EXTRACTION OF XENON USING ENRICHING REFLUX PRESSURE SWING ADSORPTION

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ABSTRACT

Measuring radioactive xenon isotopes in the atmosphere is an important technique used for monitoring within the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Several process steps are needed to capture and prepare a xenon sample suitable for transfer to a nuclear detector. These processes include air drying, xenon collection, concentration, and purification. The ideal xenon sampling system would be small, have low power consumption, not use consumables (such as helium gas or liquid nitrogen), and be fully automated, robust, and dependable. Due to the low concentration of xenon in the air, the most energy-intensive part of the gas processing is the first stage collection and concentration. Pacific Northwest National Laboratory has developed a batch-mode enriching-reflux pressure-swing-adsorption (ER-PSA) process that shows promise as a xenon collection and concentration technique. The development of this process was guided by finite element models of the process chemistry. The modeling showed that minimizing the xenon dispersion in the adsorption columns is critical to achieving a good separation. Prior to hardware construction, models were used to determine appropriate trap dimensions, adsorbent particle size, and optimum process variables such as cycle steps, step times, and flow rates. A benchtop ER-PSA unit was constructed, and testing under various operating conditions has begun. The results obtained in these initial parametric experiments have provided insight into the physics of the process and have refined the mathematical models. The combination of modeling and experiment provides a better understanding of process physics than either experiment or models alone. The benchtop system has demonstrated room-temperature collection of xenon with a xenon enrichment of 1000 (starting from air) and a modest pressure ratio of 7–10, resulting in an energy-efficient separation technique. The technique does not use exotic adsorbents, cryogenic temperatures, or high-pressure compressors, enabling a small, low-power, robust system. This ER-PSA process is an enabling technology for small energy-efficient xenon collectors, desirable qualities for next-generation international xenon systems.

OBJECTIVE

The objective of this research project is to build and test a unique gas collection scheme aimed at preconcentrating xenon without the use of any form of cooling. The collection scheme utilizes activated charcoal (AC), a well-proven, reliable, and easily obtained adsorbent material. To achieve this task a basic experimental apparatus was designed and built based on results from realistic computer simulations of the process chemistry. Initial tests were conducted to demonstrate that, in fact, the gases of interest could be collected. These early results are very encouraging and confirm that AC can be used to preconcentrate xenon to useful levels without cooling.

RESEARCH ACCOMPLISHED

Pressure Swing Adsorption

The gas preconcentrating approach that has been explored here is a special variant of a pressure swing adsorption (PSA) method, a common approach used in many small- and large-scale gas-separation applications (e.g., heatless air drying, N_2/O_2 separations, methane and hydrogen purification). The basic notion behind any PSA scheme is that the adsorption capacity of a given material is greater at high pressure than at lower pressure. Additionally, if there is a difference in the capacity of the adsorbent material for two (or more) different adsorbing species (adsorbates), it is possible to develop a separations scheme that takes advantage of the selectivity of the material and the pressure dependence of the adsorption capacity. Figure 1 shows a series of conceptual curves representing “typical” adsorption isotherms that can be used to further explain the phenomena behind PSA. In this diagram, temperature is also an adjustable variable (between adsorption and desorption) that can be used to enhance the relative difference in capacity between adsorption and desorption. Maximizing this difference leads to improved collection efficiency for a given trap size. For a given isothermal system, it can be seen that if adsorption occurs at high pressure, where capacity is large, then the capacity of the adsorbent drops if the trap is suddenly depressurized, and the previously adsorbed species must be released into the gas phase. This forms the basis of a PSA cycle: adsorption at high pressure followed by desorption at lower pressure. Typical PSA systems consist of two adsorption beds, one operating at high pressure (adsorbing mode) and the other at low pressure (desorbing or regenerating mode). In such a dual-bed configuration, the system can operate continuously by cycling back and forth between the two beds. Other PSA schemes have multiple beds used in more-complex arrangements to maximize yield.

