Characterizing a Cu/Mn Alloy for Extracting Oxygen from Inert Gas Streams

Grace Lenhard

Prattsburgh Central School

LLE advisors: Walter Shmayda and Matthew Sharpe

Laboratory for Laser Energetics

University of Rochester

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Abstract

Gloveboxes filled with inert gases are used to reduce the release of tritium, a radioactive isotope of hydrogen used in fusion studies at LLE, into the atmosphere. A zirconium/iron (Zr-Fe) alloy is used to remove tritium chronically released into the gloveboxes. However, some atmosphere permeates into the gloveboxes through the gloves and seals. Oxygen and water deactivate the Zr-Fe bed, so they must be removed from the gas stream. A copper/manganese (Cu/Mn) alloy was investigated as an alternative to nickel, the current oxygen getter. Oxygen in a carrier stream of helium is flowed over the alloy, allowing it to getter oxygen. The amount of oxygen exiting the bed is measured as a function of time to determine the bed capacity. When the amount of oxygen leaving the bed is nearly equal to the amount of oxygen being flowed into the bed, the bed is considered full. This procedure was repeated for alloy temperatures of 200°C, 300°C, and 400°C with a helium flow rate of 1 LPM containing 1% oxygen. As the temperature increased, the bed capacity increased. However, a change in the bed temperature had no significant effect on the bed efficiency. Flowing oxygen over the bed also produced a small quantity of water, even if the bed had been dried beforehand, suggesting water creation from hydrogen within the alloy.

1. Introduction

At LLE, gloveboxes are used to reduce tritium escape into the environment [1]. Tritium and inert gasses are run through a system which utilizes a Zr-Fe bed to recapture escaped tritium. However, small amounts of oxygen and water that seep into the gloveboxes can deactivate the Zr-Fe bed. A molecular sieve collects the water vapor and an oxygen getter collects the oxygen before the gas stream is passed over the Zr-Fe bed [2, 3, 4, 5]. The current oxygen getter is a nickel bed [6], but alternatives such as a copper/zinc alloy have been tested [4]. After the bed is full, it is regenerated with hydrogen, forming water. The reactions are:

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

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

In this experiment, Cu/Mn was tested as a possible oxygen getter for tritium gloveboxes. Its gettering capacity (the amount of O_2 absorbed by the bed) was tested at 200°C, 300°C, and 400°C with a constant flow rate of 10 sccm oxygen to determine the most efficient temperature for oxygen gettering with Cu/Mn. At lower temperatures, the copper oxidized, but at higher temperatures the manganese also oxidized. The reactions are:

Copper oxidation: $O_2 + 2Cu \rightarrow 2CuO$ (3)

Manganese oxidation: $O_2 + Mn \rightarrow MnO_2$ (4)

After the bed is loaded (filled to capacity), it is regenerated with hydrogen, yielding the reactions:

Copper reduction: $CuO + H_2 \rightarrow Cu + H_2O$ (5)

Manganese reduction: $MnO_2 + 2H_2 \rightarrow Mn + 2H_2O$ (6)

2. Experimental

A system was built to test the gettering capacity of Cu/Mn (fig. 2.1). The flow of the gasses used (He, H_2, and 1% O_2 in He) was controlled using mass flow controllers (MFC) and valves (1-6) allowed the gas to be flowed either through the Cu/Mn bed or through a bypass. At the end, the gasses were sent through a dew point sensor to record temperature and relative humidity. A residual gas analyzer (RGA) determined the composition of the gas. The RGA monitored for helium, hydrogen, and oxygen. Nitrogen was also monitored to ensure against leaks into the gas system.

The stainless-steel piping was heated to 100°C to prevent condensation on the plumbing surfaces. The temperature of the Cu/Mn bed could be adjusted. Temperatures of 200°C, 300°C, and 400°C were used.

The bed contained 174 ml Cu/Mn in a ratio of 14% Cu (0.29 mol), 56% Mn (1.22 mol), and 30% inert medium. The pellets were 2-3 mm in diameter with a surface area of 200 m^2/g.[1]

Helium was used to purge the system and as a carrier gas for hydrogen. It was flowed at a rate of 1 L/min at most times. Hydrogen was flowed with the helium to unload the bed. Various flow rates were tested until it was determined that the best flow rate for hydrogen was 10 sccm hydrogen in 1 L/min helium. The hydrogen flow rate was inhibited by water production because if the humidity rose above 40% water would begin to condense out of the gas stream. 1% oxygen in helium was run at 1 L/min to test the capacity of the bed for absorbing oxygen.

