

## SO<sub>2</sub> Removal by Using Jordanian Oil Shale Ash

*Adnan Al-Harashseh<sup>1</sup> and Reyad Shawabkah<sup>2</sup>*

1- Institute of Earth & Environmental Sciences, Al al-Bayt University, Jordan

2- Department of Chemical Engineering, Mutah University, Jordan

### *Abstract*

Oil shale ash was used to absorb sulfur dioxide to avoid releasing it into atmosphere. Slurries of different concentrations of this ash showed uptake capacity of  $6 \times 10^{-4}$  mol/1.5 g ash obtained after 250 s. This value is increased by increasing the solution pH, solution temperature, and ash concentration, or by decreasing the particle size of the ash. The process of uptake is coupled with both adsorption of SO<sub>3</sub><sup>2-</sup> on the surface of metal oxides or reaction with alkali and alkali earth metal hydroxides.

### *Introduction*

Air pollution is considered one of the undesired changes in the environment associated with the development of chemical and related industries. The main source of air pollution is the emission of toxic gases such as SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>x</sub>, CO, and CO<sub>2</sub>. The main source of these gases is the thermal conversion processing of liquid and solid fuels in power plants, refineries, and petrochemical industries and automobile emissions.

Sulfur dioxide is usually produced from desulphurization processes of petroleum, coal and oil shale. The content of sulfur in petroleum ranges from less than 0.5 w% up to 2 % and more (Erikh et al. 1985). This value is as high as 7-9 wt % in the oil extracted from Jordanian oil shale (Al-Harashseh et al., 2004). This sulfur is converted into H<sub>2</sub>S and SO<sub>2</sub>, depending on the type of processing (Wieckowska, 1995). Acidification of soil surfaces, poisoning of vegetation and organisms and corrosion are the negative effects of SO<sub>2</sub> in the atmosphere (Great Britain Patent 2015976; German Democratic Republic Patent 144676,AX; Japan Patent 6081138).

Adsorption is one of the widely used methods of SO<sub>2</sub> removal, using different types of absorbents such as activated carbonaceous material, including activated coal impregnated with silica and alumina, (Japan

Patent 314965), activated coal treated with sulfuric acid (USA patent No.4140752), or with nickel and potassium compounds (Tang, et al., 2005). Aluminum oxides and silica gels are commonly used as adsorbents for SO<sub>2</sub> (Laperdrix et al., 2000). Quick lime (CaO) and hydrated lime (CaO<sub>2</sub>) are the most widely used adsorbent of SO<sub>2</sub> from hot flue gases (Bouzaza, et al., 2004; Davini, 1996). Different types of natural and synthetic zeolites show a strong adsorption capacity for sulfur dioxide and hydrogen sulfide (Karge and Raskó, 1978; Khulbe and Mann, 1994).

Oil shale ash, which is obtained as a by-product of retorting and combustion of oil shale, contains different types of metals as

Table 1: Chemical composition of untreated oil shale from El Lajjun area.

Component	Wt %
SiO <sub>2</sub>	15.1
Al <sub>2</sub> O <sub>3</sub>	2.64
Fe <sub>2</sub> O <sub>3</sub>	1.2
P <sub>2</sub> O <sub>5</sub>	2.24
CaO	32
MgO	1.42
CO <sub>3</sub>	20
S	2.0
TiO <sub>2</sub>	0.2
Na <sub>2</sub> O	0.07
Organic matter and others	23.13

silicates and oxides. Table 1 illustrates the composition of the El Lajjun oil shale (Jordan), reported as oxides. Disposition of the ash is considered to be one of the most important factors in selecting suitable and economical utilization technology for Jordanian oil shale. There is no available literature on the use of this ash as an adsorbent for toxic gases. The present work is part of an ongoing project to study the characteristics of Jordanian oil shale ash and the possibility to use it as an adsorbent of SO<sub>2</sub> and other toxic gases.

### Experimental Setup

Samples of oil shale were taken from the El-Lajjun area of Jordan. These rocks were crushed, sieved to different particle sizes and stored in closed containers for further use. Ashing of the oil shale was performed by placing a fixed weight of known size of oil shale in a muffle furnace operated at 950 °C for 8 hours. Then the ash was directly placed in closed containers to prevent hydration. High purity sulfur dioxide came from the Jordanian gas company and

all chemicals were analytical grade reagents from Scharlau, Spain. All glassware was Pyrex, washed several times with soap and deionized water to remove any adhered impurities.

