Catalytic Oxidation of Hydrogen in Air Streams

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Abstract

At LLE, a zirconium-iron (ZrFe) alloy recovers tritium that has escaped from process systems. Tritium in air streams cannot be captured with ZrFe alloy because oxygen retards the alloy's function to remove tritium and consumes the alloy. A copper/zinc (Cu/Zn) alloy bed was tested as an alternative method for capturing hydrogen. Helium, oxygen, and hydrogen were all flowed through a Cu/Zn bed pre-loaded with oxygen at the same time, and the hydrogen concentration was not elevated in the outlet stream; it was captured and formed water. The alloy was determined to have the ability to function as a catalyst. To increase the efficiency of the catalytic function, tests were performed analyzing oxygen gettering and oxidation of hydrogen. Increasing the temperature of the alloy bed increases the time it takes to fill the bed to full capacity, along with the amount of oxygen that can be absorbed by the Cu/Zn alloy. Hydrogen oxidation improves when the flow rate of the carrier gas (helium) is increased and when the temperature is also increased.

1. Introduction

Tritium is usually contained in gloveboxes to decrease its escape to the environment. The inert gas helium is used in process equipment because elemental hydrogen (T_2) can be recaptured in a zirconium-iron alloy (ZrFe) bed. Minute amounts of nitrogen, oxygen and water (N_2, O_2, H_2O) seep into the glove box along with the tritium. These gases contaminate the helium gas. The ZrFe bed can be consumed by oxygen and hydrogen in water molecules which decreases the effectiveness of the ZrFe bed and retards its ability to capture tritium.[1] These contaminant gases are currently cycled through a drier to capture the water, and an oxygen getter to remove the oxygen.

Upstream of the ZrFe bed, a molecular sieve bed is placed to remove water from the air stream. Currently at LLE, a nickel bed is placed after the molecular sieve to remove oxygen.[2] Once the bed is consumed, the bed can be regenerated with hydrogen.[3] The equations for the nickel bed are:

Oxygen Uptake: $O_2 + 2Ni \rightarrow 2NiO$ (1)

Nickel Reduction: $NiO + H_2 \rightarrow Ni + H_2O$ (2)

The oxygen is being absorbed by the bed, and then the bed is regenerated and water is formed.

In this experiment, a copper/zinc alloy (Cu/Zn) was tested for its ability to remove oxygen from an air stream and be regenerated with hydrogen. The purpose of this experiment was to test the Cu/Zn alloy's oxygen getting and hydrogen regeneration capacity and to understand how conditions such as temperature, flow rate and pellet size affected the efficiency. The equations for this process are:

Oxygen Uptake: $O_2 + 2Cu \rightarrow 2CuO$

Copper Reduction: $CuO + T_2 \rightarrow Cu + T_2O$

The alloy's ability to function as a catalyst when both air and tritium were flown through the bed, where the tritium was captured by the bed and then removed by bonding with the oxygen to form tritiated water, was also tested. The parameters which affected the ability of the alloy to capture tritium and convert it into tritiated water were tested. This could be used in situations other than in the glovebox, where air has been contaminated by tritium.

2.Experimental

A system was built to test how oxygen gettering by Cu/Zn alloy is affected by temperature and flow rates. As seen in Figure 1, there are three cylinders containing He, 1% O_2 in He, and H_2.

The gases flow either through the bed or through the bypass. The gases are monitored after the bed by the atmospheric sampling system. An RGA (residual gas analyzer) measures the partial pressures of gases in the system. Oxygen, nitrogen, helium, hydrogen and water were monitored.