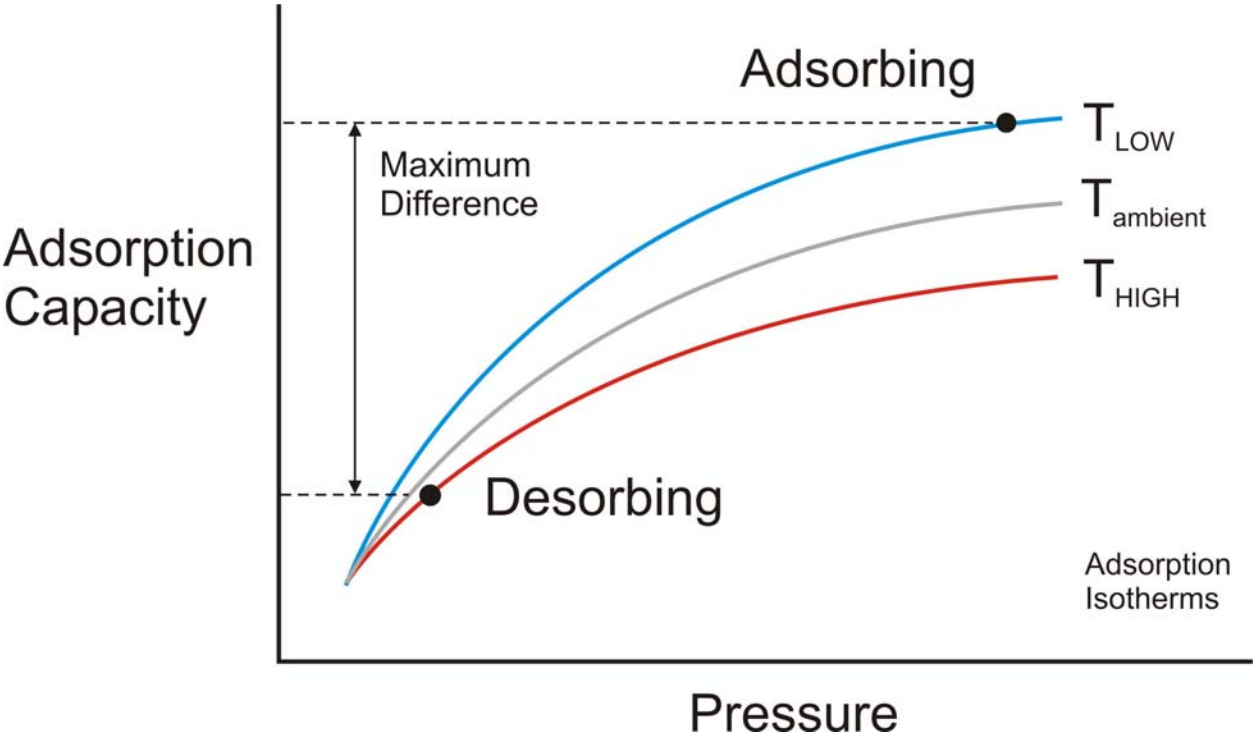

Figure 1. Depiction of the adsorption/desorption process, where temperature and pressure can be used to maximize the relative difference between adsorption capacity.

In order to develop a separations or selective pre-concentration process using PSA, it is useful that a difference exist in adsorption capacity of the adsorbent material for the different chemical species involved; this is referred to as selectivity. While a difference in capacity is useful, it is not completely necessary for a selective separations process to be practical. This is because the adsorption capacity of a given material is considered an equilibrium property. In a PSA system, gases are flowing at high rates through the beds, and the cycling between the beds can occur on short time scales. Under these nonequilibrium conditions, kinetic factors of the different chemical species begin to play a significant role in the actual separations performance of the system. The most common practical example of this difference between equilibrium and kinetic behavior is in the industrial separation of N_2 and O_2 using carbon molecular sieve (CMS) adsorbent in a PSA scheme. Evaluation of the equilibrium adsorption isotherms for these adsorbates on CMS suggests that separations would not be practical; however, it was found that the differences in kinetic behavior between these two species was sufficiently large that a separations process was economically viable, and many PSA air-separation units are now in large-scale production. On the other hand, PSA air driers function on the principle of equilibrium adsorption of water onto a zeolite molecular sieve while letting the rest of the air components pass through; kinetics play a small role in the function of PSA air driers.

