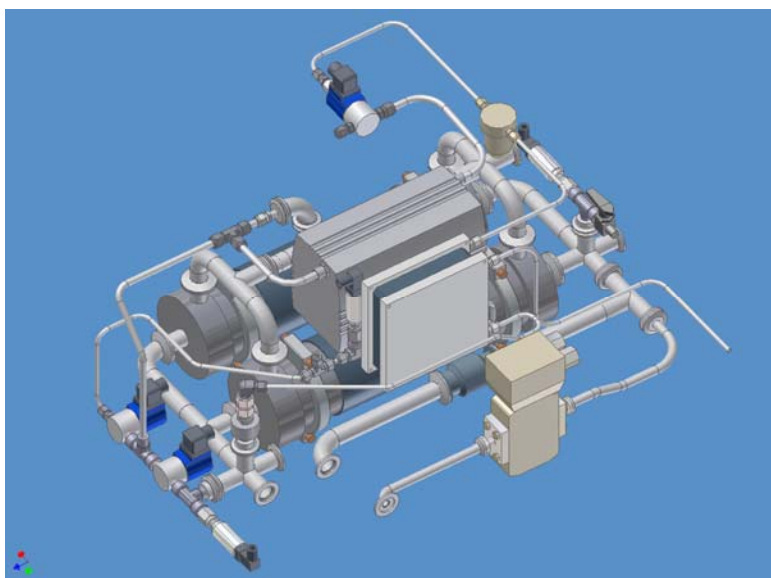




**GAMA: AMBIENT GROUNDWATER
MONITORING & ASSESSMENT PROGRAM
SPECIAL STUDY**



***California GAMA Program: Development of a Field
Deployable Dissolved Gas Extraction Apparatus***



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EXECUTIVE SUMMARY

The State Water Board has developed a comprehensive ambient groundwater quality monitoring plan to address concerns by Californians about groundwater quality. The main objectives of the Groundwater Ambient Monitoring Assessment (GAMA) Program are to improve statewide ambient groundwater quality monitoring and assessment and to increase the availability of information about groundwater quality to the public. Participation in the GAMA Program is voluntary. The GAMA program funds Special Studies to address specific issues that affect groundwater quality, including nitrate contamination, groundwater recharge, and development of innovative monitoring techniques.

The analysis of dissolved gases in groundwater provides valuable information for investigations of groundwater flow, contaminant transport, and augmented and natural bioremediation. Current methods for the extraction of dissolved gases from groundwater are unsatisfactory for extracting gases from large volumes of groundwater and severely limit the use of krypton-85 (half-life = 10.76 years) for dating young groundwater. The objective of this study was to improve upon and expand applications of dissolved gas measurements in water quality assessments.

To address the need for a system capable of extracting gas from large volumes of groundwater, a field deployable gas extraction system (GES) was built and tested for collecting dissolved gas from groundwater during sampling. The system consists of commercially available components. The primary components are two gas permeable membrane cartridges and a small compressor/vacuum pump. These are combined with plumbing, valves, flow monitoring and control, and manifold for collection of sample bottles. This system could potentially replace the current methods for collecting water samples for dissolved gas analysis, which rely on collecting water in soft copper tubing using pinch clamps to seal the sample. Extensive duplicate sample analyses indicate that difficulties persist with gas loss during sampling and occasionally with the formation of bubbles during this current method of sample collection.

The new gas extraction system offers several benefits over existing techniques.

- Removing all gas, both dissolved and exsolved, during sampling, will improve sample quality.
- Larger quantities of water will be degassed providing less opportunity for introduced heterogeneity during collection of small samples (currently 10 ml), and allowing analysis of samples for rare radionuclides such as ^{85}Kr and ^{39}Ar .
- Field extraction will facilitate the measurement of dissolved oxygen and nitrogen. The current copper tube sampling method does not preserve oxygen.
- By extracting the gas in the field and storing it in stainless steel bottles, all of the non-inert gases will be stable for long periods. Sample preparation for all dissolved gas analyses will be greatly reduced, and sample throughput will be greatly enhanced.

This system is necessary for developing the use of ^{85}Kr for dating young groundwater, which requires the extraction of dissolved gas from a large volume of groundwater (>50 gallons) to provide a suitable sample for analysis. Tests carried out using the GES on air-equilibrated water and groundwater indicate that the extraction efficiency is >90%, and that the ratios of gases (e.g. N_2/Ar) are preserved during extraction from groundwater.

INTRODUCTION

The elemental and isotopic composition of gases dissolved in groundwater reveals unique information about groundwater transport and biogeochemical history, and about conditions under which recharge took place. Several key components of both the GAMA statewide assessments and GAMA special studies rely on measurements of dissolved gases in groundwater. The objective of this study was to improve upon and expand applications of dissolved gas measurements in water quality assessments through development of a field deployable apparatus for extraction and collection of dissolved gases from groundwater.

Applications that rely on knowledge of dissolved gas elemental composition include *in situ* dehalogenation and bioremediation schemes that use atmospheric gas, hydrogen, or oxygen (MCNAB et al., 2000; ROGGY et al., 2002; SALANITRO et al., 2000), determination of saturated zone denitrification using excess dissolved nitrogen (BOHLKE and DENVER, 1995; SINGLETON et al., 2007), and paleotemperature determination using dissolved noble gas concentrations (AESCHBACH-HERTIG et al., 2002; CLARK et al., 1997; STUTE et al., 1995; STUTE et al., 1992). In addition, several of the most widely applied isotopes for groundwater age dating, such as ^3He (in the tritium- ^3He method) and ^{85}Kr , occur as dissolved gases. Groundwater age is used to determine subsurface residence time and flow rate (CLARK et al., 2004; EKWURZEL et al., 1994; POREDA et al., 1988; SCHLOSSER et al., 1988; SOLOMON et al., 1992), assess contamination vulnerability (MANNING and THIROU, 2005; MORAN et al., 2002; MORAN et al., 2004a; MORAN et al., 2004b), and calibrate or validate groundwater flow models (TOMPSON et al., 1999; WEISSMANN et al., 2002).

