

**ADSORPTION PURIFICATION OF NATURAL GAS FROM SULFUR COMPOUNDS
USING ACID-MODIFIED CLINOPTILOLITE**¹Aripdjanov Oybek Yusupdjanovich, ²Maxammatov Mirshoxid Maxmudjon ugli³Mo'minov Bekmurod Qobil ugliAssociate Professor of the Department of Chemical Technology of Oil Refining Tashkent
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Refining Tashkent Institute of Chemical Technology Republic of Uzbekistan, TashkentE-mail: muminovbekmurod0910@gmail.com**Abstract**

This paper investigates the enhancement of the adsorption properties of natural clinoptilolite for the purification of natural gas from harmful sulfur-containing components, specifically hydrogen sulfide (H₂S) and organic sulfur compounds (mercaptans, COS). The study focuses on the acid modification process (dealumination) to optimize the pore structure and increase the dynamic capacity of the adsorbent. Experimental results demonstrate that modified clinoptilolite exhibits significant efficiency, comparable to synthetic zeolites, while offering substantial economic and environmental advantages. The industrial feasibility of the proposed sorbent was validated through pilot tests.

Keywords

Natural gas, Clinoptilolite, Adsorption, Sulfur compounds, Acid modification, Dealumination, Zeolites.

1. INTRODUCTION**2.**

The increasing global demand for clean energy has made the efficient processing of natural gas a critical industrial priority. Many natural gas deposits contain significant concentrations of sour components, primarily H₂S, CO₂, and various mercaptans. These impurities are not only toxic and corrosive to pipeline infrastructure but also act as catalytic poisons in downstream chemical synthesis.

Traditional gas purification relies heavily on synthetic zeolites (e.g., NaX, CaA). However, their high production costs and sensitivity to acidic environments limit their economic efficiency. Natural zeolites, particularly clinoptilolite, represent a cost-effective alternative due to their high thermal stability and abundance. This research addresses the limitation of natural clinoptilolite—its narrow pore diameter—by applying chemical modification techniques to broaden its applicability in deep gas desulfurization.

1. Classification of Sulfur Removal Processes

Currently, more than 20 processes are used in the industry to treat gases containing sulfur compounds. These processes are categorized into two primary groups:

- **Group I:** Designed for the removal of hydrogen sulfide (H₂S) only. The chemical mechanism is based on the acidic properties of H₂S, utilizing weak bases and metal oxides as absorbents.

- **Group II:** Designed to simultaneously extract H₂S and organic sulfur compounds (such as COS, CS₂, and mercaptans). These processes are primarily characterized by physical absorption.

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- **Table 6. Chemical composition of clinoptilolite-bearing tuffs from various deposits**

Chemical composition, wt. %	Shutsima, Japan /89/	Itaya, Japan /89/	Rhodope, Bulgaria /90/	Patagonia, USA /91/	Kermine, Uzb.SSR /92/	Balkhiz, Az.SSR /77/	Noyib Kokhb, Arm.SSR /77/	Dzegvi, Geo.SSR /91/
SiO ₂	65.17	66.68	65.46	69.07	61.74	67.00	65.45	61.30
TiO ₂	0.16	0.16	—	—	0.12	0.19	0.17	—
Al ₂ O ₃	13.38	11.30	12.11	10.88	12.51	12.90	12.92	13.00
Fe ₂ O ₃	1.06	0.89	0.23	0.08	0.50	1.01	0.84	3.00
FeO	—	—	—	—	—	0.18	0.37	—
MnO	none	traces	—	—	—	—	—	—
MgO	0.53	1.44	0.49	0.18	2.05	0.57	0.90	1.80
CaO	3.22	1.86	4.41	0.39	1.30	3.35	4.13	6.30
Na ₂ O	1.62	0.43	0.38	2.52	5.00	2.55	0.84	2.00
K ₂ O	2.82	4.25	1.75	4.23	1.18	1.18	1.96	1.18
H ₂ O (+)	6.48	9.48	—	5.82	—	6.20	7.22	—
H ₂ O (-)	4.95	4.53	14.79	6.56	14.25	5.25	5.30	10.5
P ₂ O ₅	—	—	—	—	—	—	—	—
CO ₂	—	—	—	—	—	1.40	0.13	—

2. Liquid-Phase Purification Processes

- **Chemisorption (Amine Scrubbing):** This is the most common method for H₂S removal. Aqueous solutions of organic bases—amines like **MEA**, **DEA**, **MDEA**, and **DIPA**—are used. Regeneration occurs in a reboiler at temperatures between 70-150°C.

