Comparative Analysis of Oxygen Uptake in Nickel and Copper-Zinc Beds

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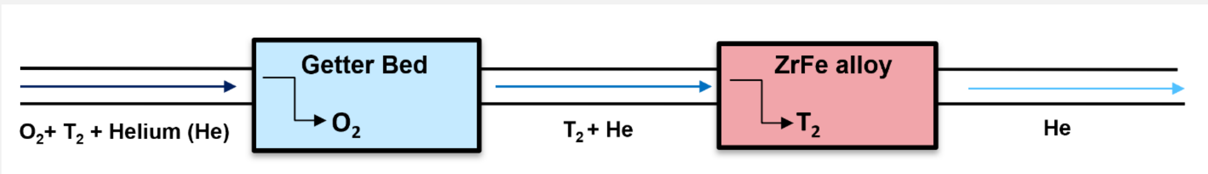
Abstract

Nickel (Ni) and copper-zinc (CuZn) getter beds were analyzed for their relative efficiency in extracting oxygen from inert gas streams. The Ni bed was oxidized at various temperatures and carrier-gas flow rates. These results were compared with previously collected CuZn data. The length of the mass transfer zone (MTZ) was used as a measure of effective use of the beds' capacity for oxygen gettering. It was found that the Ni bed at 350°C has a shorter MTZ over the carrier gas flow rates examined in comparison to the CuZn bed at 150°C. Additionally, the MTZ was found to decrease in length as the temperature of the Ni bed increased from 350°C to 450°C. The shorter MTZ length of the Ni bed is indicative of a greater oxygen breakthrough capacity in comparison with the CuZn bed.

1. Introduction

Tritium (T_2) handling equipment is encased in gloveboxes to minimize environmental releases. The inert gas flow circulating through the glovebox is processed by a system designed to remove gaseous T_2, a radioactive isotope of hydrogen, from the gas flow. In this system, a zirconium-iron (ZrFe) alloy is utilized to capture T_2. Trace amounts of oxygen that permeate the glovebox environment through the elastomeric glove material can irreversibly oxidize the ZrFe alloy, preventing the absorption of T_2 and reducing the alloy's capacity for T_2 storage.[1] To prevent this degradation, a getter bed removes O_2 from the gas stream prior to the ZrFe alloy as shown in Fig.1.

Figure 1: Schematic of the glovebox inert gas flow cleanup system.



Two getter bed options that capture oxygen through oxidation are Ni and CuZn alloy. After the full oxygen capacity of the getter bed is reached, the bed is removed from the system and regenerated through reduction by creating water with hydrogen gas.

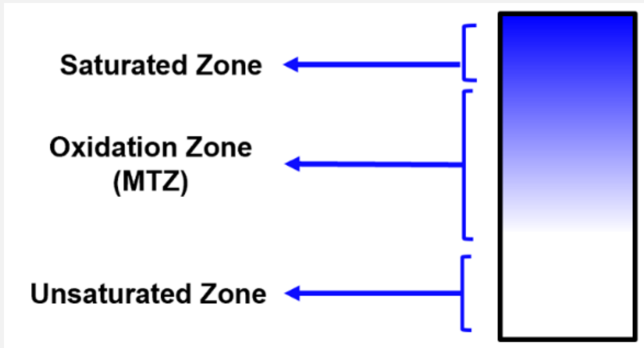
$$\text{Oxidation: } 2Ni + O_2 \rightarrow 2NiO$$
$$\text{Reduction: } NiO + H_2 \rightarrow Ni + H_2O \qquad (1)$$

or

$$\text{Oxidation: } 2CuZn + O_2 \rightarrow 2CuO + 2Zn$$
$$\text{Reduction: } CuO + Zn + H_2 \rightarrow CuZn + H_2O \qquad (2)$$

As the getter bed undergoes oxidation, a mass transfer zone is developed immediately upon introduction of oxygen flow to the bed and progresses down the length of the bed (Fig. 2). The MTZ is defined as the oxygen-getter reaction zone in which getter is being oxidized.[2] As the MTZ progresses down the length of the bed, it creates a saturated zone in which the getter bed is fully oxidized. The MTZ was previously measured for CuZn for areal flow rates from 0.1 to 3.5 cm/s at 150°C.[3] In this work, data was collected to characterize the MTZ of Ni at similar flow rates for two temperatures: 350°C and 450°C. This data was then compared with the CuZn bed data for the purpose of determining which of the two is the more efficient oxygen getter bed.