Advanced methods for analyzing dissolved gas composition include a step during which gas is extracted from a water sample under vacuum. Samples may be collected in vials without head space or in crimped copper tubes, so that they are not exposed to the atmosphere and gases are not allowed to volatilize during sampling. In the case of noble gas mass spectrometry, which is used for both tritium- ^3He groundwater age dating and determination of groundwater recharge temperature, samples collected in crimped copper tubes are mounted on a gas handling manifold under vacuum, water is frozen out using frozen CO_2 , and the gas is released into an evacuated headspace. This method of sampling and gas extraction has the advantage of being reasonably simple, but suffers from relatively poor reproducibility. For dating techniques that use a very low abundance isotope, such as ^{85}Kr , ^{81}Kr , or ^{39}Ar , gas must be extracted from a very large volume of water, from 200 L for ^{85}Kr up to 16,000 L for ^{39}Ar . Dissolved gas sampling for these large volumes has been accomplished by cumbersome, low-efficiency, flow-through vacuum extraction in the field (EKWURZEL et al., 1994). The long time period and large sample vessels required have severely limited the application of low abundance isotope dating methods. More recently, a gas extraction system using a hydrophobic semi-permeable membrane contactor has been reported (PROBST et al., 2006).

The gas extraction system described here was designed to replace the current sampling techniques for dissolved gas samples. LLNL's current sampling techniques for dissolved gas samples use copper tubes or volatile organic analysis (VOA) vials, and only allow extraction of

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gas from small volumes (10-40 mL) of water. The following are the key characteristics of the gas extraction unit developed at LLNL:

- Field deployable; uses 120V power from generator or a truck
- Compact; can be transported easily in a pickup truck
- Easy to use
- Collects large volume samples (e.g. Kr isotopes) in less than 3 hours
- Collects small volume samples (e.g. isotopes of N₂, O₂, and Ar) in less than 30 minutes
- Very high efficiency (>92% total gas extraction) for low water flow rate (< 2 gpm)
- High efficiency (65% to 90% total gas extraction) for high water flow rate (5 to 15 gpm)
- Gas sample is collected in a small, pressurized vessel meeting U.S. Department of Transportation (DOT) requirements, and easily shipped to a laboratory
- Produces no wastewater requiring disposal

KEY SYSTEM COMPONENTS

A three dimensional drawing of the apparatus in its present configuration is shown in **Figure 1**. An engineering drawing, showing the routes of water and gas flow, is shown in **Figure 2**. Essential components of the system are described here.

Contactor

Several technologies were qualitatively considered for the extraction of dissolved gases, including gas stripping, liquid atomization, and membrane extraction. Of these, a membrane based technology was chosen because it is the most compact and most easily packaged into a field deployable unit, and because of its reasonably high (> ~ 85%) designed removal efficiencies. This technology is based on the mass transfer of gases between the liquid and gas phases through a multitude of fiber membranes, which are housed in larger (e.g. 4" diameter) vessel. Based on manufacturer specifications and calculations of diffusion and solubility for various gas components, a 'contactor' (gas permeable membrane cartridge unit) was identified from Membrana™. The X-40 model that was chosen is rated for water flow rates of 5 to 15 gallons per minute. Known applications of membrane contactor technology include degassing of boiler feed water, which reduces corrosion by removing oxygen, and infusing water with gases, such as carbonation of water for the beverage industry. In the present application, groundwater flows through the Membrana™ contactor, and a vacuum is applied to the internal, or "lumens", side of the membranes. Dissolved gases are drawn out of the water, across the membranes, and ultimately collected in a pressurized vessel that can be shipped to a laboratory for analysis.

Pumps

Significant effort was focused on selection of pumps for the vapor treatment portion of the gas extraction apparatus. One pumping requirement is a relatively high vacuum for efficient operation of the membrane contactors. For applications requiring extraction from a large water volume, there is a need to pressurize the extracted gases for downstream enrichment of noble gases (as described below), and allow the possibility of delivering a final gas sample in a pressurized vessel. A Welch swing piston (WOB-L) pump was identified, which met both requirements, but was found to draw atmospheric air into the sample during testing. This is unacceptable, because the isotopic signature of the extracted gases would be altered in the final sample. A seal-less, pressure equalized diaphragm pump was then identified which met the vacuum specification, which does not introduce atmospheric air into the sample because of its seal-less design. However, a second, smaller pump is required downstream of the vacuum pump in order to pressurize the extracted gases. To insure that both pumps can work together in this configuration, one manufacturer (KNF Neuberger) was selected for both pumps. Specifications provided to the manufacturer required the vacuum and pressure pumps be connected in series and still meet a minimum vacuum of 29.5 in Hg and generate final gas samples at pressures up to 150 psig.

Flow Meters

In order to monitor the flow of gas from the membranes, a sensitive, high-precision, gas mass flow meter (Sierra Instruments Inc) was installed on the gas side of the gas extraction test unit. Two separate flow meters for measuring water flows were selected: a low-flow meter (Endress Hasuer) for flows of less than 2 gpm, and a high-flow meter (Flow Technologies, Inc.) for flows of 2 to 20 gpm. A turbine type flow meter (Omega) was used to monitor the gas condenser cooling water.

Gas Treatment

A method of removing water vapor from the effluent gas is required both for sample integrity and in order to prolong equipment lifespan. An in-line condenser (TECA Corporation), based on Peltier technology, was installed immediately downstream of the pumps, to remove the bulk of the water from the vapor stream. This device relies on a pressurized inlet stream to remove water vapor, and does not require additional power. A coalescent filter is in place upstream of the Peltier cooler, and provides the initial, bulk water removal from the gas stream.

Electronic Interface

A Programmable Logic Controller (PLC) from Automation Direct was selected, which has data display and data logging capabilities (**Figure 5**).

