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Sorbents for High Temperature Removal of Arsenic from Coal-Derived Synthesis Gas

Key Words: Sorbent, arsenic removal, syngas cleaning

Abstract

Gasification technologies convert coal and other heavy feedstocks into synthesis gas feed streams that can be used in the production of a wide variety of chemicals, ranging from hydrogen through methanol, ammonia, acetic anhydride, dimethyl ether (DME), methyl tertiary butyl ether (MTBE), high molecular weight liquid hydrocarbons and waxes. Syngas can also be burned directly as a fuel in advanced power cycles to generate electricity with very high efficiency. However, the coal-derived synthesis gas contains a myriad of trace contaminants that may poison the catalysts that are used in the downstream manufacturing processes and may also be regulated in power plant emissions. Particularly, the catalysts used in the conversion of synthesis gas to methanol and other liquid fuels (Fischer-Tropsch liquids) have been found to be very sensitive to the low levels of poisons, especially arsenic, that are present in the synthesis gas from coal.

TDA Research, Inc. (TDA) is developing an expendable high capacity, low-cost chemical absorbent to remove arsenic from coal-derived syngas. Unlike most of the commercially available sorbents that physically adsorb arsenic, TDA's sorbent operates at elevated temperatures and removes the arsenic through chemical reaction. The arsenic content in the coal gas stream is reduced to ppb levels with the sorbent by capturing and stabilizing the arsenic gas (As$_4$) and arsenic hydrides (referred to as arsine, AsH$_3$) in the solid state.

To demonstrate the concept of high temperature arsenic removal from coal-derived syngas, we carried out bench-scale experiments to test the absorption capacity of a variety of sorbent formulations under representative conditions. Using on-line analysis techniques, we monitored the pre- and post-breakthrough arsine concentrations over different sorbent samples. Some of these samples exhibited pre-breakthrough arsine absorption capacity over 40% wt. (capacity is defined as lb of arsenic absorbed/lb of sorbent), while maintaining an arsine outlet concentration at less than 10 ppb.

Introduction

U.S. Department of Energy (DOE) is working to furnish the U.S. market place with a number of advanced, highly efficient and environmentally responsible coal-based processes that can overcome the economic and environmental impediments that limit the full utilization of coal. In this context, DOE supported the development of "showcase" facilities across the country as part of the Clean Coal Technology Program (CCT), a joint effort co-funded both by the government and industry. The Liquid Phase Methanol Process (LPMEOH^{TM}) is such a "showcase" project, designed to convert synthesis gas derived from the gasification of coal into methanol to be used as a chemical intermediate or as a low sulfur dioxide emitting fuel. It has been demonstrated that the plant design capacity of 260 tons per day can be achieved and methanol can be produced for under $0.50 per gallon (DOE Clean Coal Technology Topical Report, 2000). The project also provided an excellent basis and life data for similar processes (i.e., Fischer-Tropsch synthesis, oxo processes).

However, during the demonstration tests, it was observed that the activity of the copper-based methanol synthesis catalyst was substantially reduced by the poisons (primarily arsenic) in the coal-derived synthesis gas. Catalyst deactivation rates as high as 2% per day were reported during the extended operation. Because most of these poisons are unique to coal (or can be found in coal-derived syngas at greater concentrations than they are in other type of feedstocks), their effective removal is critical for the successful demonstration of the production of chemicals and fuels from coal and coal-derived syngas.

Any commercial methanol synthesis process that uses the conventional $Cu/ZnO/Al_2O_3$ catalyst requires an essentially contaminant-free synthesis gas stream. Coal-derived syngas contains arsenic gas (As_4) and arsenic hydrides (i.e., arsine AsH_3) in low ppm levels, which interact very strongly with the copper-based methanol synthesis catalysts. The effect of arsenic on the copper catalyst is two-fold: (1) the strong affinity between arsenic and copper leads to irreversible chemisorption of arsenic on the active sites, and (2) at the temperatures of interest, arsenic and copper form a solid-solution that increases the mobility of the copper crystallites at the surface. These "micro-fluxes" promote the rapid sintering of copper, decreasing catalyst activity even further.

It is also anticipated that arsenic will act as a poison both for the iron or cobalt-based Fischer-Tropsch catalysts, rendering the catalyst inactive through the deactivation mechanism described above. Although iron and cobalt have higher melting points than copper, which may slow down the mobility of the cobalt and iron crystallites at the surface, the formation of cobalt and iron arsenides are thermodynamically very favorable. The relative stability of the cobalt and iron

arsenides (indicated by their existence at high temperatures) will cause irreversible absorption of arsenic over these metals and lead to a decrease in their activities as Fischer-Tropsch catalysts. Removing these contaminants is critical to adoption of coal-derived synthesis gas as a feedstock into the production of chemicals and transportation fuels.