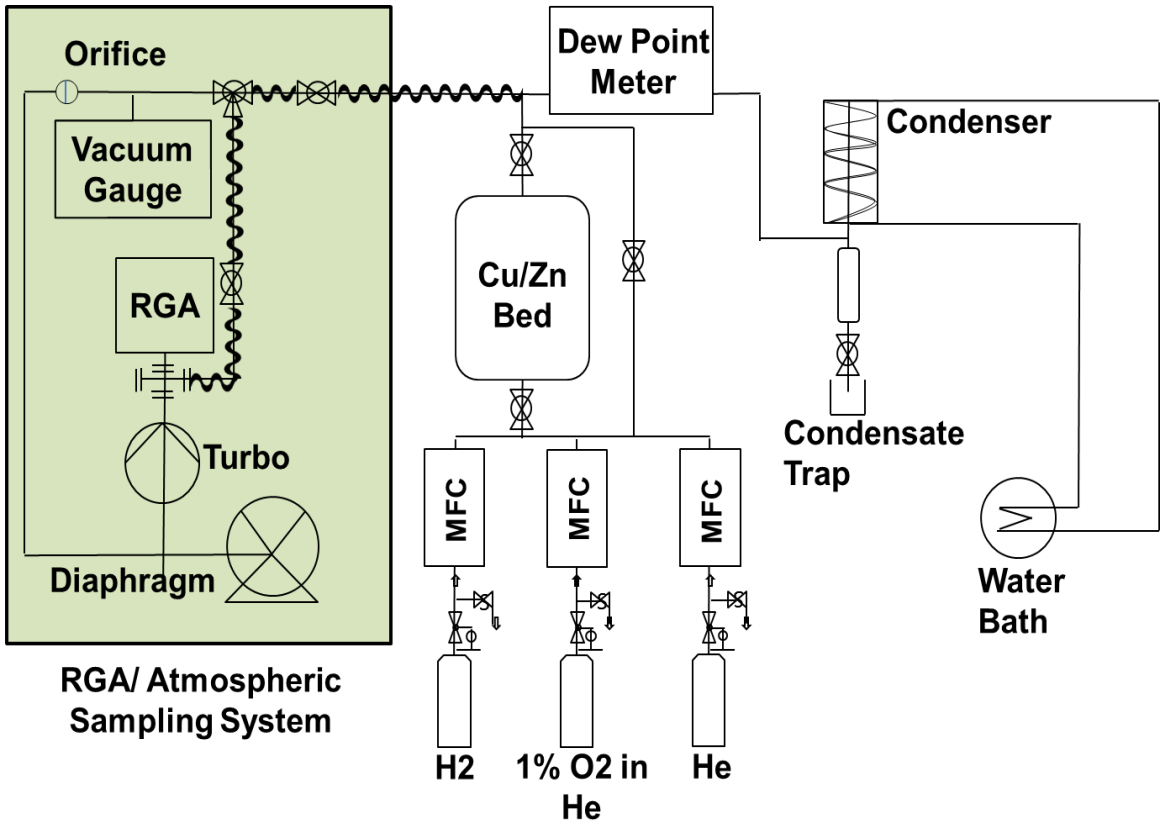

Figure 1. Schematic of experimental system

Nitrogen was measured to ensure that no air leaked into the system. The total pressure could also be measured. Thermocouples were located on the inlet and outlet streams, as well as on the bed and were monitored using a National Instruments data acquisition system. A dew point meter was placed after the bed and was recorded with the National Instruments system.

The catalyst bed and the capillary tubing were heated. The capillary tubing heated the gases from the outlet of the bed to the RGA. The alloy's temperature ranged from room temperature to 200°C. The capillary tubing was set to 120°C.

The Cu/Zn catalyst used for this experiment is 40% copper and 40% zinc, with alumina for balance. Two size pellets were used, 3mm (width) x 3mm (diameter) and 3mm x 5mm cylinders. The surface area was about 100 m^2/g for both sizes.

Three gases were used to test the Cu/Zn alloy bed. Mass flow controllers (MFC's) regulate the flow rates of these gases. Helium was flowed at the rate of 5 L/min as a carrier gas and to purge the system of air or previous gases. Helium flowed at rates between 1 L/min and 2 L/min. 1% oxygen in helium was used to load the bed with oxygen, for both oxygen getting testing and catalytic experiments. Hydrogen was used to regenerate the bed and in the catalytic experiment. H_2 was flowed at rates of 10 sccm-100 sccm (standard cubic centimeters per minute). Gases were flowed through the bypass for calibration.

