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Paper for Tritium 2004

PERFORMANCE IMPROVEMENTS OF A TRITIATED WATER RECOVERY SYSTEM

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Tritium processing equipment is installed inside gloveboxes. Leaks of tritium are captured by a tritium stripping system using an oxidation-absorption process. Tritium is captured as tritiated water in zeolite beds and is recovered by desorption and reduction. The regenerated zeolite beds are reused. Reduction of the tritiated water is accomplished by a zeolite bed recovery system using hot magnesium beds. The system has been in operation for about 10 years and met original design requirements. Recent expansion of the facility requires a higher capacity of the system. Operation data are collected and analyzed. Ways to increase the system capacity are discussed.

I. INTRODUCTION

The tritium facility at Savannah River Site (SRS) of USA processes kilogram quantity of tritium every year. The operation includes hydrogen isotope purification that purifies hydrogen isotopes from other gases, and hydrogen isotope separation that produces high purity tritium, deuterium and protium. In order to minimize tritium release to the environment all process equipment handling tritium is enclosed inside nitrogen filled gloveboxes. Any normal and accidental tritium release in the gloveboxes is removed by a stripper system. The system oxidizes and captures the tritium in zeolite beds. A general description and performance of this glovebox-stripper system is available from Reference 1. The captured tritiated water is reduced and the elemental tritium recovered. Reduction of the tritiated water is accomplished by a zeolite bed recovery system using hot magnesium beds. Continuing modernization of the facility has placed more equipment inside gloveboxes. This increases the number of gloveboxes and the amount of tritiated water to be reduced. The existing zeolite bed recovery system (water reduction system) was originally designed to recover 6.7K mole/year is now required to handle 10.7K mole/year. The system was originally designed to operate in a cycling mode. It has recently been modified to permit operation in a steady mode. This paper discusses the performance of the system operated in both cycling mode and steady mode, and explains how the system capacity may be increased.

II. TRITIATED WATER CAPTURED IN THE GLOVEBOX STRIPPER SYSTEM

The SRS tritium facility uses 30 nitrogen gloveboxes, total volume about 1,000 m^3. Two primary stripper systems support the normal tritium removal from the nitrogen atmosphere. Each primary system circulates the glovebox nitrogen at 170 m^3/hr to strip the tritium from the glovebox nitrogen. A third identical system named the secondary stripper handles accidental tritium release in any of the gloveboxes. Each of these three systems has 3 zeolite beds. Each of these beds holds 104 kg of zeolite type 3A, and can absorb up to 870 moles (15 wt%) of water at equilibrium with 200 ppm water vapor pressure. A fourth stripper system named the purge stripper, that controls the purge of nitrogen from the gloveboxes to the atmosphere, has 3 smaller zeolite beds. Each of these smaller beds holds 27 kg of zeolite type 4A. Each of these 12 zeolite beds, when saturated with water, is regenerated and reused. The total amount of captured tritiated water has been about 6.7K moles per year when 30 gloveboxes are in service. The amount is expected to increase to about 10.7K when the newly added gloveboxes increased the total number to 33. A general arrangement of this glovebox stripper system is shown in Figure 1. The average amounts of water and tritium captured in the glovebox-stripper system is illustrated in Figure 2.

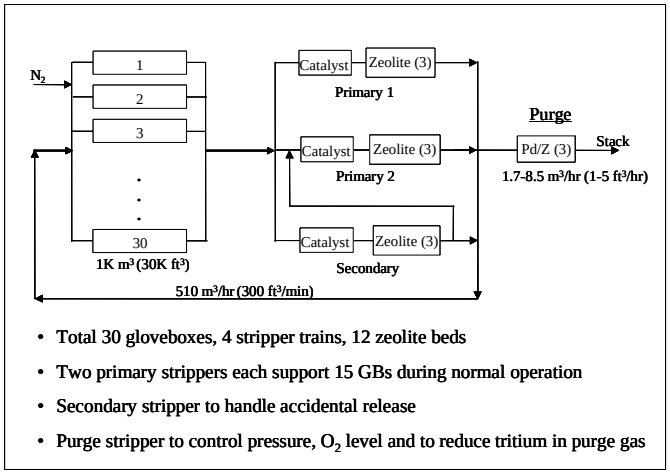

Figure 1. Glovebox-stripper system.

