

## Adsorption of Sulphur Dioxide on Clinoptilolite Volcanic Tuff

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**ABSTRACT:** The adsorption behaviour of  $\text{SO}_2$  on thermally and chemically activated clinoptilolite volcanic tuff is studied. The isotherms were obtained on a gravimetric laboratory equipment with quartz spring balance. A clinoptilolite sample from the Mirsid deposit (Romania) in crushed form (0.125-1.00 mm particle size) and activated either by heating to 500°C or by treating with hydrochloric acid was used in the experiments. The samples were characterized by chemical analysis and BET analyses of the specific surface area and pore size distribution. The maximum adsorption capacity of the samples ranged from 9 to 13 g  $\text{SO}_2$ /100 g sample. The sample activated by acid treatment exhibited a 20% higher adsorption capacity than the thermally activated one.

### INTRODUCTION

Sulphur dioxide from flue gases creates serious ecological problems, especially recently when, due to energy demands, the use of high sulphur fuels is increased. Between 1980 and 1993 the emissions of  $\text{SO}_2$  in the atmosphere were 1.8 millions of tons per year in Romania and about 7 millions of tons in the neighbouring countries [1]. The 1995 international standards for the  $\text{SO}_2$  content in flue gases fixed a level below 250 mg/Nm<sup>3</sup> which makes the problem of finding new, more efficient procedures for removal of this pollutant from waste industrial gases extremely important [2]. Thus, besides more than 30 commercial procedures on these problems already existing [3] new ones frequently appear. Among them are such that utilize adsorption of  $\text{SO}_2$  on natural and synthetic zeolites [4].

Zeolitized volcanic tuff in natural state exhibits poor adsorptive properties, its BET specific surface determined after degasation at 350°C (for 3 h and pressure of 10<sup>-3</sup> mm Hg) being 40-50 m<sup>2</sup>/g. After treatment with a HCl acid solution followed by calcination the specific surface becomes greater than 100 m<sup>2</sup>/g [5]. According to other authors [6], the removal of part of the exchangeable cations and partial dealumination take place after acid treatment of volcanic tuff samples which lead to an increase in the voids in the crystal structure of the adsorbent (namely the zeolite). With an increase in the acid concentration the specific surface grows up to a certain limit after which the zeolite crystal structure is destroyed.

Accounting for how expensive synthetic zeolites are the present paper aims to provide experimental data on  $\text{SO}_2$  adsorption on clinoptilolite volcanic tuff in both natural and chemically activated forms in order to establish possible performances of these adsorbents towards sulphur dioxide from dilute industrial gases.

### EXPERIMENTAL

Clinoptilolite tuff from the Mirsid deposit (Romania) containing about 70 wt.% clinoptilolite [7] was used as adsorbing material.

The specific surface of the samples was determined by a BET- gravimetric plant fully described previously [5]. Pore size distribution of the samples was determined by an AG/65 type mercury porometer.

The samples were treated with HCl solutions of 3, 5, and 7% concentrations, at a liquid-to-solid ratio of 3:1, at 90-100°C for 3 hours, under stirring and refluxing conditions. Afterwards, the samples were washed with distilled water until free of chlorine ions, followed by drying and calcining for 2 h at 300°C.

The isotherms of  $\text{SO}_2$  adsorption on the clinoptilolite tuff samples, processed as noted above, were performed at 20°C by the static gravimetric method on a quartz spring balance under  $\text{SO}_2$  pressures of 1.0 to 100 mm Hg. The quartz spring balance is a component of the installation for adsorption isotherms determination (Fig. 1). For a correct use of the balance first a calibration