In devising a new PSA gas-separations process, it is key to have a complete understanding of both the equilibrium and kinetic behavior of the gases involved. This information can then be fed into numerical simulations of the PSA scheme to predict the overall behavior and performance of the process. The simulation approach is extremely valuable and can save considerable time when designing a process and also during initial testing, as many of the variables can be optimized in the simulation first and then verified on a test bench system.

Enriching-Reflux Pressure-Swing-Adsorption (ER-PSA)

Before describing the specific process that has been studied here, it is useful to focus more on how a traditional PSA system operates. Typically, the input gas stream is compressed up to a high pressure (e.g., several atm), then passed through an adsorbent bed that retains some of the gas species while passing others to yield a “purified” product stream. A portion of this product stream is split off and used to purge a second depressurized adsorbent bed. The PSA system cycles back and forth between the two beds; in this way the high-pressure bed is always yielding a product stream while the low-pressure bed is being regenerated prior to the next cycle. The gases that are removed are usually referred to as the heavy products, typically the more-retained species, while the lesser-retained species are referred to as the light products. In a PSA air drier, for example, the light-product stream is dry air and the discarded waste stream is wet air (the heavy product being actual water vapor) coming from the low-pressure bed being regenerated by a supply of dry air split off from the product stream. It is important to note here that in a traditional PSA unit, the heavy products are not recovered for further use and are treated as waste. Therefore, if the desired outcome were to recover the water vapor from this traditional PSA air-drying system, it would be challenging because *the heavy product is rediluted and lost on every cycle of the system*.

The gas separations process that is relevant to this project is one in which xenon from the atmosphere needs to be concentrated and then passed onto a secondary unit for purification, etc. In this case, the light products are nitrogen and oxygen, while xenon is the heavy product. The overall goal is not to dilute and vent the xenon heavy product in the waste stream, but rather to continuously increase its concentration up to a high level within the system, then extract it a batch mode for further processing. This can be accomplished by recycling the xenon heavy product back into the PSA system on each cycle (rather than venting it); this process is referred to as enriching reflux (ER).

Enriching-reflux pressure-swing-adsorption (ER-PSA) has previously been demonstrated to preconcentrate trace atmospheric species by several hundred times (Yoshida et al., 2003). In ER-PSA the feed air comes into an atmospheric pressure bed and is used to strip or purge the adsorbed heavy products from the previous high-pressure adsorption cycle. The exit stream from this low-pressure bed is then directed to the inlet of an air compressor, which boosts the pressure up to 80–100 psig and feeds it into the high-pressure adsorption bed. The flow continues for a duration set by the cycle period, and then the flow is reversed; the cycle continues in this manner for however long is required. Upon each cycle, fresh atmospheric air is used to strip off the xenon from the low-pressure bed and sweep it into the compressor, where it is boosted to a higher pressure and readsorbed in the high-pressure bed. In addition to adsorbing the previously retained xenon during this phase of the cycle, an additional new amount of xenon is added to the adsorption bed from the incoming air stream (this is not adsorbed in the first bed because it is operated at a low pressure).

The notional concept behind ER-PSA is that adsorption of xenon occurs in the high-pressure bed, just as in any PSA scheme, but rather than its being vented during the subsequent purge, it is recycled back into the adjacent bed during the next cycle. In this way, the heavy product builds up within the system during each cycle and (in theory) would continue to build up until the bed reached saturation. However, the maximum concentration in the system will be limited by the dispersion of the gases, which causes them to “bleed out” or “break through” the exit of the high-pressure adsorption bed before the cycle is complete. Ideally, the xenon would stay physically isolated on the feed ends of the two adsorption beds as the system cycles back and forth and not migrate toward the exit ports, where it would be lost in the light-product stream. The mechanism that controls this migration or physical concentration profile of the gas is the dispersion of the adsorbing species within the bed. Higher dispersion causes the concentration profile to “smear” out along the length of the bed during the adsorption step. Several factors influence the dispersion of gases in adsorbent beds, including gas-flow velocity, particle size, and the diffusivity of the gas in the various pores of the adsorbent. Particle size and flow velocity are factors that can be adjusted for a given system, while diffusivity is an adsorbate/adsorbent physical relationship.