Although commercial sorbents are available for removing arsenic from hydrocarbon streams, these sorbents are designed to operate at low temperatures and were developed to remove arsine from LPG, LNG or high-pressure hydrocarbon streams to prevent condensation of arsenic in the heat exchangers and other process equipments used to process these gases. These sorbents remove arsenic impurities based on physical adsorption. Because the nature of interaction between the sorbent and adsorbate is relatively weak (governed by the weak Van Der Waal forces), these sorbents can generally only be used at low temperatures (very close to ambient). However, cooling the coal gas to temperatures less than the operation temperatures of the catalysts used in the downstream conversion processes (i.e., methanol synthesis, Fischer-Tropsch) will impose a large energy and cost penalty. Thus, there is a clear need for sorbents that can remove arsenic from coal-derived syngas at elevated temperatures to prevent catalyst deactivation. Since these sorbents will be operated in an expendable manner, they must be very active and have a high arsenic absorption capacity.

Results

Sorbent Preparation
During the course of our research, we prepared more than 50 different sorbent formulations using various sources of active materials, different inert substrates and additives (i.e., clays, binders). We first screened the formulations according to their physical properties, including pellet strength, porosity, surface area and active material loading level. In the selection of proper active material and support, the cost of the material (both for the active phase and the substrate) were also taken into consideration. Our choice of substrate materials included conventional supports such as γ-alumina, titania, silica, activated carbon and boehmite [$AlO(OH)_3$]. All these materials satisfied the criteria of being low-cost and high surface area (100 to 580 m^2/g as measured by the manufacturers). The support and the active material precursors were combined using TDA's geode technology, enabling the incorporation of large quantities of active material into the final formulation, without plugging the pores of the substrate material and without reducing its porosity.

The best formulations with the desired physical properties were tested for their arsenic absorption capacities under simulated reaction conditions in an automated testing apparatus.

Sorbent Screening
Sorbent Testing Apparatus: The testing apparatus was built at TDA for the specific purpose of measuring activity of the sorbents used for trace contaminant removal (Figure 2). The sorbent reactor consists of a 2.5 cm-OD stainless steel reactor tube that contains a frit at its mid-point to support pellets of 1/32" to 1/8" in diameter. A Mellen tube furnace surrounding the reactor is used to control the temperature. The pressure of the system was controlled with a Badger pressure control valve located at the downstream of the test section.

All gas flows to the reactor were controlled with electronic mass flow controllers. The gas streams of CO, H_2, CH_4, CO_2, AsH_3 and N_2 were introduced through Porter mass flow controllers. We used the most common arsenic hydride, arsine (AsH_3) as the source of arsenic in the feed stream. The arsine was acquired as a calibration gas standard mixture (Matheson Tri-Gas, Longmont, CO), where 1 to 10 ppm AsH_3 was mixed with H_2. Its controlled introduction into the system was easily achieved through mass flow controllers. After mixing in a manifold, the gas stream was preheated above the dew point of water to prevent condensation. The mixture then passed through a saturator where water was mixed into the feed stream by a peristaltic pump. The saturator design allowed complete evaporation of the liquid and ensured good mixing of the gases prior exiting the device. In some experiments, we also used a sparger to humidify the gas stream (i.e., 2 to 10% Vol. H_2O). With this setup, it was possible to generate feed streams of simulated coal-derived synthesis gas and pass them over sorbent formulations at the desired rates. The preheated feed mixture was then directed into the reactor. The feed gases could also bypass the reactor through a valve combination and flow directly to the analytical system for accurate measurement of the feed gas composition.

The arsine concentration at the outlet of the reactor bed was measured with an on-line arsine analyzer. An SRI Model 8610A gas chromatogram (GC) was used to measure concentrations of the other reaction gases CO, H_2, CO_2 and CH_4. After exiting the analyzer, the effluent gas stream was scrubbed by a strong NaOH/oxidizer solution to capture arsenic, forming highly soluble sodium arsenate and preventing the release of arsine to the atmosphere. The apparatus was fully automated and ran without an operator for long periods of time, including overnight. We used Control CB software on this apparatus to control test conditions, log analytical data, and to safely shut down the apparatus in case of a malfunction.

Testing Procedure: We tested each sorbent formulation using gas concentrations representative of coal-derived synthesis gas (Table 1). We simulated the syngas by blending certified mixtures of AsH_3 in H_2 (Matheson Tri-Gas, Longmont, CO), N_2, CO, H_2, and CO_2 (Air Gas, Inc., Colorado Springs, CO). Prior to each test, we calibrated the arsine analyzer and measured the arsine concentration at the reactor inlet via the reactor by-pass line. Once the preliminary tests were completed and a stable baseline for the inlet arsine level was established, we directed the gas flow through the sorbent bed.

