

# Impacts of temperature on nitrogen adsorption of common cryogenic purification materials

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**Abstract.** As hydrogen continues to gain adoption as a global energy carrier, a renewed focus on hydrogen liquefaction technologies has emerged. The hydrogen liquefaction process requires extremely pure hydrogen feed gas to prevent the freeze out of impurities which can damage equipment and disrupt operations. This study investigates the impact of temperature on the nitrogen adsorption performance of four widely used materials: silica gel, carbon-based molecular sieve, 13X zeolite and 5A zeolite. The aim is to examine the thermal dependence of nitrogen uptake in these materials, providing insights into their efficiency and suitability for cryogenic purification of hydrogen. Comparative results for equilibrium capacity at temperatures between 80 K and 110 K are presented.

## 1. Introduction

As the demand for hydrogen grows, liquefaction will continue to be a vital step in the hydrogen supply chain due to its advantages in storage and transportation. Hydrogen production methods, such as electrolysis, steam methane reforming, chemical processing, and biomass reforming, produces hydrogen feed gas with varying types of impurities and impurity concentrations. All impurities, except for helium, will freeze throughout the hydrogen liquefaction process. When impurities in the feed gas solidify, they can create blockages which disrupt operations and damage equipment. Oxygen in particular poses a significant explosion hazard in the hydrogen liquefaction process [1]. As the need for hydrogen liquefaction continues to grow, there will be an increasing demand for highly efficient hydrogen purification systems capable of handling a broad range of feed gas compositions and process conditions.

A variety of technologies are available to purify hydrogen depending on the impurity composition of the process gas and the required purity levels [2-3]. For industrial hydrogen liquefiers, pressure swing adsorbers (PSAs) and temperature swing adsorbers (TSAs), both using molecular sieve materials, are commonly employed. PSAs are typically used for initial hydrogen purification to achieve impurity levels in the low parts per millions, while cryogenic TSAs are employed within the liquefier for final purification to achieve impurities levels in the low parts per billions levels before the final liquefaction stage. While the types of adsorbents (silica gel, activated carbon, and zeolites) used in industrial liquefaction applications are generally known, detailed information on their specific adsorption properties at cryogenic temperatures is often scarce.

Temperature swing adsorbers inside hydrogen liquefaction units are generally operated at a temperature of 80 K. There is little data available in the literature to characterize how the