While the bed is being loaded with oxygen, breakthrough is defined when the O_2 concentration reaches 0.01% in the outlet stream, which is monitored using the RGA. During the oxygen gettering capacity tests, the partial pressure of the oxygen gas in the outlet stream during the loading phase is less than the inlet stream because oxygen is being removed from the stream by the alloy bed. The alloy bed is no longer absorbing all of the oxygen from the inlet stream when breakthrough occurs, and its ability to effectively remove oxygen deteriorates at breakthrough.

3. Results and Discussion

3.1 Oxygen Uptake

The Cu/Zn alloy bed's capacity for "gettering", or removing oxygen from air streams, was tested at 30°C, 100°C and 200°C. 1% O_2 in He was flown at 5 L/min through the bypass in

order to get a reference reading of the inlet partial pressure of the oxygen. Then the Cu/Zn alloy bed's valve was opened and the bypass was shut off, and the partial pressure of oxygen in the outlet stream was measured as a function of time. Breakthrough was defined to occur when the O_2 concentration in the outlet stream reached 0.01%. The results can be seen in Figure 3.1 and Table 3.1. The two curves at each temperature corresponds to the two different particle sizes, with the color code given in Table 3.1.

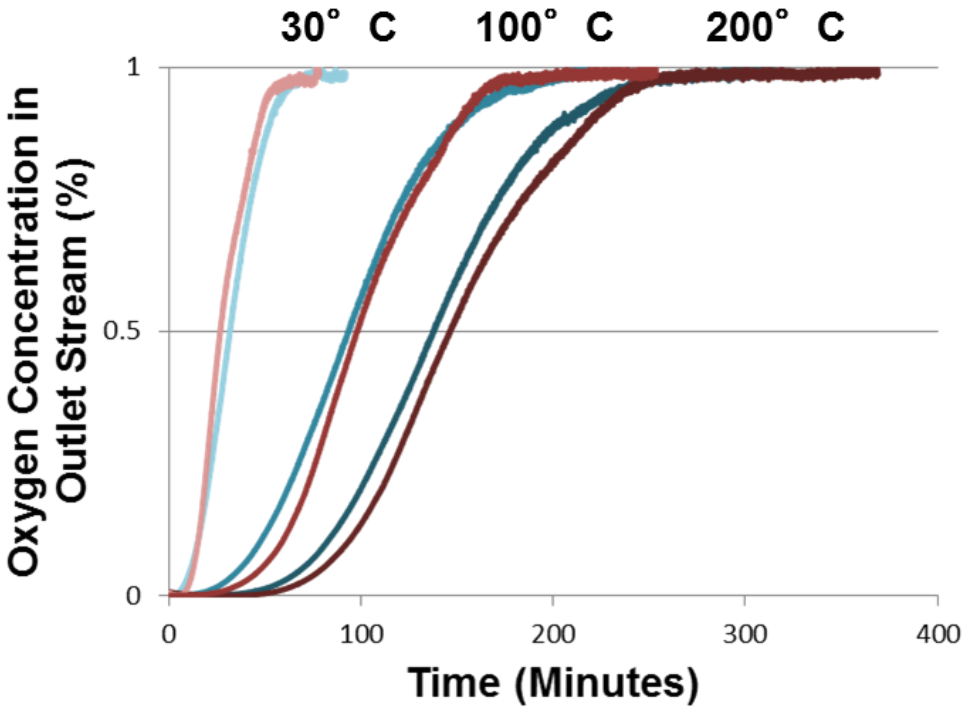

Figure 3.1 The concentration of oxygen in the outlet stream over time for different temperatures.

	3mm x 3mm				3mm x 5mm		
Temperature (° C)	30	100	200		30	100	200
Time to *Break-through (Minutes)	9.1	29.4	58.2		6.2	21.3	46.7
Time to 90% Capacity (Minutes)	37.2	114.8	165.1		41.2	144.5	154.5
Capacity (% Cu consumed)	11.3	38.7	57.6		13.2	38.7	55.9

Table 3.1 Breakthrough times and capacity of Cu/Zn beds

It was found that as temperature increases, the time to reach breakthrough increased. This can be seen in Table 3.1. The time until breakthrough increased with the 3mm x 3mm particle bed because there is less gas channeling around the particles on the side of the bed container.