In every test, a known quantity of sorbent was placed in the reactor. Each test started with heating up the reactor to the desired temperature under a flow of nitrogen. Once the temperature was stabilized, the reactor cell was pressurized under nitrogen to the desired pressure. We carried out tests at temperatures ranging from 30 to 250°C, and pressures from 100 psig to 750 psig. We also employed different space velocities in our tests to observe the effect of gas contact time on the arsenic removal capacity. Due to the very high arsenic absorption capacity of the sorbent formulations, we employed space velocities much higher than that of those expected in conventional gasifier effluent clean-up systems to reduce the testing time for each formulation and to accomplish a quick screening of many samples as possible (this provided a very conservative measurement of the capacity of our sorbents).

We carried out two different sets of tests to measure the sorbents' performance: 1) breakthrough tests and 2) saturation capacity (post-breakthrough capacity measurement) of the sorbents

(Figure 3). In the breakthrough tests, we measured the arsine concentration in the simulated syngas exiting the sorbent bed. The absorption capacity was determined at the breakthrough point. In most of the tests, we used 99% arsine removal as the criteria for stopping the test and calculate the absorption capacity (i.e., for a 2.5 ppm arsine inlet concentration, we used 25 ppb as the breakthrough point, providing 99% removal of the arsine fed to the reactor).   The amount of arsenic absorbed over the sorbent was calculated by integrating the area above the breakthrough curve. We then defined the capacity as the mass of arsine absorbed per unit mass of sorbent (i.e., lb arsenic/lb sorbent). Measuring the saturation capacity (or ultimate absorption capacity of the sorbent) we loaded a very small quantity of sorbent material into the reactor, 10-20 mg (an order of magnitude less than we used previously in the pre-breakthrough measurements) in order to minimize the testing time. Since the quantities were so low, we homogeneously mixed them with inert materials to prevent any channeling through the bed. Using such small quantities of sorbent caused extremely high gas hourly space velocities (or very short contact times) followed by almost instantaneous arsine breakthrough. We then ran the sorbent until the sorbent was completely saturated and absorbed no more arsine.   The arsine absorption capacity was calculated following similar procedures as we used in the pre-breakthrough calculations (the shaded area in Figure 3) with the only difference being in the shape of the arsine breakthrough curves.

Diagnostic Tests: Prior to testing of the sorbent, we carried out several diagnostic tests to measure the effects of dead volume and other reactor components (i.e., stainless steel tubing) on the breakthrough time and arsine outlet concentrations. The time elapsed from introducing arsine into the manifold and its detection in the gas monitor was less than a minute under representative operation conditions, indicating that the reactor design allowed an acceptable time lag to carry out the intended tests.

Once the blank reactor tests were completed, we loaded the reactor with inert alumina pellets (high surface area and high porosity) to measure the effect of typical support material that we plan to use on arsine absorption. We tested the inert pellets with arsine inlet concentrations changing from 1.0 to 5.0 ppm. These tests indicate that the high surface area substrates (i.e., alumina or silica) have very little or no affinity for arsine, and essentially act as an inert during the absorption process. These tests allowed us to use these materials as a diluent in the reactor during the saturation tests (where we mixed small quantities of sorbent materials with inerts to prevent the reaction gases from channeling through the bed).

Test Profile: Figure 4 illustrates a typical test profile for the breakthrough tests. In this particular test, after waiting for temperature and pressure stabilization, we introduced 500 sccm mixture of AsH_3/H_2 and 500 sccm nitrogen to yield a 2.7 ppm arsine inlet concentration and 50% H_2 (balance nitrogen). We monitored the arsine outlet concentration exiting the reactor in 20 sec time intervals.   In the initial screening tests, the gas hourly space velocity (GHSV) was maintained at 200,000 hr^{-1}, corresponding to a contact time of 0.018 sec. Although we selected an extraordinarily low contact time, it was necessary to minimize the breakthrough time so that we could test a large number of sorbents in a short time, which might otherwise take days for some of our samples.

Once the arsine concentration from the bed exceeds a pre-determined concentration, the automated system initiated a shutdown sequence, stopping the gas flow, depressurizing and cooling the reactor. The samples were recovered, so we could carry out physical characterization tests (i.e., surface area). Some samples were shipped to Huffman Laboratories who measured the arsenic content of the sample. The chemical analysis results and our calculations based on the breakthrough profile were in very close proximity ($\pm$ 5%). For this particular sample, arsine was first detected by the analyzer after 780 minutes of operation and its concentration slowly crept up to above 10 ppb reaching to 27 ppb in 1030 minute. At this point, we stopped the run and purged the system with nitrogen until we observed a zero signal in the analyzer. We selected 27 ppb as the breakthrough point $1/100^{th}$ of the inlet concentration to ensure 99% removal. The arsine absorption capacity of the sorbent was calculated as 4.58% wt. at 30^oC. We repeated tests in similar nature at different operation conditions, where we varied the temperature, pressure and contact time, as described in the section below. Of course, the breakthrough capacities would have been higher, if we had tested them at a lower space velocity.