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[1] Surface area of gettering material is measured by the total surface area of all particles in a certain mass of the material. In this case, the total surface area of one gram of particles is 200 m^2.

This resulted in an oxygen flow rate of 10 sccm. When the 1% oxygen in helium was flowed, the flow of pure helium was shut off.

The RGA used to measure the partial pressures of the gas in the stream had to be calibrated because the RGA works under a partial vacuum and the proportions of gasses in the RGA are not the same as in the gas stream. Correction factors had to be calculated for each gas using the equations

Hydrogen:

$$C_{H_2} = \frac{\frac{F_{H_2}^{avg}(LPM)}{F_{total}(LPM)} \cdot 101325(Pa)}{P_{H_2}^{RGA}(Pa)} \tag{7}$$

Oxygen:

$$C_{O_2} = \frac{0.01 \cdot 101325\ (Pa)}{P_{O_2}^{RGA}(Pa)} \tag{8}$$

Water:

$$C_{H_2O} = \frac{P_{H_2O}^{carrier}(Pa)}{P_{H_2O}^{RGA}(Pa)} \tag{9}$$

where 101325 Pa is the total system pressure, C_{H_2} is the correction factor for hydrogen, C_{O_2} is the correction factor for oxygen, C_{H_2O} is the correction factor for water, $F_{H_2}^{avg}$ is the average flow of hydrogen, F_{total} is the total gas flow, $P_{H_2}^{RGA}$ is the partial pressure of hydrogen in the RGA, $P_{O_2}^{RGA}$ is the partial pressure of oxygen in the RGA, $P_{H_2O}^{RGA}$ is the partial pressure of water in the RGA, and $P_{H_2O}^{carrier}$ is the partial pressure of water in the carrier stream found from the relative humidity and the vapor pressure of water at the given temperature using the equation

Partial pressure of water:

$$P_{H_2O}^{carrier}(Pa) = RH \cdot P_{vap}(Pa) \tag{10}$$

where RH is relative humidity and P_{vap} is the vapor pressure of water at a given temperature. The partial pressure of gasses in the RGA are multiplied by the conversion factors to get the partial pressure of the gasses in the carrier stream.

3. Results and discussion

3.1 Oxygen absorption

The main objectives of this work were to test the rate of oxygen absorption and to measure the capacity of Cu/Mn at multiple temperatures to determine its usefulness in scavenging oxygen from inert gas streams. To test this, multiple steps were taken. First, 1% oxygen in helium was flowed through the bypass to determine the partial pressure measured by the RGA for that specific run so the conversion factor could be found using equation 8. The bed was then opened to the gas flow. The concentration of oxygen in the outflow quickly dropped to nearly 0, before increasing and eventually leveling out at about the same concentration as when the gas was running through the bypass, creating a breakthrough curve like the one in figure 3.1. After the measured oxygen concentration was level for several minutes, the gas flow was switched back to bypass before the bed was unloaded by flowing hydrogen over it producing water as shown in equations 5 and 6.

The volume of oxygen absorbed was found using the flow rate into the bed (known) and the flow rate out of the bed (determined using the partial pressure of oxygen in the RGA multiplied by the correction factor found using equation 8). The oxygen flow out of the bed (the shaded area in figure 3.1) was determined using

Oxygen flow out: $$V_{O_2}^{out}(\mu mol) = \int F_{O_2}^{out}\left(\frac{\mu mol}{s}\right) dt \qquad (11)$$

where $V_{O_2}^{out}$ is the volume of oxygen not captured by the bed and $F_{O_2}^{out}$ is the flow rate of oxygen out of the bed.