The fraction of the Cu/Zn bed consumed as a function of time was also examined for each temperature and presented in Figure 3.2, which has the same color code as Table 3.1. The time until 90% capacity can be seen in Table 3.1. At 200°C, 57.6% of the bed was consumed by oxygen, compared to 11.3% consumed at 30°C. The bulk of the alloy is being consumed at the higher temperature whereas only surface copper is oxidized at room temperature. At the higher temperature, both the time to breakthrough and the capacity of the Cu/Zn alloy to consume oxygen increase.

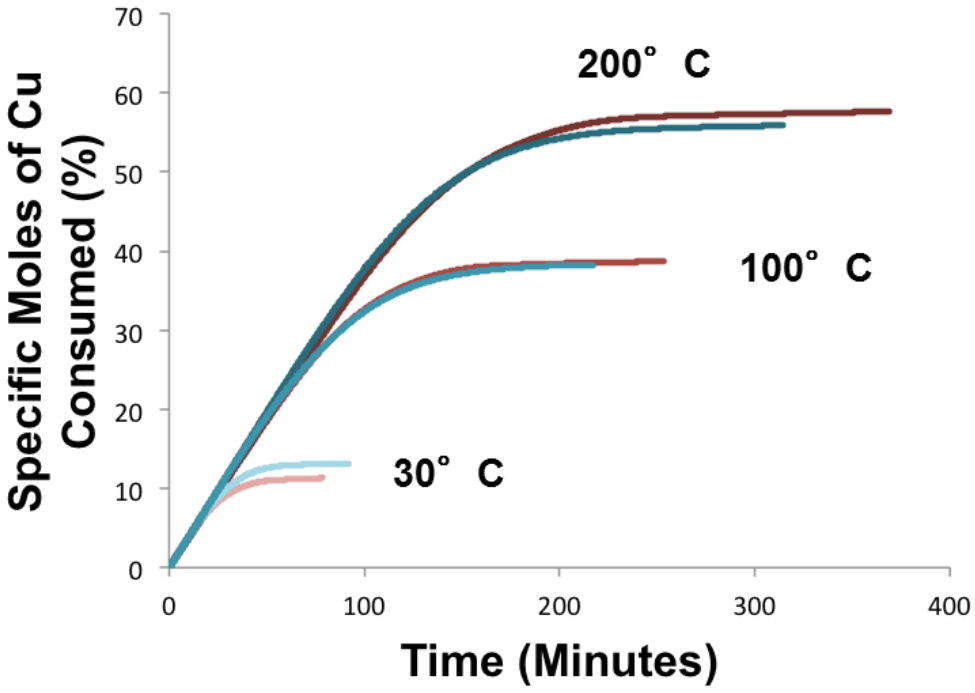

Figure 3.2 Consumption of CuZn bed over time

3.2 Copper Regeneration using Hydrogen

The cupric oxide formed by oxygen gettering can be reduced back to copper using hydrogen. The bed can then be re-used for additional oxygen gettering. Hydrogen was flown at 100 sccm for all tests. The ability to regenerate the oxidized alloy was tested at 100°C, 150°C, and 200°C, and at helium purge gas flow rates of 1 L/min, 1.5 L/min, and 2 L/min. The hydrogen partial pressure and water partial pressure were measured. The effect of varying the carrier (Helium) gas concentration can be seen in Figure 3.3. Starting with 1 L/min, the concentration of hydrogen in the outlet stream decreased with each increase in carrier gas concentration. This is because the efficiency of the regeneration process improved with increased purge rate. As the copper oxide is reduced, water vapor is formed and must be removed from the vicinity of the alloy in order for more copper oxide to be reduced. The increased flow rate decreases the amount