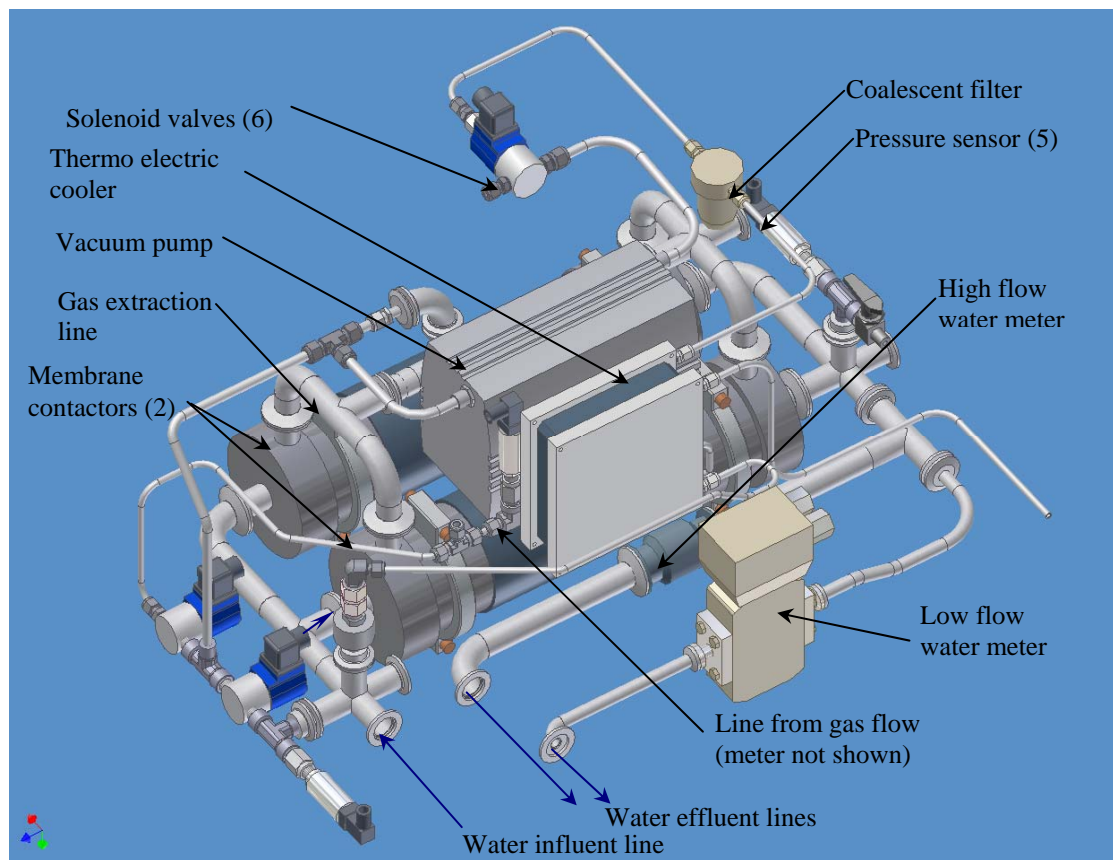


Figure 1. LLNL Gas Extraction System with key components labeled.

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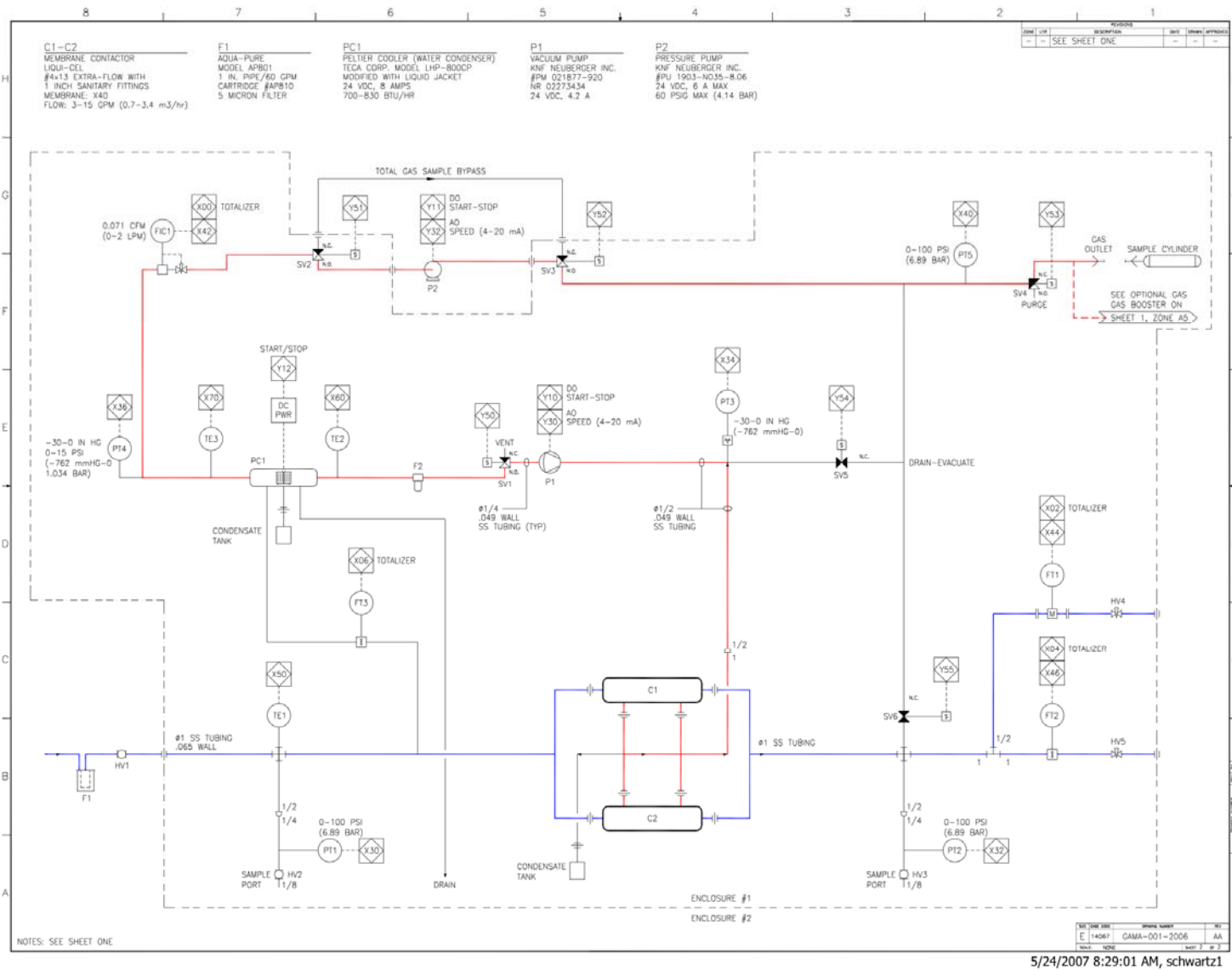


Figure 2. Engineering drawing of LLNL Gas Extraction System. Water flow line shown in blue; vacuum lines in black and final gas sample flow in red.

TESTING – BENCH SCALE APPARATUS

The three major technical challenges in designing and building the gas extraction system are achieving very high removal efficiencies of dissolved gases; packaging the final gas sample in a vessel that can be conveniently shipped to a laboratory for analysis; and making the device compact enough to be easily used in the field. A bench scale test stand was designed and assembled in order to determine the efficiency of the membranes at different water flow rates.

A photograph of the test apparatus is shown in **Figure 3**. The configuration allows the contactors to be tested in both series and parallel arrangements with respect to influent water. The parallel arrangement was expected to give the greatest gas removal efficiency, because it increases the residence time of the water inside the contactors.