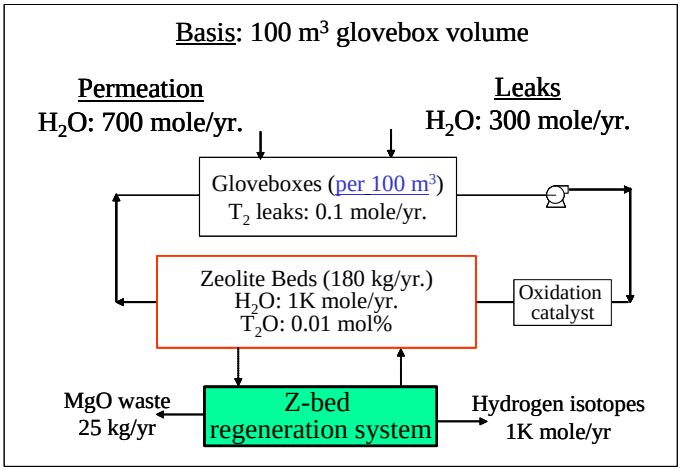

Figure 2. Hydrogen source and recovery of the zeolite beds.

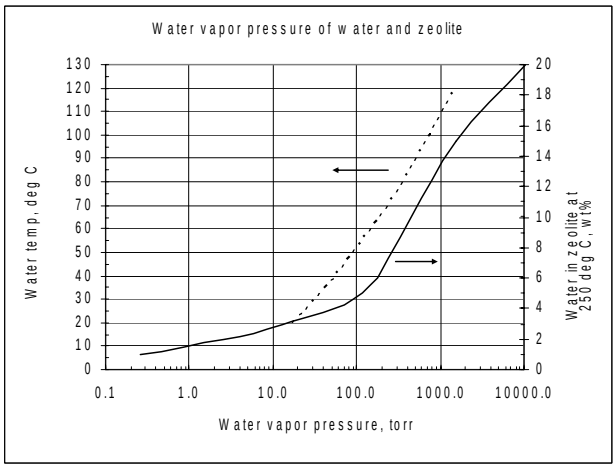

Figure 4. Vapor pressure of water and zeolite.

III. ZEOLITE BED RECOVERY SYSTEM

The regeneration and recovery of hydrogen isotopes from the above zeolite beds is accomplished by a zeolite bed recovery system. The system consists of magnesium beds, furnace, circulation pumps, pressure regulators, mass flow meters and recycle tanks. A schematic of the system is shown in Figure 3. The magnesium bed is a 25-cm diameter vessel and holds 20 kg (823 mole) magnesium turnings supported by a porous plate at the bottom. The magnesium container is heated in a furnace equipped with resistant electric heaters. Layers of heat shields and a vacuum jacket provide thermal insulation. Inlet gas containing water moisture flows through a stand pipe to the lower side of the porous plate. As the gas mixture rises through the Mg bed, the moisture reacts with Mg to form MgO and elemental hydrogen. The hydrogen gas exits the top of the bed and is circulated in the loop. During operation the Mg bed is maintained between 450 to 500 ^{o}C. The 20 kg of Mg can reduce a maximum of 823 moles of water generating 18K STP liters of H_2 according to the reaction below.

$Mg + H_2O \rightarrow MgO + H_2$ 86 kcal/mole.....(1)

When the Mg is consumed the bed is removed and disposed of as low level radioactive waste. The hydrogen isotopes are collected in recycle tanks and later separated to recover the tritium.

The system was originally designed to operate in a cycling mode for an expected capacity of 7K moles per year. It has been operated in this mode for about 10 years and the average amount of tritiated water reduced is about 6.7K mole per year. Due to the addition of equipment and gloveboxes to the facility, the required capacity is expected to increase to about 10.7K mole/year, an increase of about 60%.