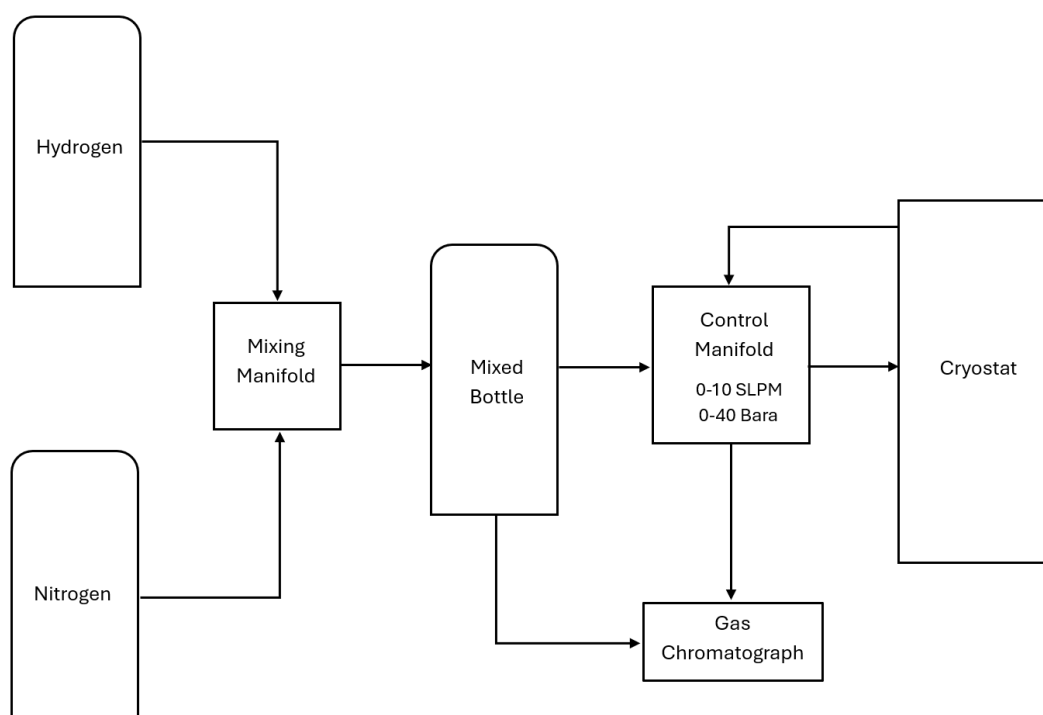


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performance of adsorbent materials are affected by elevated operating temperatures. Several studies have been published on the performance of industrial adsorbents at 77 K and ambient temperature, but there is little information available on performance between these temperature extremes [5-7]. Comparative results for equilibrium adsorption capacity of nitrogen on silica gel, carbon molecular sieve, zeolite 5A, and zeolite 13X from 80 K to 110 K are presented in this paper.

## 2. Experimental System

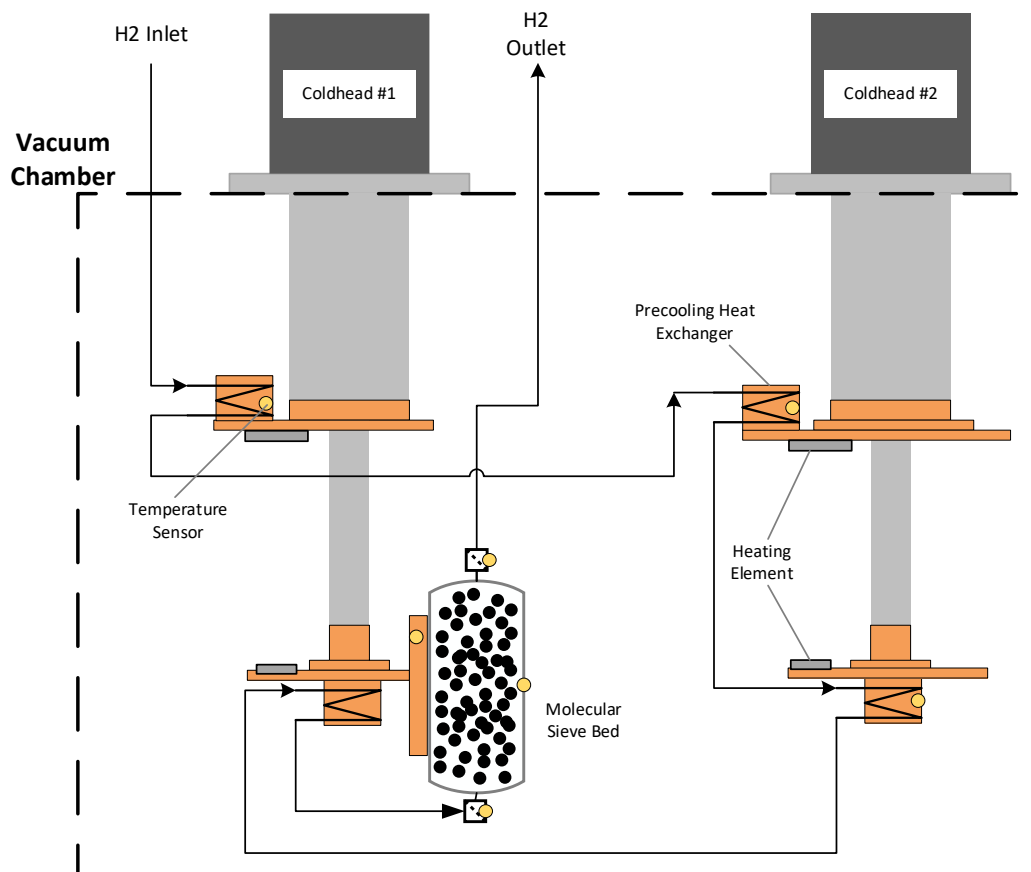
The experimental system previously used to characterize molecular sieve materials in prior work has been upgraded with an in-line gas chromatograph to provide real time impurity measurements during adsorption and breakthrough [4]. This experimental system features three major subsystems: a mixing manifold, a control manifold, and a cryostat. Mixtures of approximately 500 ppm nitrogen in a hydrogen balance were made for each adsorption test. Ultra-high purity grade hydrogen and nitrogen cylinders were mixed in a third cylinder to serve as the feed gas for the experiment. A gas chromatograph with a pulsed discharge helium ionization detector (PDHID) having a lower detection limit of 0.04 ppm nitrogen was used to verify the nitrogen concentration. Figure 1 shows a simple block flow diagram of the experimental system.