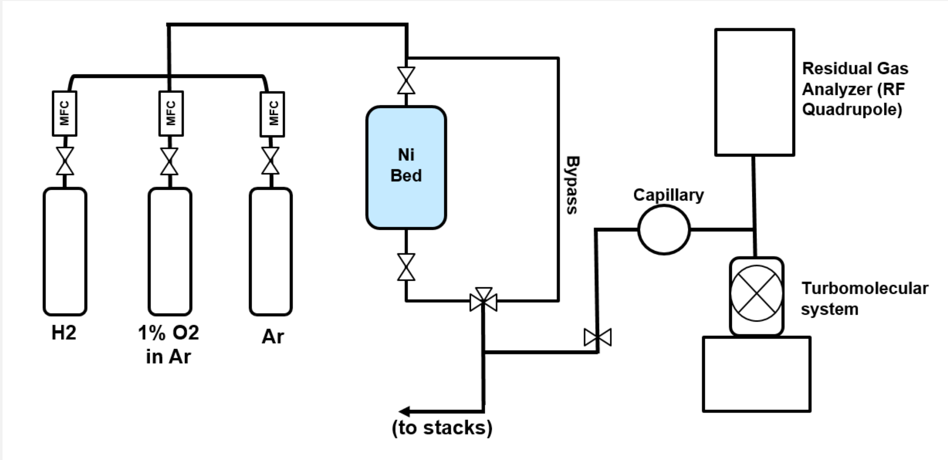
Figure 2: Mass transfer zone of the getter bed.



2. Experimental

The experimental set up shown in Fig. 3 allowed for control of the route and rate of the gas flow in order to simulate the flow conditions of a typical glove box inert gas stream. The bypass, which provided an alternative path for the gas flow around the Ni bed, was used for calibration prior to oxidation data collection. After traveling through either the bypass or the Ni bed, a small portion of the gas flow was siphoned off with capillary tubing in order to sample the composition of the gas leaving or bypassing the Ni bed. The chemical composition of the bed's outlet gas stream was measured with a residual gas analyzer (RGA). In the RGA system, the gas molecules were ionized by a hot cathode, then accelerated through an oscillating electric field (provided by the radio frequency quadrupole) for the purpose of finding the mass to charge ratio of the gas ions.[4] The remainder of the gas was released to the stacks. A turbomolecular system was used to create the high vacuum conditions necessary for the operation of the RGA. The bed was heated to temperatures ranging from 350°C to 450°C for the experiments while the overall system was kept at 150°C and insulated to prevent water condensation. The temperature was measured by thermocouples. The pressure of the system was monitored by a cold cathode gauge (not shown in Fig. 3) and a capacitance manometer (not shown in Fig. 3).

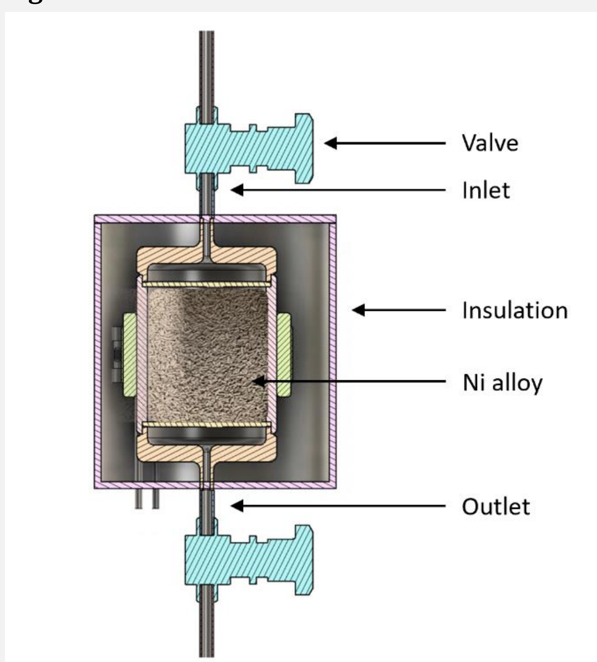
Figure 3: Schematic of experimental set up.