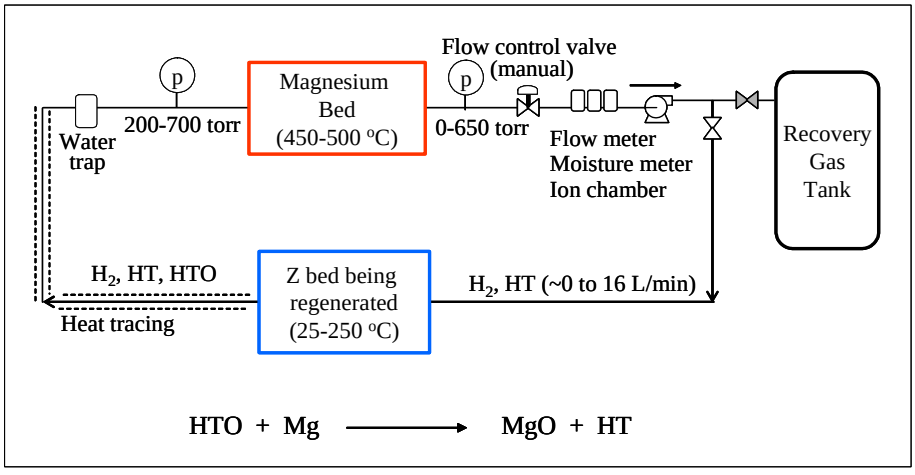

Figure 3. Zeolite bed regeneration system.

IV. KEY OPERATION PARAMETERS

IV.A. Desorption Temperature and Pressure of Zeolite Bed

Water is desorbed from a zeolite bed by heating with circulating hydrogen gas. Water content, temperature, system pressure and gas circulation rate all affect the rate at which the water leaves the bed. At a given water content the vapor pressure increases as temperature increases. High temperature increases the desorption rate, but the temperature is limited to about 250 ^{o}C due to the physical stability of the zeolite pellets. At a given temperature the vapor pressure decreases as the water content

decrease. The dependence of water vapor pressure on water content at 250 °C is shown Figure 4. The vapor pressure decreases rather rapidly as the water content decreases. This means it becomes much harder to desorb the last bit of water from the zeolite. It is impractical to decrease the water content to less than about 2 wt%. Gas circulation removes water vapor from the bed, and increase the driving force for desorption. High circulation therefore favors desorption rate. Gas pressure should not affect the desorption rate, but pressure improves heat transfer, and therefore should improve desorption, since deorption requires heat.

IV.B. Tracing Temperature

After the water vapor leaves the zeolite bed in hydrogen gas, it flows through the piping connecting the zeolite bed to the Mg bed. This section of piping must be kept hot to prevent or control condensation. Condensation some times is necessary in order to limit the water rate entering the Mg bed. Vapor pressure of liquid water at tracing temperature is compared to the water vapor pressure of the zeolite bed. If the latter is higher than the former, condensation will occur. Otherwise it will not. **Figure** 4 compares the liquid water vapor pressure with that of zeolite at 250 °C. It shows that at 15 wt% the zeolite generates a vapor pressure of about 2000 torr. To prevent condensation the heat tracing temperature will have to be higher than 120 °C. At lower tracing temperatures, a vertical line drawing from the water curve to the zeolite curve locates the water level above which condensation will occur. This tracing temperature is important since it controls the water vapor partial pressure entering the Mg bed when condensation occurs. When condensation does not occur the desorption rate of the zeolite bed becomes the controlling factor. The tracing temperature can help the regeneration rate only to a degree.

IV.C. Mg Bed Temperature

For the reduction reaction to proceed rapidly the Mg bed must be kept at high temperatures. The high temperature is also necessary to prevent the formation of MgH_2 and $Mg(OH)_2$, since both of them hold up the hydrogen. The melting point of Mg is 650 °C. The bed temperature must not be close to this temperature to prevent accidental melting and excessive Mg vapor. As shown by equation (1) the reduction of water is exothermic and produces 86 kcal/mole. This heat must be dissipated to prevent local melting. High pressure and circulating gas flow help heat dissipation.

IV.D. Mg Utilization

The Mg bed is operated in a flow-through fashion. Mg in the entrance end will be consumed first. The gas must travel a distance before the water it carries has been reacted. This distance is called the reaction zone. The size of this reaction zone defines the utilization of the Mg in the bed. For 100% utilization the reaction zone size has to approach zero. For 80% utilization the reaction zone size is 20% of the bed. In general, large length/diameter of the bed, high residence time (slow mass flow rate and high pressure), and large surface area of the Mg particles all favors high utilization.