The objective of this research was to design, construct, and conduct preliminary tests of a prototype ER-PSA system to determine if xenon in air could be preconcentrated using activated charcoal at room temperature. These results are presented below and show that these early tests appear very promising and that useful quantities of xenon were recovered from both 2- and 4-hour collection intervals using PSA cycles of less than 2 minutes.

ER-PSA System Research

As mentioned earlier, a prototype ER-PSA system was designed and constructed. In order to provide for maximum flexibility, a three-bed system was built with individually controlled electronic valves. Figure 2 is a flow schematic for an ER-PSA prototype; this flow schematic is also used in the web-based graphical user interface, where all the functions of the system can be either independently controlled by an operator or set to run in an automated process mode.

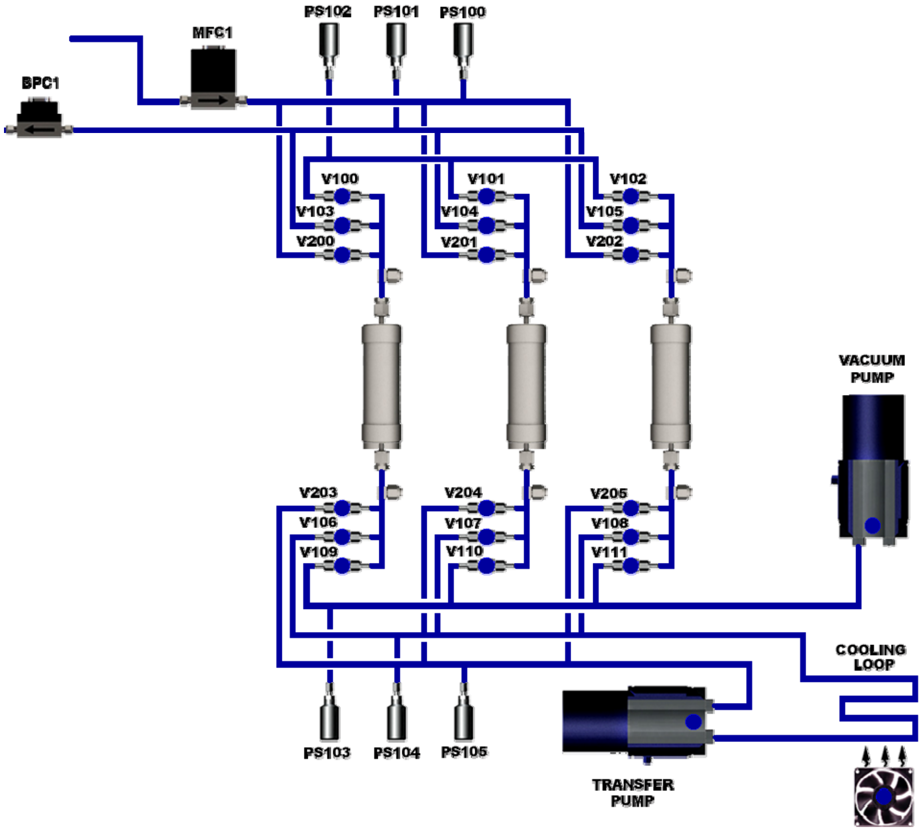

Figure 2. Flow schematic and GUI display of the ER-PSA prototype.

In the ER-PSA system, air flow enters the system through a mass flow controller and is directed through one of the low-pressure beds (filled with ~200 grams of AC). This flow is routed to the inlet of the transfer pump (compressor), where it is boosted up to 80 psig and routed into the high-pressure adsorption bed. The pressure in this bed is kept high with the use of a back-pressure regulator located at the flow exit of the system. Adsorption is cycled back and forth between two of the beds with cycles times as short as 8 seconds and as long as desired (typically less than 3 minutes). Build-up of xenon was monitored in real time by sampling the outlet of the compressor with a capillary connected to a quadrupole mass spectrometer. Initial experiments were conducted in which the cycle time and/or flow rate were varied and the build-up of product monitored. Very recently a secondary module was added to the test bench, which allows for manual batch-mode extraction of the xenon into a small-volume charcoal trap after some number of cycles have been completed (usually 2 or 4 hours). This step was added so that the samples could be concentrated further (by removing excess nitrogen and oxygen) and be analyzed on a commercial gas chromatograph (GC) for a more quantitative evaluation of the system performance. To date, samples have been extracted from the system and analyzed on a separate mass spectrometer but not yet on a calibrated GC. Figure 3 shows a recent photo of the ER-PSA test bench. The instrumentation on the right in Figure 3 is the quadrupole mass spectrometer used to measure the real-time build-up of xenon. The small tubing, traps, and manual valves on the left are part of the secondary collection portion used for quantifying the gas collected. No consideration was given to the overall size or weight of this test bench. Rather, it was designed for maximum flexibility and ease of access to all the elements; however, it can be seen that a system this simple could be easily engineered to be relatively compact.

