

Oxygen Uptake Using a Nickel Catalyst

MaryKate Hanchett

Fairport High School

LLE Advisor: Walter Shmayda

Laboratory for Laser Energetics

University of Rochester

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Abstract

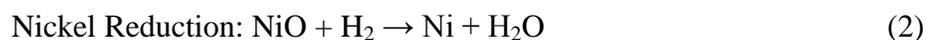
A Zirconium-iron alloy is used to absorb tritium that has escaped from process systems at LLE. Oxygen deactivates the alloy and decreases its ability to remove tritium from effluent streams. A nickel catalyst is used to crack tritiated hydrocarbons and to capture elemental oxygen. The capacity of nickel beds is finite and they require periodic reactivation using hydrogen in a helium carrier stream. Experiments have been conducted to study the efficiency of oxygen uptake and the efficiency of reactivation. Increasing the temperature of the catalyst from room temperature to 400 °C increases the amount of oxygen that can be absorbed by the catalyst. Catalyst reactivation is more efficient as the flow rate of hydrogen increases. Water vapor in the vicinity of the nickel inhibits reactivation; increasing the carrier flow rate decreases the water vapor pressure and improves the reactivation efficiency.

1. Introduction

Tritium process equipment is typically encased in gloveboxes to minimize tritium losses to the environment and to protect operators from tritium exposure. An inert gas is the preferred cover gas in a glovebox because elemental hydrogen (T_2) that has escaped from the process loops can be recaptured. Helium is the inert gas of choice. However, small amounts of air (N_2 , O_2 , H_2O) permeate through the gloves in the box. These impurities contaminate the helium cover gas at the rate of a few parts per million per hour. The impurities are removed from the cover gas by circulating it through a drier to remove water, an oxygen getter to remove oxygen, and finally a zirconium-iron alloy (ZrFe) to capture the tritium. The function of the drier and the oxygen getter is to protect the ZrFe bed.

Air that diffuses into the glovebox and its streams provides an obstacle to absorbing tritium with the ZrFe alloy. Oxygen coats the surface of the ZrFe alloy and retards the ability of the alloy to remove tritium. Oxygen also consumes the ZrFe alloy, reducing its capacity to store hydrogen. The ZrFe alloy can also crack water to absorb the hydrogen and oxygen. This process is irreversible like the absorption of oxygen, and therefore decreases the effectiveness of the alloy to capture tritium and increases the number of times that the alloy must be replaced.

A molecular sieve bed is placed upstream of the ZrFe alloy to remove the H₂O vapor. However, the issue of oxygen consumption remains. This issue can be resolved by the use of nickel or copper catalysts placed in the glovebox's stream. These catalysts can crack tritiated hydrocarbons and capture elemental oxygen. With heat and hydrogen gas, the catalysts can be regenerated. The reaction equations are:



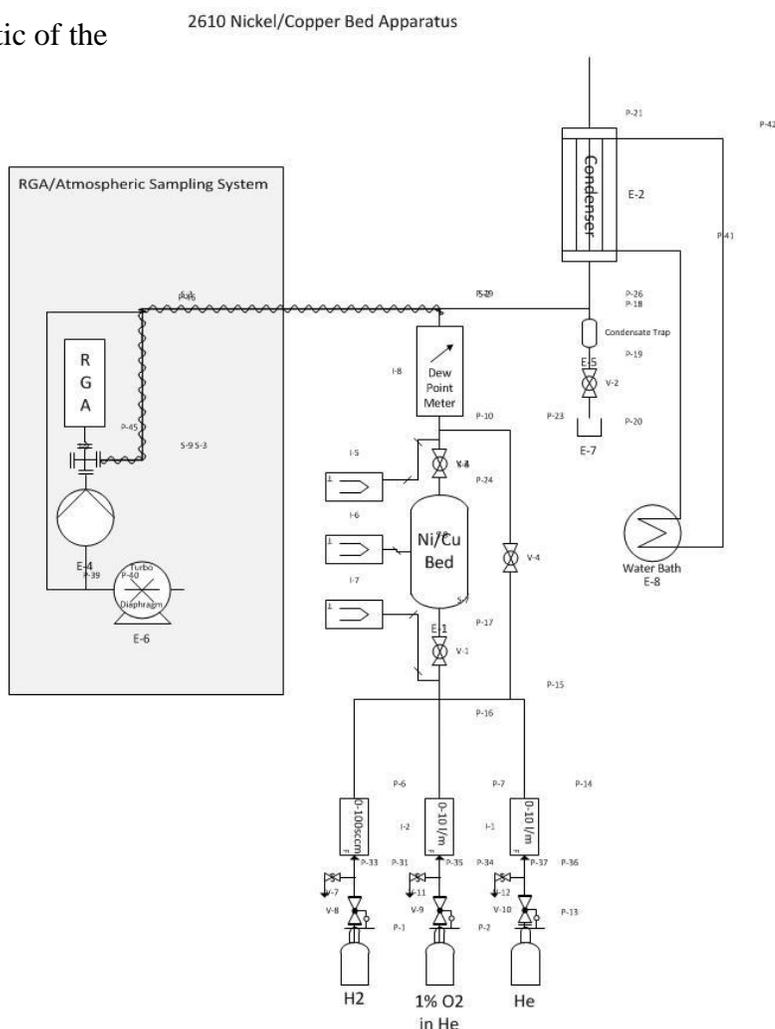
It can be seen that one mole of oxygen will react with 2 moles of activated nickel. In the second equation, one mole of hydrogen gas is required to decompose one mole of NiO. One mole of water is generated in the process.^{1,2}

