Oxidation of Copper Zinc Alloy

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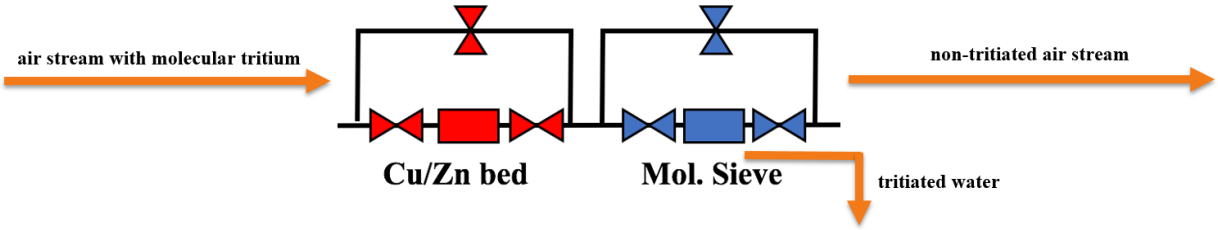
Abstract

A copper zinc (Cu/Zn) alloy was characterized for its use as an alternative concept to traditional techniques for extracting tritium from air streams. The molecular tritium is oxidized to form tritiated water which is then captured on a molecular sieve. The Cu/Zn alloy consists of 40 wt% of Cu and Zn and balance support alumina. In this work, hydrogen is used in place of tritium to mitigate any radiological hazards. Oxygen is loaded onto the bed preceding the hydrogen oxidation. The oxygen gettering dependence on alloy temperature has been measured at various bed temperatures. Gettering capacity increases as the temperature increases from 30°C to 150°C and approaches 100% at 150°C. Oxygen gettering efficiency of the bed is not influenced by temperature and is also independent of the range of total flow rates and oxygen concentrations examined. During hydrogen oxidation, conversion efficiency of hydrogen to water decreases as oxygen inventory on the bed increases. The results indicate that the Cu/Zn alloy can oxidize hydrogen at significantly lower temperatures than the traditional method and can be implemented as an alternative in the nuclear industry to remove molecular hydrogen isotopes from air streams.

1. Introduction

Catalytic oxidation of molecular hydrogen species has potential applications in industry to treat hydrogen waste streams to form non-hazardous waste water. This same process can also be used in the nuclear industry to remove molecular tritium from air streams [1]. Tritium process systems are typically enclosed in gloveboxes to minimize exposure to radioactive material. An inert gas, helium, is utilized in the glovebox because elemental hydrogen that escapes from process loops can be recaptured and re-used [2]. Traditionally, a copper (Cu) bed operating in the realm of 700°C is used to convert molecular tritium to tritiated water, which is then captured on a molecular sieve. This process can be repeated once the Cu bed is reloaded with oxygen. The equation for reducing the Cu alloy is: $T_2 + CuO \rightarrow T_2O + Cu$. Alternatively, a Cu/Zn alloy is able to oxidize tritium at significantly lower temperatures (~150°C) than the tradition Cu metal [3]. The equation for reducing the Cu/Zn alloy is: $T_2 + Cu/ZnO \rightarrow T_2O + Cu/Zn$. The alternative tritium removal system is shown in Fig. 1.1.

Figure 1.1: Schematic of alternative elemental tritium removal system where the Cu/Zn alloy is employed. An air stream containing molecular tritium is flown over a Cu/Zn bed that converts molecular tritium to tritiated water which is then captured on a molecular sieve.

