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MULTI-METAL OXIDE AEROGEL FOR CAPTURE OF POLLUTION GASES FROM AIR

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ABSTRACT

Utilization of fossil fuels results in the emission of pollution gases such as CO₂, SO₂, CO, NO_x and H₂S. Currently available commercial technologies for reducing SO₂ and NO_x emissions from power plants are costly and produce hazardous wastes. The concept described in this paper uses advanced aerogel materials containing components such as CaO and MgO in their structure to capture/adsorb gaseous wastes from fossil fuel combustion. Aerogels are typically highly porous materials, which can have over 90% porosity, very low density, and extremely high surface area (several hundred m²/g). The test results of this work indicated that an aerogel sorbent containing CaO, MgO and SiO₂, which is prepared in the laboratory "by the advanced sol-gel technology", can be used efficiently to capture/adsorb pollution gases such as CO₂, SO₂, NO_x, CO and H₂S through both physical and chemical sorption mechanisms. Aerogels can be engineered to different forms, sizes, and chemical compositions to be used as gas filters in the different workplaces and indoor living spaces.

KEY WORDS

Aerogel materials, Sol-gel process, Fuels, Pollution gases, Gas adsorption.

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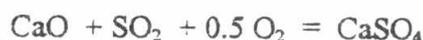
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INTRODUCTION

Utilization of fossil fuels (coal, oil and gas) in stationary (e.g., diesel generators, electric power, metallic, cement, ceramic, chemical, and other plants) and mobile (e.g., diesel trucks, buses, automobiles, air planes, etc.) results in the emission of gases such as CO₂, CO, SO₂, and NO_x (greenhouse gases) into the atmosphere, in addition to H₂S which is mainly produced from the petrochemical industries. These gases are blamed for environmental problems such as acid rain, global warming, ozone depletion, corrosion, and increased toxicity of breathing air.

The currently available commercial technology for reducing SO₂ and NO_x emission from power plants is wet scrubbing. However, since this technology is costly and creates hazardous slurry wastes, it has not found wide acceptance from power utilities and the various manufacturing plants. Further, wet scrubbing is not suitable for mobile applications. Dry sorbent injection technologies seem to be more promising, however, they also produce dry hazardous wastes. In a power plant, the dry sorbents are injected either in the combustion furnace (1204°C), the economizer zone (538°C), or the "cool side" ducts (70°C), [1]. Typical sorbents include finely ground limestone, dolomite, hydrated lime, sodium bicarbonate and sodium sesquicarbonate. The sorbents react with SO₂ emissions to form solid products such as CaSO₄ or Na₂SO₄, which are then removed with the coal ash or with the dust by the particulate collection system (e.g., electrostatic precipitator or baghouse), depending on the point of injection. Of these approaches, limestone injection is considered to be commercially proven. Typical removal levels of SO₂ by calcium and magnesium sorbents at Ca/S ratio = 2 are: limestone; 25-40%, dolomite; 40-60%, and hydrated dolomite; 60-80%, [1].

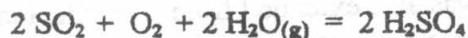
As mentioned earlier, SO₂ can be removed from the flue gases by adding calcium-based sorbent according to the following chemical reaction :



Electron microscope examination, [2], showed that this reaction takes place only within a thin layer on the outer surface of the sorbent particles. Thus, the finer the particle the higher the utilization rate of the sorbent. However, finer particles are more easily carried out of the bed by the flue gas; as a consequence, their reaction time is shortened leading to incomplete reaction and inefficient utilization of the sorbent. To solve this problem a method of agglomerating fine limestone particles with some adhesive substances, has been developed and used in China, [2,3]. This is called synthetic Ca-based sulfur sorbent with high reactivity.

For natural limestone, reactant gases (SO₂ and O₂) diffuse into the inside particles only through the small pores and react with CaO grains to produce solid CaSO₄ which then covers the surface of CaO grains. In a short time, these small pores are filled, which limits the diffusion of reactant gases into the particles. So the overall CaO conversion rate of natural limestone particles is very low. However, with synthetic sorbents which are prepared by agglomerating small particles of limestone with a binder, reactant gases not only directly diffuse into grain groups near the surface, but also directly penetrate to internal groups through the large pores between the grain groups. This is beneficial for increasing the overall CaO conversion rate.