Dissolved gases are drawn from the water by applying vacuum to the lumens side of the membrane fibers within the contactors, as indicated by the green lines on **Figure 2**. A diaphragm type vacuum pump was used for the test stand, in order to minimize introduction of atmospheric air into the vapor sample. Additional piping and valves (not shown) allowed the vacuum pump to evacuate the entire apparatus, which minimized carry over of atmospheric air, and hastened the drying of the contactors between uses. A cold trap immediately before the pump minimized the impact of water vapor on the pump, and reduced the amount of water vapor in the final gas sample.

Groundwater gases extracted by the vacuum pump (red line, **Figure 2**) were collected by sending the vacuum pump discharge directly to an evacuated sample bottle or Tedlar® bag.

As shown in **Figure 4**, the gas extraction test apparatus removes all of the major gases with an efficiency of nearly 100% after about 10 minutes of operation (the lag in the Horiba dissolved oxygen reading is likely due to the time required for equilibration of the dissolved oxygen (DO) sensor). Of the variables examined, vacuum pressure had the greatest effect. Lower efficiencies (down to 80%) were observed at higher water flow rates (10 gpm), but there was little difference in extraction efficiency for flow rates below about 5 gpm. Results were nearly identical for single pass versus double pass runs. At vacuum pressures less than about 28 in. Hg, removal efficiencies were less than 90% even for low flow rates.

A series of tests were performed to examine the efficiency of the contactors at different flow rates. The test system was operated at a variety of low rates. For each flow rate, a copper tube sample, a volatile organic analysis (VOA) vial sample for water analysis, and an extracted gas sample were collected. Results from MIMS analysis of the gas samples are shown in **Table 1**. Results from noble gas mass spectrometry analysis of the gas-stripped effluent water samples are shown in **Figure 6**, in order to determine the extent to which noble gases are extracted at different flow rates. In general, the heaviest gases are most sensitive to flow rate, and the lowest flow rates achieve the most efficient extraction of all gases.

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Table 1 Efficiency percentages for 1 and 2 contactors (in parallel) for different water flow rates. Measurement uncertainty is approximately 2 %.

Test	N ₂ Extraction
1GPM/1 Contactor	92%
2.5GPM/1 Contactor	87%
2.5GPM/2 Contactors	92%
1GPM/2 Contactors	89%

Table 2. Composition of gas extracted from water by the GES (“gas”) determined using membrane-inlet mass spectrometry (MIMS). Dissolved gas in groundwater (“water”) was also determined in VOA vial samples using the same analytical method. Samples were collected during the July 1, 2008 test.

Gas concentration	Gas N ₂ (atm)	Gas O ₂ (atm)	Gas Ar (atm)	Gas N ₂ /Ar	Water N ₂ /Ar	N ₂ /Ar (% difference)
Room air	0.77	0.21	0.009	83.51		
0.2GPM_AEW_gas	0.63	0.51	0.015	41.93	40.52	-3.47%
0.4GPM_AEW_gas	0.62	0.45	0.015	40.86	40.49	-0.90%
0.2GPM_TFD_gas	0.56	0.21	0.012	45.38	46.23	1.86%
0.4GPM_TFD_gas	0.55	0.23	0.013	42.75	44.28	3.45%



Figure 3. Gas Extraction test apparatus at LLNL. Membrane contactors are housed in white vertical cylinders; diaphragm pump sits on the floor.

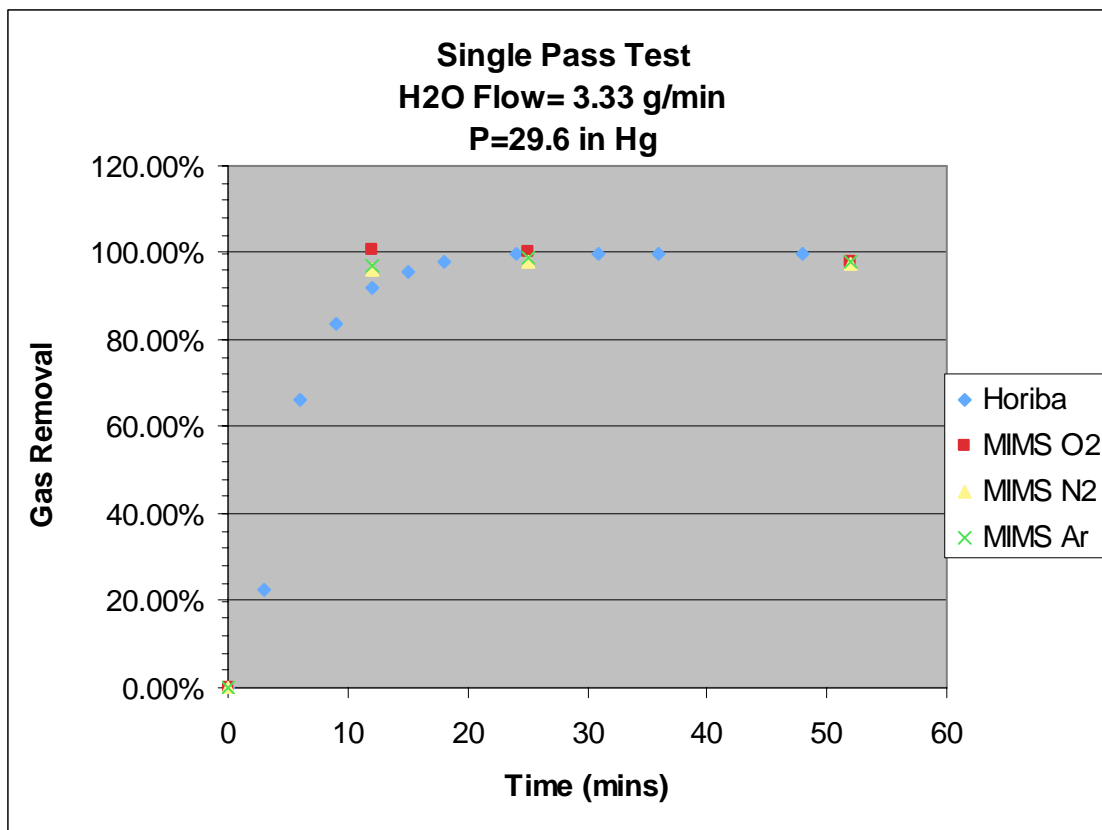


Figure 4. MIMS and dissolved O₂ (Horiba) results of bench-scale test of gas extraction apparatus.