Theoretically, subtracting the amount of oxygen flowed out of the bed from the amount of oxygen flowed into the bed would equal the amount of oxygen gettered by the bed. However, there was also water output when the oxygen was being flowed through the bed (discussed in section 3.2 below), so the volume of water production also had to be taken into consideration using the equation

Oxygen gettered:

$$V_{O_2}^{get}(\mu mol) = V_{O_2}^{in}(\mu mol) - V_{O_2}^{out}(\mu mol) - \frac{V_{H_2O}^{out}(\mu mol)}{2} \qquad (12)$$

where $V_{O_2}^{get}$ is the total volume of oxygen gettered by the bed, $V_{O_2}^{in}$ is the volume of oxygen that entered the getter bed, and $V_{H_2O}^{out}$ is the total volume of water produced by the bed. The last factor is divided by two because one µmol of oxygen is needed to form two µmols of water.

Using these equations, the volume of oxygen gettered by the bed at each temperature was determined. As the temperature increased, the amount of oxygen the bed could hold, or bed capacity, increased, as shown in figure 3.2.

An important extension of this information is the efficiency of the bed. The percentage of oxygen flow that was gettered or converted to water over time was calculated using the equation

$$Efficiency(\%) = \frac{F_{O_2}^{in}(\frac{mol}{s}) - F_{O_2}^{out}(\frac{mol}{s})}{F_{O_2}^{in}(\frac{mol}{s})} \cdot 100\% \tag{13}$$

where $F_{O_2}^{in}$ is the flow rate of oxygen in. As seen in figure 3.3, bed efficiency exceeds 98% when the getter is operating at 200 ^oC and improves slightly with increasing temperature. When the bed approaches capacity, the gettering efficiency drops off rapidly.

Bed efficiency is a critical consideration in how well a material can perform as an oxygen getter in glove boxes. Although the calculations above provide a total bed capacity, the useful bed capacity is the amount of oxygen absorbed before breakthrough. Breakthrough is defined as the point at which more than 1% of the oxygen above background levels gets through. In other words, it is when efficiency drops 1% below the highest efficiency recorded. For Cu/Mn at 200°C, oxygen absorbed before breakthrough is approximately 4% of the theoretical bed capacity (the amount of oxygen that could be absorbed if every atom of copper and manganese were oxidized) and at 400°C oxygen absorbed before breakthrough is 24% of the theoretical bed capacity. For the Ni beds currently used, however, oxygen absorbed before breakthrough is roughly 12% of the theoretical bed capacity at 200°C and 50% of the theoretical bed capacity at 400°C [6]. It is clear that the useful capacity compared to the theoretical capacity of the nickel beds currently used is much higher than that of Cu/Mn.

3.2 Water production during unloading

An interesting artifact of bed loading was water production. Although no water should have been produced during the oxidation of the alloy, approximately 30 mmol of water were produced during each loading run as shown in Table 1. This is substantial considering that average oxygen uptake was between 54 mmol and 324 mmol, depending on the alloy temperature. Water production did not appear to depend on the alloy temperature, as shown in figure 3.4.

Water production was measured using two methods: with a dew point sensor installed in the main stream and by sampling the stream with the RGA. In the first case, the relative humidity is directly proportional to the vapor pressure of water in the carrier provided the carrier temperature is fixed. In the second case the vapor pressure in the carrier can be inferred from the RGA signal once the RGA is calibrated using equation 9.

In the first approach the quantity of water produced in the getter bed is:

$$V_{H_2O}(mol) = \int \frac{P_{H_2O}^{carrier}(Pa)}{101325} * F_{total}\left(\frac{mol}{s}\right) dt \qquad (14)$$

where F_{total} is the total gas flow.

The source of water production is unclear but is most likely related to reactions of the hydrogen with the manganese or the binder in the Cu/Mn bed.

4. Conclusion

This experiment measured the oxygen gettering capacity of a Cu/Mn bed at different temperatures to determine if it would be a good alternative to nickel, the current oxygen getter used in tritium glove boxes. As temperature increased, the bed was able to getter more oxygen. The efficiency rose slightly from 98% to 99.5% as the temperature of the alloy increased from 200 to 400°C. The useful gettering capacity was between 4% and 24% of the theoretical bed capacity at temperatures of between 200°C and 400°C. Water was also produced during the oxidation of the bed. The latter two observations suggest that Cu/Mn would be a poor replacement for the current Ni beds because of the production of water and the significantly lower useful gettering capacity per amount of material.