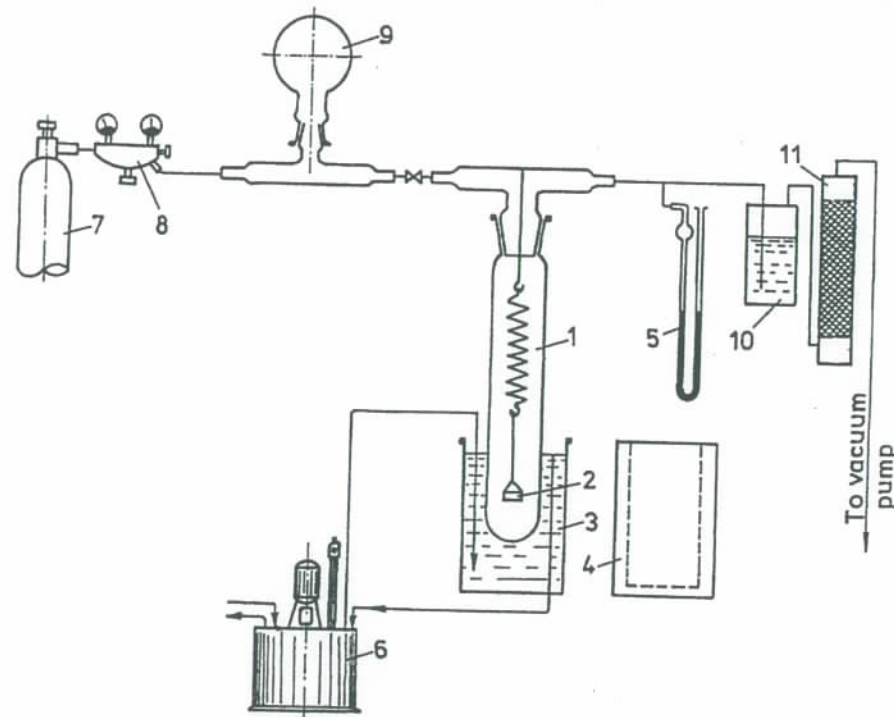


Fig.1. Gravimetric laboratory installation for adsorption studies by the static method:  
1 - quartz spring balance; 2 - platinum basket; 3 - thermostatic vessel; 4 - electric furnace; 5 - U-shaped mercury manometer; 6 - thermostat; 7 - cylinder with liquified sulphur dioxide; 8 - pressure reducer; 9 - ballon; 10 - bubbling vessel with iodine solution; 11 - drying tower.

curve in mass-elongation coordinates was created - under vacuum the weights were placed in basket 2 of the balance 1 (Fig. 1) followed by an elongation reading with a cathetometer. All calibration measurements were performed within the range of linear dependence of elongation on weight proper to the available quartz spring.

Each adsorption isotherm was determined as follows: sample of about 0.2 g was placed in basket 2 of balance 1 and, under vacuum, was degassed at 300°C for 3 h by heating with electric furnace 4 until no change in elongation of the quartz spring was detected. Then the furnace was removed and after cooling at room temperature the thermostatic vessel 3 was placed (Fig. 1). Then, from ballon 9, a small quantity of sulphur dioxide was admitted in the space of balance 1 through the valve connecting 9 and 1 (Fig. 1). For the first point the amount of SO<sub>2</sub> is that corresponding to a pressure of about 5 mm Hg and for the next points the pressure is increased step by step up to 100 mm Hg. For each pressure the gas-solid equilibrium is considered reached when no change in the quartz spring elongation was detected. The amount of sulphur dioxide adsorbed on the sample causes a change in the quartz spring elongation which is measured by means of a cathetometer. Using the calibration curve noted above the amount of adsorbed sulphur dioxide was estimated. The equilibrium pressure for each determination was controlled by manometer 5 (Fig. 1).

## RESULTS AND DISCUSSION

The mean chemical composition of the used clinoptilolite tuff sample is presented in Table 1.

The adsorption isotherm of gaseous nitrogen (at -196°C) for the studied sample is shown in Figure 2 and is of type II, a fact that points out the presence of large pores in the sample. The BET specific surface calculated on the basis of this isotherm is 46.81 m<sup>2</sup>/g.

The cumulative distribution of the macropores volume in the sample is given in Figure 3. The total volume of the macropores is 0.19609 cm<sup>3</sup>/g. Macropores with radii of 83.3, 125.0, and 600.0 Å predominate but the sum of their area is only 14.60 m<sup>2</sup>/g. The difference of 32.21 m<sup>2</sup>/g in respect to 46.81 m<sup>2</sup> calculated from the isotherm (Fig. 2) corresponds to pores with radii less

than 75 Å including the clinoptilolite micropores with a specific surface of about 30 m<sup>2</sup>/g (determined by the BET method).

The adsorption isotherm of nitrogen (at -196°C) for the sample treated with a 5% HCl solution is represented in Figure 4. On the basis of this isotherm the BET specific surface of the treated sample is 103.4 m<sup>2</sup>/g. The values of BET specific surfaces for the sample untreated and treated with solutions of 3%, 5%, and 7% HCl are 46.81, 80.6, 103.4, and 110.2 m<sup>2</sup>/g, respectively.

The data of SO<sub>2</sub> adsorption on clinoptilolite volcanic tuff are represented in Figures 5 and 6 as adsorption isotherms in coordinates: g SO<sub>2</sub>/100g sample - pressure of SO<sub>2</sub>, and it is seen that all adsorption isotherms are of type I - favourable for

Table 1. Chemical composition of the clinoptilolite volcanic tuff.