V. CYCLING OPERATION MODE

In the cycling mode of operation, the zeolite bed to be regenerated is connected to the circulation loop of the recovery system as shown in Figure 3. To begin, the circulation loop is filled with hydrogen to 200 torr., and the magnesium bed is heated to 450 °C. The pump is then started to circulate the gas through the zeolite bed and the magnesium bed. The zeolite bed is heated gradually to 250 °C. The circulating hydrogen carries the moisture from the zeolite bed to the magnesium bed, where the moisture is reduced and the hydrogen is freed. As hydrogen gas is accumulated in the loop, the loop pressure increases. When the pressure reaches 700 torr, the loop is opened to the recycle tank to remove the hydrogen and the loop pressure is reduced back to 200 torr. The pressure cycles this way until the zeolite bed is considered dry as indicated by much slower rate of pressure increase. At this point the water content in the zeolite is estimated to be about 2 wt% and the water vapor pressure is about 2 torr. A typical trace of the Mg bed inlet pressure and the gas flow rate is shown in Figure 5. Both the pressure and the gas flow rate cycled. The upward slope of the pressure was nearly constant indicating the water reduction rate is about constant

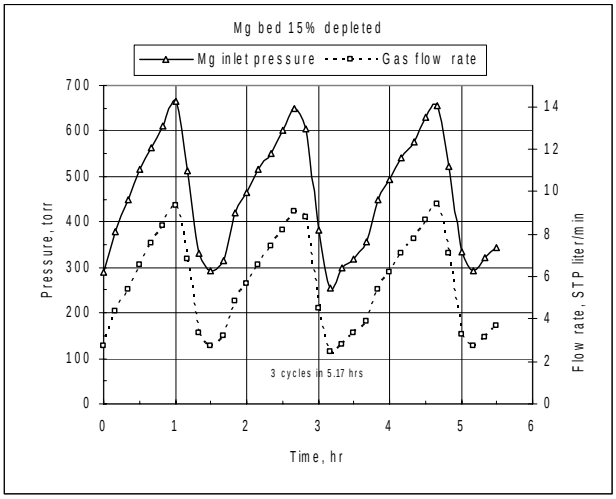

Figure 5. Pressure and flow rate of the cycling mode of operation.

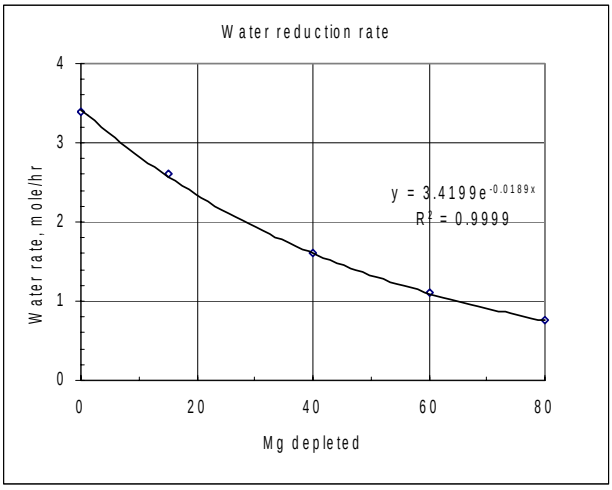

Figure 6. Water reduction rate depending on Mg depleted.

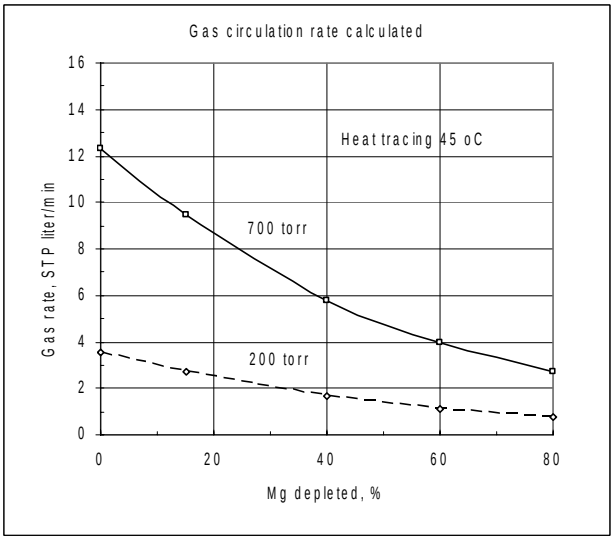

Figure 7. Gas circulation rate if saturated with water.