Parametric Tests
Once we completed the screening of the sorbent formulations, we identified a single-best material and conducted the parametric tests where we measured the effects of operation parameters (i.e., temperature, pressure) on the performance of the sorbent.

Effect of Temperature: Although our main interest is in the high temperature removal of the catalyst poisons from the coal-derived syngas, we carried out tests at a range of temperatures to identify the effect of temperature on the arsenic absorption capacity of the sorbent. We carried out tests at 30^oC, 140^oC and 230^oC temperature, systematically increasing the temperature using the same sorbent. We flowed simulated coal gas until we observed arsine breakthrough and estimated the arsine absorption capacity of the sorbent. Figure 5 summarizes the results of these tests, where we measured the arsenic absorption capacity of three sorbents using the same active absorbent phase and substrate (active material content is in the order of 68A<68B<68C) at different temperatures. It is important to note that the arsenic absorption capacity of the sorbents increases with increasing temperature because the absorption of arsenic on the sorbent is a chemical process. The sample with the highest fraction of active material exhibited the highest absorption capacity at 230^oC.

Effect of Pressure: We also measured the performance of the sorbent at different pressures. Although the LPMEOH^{TM} plant operates at 700-750 psig, the absorbents developed for the syngas cleanup should demonstrate sufficient activity at a range of pressures, for easy integration into a wide spectrum of downstream syngas conversion processes. We conducted breakthrough measurements where we varied the pressure in the range of 100 to 900 psig. As illustrated in Figure 6, the absorption capacity of the sorbent increased with increasing pressure. However, we observed a saturation effect at pressures over 750 psig, and further increase in pressure has less much smaller increase on the absorption capacity of the sorbent.

Effect of Arsine Inlet Concentration: The commercially successful sorbent must be able to work over a very wide range of inlet arsine concentrations. The arsenic content of the coal-derived syngas varies significantly depending on the type of the coal used in the gasification process and the type of the gasifier (i.e., whether it uses water quench or not). Thus, we tested the

performance of our sorbents at a range of arsine inlet concentrations (Figure 7). We observed a dramatic increase in the breakthrough absorption capacity of the sorbent by lowering the arsine inlet concentration from 2.5 ppm to 1.0 ppm, under identical operation conditions (T=230°C, P=450 psig, GHSV=2,000,000 h^{-1}). We also observed a further increase in the absorption capacity from 37.29% wt. to 44.56% wt. by decreasing the inlet concentration from 1.0 ppm to 0.5 ppm. This trend shows that the breakthrough capacity strongly depends upon the solid diffusion rate (the rate limiting step) in which the surface bound arsenic can be transferred to the inner layers of the active material and stabilized.

Effect of Gas Hourly Space Velocity: We tested the effect of gas hourly space velocity (reciprocal contact time) on the arsenic absorption capacity (Figure 8). The arsenic absorption capacity showed a strong dependence to the gas/solid contact time at 230°C and 450 psig. Given enough time, the surface-bound arsenic diffuses into the inner active material matrix, even if the substrate does not possess a very high porosity. Figure 8 also indicates that increasing the contact time to more than 4.0 miliseconds generates smaller gains on the capacity of the sorbent. It is also important to note that 4.0 milisecond contact time is almost two orders of magnitude lower than that is encountered in the state-of-the-art sorbent systems, indicating extremely fast arsenic absorption and solid diffusion rates at the operation temperature.

Estimation of Cost of Removal of Arsenic

Based upon the experimental data we carried out a cost assessment for the removal of arsenic from coal-derived syngas. Our preliminary economic analysis indicates that for the sorbent-based removal of catalyst poisons, sorbent replacement cost will be a major cost driver. Other costs include sorbent disposal, annualized capital costs and operating expenses. There will also be a relatively small cost due to parasitic losses associated with the pressure drop through the bed (i.e., an efficiency loss).

The sorbent cost and the sorbent life (i.e., arsenic absorption capacity of the sorbent) determine the sorbent replacement costs. Since the sorbent is expendable, low sorbent cost is critical to cost-effective removal of the poisons. Although we selected very inexpensive materials to be used in the sorbent formulations, the unavoidable fabrication costs constitute a large fraction of the cost of the final sorbent (usually 50-60% of the sorbent cost). Since our materials are already inexpensive, there are no ways to easily reduce the cost of sorbent, thus it is important to maximize the sorbent arsenic loading without increasing the sorbent cost.