5. Acknowledgements

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6. References

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Figures

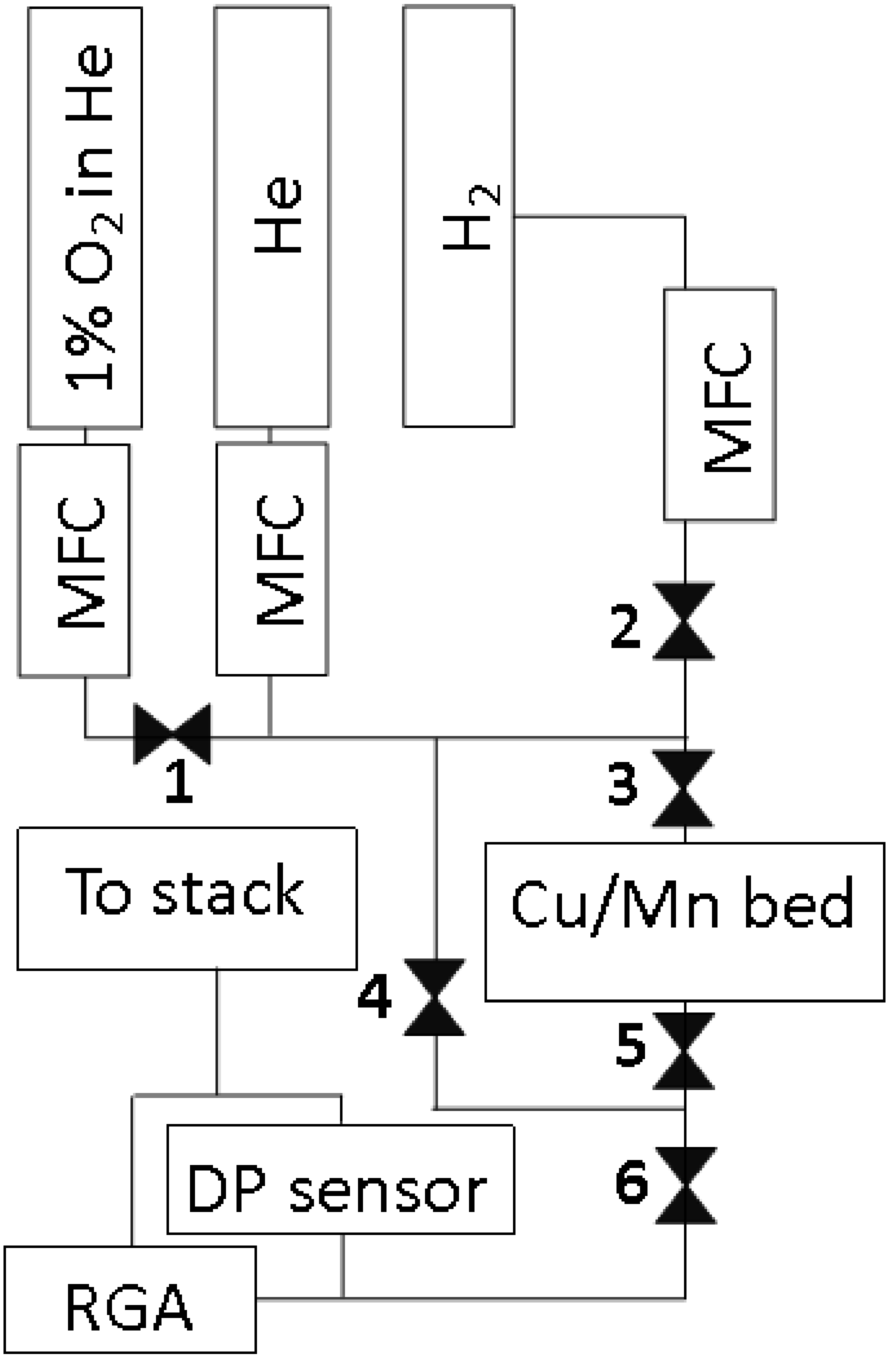

Figure 2.1 Experimental setup. MFC is mass flow controller; RGA is residual gas analyzer; DP is dewpoint

