MV. Physicochemical properties of the solid component of welding aerosol. I. Phase composition. *Odesa Natl Univ Her Chem.* 2015; 19: 6-13. doi: 10.18524/2304-0947.2014.1(49).38308.
4. Grigoryan FA. Issledovanie adsorbtsii oksida sery prirodnym tseolitom Armenii [Investigation of SO<sub>2</sub> adsorption on natural zeolites of Armenia]. *Chem J Armenia.* 2010; 63(2): 214-219. (in Russian).
5. Mahmoodi Meimand M, Javid N, Malakootian M. Adsorption of sulfur dioxide on clinoptilolite/nano iron oxide and natural clinoptilolite. *Health Scope.* 2019; 8(2): e69158. doi: 10.5812/jhealthscope.69158.
6. Gani A, Wattimena Y, Erdiwansyah, Mahidin, Muhibbuddin, Riza M. Simultaneous sulfur dioxide and mercury removal during low-rank coal combustion by natural zeolite. *Heliyon.* 2021; 7: e07052. doi: 10.1016/j.heliyon.2021.e07052.
7. Allen SJ, Ivanova E, Koumanova B. Adsorption of sulfur dioxide on chemically modified natural clinoptilolite. Acid modification. *Chem Eng J.* 2009; 152: 389-395. doi: 10.1016/j.cej.2009.04.063.
8. Lee KT, Bhatia S, Mohamed AR. Removal of sulfur dioxide using absorbent synthesized from coal fly ash: role of oxygen and nitrogen oxide in the desulfurization reaction. *Chem Eng Sci.* 2005; 60: 3419-3423. doi: 10.1016/j.ces.2005.01.002.
9. Rakyts'ka TL, Kiose TO, Kameneva AV, Mykhaylova OV. The performance of natural sorbents in the sulfur dioxide adsorption. *Odesa Natl Univ Her Chem.* 2015; 16(13): 24-33. doi: 10.18524/2304-0947.2011.13.38085.
10. Petrosov IH, Jrbashyan RT, Mnatsakanyan AH. *Glavneishie mestorozhdeniya tseolitov Armenii* [Major deposits of zeolites in Armenia]. Yerevan: Armenian NAS Publisher; 1999. (in Russian).
11. Tsitsishvili V, Panayotova M, Miyamoto M, Dolaberidze N, Mirdzveli N, Nijaradze M, et al. Characterization of Georgian, Kazakh and Armenian natural heulandite-clinoptilolite. *Bull Georgian Natl Acad Sci.* 2022; 16(4): 39-46.
12. Tran YT, Lee J, Kumar P, Kim KH, Lee SS. Natural zeolite and its application in concrete composite production. *Compos B Eng.* 2019; 165: 354-364. doi: 10.1016/j.compositesb.2018.12.084.
13. Aghbalyan SG, Hovsepyan AH, Zakaryan FH, Zurnachyan MGH. Optimum parameter research and definition of Kajaran molybdenite concentrate annealing process. *Proc NAS RA and SEUA Tech Sci.* 2004; 57(3): 388-392.