**Figure 1.** A simplified block flow diagram of the experimental system.

A custom cryostat consisting of a vacuum chamber, radiation shield, heater controller, and two helium cryocoolers was used to control the temperature of the hydrogen feed gas and the cryogenic purification bed. The system was designed to operate between 20 K and 120 K. Each cold head features two copper heat exchangers to precool the hydrogen stream. Temperature sensors and heaters embedded in the copper blocks are used to control and monitor the temperature on each cooling stage. Figure 2 shows a schematic of the cryostat setup. A valve manifold regulates the pressure and flowrate of the hydrogen to the cryostat and cryogenic adsorbent bed. The manifold includes a flow controller, source pressure regulator, and back pressure regulator to moderate the flow and pressure of the hydrogen throughout the system to

simulate the pressure, temperature, and flow velocities expected within the hydrogen liquefaction process.



**Figure 2.** Schematic of the cryostat configuration.

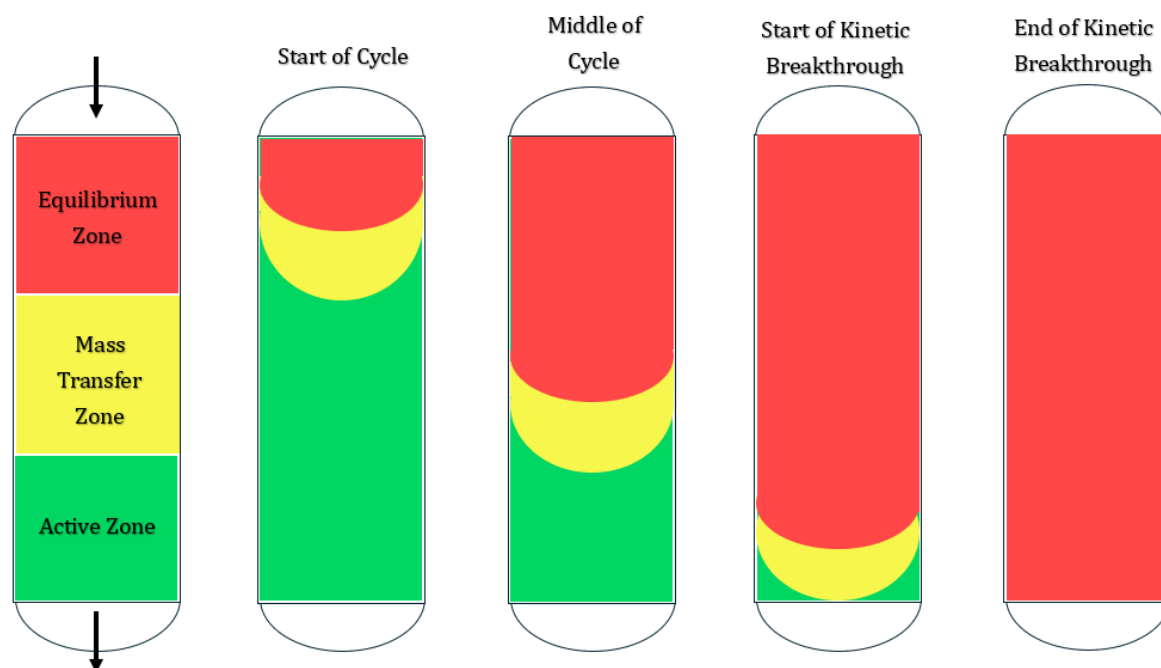
The adsorbent bed used for this test was an eight inch long, 12.7 mm (0.5 in.) diameter copper tube, sized to have a comparable L/D ratio to a full-scale adsorber bed. One inch at either end of the bed was packed with ceramic beads and quartz wool to inhibit migration of the adsorbent material during operation, and the remaining volume was packed with adsorbent material. The mass and volume of each material was measured before adding to the bed. The copper tube was thermally anchored to a copper block to promote heat transfer and isothermal conditions. Temperature sensors were located at the inlet, outlet, and along the axis of the tube to monitor the temperature. The temperature of the incoming hydrogen gas was cooled to match the temperature of the mole sieve bed to ensure steady state conditions.