In this experiment, nickel supported on 1/8" alumina spheres was tested. This type of catalyst is currently in use at LLE. It has a spherical form to maximize surface area within the bulk. The purpose of the experiment was to understand which parameters need to be controlled to maximize the efficiency of this particular nickel bed by adjusting variables such as carrier flow rates and temperature. The objective of this work was to establish a baseline against which new catalysts will be compared.

2. Experimental

An apparatus was constructed to test for the desired temperatures and gas flow rates for maximum efficiency of oxygen uptake and nickel reduction. As shown in Figure 1, paths are available for gases to flow through the nickel bed or around the nickel bed. Heating components, placed around the bed and tubing, prevent water vapor from condensing in the circuit. A condensation unit to collect water vapor produced during the reactivation of the nickel is placed at the top right of the schematic. The Residual Gas Analyzer (RGA), dew point monitor, and thermocouples are used in data acquisition.

Figure 1: A schematic of the apparatus.



2.1 Gases

Three gases were used to test the nickel getter bed. Three mass flow controllers were used to turn on and off the gas flow and to control flow rates. Helium was used to purge the air from the system, as a carrier gas, and to calibrate the data acquisition systems. Helium was flowed at flow rates varying between 100 scc/min and 4 L/min (equivalent to 4,000 scc/min). A mixture of 1% oxygen in helium was used to load the bed with oxygen. Hydrogen was flowed at varying flow rates from 2 to 50 scc/min with varying flow rates of helium to regenerate the bed. The gases can either be flowed through the nickel bed or through a bypass for control and calibration. The sensors for the data acquisition are placed at the junction of the exhaust from both the bed and the bypass.

Breakthrough occurs when the partial pressure of oxygen downstream of the catalyst increases above the background partial pressure during the load phase. The progressive deterioration of the nickel's ability to collect oxygen can be viewed on the RGA computer display as a function of time. When the bed is being loaded, the partial pressure of oxygen read at the exhaust is lower than the feedstock concentration because the oxygen is being removed from the gas stream by the bed. Breakthrough indicates that the bed can no longer absorb all of the oxygen present in the stream; it is approaching its maximum capacity at that temperature.

2.2 Properties of the Nickel Catalyst

The nickel catalyst used for this experiment is manufactured by Johnson Matthey. It is 1/8" nickel supported on alumina spheres, Type 0104. It is 60% nickel by weight and has a surface area of around 125 m²/kg.³

2.3 Data Acquisition Equipment

A Residual Gas Analyzer (RGA) and a National Instruments data acquisition system were used. The RGA has the capability to measure the partial pressure of different species in the carrier and the total pressure of the gas mixture. Thermocouples for the National Instruments system were placed before the nickel bed, on the nickel bed, and at the exhaust of the nickel bed to determine the temperatures of the gases entering the bed, the temperature of the nickel bed, and the temperature of the gases leaving the bed. They are represented in Figure 1 by the horizontal rectangles to the left of the nickel bed. The dewpoint (DP) was also tracked with a National Instruments card. The DP sensor was placed at the exhaust of the nickel bed.