The sorption procedure was carried out by introducing 200 ml deionized water containing 0.3 g of different particle sizes (45 μm-1.2 mm) of oil shale ash in a glass tube (2.5 cm ID, 100 cm length). The tube is surrounded by a glass jacket and controlled-temperature water is circulated through this jacket to maintain isothermal conditions (Figure 1). Pure SO<sub>2</sub> is allowed to enter the bed from the bottom of the column at a constant flow rate of 1.5 L/min, while the exit stream is connected to a deionized water reservoir with a pH meter attached. Samples of known volumes of pure SO<sub>2</sub> were introduced in the upstream end at atmospheric pressure and room temperature (22±1 °C). The concentration of the SO<sub>2</sub> at the exit of the column was measured as a function of the difference in pH of deionized water. This procedure was repeated at different bed

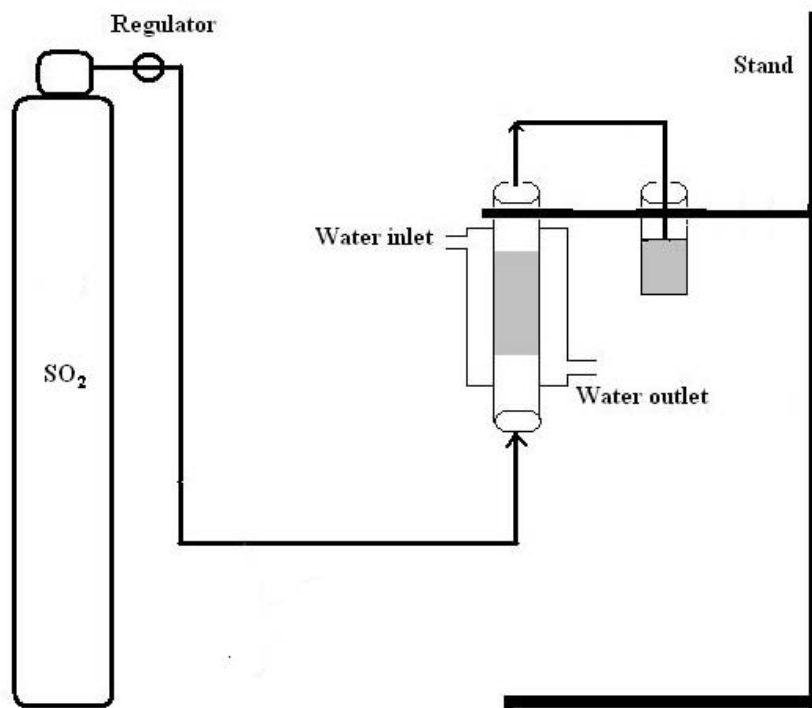


Figure 1: Fixed bed adsorption apparatus.

Table 2: Percentage of ash in oil shale samples.

Sample number	Sample weight before burning (g)	Sample weight after burning (g)	Amount of evaporated water & hydrocarbons (g)	Percentage of remaining ash (%)
1	116.09	77.06	39.03	66.38
2	94.73	62.56	32.17	66.04
3	69.97	23.44	46.52	33.05
4	77.04	25.89	51.18	33.61
5	71.48	24.05	47.40	33.65
6	79.18	26.30	52.88	33.74

temperature values, masses and particle sizes of the ash, and acidity of the solution containing the ash.

*Results and Discussion*

Samples of oil shale were tested at the Royal Scientific Society - Jordan for their chemical composition (Table 1). The samples show high content of silica, alumina and calcium oxide. These samples were then ashed at 950 °C for 8 hours to evaporate the water content and the or-

ganic matter.

