

Design and Fabrication of a Tin-Sulfide Annealing Furnace

By

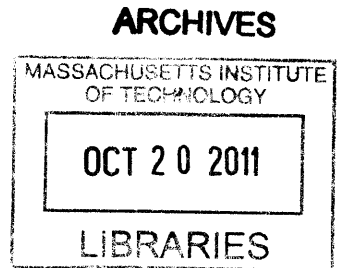
Raymond Lewis

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS OF

BACHELOR OF SCIENCE IN MECHANICAL ENGINEERING
AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2011

©2011 Raymond A. Lewis. All rights reserved



The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part in any medium now known or hereafter created.

Signature of Author: _____
Department of Mechanical Engineering
May 20, 2011

Certified by: _____
SMA Assistant Professor of Mechanical Engineering and Manufacturing
Thesis Supervisor
Tonio Buonassisi

Accepted by: _____
Samuel C. Collins Professor of Mechanical Engineering
Undergraduate Officer
John H. Lienhard V

Design and Fabrication of a Tin-Sulfide Annealing Furnace

by

Raymond A. Lewis

Submitted to the Department of Mechanical Engineering on May 20, 2011 in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Mechanical Engineering

ABSTRACT

A furnace was designed and its heat transfer properties were analyzed for use in annealing thin-film tin-sulfide solar cells. Tin sulfide has been explored as an earth abundant solar cell material, and the furnace was developed to test the properties of annealed tin-sulfide thin films. Annealing is a highly temperature and time dependent process so the furnace must be able to reach the temperature to be tested quickly, maintain that temperature and once finished, cool down quickly. The furnace is composed of a quartz tube with two heated zones, both heated with nichrome wire and cooled with fans. The two zones were designed to reach temperatures of 600 C and 200 C and to be cooled at a rate of 10 C per minute.

Thesis Supervisor: Tonio Buonassisi

Title: SMA Assistant Professor of Mechanical Engineering and Manufacturing

Acknowledgements

The author would like to thank James Serdy for providing guidance on the project and Prof. Tonio Buonassisi and Katy Hartman for providing the opportunity to work on it.

Table of Contents

1 Introduction	6
1.1 Requirements of Furnace Design	6
2 Design and Components of Furnace	6
2.1 Heated Section of Furnace	7
2.2 Supplemental Vendor Supplied Components	9
3 Rational Behind Design Decisions for Furnace	11
3.1 Heating Elements	11
3.2 Cooling Method	12
3.3 Insulation	12
4 Properties of Furnace	12
4.1 Heat Transfer Results	12
4.1.1 Cooling	13
4.1.2 Maintaining Temperature	14
4.1.2.1 Isothermal Sections	15
4.1.2.2 Fin in Between Hot Sections	15
4.1.2.3 Fins on Ends	15
4.1.2.4 Total Heat Transfer	16
4.2 Nichrome Wire	17
4.2.1 Wire Selection	17
4.2.2 Preliminary Experiments	19
5 Hydrogen Sulfide Concerns	21
5.1 Information from the MSDS	21
5.2 Miscellaneous Chemical Reactions Possible Inside the Furnace	22
6 Conclusion	22
REFERENCES	22

1 Introduction

Solar cells are semiconductor devices that convert solar radiation into electrical energy. They are being studied as an alternative to conventional energy sources based on fossil fuels. However, the materials used in the active layers tend to be expensive, which drives up the cost significantly. If photovoltaic systems are to be a viable alternative to conventional sources of energy then cheaper, more abundant materials must be developed and studied as alternatives.

Tin-sulfide is an example of an earth abundant alternative to conventional solar cells materials. However the current energy conversion efficiency of tin-sulfide is low compared to other materials. A portion of this energy loss is due to impurities in the crystal structure of tin-sulfide films. The crystal structure of thin films is dependent on the annealing process used to create the cells. The two relevant parameters of interest in this project are the temperature of the process and the time involved. This project was part of an effort to study this material by annealing tin sulfide films.

1.1 Requirements of Furnace Design

The purpose of this report was to propose a design for a furnace to be used to anneal these films. The tube furnace used in this case consists of a quartz tube with two heated sections, one at 200 C where reactants are evaporated and one at temperatures as high as 600 C where the solar cell material is annealed. The furnace must be able to maintain these temperatures while losing as little heat to the environment as possible. In addition, since temperature and time play such an important role in the process being studied the cooling time must be quick enough so that the only effects being measured are those of the process being performed. For this reason a constant cooling rate of 10 C per minute was set as a target.

These are unconventional functional requirements, which a typical furnace would not be able to satisfy completely. The temperature range is reasonable compared to the ranges that typical furnaces could reach, but the cooling requirements are not. Typical furnaces maintain high temperatures with thick layers of insulation. These layers provide insulation during heating and cooling, which lowers the cooling rate below 10 C/minute. Therefore, a new design was developed.

The furnace was built around a quartz tube. Through the tube a mixture of gases will be flowing. In particular up to four gases will be flowing through the furnace; hydrogen sulfide, argon, nitrogen and forming gas. The furnace is intended for pure hydrogen sulfide, but for the initial stages of the furnace operation a lower concentration mixture of hydrogen sulfide in nitrogen will be used. Forming gas is a mixture of hydrogen and nitrogen provided to serve as a source of hydrogen while minimizing its dangerous properties, in particular its explosive nature.

The furnace will be used to anneal thin-film solar cells, on the order of several microns, so the pressure of the procedure will be up to, but usually below, atmospheric pressure. The lowest pressure to be expected in the furnace is 1 millitorr at the beginning of the process to evacuate the furnace of excess material left from previous procedures. To reach these temperatures, a roughing pump will be used. The purpose of this project was to describe a furnace designed to work at these specific conditions.

2 Design and Components of Furnace

The furnace can be separated into separate subassemblies. The heated section of the furnace contains all of the components needed to ensure that the furnace can reach and maintain the relevant temperatures described earlier. This section includes the tube, heating elements and a shield to thermally isolate the furnace during heating and greatly increasing the thermal interaction during cooling.

Supplemental components of the furnace include temperature and flow controllers, tubing outside of the furnace, a filter and a pump to evacuate the tube within the furnace.

2.1 Heated Section of the Furnace

The innermost section of the furnace was an 18 in. quartz tube with inner and outer diameter of 48mm and 52mm, respectively. The sections of the quartz tube heated up to 200 C and 600 C were 3 in and 4 in long respectively, spaced 2 in apart. Heating was accomplished with nichrome wire wrapped around the tube in a coil.¹The two sections were placed two inches apart to create a distance large enough so that the temperature at one zone would not affect the other. The placement of the two rolls of nichrome wire was displayed in the figure below.