2.4 Heating Components

Both the bed and capillary tubing were heated. The capillary tubing carries the gases from the exhaust of the bed to the RGA. A heating band was placed around the nickel bed and was monitored by the National Instruments system. The temperature of the nickel bed was set to range from ambient to 500 °C. Heating tape was placed around the capillary tubing and the entrance to the RGA to keep water in a vapor form. The heating tape was kept at 120 °C.

2.5 Water Collection

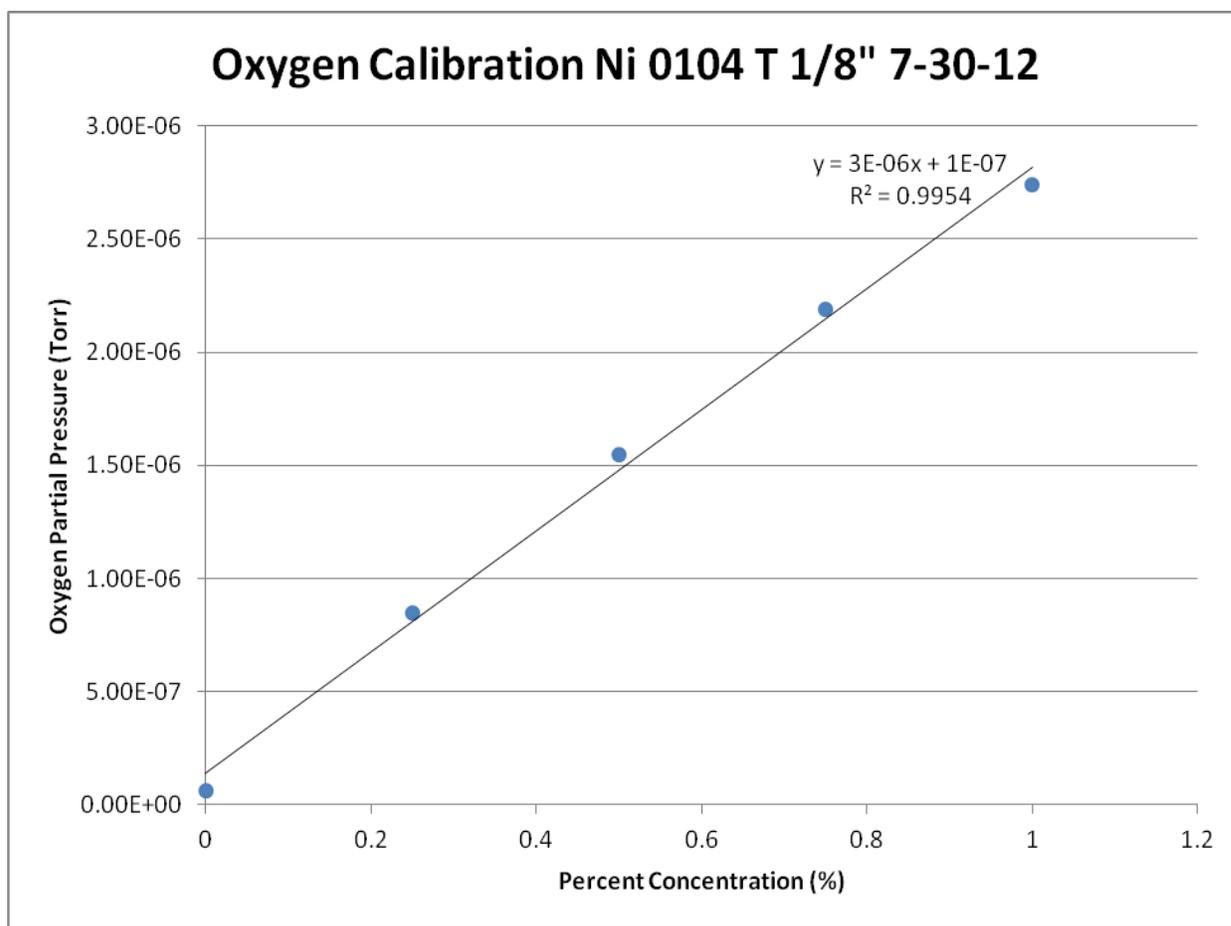
When the bed is regenerated, water is produced. To measure the amount of water produced, and to remove it from the apparatus and experimental system, a condensation unit is placed after the RGA at the exhaust – it is at a lower elevation with sloping tubing so gravity aids the removal of water. A water bath was used to cool the tubing to condense the water vapor into

liquid form. After condensation, the water collected and the amount produced could be measured using a graduated cylinder.