Activated carbon (coke) has been used in Germany, [4], to adsorb SO_2 from the hot gases in the presence of O_2 and H_2O vapor according to the following reaction:



Sulfuric acid (H_2SO_4) is later desorbed (released) from the activated carbon by heating with hot sand according to the following reaction:



The degree of desulfurization achieved by this method has not been reported. Activated carbon is expected to capture gases by physical adsorption mechanism as there are no chemisorption mechanisms available.

Because of the obvious benefits of having porous agglomerates of the calcium based sorbents, or porous activated carbon, in increasing the efficiency of SO_2 capture and reactivity, [1-5], we believe that aerogel materials containing CaO and/or other metallic oxides in their structure, will be much more efficient sorbents than calcium based powders, agglomerates, or activated carbon, due to the aerogel's extremely high porosity, high surface area, and the incorporated metallic oxides. Also, aerogels can be molded to any shape and size, and thus are more flexible than the powder or agglomerate.

Development of Aerogel Sorbents:

Aerogel sorbent materials are made by the sol-gel process, shown schematically in Fig. 1, in which an alcoholic solution of a metal alkoxide e.g., magnesium ethoxide, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, or of a mixture of metal alkoxides and salts (e.g., nitrates), is hydrolyzed to form a sol (a colloidal suspension of the metal hydroxide, e.g., $\text{Mg}(\text{OH})_2$ in alcohol). A catalyst is then added to start the condensation polymerization process to form a gel (a continuous solid skeleton of the polymerized hydrolyzed material enclosing a continuous phase of the liquid alcohol). The aerogel is formed by removing the alcohol from the pores of the gel by supercritical drying in an autoclave, which minimizes shrinkage and cracking. The volume of the resulting aerogel is similar to that of the original sol, which makes the production of highly porous materials possible.

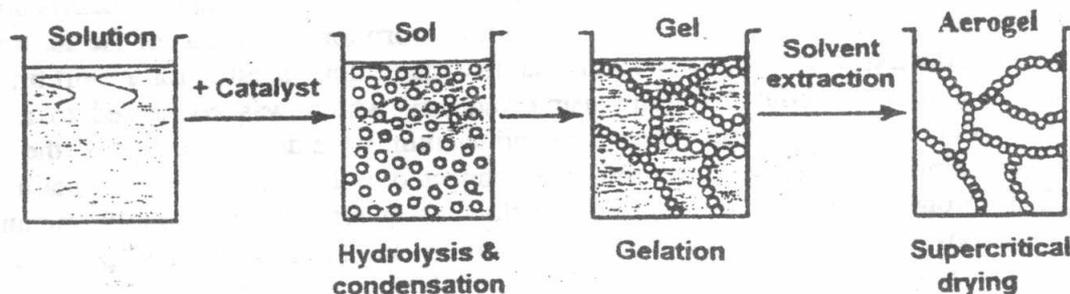


Fig. 1. Schematic diagram of the preparation of aerogel by sol-gel processing and supercritical drying for solvent extraction.

Several investigators, [6,7], have developed and discussed the production of aerogel materials. Optimization of the various parameters involved was achieved, and improvements of the process were developed. The method was also extended from pure silica to various multi-systems. The very large surface area characterizing these materials, currently of several hundred m^2/g (a pore diameter distribution extending from the nm to the μm range) made them attractive for several applications, e.g., the field of catalysis and thermal insulation, [6,7].

The main objective of this work was to investigate the feasibility of using an aerogel sorbent which is prepared in the laboratory, to adsorb/capture waste gases such as: SO_2 , NO_x , CO_2 , CO and H_2S

EXPERIMENTAL PROCEDURES

(1) The Aerogel Sorbent:

The tested aerogel, containing CaO , MgO and SiO_2 , was manufactured through the preparation of the corresponding alcogel by the sol-gel processing technology, and then by subjecting the alcogel to supercritical drying in an autoclave to remove the alcohol. The produced aerogel specimens were then heat treated in air at 650-700 C to eliminate the organic residues after autoclave drying. The chemical and physical compositions of the prepared aerogel were adjusted through the molar ratio of the main components, type of precursors (chemical feed stock), catalyst type and concentration, and method of preparation. Figure 2 shows a flowchart of the procedure and precursors used.