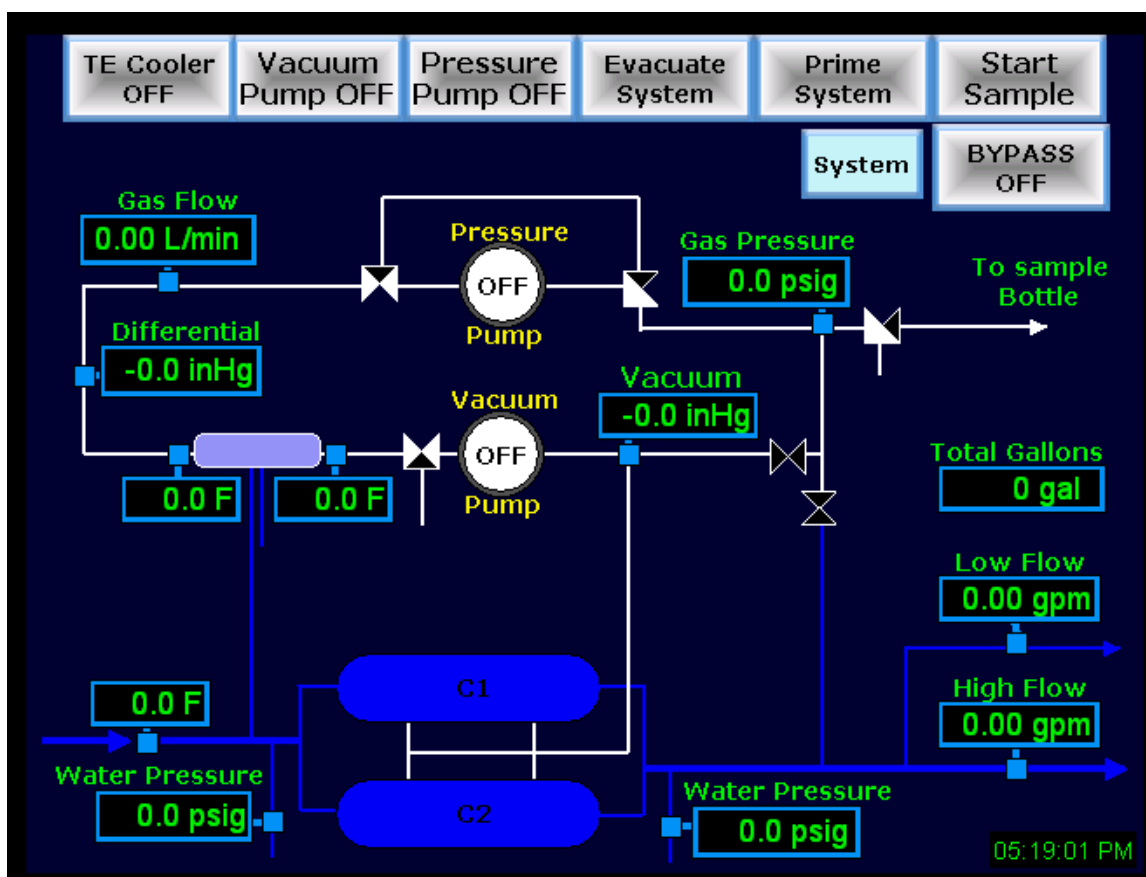


Figure 5. Screen capture of Programmable Logic Controller user interface in sample collection mode.

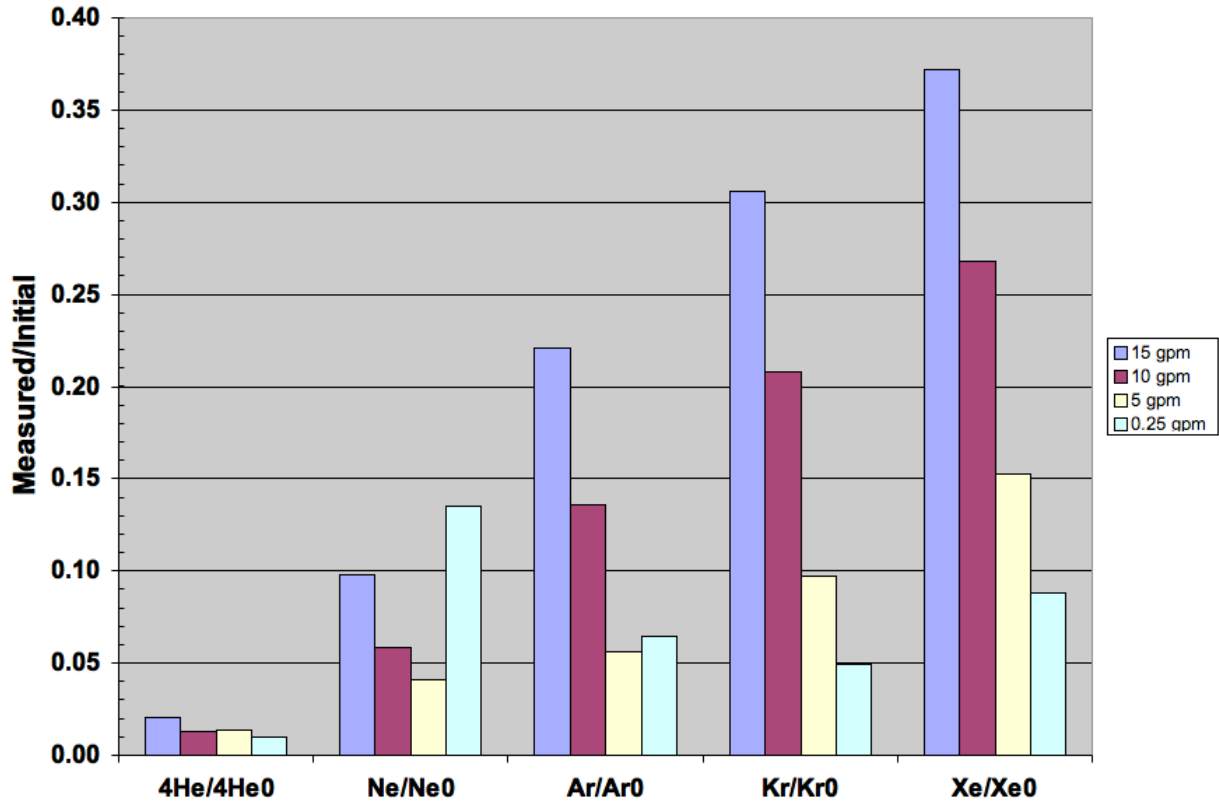


Figure 6. Results of analysis of GES effluent water samples from which gases have been extracted by the GES. The concentrations of gases measured in the gas-stripped effluent waters at different flow rates are normalized to their concentrations in the influent water. Analyses were performed by noble gas mass spectrometry using copper tube samples. Influent water was an untreated groundwater from Treatment Facility D on the LLNL main site.