2.6 Calibration

Before starting the experiment, the system was calibrated to determine the partial pressure of oxygen, in Torr, measured by the RGA when different concentrations of oxygen were passed through the system. This was done to provide a reference for when oxygen was loaded onto the bed during the experiment. One can tell from the partial pressure of oxygen measured by the RGA if the bed is nearing its full capacity for oxygen.

Figure 2: Oxygen Partial Pressure vs. Percent Concentration



3. Results and Discussion

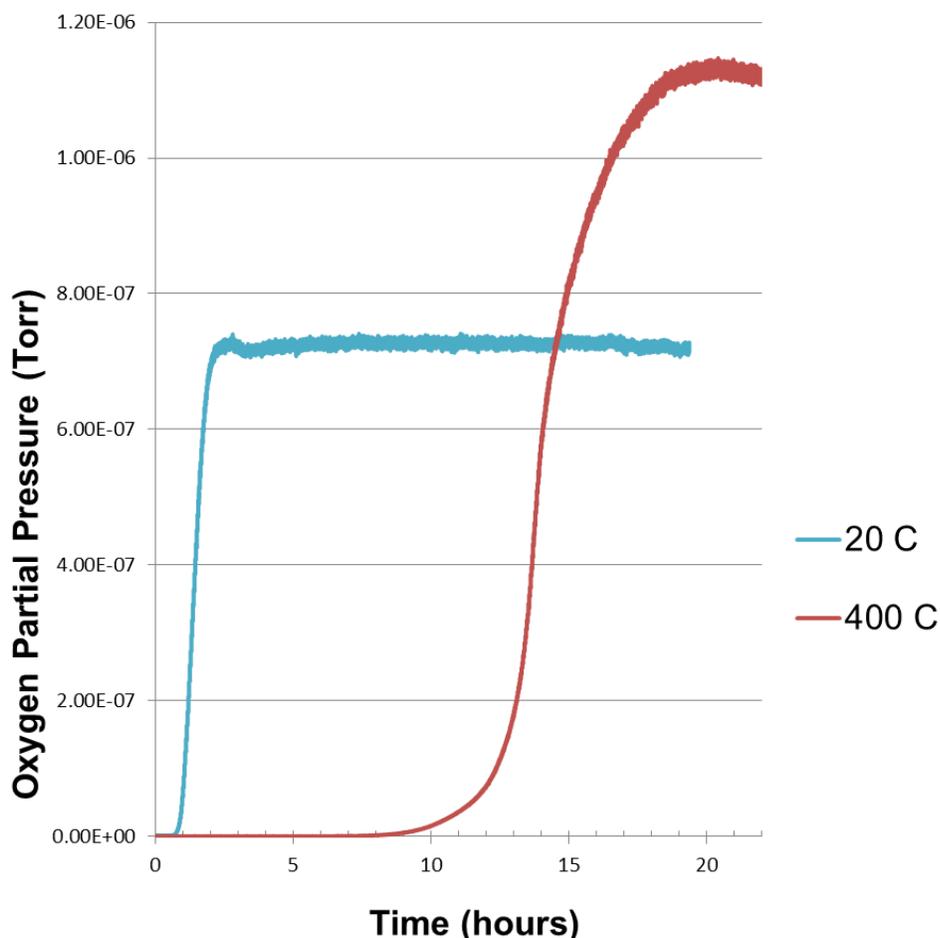
3.1 Oxygen Uptake

The efficiency of oxygen uptake by the Ni bed was investigated in experiments in which the flow rate of a homogeneous mixture of 1% oxygen in helium was held constant at 2 L/min while the temperature of the bed was varied. Results for the oxygen partial pressure as measured by the RGA are shown in Figure 3.1. Defining breakthrough as the time at which the amount of oxygen leaving the bed exhaust is equivalent to 1% of the feedstock concentration, it is found that as the catalyst temperature increases from 20 to 400 °C, the time for oxygen breakthrough to occur increases. The breakthrough time is shown for three bed temperatures in Table 3.1. 400 °C is a practical maximum temperature for loading. At this temperature the nickel exhibits good oxidation properties without generating an excessive heat load around the bed or carrier stream. As demonstrated in Table 3.1 and Figure 3.2, oxygen took around 10 times as long to break through at 400 °C as it did at 20 °C . Clearly, bulk nickel is participating in the oxidation process.