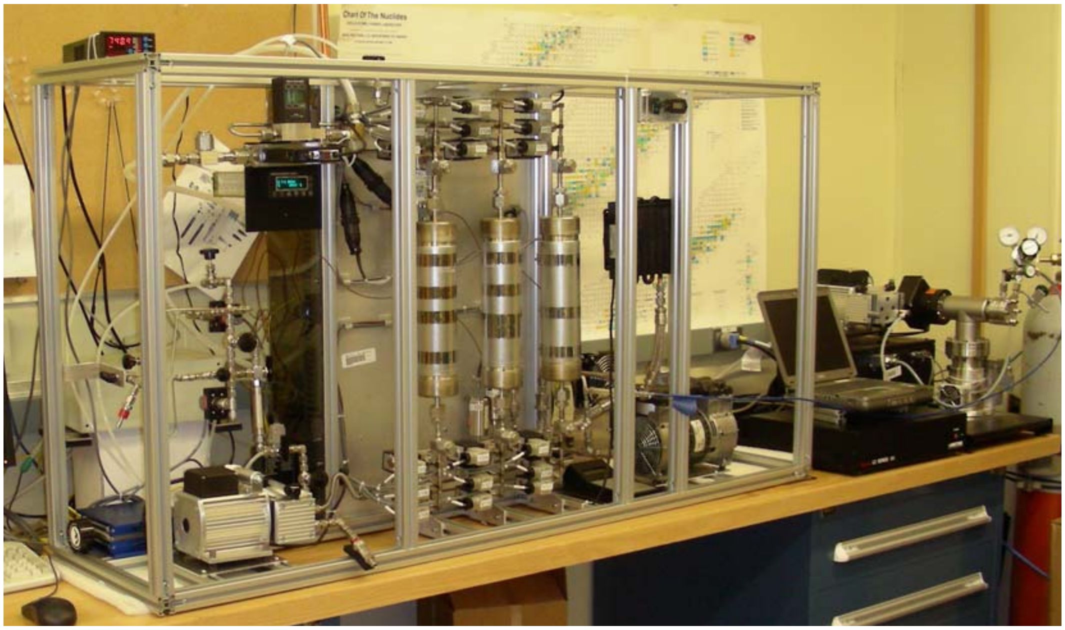

Figure 3. Photo of the ER-PSA test bench, along with the mass spectrometer and manual secondary collection module for sample quantification.

ER-PSA Results

Figure 4 shows the xenon build-up from one of the preliminary tests of the ER-PSA. In this particular comparison, the only change that was made was in the inlet flow rate. The upper black trace shows the gas-phase xenon concentration build-up under an inlet flow of 35 standard liters per minute (SLPM), while the blue trace is at half the previous flow (or 17.5 SLPM). In both experiments the cycle time was fixed at 30 seconds. The lower-flow-rate experiment was allowed to operate for twice as long so that the total amount of air that moved through the system was the same (i.e., 4.2 std. m^3 of air). If the system retained xenon with the same overall efficiency under these two conditions, it is expected that the measured xenon concentration for the lower flow rate at 240 minutes would match the xenon level from the higher flow rate at 120 minutes because both experiments would have processed the same amount of whole air. It can be seen from the data that the system was less efficient at collecting xenon at the lower flow rate than it was at the higher flow rate. The results suggest that xenon dispersion in the bed is not the likely cause of product loss, as dispersion (and breakthrough) would have occurred to a higher degree in the higher-flow-rate experiment. In addition to potential product loss from dispersion, a second source of loss in the ER-PSA system arises from the pressure equalization step that occurs just prior to switching flow between the two adsorption beds. During these first trial experiments of the ER-PSA system, the pressure equalization occurred through the feed ends of the adsorption beds. This involved gas exiting the high-pressure adsorption bed from the end near the zone of highest xenon enrichment and flowing at high rate directly into the low-pressure bed. This turns out to be a very inefficient pressure-equalization process due to the fact that the desorbing xenon from the high-pressure bed flows into the low-pressure bed and ends up being distributed throughout the entire column. Under an ideal pressure-equalization step, the enriched gas would be transferred to only the feed end of the low-pressure column prior to flow. With the product being dispersed throughout the whole column, a significant fraction is then lost (out of the vent) during the subsequent adsorption cycle. A series of experiments is planned that will explore alternative pressure-equalization schemes that minimize (or eliminate) loss due to pressure equalization prior to column switching.