Table 2 shows the weight of 6 samples before and after the ashing. It appears that as the initial sample weight increases, the percentage of ash remaining increases (Figure 2). This effect could be attributed to trapping of some hydrocarbons in the ash that were protected by the larger mass of shale. The average percentage of ash content in all samples is 44.4 wt %. From these results it appears that the ash contains several oxides of alkali and alkali

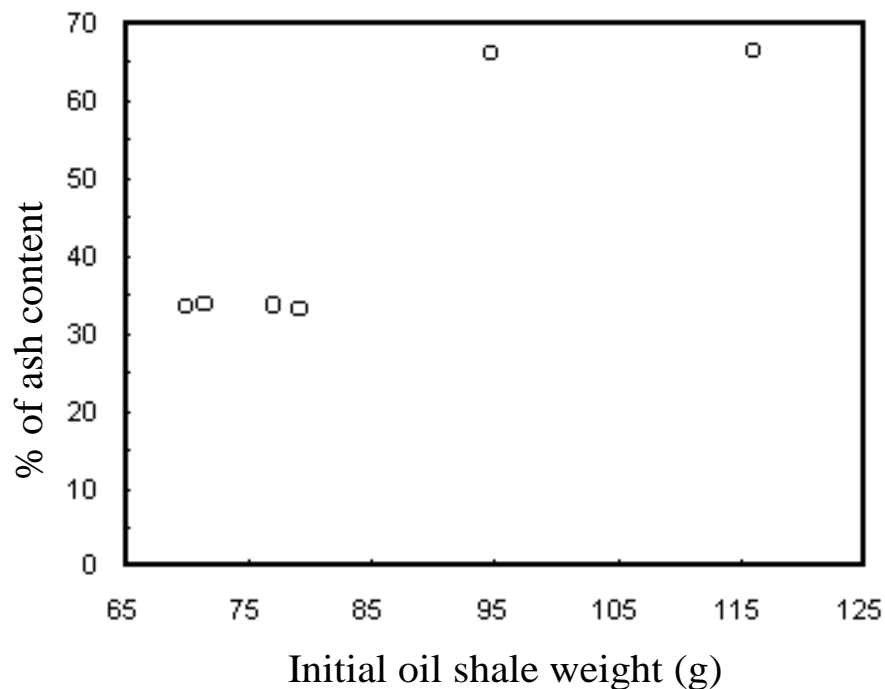
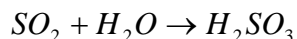


Figure 2: Relationship between the initial weight of the oil shale and the percentage of remaining ash.

earth, which could play a significant role in absorption of acidic gases such as SO<sub>2</sub>.

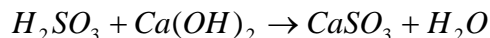
Absorption of SO<sub>2</sub> was established by introducing a fixed molar flow rate of 6 x 10<sup>-4</sup> mol /min into the ash solution while the exit stream was directed into fresh water and the pH of the solution was monitored as a function of time.

Figure 3 shows the effect of ash concentration on the absorption kinetics of SO<sub>2</sub>. As the amount of SO<sub>2</sub> injected into the ash solution increases with time, the pH of the detection solution decreases. This effect is attributed to the attainment of the saturation value of SO<sub>2</sub> in the first solution containing ash. It is noted that the decrease in pH was large in a short period of time for the samples with a low mass of ash, whereas this decrease was sluggish for the samples that contained higher ash content. In all cases SO<sub>2</sub> reacts with water in the ash solution to produce sulfurous acid as:



Sulfurous acid then undergoes a series of either chemical reactions and/or adsorption

with the metal oxides present in the ash. For example, it may be adsorbed on the surface of silica and alumina to yield a monolayer of adsorbed SO<sub>3</sub> on the surface of these oxides or reacted with hydrated lime to produce calcium sulfate according to:



Increasing the amount of ash in solution will provide more metal oxides and as a result more sorption of SO<sub>2</sub> gas by this solution. This was clear in Figure 3 where 1.3 x 10<sup>-3</sup> mol SO<sub>2</sub> was detected at the exit of the absorption column containing 0.5 g achieved after 250 s, whereas a maximum of 5.6 x 10<sup>-12</sup> mol was reached in a solution containing 1.5 g ash obtained over the same period of time.

Figure 4 shows the amount of sorbed SO<sub>2</sub> as a function of pH change in the solution at the exit stream. It is obvious that increasing solution temperature favors sorbent uptake of SO<sub>2</sub>. The maximum of SO<sub>2</sub> left over at the exit stream increased with decreasing solution temperature. This decrease was moderate at elevated tem-