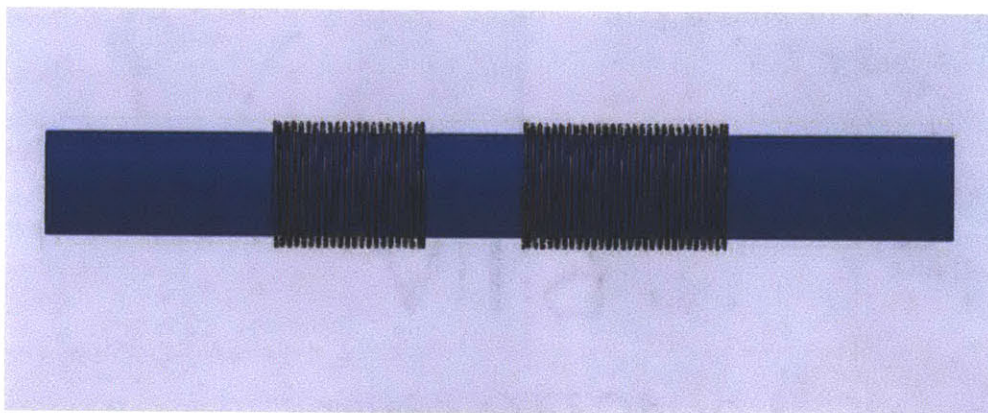


Figure 1: Quartz tube shown with nichrome wire placement scheme.

In order to close off the tube and provide a connection to other components of the assembly two quartz caps were provided. Over each cap a sleeve of silicone rubber was placed to hold the caps in place and to provide a seal. The inner diameter and length of the silicone rubber sleeves were 2 in and 3 in respectively, small enough compared to the outer diameter of the quartz tube and the quartz cap to allow both components to slide into them providing a press fit, as shown in the figure below. The fit was tight enough that external force was needed to pull the assembly apart, ensuring that in a vacuum the seal would not become undone.

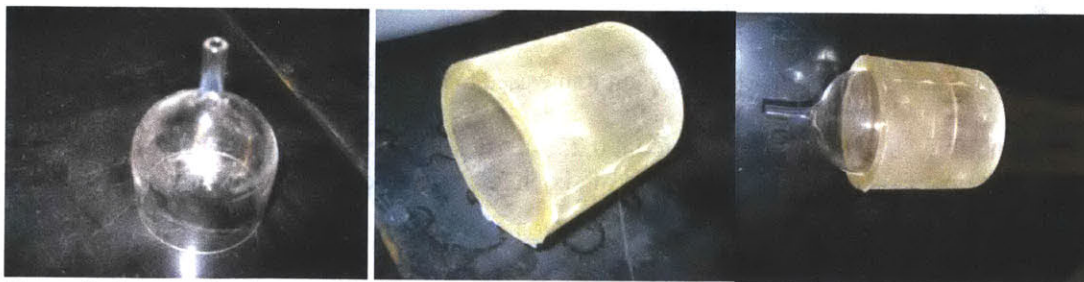


Figure 2: Quartz tube shown with silicone rubber sleeves and quartz caps. To the right the quartz cap that was placed at the end of the tube. At center the silicone rubber sleeve placed over the cap and the tube. At left the entire end connection assembled on one end of the cap. The sleeve fit over the tube and the cap and was

An aluminum shield was placed around the tube and lined with aluminum foil to act as a radiation shield. The purpose of the aluminum was to provide a low emissivity reflector so that radiation heat transfer could be minimized. The inner diameter of the aluminum tubing was lined with aluminum foil, which due to its even lower emissivity would further enhance the reflective properties of the shield.

A ceramic end was placed on each side of the tube to hold it up. Equipment cooling fans were added to blow air along the length of the furnace to allow for forced convection cooling. This entire section was held up using an 80/20 Aluminum Frame and around this a second aluminum shield will be placed to completely enclose the entire furnace. The dimensions of the 80/20 chosen to form the frame were 1.5 in X 1.5 in. This was chosen because this form of 80/20 was common in the lab and in the event that more was needed stock could easily be found. An example of the design of the frame was shown in the figure below.



Figure 3: Example of the 80/20 Aluminum frame used to house the thermal system.

Around this 80/20 frame an additional 0.25 in thick layer of aluminum was provided to add a layer of protection. This layer was composed of six sheets bolted to the slots in the 80/20 so that it would be quickly removed if need be.

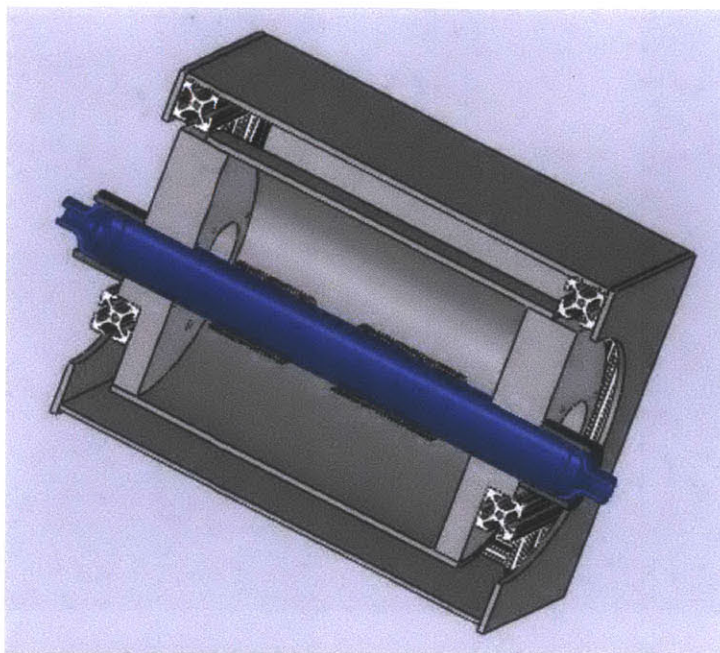
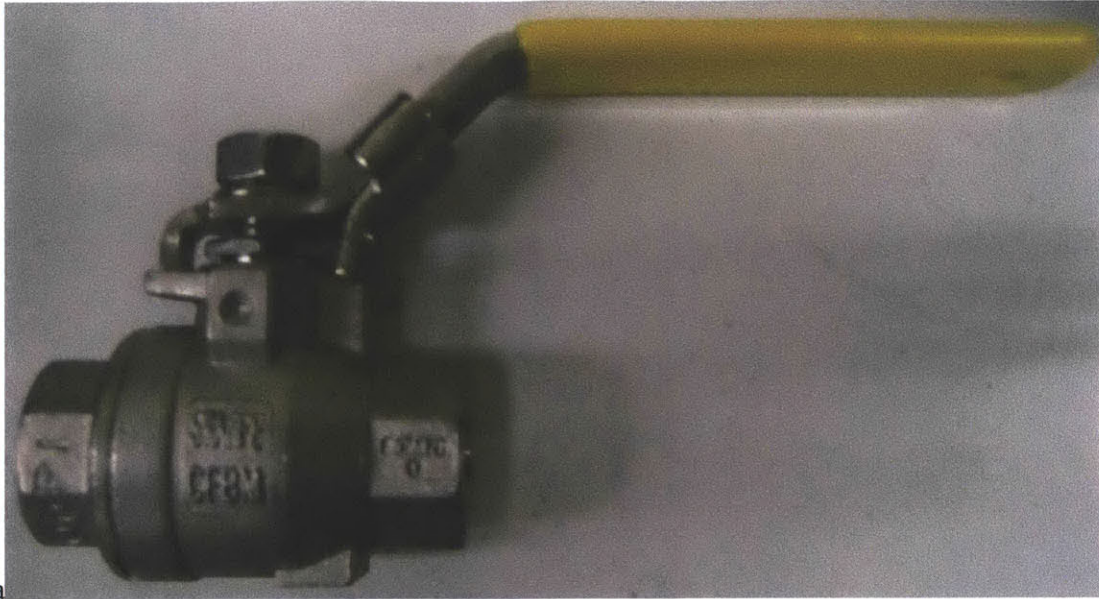


Figure 4: Cross Section of Inside of Furnace.