Our preliminary cost assessment predicts an arsenic removal cost of $10 to $40/lb of arsenic, depending on the arsenic absorption capacity of the sorbent and sorbent cost. Figure 9 shows the cost of removal of arsenic reflected per unit mass of coal processed through a gasifier, and illustrates that the relative sensitivities of sorbent cost and absorption capacity on arsenic removal. For coal containing 2.0 ppm of As, TDA's sorbent system offers the potential to remove arsenic at a cost less than $0.4/ton of coal, provided that sorbent cost is approximately $5/lb and sorbent loading levels are on the order of 30 lb of arsenic/100 lb of sorbent (Figure 9). If the cost of coal is assumed to be about $30-40/ton, the removal of arsenic would cause about 1-2% increase. This will correspond to a much smaller increase in the cost of methanol produced (~0.1-0.2 cents/gallon out of approximately $0.5/gallon, or a 0.2 to 0.4% increase).

Conclusions

TDA's sorbent achieved an arsenic absorption capacity over 40% on weight basis at $230^{o}C$, under simulated conditions (where we intend to operate) and a capacity of 15.1% wt. at $30^{o}C$.

We carried out parametric tests where we varied operation parameters such as temperature, pressure and inlet arsenic concentration and demonstrated that the sorbent can operate effectively at a wide range of conditions. The bench-scale test results clearly demonstrate that:

1) TDA's sorbents have a very high capacity for arsenic absorption
2) These sorbents can be used both at low and high temperature applications (temperature range of 30 to $250^{o}C$)
3) High absorption capacities can be achieved by operating the sorbent at high temperatures
4) The sorbent pellets maintain their mechanical integrity during the large expansion associated with the changes in molar volume resulting from arsenic absorption

Based upon the experimental results, we carried out a preliminary cost assessment for the removal of arsenic from coal. We showed that the sorbent replacement cost to remove arsenic from coal-derived syngas will be less than $40/lb, (anticipated to be the primary cost driver in the syngas clean-up system). This will translate into less than $0.40 increase in the cost of coal per ton.

References

DOE Clean Coal Technology Topical Report (2000). "Commercial-scale Demonstration of the Liquid Phase Methanol Process", No.11.
DOE Clean Coal Technology Technical Progress Report (2000). "Commercial-scale Demonstration of the Liquid Phase Methanol Process", April-June 2000.

Table 1. Typical gas compositions.

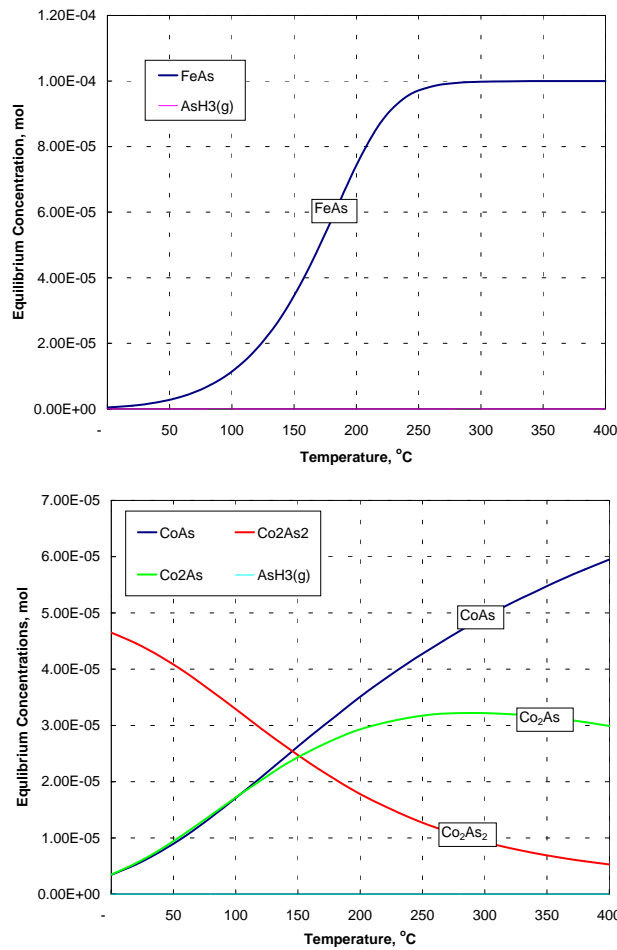| Components	Composition
H_2	40-45%
CO	30-35%
CO_2	10%
N_2	0-5%
H_2O	20-25%
AsH_3	0.5-2.7 ppm

Figure 1. Equilibrium distributions of iron and cobalt arsenides (1.0 ppm arsenic and simulated coal-derived syngas is used with excess metals for the simulation).