(2) Gas Adsorption Testing:

Gas adsorption was measured by passing the test gas mixture with air over the aerogel sample enclosed in a stainless steel pressure filter vessel (adsorption chamber) and recording the change in gas concentration before and after the adsorption chamber as an indication of the extent of gas adsorption. It was found that the presence of water vapor (steam) enhances the gas adsorption of the process, [8]. Thus before adsorption, activation of the aerogel was made by introducing water vapor (steam) into the adsorption chamber for a short time (3-5 seconds) at a rate of about 0.7 l/min using vacuum, which was connected to a steam generator. After the selected time, the steam and vacuum were disconnected, and the air-gas mixture (containing the gas in question) was connected to the pressure filter containing the humidified aerogel. The gas was allowed to flow at about 0.7 l/min under vacuum, for selected periods of time. Prior to the humidification and gas adsorption steps, the aerogel sample was evacuated for a period of time and its weight was recorded.

To simulate flue gas system from high sulfur coal combustion, gases of SO_2 , CO_2 and air were premixed to a desired composition range, i.e., about 1000-2500 ppm SO_2 and 6 -15.5% (vol.) CO_2 , by adjusting the valves of SO_2 and CO_2 cylinders directly so that the output of

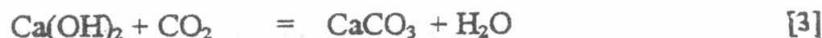
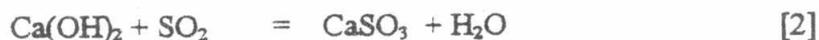
SO₂ and CO₂ from the cylinders were controlled. The pressures of these gases from the cylinders were only slightly above the atmospheric pressure (about 3 psi). Air was introduced directly from the atmosphere. NO gas was introduced in this simulation, but was tested in mixtures with air separately. CO and H₂S were each tested in mixtures with air also. At the beginning of each gas adsorption test, the concentration of each gas in the air mixture was tested by Drager Gas Detector Tubes supplied by SKC Inc., PA, U.S.A. The concentration of each gas coming out of the adsorption chamber was measured at different times also using the Drager gas analysis detector tubes. The inlet concentrations of each gas in the mixed gas stream before adsorption were again determined at the end of the test, (i.e., without passing through the aerogel filter first), to ensure that there was no change in the gas composition with time. Figure 3 is a schematic representation of the experiment setup. Approximately 10-13 grams aerogel granules (grain size < 5 mm) were tested in each experiment, although monolithic aerogel could also be used.

RESULTS AND DISCUSSION

The primary objective of this research program was to ascertain whether CaO and MgO containing aerogels can adsorb the greenhouse gases from air, specifically, SO₂, NO, CO₂, CO and H₂S gases. Such adsorption has not been reported before. Once this has been ascertained, then research will continue to refine the aerogel preparation and gas adsorption processes to maximize the capacity of the aerogel to capture these gases.

Both small (200 ml) and large (1500 ml) monolith and granulated aerogel specimens (grain size < 5 mm), containing oxides of Ca, Mg and Si, were prepared. Its density is approximately 0.12 g/cm³, porosity is greater than 90% (estimated at about 96%), color is white, and appearance is opaque.

Adsorption of single gases SO₂ and CO₂ by the prepared aerogel has been ascertained by X-ray diffraction (XRD), and was reported earlier (Fig. 4), [8]. XRD spectrograms for the aerogel tested before and after adsorption of SO₂ and CO₂ show the existence of MeSO₃ and MeCO₃ (Me refers to Ca and Mg) in adsorption-tested aerogel specimens, which proves that this aerogel can adsorb these gases effectively. The adsorption test results also showed that the gas adsorption rate can be significantly increased by introduction of water vapor (steam). The role of the steam was considered to activate the gel surface by forming surface hydroxyl groups and therefore enhances the kinetics of chemisorption reactions on the gel surface according to the following equations:



The possible chemisorption mechanisms for the gases considered in this investigation by CaO and MgO containing aerogels are listed in Table 1.