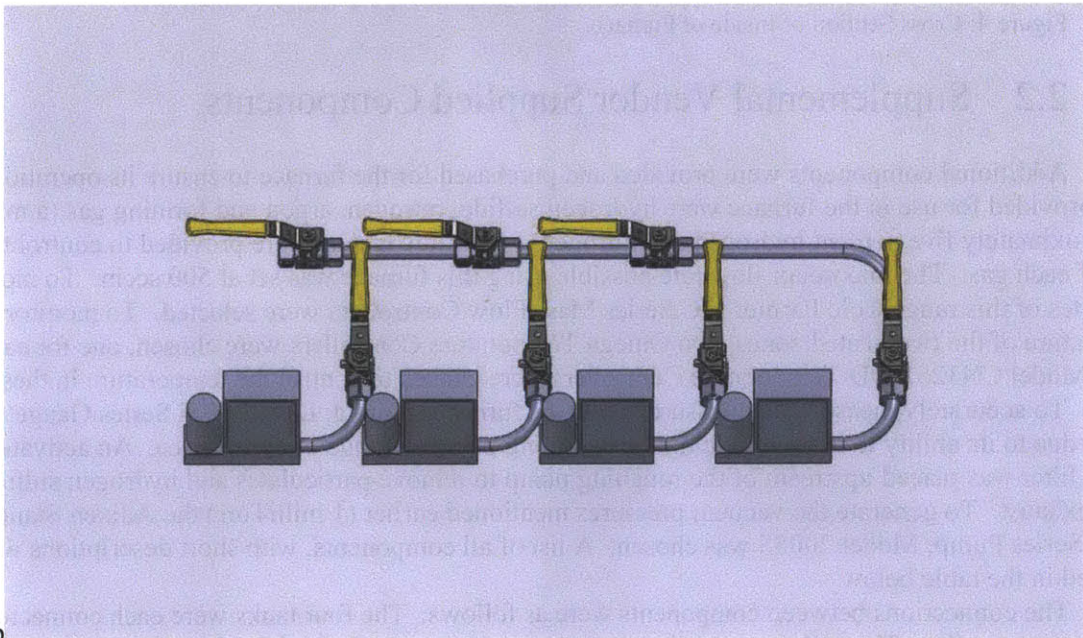
2.2 Supplemental Vendor Supplied Components

Additional components were provided and purchased for the furnace to ensure its operation. Four gases provided for use in the furnace were hydrogen sulfide, nitrogen, argon and forming gas (a mixture of approximately five percent hydrogen and nitrogen). Gas flow meters were provided to control the flow rates of each gas. The maximum flow rate possible using this furnace was set at 500 sccm. To monitor flow rates of this range Cole Parmer MC Series Mass Flow Controllers were selected. To monitor the temperature of the two heated zones, two Omega Temperature Controllers were chosen, one for each zone. Model CN3251-DD Temperature Controllers were chosen to control the temperature in these ranges. To accurately measure the pressure inside the furnace a Kurt J. Lesker 275i Series Gauge was chosen due to its ability to measure within the operating pressure range of the furnace. An activated carbon filter was placed upstream of the roughing pump to remove particulates and hydrogen sulfide out of the exhaust. To generate the vacuum pressures mentioned earlier (1 milliTorr) the Adixen Standard Pascal Series Pump, Model 2005S was chosen. A list of all components, with short descriptions was provided in the table below.

The connections between components were as follows. The four tanks were each connected to mass flow controller. These flow controllers were connected to the feed of the furnace as shown in the figure below. The valves shown were placed so that at any given instant during the furnace's operation any connections could be quickly shut off. Another important feature in this subassembly was the placement of hydrogen sulfur as the last gas to be added to the furnace. This was done to minimize the risk of any unwanted mixtures and to minimize the number of places where hydrogen sulfide can interact with other materials before the actual furnace. This was then fed into the furnace.



a



b

Figure 5: Mass flow controllers with valves and connections included. Figure 5a shows one of the ball valves. Figure 5b shows the configuration. The controllers, arranged from left to right are those for Hydrogen Sulfide, Forming Gas, Nitrogen and Argon. This arrangement was chosen so that H_2S was the last gas to be added to the mixture.

Downstream of the furnace additional sensors and monitors were added. A pressure sensor was connected to the piping by means of a t-connector, upstream of a filter with activated carbon in it. This spot was chosen because placing the pressure sensor downstream of the activated carbon filter would have meant that pressure drop across the filter would affect the readings. However, particulates from the furnace could potentially damage the sensor so a smaller filter was placed between the t-connector and the pressure sensor ease the damage of the particulates. Downstream of the t-connector a filter with activated carbon was placed to remove dangerous chemicals, and a roughing pump was placed at the end to generate vacuum pressures.

Table 1: Parts List with Prices.

Description of Part	Vendor	Price per part	Notes
Adixen™ Standard Pascal Series (Model 2005 SD) 275i Series Gauge with Integrated Controller and Display 316 Stainless Steel Full-Port Ball Valve, Lever Handle Mass Flow Controller	Kurt J. Lesker ²	\$2,200.00	-roughing pump -capable of 10 ⁻⁴ Torr
	Kurt J. Lesker Company	\$295.00	-pressure sensor -Operating Temperature 0-40 C
	McMaster-Carr ³	\$29.09	-7 valves
	Cole-Parmer ⁴	\$1291.00	-measure/regulate flow -4 meter (one for each gas)
Hydrogen Sulfide Tank (Size 33A)	Airgas, Inc. ⁵	\$203.86	-9 in diameter, 6 in tall -replaceable -4% H ₂ S
Power Strip	Any Electronics Store ⁶	\$3-\$5	-Power small electrical equipment -NOT the Temperature Controllers
Omega Temperature Controller (CN3251-DD)	Omega Engineering, Inc. ⁷	~\$800.00	-Controller, relay and heat sink all included in casing -Two Controllers (one for each zone)
Biosystems ToxiPro Single Gas Detector	Sperian Protection ⁸	\$239.00	-H ₂ S detector -Vibrating alarm and data logger

3 Rationale Behind Design Decisions for Furnace

Important features involved in this furnace design were the nichrome heating elements, the aluminum shielding, the end caps with fans and the 80/20 Frame. Each component was inspired by work done to build previous furnaces, vendor supplied models studied online, and personal experience and intuition.

