Sulphur Dioxide Removal by Zeolitic Tuff: An Experimental Study

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Talk Outline

• Background Information
• Aims and Objectives
• Experimental Work
• Results and Discussion
• Conclusions
Jordan has huge reserves of oil shale but its utilization is limited due to several factors including the high sulfur content.

Combustion of OS generates large quantities of $\text{SO}_2$ \(\rightarrow\) Air pollution problem & acid rain.

Solutions for such problem might be:

- Utilization of the high calcium content in the oil shale
- Use sulphur removal technologies based on adsorption or absorption
  - Regenerative
  - Non-regenerative
The aim of this project was to study various scenarios for removal of SO$_2$ from off streams utilizing the natural resources available in Jordan.

Materials tested so far

- Absorption of SO$_2$ by Dead Sea, Red Sea and Saline water
- Adsorption of SO$_2$ by Oil shale ash
- Adsorption on Zeolitic Tuff
Zeolite occurs as a cementing material to volcanic tuff granules.

Zeolites are hydrated aluminosilicates of the alkali and alkaline earth metals.

- Consist of three-dimensional frameworks of \( \text{AlO}_4 \) and \( \text{SiO}_4 \) tetrahedra.

Jordanian ZT contains 20-70% (avg 50%) zeolite minerals:

- Phillipsite and Chabazite are most predominant.
- Faujasite less common.
<table>
<thead>
<tr>
<th>Area</th>
<th>Geological reserves (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tall Rmah</td>
<td>46</td>
</tr>
<tr>
<td>Al-Aritain</td>
<td>170</td>
</tr>
<tr>
<td>Tlol</td>
<td>9.2</td>
</tr>
<tr>
<td>Al-Shahba</td>
<td></td>
</tr>
<tr>
<td>North east Areas</td>
<td>472</td>
</tr>
<tr>
<td>Other areas</td>
<td>1340</td>
</tr>
</tbody>
</table>
EXPERIMENTAL WORK
Experimental system

A UIC sulfur coulometer (model number CM50155) was used for the continuous determination of total sulfur.
Experimental system
Experimental work

- 5000 ppm SO₂ in balance of N₂
- 30 ml/min (chosen so that the instrument can cope with SO₂)
- 5 g sample
- Bed diameter: 10mm & bed length 100-160 mm
- Main ZT sample was from Aritain area (red in colour)
- Characterization: XRD, XRF, SEM, BET SA, TGA & DTA
- Parameters studied:
  - Effect of particle size
  - Effect of Drying
  - Effect of locality (zeolite content)
  - Effect of Ads. temperature
  - Effect of thermal pre-treatment of ZT on Ads at room T
  - Regeneration options: Thermal
RESULTS AND DISCUSSION
XRD of the main sample

# - Phillipsite
* - Chabazite
+ - Diopside (CaMgSi$_2$O$_6$)
## BET surface area

<table>
<thead>
<tr>
<th>Particle size, µm</th>
<th>Surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-500</td>
<td>91.1</td>
</tr>
<tr>
<td>2000-4000</td>
<td>85.9</td>
</tr>
<tr>
<td>2000-4000 dried at 105°C</td>
<td>86.79</td>
</tr>
</tbody>
</table>
ADSORPTION EXP. WORK
Effect of particle size

SO$_2$ adsorbed, µmol/g

Time, min.

SO$_2$ out, µmol/g

Breakthrough times: 28.5, 27.5, 20.5 and 17 min

- 250-500 µm
- 500-1000 µm
- 1000-2000 µm
- 2000-4000 µm
Effect of Temperature

SO₂ Adsorbed, µmol/g

2000-4000 µm
30 mL/min
5 g sample

Time, min.

0 50 100 150 200 250 300 350

150°C
200°C
100°C
18°C
300°C
500°C
Effect of drying

$\text{SO}_2, \mu\text{mol/g}$

2000-4000 $\mu$m
30 mL/min
5 g sample

Non Ads. $\text{SO}_2$ on As Received

Ads. On as Received sample

17 min
Effect of drying 1

Moisture removed: 4.5%

SO₂ Adsorbed, µmol/g

2000-4000 µm
30 mL/min
5 g sample

As Received -out
Dried at 105°C -Ads

Dried at 105°C-out

Time, min.

0 50 100 150 200 250 300 350

88 min
Effect of drying 2

SO₂ Adsorbed, µmol/g

- As received
- Dried at 105°C
- Microwave dried
- As received - out
- Dried at 105°C - out
- Microwave dried - out

Moisture removed by MW: 6.5%

Time, min.

95 min
Effect of sample source (zeolite content)

- SO2 out, µmol/g
- SO2 Ads. µmol/g
- Time, Min

- Main Sample No1-
- Red Magais & Quais
- JGTGC red
- JGTGC Black
Effect of Thermal Pretreatment on Uptake capacity

- **Ads. @ room T**
  - 2000-4000 µm
  - 30 mL/min
  - 5 g sample

**Graph Details**
- **SO₂ Adsorbed, mmol/g**
- **Time, min.**
- Curves represent adsorption at different temperatures:
  - 18 °C
  - 200 °C
  - 250 °C
  - 300 °C
  - 400 °C
  - 500 °C
Effect of Thermal Pretreatment Breakthrough Time

[Graph showing the relationship between Pretreatment Temperature (°C) and Breakthrough time (min), with lines indicating SO2 adsorbed at BTT (µmol/g).]

- Breakthrough time, min
- SO2 adsorbed at BTT, µmol/g
Effect of Thermal Pretreatment
Phase Change

@ 250 °C intensity of Ph. Peaks increased
@ 300 °C Ph. disappeared

# - Phillipsite
* - Chabazite
◊ - Diopside
Effect of Thermal Pretreatment: Phase Change

# - Phillipsite
* - Chabazite
◊ - Diopside

Intensity, counts

Angle, $2\theta$, °
Effect of Thermal Pretreatment

Phase Change

# - Phillipsite
* - Chabazite
◊ - Diopside

Intensity, counts

Angle, $\theta$, °

400°C
300°C
250°C
200°C
untreated
Thermal Regeneration

SO$_2$ Ads., µmol/g

Time, min

- First Ads. cycle
- First Regen Cycle
- Second Regen Cycle
- Third Regen Cycle
Thermal Regeneration of 3rd Ads. cycle

- Flushing with N\(_2\) @ Room T
- Flushing with N\(_2\) @ heating at 100\(^\circ\)C
- Flushing with N\(_2\) @ heating at 200\(^\circ\)C

![Graph showing SO\(_2\) removal over time with different flushing conditions.](Image)

- 27% removed
- 60% removed
- 12% removed

Amount of SO\(_2\), µmol/g vs Arbitrary Time, min.
Conclusions

• The effect of various parameters on the adsorption of SO$_2$ by ZT tuff has been investigated; including Particle size, locality, temperature, thermal pretreatment

• The optimum adsorption temperature for SO$_2$ is between 150 and 200°C

• Moisture removal from ZT is crucial for better adsorption results.

• The change of SO$_2$ Adsorption capacity of ZT after thermal treatment is related to moisture removal and minerals phase change.
  • It is recommended to carry out adsorption at 200°C or above 400°C
  • The type zeolite phase present in ZT dictates the thermal treatment T

• Thermal regeneration is possible and it has positive effect on adsorption capacity of ZT
THANK YOU FOR YOUR ATTENTION ANY QUESTION?