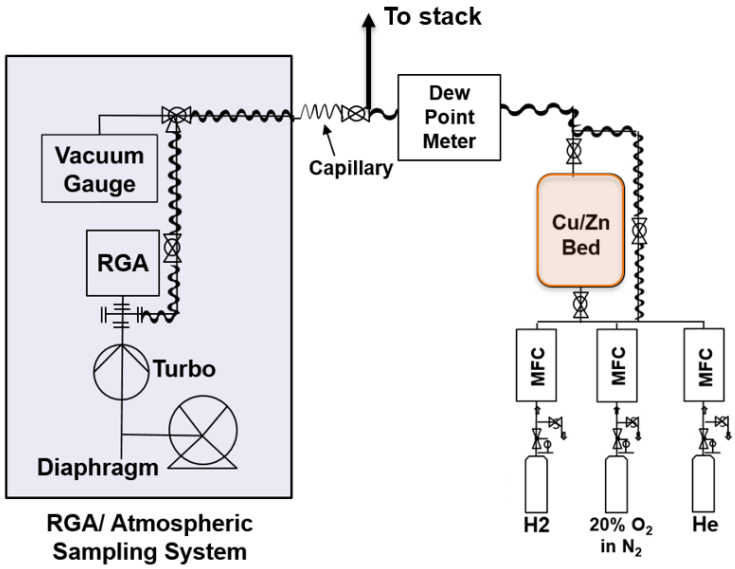


In this experiment, a Cu/Zn alloy was characterized as an alternative to replace Cu. Specifically, this experiment investigated the oxygen gettering efficiency (defined as the bed's efficiency of adsorbing oxygen) and capacity (the percentage of copper that is oxidized) as a function of bed temperature during the oxygen regeneration process and the bed's conversion efficiency of hydrogen to water as a function of oxygen inventory during the hydrogen oxidation process.

2. Experimental

The gettering experimental setup is shown in Fig. 2.1. This setup was used to determine the hydrogen oxidation oxygen gettering efficiencies of the Cu/Zn bed at various temperatures. Gas flow (H_2, 20% O_2 in N_2, and He) can travel over the Cu/Zn bed or through a bypass line. The bypass line, system lines, and capillary tubing are heated to prevent water from condensing in the system. The bypass line and system lines were heated to 100° C and the capillary tubing was heated at 150° C. To monitor these temperatures, thermocouples are located in the outlet stream of the Cu/Zn bed and adjacent to the Residual Gas Analyzer (RGA). The RGA is a mass spectrometer that finds the chemical composition of a gas by measuring the distribution of mass to charge ratios of the ionized gas molecules. The bed is surrounded by a heater and packed with insulation to preserve the desired temperature for each experiment. The bed's temperature ranges from 30° C to 200°C and is measured with a thermocouple attached directly to the bed. The dew point monitor, thermocouples, and RGA are utilized in data acquisition.

Figure 2.1: Schematic of experimental system.

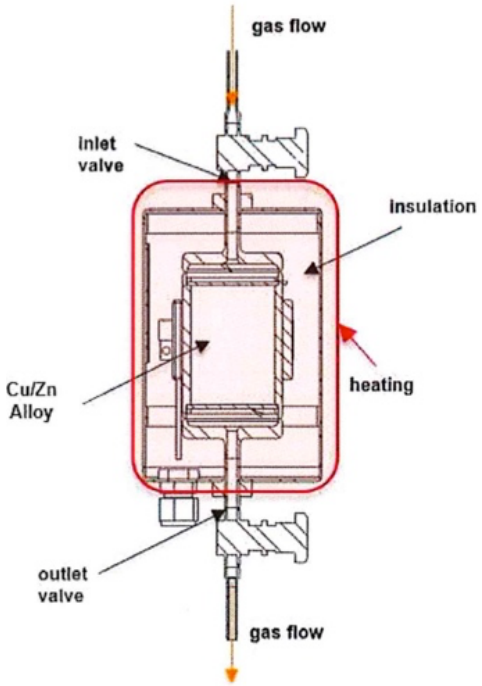


2.1 Properties of the Cu/Zn Alloy and the Bed

The 188 gram Cu/Zn alloy (Gettermax 133), 140 cm^3 internal volume bed utilized for this experiment was comprised of 40% Cu and 40% Zn with alumina for balance. The particle size/shape of the pellets composing the Cu/Zn alloy is 3 × 3 mm. The bed cavity is cylindrical with a diameter of 5.4 cm and length of 6.1 cm. The tapped density (defined as the increased density of the bulk attained after mechanically tapping the container) of the alloy in the bed is 1.35 g/cm^3. The ratio of the particle diameter to the bed diameter is 0.0556, which implies that slippage flow between the alloy and the wall represents less than 1% of the total flow through the alloy (according to calculations).

The gas flow enters through the inlet valve, passes through a 100 µm stainless steel filter, interacts with the Cu/Zn alloy, and then leaves the bed through a second 100 µm filter, as shown in Fig. 2.2. At a flow rate of 1 L/min the superficial velocity through the bed (=volumetric flow rate ÷ cross-sectional area of the bed) is 1 cm/s and the residence time in the bed (= bed volume ÷ volumetric flow rate) at the flow rate is 8.4 s. Under these conditions the modified Reynolds number (=particle diameter × superficial mass flux ÷ gas viscosity) is 0.2 and indicates the flow through the bed is laminar. The flow can be visualized as a slug of gas moving through the getter material.