Bed Temperature (°C)	Break Through Time (hours)
20	1
200	2.5
400	10

Table 3.1: Breakthrough time for oxygen flowing over the nickel bed at varying temperatures, obtained from graphs such as that of Figure 3.1.

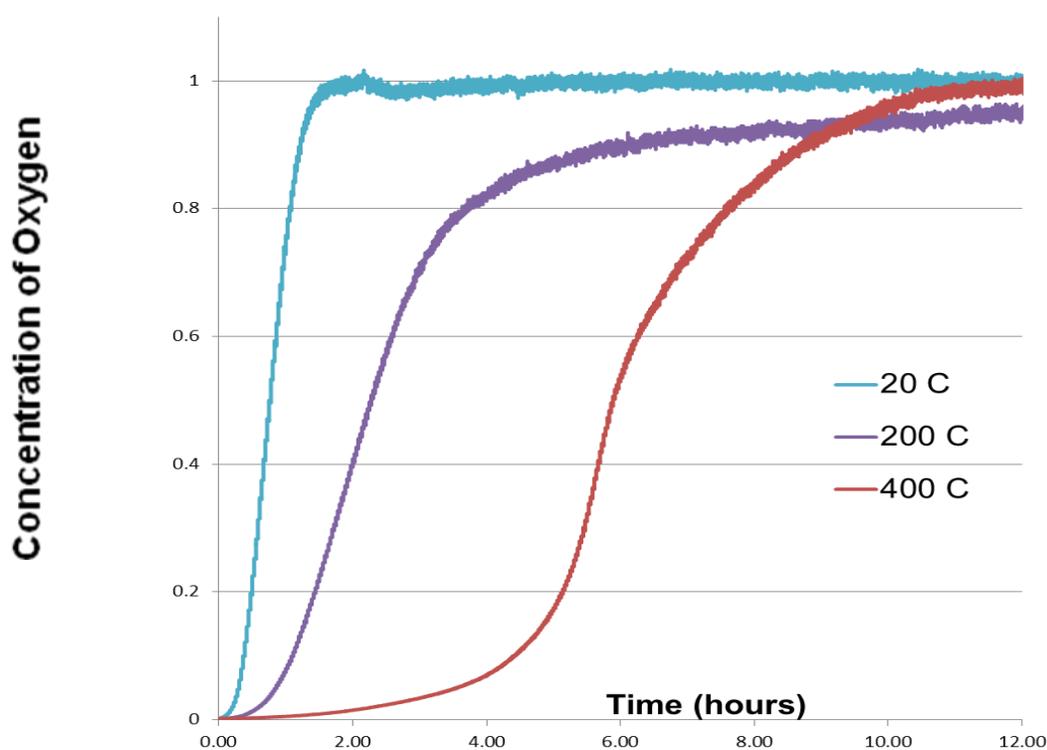
Figure 3.1: Oxygen partial pressure measured by the RGA as a function of time for two different temperatures of the nickel bed at a helium flow rate of 2 L/min.



The Mass Transfer Zone (MTZ) is the transition region in which the oxygen concentration in the carrier changes from the inlet value to the outlet value. In Figure 3.1, the MTZ is on the order of 3 cm, or half the length of the bed, for the flow conditions and operation at 400 °C. The MTZ and capacity for oxygen uptake increase with temperature. Higher operating temperatures are preferred. At lower temperatures the reaction between the oxygen and nickel is limited to a surface reaction; the bulk does not participate. As shown in Table 3.2, the capacity of the nickel to absorb oxygen increases tenfold by increasing the operating temperature from 20 °C to 400 °C.

Table 3.2: Comparison of capacity of nickel bed and fraction of nickel bed at differing temperatures.		
Bed Temp. (°C)	Capacity (mol of O₂ loaded onto nickel bed)	Fraction of Ni Bed
20	.05	.05
200	.13	.12
400	.54	.50

Figure 3.2: Concentration of oxygen measured by the RGA relative to the concentration of oxygen in the incoming helium flow as a function of time for three different temperatures.



The evolution of the oxygen concentration in the carrier leaving the bed is illustrated in Figure 3.2 for three different operating temperatures. The carrier flow rate is fixed at 2 L/min and

contains 1% oxygen. Nickel removes the oxygen from the incoming stream to form nickel oxide. Oxygen-free helium leaves the bed and oxygen is absent from the outlet stream until some fraction of the nickel has been converted to nickel oxide. Once breakthrough occurs, the oxygen concentration in the outlet increases toward 1%, the inlet value. Inspection of Figure 3.2 indicates that the time for breakthrough increases with increasing operating temperature.

