Monitoring and Containment of Fugitive Emissions from Valve Stems – Electrical Conductivity and Gas Adsorption Measurements on Metal Oxides

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Introduction

Regulatory bodies in North America and Europe recognize that fugitive emissions from process equipment contribute to the release of hazardous and/or harmful chemicals to the environment. Long term objectives are to reduce leaks to near zero and to further develop accurate detection methods. The focus of the present research is to demonstrate the concept of using adsorbents, doped with catalysts that will enhance electrical conductivity of the solid when exposed to certain gas components, to monitor and control emission levels.

Fugitive emissions are leaks that occur from process equipment such as valves, pumps, compressors, and flanges. Fugitive emissions account for over 125,000 metric tones of lost product per year in the United States alone [1,2]. The percentage of fugitive emissions that come from valve stems is estimated to be 60% to 85% [1,2] due to the cumulative effects of large numbers of valves in processing plants. Regulatory requirements have evolved that require process industries such as refining and chemical processing to utilize Leak Detection and Repair (LDAR) programs. Further developments of LDAR techniques are needed that can accurately detect and monitor very small leaks.

Current technology for leak detection is labor intensive, expensive, does not contain leaks when they occur, and reduces the flexibility of maintenance scheduling since the task can take up so much of the maintenance resources. The present study focuses on developing the concept of combining the monitoring and control of fugitive emissions from valve stems into a single system that is contained within the valve. The combination of adsorbent and emission sensor will be achieved by adsorption on porous metal oxides and detection by monitoring changes in electrical conductivity on metal/metal oxides as they are exposed to the emission gas.

Gas adsorption studies on porous metal oxides are well established and, for example, hydrocarbon uptakes on various zeolites, silica-alumina, silica gel and activated carbons are reported in the literature [3-4]. Grande et al. report equilibrium and kinetic results for propane and propylene adsorption on commercial pellets and crystal of 5A zeolite in the temperature range of 323-423 K. The pellet adsorption loading measured by gravimetry is 1.7 mmol/g for propylene and 1.3 mmol/g for propane at 100 kPa and 423 K. [3]. Valve fugitive emission leakage rates vary depending on the size of the valve and stem diameter. On a per unit basis, a typical valve leakage rate is estimated to be 6.6×10^{-7} kg/hr/source [5]. For containment of propylene, for example, using the uptake data reported by Grande et al. [3], a valve would require approximately 81 grams of 5A zeolite to contain the emissions for a one year period. The estimate suggests that developing an on valve containment system of reasonable size using a solid adsorbent is feasible.

Studies have been reported on the electrical properties of solid oxides with a wide range of results. On γ-alumina, conductivity variation among samples is attributed to differences in surface area, average pore size, and crystallinity among samples. Conductivity is also dependent upon the hydration state of the starting sample and conductivity values have been reported to range over several orders of magnitude [6-9]. Electrical sensitivity experiments have also been carried out at 50 – 450 °C for a semi-conducting tin dioxide gas sensor with different Pd and $Al_2Si_2O_7$ loadings, in order to optimize this material as a gas sensor [10].

The above indicates that both adsorption and electrical properties have the potential to be utilized to monitor and control fugitive emissions from valve stems.

Results and Discussion

An experimental unit has been commissioned that allows simultaneous measurement of the gas uptake and the change in conductivity of an adsorbent bed. The adsorbent bed is approximately 2cm x 5cm in size and is placed in a quartz reactor. The bed is held within two co-centric, cylindrical tantalum electrodes used to measure the conductivity of the bed. Using breakthrough analysis following a step-change in feed gas composition, both the adsorption characteristics and changes in conductivity of the adsorbent bed are determined. Results from experiments using propylene over a number of adsorbents will be presented. An assessment of the approach to utilize an adsorbent for both containment and detection of leaks from valve stems will be presented based on the reported results.

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