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Adsorption Study of SF_6, H_2 and N_2 over 13X Molecular Sieve

Summary
This is a short study on SF_6, H_2 and N_2 adsorption over 13X Molecular Sieve. It is confirmed that 13X can be used to remove SF_6. At cryogenic temperature, 13X adsorbs significant amount of H_2 which can be purged out with He or He with N_2 doses. The N_2 adsorption was not affected with pre-adsorbed H_2.

Background
Molecular sieves are widely used to purify various streams in tritium process: either by removing hydrogen isotopes from, e.g., He-3 streams at cryogenic temperature; or by removing trace impurities from hydrogen stream at a relative higher temperature. Sulfur hexafluoride (SF_6) is used in the circuit breakers, switchgear, and other electrical equipment due to its unique dielectric property. Questions have been raised when a tritium stream is contaminated with SF_6, can the SF_6 be easily removed using a molecular sieve, and if it is a cryogenic adsorption condition, would the adsorbed tritium be recovered by displacement adsorption with nitrogen gas (N_2).

Materials
Sulfur hexafluoride (SF_6) is an inorganic, colorless, odorless, and non-flammable gas. SF_6 has an octahedral geometry, consisting of six fluorine atoms attached to a central sulfur atom. It is a hypervalent molecule, has poor water solubility (typical for a nonpolar gas), but is soluble in nonpolar organic solvents. It has a density of 6.12 g/L at sea level conditions, which is considerably higher than the density of air (1.225 g/L). It has a boiling point of -64°C (1 torr) and a melting point of -50°C.

The following materials were used for the experiments:

13X molecular sieve, UOP MS-1347, Lot#2890000438
Sulfur hexafluoride, Sigma-Aldrich 295701-227G, Lot#MKB0598V
Nitrogen, Air Liquide Alphagaz 2, 99.9995%
Hydrogen, Air Liquide Alphagaz 2, 99.9995%
Helium, Air Liquide Alphagaz 2, 99.9999%

Adsorption Study

Molecular sieve 13X was selected for SF_6 adsorption study based on its large pore size and the relatively bulky SF_6 molecule. The adsorption was measured as SF_6 uptake at corresponding equilibrium vapor pressure in a Micromeritics TriStar II 3020 instrument. Prior to the study, the 13X molecular sieve was degassed at 350°C under vacuum for 10 hours. Since SF_6 is a condensable gas at cryogenic temperature, two adsorptions were performed at ambient (22°C) and ice-water (0°C) temperatures, respectively. Figure 1 shows the adsorption / desorption isotherms for the 13X material. Even at ambient temperature, the 13X material adsorbed more than 10 std cc/g SF_6 at a pressure of about 20 torr, and 44 std cc/g at 800 torr. After the analysis, the 13X sample was shown to have gained about 9% mass, indicating that SF_6 was not removed during sample evacuation. Bake out of the 13X is probably needed for SF_6 removal. At 0°C (273 K), 13X adsorbed more SF_6 and had a steeper slope at low pressure. The removal of SF_6 at cryogenic temperature from a process stream is expected to be complete since the temperature is below its freezing point of SF_6.

The heat of adsorption information is derived from the above adsorption data at two different temperatures. Figure 2 shows that the heat of adsorption is mostly in 30 - 45 kJ/mole range. This information indicates the sensitivity of adsorption to temperature, and allows estimation of adsorption at different temperatures.

In a parallel test, the 13X molecular sieve was loaded in a Micromeritics AutoChem II 2920 instrument, degassed with a He flow at 450°C for 1.0 hour. The 13X molecular sieve sample was then cooled in a liquid nitrogen bath (-196°C), saturated with flowing H_2 (about 90 std cc/g uptake in flow conditions - in static equilibrium conditions the measured uptake was 125.1 std cc/g at 800 torr), injected with N_2 gas in doses to the He carrier stream. The effluent off-gas was monitored by a Pfeiffer Prism Plus RGA (Residue Gas Analyzer by mass spectrum).