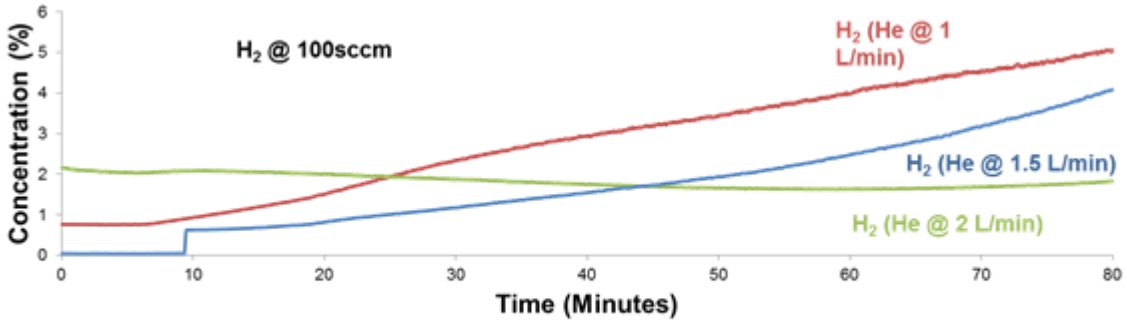

Figure 3.3 Concentration of hydrogen in outlet stream over time

of water vapor present around the alloy and allows more hydrogen to be used, thereby decreasing the outlet concentration of hydrogen.

Increasing the temperature also affected the regeneration, as can be seen in Figure 3.4, which shows the concentrations of hydrogen and water as a percent of their total possible concentrations in the outlet stream, or the concentrations of the gases compared to their total

bypass of the alloy bed concentrations (100%). As the temperature increased over time, the regeneration increased until the bed was completely regenerated. With each increase in temperature, more hydrogen was consumed for copper oxide reduction, and more water was produced. In the beginning of the run, the low temperature allows almost no capture of hydrogen,

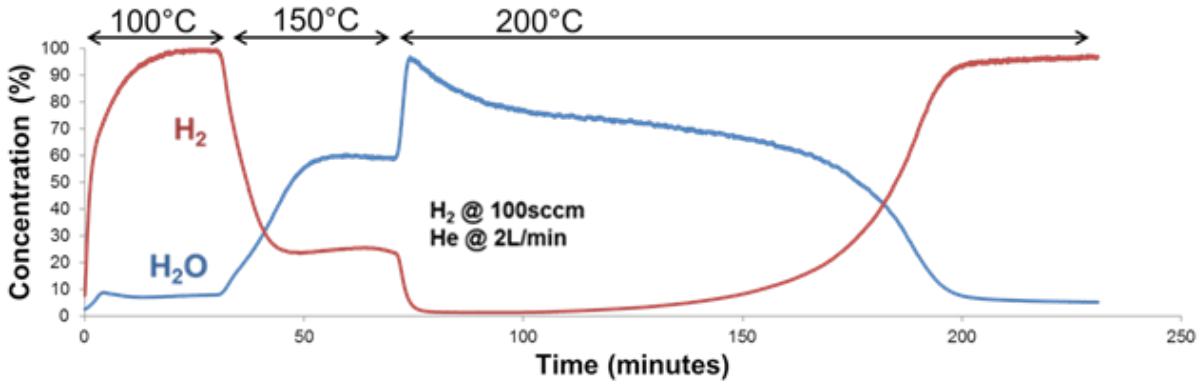

Figure 3.4 Concentrations of hydrogen and water in outlet stream over time with increasing temperature

so most of it passes through the bed and the concentration is very high. Towards the end of the run, the alloy is nearly regenerated and the amount of copper oxide available to be reduced drops. Consequently the water concentration in the outlet drops. Increasing the temperature decreases the time needed to regenerate the bed.

3.3 Catalytic Ability

The ability of the Cu/Zn alloy to function as a catalyst was tested. A catalytic bed would use oxygen from an air stream to transform elemental hydrogen into water without altering the alloy. In this case, the Cu/Zn functions as a pseudo-catalyst in that hydrogen can remove oxygen from the alloy but oxygen in the carrier will replace the missing oxygen on the alloy.