TESTING –FIELD APPARATUS

Air Equilibrated Water and Treatment Facility D Well

On July 1, 2008 the completed field apparatus (**Figure 7**) was tested with air equilibrated water (AEW), and groundwater from the LLNL Test Facility D well (TFD). Samples were collected from pumped influent water and extracted gas while running the GES at 0.2 and 0.4 GPM. These samples were then analyzed on the MIMS in order to determine whether the system is leak tight, and if there is any evidence for gas fractionation during the extraction process. The ratio of N₂ to Ar gas is an indicator of both of these conditions. Furthermore, it is important that the N₂/Ar value of the extracted gas represents the dissolved gases present in water since this value is used to determine the presence of excess N₂ from denitrification. Under successful operation, the N₂/Ar of the extracted gases should match that of the influent water. As shown in **Table 2**, the N₂/Ar for the extracted gases are within 3% of the influent water. Given measurement uncertainty (approx. 5%) in the MIMS analyses, the extracted gases match the dissolved gases in the influent water. There does not appear to be a major difference between 0.2 and 0.4 GPM in the MIMS data. This test also confirms that the system is leak tight. Any air entering the system would have resulted in elevated N₂/Ar ratios in the extracted gas.

Figure 8 shows the relation of noble gas concentrations and isotopic ratios between the influent waters and the gases extracted using the GES. Ideally, the concentration and isotopic ratios for extracted gases should be the same as the influent water. However, some gases may be transported across the membrane more readily than others, which will result in differences in the observed ratios. In most cases, it is expected that the lighter gas such as He will be transported more rapidly across the membrane than heavier gases such as Xe. For this reason, each of the gases is normalized to Xe, the heaviest noble gas that was measured. **Figure 8a** shows that in a test conducted on July 1, 2008, the largest difference between gas and water is observed in the He/Xe ratios, and progressively smaller differences are observed for Ne/Xe, Ar/Xe, and Kr/Xe. Such a pattern is consistent with gas transport across the membrane controlling fractionation during extraction of gases by the GES. The gases for the 0.2 GPM groundwater from Treatment Facility D (TFD) were slightly more fractionated than the air-equilibrated water (AEW) at the same flow rate. This difference may be related to the higher dissolved gas load present in the TFD water, which could result in slightly lower extraction efficiencies.

Figure 8b plots ³He/⁴He atom ratio for both influent water and extracted gas. The TFD gas helium atom ratio is within measurement error of the TFD influent water at the only flow rate where both gas and water were measured (0.2 GPM), and the AEW gas helium isotope atom ratio is within 1.5% of influent water for both flow rates measured (0.2 and 0.4 GPM). For TFD, the helium isotopic composition of water collected at 0.2 GPM is distinctly different than water collected at 0.4 GPM. Elemental gas compositions in the two water samples also differ, as observed in both copper tube samples (analyzed by noble gas mass spectrometry) and VOA vial samples (analyzed by membrane-inlet mass spectrometry) (**Table 2**). The reason for this difference is not known – TFD is a gas-rich groundwater that may be heterogeneous or affected by variable gas loss during groundwater pumping and processing at the facility. For AEW, two different copper-tube samples collected at a flow rate of 0.2 GPM on July 1, 2008, have distinctly different ³H/³He isotopic compositions. Elemental gas compositions also differ with

lighter gases enriched in the sample with the higher $^3\text{He}/^4\text{He}$ ratio. During the nearly 3-hour test, AEW water temperature rose from 22.2 to 24.4 °C. Re-equilibration of AEW with atmospheric gases over the course of the 2.2-degree temperature rise may be responsible for some of the compositional and isotopic difference between the two AEW water samples

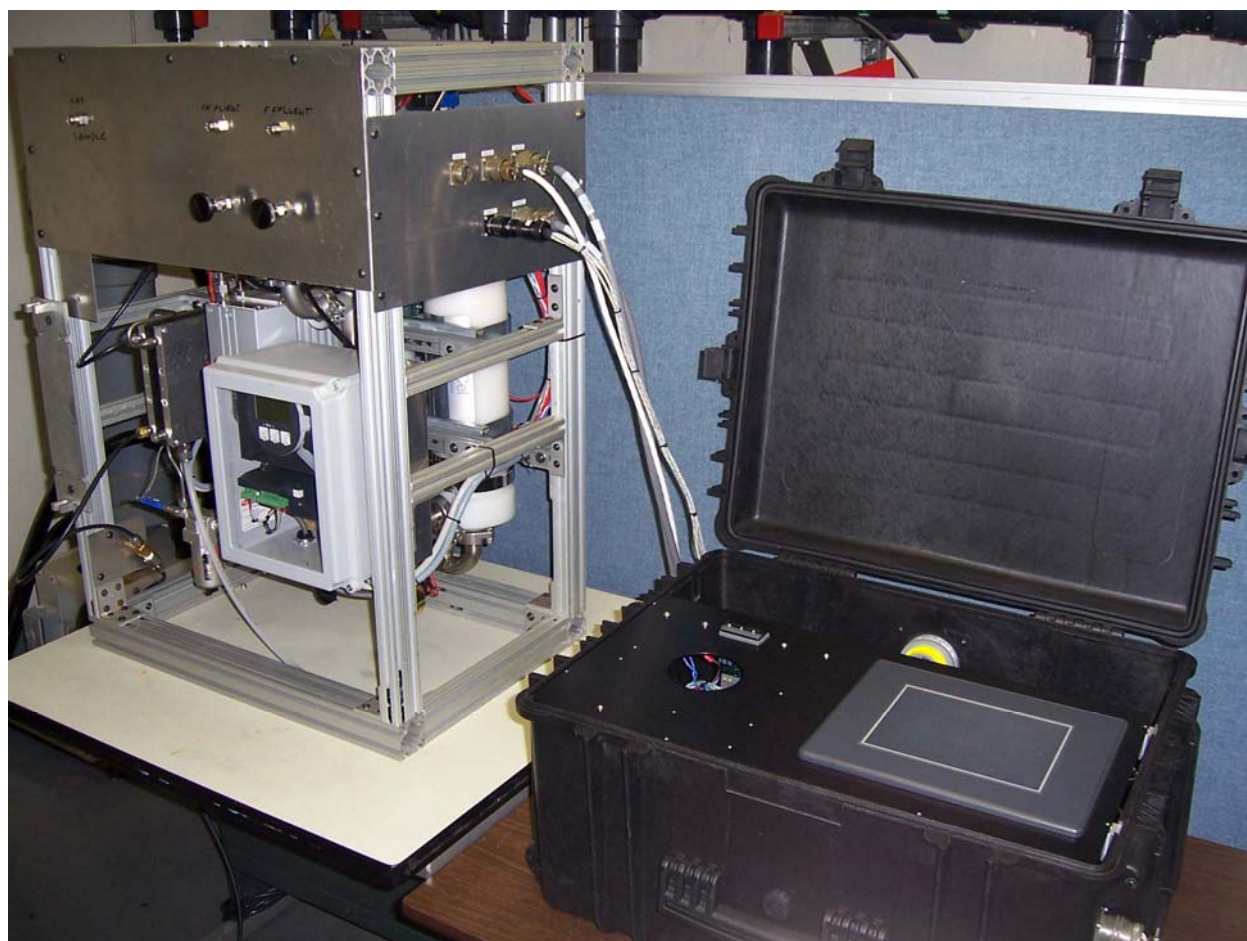


Figure 7. Photograph of LLNL field deployable Gas Extraction System.