2.1 Getter Bed

The Ni bed used in this experiment consisted of a cylinder with diameter and length dimensions of 5.4 cm × 9.144 cm packed with 1.2 mm × 3 mm Ni pellets. The bed, shown in Fig. 4, was surrounded by insulation to minimize heat loss. To make the data gathered in this project applicable to any Ni bed rather than exclusively to the Ni bed dimensions used, the MTZ was measured as a function of areal velocity, defined as total gas flow rate (cm^3/s) ÷ bed cross sectional area (cm^2).

Figure 4: Schematic of Ni bed.



2.2 Gases and Gas Flow

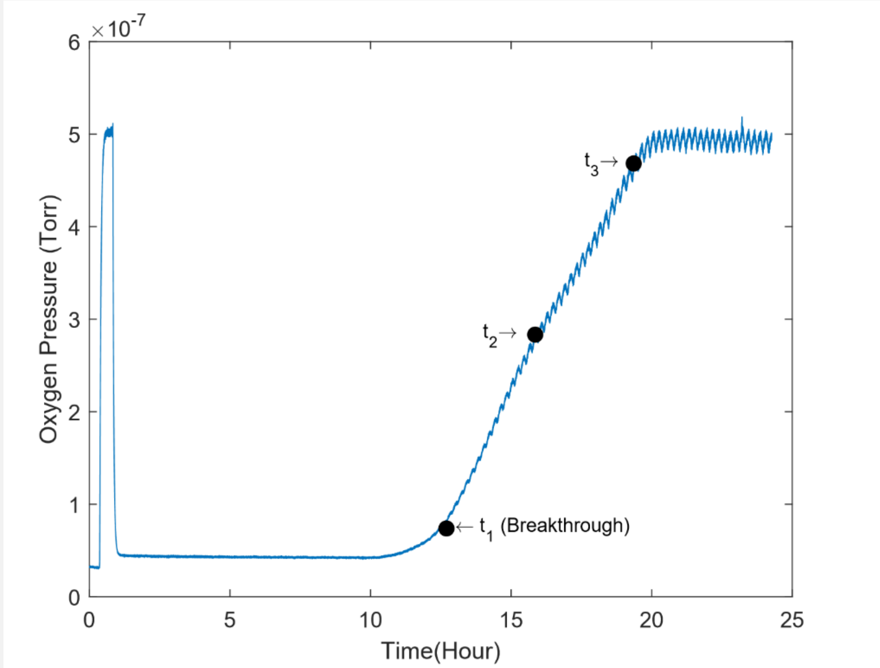
Argon, 1% oxygen in argon, and hydrogen were used in this experiment. Argon, an inert gas, was used for purging the system of residual gases between oxidations and as a carrier gas for oxygen and hydrogen. The flow rate of argon was adjusted for each oxidation to make areal velocity an independent experimental variable. The total gas flow rate considered in the calculation of areal velocity is the sum of the 0.97 LPM 1% O_2 in Ar (or 0.0238 mol O_2 per hour) and the varied Ar flow rate (0.1 to 2.75 LPM). After the bed was oxidized, 50 standard cubic centimeters per minute (sccm) of hydrogen gas reduced the bed by creating water in the regeneration process.

Within the flow rate range used for this experiment (0.1 to 2.75 liters per minute (LPM) of Ar + 0.97 LPM O_2 in Ar), the areal velocity through the bed is 0.7 to 2.7 cm/s and the residence time in the bed (bed volume ÷ volumetric flow rate) is 1.4 to 52 s. Under these flow rate conditions and the temperature range used (350°C to 450°C) the modified Reynolds number (particle diameter × areal velocity × density of fluid ÷ gas viscosity) is 0.17 to 0.46. This value indicates that the gas flow is laminar and its velocity profile can be visualized as a plug flow.

2.3 Oxidation

The graph of the partial pressure of oxygen over time throughout a typical oxidation cycle of the Ni bed is shown in Fig. 5. Before oxidizing the bed, the bypass line and bed were purged with an argon flow to remove trace gases from the previous run. This is shown by the low levels of oxygen at the start of the graph. After the argon purge, a fixed flow rate of 1% oxygen in argon was passed through the bypass for calibration of the RGA, creating a sudden increase in oxygen partial pressure near the beginning of the graph. After half an hour of calibration, the gas flow route was switched to the Ni bed, resulting in a rapid decrease in the partial pressure of the oxygen flow in the outlet stream as the Ni bed began consuming oxygen through oxidation of the alloy. As the Ni bed nears maximum oxygen capacity (see "breakthrough" in Fig. 5), it is no longer able to absorb the majority of the oxygen flow, causing a gradual increase in the partial pressure of oxygen that is able to flow past the Ni bed to the outlet stream.