Figure 3.3: Partial pressure of oxygen as a function of time, illustrating the mass transfer zone for nickel at 200 °C.

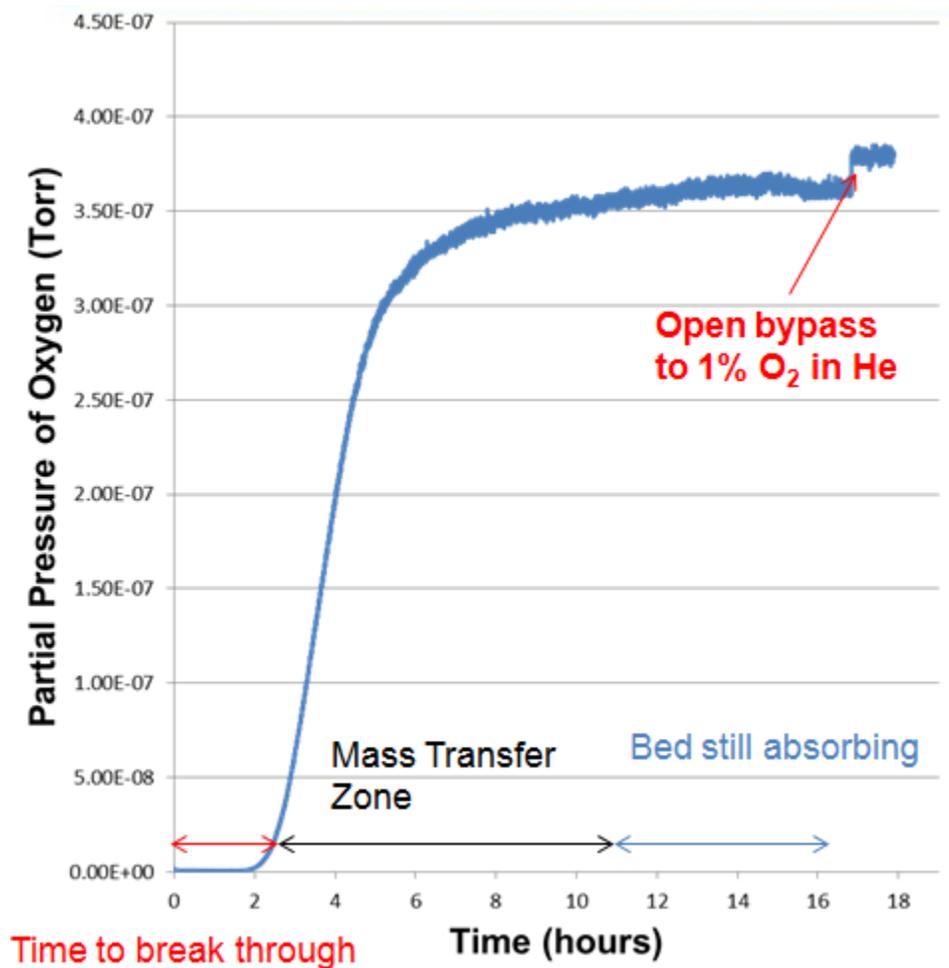


Figure 3.3 indicates that saturation is approached asymptotically. At hour 17, the nickel bed was bypassed to measure the oxygen concentration of the inlet stream. It is evident that the nickel bed continued to remove some oxygen from the stream, albeit not very efficiently. At hour 17, only 12% of the nickel had been converted to oxide. The oxidation process appears to be diffusion limited, either by nickel atom diffusion through the oxide layer or oxygen diffusion into the nickel bulk. Increasing the operating temperature to 400 °C increases the oxygen removal rate. Clearly the diffusion rate at the nickel/nickel-oxide surface has increased. The outlet concentration approaches the inlet concentration in the 400 °C case in Figure 3.2 at hour 12. Fifty percent of the nickel has been oxidized by this time.

3.2 Nickel Reduction (Hydrogen Regeneration)

Nickel oxide can be reduced to nickel at 500 °C in the presence of hydrogen. This means that spent nickel beds can be regenerated with hydrogen to recover their ability to scavenge oxygen from carrier streams. The beds can be re-used.