Adsorption of Gas Pollutants from Air :

Adsorption of mixed SO₂ and CO₂ from simulated flue gas stream by the tested aerogel is shown in Fig. 5. It can be seen that SO₂ and CO₂ gases are adsorbed readily by the aerogel sorbent. Adsorption of SO₂ ranged from 95% to nearly 100%, while adsorption of CO₂ ranged from 85% to about 100%. The high concentration of CO₂ (12.5% vol.) did not retard the adsorption of SO₂ in the simulated flue gas mixture.

Adsorption of NO, CO and H₂S, each from mixtures with air by the tested aerogel sorbent, are shown in Figs. 6, 7 and 8 respectively. Excellent adsorption of NO and CO can be seen in Figs. 5 and 6. CO adsorption ranged from 90% to 98% and NO adsorption was nearly complete (i.e., 98-100%). Adsorption of H₂S, in Fig. 7, on the other hand, started at 90% then decreased with time to about 40% after about 105 minutes of contacting with the aerogel sorbent. The exact reason for this behavior is not known, but it is believed that the presence of water vapor from the activation step might have interfered with adsorption reaction between H₂S and CaO & MgO, which results in the release of water molecules, as shown in Table 1. Therefore, H₂S adsorption should be improved (a) at higher temperatures where water would be removed by drying, (b) with no activation of the aerogel by steam.

CONCLUSIONS

Based on the experimental results for mixed gas adsorption, it can be concluded that calcium and magnesium oxides containing aerogels can effectively adsorb polluting gases such as SO₂, NO, CO₂, CO and H₂S from air or flue gas streams. Similarly, aerogels containing other metallic oxides capable of reacting with these gases should provide excellent adsorbent materials. Furthermore, aerogel sorbents can be engineered to different forms, sizes, and chemical compositions to be used as gas filters for removal of pollution gases from air in the different workplaces and indoor living spaces.

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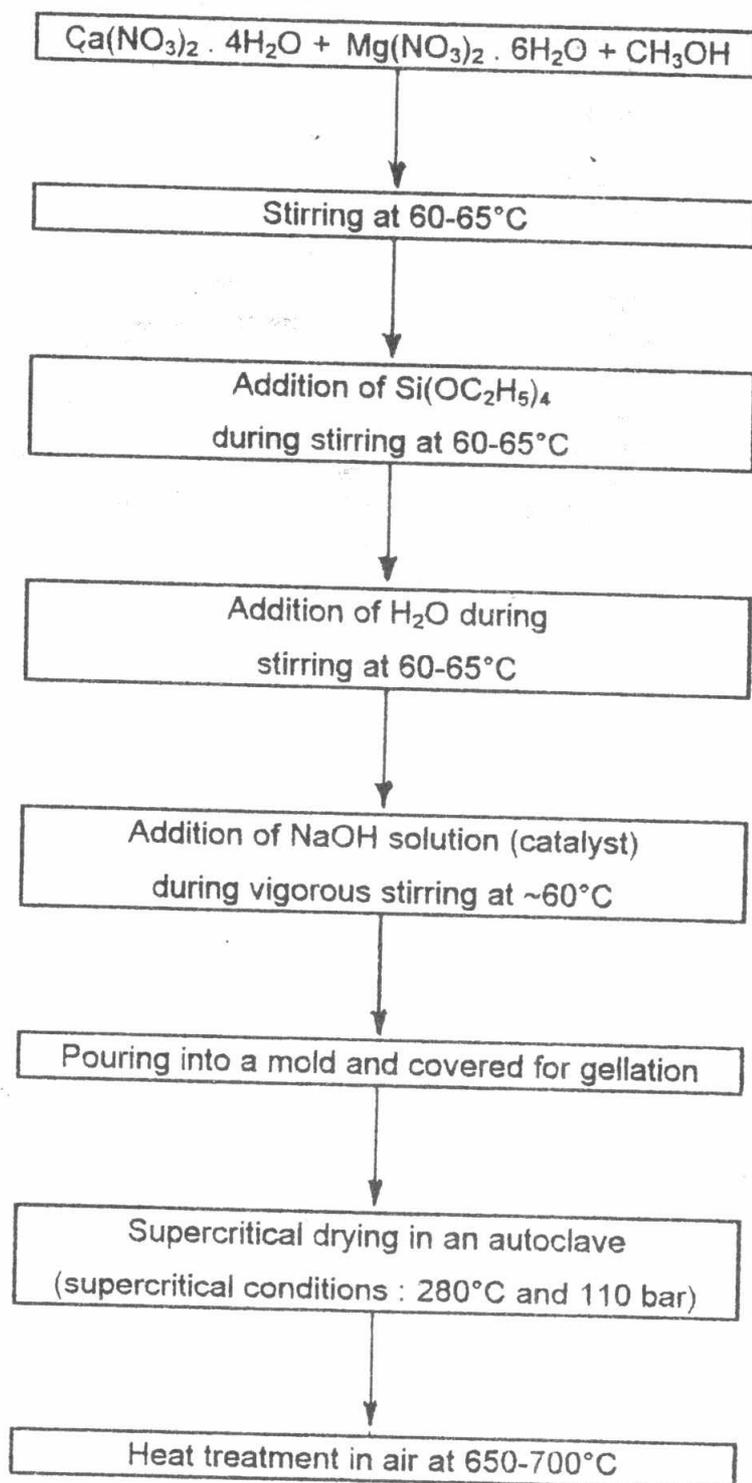