A regeneration oven was used to perform reactivation procedures on sieve materials prior to testing. The oven features a resistive heater contained in an insulated enclosure, in which materials were heated at 394 K for eight hours with a dry nitrogen flow. At the end of the regeneration process, the adsorbent bed was flushed with ultra-high purity hydrogen to remove the nitrogen from the system.

Each material underwent a full breakthrough cycle at approximately 80 K, 97 K, and 110 K. The material was heated to at least 280 K and flushed with dry hydrogen for one hour between each test. All other factors that affect adsorption behavior including pressure, flow rate, and nitrogen impurity concentration were kept consistent between all tests.

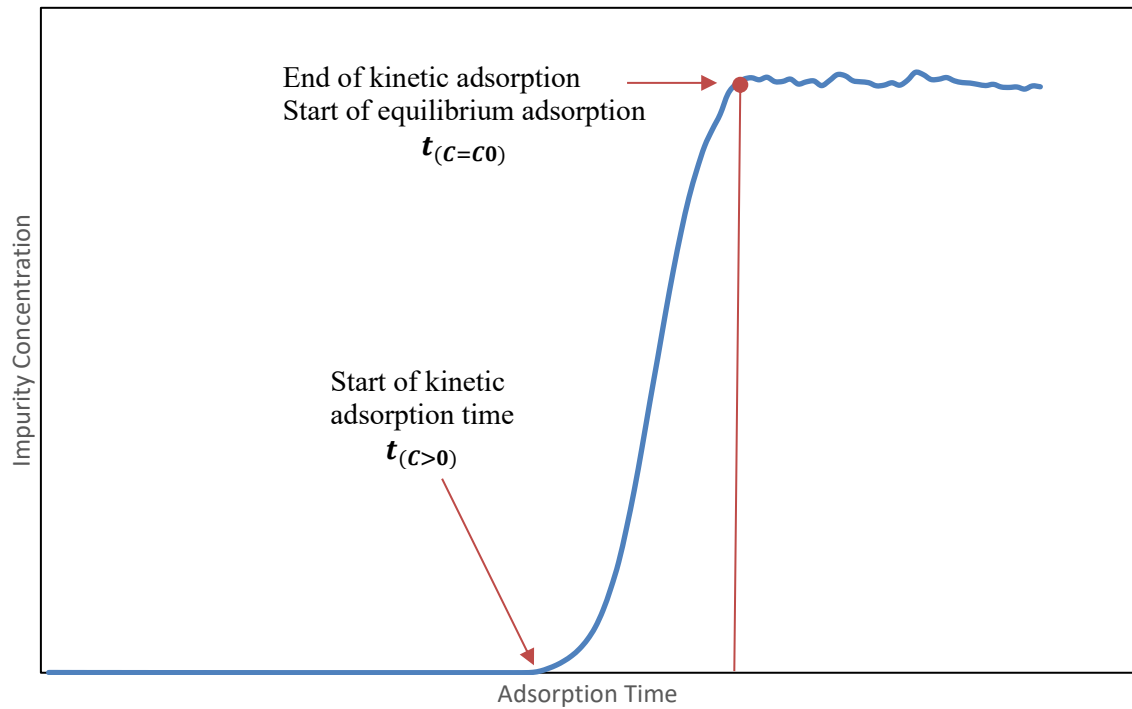
To begin a test, the bed was cooled to the desired temperature with a flow of ultra-high purity hydrogen until steady state conditions were achieved. Once the steady state temperature was

reached, the ultra-high purity hydrogen feed gas was shut off and replaced by the hydrogen-nitrogen mixture. The mixture flowed through the bed for the duration of the breakthrough cycle, similar to what is shown in Figure 3. In the example adsorbent bed depicted in Figure 3, hydrogen gas which is contaminated with nitrogen enters the top of the cylinder, and pure hydrogen flows out the bottom. The red area, known as the equilibrium zone, represents the adsorbent material that has already adsorbed the maximum amount of nitrogen and is fully saturated. The mass transfer zone depicted in yellow is the portion of the adsorbent bed that is actively adsorbing nitrogen out of the hydrogen stream. The green area, known as the active zone, represents virgin adsorbent material that has only been exposed to pure hydrogen since the nitrogen has already been removed upstream in the bed.