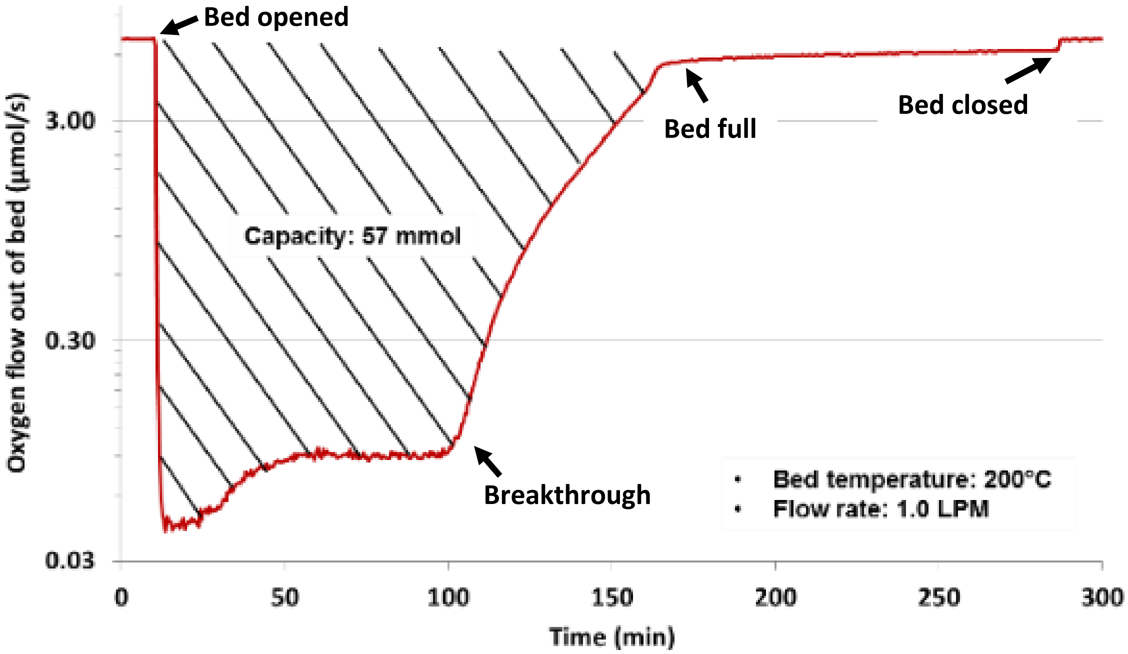

Figure 3.1 Typical oxygen collection profile for Cu/Mn. The shaded area provides an estimate of the bed oxygen capacity. Note that the oxygen concentration in the carrier stream increases when the bed is closed because collection efficiency is not 100%.