3.1 Heating Elements

Nichrome was chosen as the heating element because it was capable of reaching the desired temperatures and would not contribute greatly to the design of the furnace. Ceramic rods running parallel to the furnace were the only additions needed to hold the nichrome wire up, and they could be connected to the ceramic cover. Grooves placed along the rods held the wire up and gave it room to expand when heating. Alternatives to bare nichrome wire which were rejected included a wire with a protective sheath and quartz heating lamps. The sheathed wires that were considered were capable of a maximum temperature of 600 C.⁹ While this would reach the value required of the furnace, the temperature of the wire would in actuality be higher than the temperature of the section of the furnace. This is due to the fact that heat transfer requires a temperature gradient in order to flow. Due to this fact the temperature of the wire would be higher than the temperature of the heated zone in the tube, and would run the risk of being higher than its pre-determined maximum temperature of the sheath. Another possibility that was considered included infrared heating lamps.¹⁰ This idea was rejected because heating lamps would have

been an example of overdesign in the furnace. Some heating lamps can go to temperatures several hundreds of degrees higher than the intended range of the furnace, which would have been unnecessary. Nichrome wire appeared to be an elegant and simple solution.

3.2 Cooling Method

Cooling was accomplished by placing a series of cooling fans at the front and rear end of the furnace to allow for forced convection cooling. This was chosen because by switching the fans on and off the cooling properties of the furnace could be quickly changed. During the actual process the fans would be turned off, and once cooling was required the fans would just turn on and blow air across the furnace. With this system in place it became possible to quickly change the properties of the furnace. The material chosen for the shield was aluminum foil, due to its reflective properties. Other materials that were considered were gold and coated quartz. Gold was rejected because it was more expensive per pound than gold and gold tubing of the size required to cover the entire tube section was hard to find. Quartz coated with a thin layer of reflective material was rejected because quartz is a relatively brittle material and in case the furnace was to be moved, the quartz tube would break if handled roughly.

An alternative design which was rejected involved encasing the quartz tube within an adjustable vacuum/ low pressure environment. This section would then be connected to a source of recirculating air to help aid the cooling process when needed. This idea was rejected because, again the added complexity was considered unnecessary. This would have constituted overdesigning the furnace, especially since the majority of the heat transfer was by radiation. A vacuum would lower the density and inhibit natural convection, but since radiation dominated the heat transfer dynamics in this system that method seemed unnecessary.

3.3 Insulation

Finally the system had to be capable of not losing heat to the environment during the processing stage and losing heat quickly when cooling. Most furnaces on the market don't have this ability so a new method had to be devised. This was achieved in the design by enclosing the entire furnace in an aluminum shield and having the fans blow air through the section in between the quartz tube and said shield. The aluminum shield was added to act as a shield to prevent radiation related heat loss while still providing room for fluid to flow through it when cooling. Adding additional layers of low conductivity insulation were rejected for two reasons. First, a separate mechanism would have to be devised to move the insulation when it was time to cool. Second, the insulation available had the potential to produce large amounts of dust, which would interfere with the ventilation system in the lab.

The decision to line the aluminum shield with foil was due to the fact that the emissivity of aluminum foil was, at most 0.05. This property means that at least 95 percent of all radiation incident on the aluminum foil would be reflected. Since the dominant heat transfer mode in this section was expected to be radiation, this was expected to have a large effect on the behavior of the furnace. For comparison, normal aluminum could have an emissivity as high as 0.2. Letting the tube radiate to the environment would have led to an outer surface with an effective emissivity of 1. The addition of aluminum foil therefore, represents an improvement in reflectivity of the outer surface of the furnace.

4 Properties of the Furnace

4.1 Heat Transfer Results

The most important aspect of the furnace design was its ability to manage heat transfer in and around the quartz tube. The three most relevant modes of heat transfer available in this furnace are

conduction, convection and radiation. Conduction is heat transfer through the material as adjacent atoms vibrate and collide with one another. Convection involves the movement of fluid over a surface, which serves to carry the heat away. Radiation involves the emission and absorption of electromagnetic radiation. The two cases studied were during the process, when the furnace must maintain the temperature and minimize heat loss to the surroundings and during the cooling process during which heat transfer must be accelerated to provide good heat loss to the environment.

4.1.1 Cooling

Here is presented an analysis of the heat transfer processes expected to occur during the cooling process, achieved largely through forced convection. This behavior could be approximated by Newton's Law of Cooling, expressed as a function of the heat transfer rate Q , the heat transfer coefficient h , exposed area A , and the change in temperature ΔT .

$$q = hA\Delta T \quad (1)$$

Using the first law to equate the heat transfer rate to the change in internal thermal energy of the system this could be rewritten as:

$$mc \frac{d(\Delta T)}{dt} = hA\Delta T \quad (2)$$

Here m is the mass of the system being cooled and c is the specific heat capacity.

An approximation was made here to simplify the analysis of this phenomenon. Because the outer wall of the quartz tube was rather small it was assumed that the quartz tube was essentially isothermal in the radial direction, i.e., the lumped parameter model would be sufficient. Because the sink temperature was constant (20 C) this situation was modeled as exponential decay. Since the required cooling rate was 10 C/minute and the highest temperature was about 600 C it was assumed that the cooling should be essentially complete within one hour.

Ninety percent decrease in temperature was assumed to be "done" for the purpose of the model. This corresponds to a time passage equivalent to about 4.6 time constants, i.e., one hour must be equal to about 4.6 times the time constant, equal to:

$$\tau = \frac{mc_p}{hA} \quad (3)$$

The heat transfer coefficient required to reach this value was approximately 1.2 W / (m²K). As a sanity check, the Biot number was calculated by taking the characteristic length as the volume of the quartz tube divided by the area of the outer section of the tube. Blowing air through the tube would interfere with the process, so in this furnace that was avoided. The Biot Number calculated for this case was about 0.0066, demonstrating that the lumped parameter model was valid here.¹¹

In order to calculate the flow rate needed to generate a heat transfer coefficient of 1.2 W/(m²K), a heat transfer correlation was used to model flow across a cylinder. These correlations were developed to estimate the thermal properties of situations such as this which are non-trivial, and thus, very difficult to model. Flow across a cylinder was modeled using the following equation:

$$Nu = \frac{hd}{k} = 0.3 + \frac{0.62Re^{1/2}Pr^{1/3}}{[1+(0.4/Pr)^{2/3}]^{1/4}} \quad (4)$$

$$Pr = \frac{\nu}{\alpha} \quad (5)$$

$$Re = \frac{vd}{\nu} \quad (6)$$

Here h is the heat transfer coefficient, d is the diameter of the tube, k is the thermal conductivity of the liquid, ν is the kinematic viscosity of the fluid, α is the thermal diffusivity of the fluid, v is the velocity of the fluid and Nu , Pr , and Re are the non-dimensional Nusselt, Prandtl and Reynolds numbers respectively.

In this case d was assumed to be 52 mm, Pr was 0.7, k was 0.025, ν was assumed to be 1.75×10^{-5} m²/s. Using these values Re was found equal to 21 indicating laminar flow. This corresponded to a velocity of 7 mm/s, meaning that any fan could be used to cool the sections of the furnace when needed. The smallest fan found on McMaster Carr had an area of 25 mm X 25mm and reach a flow rate of 1 cfm, indicating a velocity of 0.76 m/s. Since this was a full order of magnitude larger than the minimum velocity required it was concluded that a fan would be an adequate cooling method for this furnace.