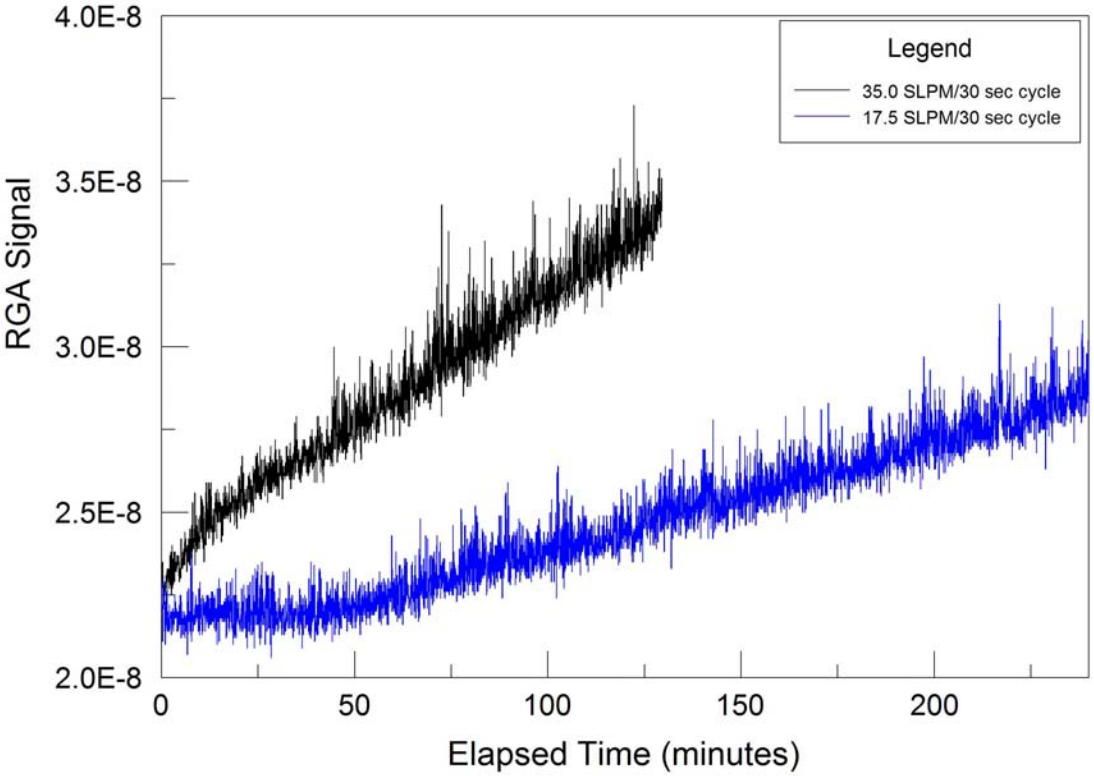

Figure 4. Build-up curves for xenon in the ER-PSA test bench under different flow-rate conditions.