- **Physical Absorption:** These processes use organic solvents where absorption capacity increases proportionally with partial pressure, making them economical for high-pressure gases with high concentrations of acid components. Key industrial processes include:

- Fluor (propylene carbonate).
- Purisol (N-methylpyrrolidone).
- Rectisol (methanol cooled to -30°C).
- Selexol (dimethyl ether of polyethylene glycol).

- **Physico-Chemical Solvents:** Mixed solvents like **Sulfinol** (sulfolane + DIPA + water) combine chemisorption and physical dissolution to treat gases containing both H₂S and organic sulfur.

3. Oxidative and Alkaline Processes

- **Oxidative Processes:** These involve the liquid-phase oxidation of H₂S into elemental sulfur. Examples include the **Stretford** (using ADA catalyst) and **Tayioks** processes. They are highly selective for H₂S but are generally limited to small-scale operations (less than 10 tons of sulfur per day).

- **Alkaline Processes:** Used primarily for mercaptan removal. To improve the solubility of mercaptans, "solutizers" (organic additives like methanol or naphthenic acids) are added to the alkaline solutions.

4. Adsorption Processes and Zeolites

- **Industrial Adsorbents:** While active carbons, silica gels, and alumina gels can be used, they often have low sulfur capacity due to the co-adsorption of heavy hydrocarbons.

- **Synthetic Zeolites (Molecular Sieves):** Zeolites are currently the preferred choice for sulfur removal because of their high affinity for polar molecules and their molecular-sieve properties.

- **Zeolite Types and Selectivity:**

- **NaA (4Å):** Adsorbs H₂O, CO₂, and CH₃SH (methyl mercaptan) but excludes propane and larger molecules.

- **KA (3Å):** Primarily used for dehydration, as it excludes ethane and larger molecules.

- **Natural Zeolites:** Recent interest has shifted toward natural zeolites due to their abundance and low cost. However, their industrial use is often limited by small pore sizes (approx. 4Å), necessitating chemical modification to expand their application in gas purification.

2. MATERIALS AND METHODS

3.

The primary raw material used was natural clinoptilolite. To enhance its adsorption capacity, a chemical modification (acid treatment) method was employed.

2.1. Modification Process:

The zeolite samples were treated with hydrochloric acid (HCl) under varying conditions:

- Concentration: 0.5 to 10.0 N.
- Temperature: 20 °C to 90 °C.
- Duration: 2 to 10 hours.
- Solid-to-Liquid Ratio: 1:5.

2.2. Characterization:

The modification leads to dealumination—the selective removal of aluminum ions from the zeolite framework. This process was monitored to ensure the expansion of the "entry windows" of the pores without collapsing the crystalline structure.

3. RESULTS AND DISCUSSION

3.1. Structural Transformation

The study found that the degree of dealumination is the key factor determining the sorbent's efficiency. When the dealumination level reaches approximately 30-40%, the specific surface area and pore volume increase significantly. Beyond 40%, the structural integrity of the zeolite starts to degrade, leading to a decrease in mechanical strength.

3.2. Adsorption Dynamics

Experimental data indicates that acid-modified clinoptilolite shows a higher dynamic activity for H₂S compared to its natural state.

- **Isosteric Heat of Adsorption:** The heat of adsorption for H₂S and COS on modified clinoptilolite is lower than on synthetic NaX zeolites. This suggests that the regeneration of the adsorbent (desorption) can be achieved at lower temperatures, leading to significant energy savings.

- **Mercaptan Removal:** While natural clinoptilolite is ineffective for large molecules like methyl mercaptan, the modified version demonstrates a high degree of capture due to the expanded pore structure.

3.3. Pilot Testing

Industrial trials conducted at the Orenburg Gas Processing Plant confirmed that the modified clinoptilolite maintains its activity over multiple adsorption-regeneration cycles, proving its durability in harsh industrial conditions.

4. ECONOMIC ANALYSIS

The production of modified clinoptilolite is highly cost-efficient. The technological flowchart includes standard industrial equipment: reactors, washing filters, dryers, and sifting units.

- **Cost Comparison:** The estimated cost of modified clinoptilolite is several times lower than that of synthetic 13X (NaX) zeolites.
- **Scalability:** The abundance of natural deposits ensures a stable supply chain for large-scale gas processing facilities.

5. CONCLUSION

Acid modification (dealumination) is an effective method to tailor the pore structure of natural clinoptilolite for specific gas purification tasks. The modified sorbent achieves high-purity levels in removing H₂S and organic sulfur compounds, meeting international pipeline standards. Lower regeneration energy requirements and lower production costs make modified clinoptilolite a superior alternative to synthetic adsorbents in the context of sustainable industrial development. Here is the literature review based on your document, translated into English for your article:

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