4.1.2 Maintaining Temperature

The furnace was designed to transfer heat from the nichrome wire to the two sections of the quartz tube, while minimizing heat loss to the surrounding environment. To quantify the reduction in heat loss, the power required to maintain the required temperatures with and without the surrounding aluminum case were calculated using the basic principles of heat transfer.

Consider a quartz tube of the same dimensions as previously stated, with two heated zones. Heat loss from the tube was expected to occur from conduction across the tube and from convection and radiation to the outer environment. Radiation to the environment was initially determined using the Stephan-Boltzmann Law.¹²

$$q = \varepsilon\sigma(T_S^4 - T_E^4) \quad (7)$$

Here ε is the emissivity of the material (quartz in this case), σ is the Stephan-Boltzmann Constant (5.67×10^{-8} W/m²K⁴) and T_S and T_E are the temperatures of the surface of the tube and the environment, respectively. Natural convection was modeled using a heat transfer correlation, relating the Raleigh Number to the Nusselt Number.

$$Nu_d = \frac{h*d}{k} = f(Ra, Pr) \quad (8)$$

$$Ra_d = \frac{g\beta(\Delta T)d^3}{\alpha\nu} \quad (9)$$

The function $f(Re)$ represents a complex, non-trivial relationship that is difficult to model analytically. For this reason correlation equations were provided which attempt to represent the phenomena at work.

$$Nu = 0.36 + \frac{0.518Ra^{1/4}}{\left[1 + \left(\frac{0.559}{Pr}\right)^{9/16}\right]^{4/9}}, 10^4 < Ra \leq 10^9 \quad (10)$$

$$Nu = 0.36 + \frac{0.518Ra^{1/4}}{\left[1 + \left(\frac{0.559}{Pr}\right)^{9/16}\right]^{4/9}}, 10^9 \leq Ra \quad (11)$$

These correlations attempt to model natural convection along a horizontal cylinder, which was determined to be an adequate model for the situation in question.

The total heat transfer loss was equivalent to the sum of convection and radiation heat transfer. The two hot zones were approximated as isothermal i.e. all heat transfer was convection. The other

sections were modeled as fins since conduction along the tube as well as convection and radiation contributed to the heat transfer away from the hot zones. The heat transfer to the environment was calculated as follows using Microsoft Excel.

4.1.2.1 Isothermal Sections

The temperature in these sections was isothermal, meaning that the total heat transfer to the environment was equal to:

$$Q = q * A = \pi \frac{d^2}{4} L [\epsilon \sigma (T^4 - T_e^4) + h(T - T_e)] \quad (12)$$

Here A is the wetted area of the section of the quartz tube and all other variables are as previously defined. Assuming a temperature of 600 C in the “hot” section and 200 C is the “cold” section the heat transfer associated with each temperature drop was recorded in the table.

Table 2: Heat Transfer out of the “hot” 600 C and “cold” 200 C sections of the furnace, separated into natural convection and radiation.

Heat Transfer (W)	“Hot Section”	“Cold Section”
Radiation	501	28
Natural Convection	4	1
Total	505	29

4.1.2.2 Fin In Between Hot Sections

In an attempt to compare radiation and convection an effective heat transfer coefficient was calculated by taking the ratio of the heat flux per unit area calculated by the Stephan-Boltzmann Law and the temperature difference for the hot zone. The temperature used to solve for the heat transfer coefficient was the average of the end temperatures of the section of the pipe. The heat transfer coefficients found using this manner were 28 W/ (m²K) for radiation and 0.4 W/ (m²K) for natural convection.

Assuming a constant heat transfer coefficient allowed the section to be modeled as a fin with two ends at predetermined temperatures, 600 C and 200 C which could be modeled using the following equations.⁴

$$m = \sqrt{\frac{hP}{kA}} \quad (13)$$

$$M = \sqrt{hPkA\Delta T_b} \quad (14)$$

$$Q = M \left[\frac{\cosh(mL) - \frac{\Delta T_L}{\Delta T_b}}{\sinh(mL)} \right] \quad (15)$$

These equations, assuming a length of 2 in predict a heat transfer of 3 Watts out of the base of the heated section and 1 Watt into the “cold” section of the tube furnace. The rest (2 Watts) was released to the environment.

4.1.2.3 Fins on Ends

Using the same approximation and variables introduced before the fin equation became.¹³

$$Q = \sqrt{hPkA}[\Delta T]\tanh(mL) \quad (16)$$

The heat transfer correlations developed for the two fins, one in contact with the “hot” section and one in contact with the “cold” section were as follows.

Table 3: Heat Transfer Coefficients used for the fins at either end of the furnace. The temperature used was the temperature of the heated section closest to the fin. This would act as an upper bound to the heat transfer rate of the system.

Heat Transfer Coefficient(W/m ² K)	Radiation	Natural Convection
“Hot” Section Fin	53	0.4
“Cold” Section Fin	13	0.4

Because the length of the tube was set at 18 inches which included 4 inches of a hot zone, 3 inches of a cold zone and 2 inches in between to allow for separation between the sections, the length of each fin was set at 4.5 inches. The heat transfers out of the “hot” and “cold” section to these fins were 2.8 W and 0.8 W respectively.

4.1.2.4 Total Heat Transfer

The additions mentioned in the furnace act as a series of shields to add thermal resistance between the quartz tube and the environment. Rather than transferring air to the environment, the quartz tube transferred heat to the aluminum tubing and the end cap, which transfer heat to the outer aluminum. It was this outer shield which, through natural convection and radiation, transfers heat to the environment rather than the quartz tube.

The effect of the aluminum shield was to reflect the radiation back onto the quartz tube. This changes the behavior because the effective emissivity of the environment is lower. For a body emitting to the environment it is often assumed that the environment is a body with an emissivity of 1. This approximation was valid because the area of the environment was assumed to be large enough so that only a small amount of the radiation was reflected back onto the tube. This is characteristic of a black body.

Because the aluminum was added to reflect radiation back onto the surface, this approximation was no longer valid. The system could be modeled as two thin-walled concentric cylinders of radii R and r, respectively. If R is the radius of the aluminum shield and r is the outer radius of the quartz tube, the heat transfer relationship is as follows. Here ϵ_Q and ϵ_{al} are the emissivity of quartz and aluminum respectively. The radiating/absorbing area of the quartz and aluminum tubing in question are A_Q and A_{al} respectively.

$$Q = \frac{1}{\frac{1-\epsilon_Q}{\epsilon_Q A_Q} + \frac{1}{A_Q} + \frac{1-\epsilon_{al}}{\epsilon_{al} A_{al}}} \sigma(T^4 - Te^4) = \frac{A_Q}{\frac{1-\epsilon_Q}{\epsilon_Q} + 1 + \frac{A_Q(1-\epsilon_{al})}{A_{al}\epsilon_{al}}} \sigma(T^4 - Te^4) \quad (17)$$

This equation was derived by modifying a formula for radiation between two finite surfaces.⁵

$$Q = \frac{1}{\frac{1-\epsilon_Q}{\epsilon_Q A_Q} + \frac{1}{F_{Q-al} A_Q} + \frac{1-\epsilon_{al}}{\epsilon_{al} A_{al}}} \sigma(T^4 - Te^4) \quad (18)$$

In this formula F_{Q-al} , is the view factor, representing the fraction of irradiated energy emitted by a surface (in the case the quartz surface) that reaches the second surface (the aluminum shield). Since the quartz tube was essentially surrounded by the aluminum shield the view factor was taken as equal to 1.