In the first test to determine if catalytic function was possible, hydrogen was flown at 100 sccm, and 1% oxygen in helium was flown at 5 L/min. The alloy temperature was set at 200°C because the efficiency for both oxygen gettering and hydrogen regeneration improved with increased temperature. The results can be seen in Figure 3.5. Concentrations of hydrogen,

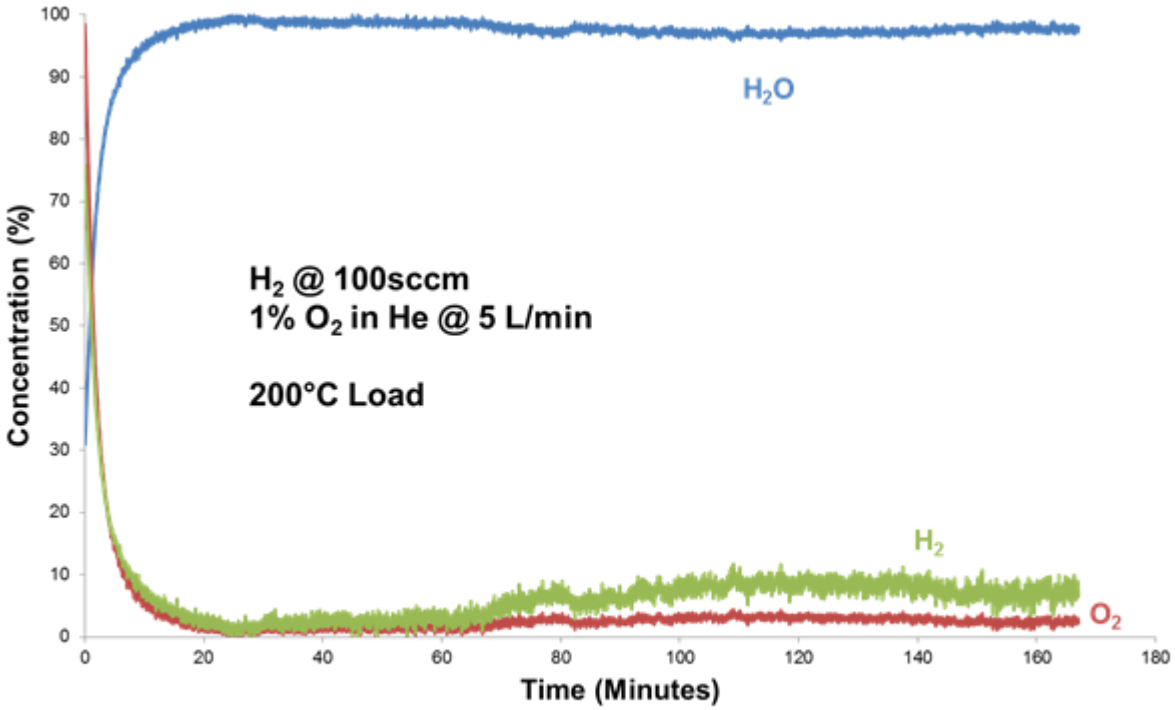

Figure 3.5 Catalytic function of Cu/Zn alloy

oxygen and water compared to their individual complete bypass concentrations are shown. Hydrogen was only seen with very small concentrations in the outlet stream, and oxygen breakthrough did not occur even though the experiment ran beyond when breakthrough would normally occur for the 200°C case. This indicates that the oxygen was being removed from the bed while the oxygen entrained in the carrier oxidized the alloy. Catalytic function is shown to be possible.

Since slight concentrations of hydrogen were seen in the outlet stream, it seems that the conversion efficiency was less that 100% in this case. The amount of hydrogen in the air stream overwhelmed the alloy's ability to convert the hydrogen to water. As H_2O is formed, there is twice as much hydrogen as oxygen in the air stream. It appears that it is necessary to operate in a condition where excess oxygen is present for complete oxidation of the hydrogen to occur.