Figure 2.2: Schematic of the getter bed.



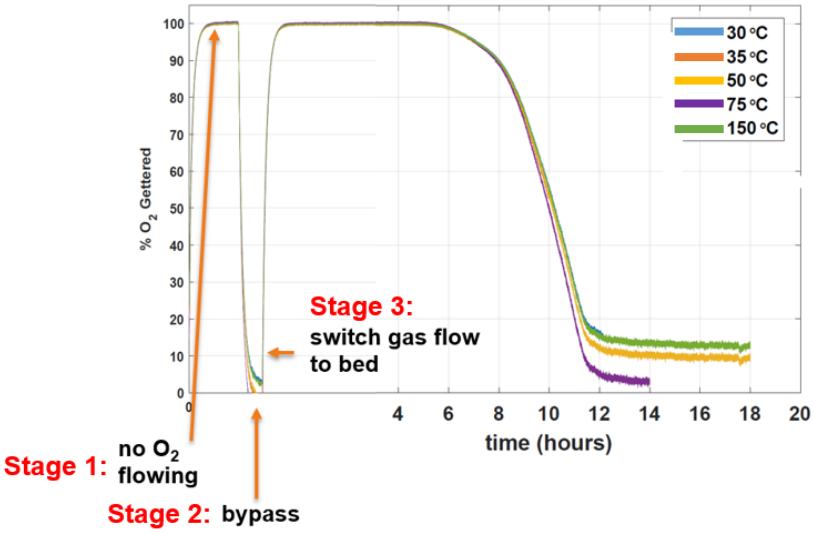
2.2 Gases

Three gases, helium, hydrogen, and 20% oxygen in nitrogen were used during the experiment. Helium gas functioned as a carrier gas while the hydrogen and 20% oxygen in nitrogen were the actual experimental gases used to test the bed's oxygen gettering capacity, oxygen gettering efficiency, and conversion efficiency of hydrogen to water. The flow rates of the gases were controlled by three mass flow controllers (Alicat) which were controlled by a LabVIEW program. The gases could either be sent over the Cu/Zn bed or through the bypass line for control and calibration (see Fig. 2.1). Helium was used as an inert carrier gas flown at a rate of 1 L/min to purge the system of atmospheric air and other residual gases as well as to carry the low quantities of hydrogen and oxygen through the system. A mixture of 20% oxygen in nitrogen was passed over the Cu/Zn bed during oxygen gettering experiments to load the bed with oxygen. Hydrogen was sent over the oxidized Cu/Zn species to regenerate the bed during hydrogen oxidation experiments.

2.3 Oxygen Gettering Experiment

For an oxygen gettering experiment 47.6 sccm (standard cubic centimeters per minute) of 20% oxygen in nitrogen is co-blended with 1 L/min of helium. Figure 2.3 is a graph of the percentage of oxygen gettered over the course of the experiment.

Figure 2.3: Percentage of oxygen adsorbed (gettered) by the Cu/Zn bed over the course of an oxygen gettering experiment. A nonlinear scale is used during the initial portion to better display the early time behavior.