during a cycle. It took 5.17 hours to complete 3 cycles. Each cycle produced 100 STP liters of hydrogen. The water reduction is then 100*3/5.17=58 STP liter/hr=2.6 mole/hr. At the tracing temperature of 45 ^{o}C, the water vapor pressure is 72 torr. When the Mg bed inlet pressure is 200 torr, if the gas is saturated, the water vapor concentration in the gas would be 72/200=0.36. The required gas flow rate to give 58 STP liter/hr would be 58/0.36=161 STP liter/hr=2.7 STP liter/min. The same calculation at 700 torr Mg bed inlet pressure would give a gas rate of 9.4 STP liter/min. Compared with the flow rate data shown in Figure 5, which has low values of about 2.5 and high values of about 9.4, they are surprisingly close. This indicates that the gas entering the Mg bed is saturated with water vapor. The inlet flow rate is controlling the water reduction rate and the pressure is not. Note that this set of data is generated when the Mg bed depletion was about 15%. Data showed that the rate depends on the amounts of Mg that had been depleted.

Data in Figure 6 show that the water reduction rate decreases from 3.4 mole/hr to 0.75 mole/hr as the Mg depletion increased from 0 to 80%. This is mainly due to the increase of MgO in the bed which increased the flow resistance. Using the saturation conclusion derived above, the gas flow rates at the low and high pressures were calculated and plotted in Figure 7. The results covers a range from 0.9 to 12.3 STP liter/min, Actual operation is from about 1 to 16 STP liter/min. Therefore on the average the gas entering the Mg bed is 70 to 90% saturated.

Figure 8 is a time trend showing the zeolite bed temperature, the Mg bed temperature and the amounts of hydrogen recovered. It took 30 days to regenerate the fully saturated zeolite bed (104-kg bed containing 870 mole or 19000 STP liter of water). Since one pressure cycle produces 4.46 moles (100 STP liters) of gas, it takes 195 cycles to complete a bed. The average time to complete a cycle is then 3.69 hours, and the average water reduction rate is 1.21 mole/hr (=4.46/3.69). The actual water reduction rate varies from 0.75 to 3.4 moles/hr. It took about 8 days to ramp up the zeolite bed temperature to 240 ^{o}C. The slow heat up rate is to control the water deorption rate, so that the Mg bed temperature would not go too much above 500 ^{o}C. Besides controlling the heat up rate, the gas circulation rate is also adjusted manually through a control valve in the loop. At the end of regeneration it took 3 days to cool down the bed to room temperature.

Heat tracing between the zeolite bed outlet and the Mg bed inlet is important. The tracing temperature controls the water vapor pressure entering the Mg bed when the vapor pressure from the zeolite bed is higher than what is generated by the tracing temperature. It

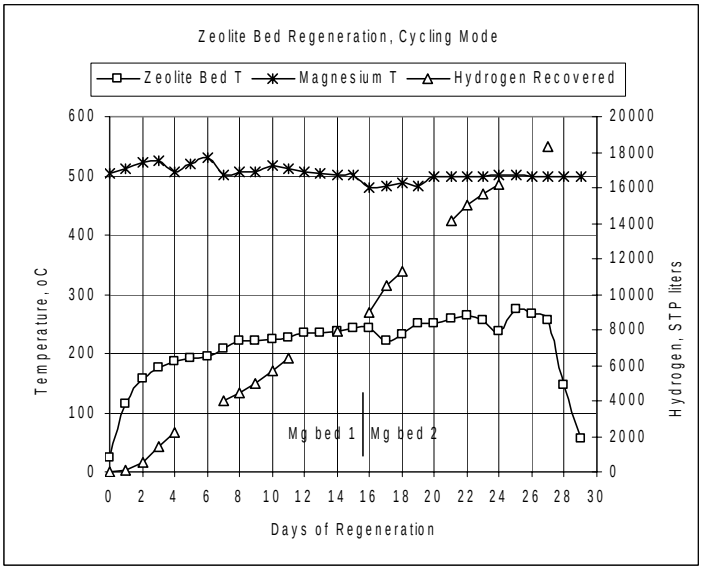

Figure 8. Time trend of cycling mode of operation.