In the second catalytic test the oxygen concentration was increased so that the ratio of hydrogen to oxygen was 1:5, but since the molecular formula for water contains twice as many hydrogens as oxygens, the ration for the amount of possible water formation is 1:10. This is a more realistic approach, as there will be at least 5 times more oxygen in the carrier as there would be in any conceivable tritium release to the air, as much as $1:10^9$. The hydrogen flow was decreased to 10 sccm for this experiment. The results can be seen in Figure 3.6. H_2 was flown at

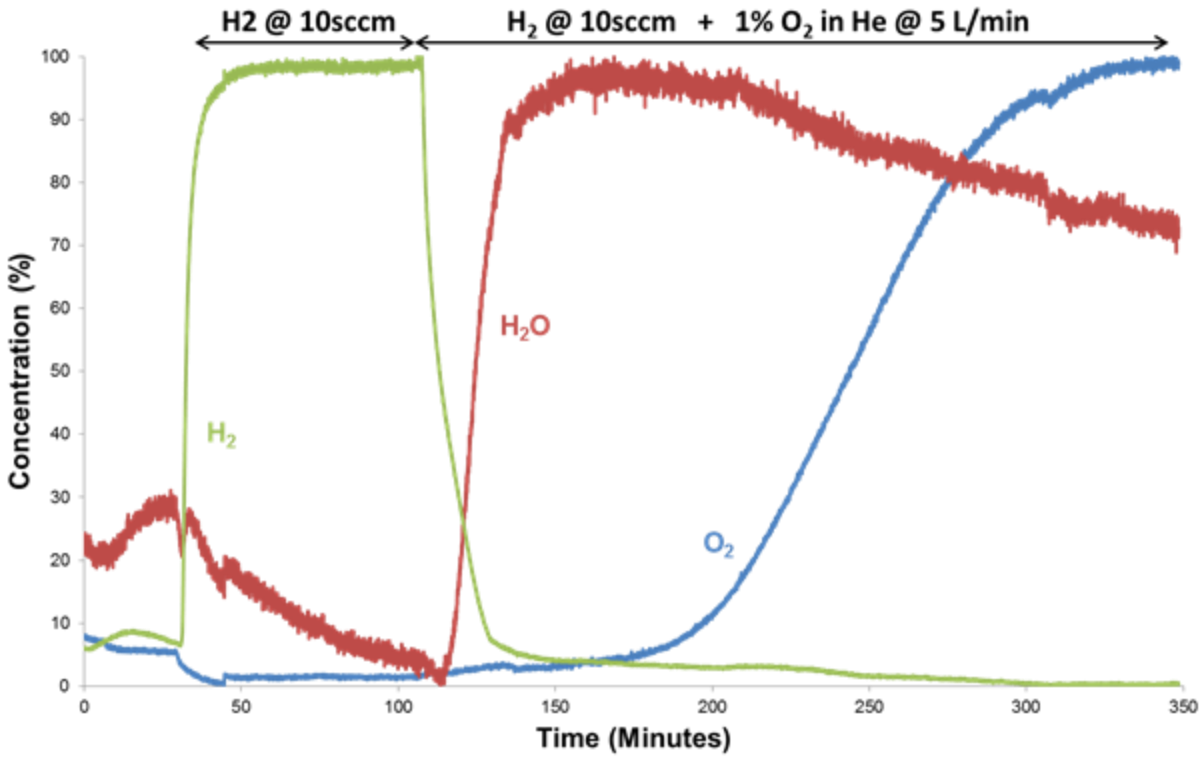

Figure 3.6 Catalytic function with 10:1 oxygen to hydrogen ratio

10 sccm until approximately 100 minutes, and then 1% O_2 in helium was flown at 5 L/min. When oxygen was introduced, the hydrogen concentration dropped to zero over the next 100 minutes. The addition of oxygen captures the hydrogen from the air and bonds into water, which is why the water concentration suddenly increases when oxygen is added. Oxygen overwhelms the hydrogen as there is much more than needed to fully capture the hydrogen so its concentration rises, as expected, when the alloy becomes fully oxidized. This experiment indicates that the Cu/Zn alloy has the ability to function as a catalyst for tritium removal at realistic ratios of hydrogen to oxygen.