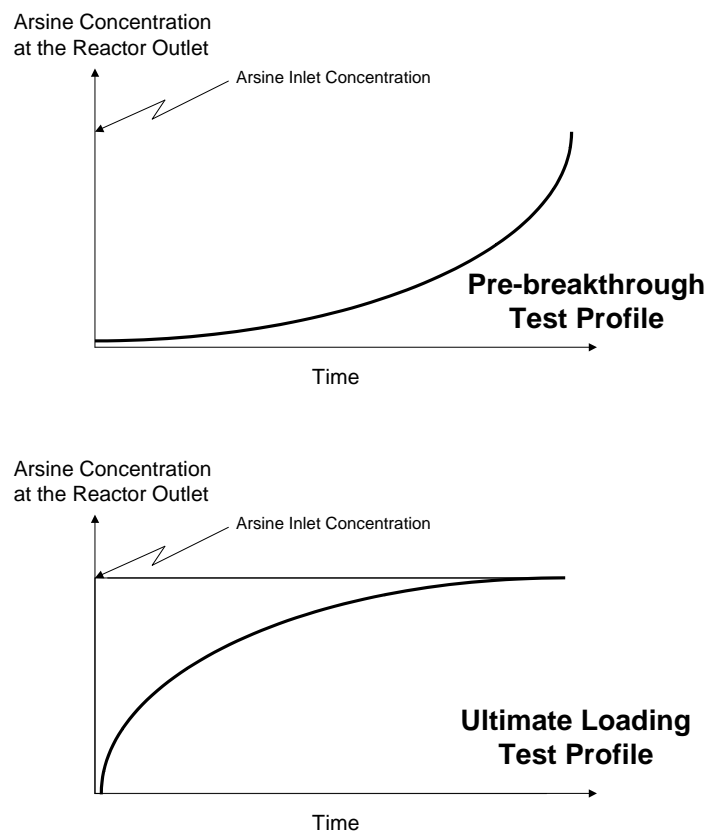Figure 2. A photograph of the testing apparatus.

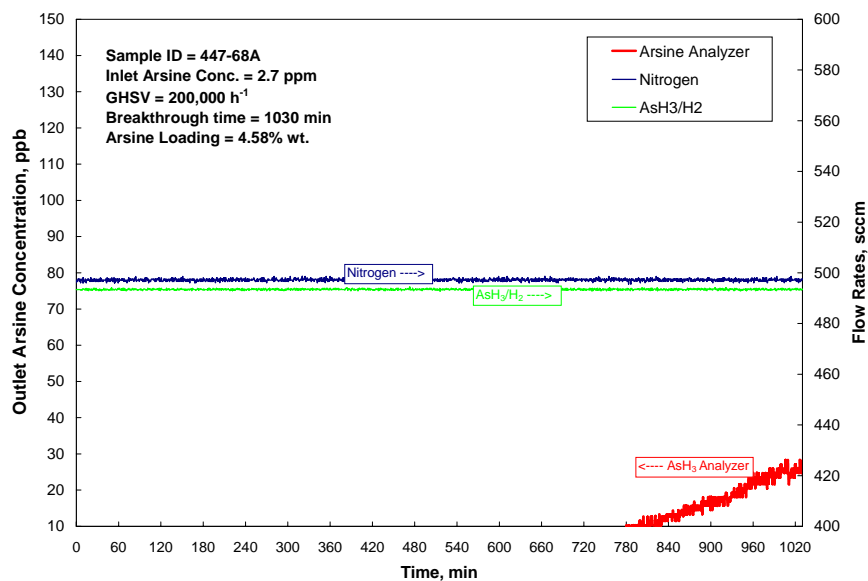Figure 3.   Arsine concentration profiles for pre-breakthrough and ultimate loading tests.