The temperature profile was calculated using a Finite Element Analysis package in Solidworks using only radiation heat transfer and a section view of the results were displayed in the figure below. This was done since the results in the previous section concluded that heat transfer to the environment as a result of natural convection was always significantly smaller than that due to radiation. The results were shown in the figure below.

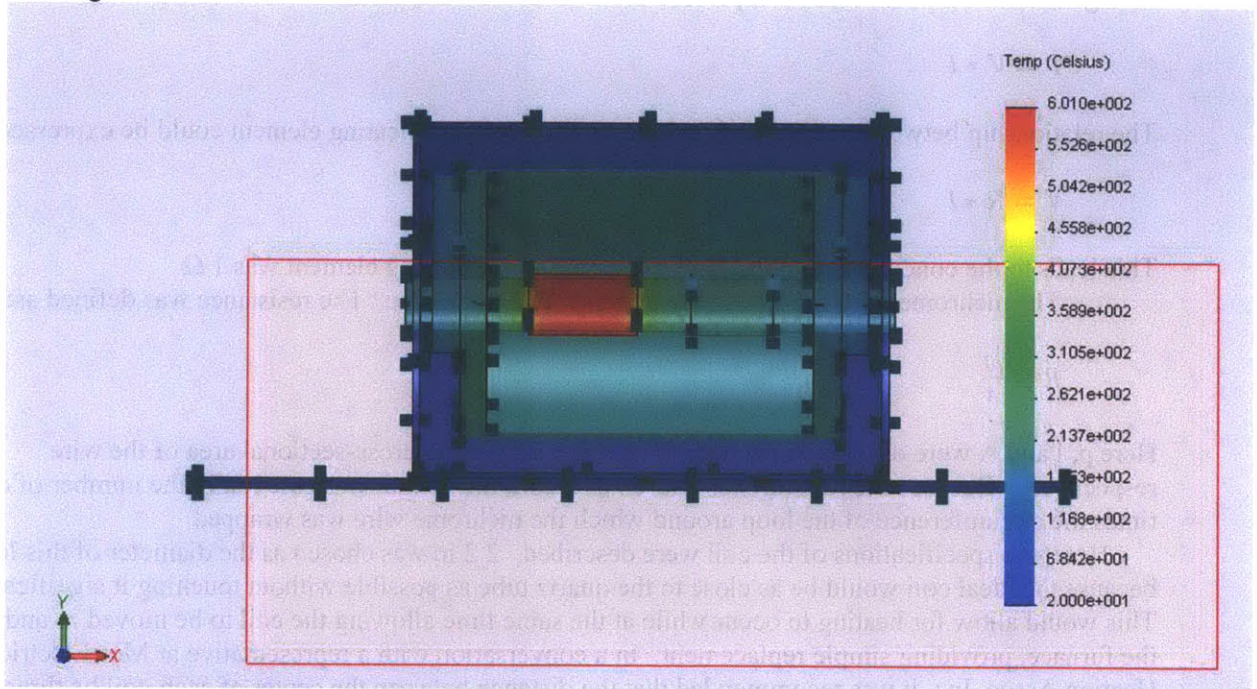


Figure 6: Temperature Distribution Inside of Furnace

It was assumed that the temperature of the environment surrounding the quartz tube was 150 C and the model was solved again, to determine the change in heat transfer properties. The results were compared in the table below. Since, in the baseline case radiation was the largest source of heat transfer, the addition of a radiation shield greatly decreased the amount of heat lost to the environment.

Table 4: Heat Transfer for the two cases under question. The addition of an Aluminum shield shows a decrease in heat transfer because the temperature of the aluminum is higher than that of the environment and the Aluminum serves as a radiation shield to reflect light back towards the quartz tube.

Heat Transfer (W)	Radiating/Convecting to Atmosphere	Within Al Shield with Al foil Layer
“Hot” Section	504	85
“Cold” Section	29	1.9
Fin in Between	2.3	1.4
“Hot” Section Fin	2.8	2.1
“Low” Section Fin	0.8	0.2

4.2 Nichrome Wire

4.2.1 Wire Selection

Nichrome wire was selected for heating up the hot zone, and the type of wire to be used was calculated using the heat transfer data calculated before. It was estimated that a reasonable upper bound on heat loss to the environment was 100 Watts. The maximum amperage available in the temperature

controllers being considered was 10 A. Based on this information it was concluded that a reasonable upper bound for the behavior of nichrome wire was the ability to supply 100 W with 10 A.

By conservation of energy it was assumed that, during steady state, the power being dissipated in the resistive windings was equal to the heat dissipated to the furnace. The relationship between, power P, voltage V and current I could be expressed as:

$$P = V * I \quad (19)$$

The relationship between voltage and current across a resistive heating element could be expressed as:

$$V = R * I \quad (20)$$

This leads to the conclusion that the total resistance of the heating element was 1 Ω .

The nichrome wire was chosen to generate that resistance. The resistance was defined as:

$$R = \frac{\rho l}{A} \quad (21)$$

Here ρ , l and A were defined as the resistivity, total length and cross-sectional area of the wire respectively. Because the resistor was chosen as a coil, the length was essentially the number of coils times the circumference of the loop around which the nichrome wire was wrapped.

Here, the specifications of the coil were described. 2.2 in was chosen as the diameter of this loop because the ideal coil would be as close to the quartz tube as possible without touching it significantly. This would allow for heating to occur while at the same time allowing the coil to be moved in and out of the furnace, providing simple replacement. In a conversation with a representative at Mor Electric Heating Assoc. Inc. it was recommended that the distance between the center of each coil be three times the diameter of the wire, as shown in the figure below.

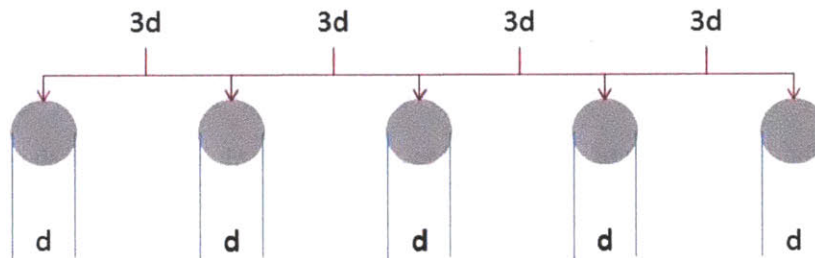


Figure 7: Spacing Scheme Used to Determine Nichrome Wire Size. The idea behind this arrangement was to space the wires so that the distance between the center of each wire was equal to three times the diameter. Therefore, once the wire is completely wound around the tube it would experience a three-fold expansion in overall length.