The temperature of the alloy bed was varied in the third catalytic experiment to try and find

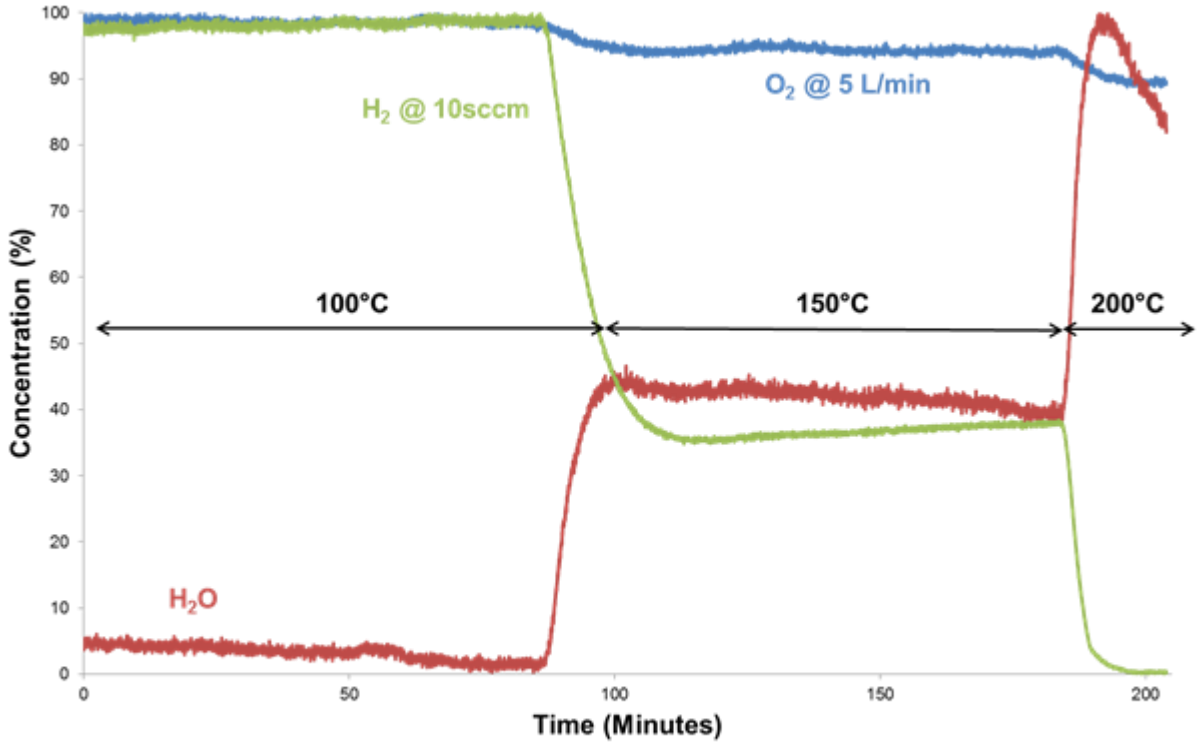

Figure 3.7 Catalytic function with increasing temperature over time

the optimal temperature for continuous catalytic function. The alloy bed was started at a low

temperature, with 0.01% O_2 in He at 5 L/min, and H_2 at 10 sccm, or the same ratios and setup as the previous experiment, beside temperature. Alloy temperatures of 100°C, 150°C and 200°C were used. The results can be seen in Figure 3.7. Each time the temperature was increased, less hydrogen was seen in the outlet stream. At the final temperature, 200°C, the hydrogen concentration at the bed outlet dropped to background values. This test reveals that higher temperatures improve catalytic function significantly. Operating the bed at 200°C ensures that hydrogen is being captured fully.

Conclusion

Experiments were performed to find optimal conditions for Cu/Zn oxygen gettering, hydrogen regeneration, and catalytic function. Increasing the bed temperature from 30°C to 200°C improves oxygen gettering capacity and increases the time until oxygen breakthrough. Regeneration is more efficient as flow rate of the carrier gas and temperature increase. Catalytic function is possible with the Cu/Zn alloy. Conversion efficiency improves with higher ratios of oxygen to hydrogen and increasing temperature. Higher temperatures are preferred for oxygen gettering, hydrogen regeneration and catalytic function.

Discovering that the Cu/Zn has the ability to be a catalyst is very beneficial to LLE. It can be operated at much lower temperatures than other catalyst options, and it would eliminate the need for an oxygen getter and its frequent regeneration. This is a very efficient solution to tritium removal from air streams.

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