Adsorption of H$_2$S from Thermal Water Using Clinoptilolite

Lali Akhalbedashvili$^1$, Tsira Beruashvili $^1$, Sophio Jalagania$^1$, Nona Janashvili$^1$, Nino Merabashvili $^2$

$^1$Ivane Javakhishvili Tbilisi State University, Alexandre Tvalchrelidze Caucasian Institute of Mineral Resources, Mindeli str., 11, Tbilisi, 0186, Georgia
$^2$JSC “Rustavi Azot”, No 2, Peace str., Rustavi, 3700, Georgia

lali.akhalbedashvili@tsu.ge

Abstract. The goal was to study and develop the composite adsorbents to uptake H$_2$S from thermal water on the base of natural zeolite clinoptilolite (CL) from deposit of Georgia and activated carbon (AC). Cation-modified forms of CL have been prepared by wet-milling method. The crystalline structure and content of prepared adsorbents have been studied by X-ray diffraction (XRD) technique, IR- and AAS methods. Adsorption experiments carried out varying the ratio zeolite: AC, composite: solution, duration of contact, granulation degree. The results obtained showed that modification of CL by ion-exchanging method with metal ions (Zn$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Cu$^{2+}$) has improved the adsorption capacity. Adsorption equilibrium reached in seven-fifteen minutes, and adsorption activity grows in a row: DeCL $<$ CL $<$ CuDeCL $<$ MnDeCL $<$ FeDeCL $<$ ZnDeCL $<$ AC/CL. The sorption capacity ranged from 0.68 mg/g to 28.17 mg/g. pH of thermal water before sorption was 8.97 and in filtrates changed in very wide ranges – from 10.44 until 3.55 depending on type of modification. Presence of multivalent cations of metals in the zeolite confirmed to be an essential factor determined the adsorption activity in relation to H$_2$S, adsorption occurs via both physical sorption and chemisorption. Most active was composite AC/CL with ratio AC:CL, equal 3:2. The difference for H$_2$S between decationated and cation-exchanged forms of CL may be explained by the change of surface potential. Polarity of zeolites depends on Si/Al ratio, which by-turn depends on conditions of acid treatment.

1. Introduction
The deep heat of the Earth's in the form of thermal waters is the cheapest, environmentally friendly, stable, safe and inexhaustible sources of energy. Their use plays an essential role in the fight against climate change and the improvement of atmospheric air, since using underground hot water and heating systems will save million tons of organic fuel, electricity, drinking water and gas.

Georgia is a rich country with natural sources of underground high-temperature thermal waters, known from ancient times. However, widespread use of geothermal water is limiting due to the presence of toxic H$_2$S+HS$^-+S_2O_3^{2-}$. Contents of sulphides (concentration of H$_2$S+HS$^-$) in the water extracted from 44 boreholes is within the range of 5-18 mg/l, out of which hydrogen sulphide makes 1mg/l, and the rest is HS$^-$, dissolved in the water.

Hydrogen sulphide is strong poisonous to the human organism, because it binds to iron in the mitochondrial cytochrome enzymes, and thus interfering cellular respiration and especially damaging the nervous system [1].


H₂S very weakly dissolves in water at ambient conditions and only in small degree dissociates according to equation H₂S+H₂O→HS⁻+H⁺, forming a weak acid areas (pH=6.8). Consequently, the problem of purification the water from H₂S has obtained big topicality that is confirmed by the large number of literature data on this issue [2-5].

Different methods have been tested to remove hydrogen sulfide from water such as aeration, ozonation, ion exchange, reverse osmosis, biological treatment and chemical oxidation [6, 7]. Activated carbon (AC) can be one of the best options for H₂S removal, but the preparation of this adsorbent requires high temperature, high pressure, and an activation process [5]. Recently, many solid adsorbents developed for the removal of H₂S; they are metal oxides, different types of activated carbons and natural and synthetic zeolites. The use of natural zeolites as adsorbents acquires importance due to their availability and low cost. Being a successful adsorbent for removal of hydrogen sulphide, zeolites should have high activity regard to sulphur adsorption, good regenerability and safety of structure. Clinoptilolite (CL), which is one of the most abundant zeolite in nature and widely used, attracted the attention and interest of many researchers [8-12].