Figure 3.4: Partial pressure of hydrogen and water, measured by the RGA, as a function of time. Helium carrier flow rate and temperature were held constant at 2 L/min and 500 °C, respectively.

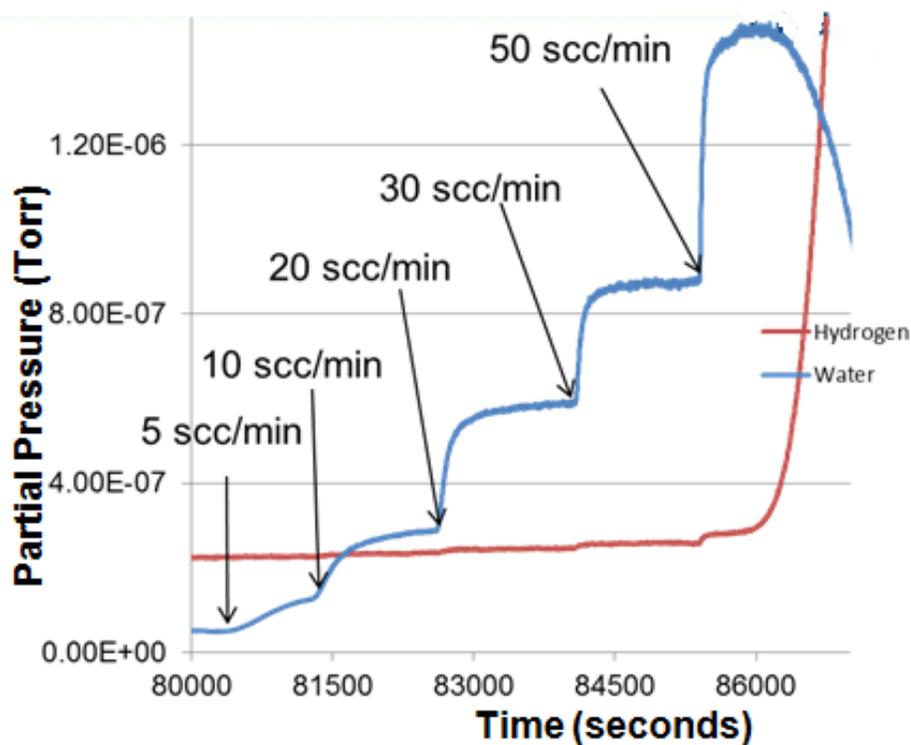


Figure 3.4 illustrates a typical regeneration at 500 °C using a helium purge rate of 2 L/min. As the hydrogen flow rate is increased from 5 scc/min to 50 scc/min the water partial pressure in the carrier at the bed outlet increases proportionately. Towards the end of the run, the water partial pressure is observed to drop and concomitantly the hydrogen partial pressure increases as the quantity of residual nickel oxide in the bed disappears.

Figure 3.5: Partial pressure of water vs. flow rate of hydrogen at three different helium carrier flow rates.

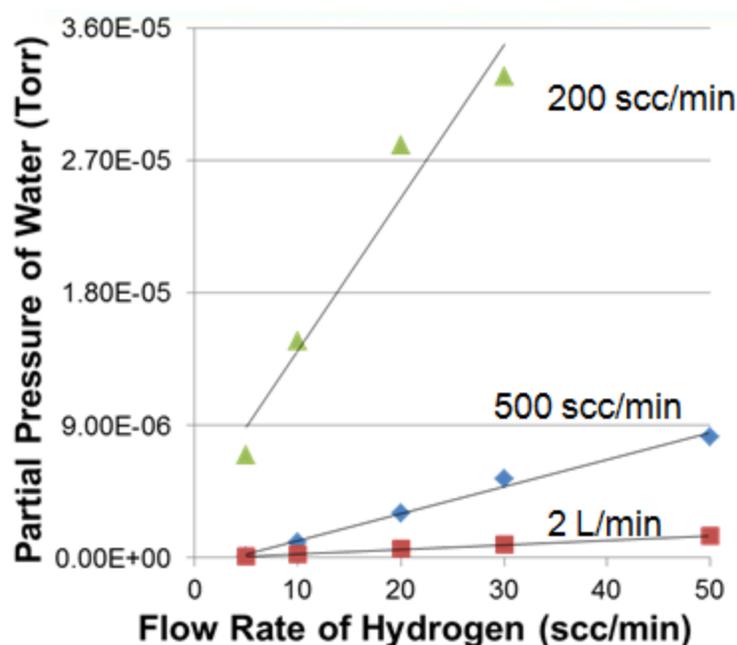


Figure 3.5 summarizes three regenerations at 500 °C for varying helium and hydrogen flow rates. At a helium purge rate of 500 sccm and 2 LPM, the partial pressure of water appears to increase linearly with increasing hydrogen flow rate (or partial pressure). For a helium purge rate of 200 sccm, the water production rate deviates from linearity and appears to approach a saturation value that is independent of the hydrogen partial pressure in the carrier.