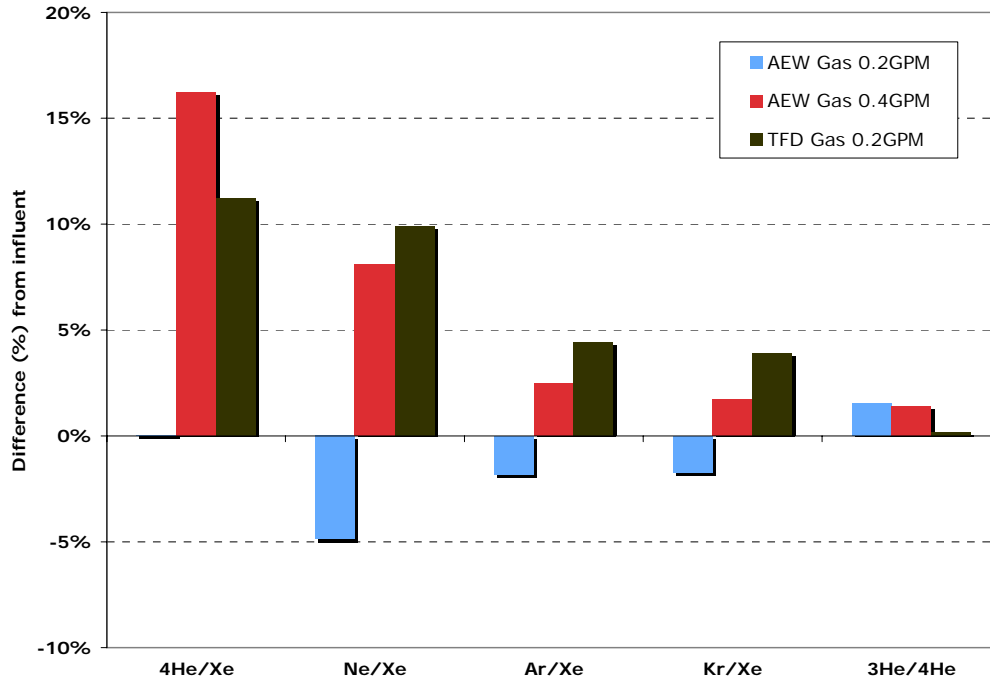


Figure 8a. Comparison of noble gas concentration ratios between dissolved gas measured in influent water using the current copper-tube approach and dissolved gas measured in gas extracted using the GES, shown as the fractional difference between the gas and water sample. Results are shown for different flow rates, measured in gallons per minute (GPM), for air-equilibrated water (AEW) and Treatment Facility D groundwater (TFD) in a test conducted on July 1, 2008. A sample was collected for the TFD water at 0.4 GPM, but was impacted by gas loss during the collection process. Plotted data for the 0.2-GPM AEW test use the average of two water samples.

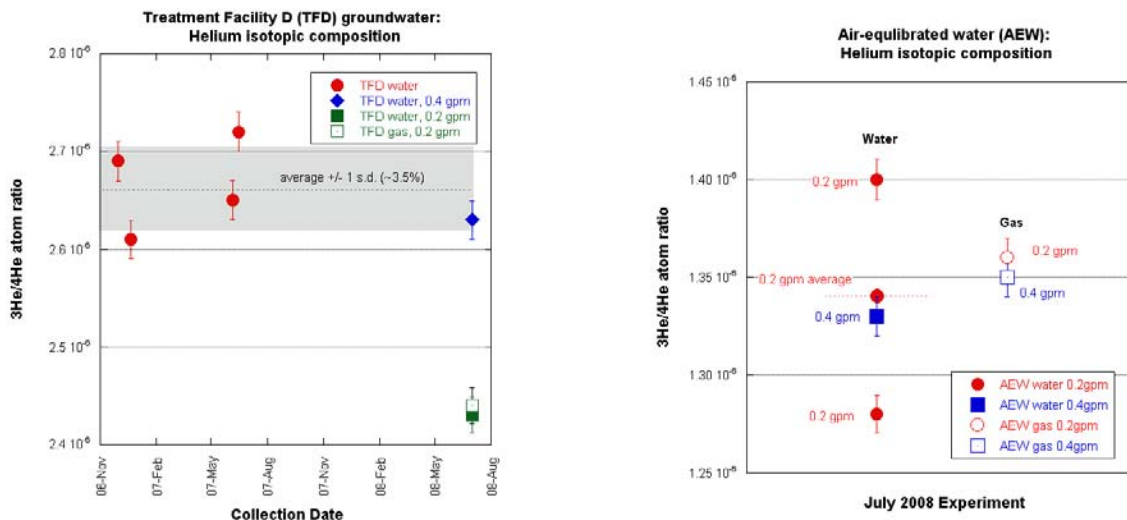


Figure 8b. Helium isotopic composition ($^3\text{He}/^4\text{He}$) in influent water (copper tube samples, solid symbols) and in extracted gas (GES gas samples, open symbols).