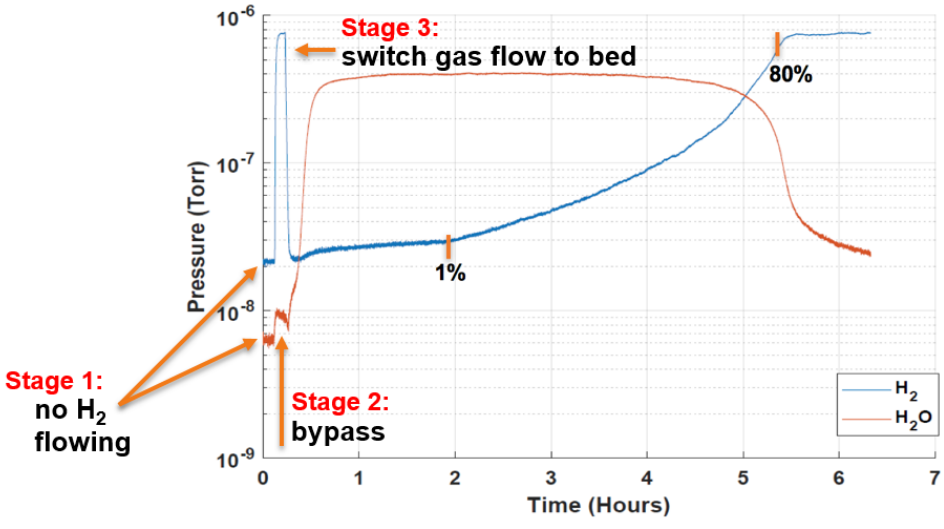


At the beginning of the experiment (Stage 1 in Fig. 2.3), there is no oxygen being passed through the system. During Stage 1, there appears to be 100% oxygen gettered according to the figure. This is because there is close to 0% oxygen in the outlet stream of the bed. Oxygen flow is then sent through the bypass line to calibrate the RGA signal (Stage 2 in Fig. 2.3). Once calibrated, the gas flow is then sent over the Cu/Zn bed (Stage 3 in Fig. 2.3), which is expected to getter oxygen to form Cu/ZnO. Close to 100% of the oxygen is gettered until the bed is no longer able to absorb all of the oxygen in the gas stream at that temperature. This is known as break through. Break through level in these experiments is arbitrarily defined as the point when the oxygen gettering efficiency drops to 80% i.e., when the fraction of oxygen in the outlet stream is 20% of the total oxygen in the inlet gas stream. Figure 2.3 shows that the bed has a relatively high gettering efficiency, meaning the bed is absorbing all of the oxygen in the inlet stream. This experiment determined the gettering efficiency of the bed for several temperatures between 30°C and 150°C.

2.4 Hydrogen Oxidation Experiment

During hydrogen oxidation experiments, 10 sccm of hydrogen was co-blended with 1 L/min of helium and passed over the Cu/Zn bed loaded with oxygen from the preceding oxygen gettering experiment. The bed was heated at 200°C and experiments were conducted at varying oxygen inventory levels on the copper alloy. Figure 2.4 is a data graph of the hydrogen and water flow in the system over the course of a typical run.

Figure 2.4: Partial pressure of H_2 and H_2O in the outlet stream of the Cu/Zn bed over the course of a hydrogen oxidation experiment.



Initially, there is no hydrogen being sent through the system (Stage 1 in Fig. 2.4). Hydrogen is then passed through the bypass line to calibrate the RGA signal (Stage 2 in Fig. 2.4). Once the RGA signal is calibrated, hydrogen gas is passed over the Cu/Zn bed (Stage 3 in Fig. 2.4). When the gas flow is initially switched to the bed, the hydrogen concentration in the outlet stream decreases rapidly and the water concentration increases because the hydrogen being passed over the bed bonds with the adsorbed oxygen to produce water. Once the oxygen inventory on the bed is exhausted, the hydrogen concentration in the outlet stream increases while the water concentration decreases. Break through level is defined as the point when the hydrogen concentration in the outlet stream returns to 80% of the feedstock concentration. Once the partial pressure of hydrogen in the outlet stream matches that of the inlet stream, there will be no oxygen bonded to the copper alloy and the alloy will be fully regenerated.

3. Results and Discussion

3.1 Oxygen Gettering Capacity

Oxygen gettering capacity is defined as the percent copper oxidized on the bed at a specified temperature when the maximum quantity of oxygen has been adsorbed onto the bed. The temperature dependence of the oxygen gettering capacity and efficiency was determined by fixing the flow rate of oxygen and helium and changing the temperature of the bed over several runs. The concentration of oxygen in the outlet stream was measured as a function of time. The results for the percentage of oxygen gettered as a function of time measured by the RGA are show in Fig. 2.3. It is found that the oxygen gettering capacity of the Cu/Zn alloy increases with increasing bed temperature from 30°C to 150°C. The percentage of the copper oxidized up to the breakthrough for five bed temperatures is shown in Table 3.1 and demonstrates that the percentage of copper oxidized increases with increasing temperature.