Component	Content, wt. %
SiO <sub>2</sub>	68.12 - 70.06
Al <sub>2</sub> O <sub>3</sub>	11.77 - 12.62
Fe <sub>2</sub> O <sub>3</sub>	0.67 - 1.06
CaO	3.36 - 4.82
MgO	0.55 - 0.82
K <sub>2</sub> O	2.20 - 3.52
Na <sub>2</sub> O	0.40 - 0.60
TiO <sub>2</sub>	0.18 - 0.24
ign. loss	8.40 - 10.61

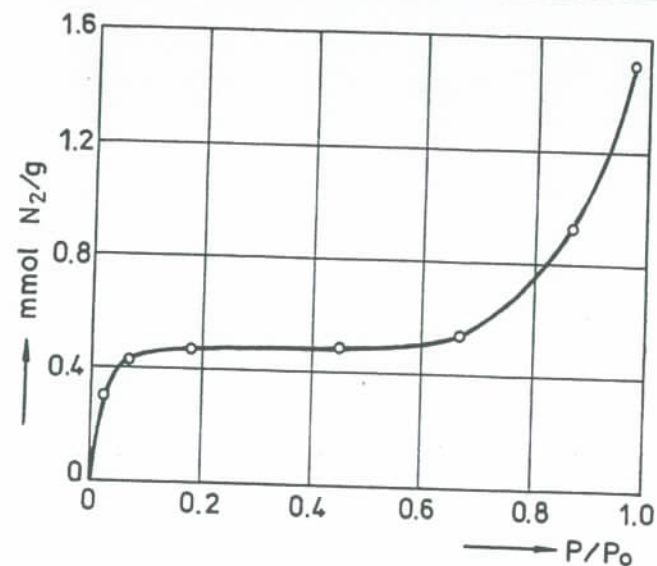


Fig. 2. Isotherm of nitrogen adsorption (at -196°C) on clinoptilolite volcanic tuff sample with granular size of 0.125 to 1.00 mm.

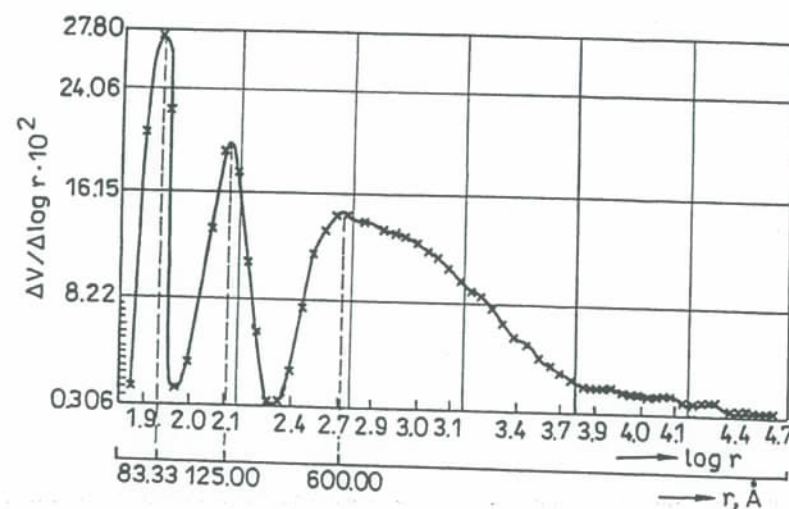


Fig. 3. Cumulative macropore distribution in clinoptilolite volcanic tuff sample with granular size of 0.125 to 1.00 mm.

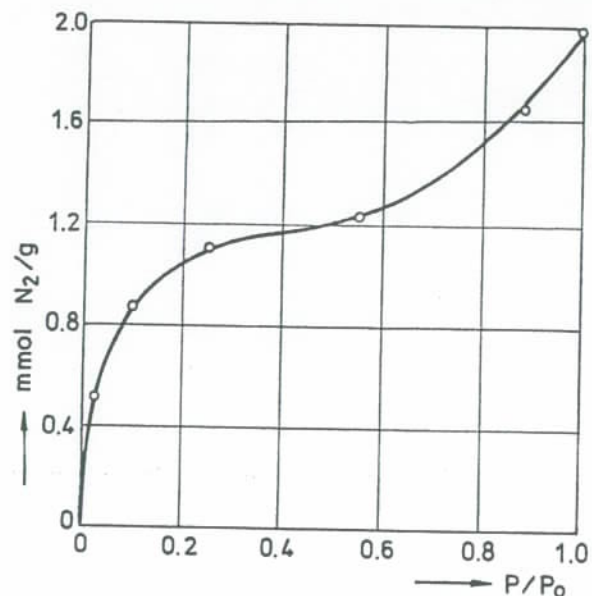


Fig. 4. Isotherm of nitrogen adsorption (at  $-196^{\circ}\text{C}$ ) on clinoptilolite sample treated with a 5% HCl solution for 3 hours.