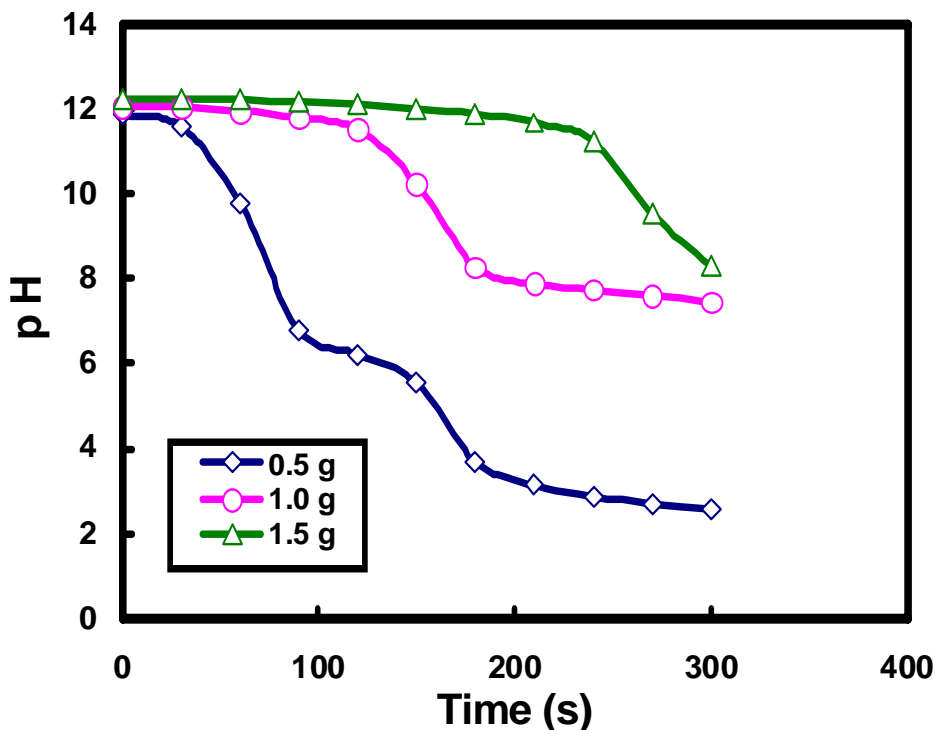


Figure 3: Effect of ash dose on the absorption of SO<sub>2</sub>

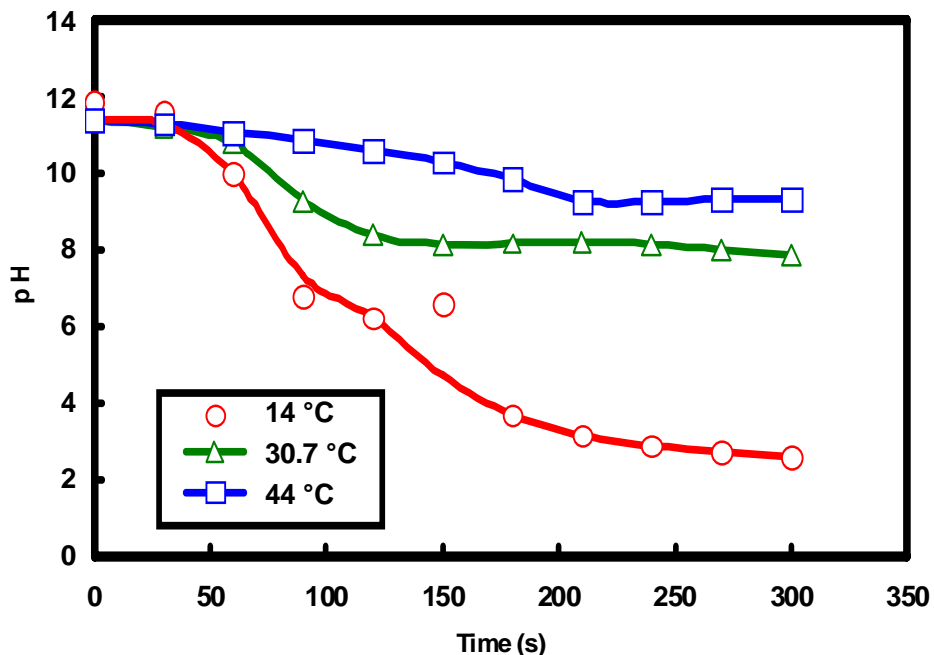


Figure 4: Effect of solution temperature on the absorption of SO<sub>2</sub>

perature values greater than 30 °C.