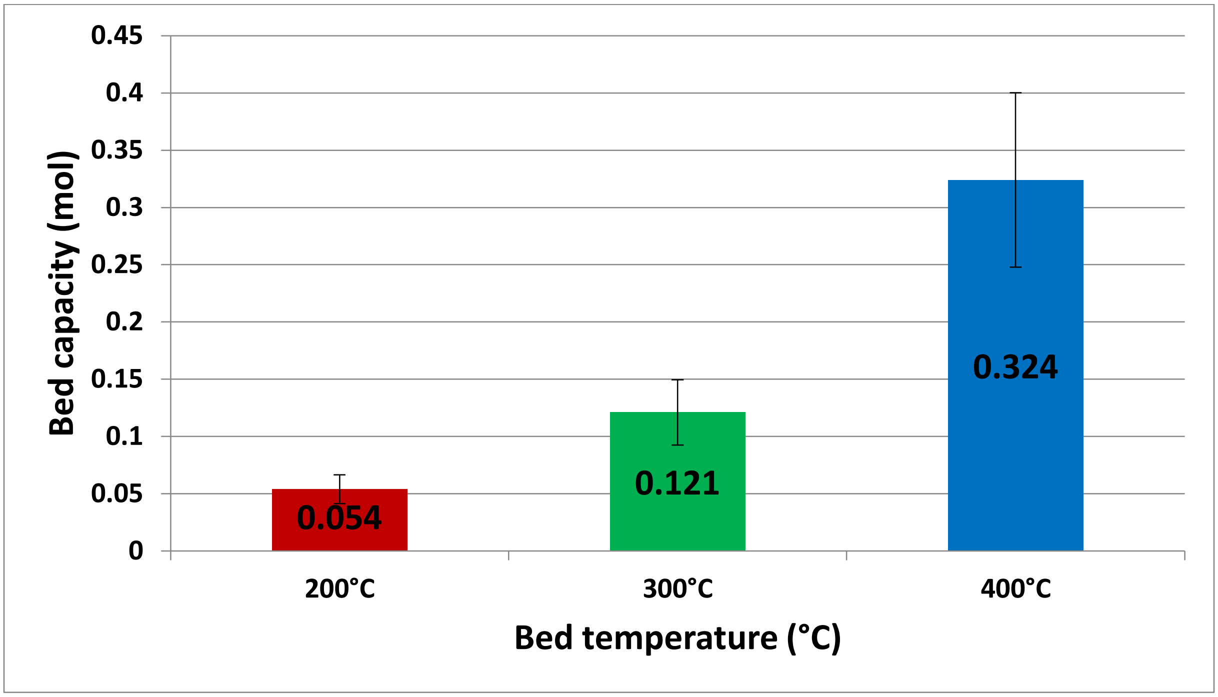

Figure 3.2 Bed capacity versus temperature. As bed temperature increases, bed capacity also increases.