Taking these factors into account the relationship between the resistance R, coil diameter D, wire diameter d and heated quartz tube length L (i.e. the length of the quartz tube over which the wire will be placed) was:

$$R = \frac{\rho DL}{3d^3} \quad (22)$$

This was most critical when determining the coil size for the higher temperature section since that section experienced the highest, theoretical heat loss. The resistivity of Nichrome 60 wire found of MATWEB was $1.1 \mu\Omega \cdot m$.¹³ Using that and the fact that the length of the heated zone was to be 4 in yielded a diameter of $d=1.28 \text{ mm}$ ($\sim 0.05 \text{ in}$). The closest vendor supplied size of nichrome wire available was 16 Gauge wire, with an outer diameter of 0.051 in (1.2954 mm).

With this spacing scheme the total length of the heated section covered by the nichrome wire was approximately equal to one third the length of the entire section. Assuming this covered length was equal to the diameter of the coils times the number of windings, yield the relationship:

$$N = \frac{L}{3d} \quad (23)$$

Here N is the number of coil turns around the tube. Solving this equation for N with the information gathered so far yielded 26.15 turns, which was rounded up to 27. By taking the product of N and the circumference of each coil turn (given that the diameter of a coil turn was taken as 2.2 in) led to an estimation of 15.5 feet of wire.

4.2.2 Preliminary Experiments

A bench level experiment was performed to determine if the nichrome wire was in fact capable of reaching 600 C . The wire was wrapped around a quartz tube in a quick-and-dirty manner shown in the figure below.

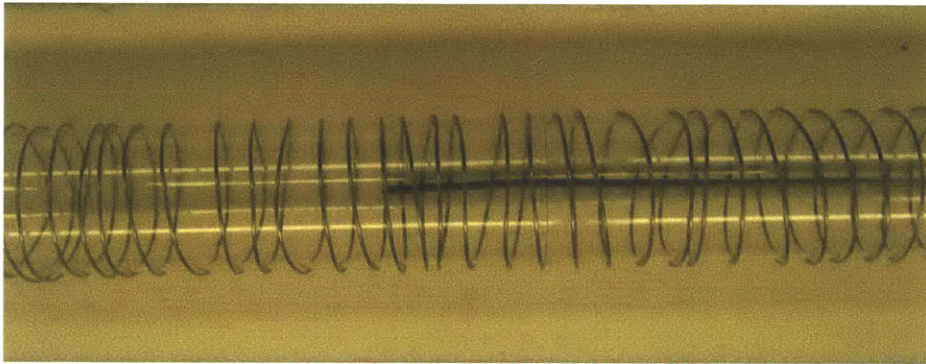


Figure 8: First test of nichrome wire coiled around a quartz tube for preliminary heating trial. A thermocouple was placed inside of the tube to measure the temperature of the environment inside of the Quartz tube.

This was tested before a structure was available to hold up aluminum foil insulation so insulation blocks were placed around the tube to create the effect of thermal insulation, as shown in the figure below.



Figure 9: Insulation blocks placed around the quartz tube to provide a quick-and-dirty test of the nichrome wire.

Three tests were performed with this setup. The first applied and input amperage and voltage of 9.7 A and 53 V respectively along the nichrome wire. The second used 19A and 120 V. The third used an Omega temperature controller of a model similar to that considered for the furnace. The resulting temperature profiles were recorded manually and shown in the figure below.

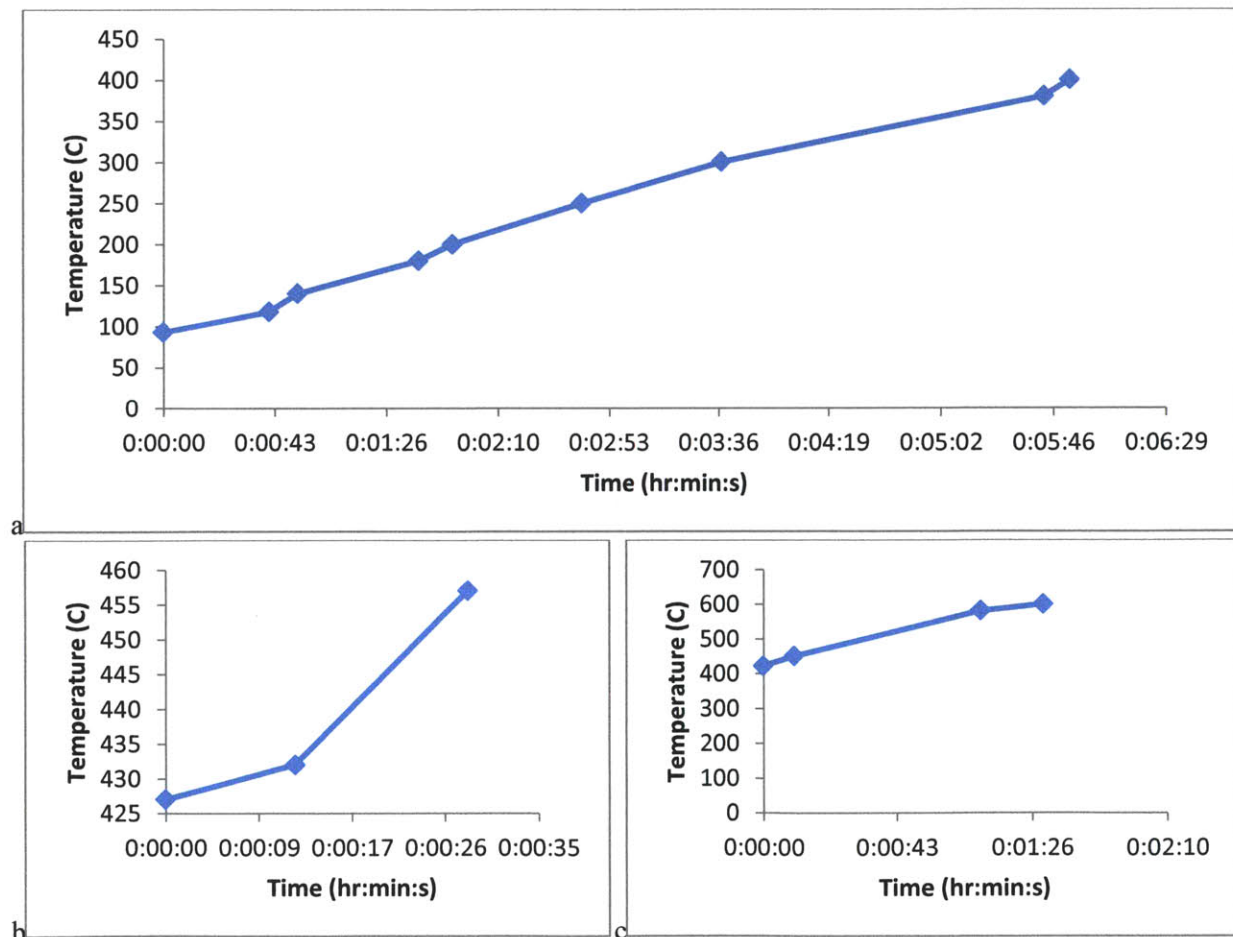


Figure 10: Preliminary data taken from quick-and-dirty test runs. Test a was the test performed at 9.7 A and 53 V. Test b was performed at 19 A and 120 V. Test c was performed using an Omega Temperature Controller.