Georgia is rich with high-temperature thermal waters (303-385 K), which contain the high content of hydrogen sulphide and needed the cleaning from it. At the same time, there are the rich deposits of zeolites, especially of clinoptilolite, in Georgia.

So, the goal of current research was to study and develop adsorbents to uptake H₂S from thermal water on the base of natural zeolite clinoptilolite (CL) from deposit of Georgia and the composite on the base of clinoptilolite and activated carbon (AC).

2. Materials and methods

Natural zeolite CL from Tedzami deposit (Georgia) was crushed, sieved and three fractions 0.25÷0.5, 0.5÷1 and 1.5÷3 mm were choosen for adsorption experiments. The chemical content of initial CL, determined by classical chemical analysis, is given in table 1.

Natural zeolite was be modified by combined treatment such as heating and chemical modification with acids and inorganic salts. Decationation of initial zeolite carried out twice with 0.5 or 1N HCl at 363-368 K during 1 hour with following washing and drying at 393 K. Cation-modified forms of CL were prepared from decationated samples by wet-milling method, using chloride or sulphate of corresponding metal. Crystalline structure of the adsorbents was analysed by X-ray diffraction (XRD) technique using DRON-2 diffractometer with CuKα radiation. IR-investigation carried out on Cary 630 FTIR spectrometer of “Agilent Technologies”. The amount of adsorbed H₂S determined by back titration with iodometric method before and after filtration; the content of exchanged ions were determined using AAS method on apparatus A Analyst-200 of firm “Perkin-Elmer” and flame photometer. Adsorption of H₂S was been studied at 323 K and ambient temperature and normal pressure by stirring the samples with thermal water, varying the ratio zeolite / AC, composite / solution, duration of contact, granulation degree and calcine temperature of zeolite. The optimal ratio zeolite : thermal water in static conditions was 2 / 50, zeolite / AC equal 2/3. The adsorption tests in dynamic regime included the following conditions: mass of adsorbents varied from 10 to 80 g, volume of passed water from 0.25 until 6.0 l, flow rate 3.0 l/h.

The chemical content of initial CL and decationated form (DeCL), determined by classical chemical analysis, is given in table 1. The exchanged degree of transition metal cations equal 5.95% for FeDeCL, 4.2% for CuDeCL and 2.1% for MnDeCL.
Table 1. The chemical composition of natural zeolite clinoptilolite from deposit of Tedzami (Georgia)

|       | Cl   | SiO₂ | Al₂O₃ | CaO  | MgO  | P₂O₅ | Fe₂O₃ | TiO₂ | MnO  | SO₃  | Na₂O | K₂O | Loss on calcination | Humidity |
|-------|------|------|-------|------|------|------|-------|------|------|------|------|-----|---------------------|----------|
| Conten. % | 58.24 | 19.43 | 5.71  | 0.08 | 0.05 | 5.15 | 0.20  | 0.03 | 0.3  | 1.90 | 1.80 | 4.55 | 1.96 |
| DeCL | SiO₂ | Al₂O₃ | CaO  | MgO  | P₂O₅ | Fe₂O₃ | TiO₂  | MnO  | SO₃  | Na₂O | K₂O | Loss on calcination | Humidity |
| Conten. % | 65.72 | 10.21 | 2.74  | 0.09 | - | 1.84 | - trace | - | 0.76 | 4.24 | 8.68 | - |

The investigated thermal water from borehole contained about 11.22 ppm of total H₂S in winter, but in summer, the content of H₂S decreased to 9.18 ppm. Only 1-3 ppm of H₂S exists in molecular form, the rest as HS⁻.

3. Results and discussions

3.1. Adsorbents characterization

XRD patterns of raw and treated samples indicated that acid treatment and following introduction of cation made a little shift at the peak points of diffraction spectrum: the intensity of decationated clinoptilolite decreased that explained by changes in crystalline lattice (figure 1, 2), and forming of amorphous structure. Raw zeolite contains 70-75% of CL, about 10 % of clay, 10-15% of feldspar, montmorillonite, and quartz.

IR-spectroscopy results showed that during the acid treatment (that causes dealumination, decationation) and ion exchange of zeolites, the oscillations of the external bonds of the Si (Al) -O tetrahedrons are affected. These bands are the low-intensity tetrahedral deformation oscillation band in the range of 593-602 cm⁻¹ also of the strip 665 cm⁻¹, which characterizes the structure of zeolite clinoptilolite. This oscillation band in the spectrum disappears after the introduction of copper cations into the zeolite, as well as in the dealuminated zeolite spectrum. The frequency of the intra-tetrahedral valence band after acid treatment of zeolite shifted from ~ 1060 to 1089 cm⁻¹, indicating a process of dealumination of zeolite.