A similar trend was noticed when the particle sizes of the ash was increased from <63 to 710 μm (Figure 5). Increasing the ash particle size appears to allow less interaction between the SO<sub>2</sub> bubbles and ash

particles in the solution. In the larger particle size runs, the diffusion of SO<sub>2</sub> into the ash particle is the dominant resistance. At smaller particle sizes, there is more surface contact between the sorbed SO<sub>2</sub> and the ash particles.

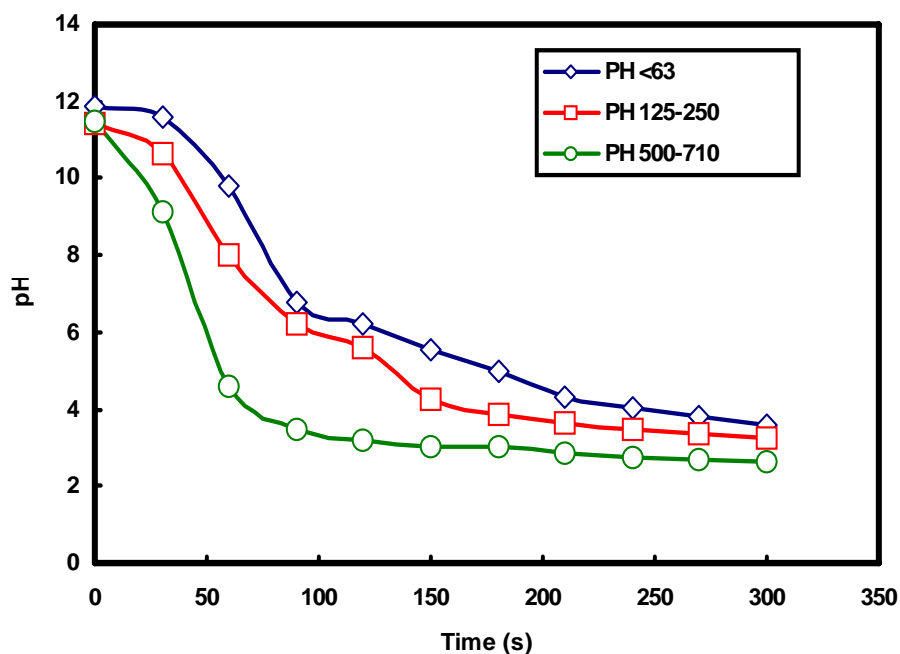
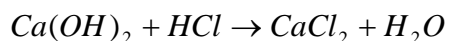
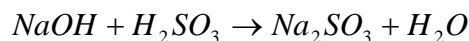


Figure 5: Effect of ash particle size of SO<sub>2</sub> uptake.

To predict the effect of solution acidity on SO<sub>2</sub> uptake, three different solutions were initially prepared with the addition of either HCl or NaOH to obtain solution pH of 3.68, 7.03 and 11.89. For all solutions there was a linear increase in the amount of SO<sub>2</sub> sorbed at a fixed concentration of ash (Figure 6). The rate of increase of SO<sub>2</sub> uptake in the acidic solution is lower than that of neutral and basic ones. This decrease in rate of uptake in acidic solution is ascribed to the effect of the hydrogen ions which either desorb the sulfate ions on the metal surface or hold back the reaction of SO<sub>3</sub> with lime through reaction between calcium hydroxide and chloride ions in solution as:



On the other hand, the addition of sodium hydroxide will increase the concentration of OH<sup>-</sup> in the solution and either provides a repulsion force with (SO<sub>3</sub>)<sup>2-</sup> in the solution and thereby enhances the adsorption of the latter on the surface or consumes the amount of introduced SO<sub>2</sub> into the column by means of a side reaction between the sodium hydroxides and the sulfate ions, such as



### Conclusion

A sulfur dioxide gas stream was sweetened by passing it through a slurry of oil shale ash. The rate of uptake of SO<sub>2</sub> was directly affected by the amount of ash added to the solution mixture, the temperature of the solution, particle sizes of the ash and the solution acidity. This process is economical, safe and efficient.

### References:

Al-Harashsheh, A., Awni Y. Al-Otoom and Reyad A. Shawabkeh, 2004, Sulfur distribution in the oil fractions obtained by thermal cracking of Jordanian El-Lajjun oil shale, Submitted for publication, 2004.