Figure 5: Partial pressure of oxygen as a function of time during oxidation at 350°C with 1 LPM Ar and 0.97 LPM 1% O_2 in Ar.



2.4 Mass Transfer Zone

Prior to breakthrough (see Fig. 2), there exists a region of the bed below the MTZ in which there is little to no oxygen present, resulting in a low partial pressure of oxygen in the outlet. The length of the MTZ is calculated with three specific time markers on the MTZ curve, shown in Fig. 5. The first time marker t_1 (i.e., breakthrough) is defined as the time at which the oxygen concentration in the outlet is 15% of the feedstock and t_3 when the oxygen concentration is 85%. The second time marker t_2 is when

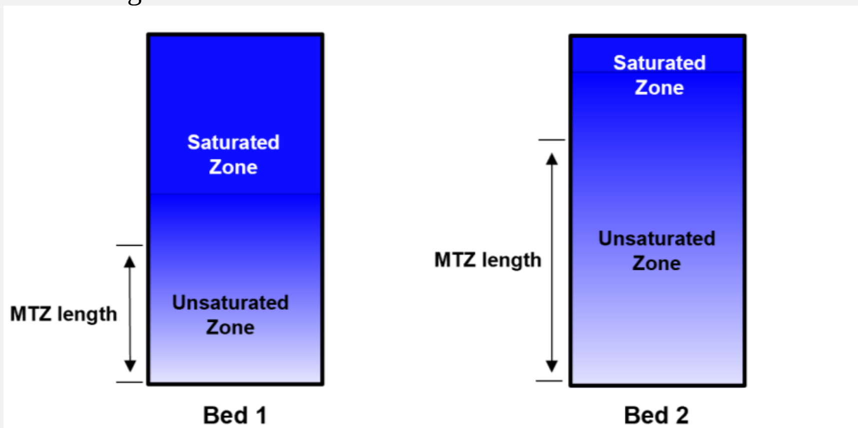
$$\int_{t1}^{t2} P(t)\, d(t) = \int_{t2}^{t3} (P(t_3) - P(t))\, d(t)\,, \tag{3}$$

where P(t) is the partial pressure of oxygen in the carrier gas over time. From the values of t_2 and t_1, the MTZ length can be calculated by:

$$MTZ\ length = \frac{length\ of\ bed}{(t_2)} \times (t_2 - t_1) \times 2\,. \tag{4}$$

Beds 1 and 2 represent two different getter beds at breakthrough in Fig. 6. The MTZ length of Bed 1 is shorter than that of Bed 2. Correspondingly, the volume of the bed which is incompletely saturated is smaller in Bed 1 in comparison to Bed 2. This indicates that Bed 1 has utilized the oxygen capacity of the bed more effectively than Bed 2 because a greater fraction of the bed is used to capture oxygen. For the purposes of this work, the effective use of the beds' oxygen capacity, or MTZ length, was used as a comparative measure of the beds' efficiency.

Figure 6: MTZ length comparison of two different getter beds at breakthrough.



2.5 Oxygen Gettering Capacity

Capacity is defined as the maximum number of moles of oxygen that the bed can absorb at a given flow rate and temperature. The flow rate of oxygen was kept constant at 0.0238 mol/hour throughout all of the oxidation experiments. The fraction of the oxygen flow rate that is unabsorbed by the bed is proportional to the pressure of oxygen at the outlet of the bed (Fig. 5). The bed is absorbing the majority of the flow rate before t_1 and gradually decreases in the amount of oxygen absorbed from t_2 to t_3. The oxygen capacity in moles was approximated to be

$$Oxygen\ Capacity = 0.0238 \times t_2 \tag{5}$$

where t_2 is measured in hours.

3. Results and Discussion

The MTZ length and capacity calculated from the Ni oxidations gathered throughout this work are shown below in Table 1.