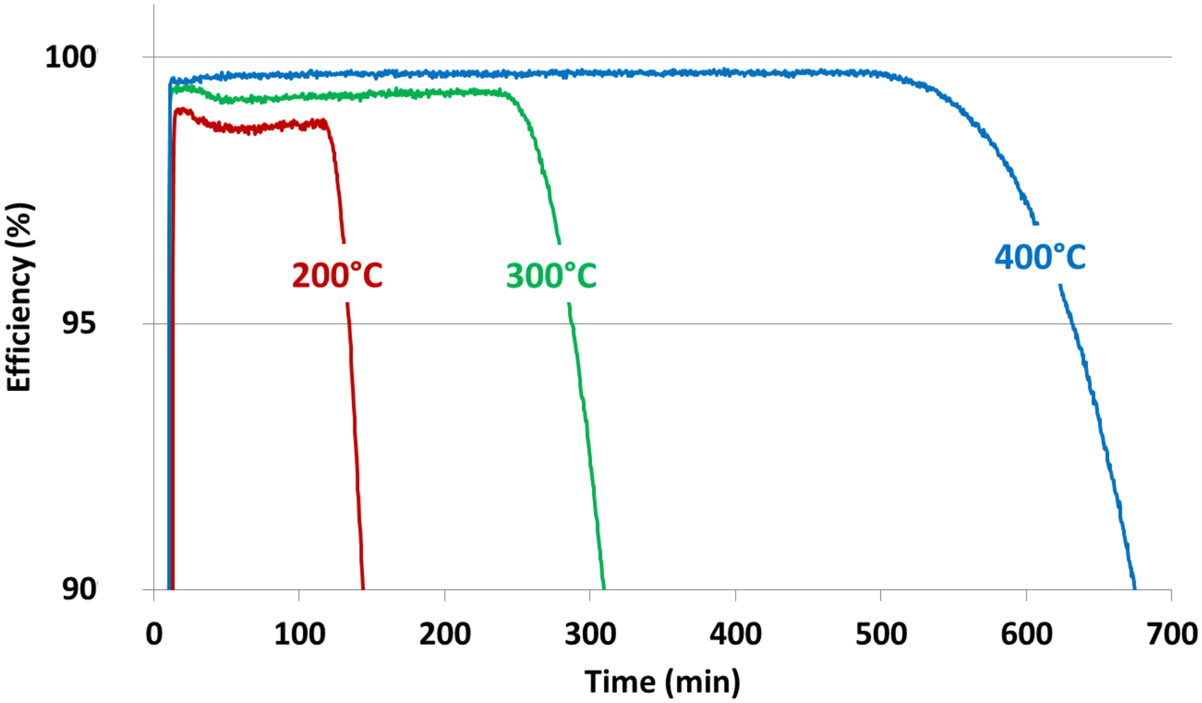

Figure 3.3 Dependency of gettering efficiency on temperature

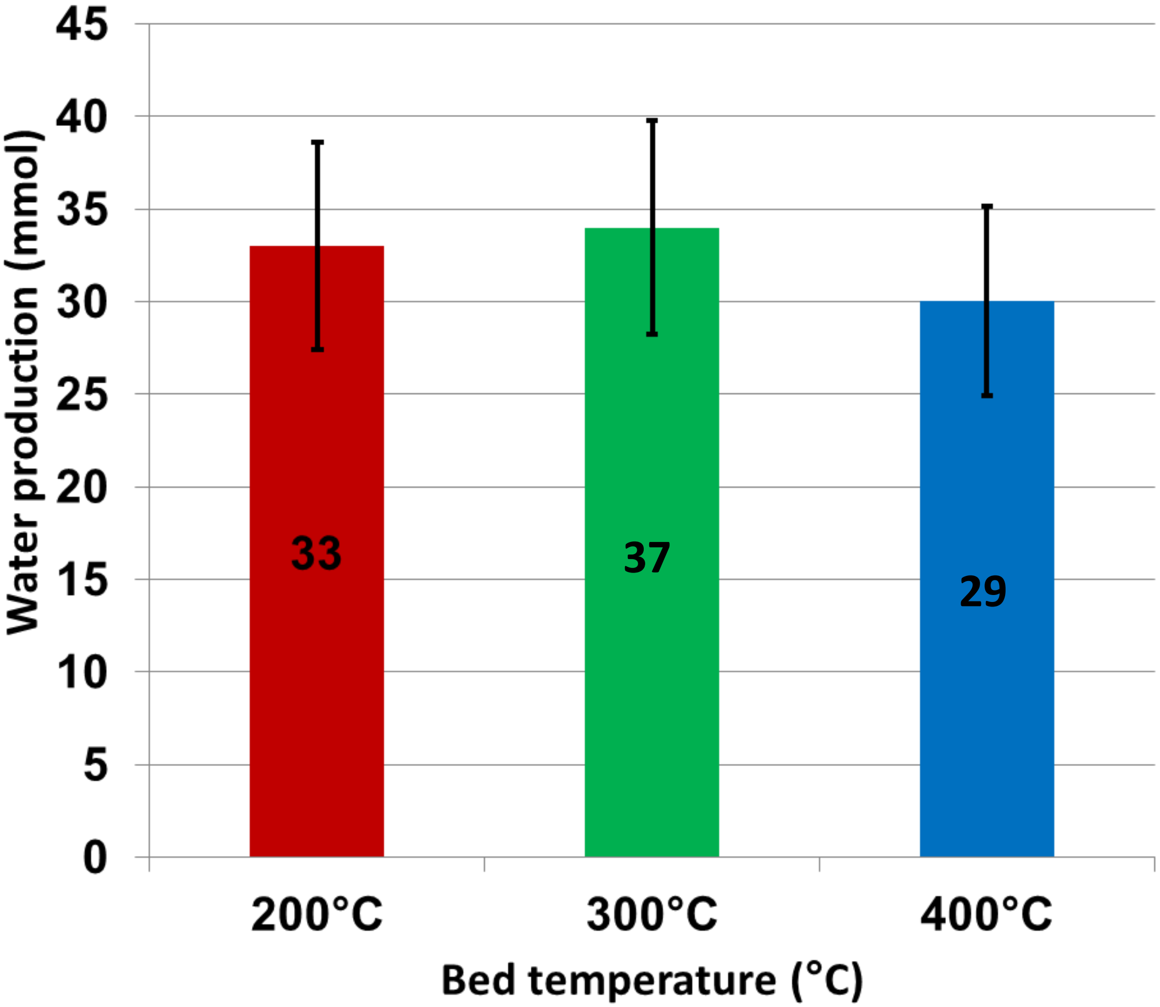

Figure 3.4 Dependency of water production on bed temperature

Temperature (°C)	Oxygen consumed (mmol)	Water production (mmol)
200	65.0	38.6
200	40.2	27.6
200	57.2	31.2
300	121.0	34.2
300	122.0	39.6
400	324.0	31.1
400	325.0	26.6

Table 1: Oxygen consumption and water production for all runs organized by temperature.