Figure 1. X-ray diffraction spectrum of raw clinoptilolite
3.2. Adsorption experiments

The results showed that modification of clinoptilolite by ion-exchanging method with metal ions (Zn$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Cu$^{2+}$) has improved the adsorption capacity. Adsorption equilibrium has been reached in five-fifteen minutes in static and flow mode (figure 3), and adsorption activity grows in a row: DeCL < CL < CuDeCL < MnDeCL < FeDeCL < ZnDeCL < AC/CL < AC (figure 4). The dynamic sorption capacity (DSC) ranged from 0.68 mg/g to 8.17 mg/g. With an increase in the degree of dealumination, decationization and partial amorphization also occur as a result of severe acid treatment, and the sorption activity of the DeCL sample with respect to hydrogen sulfide sharply decreased. This effect is apparently associated with the removal of both intrazeolitic and impurity cations, a change in the porous structure and chemical nature of adsorption centers.

![Figure 3. Kinetic curves of H$_2$S concentration dependence on time for initial CL and activated carbon](image-url)
According to water analysis, resulted before and after filtration the ions of Fe, Mn, Ca and Mg were adsorbed simultaneously with H$_2$S. The hardness, alkalinity, permanganate oxidizability, smell, water colour and colony count decreased too. The cupper (II) and Fe (III) exchange in preliminary acid decationated and thermal treatment CL significantly improved the H$_2$S adsorption capacity of this natural zeolite and the highest values were reached 6.24 mg/g for CuDeCL and 8.17 mg/g for FeDeCL (figure 4).

### 3.3. Dependence on pH and temperature of water

It is known that the existence of ionic forms of hydrogen sulphide in groundwater is highly depends on pH [1]. At pH<4 prevails the molecular form of hydrogen sulphide. The growing of pH promotes the increasing of HS$^-$ and very rarely S$^{2-}$ ions. pH of studied thermal water before sorption was 8.97, but in filtrates changed in very wide ranges – from 10.44 until 3.55 depending on type of modification the zeolite – in acid or alkali medium.

Experiments carried out with preliminary acidification of thermal water to pH = 3 showed that the adsorption of total hydrogen sulfide decreases on cationic forms of clinoptilolite by 30-35%. Consequently, the chemisorption of HS$^-$ ions occurs mainly on cationic samples, and competitive water molecules with a higher dipole moment block the electrostatic interaction of molecular H$_2$S with surface (dipole moment for water molecular is 1.85 D and 0.95 for H$_2$S).

The temperature of flowing thermal water (323-343 K and 293-298K) did not influence the sorption capacity of zeolite samples and activated carbon. However, rise of temperature of thermal processing all studied adsorbents from 573 to 873 K significantly decreases the sorption activity that may be explained by narrowing of entry windows and channels at heating and partially distruction the structure at 873 K already.

### 3.4. Influence of granulation degree

Using the initial CL as an example, the effect of the size of zeolite granules on its adsorption capacity with sizes in the range 0.25–0.5, 0.5–1 and 1.5–3 mm was studied only in the flow mode. Since in the static mode the degree of granulation did not affect the sorption capacity of the sample: the equilibrium concentration of H$_2$S in the filtrate was reached within 10-15 minutes, the sorption capacity was also equal to 7 mg / g. But in the flow mode, when thermal water was passed through an adsorbent with dimensions of 0.25–0.5, the flow rate dropped almost to zero, and above 3 mm, a skip was observed. The most optimal degree of granulation was found to be a fraction of 0.5–2.0 mm.

It is known that at adsorption of H$_2$S the determining factor is the size of the entrance windows into large channels of zeolite [13, 14]. Introduction of transition metal ions in zeolite, natural or synthesised, causes the increasing of micropores’ volume An increase in the availability of zeolite upon replacement of Na$^+$ with divalent cations by 30-40% leads to the fact that exchanged forms absorb hydrogen sulfide in a dynamic mode more than initial form. The adsorption capacity of clinoptilolite in relation to H$_2$S was significantly improved after modification with copper, iron,
manganese or zinc cations, especially for Fe (III)-exchanged form. This is due to the decrease in the number of extraframework cations, while two or three monovalent sodium and potassium ions are replaced with one divalent or trivalent copper, iron or zinc ions.