defines how much water still has to be recovered when the zeolite bed vapor pressure becomes the controlling factor. For the cycling mode of operation the tracing temperature was set at 45 ^{o}C, generating a vapor pressure of 72 torr. From Figure 4, this is the vapor pressure of the zeolite at 250 ^{o}C and 4 % water content. Therefore, from 15% to 4% water content the tracing temperature controls the water vapor pressure entering the Mg bed. The zeolite vapor pressure becomes controlling when the water content is less than 4%. Since the target "dry" water content is 2%, the portion of water recovered when the vapor pressure is 72 torr is 0.85 fraction [(15-4)/(15-2)]. The balance of 0.15 frantion is recovered at vapor pressures much lower than 72 torr, and requires more that 15% of the time.

VI. STEADY OPERATION MODE

The recovery system was modified to permit steady operation about a year ago. "Steady" means that the loop pressure is kept constant instead of cycling during the regeneration of a zeolite bed. A pressure control valve was added between the circulation loop and the recycle tanks, a mass flow controller was added in the loop, and the water trap size was increased from about 1 liter to about 15 liters. Changes were also made to permit operation at higher pressures. The pressure control valve keeps the loop pressure constant by releasing gas out of the recycle loop as required. The mass flow controller maintains a constant gas flow through the loop. The larger water trap permits faster initial heat up of the zeolite bed without possible flooding the Mg bed.

With this steady mode of operation, the regeneration of a typical full size zeolite bed is shown in Figures 9 & 10. First in Figure 9, the heat up rate is much faster, 30 hours to reach 250 ^{o}C versus about 8 days before. **Figure**

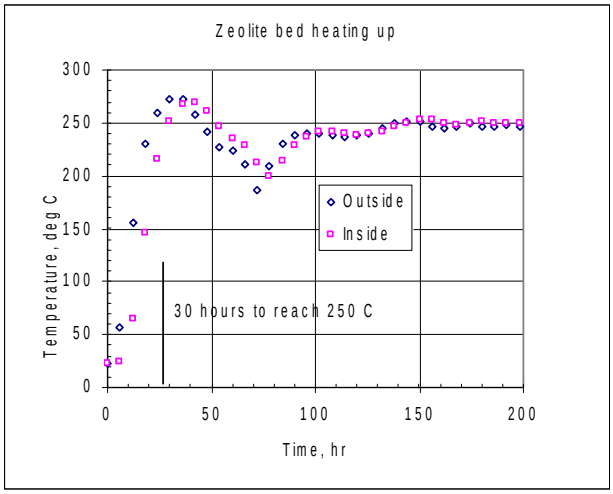

Figure 9. Heat up rate of a zeolite bed for steady mode of operation..

10 shows that the regeneration took 42 days not counting the 7 days spent on changing the Mg bed. The hydrogen gas recovered was 19000 standard liters. Looking at the recovered hydrogen data, five periods of reduction rate can be identified. The rate is nearly constant during each of these five periods as indicated by the constant slop of the data. The cause for these 5 different rates is the variation in gas flow rate and the water trap outlet temperature (tracing temperature). The loop pressure was steady at 1500 torr through out the 5 time periods. In periods 1 and 2, the main change was the gas flow rate decreasing from 8 to 5 STP liter/min. This caused the water reduction rate to decrease from 1.65 to 0.68 mole/hr. In periods 3, 4 and 5, the main change is trap outlet temperature, from 69 to 65 and to 31 ^{o}C. The water rate changed from 1.41 to 0.99 and 0.25. These variations are summarized in Table 1. The equilibrium water vapor pressure at the trap outlet temperature is shown in row 6 of the table. If the gas is saturated with water vapor at the temperature of the trap outlet, the water rate would have been those shown in row 7. They all are much higher than the data shown in row 5. The ratio of the actual rate and the calculated saturation rate is from 0.36 to 0.56 as shown in the last row. The average water vapor concentration is only about half of saturation. This large deviation from saturation might be related to the large water trap shose design might not have been optimum for obtaining equilibrium. Overall it took 42 days to recover 19000 STP liter hydrogen. The average rate is 18.4 STP liter/hr (0.82 mole/hr). This is slower than the 1.21 mole/hr achieved in the cycling mode of operation.