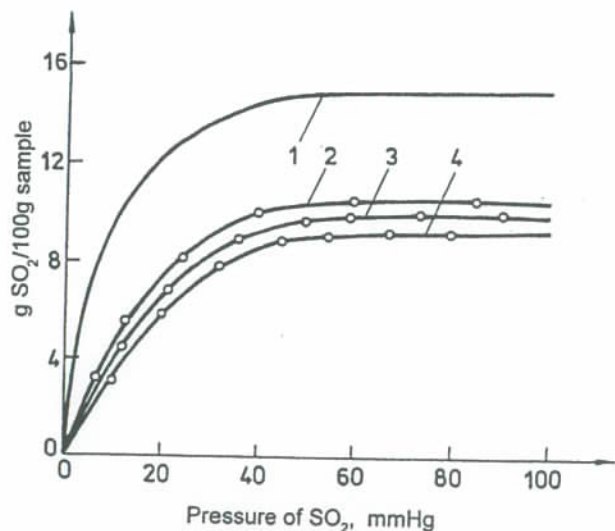


Fig. 5. Isotherms of  $\text{SO}_2$  adsorption (at  $20^{\circ}\text{C}$ ) on clinoptilolite volcanic tuff samples calcinated at different temperatures in comparison with pure clinoptilolite sample: 1 - pure clinoptilolite calcinated at  $500^{\circ}\text{C}$ ; 2, 3 and 4 - clinoptilolite volcanic tuff sample calcinated at 500, 400 and  $300^{\circ}\text{C}$ , respectively.

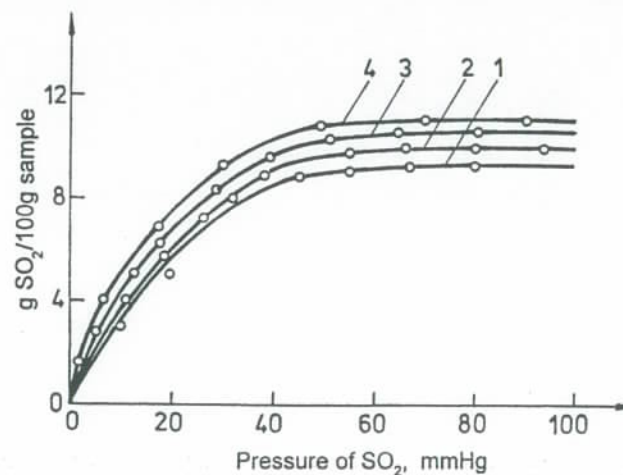


Fig. 6. Isotherms of  $\text{SO}_2$  adsorption (at  $20^{\circ}\text{C}$ ) on clinoptilolite volcanic tuff samples treated with HCl solutions of different concentrations and then calcinated at  $300^{\circ}\text{C}$ : 1 - reference; 2 - 3% HCl; 3 - 5% HCl; 4 - 7% HCl.

Table 2. BET specific surface and the adsorption capacity of the samples treated with HCl acid solutions and calcinated at  $300^{\circ}\text{C}$  for 2 hours.

Sample	HCl solution (%)	BET specific surface, $\text{m}^2/\text{g}$	Adsorption capacity $\text{g SO}_2/100 \text{ g sample}$
1(ref.)	0	46.8	9.2
2	3	80.6	10.0
3	5	103.4	10.6
4	7	110.2	11.00

$\text{SO}_2$  adsorption. Isotherms 2, 3 and 4 in Figure 5 are below isotherm 1 (of pure clinoptilolite) which may be related to the clinoptilolite content in the studied volcanic tuff which is below 70 wt.%. The effect of calcination on the adsorption capacity of the sample is negligible - the adsorption capacity is 10.6, 10.0 and 9.2  $\text{g SO}_2/100 \text{ g sample}$  calcinated at 500, 400 and  $300^{\circ}\text{C}$ , respectively.

The effect of acid treatment is represented in Figure 6 - isotherm 1 is of a sample calcinated at  $300^{\circ}\text{C}$  for 3 h (used as a reference one) and isotherms 2, 3, and 4 correspond to samples treated for 3 h with solutions of 3%, 5%, and 7% HCl, respectively, followed by calcination at  $300^{\circ}\text{C}$  for 2 h. The maximum adsorption capacity for  $\text{SO}_2$  of these samples is 10.0, 10.6 and 11  $\text{g}/100\text{g sample}$ , respectively, while that of the reference sample is only 9.2  $\text{g}/100\text{g sample}$  (Table 2). The increase is of 0.8, 1.4 and 1.8 units, respectively. Data in Table 2 show an almost linear dependence of adsorption capacity on BET specific surface, but the former increased 2.3 times while the latter only 1.2 times.