Fig. 2. Flowchart of the procedure and precursors used to prepare the aerogel sorbent in the present work.

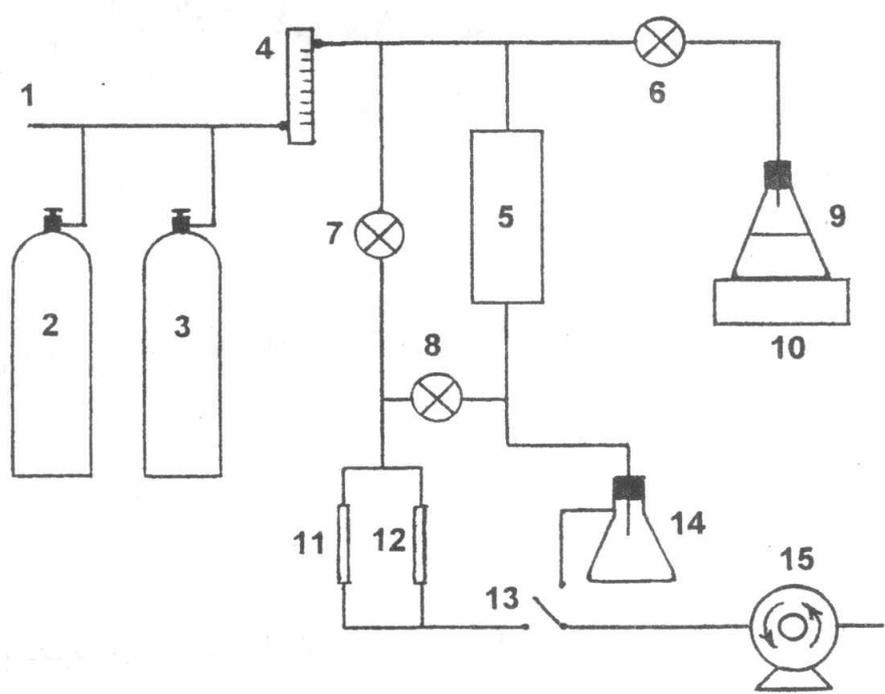


Fig. 3. Experimental setup for gas adsorption by the aerogel sorbent.

- | | | |
|---|----------------------|--------------|
| 1. Inlet air | 2 & 3. Gas cylinders | 4. Flowmeter |
| 5. Adsorption chamber containing aerogel sample | 6, 7 & 8. Valves | |
| 9. Steam generator | 10. Heater | |
| 11 & 12. Drager Gas Detector Tubes (SKC Inc., PA, U.S.A.) | 13. Switch | 14. Gas trap |
| | | 15. Pump. |