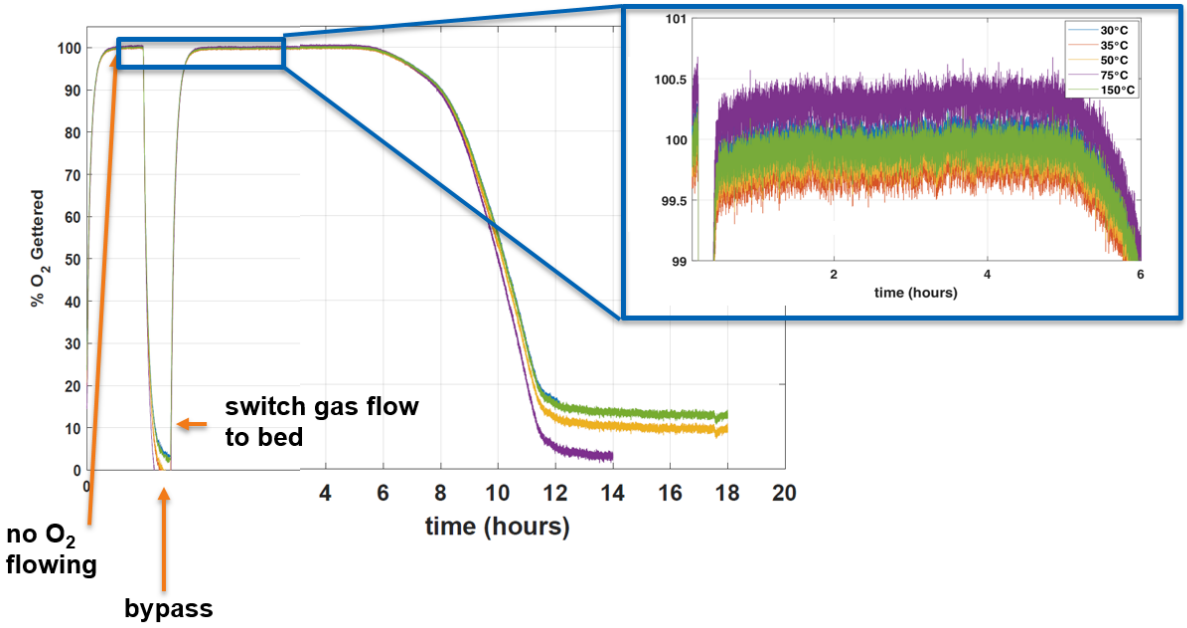
Table 3.1: Quantity of copper oxidized as a function of temperature for five different bed temperatures.

Temperature (°C)	% of Cu Oxidized
30	5.0
50	7.0
75	15.6
100	29.0
150	41.9

3.2 Oxygen Gettering Efficiency

The oxygen gettering efficiency of the Cu/Zn bed was determined by comparing the concentration of the oxygen in the outlet stream to the concentration of oxygen in the inlet stream. Fig. 3.1 shows the fraction of oxygen gettered as a function of time magnified prior to breakthrough. It reveals that there is a slight difference between the oxygen concentrations in the outlet stream when there is no oxygen flowing through the system compared to when oxygen is initially being flown over the bed. This indicates that when the oxygen is initially flown over the Cu/Zn bed the bed is gettering 99.8% of the oxygen flow. This trend perpetuates for different temperatures showing that oxygen gettering efficiency is independent of temperature.

Figure 3.1: Same as Figure 2.3 except that it is magnified at low times.

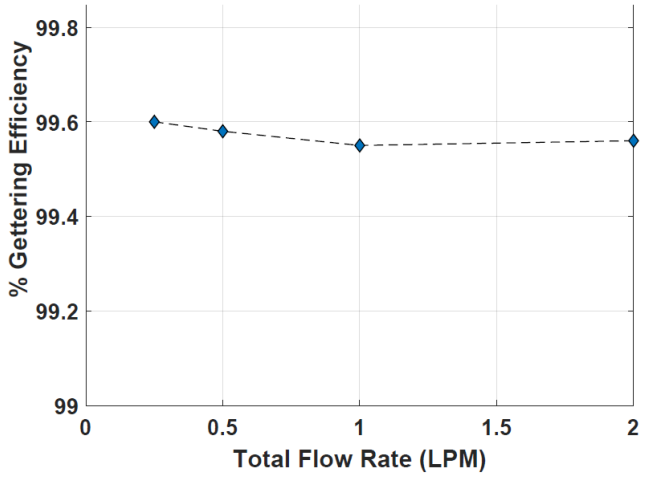


Delivering oxygen to the bed results in an exothermic reaction which produces watts of heat. When less oxygen is delivered to the bed, less heat is generated. Through a series of calculations summarized below, it was determined that varying the amount of oxygen delivered to the bed, and therefore changing the amount of heat the exothermic reaction generates, does not affect the bed's efficiency. The heat of formation of CuO is 157 kJ/mol of CuO. With 0.087 mol/L of 20% oxygen in nitrogen and 1 L/min of helium, there are 455 watts generated in the getter bed. If the helium flow rate is reduced to 0.25 L/min the heat generated by the exothermic