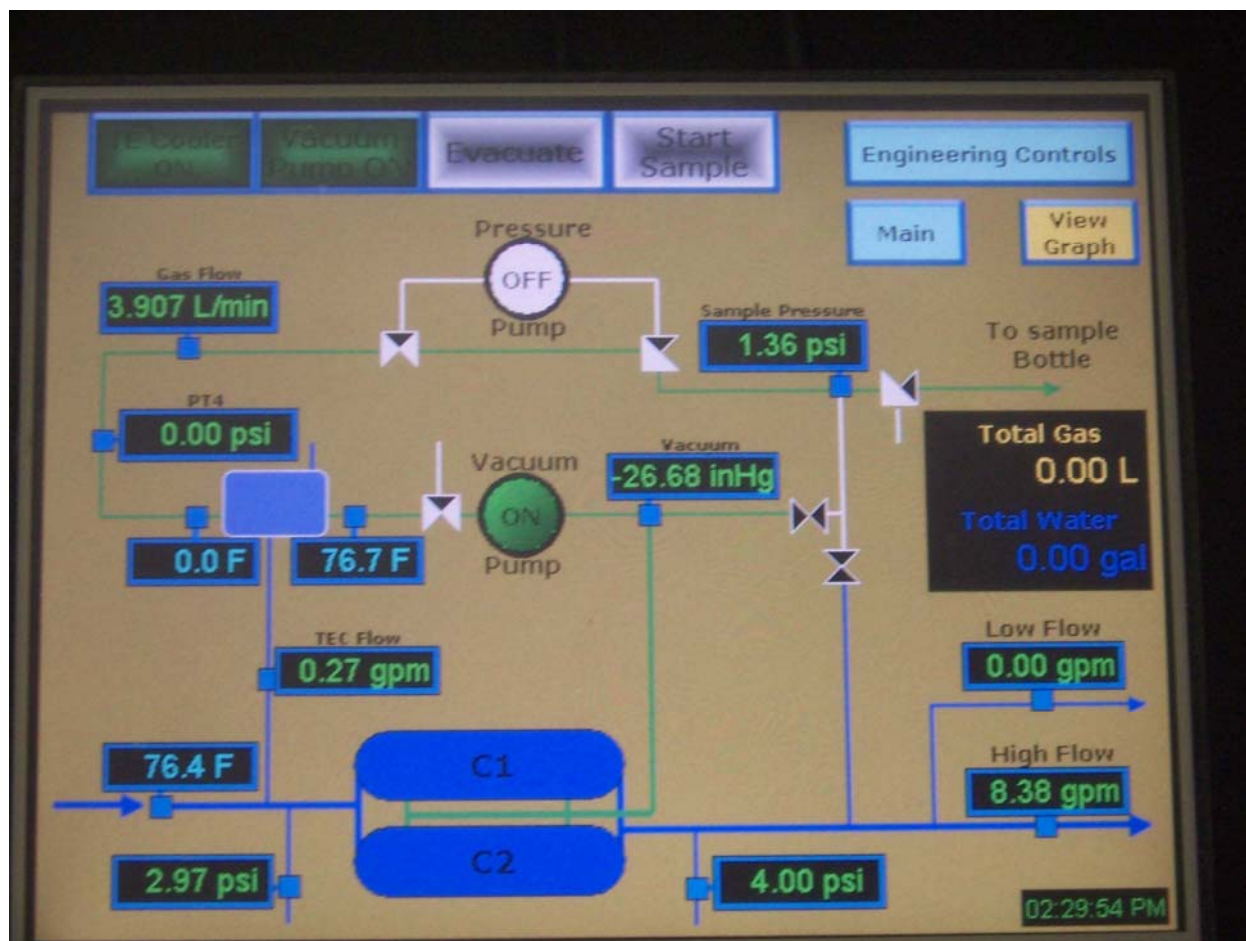


Figure 9. Screen capture of PID during operation of the Gas Extraction System (high flow mode).

GAS EXTRACTION SYSTEM OPERATION

The order of operations is as follows:

1. The Thermoelectric Cooler (TE Cooler) is turned on first to allow for adequate cool down time.
2. The Vacuum Pump along with the Pressure Pump are turned on in order to evacuate the system. They have separate controls to take into account operations without the pressure pump.
3. The Evacuate System press button opens the two 2-way solenoid valves that separate the gas and water lines along with the 3-way solenoid valve located after the vacuum pump. This process evacuates any left over media located in the gas and water lines from previous operations and ensures a clean sample.
4. The Prime System press button closes the evacuation 2-way solenoid valves along with the 3-way solenoid valve located after the vacuum pump. It is pressed after the system has been adequately evacuated. The system is now ready for the introduction of water. This process primes the system by filling the lines with sample only gas produced from the newly introduced water.
5. The Start Sample press button opens the 3-way solenoid valve that leads to the sample bottle. This action starts the total gallons sampled totalizer, the total gas produced totalizer and a timer that keeps track of how long the process is in operation.
6. The process will end automatically when the sample pressure reaches 10 psi, or by manual sample shutdown.

In addition, a cleaning method was developed and tested for preventing biological and mineral fouling of the membrane contactors. The method consists of recirculating a 100 ppm bleach solution (for elimination of biofouling) and a 3% citric acid solution (for elimination of mineral fouling), separated in between by a rinse with tap water. Although no particular problems with fouling (as might be indicated by a decrease in removal efficiency or flow rate) have been observed to date, experience with similar membranes indicates that prevention of fouling is very important for long term performance of the contactors. When not in use the contactors should be stored in tap water.

FUTURE WORK – REMOVAL OF MAJOR GAS COMPONENTS

The testing described in this report focused on the extraction and collection from groundwater of the major gases, including oxygen, nitrogen, and argon, as well as the trace gases, such as helium, neon, krypton, and xenon. To obtain a sample of very low abundance gases, such as Kr, the vapor stream will need to be passed through an additional scrubbing step to remove N₂, O₂, and CO₂, before being pressurized and captured in a sample bottle. The specific types of scrubbers have not been identified at this time, and are represented simply as “Gas Removal” in **Figure 2**.

A number of separation technologies (including zeolites, membranes, cryogenics, gas chromatography and gas-metal reactions) have potential to provide efficient scrubbing of major gases. Within the past year, researchers at the University of Illinois at Chicago have reported on their development of a system for extraction of ⁸⁵Kr from gas samples (YOKOCHI et al., 2007). The system is lab-based, and consists of cryogenic distillation, gas chromatographic separation and a titanium getter, allowing separation of pure Kr with high yield (>90%) from a large range of bulk gas quantities (5- 125 liter STP) over a period of 4-6 hours. The system includes an in-line gas composition monitoring capability using a quadrupole mass spectrometer

To manufacture a field-deployable system, zeolites and membranes are more practical than cryogenics and Ti-gettering. Various zeolites, activated carbons, and membranes have been used to separate major and some rare gases from air and various process streams. Bulk separation of oxygen and argon from air with zeolites 5A and 13X is a well developed technology, and is the basis for oxygen purifiers for medical applications. Zeolite and carbon based methods for separating nitrogen from krypton at comparable concentrations have been proposed and patented, but do not address separation of krypton from bulk air. Stern and Leone (1980) describe the use of silicone capillaries to separate krypton and xenon from air, for application in the nuclear power industry.

A field-deployable krypton enrichment train can be constructed using simple gas drying columns (Alltech) and zeolites, or using gas drying columns and silicone capillaries. One requirement of both approaches is sufficient pressure to drive the separation process. An additional pump to pressurize effluent gas from the GES would be simple to implement.

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