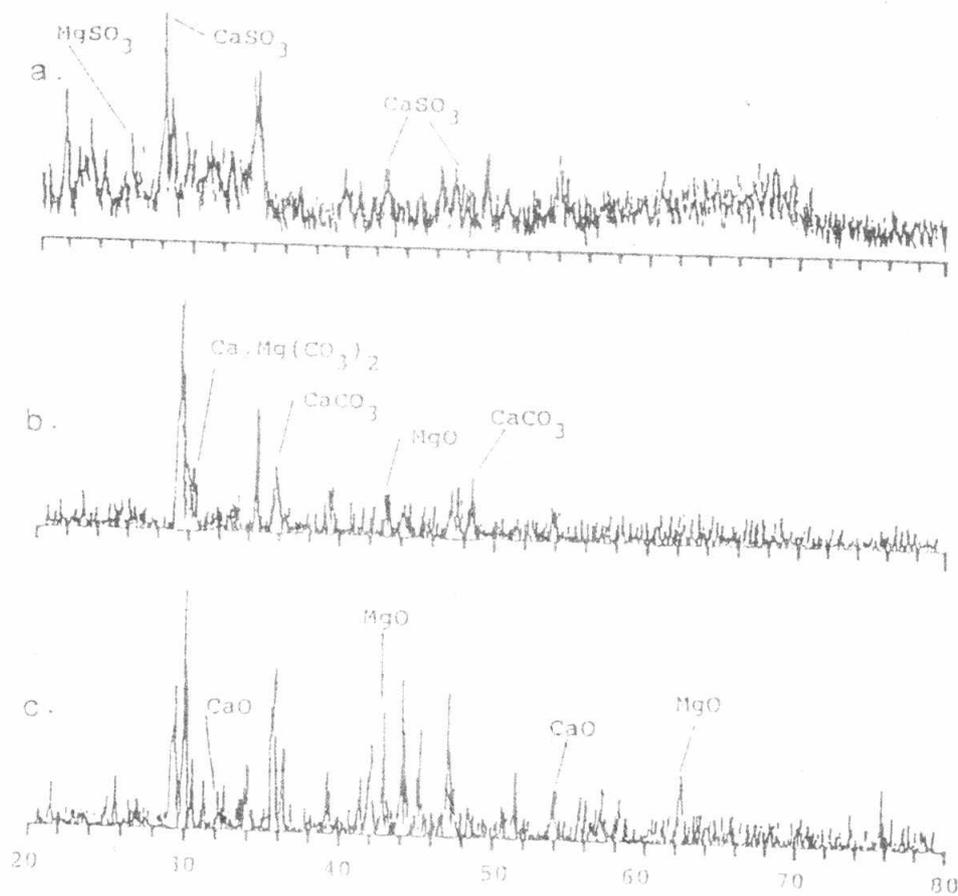


Fig. 4. X-ray diffraction spectograms of the aerogel sorbent before and after adsorption of CO_2 and SO_2 gases, [8].
(a) Aerogel after SO_2 adsorption
(b) Aerogel after CO_2 adsorption
(c) Fresh aerogel sample

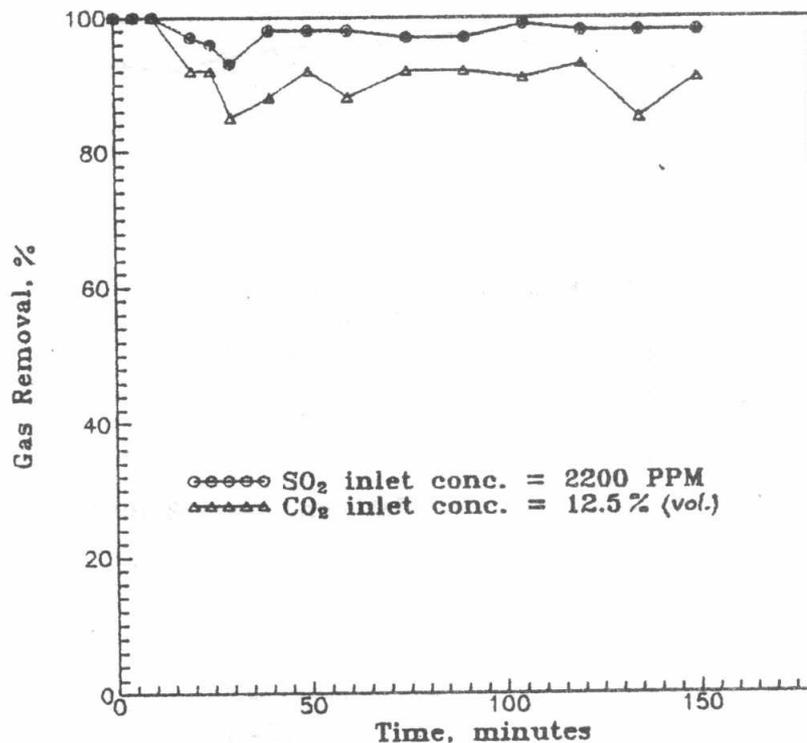


Fig. 5. Removal of CO₂ and SO₂ from air by the aerogel sorbent.