**Figure 3.** Breakthrough cycle in a cryogenic adsorber bed.

A gas chromatograph was used to monitor the breakthrough behavior during each test. A slip stream of hydrogen gas exiting the adsorption bed was diverted to the gas chromatograph for analysis. A gas sample was analyzed once every nine minutes, which was the cycle time of the gas chromatograph. The kinetic adsorption time was defined as the time from start of mixture flow to the first nitrogen concentration measurement above baseline impurity ( $C > 0$ ), indicating the start of kinetic breakthrough as depicted in Figure 3. The equilibrium adsorption time was defined as the time from start of mixture flow to the time that the inlet concentration was equal to the outlet concentration ( $C = C_0$ ), indicating the end of kinetic breakthrough. Typical breakthrough times ranged from eight hours to twenty-four hours. Figure 4 shows how kinetic and equilibrium adsorption times were identified from an experimentally measured breakthrough curve.



**Figure 4.** Identification of kinetic and equilibrium adsorption time from a breakthrough curve.

Kinetic and equilibrium adsorption capacity were calculated in terms of weight percentage nitrogen to sieve material using the equations 1 through 3, below.

$$Capacity_K = \frac{\rho_{N2,std} \cdot \dot{V}_{N2,mix} \cdot (C_0 - C) \cdot t_{(C>0)}}{m_{sieve}} \cdot 100 \quad (1)$$

$$Capacity_E = \frac{\rho_{N2,std} \cdot \dot{V}_{N2,mix} \cdot t_{sample} \cdot \sum_{n=1}^k (C_0 - C_n)}{m_{sieve}} \cdot 100 \quad (2)$$

where,

$$C_k = C_0 \quad (3)$$

and,

$Capacity_K$  [% weight] = kinetic adsorption capacity

$Capacity_E$  [% weight] = equilibrium adsorption capacity

$\rho_{N2,std}$  = Density of N<sub>2</sub> at STP ( $T = 15^\circ\text{C}$ ,  $P = 1.013 \text{ bar}$ )

$t_{(C>0)}$  [min] = kinetic breakthrough time

$t_{sample}$  [min] = time increment for gas chromatograph measurement

$m_{sieve}$  [g] = mass of adsorbent material

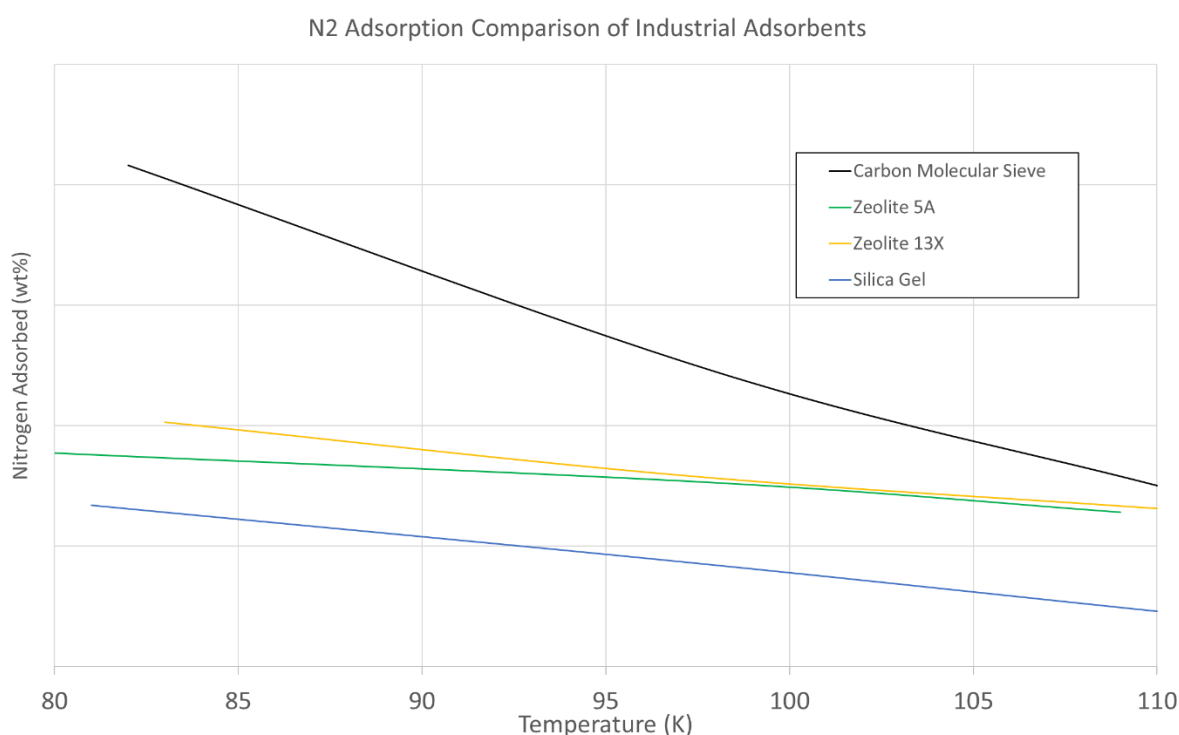
$\dot{V}_{N2,mix}$  = standard volumetric flow rate of of nitrogen in feed gas