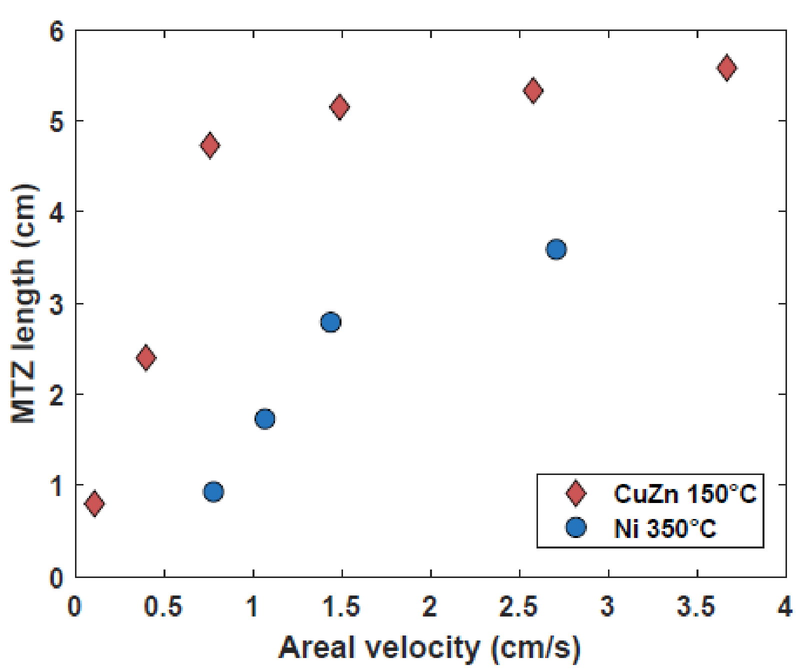
Table 1: Data collected for the Ni bed capacity and MTZ length for various flow rates/areal velocities and temperatures.

Temperature (°C)	Argon Flow Rate (L/min)	Areal Velocity (cm/s)	Capacity (moles oxygen)	MTZ length (cm)
350	0.1	0.78	0.36	0.93
350	0.5	1.07	0.28	1.73
350	1	1.43	0.35	2.79
350	2.75	2.71	0.33	3.59
450	2.75	2.71	0.31	3.2

3.1 Comparison of MTZ length in the Ni and CuZn beds

The dependency of the MTZ length on areal velocity for nickel at 350°C was compared with the CuZn data at 150°C in Fig. 7. It was found that the Ni bed has the shorter MTZ for areal velocities from 0.78 to 2.7 cm/s. These results suggest that that the Ni bed has a greater oxygen adsorption capacity prior to breakthrough, with the concession that the CuZn bed operates at a lower temperature.

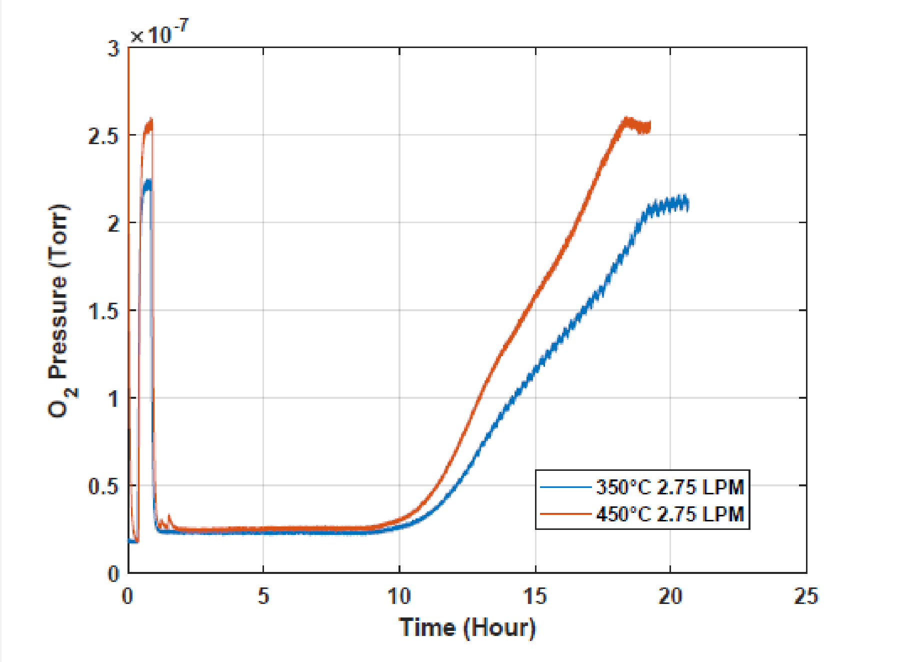
Figure 7: Comparison of MTZ lengths of CuZn and Ni beds. The CuZn data was collected in previous research.[3]