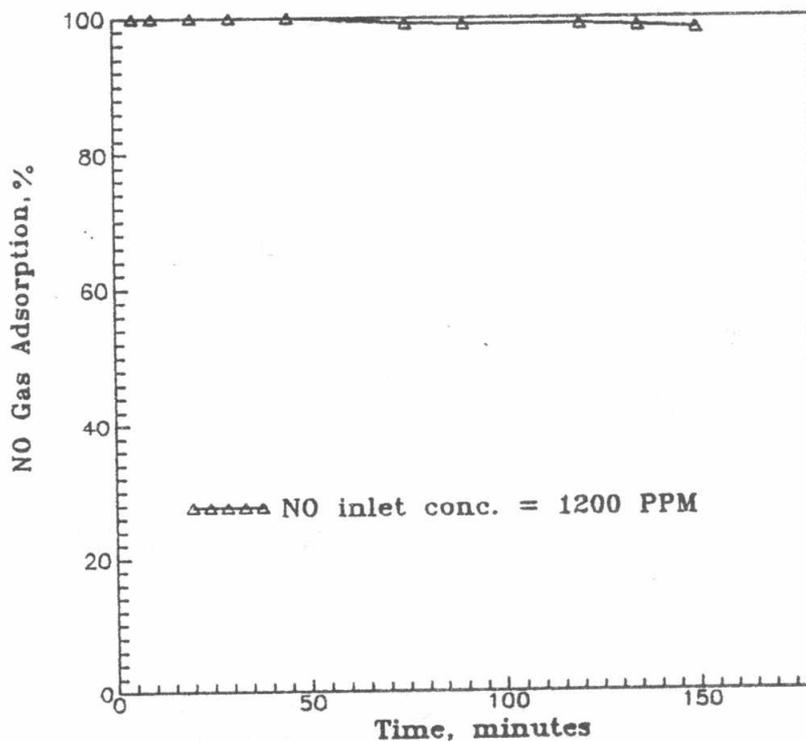


Fig. 6. Removal of NO from air by the aerogel sorbent.

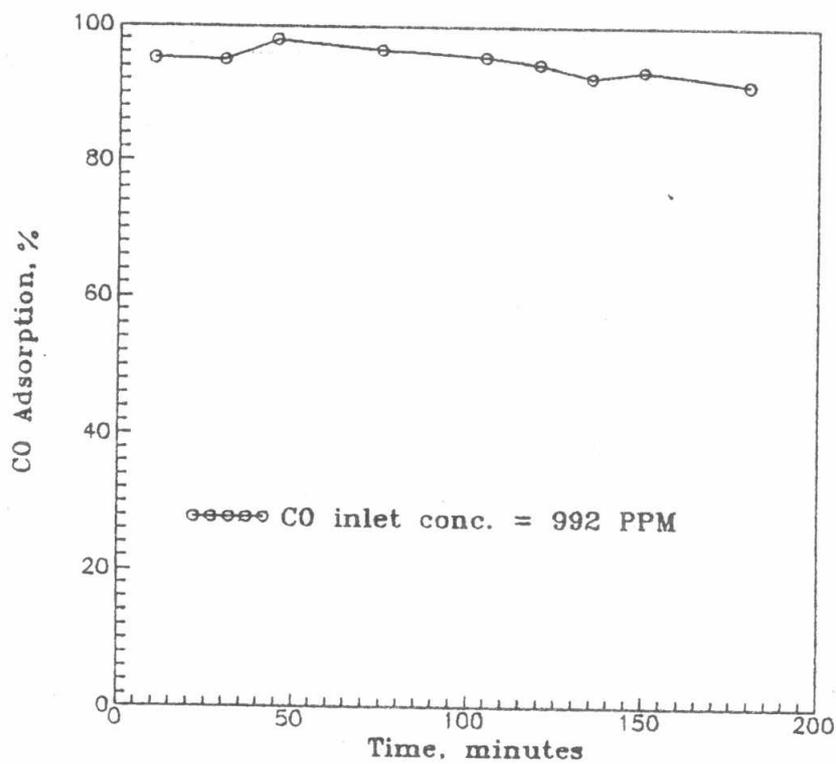


Fig. 7. Removal of CO from air by the aerogel sorbent.