The significant take away from these tests was that the wire could reach 600 C within a reasonable amount of time i.e. less than 10 minutes. The actual furnace would behave differently both because in the original design in Section 2 the heat transfer due to radiation would be minimized by the shield and because the wires would be packed closer together. The purpose of this test was to validate that the nichrome wire could work, which was demonstrated using these results.

5 Hydrogen Sulfide Concerns

The four gases flowing through the furnace are hydrogen sulfide, forming gas (a mixture of nitrogen and hydrogen), argon and nitrogen. Of all the chemicals flowing through this furnace hydrogen sulfide is the most dangerous, both to the human body and to the other chemicals that could be placed in the furnace. For this reason it was deemed important to provide a survey of the safety concerns and precautions to be taken when handling hydrogen sulfide.

For example hydrogen sulfide is a corrosive material, meaning that special care must be taken to ensure that the piping that handles H₂S doesn't wear down. Typically stainless steel is used for this purpose. However, for this application a section of the tubing would have to be movable, so that the end caps could be removed when placing samples in and out of the tube. Corrugated stainless steel hoses were chosen because they provide the corrosion resistance to H₂S, while also being flexible enough to move around.¹⁴ Because the only section of the assembly that required significant motion was the section connected to the caps, only the tubing connected to the caps would require any corrugated hose.

5.1 Information from the MSDS

Hydrogen sulfide is considered incompatible with the following materials, which were listed on the referenced Material Safety Data Sheet (MSDS).¹⁵

- Ammonia
- Bases
- Bromine pentafluoride
- Chlorine trifluoride
- Chromium trioxide and heat
- Copper (powdered copper and air)
- Fluorine
- Lead
- Lead oxide
- Mercury
- Nitric acid
- Nitrogen trifluoride
- Nitrogen sulfide
- Organic compounds
- Oxidizing agents
- Oxygen difluoride
- Rubber
- Sodium and moisture
- Water

This was not intended to be an exhaustive list as there are several other chemicals that can potentially react with hydrogen sulfide that were not placed in the MSDS. This list was provided as a warning and as a first step when considering what materials to avoid keeping around hydrogen sulfide.

5.2 Miscellaneous Reactions Possible Inside the Furnace

One possible byproduct that could accumulate in the furnace is ammonia, produced from the reaction of hydrogen and nitrogen. Hydrogen sulfide is incompatible with ammonia, so precautions were developed to ensure ammonia could not be formed in amounts that could endanger the furnace. In industry ammonia is produced using the Haber-Bosch Process. During this reaction one nitrogen and three hydrogen molecules react to form ammonia. Rubidium and Iron have been suggested as catalysts for this reaction, so care must be taken when using these materials in the furnace to prevent ammonia synthesis. While these reactants are present, however, the pressures generally required to catalyze this reaction are significantly higher than the pressures in this furnace, so this reaction seems unlikely.

In the human body, ammonia is produced at much lower temperatures than in the Haber-Bosch Process (room temperature and atmospheric pressure) using the protein nitrogenase. The active site on this enzyme is believed to be an Iron-Molybdenum cofactor with the stoichiometric formula MoFe_7S_9 , sometimes known as homo-citrate. In this reaction ammonia is produced from nitrogen, free electrons and protons (H^+ ions). Alternatively this reaction was demonstrated using a Palladium catalyst on a proton conducting oxide.¹⁶ That being said this reaction could be avoided by minimizing the presence of hydrogen ions unless necessary to the process occurring in the furnace.

These results were provided to illustrate the need for caution when running experiments in the furnace. Before any material is to be put inside of this furnace, the possible reactions with hydrogen sulfide must be studied.

6 Conclusion

A novel design for a tin-sulfide annealing furnace was developed and its heat transfer properties were explored. The furnace was designed as a tube furnace with two sections, one capable of reaching 200 C and another reaching 600 C. Analysis of the thermal interactions occurring within the furnace was done and information on possibly hazardous reactions that could occur within the furnace was provided. A brief survey of possible chemical reactions to occur within the confines of the tube was presented to advise future users of the furnace when running experiments with it. Once built, the furnace will be used to anneal tin-sulfide solar cell films, which will be tested as an alternative material in solar cell devices.

REFERENCES

- 1-“Nichrome 60 (NiCr) Resistance Wire.” Cornstock Park, MI. Mor Electric Heating Assoc., Inc. 1999-2010. <http://www.heatersplus.com/nichrome.htm>.
- 2-“Kurt J. Lesker Company | Home Page | Vacuum Science is our Business.” Kurt J. Lesker Co. Pittsburgh, PA. 2011. <http://www.lesker.com/newweb/index.cfm>.
- 3-“Stainless Steel Ball Valves.” McMaster Carr. Robinsville, NJ. 2011. <http://www.mcmaster.com/#stainless-steel-ball-valves/=cdwk2n>
- 4- “MC Series Mass Flow Controllers: Precision Gas Flow Controller Operating Manual.” Cole-Parmer Instrument Co. Vernon Hills, IL. 2011.
- 5-“Airgas – Gas, Welding, Safety Supply.” Airgas, Inc. 2011. www.airgas.com.
- 6-“Belkin F9P609-03 - PWR Strip 6Outlet w/ 3ft Cord Plastic.” Amazon.com, Inc. 1996-2011. <http://www.amazon.com/Belkin-F9P609-03-6OUT-Cord-plastic/dp/B002HHF1HG>.
- 7-“Ramp/Soak Temperature Controllers: ¼ DIN Ramp/Soak Temperature /Process Controllers with Modular Outputs and Communications.” Omega Engineering, Inc. 2003-2011. <http://www.omega.com/ppt/pptsc.asp?ref=CN3251>
- 8-“Biosystems ToxiPro Single Gas Detector.” Sperian Protection. Smithfield, RI. 2011.

- 9-“Heating Cables.” Pyrotenax. 2003.
- 10-“Infrared Industrial Heaters: Stock Emitters Manufactured by Heraeus Noblelight.” Heraeus Noblelight. Duluth,GA. 2010. http://www.noblelight.net/infrared_heaters/standard_sizes.shtml.
- 11-Cravalho, E.G., Smith, J. L., Brisson, J. G., McKinley, G. H., Thermal Fluids Engineering. Oxford University Press. 2011.
- 12-Lienhard, J.H., Lienhard J. H., A Heat Transfer Textbook. John H. Lienhard IV and John H. Lienhard V. 2000-2011.
- 13-“Online Materials Information Resource –MatWeb.” MatWeb, LLC. <http://www.matweb.com/>.
- 14-“Buy the Right Hose – Corrugated Metal Hose.” Hose Master, LLC. Cleveland, OH. 2007. <http://www.hosemaster.com/products/buytherighthose/corrugatedmetalhose/hose.php>.
- 15-Praxair Technology, Inc. “Material Safety Data Sheet: Hydrogen Sulfide.” Danbury, CT. 2009.
- 16-Rod, T.H., Logadottir, A., Nørshov, J. K. “Ammonia Synthesis at Low Temperature,” *Journal of Chemical Physics*. American Institute of Physics. 2000.