Adsorption of sulphur dioxide on clinoptilolite volcanic tuff is reversible and our results can serve as the basis for a technology for industrial gases purification from  $\text{SO}_2$  and repeated use of the natural zeolite adsorbent. We go further in the investigation of this possibility.

## CONCLUSIONS

1. The studied clinoptilolite volcanic tuff displays isotherms of  $\text{SO}_2$  adsorption of the I<sup>st</sup> type, i.e. favourable for its adsorption. The adsorption capacity ranges from 9.0 to 13.0 g  $\text{SO}_2$ /100 g tuff.
2. The HCl acid treatment increases the BET specific surface of the samples from 46.81 to 80.6, 103.4 and 110.2 m<sup>2</sup>/g for HCl solutions of 3%, 5%, and 7%, respectively.
3. By acid treatment the specific surface is increased 2.3 times while the adsorption capacity only 1.2 times which means that not the entire surface is responsible for sulphur dioxide adsorption. Acid activation of the sample with a 5% HCl solution increases its adsorption capacity by more than 29%.

## REFERENCES

1. Commission Economique pour l'Europe, l'État de la pollution atmosphérique transfrontière; mise à jour 1992, (1993) Nations Unies, New York and Geneva, 3.
2. Centi, G., A. Riva, I. Miracca, N. Passarini (1989) Riv. dei Combustibili, **43**, 6, 205-211.
3. U.S. Department of Energy, *Clean Coal Technology*, Project Status, June, 1991.
4. Breck, D.W. (1974) *Zeolite Molecular Sieves*, J.Wiley, N.Y., 771 pp.
5. Ababi, V., N. Bilba, P. Onu, Gh. Mihaila, N. Naum, C. Luca (1980) Bulet. Inst. Polit. Iasi, **26**, 3-4, 51-59.
6. Koridze, Z.I., A.Iu. Krupennikova, T.G. Andronikashvili (1974) *Clinoptilolite*. Proc. of Symp. Investigation and Use of Clinoptilolite, Tbilisi, November 2-4, A.Iu. Krupennikova (Ed.) 12. (in Russian)
7. Barbat, A., A. Marton (1989) *Zeolite volcanic tuffs*, Printing House Dacia, Cluj - Napoca. (in Romanian).

## Comparative Study of Water Adsorption and Air Enrichment by Selected Sedimentary and Synthetic Zeolites

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**ABSTRACT:** Adsorption characteristics of representative samples from different zeolite deposits of various geographic areas and selected synthetic ones are compared. Adsorption of water and enrichment of air are applied. Clinoptilolite, mordenite, chabazite, erionite, analcime and zeolite L, and synthetic mordenite are used as sorbents. Amounts adsorbed and isosteric heats for water adsorption are determined. Air enrichment is characterised by oxygen concentration and volume of the enriched gas. Chabazite is the best sorbent for water, and synthetic mordenite for air enrichment.

## INTRODUCTION

A given type of sedimentary zeolite from different deposits all over the world may possess similar characteristics but at the same time its properties can vary in different parts of a given deposit.

The object of the present study is to compare the adsorption characteristics of representative samples from different zeolite deposits of various geographic areas.

## MATERIALS AND METHODS

The studied zeolite samples are listed in Table 1.

The samples were chemically characterised by the classical silicate analyses.

A quantitative mineralogical analysis was performed by powder X-ray diffraction (DRON 3 diffractometer, Cu K<sub>α</sub> radiation).

All the studied samples were characterised and compared by their adsorption behaviour towards water vapours under various temperatures and pressures and by their selective adsorption of nitrogen from air after activating the samples at different temperatures (from 300 to 550°C).

Adsorption experiments were carried out in static conditions. Before adsorption tests the samples were dehydrated at 450°C for 4 hours. The applied water pressures were in the range 100 to 2000 Pa. The temperatures for adsorption were from 273 up to 327°C. Adsorption capacities,  $\alpha$ , were computed in gram adsorbed water for 100 grams of dehydrated zeolite. Adsorption isotherms were drawn for each temperature in the above mentioned pressure range.

## RESULTS AND DISCUSSION

The exchangeable cation compositions of most of the samples are presented on Figure 1. A modified Gibbs-Rosebom triangle [1] is used. Sodium, potassium and calcium are put on triangle tops. The content of these cations is accepted for 100 and the percentage of each cation is