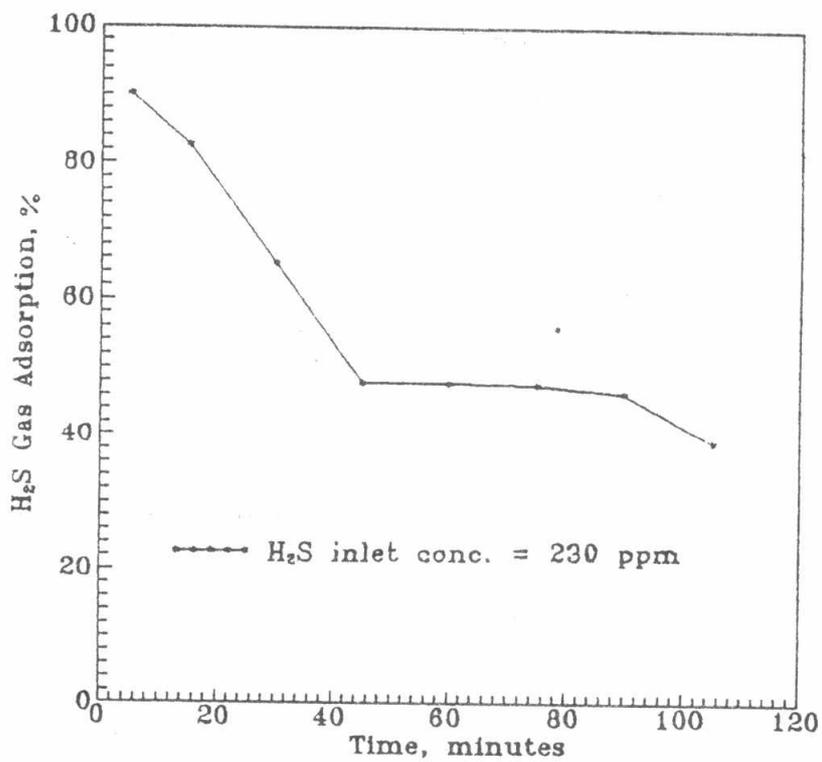


Fig. 8. Removal of H₂S from air by the aerogel sorbent.

Table 1. Possible adsorption reactions between gases and the aerogel sorbent.

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- * Active sites on aerogels : CaO & MgO
 - * Adsorption of H₂O vapor (steam)
CaO + H₂O = Ca(OH)₂ (surface)
MgO + H₂O = Mg(OH)₂ (surface)
 - * Adsorption of SO₂
Ca(OH)₂ + SO₂ = CaSO₃ + H₂O ; CaSO₃ + 1/2 O₂ = CaSO₄
Mg(OH)₂ + SO₂ = MgSO₃ + H₂O ; MgSO₃ + 1/2 O₂ = MgSO₄
 - * Adsorption of CO₂
Ca(OH)₂ + CO₂ = CaCO₃ + H₂O
Mg(OH)₂ + CO₂ = MgCO₃ + H₂O
 - * Adsorption of CO
Ca(OH)₂ + CO + 1/2 O₂ = CaCO₃ + H₂O
Mg(OH)₂ + CO + 1/2 O₂ = MgCO₃ + H₂O
 - * Adsorption of NO
Ca(OH)₂ + 2NO + 3/2 O₂ = Ca(NO₃)₂ + H₂O
Mg(OH)₂ + 2NO + 3/2 O₂ = Mg(NO₃)₂ + H₂O
 - * Adsorption of H₂S (in absence of steam activation)
CaO + H₂S = CaS + H₂O
MgO + H₂S = MgS + H₂O
-