3.2 Temperature Dependence of the MTZ length of the Ni bed

The MTZ length of the Ni bed was measured at 350°C and 450°C at the areal velocity of 2.71 cm/s (or argon flow rate of 2.75 L/min). This areal velocity was chosen to find the temperature dependency as the divergence of MTZ lengths was expected to become more evident at higher areal velocities. As shown in Fig. 8, the slope of the O_2 pressure-versus-time curve at 450°C is greater than in the 350°C oxidation case, indicating that the MTZ for the 450°C case is shorter. Table 1 shows the calculated MTZ lengths for these two operating temperatures; the MTZ length in the 450°C case is 3.2 cm in comparison to the 3.59 cm for the 350°C oxidation case.

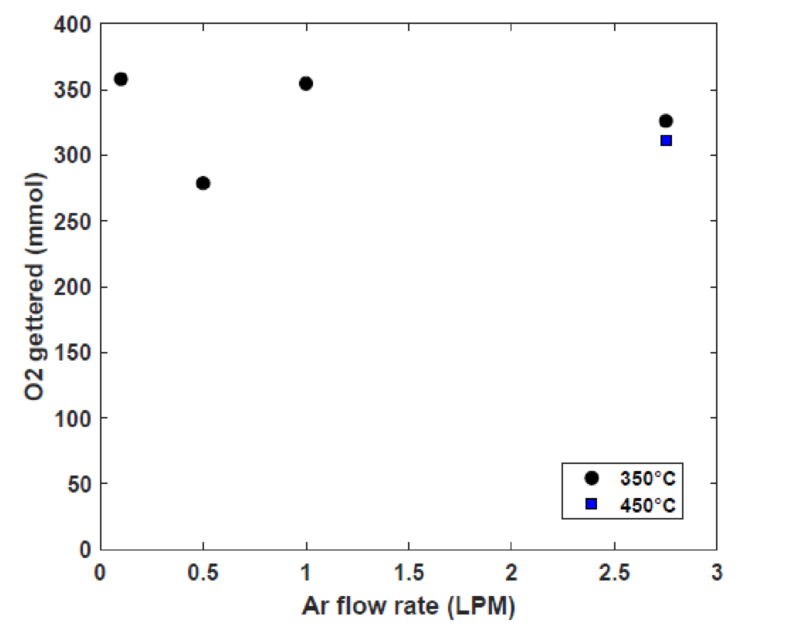
Figure 8: Oxygen partial pressure over time in 350°C and 450°C oxidation of Ni bed at an argon flow rate of 2.75 LPM.



3.3 Temperature and Flow Rate Dependency of the Ni Bed's Capacity

The dependence of the nickel bed capacity on flow rate and temperature is shown in Fig. 9. The data show a trend of decreasing oxygen capacity with increasing flow rate. This is expected because, from Fig. 7, the MTZ length increases with increasing flow rate. As discussed earlier, the capacity is expected to decrease with increasing MTZ length. The data point at 0.5 LPM is an outlier within the trend with a lower oxygen capacity suggesting that the reduction prior to the experiment was incomplete, resulting in a partially oxidized bed at the start of the oxidation. The decreased capacity of the Ni bed at 450°C in comparison to 350°C differs from the observations for the CuZn bed,[3] for which the oxygen capacity was found to increase with temperature. Further data collected from the Ni bed at 450°C may clarify the source of this difference.

Figure 9: Oxygen capacity of the Ni bed at 350°C and 450°C as a function of Argon flow rate.



4. Conclusion

The purpose of this work was to compare the efficiency of the Ni and CuZn getter beds in removing oxygen from inert gas streams. The MTZ length of the Ni at 350°C and CuZn at 150°C were compared for various areal velocities. It was observed that the MTZ of the Ni bed is shorter within the areal velocity range of 0.78 to 2.71 cm/s, suggesting that the Ni bed has greater oxygen gettering efficiency within this range. Additionally, the MTZ length of the Ni bed was found to decrease as temperature increases from 350°C to 450°C. These results suggest that the Ni bed at 350°C can be implemented within tritium glovebox systems for increased oxygen adsorption performance in comparison to the CuZn bed at 150°C.

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