Figure 4. Arsine breakthrough curve over TDA 447-68A sorbent at 30°C.
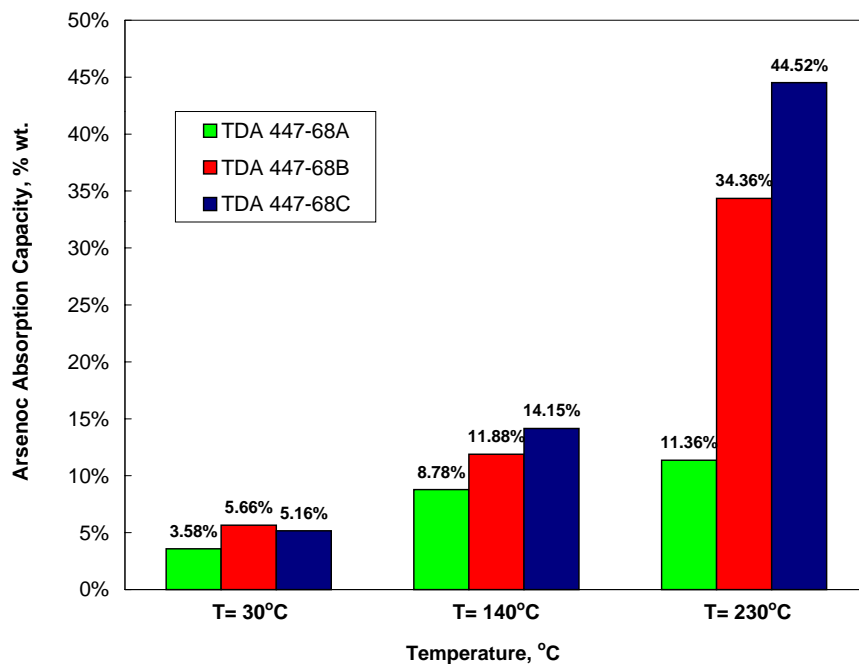
Figure 5. Effect of temperature on breakthrough arsenic removal capacity, P=450 psig, GHSV = 300,000 h^{-1}, AsH$_3$ conc.= 2.7 ppm.
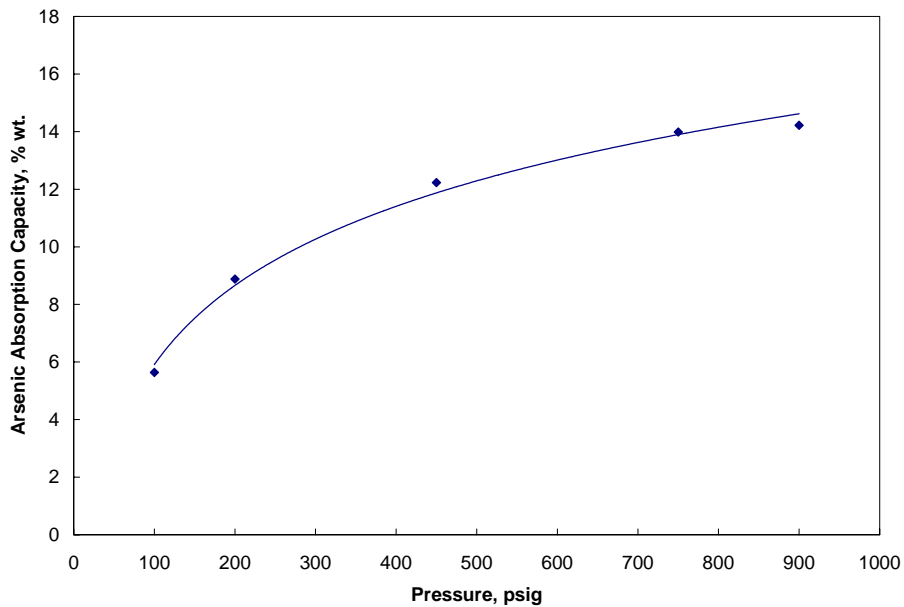
Figure 6. Effect of pressure on breakthrough sorbent performance, TDA 447-68B sorbent, T=230°C, GHSV=1,000,000 h^{-1}, AsH$_3$ inlet concentration = 2.5 ppm.
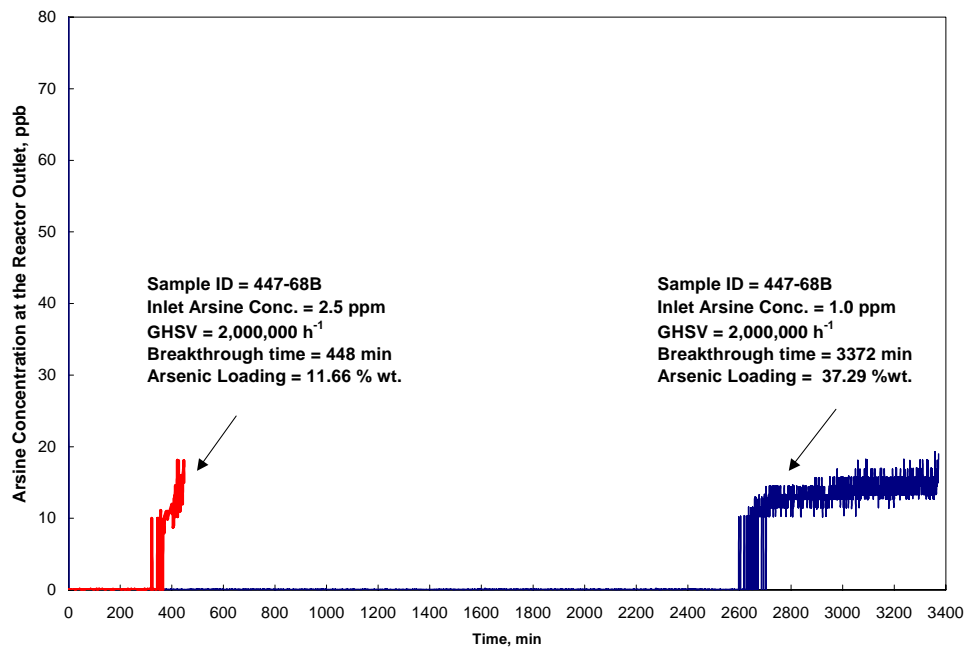