$C_0$  = inlet nitrogen concentration

$C$  (or  $C_n$ ) = outlet nitrogen concentration

### 3. Results

The methods outlined above were used to characterize the performance of four common adsorbents: Silica Gel, zeolite 5A, zeolite 13X, and carbon molecular sieve. For each adsorbent, a full breakthrough was observed at 80 K, 97 K, and 110 K. Comparative results for the kinetic and equilibrium capacity of each material over the defined temperature range are presented in Figure 5. Note that the results shown are a general representation of the adsorbent performances. There was significant variability within each type of adsorbent depending on the manufacturer and specific chemical composition of each adsorbent.



**Figure 5.** Equilibrium adsorption capacity between 80 K and 110 K.

Competitive adsorption of argon was also shown to impact the adsorption capacity and breakthrough behaviour of the adsorbent bed. Throughout this work, trace argon ( $< 0.25$  ppmv) present in the ultra-high purity hydrogen was shown to breakthrough the adsorber bed at different times and rates depending on the type of adsorbent. The weaker adsorbed molecule would exhibit a breakthrough surge as the bed reached capacity, and the more strongly adsorbed contaminant began kinetic breakthrough.

### 4. Conclusions and Future Work

Molecular sieves 5A, 13X, and carbon-based sieves are all effective in removing nitrogen from hydrogen, but their adsorption capacities differ significantly depending on the type of adsorbent and manufacturer. Temperature plays a critical role, as even small variations (10 K to 20 K) can markedly influence adsorption capacity. This can have significant operational impacts as a large quantity of adsorbed molecules can desorb during transient operations or temporary shutdowns. Hydrogen liquefaction facilities must consider methods and procedures to ensure impurities do not migrate to colder regions of the process where they can freeze out when faced with abnormal conditions that would allow the cryogenic adsorption beds to heat up beyond their normal operating temperature.

The carbon molecular sieve, commonly referred to as activated carbon, outperformed the two molecular sieve materials over the entire temperature range in terms of equilibrium adsorption capacity, however carbon showed the least resiliency with respect to temperature increase. The carbon adsorbent lost 64% of its equilibrium adsorption capacity when the bed temperature was increased from 80 K to 110 K. At equilibrium, the carbon molecular sieve adsorbed 125% more nitrogen than mole sieve 5A at 80 K, but only 20% more nitrogen at 110 K. The zeolites showed the greatest resilience over the full temperature range from 80 K to 110 K. Silica gel had a markedly worse adsorption capacity compared to the other adsorbents tested in this work and is not recommended for nitrogen adsorption at cryogenic temperatures.

Competitive adsorption among multiple impurities must also be considered as it has been shown to reduce the overall adsorption capacity and lead to premature breakthrough [1]. This work also noted that competitive adsorption will lead to premature breakthrough of the impurity with the lowest adsorption capacity, leading to a surge of that contaminant breaking through the bed.

Additional work is needed to study the relationships between impurity concentration and adsorption capacity as lower partial pressures can also impact adsorbent performance. Pilot tests under expected operating conditions are recommended to fine-tune adsorbent selection and adsorption capacities.

## 5. References

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