4. Conclusions
The adsorption of H₂S from underground thermal water using ion-exchanged clinoptilolite and activated carbon have been studied in this work. The content of transition metals in zeolite structure promotes the adsorption capacity in relation to hydrogen sulfide. The sharp decrease of sorption capacity at acid treatment is an essential factor, demonstrative the leading role of cations and may be explained by the change of surface potential during ion-exchanged processing. Polarity of zeolites depends on Si/Al ratio, which by-turn depends on conditions of acid treatment.

Adsorption occurs via both physical sorption on Bronsted centers and chemisorption over cations. Therefore the most active was composite AC/CL with ratio AC/CL with optimal ratio 3/2.

Acknowledgment
The work carried out in the frame of project CARYS-19 and authors would like to thank Shota Rustaveli National Science Foundation of Georgia for supporting this research.

References
[1] S. Edwards, R. Alharthi and A.E. Ghaly. Removal of Hydrogen Sulphide from Water. American Journal of Environmental Sciences 7 (4): 295-305, 2011.
[2] N. Q. Long, H. T. Vuong, H. K. Phuong Ha, W. Kuniawan, H. Hinode, and T. Baba. Preparation, characterization and H₂S adsorptive removal of ion-exchanged zeolites X. ASEAN Engineering Journal Part B, Vol 5, No 1, 2016.
[3] S. Shah Mansi, M. Tsapatis, and J. I. Siepmann. Hydrogen Sulfide Capture: from Absorption in Polar Liquids to Oxide, Zeolite, and Metal–Organic Framework Adsorbents and Membranes. Chem. Rev. 117, pp.9755–9803, 2017.
[4] S. Regenspurg, J. Iannotta, E. Feldbusch, F. J. Zimmermann and F. Eichinger. Hydrogen sulfide removal from geothermal fluids by Fe(III)-based additives. Geotherm Energy, 8, 21, 2020.
[5] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32(5), pp.759–769, 1994.
[6] A.J.H. Janssen, G. Lettinga and A. de Keizer. Removal of hydrogen sulphide from wastewater and waste gases by biological conversion to elemental sulphur colloidal and interfacial aspects of biologically produced sulphur particles. Colloids Surfaces. 151, pp. 384-397, 1999.
[7] A.M. Eimarsen, A. Esoy, A.I. Rasmussen, S. Bungum and M. Sveberg. Biological prevention and removal of hydrogen sulphide in sludge at Lillehammer Wastewater Treatment Plant. Water Sci. Technol., 41, pp.175-187, 2000.
[8] S. Yasyerli, I. Ar, G. Dogu, and T. Dogu. Removal of hydrogen sulfide by clinoptilolite in a fixed bed adsorber. Chemical Engineering and Processing, 41, pp.785–792, 2002.
[9] D.W. Breck, Zeolites, Molecular Sieves, first ed., Wiley-Interscience, New York, 1974.
[10] A. Arcoya, J.A. Gonzalez, G Removal of Hydrogen Sulphide from Water sieves properties of a clinoptilolite, Microporous Mater. 7, pp.1 -13, 1996.
[11] R. Hernandez-Huesca, L. Diaz, G. Aguilar-Armenta, Adsorption equilibria and kinetics of CO₂, CH₄ and N₂ in natural zeolites, Sep. Pur. Technol., 15, pp.163-173, 1999.
[12] A. Sirkecioglu, Y. Altav, A. Erdem-Senatalar, Adsorption of H₂S and SO₂ on Bigadic, clinoptilolite, Sep. Sci. Technol. 30, 13, pp.2747–2762, 1995.
[13] L. Sigot, G. Ducom, and P. Germain. Adsorption of hydrogen sulfide (H₂S) on zeolite (Z): Retention mechanism. Chemical Engineering Journal, 286, pp. 47-53, 2016.
[14] H.-L. Tran, M.-S. Kuo, W.-D. Yang and Y.-C. Huang. Hydrogen sulfide adsorption by thermally treated cobalt (II)-exchanged NaX zeolite. Adsorption Science & Technology, Vol. 34(4–5), pp. 275–286, 2016.