Bouzaza, A., A. Laplanche, S. Marsteau, 2004. Adsorption-oxidation of hydrogen sulfide on activated carbon fibers: effect of the composition and the relative humidity of the gas phase: *Chemosphere* 54 (4), 481-488.

Davini, P., 1996. Investigation of the SO<sub>2</sub> adsorption properties of Ca(OH)<sub>2</sub>-fly ash

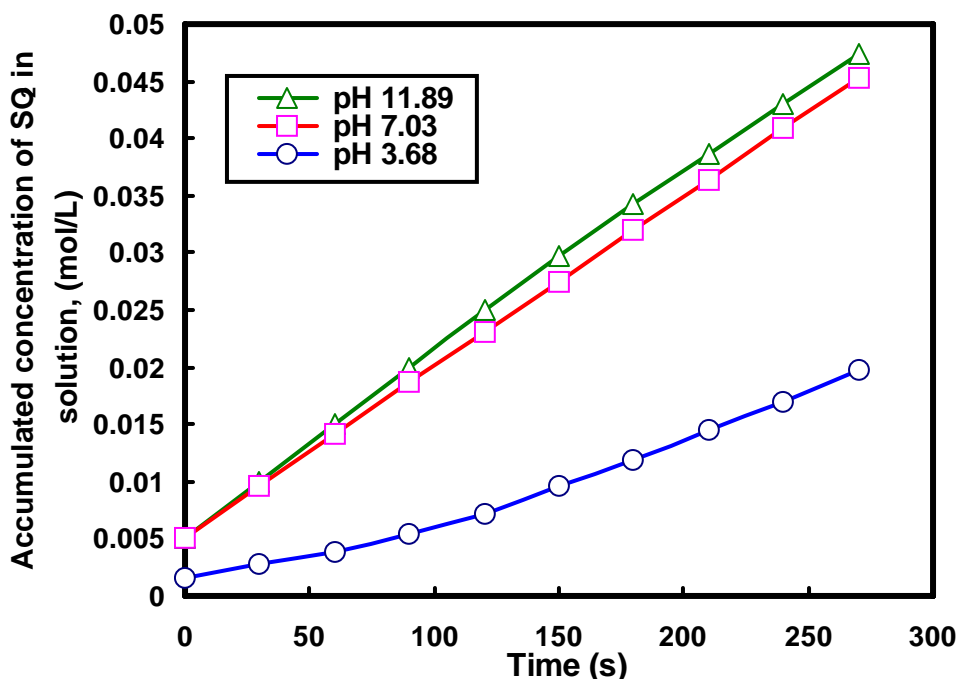


Figure 6: Effect of solution pH on SO<sub>2</sub> uptake.

systems: Fuel 75 (6) 713-716.

Erikh, V.N., M.G. Rasina, M.G. Rudin, 1985, The chemistry and technology of petroleum and gas, Mir publishers, Moscow.

German Democratic Republic Patent No 144676, AX. A.

Great Britain Patent No 2015976, Powles land Eng, Ltd.

Japan patent No. 6081133, Mitsubishi Heavy Industries K. K.

Japan patent No. 3149165, Tokyo Shibaura Electric, Ltd.

Karge, H. and J. Raskó, 1978. Hydrogen sulfide adsorption on faujasite-type zeolites with systematically varied Si-Al ratios: Journal of Colloid and Interface Science 64, 522-532.

Khulbe, K. and R. Mann, 1994. Interaction of V<sub>2</sub>O<sub>5</sub>-NaY zeolite with H<sub>2</sub>S and SO<sub>2</sub>: Zeolites 14 (6), 476-480.

Laperdrix, E., G. Costentin, O. Saur, J. Lavalley, C. Nédez, S. Savin-Poncet, J. Nougayrède, 2000. Selective Oxidation of H<sub>2</sub>S over CuO/Al<sub>2</sub>O<sub>3</sub>: Identification and Role of the Sulfurated Species formed on the Catalyst during the Reaction: Journal of Catalysis 189 (1), 63-69.

Tang, Q., Z. Zhang, W. Zhu, Z. Cao, 2005. SO<sub>2</sub> and NO selective adsorption properties of coal-based activated carbon: Fuel 84 (4), 461-465.

USA patent No.4140752, Allied Chemical Corp.

Wieckowska, J., 1995, Catalytic and adsorptive desulphurization of gases: Catalysis Today, 1995, 405-465.