As mentioned previously, a secondary module was added to the test bench, which allows the preconcentrated gases to be extracted from the ER-PSA system at the end of a collection run and transferred into a small container for further analysis. This secondary re-concentration system consists of a small-volume AC trap designed to be submerged in liquid nitrogen for complete adsorption of xenon. A small 13-X zeolite trap is installed before the AC trap to collect adsorbed CO_2 and water, which also build up in the ER-PSA system. This re-concentration module is very efficient because it reduces the total gas volume from ~ 10 std. liters of gas (in the entire ER-PSA system after collection) down to < 0.1 std. liters, while maintaining high recovery of xenon. Following this re-concentration step, the sample can be taken to a separate quadrupole mass spectrometer or gas chromatograph for analysis and comparison against a standard sample. To date the mass spectrometer approach has allowed for semi-quantitative assessment of the percent recovery of xenon in the initial trial experiments on the ER-PSA system. At the time of this writing, only a few tests runs have been completed, but all show promising results and also suggest that changes made to the running parameters do have a impact on recovery, suggesting improvements in system performance can be made with further testing. Table 1 summarizes four ER-PSA runs in the which the collected gas was analyzed using the mass spectroscopy method mentioned above.

Table 1. Summary of early test results for the ER-PSA system. Percent recovery is defined as the total volume of gas collected compared to the total possible.

Flow Rate (SLPM)	Cycle Time (sec)	Collection Duration (min)	% Xenon Recovery
35	30	120	33%
17.5	30	240	18%
17.5	15	240	18%
17.5	15	120	28%

Other experiments have been conducted with the ER-PSA system in which the flow rate and cycle time are varied and the percent recovery is measured. The results thus far suggest two likely causes of product loss during collection. In both of these scenarios, a portion of the xenon is lost out of the system exhaust vent during the adsorption cycle. The first mechanism is basic dispersion of the xenon concentration profile during the duration of the adsorption cycle. This dispersion causes the concentration profile to smear out along the adsorption bed (rather than being focused near the inlet). During the duration of the adsorption cycle, some of this xenon reaches the exit prior to the switching of the beds and is therefore lost; shortening the adsorption cycle can reduce the loss associated with this mechanism. A second loss factor that may be affecting the performance of the current ER-PSA scheme is the pressure equalization step mentioned and described earlier.

Addressing these two loss mechanisms is an important next step in improving the overall efficiency of ER-PSA for extraction of xenon from ambient whole air. Dispersion can be mitigated with modifications to the adsorption beds. The current bed design was based on the best available estimates of the kinetic behavior of xenon in AC because no experimental kinetic data are available. As the percent recovery is lower than expected, this suggests that the values used for the mass transfer coefficients (i.e., the kinetic parameters) in the simulation may have been incorrect, and the resulting dispersion in the bed is higher than expected. Methods to reduce dispersion in the bed include increasing the diameter, which causes the flow velocity to drop, and reducing the adsorbent particle size, thereby reducing the time for gases to reach the adsorption sites. Reducing particle size would have the effect of increasing the pressure drop across the column. Since the results also suggest xenon loss during the pressure-equalization step, new approaches should be investigated. Presently, several new pressure-equalization steps have been discussed that can be easily implemented on the ER-PSA test bench in the future.

CONCLUSIONS AND RECOMMENDATIONS

An ER-PSA test bench has been designed and built, and initial tests have been conducted aimed at demonstrating pre-concentration of xenon using AC (a basic adsorbent) at room temperature. Measurements have been made showing significant build-up of xenon during the collection interval. Additionally, a secondary module was added to the system, allowing for the processing of the gases after the collection duration. The module allowed for semi-quantitative analysis of the collected xenon. This analysis has shown that for this initial design the percent recovery for xenon was greater than 30%. These results show that the ER-PSA concept is capable of the original objective of room-temperature collection of xenon from ambient air. The results also point to the likely cause of product loss, that is, dispersion loss of products as they move back and forth through the beds. Several design factors can be modified now that this effect has been observed and it is expected that with a new bed design the percent recovery will increase significantly. These design modifications include beds with reduced flow velocity and smaller particle size. New pressure-equalization schemes can also be implemented aimed at reducing product loss during bed switchover.

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REFERENCE

Yoshida, M., J. A. Ritter, A. Kodama, M. Goto, and T. Hirose (2003). Enriching reflux and parallel equalization PSA process for concentrating trace components in air, *Ind. Eng. Chem. Res.* 42: 17951803.