Table 1 Steady mode of operation

Time period	1	2	3	4	5
Loop pressure, torr	1750	1750	1750	1750	1750
Trap outlet temperature, ^{o}C	71	71	69	65	31
Flow rate, slm	8	5	8.5	8.5	8.5
(1) Water reduction rate, mole/hr	1.65	0.68	1.41	0.99	0.25
Water vapor at trap temp, torr	246	246	225	192	34
(2) Water rate if saturated, mole/hr	3.01	1.88	2.93	2.49	0.44
Ratio (1)/(2)	0.55	0.36	0.48	0.40	0.56

VII. STRATEGY FOR PROCESSING RATE INCREASE

The key factors that impact the regeneration time of a zeolite bed include the heat up rate of the zeolite bed, the

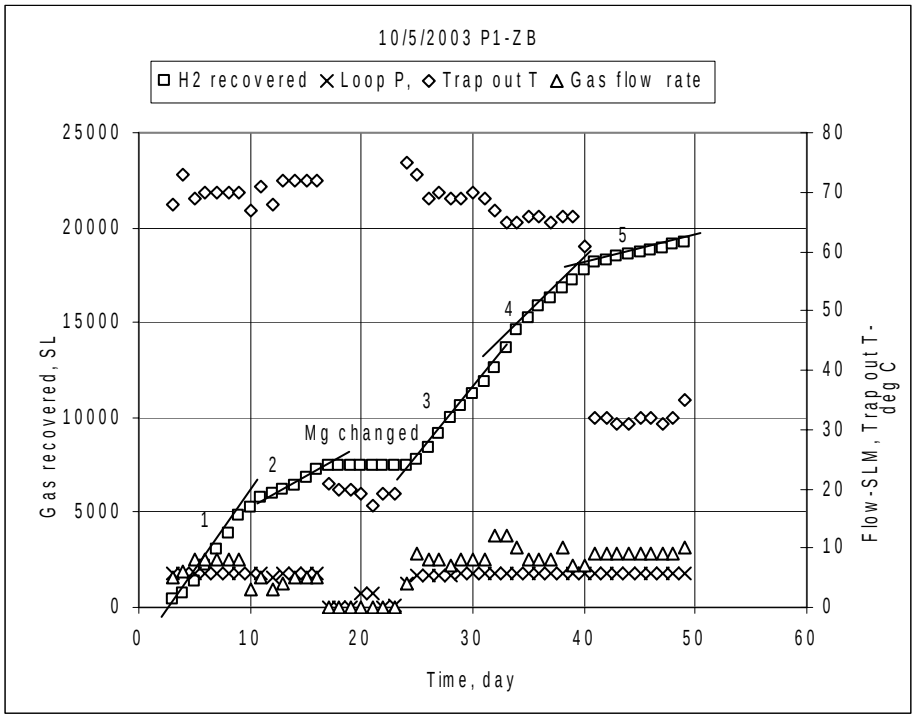

Figure 10. Time trend of key parameters of the steady mode of operation.

high temperature of the zeolite bed, the tracing/water trap temperature, and the gas circulation. The zeolite bed should be heat up to target temperature as fast as the heater power can achieve. To avoid water flooding the Mg bed, a water trap with a sufficient volume is needed in the exit line of the zeolite bed. The water trap and the gas line must be kept at a high temperature so that the water vapor concentration in the gas entering the Mg bed is high. The water trap design must facilitate mixing between the passing gas and the condensed water to achieve equilibrium. The gas circulation rate should be programmed to match the Mg depletion in the Mg bed: high rate when the Mg bed is new, slower rate when the Mg bed becomes depleted. The loop pressure should be as high as practical. High pressure increases the residence time in the Mg bed that permits higher water rate and increase the utilization of Mg in the bed. High pressure is also good for heat transfer, which helps water desorption from the zeolite and heat dissipation in the Mg bed. Steady pressure mode of operation provides better opportunity to fine tune the pressure, flow rate and tracing temperature. Using proper operation conditions the steady pressure mode of operation should yield a higher system capacity than the cycling mode of operation.

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[1]. L. K. HEUNG and M. L. RHODEN, “Performance of a Large-Scale Glovebox-Stripper System”, *Fusion Science And Technology*, **41**, 583, (2002)