reaction is only 114 Watts. Heat loss from the bed is mostly by conduction through the medium to the walls of the getter bed (although 8W will be carried away by hot gas). Despite the considerable decrease in heat produced by the reaction, it is found that there is negligible change in the efficiency. This is another indication that the oxidation rate is not sensitive to temperature.

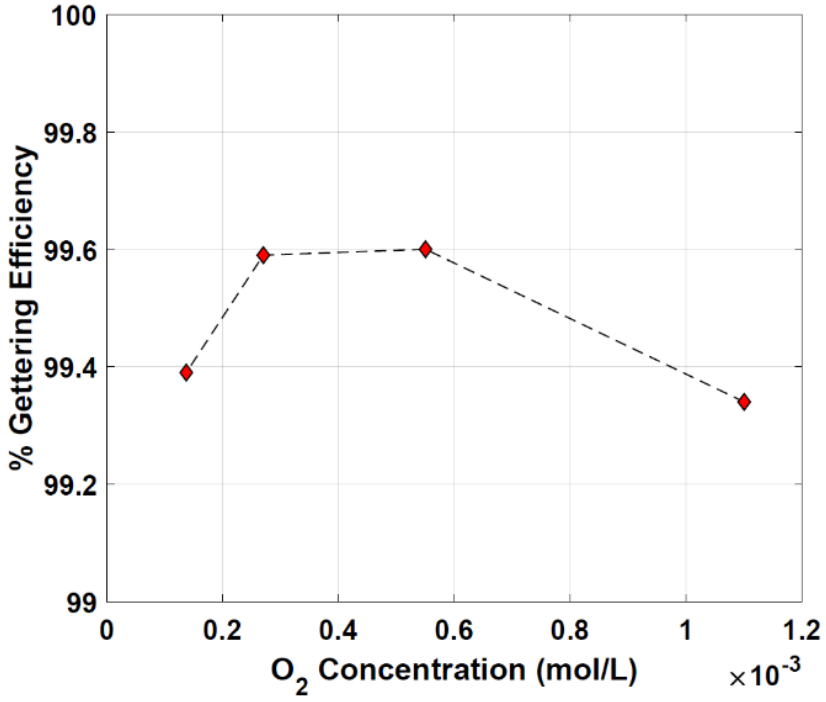
The oxygen gettering efficiency of the Cu/Zn bed was measured as a function of total flow rate. A concentration of 0.087 mol/L of 20% oxygen in nitrogen was held constant for total flow rates varying from 0.25 L/min to 2 L/min. Fig. 3.2 shows the gettering efficiency as a function of total flow rate and demonstrates that as total flow rate increases, the oxygen gettering efficiency remains constant.

Figure 3.2: Oxygen gettering efficiency dependence on total flow rate.



The gettering efficiency was also tested as a function of oxygen concentration. The concentration of oxygen in the carrier stream was varied from 0.14×10^{-3} mol/L to 1.1×10^{-3} mol/L of oxygen per liter of carrier gas. Fig. 3.3 shows the gettering efficiency as a function of oxygen concentration and demonstrates, within experimental error, that as the oxygen concentration increases the oxygen gettering efficiency of the Cu/Zn bed does not change.

Figure 3.3: Oxygen gettering efficiency dependence on oxygen concentration in the carrier. Dashed lines connect data points but there is no significant trend.