Water vapor in the vicinity of the nickel oxide appears to inhibit the reduction process. At low carrier flow rates, water vapor resulting from the nickel reduction remains in the vicinity of the remaining nickel oxide and interferes with hydrogen reaching unreacted nickel oxide. Increasing the helium carrier flow rate encourages the removal of water vapor from the nickel oxide regions and promotes more rapid reduction.³

Figure 3.6: Partial pressure of water and helium vs. time measured by the RGA as the carrier flow was increased at the indicated times.

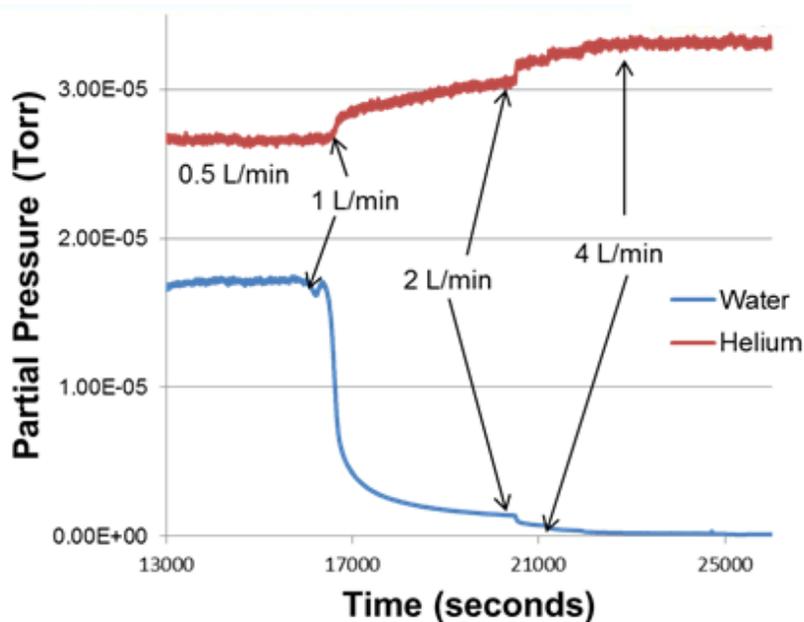


Figure 3.6 illustrates the impact of the helium carrier on the reduction process. In this experiment, the hydrogen flow rate was fixed at 50 sccm and the carrier flow rate varied from 0.5 L/min to 4 L/min. The regeneration temperature was 500 °C. If all water generated in the reduction process is purged from the bed as it is produced, one would expect the water partial pressure in the carrier stream at the bed outlet to be inversely proportional to the carrier flow rate. Doubling the carrier flow rate should reduce the water partial pressure by half. Inspection of Figure 3.6 indicates a dramatic drop in the water partial pressure when the carrier flow rate increases from 0.5 L/min to 1 L/min and significantly smaller changes in the partial pressure when the carrier flow rate is increased further to 2 L/min and then 4 L/min. Evidently the vapor pressure in the carrier at the lowest flow rate is not directly related to the rate of water generation

due to the presence of hydrogen but rather to a balance between the water vapor production rate and the water removal rate from the bed. The increasing helium partial pressure dependence on the increasing helium flow rate is an artifact of the diagnostic used to measure the gas partial pressures. The helium partial pressure should be independent of the flow rate.

Conclusion

Increasing the temperature of the catalyst from room temperature to 400 °C increases the amount of oxygen that can be absorbed by the catalyst. Catalyst reactivation is more efficient as the flow rate of hydrogen increases. Water vapor in the vicinity of the nickel inhibits reactivation; increasing the carrier flow rate decreases the water vapor pressure and improves the reactivation efficiency.

Higher operating temperatures are preferred for both oxygen uptake and nickel reduction. Higher flow rates are preferred in nickel reduction for both hydrogen and the carrier gas.

References

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