Figure 7. Effect of arsine inlet concentration on the breakthrough arsenic absorption capacity of the TDA 447-68B sorbent (T=230°C, P=450 psig, GHSV=2,000,000 h^{-1}).
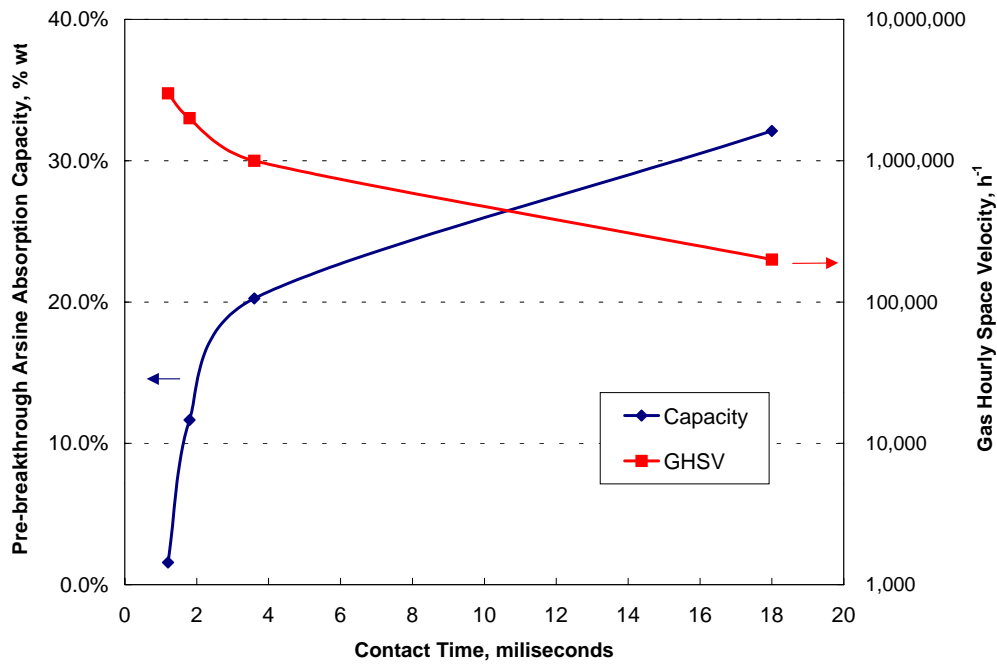
Figure 8. Effect of gas/solid contact time on breakthrough arsenic absorption capacity over TDA 447-68B sorbent, P=450 psig, T= 230°C, AsH$_3$ conc.= 2.7
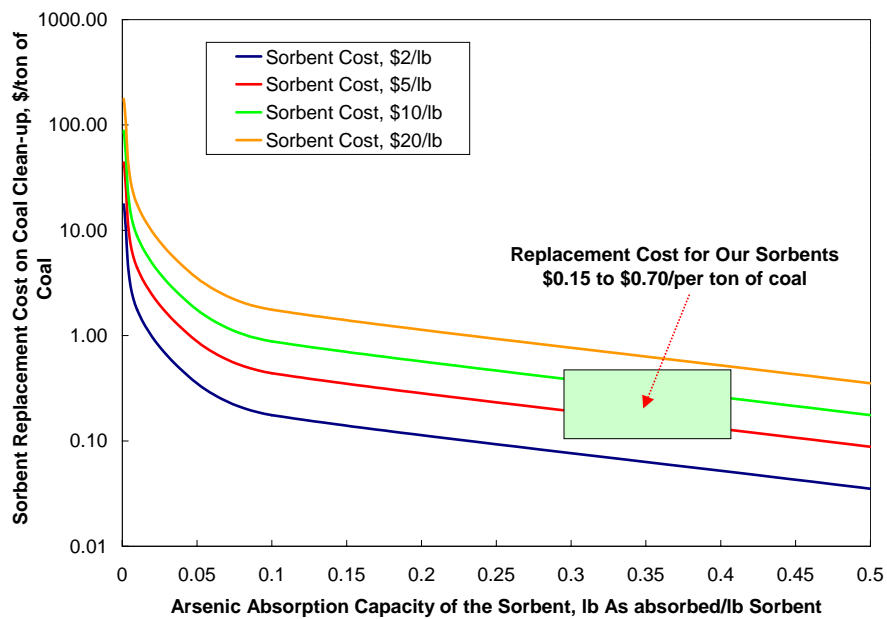

Figure 9. Cost of removal of arsenic as a function of sorbent loading and cost.