Figure 3 shows the N_2 and H_2 in off-gas. The initial 8 doses of N_2 were completely adsorbed. After a few partial peaks, the N_2 peaks reached a steady state, indicating saturation adsorption. The cumulative N_2 adsorption was 184 std cc/g. This is comparable to 229.4 std cc/g at 800 torr static equilibrium conditions (measured separately). On the other hand, the H_2 concentration decreased steadily until about 50 minutes when the adsorbed H_2 on 13X was completely stripped out. During the initial 50 minutes, the H_2 peaks trended with the N_2 injections. As a baseline comparison, H_2 elution in a He carrier gas without N_2 injection is shown in Figure 4. The figure shows the adsorbed H_2 was carried out by the He gas in about 50 minutes as well, simply by reducing its equilibrium vapor pressure over the sample.

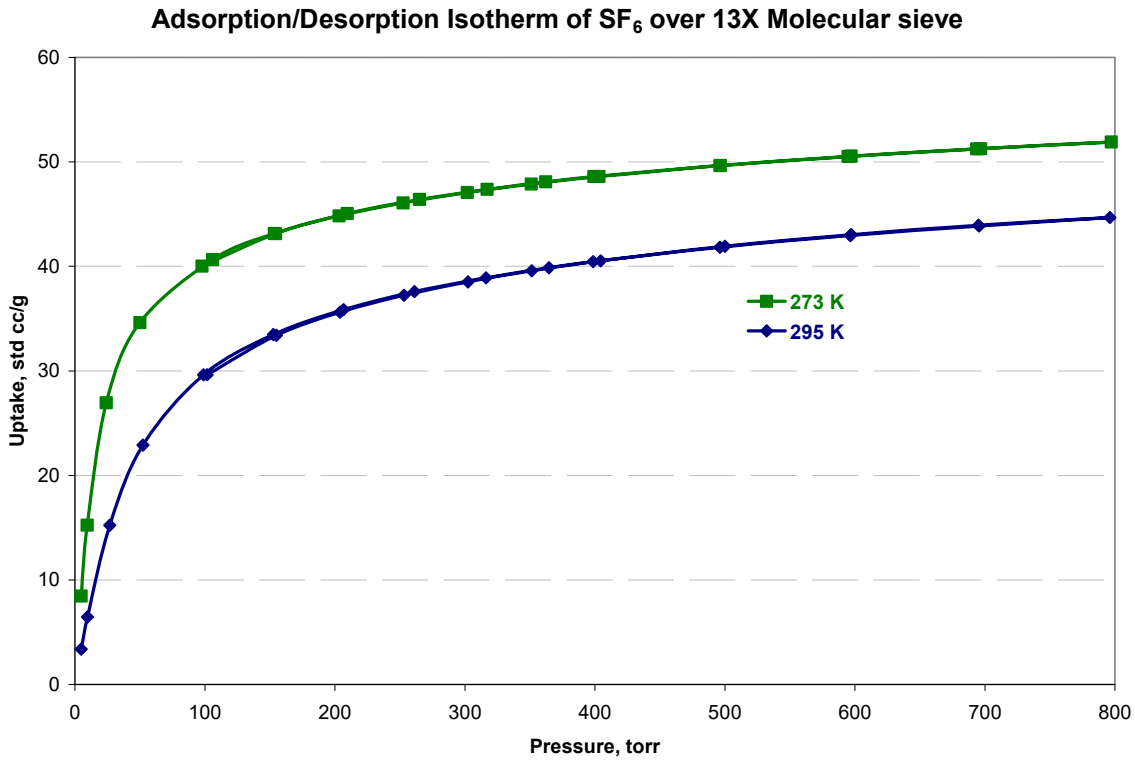

Figure 1: SF_6 Adsorption Isotherm over 13X Molecular Sieve

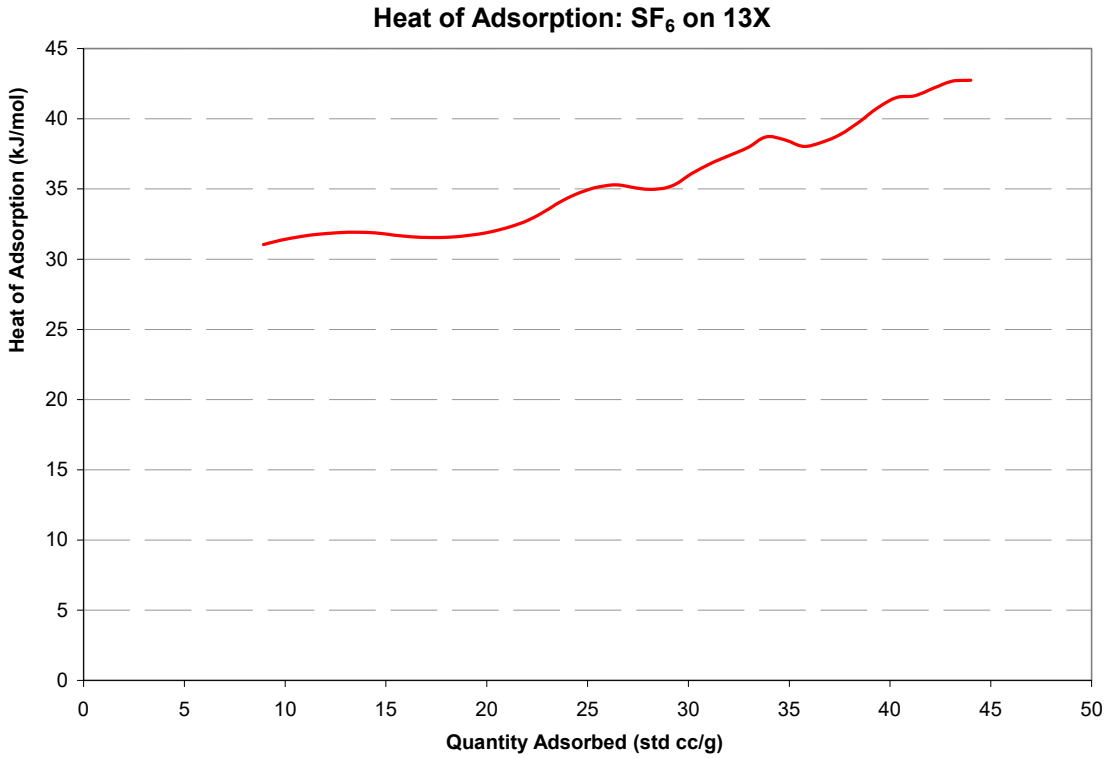

Figure 2: Heat of Adsorption of SF_6 on 13X Molecular Sieve

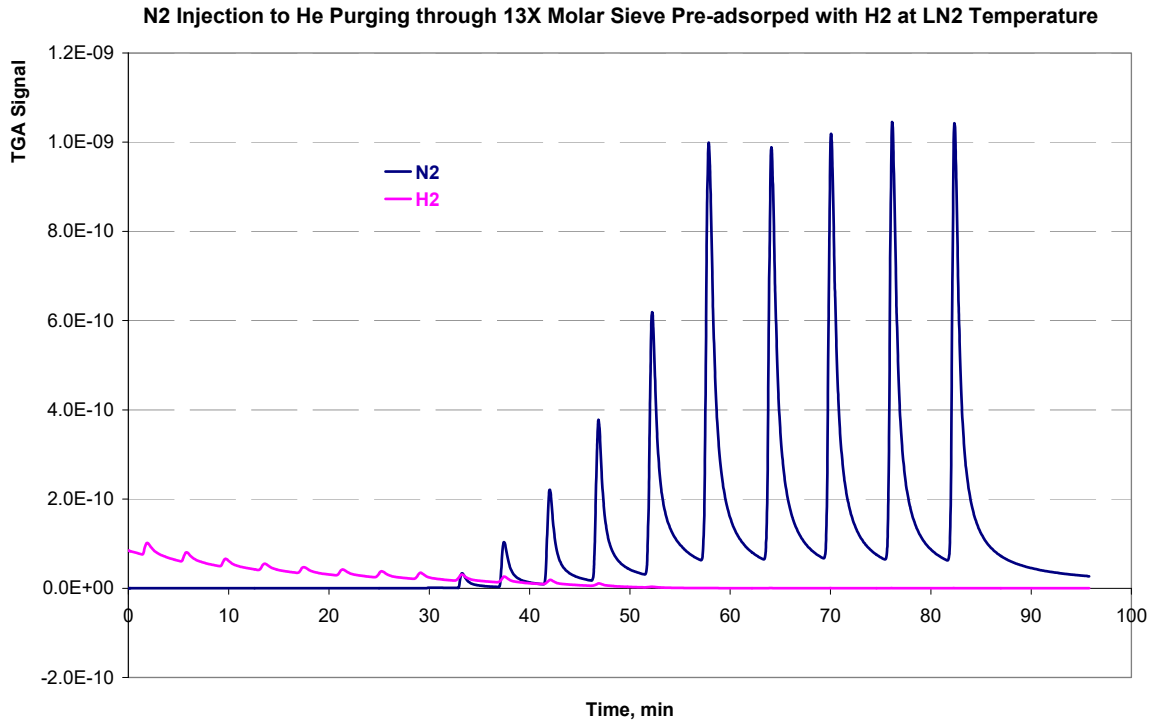

Figure 3: N_2 and H_2 in off-gas over 13X at LN_2 Temperature

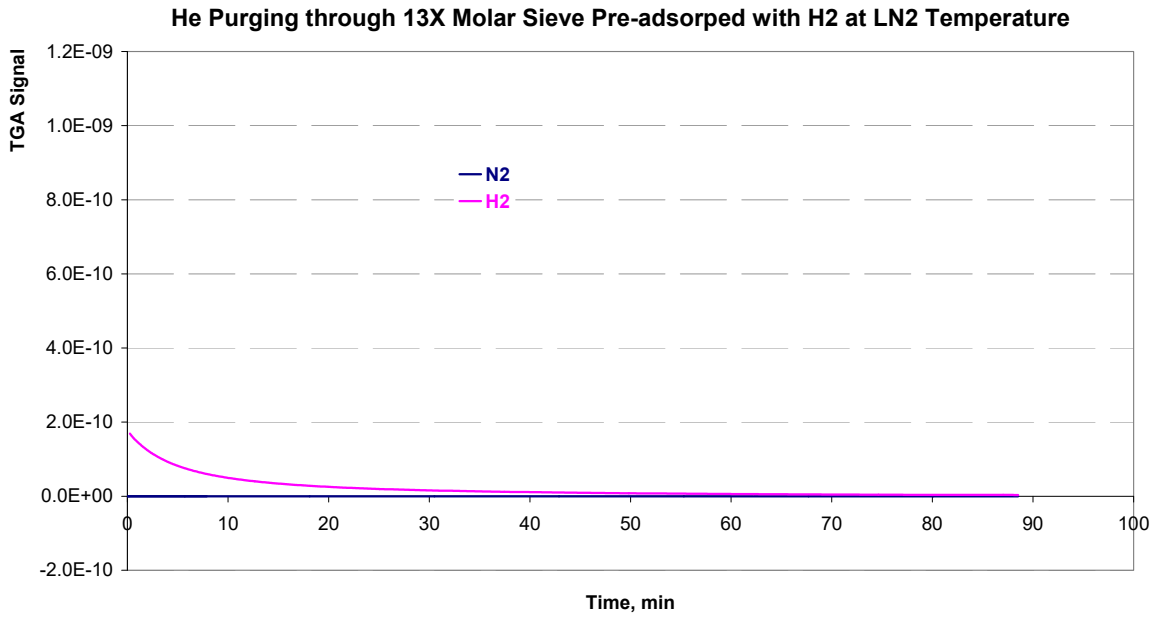

Figure 4: N_2 and H_2 in off-gas over 13X at LN_2 Temperature

Conclusions

1. SF_6 can be removed by 13 X molecular sieve. The pores of the 13X molecular sieve are big enough to adsorb SF_6 molecule. The 13X molecular sieve has significant adsorption capacity

even at ambient temperature. Complete removal of SF_6 is expected at lower temperatures. The adsorbed SF_6 will need to be baked out for removal from the 13X.

2. The adsorbed H_2 on 13X at LN_2 temperature will be purged out by either He or N_2. The N_2 doses had some effect promoting H_2 off-gas however the purging time for complete H_2 removal was about the same. The N_2 adsorption was not affected by pre-adsorbed H_2 at LN_2 temperature.

Future Work

More studies are needed at various temperatures and also use flowing adsorption to define a set of conditions to separate SF_6 from H_2. Other inert gases, e.g., nitrogen or argon may be used to get the H_2 off without removing the SF_6. The ultimate goal would be to keep the SF_6 on the 13X while recovering the H_2 (tritium) from the 13X. If successful, the data have potential to lead to a pilot scale test.