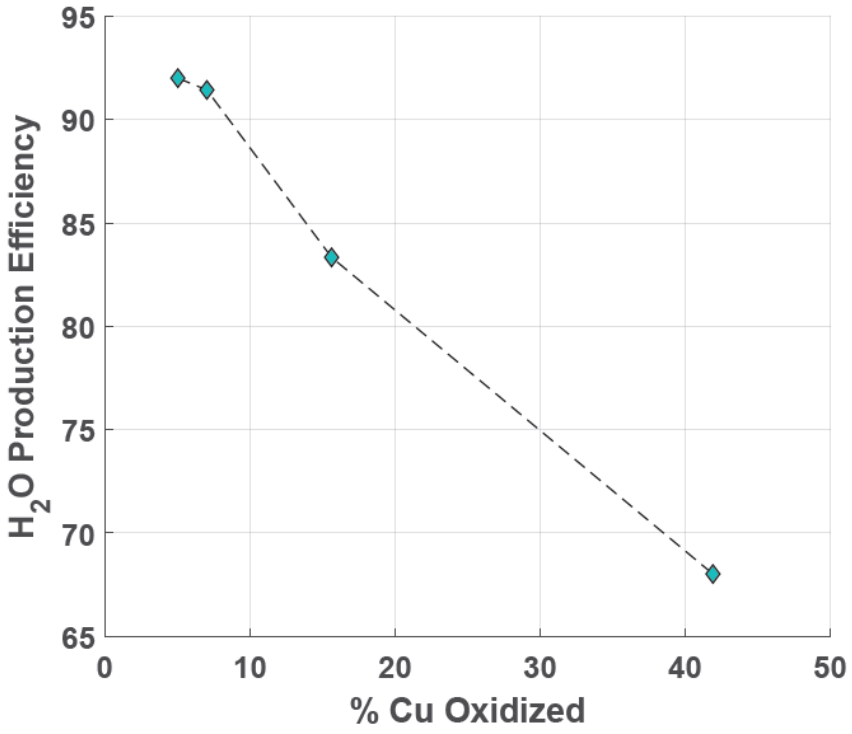


3.3 Hydrogen Oxidation Efficiency

The Cu/Zn hydrogen oxidation efficiency, shown in Fig. 2.4, was measured by fixing the hydrogen and helium flow rates as well as the alloy temperature and varying the oxygen inventory on the bed at the start of each experiment. The concentrations of hydrogen and water species in the outlet stream were measured as a function of time, as shown in Fig. 2.4. It is seen that the hydrogen concentration in the outlet stream when hydrogen is initially passed over the bed is slightly greater than the hydrogen concentration when no hydrogen is being flown through the system. This indicates that during hydrogen oxidation, the conversion efficiency of hydrogen to water is less than 100%.

The water production efficiency of the Cu/Zn bed was measured for varying oxygen inventories. The oxygen inventory of the bed is equivalent to the percentage of copper oxidized. Figure 3.4 shows the water production efficiency of the bed at varying oxygen inventories on copper.

Figure 3.4: H_2O production efficiency as a function of percentage Cu oxidized, measured at 200°C



This figure demonstrates that water production efficiency of the Cu/Zn bed decreases as the fraction of oxidized copper increases. This is due to the position of the mass transfer zone (defined as the portion of a packed column where the adsorption occurs) moving along the length of the bed with increased oxidized copper. Eventually, this zone which is required for complete conversion of $Cu/ZnO + H_2 \rightarrow Cu/Zn + H_2O$ is small enough that the conversion cannot be completed. This decreases the water production efficiency of the bed. This supports that the oxidized Cu/Zn bed will convert hydrogen to water as long as there is available oxygen on the bed, but at a reduced efficiency.

Conclusion

The goal of this research was to use Cu/Zn as a more efficient alternative of capturing tritium. This work looked at oxygen gettering dependence on alloy temperature, total gas flow rates, and oxygen concentrations. It also looked at the conversion efficiency of hydrogen to water as a function of oxygen inventory. It was found that oxygen gettering capacity increases as the temperature of the alloy increases from 30°C to 150°C. Gettering efficiency of the Cu/Zn bed is not influenced by temperature and is independent of total flow rate and oxygen concentration over the range tested. During hydrogen oxidation, conversion efficiency of hydrogen to water is less than 100% at 200°C and decreases as the oxygen inventory on the bed increases. The Cu/Zn bed will convert hydrogen as long as there is available oxygen on the bed, but at a reduced efficiency as the oxygen inventory increases. These results signal that the Cu/Zn alloy has the ability to perform at significantly lower temperatures than the traditional method. They also support the conclusion that the alloy could be implemented in the nuclear industry to remove molecular hydrogen from air streams.

Acknowledgments

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