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DESIGN, FABRICATION AND TESTING OF AN APPARATUS FOR MATERIAL COMPATIBILITY TESTING IN NITRATE SALTS AT TEMPERATURES UP TO 700°C

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ABSTRACT

Thermal energy storage is one of the key differentiators between Concentrating Solar Power (CSP) and other renewable energy technologies. Molten salt is an effective and affordable method of storing thermal energy. Current salt storage systems charge at temperatures between 390°C and 585°C (oil filled parabolic trough systems to molten salt towers). It is highly desirable to increase the operating temperature of salt storage systems in order to increase the efficiency of the power cycle and to permit the use of alternative, high-temperature cycles. However, higher salt temperatures cause increased reactivity and thus increased corrosion rates in many materials. In order to utilize molten salt at higher temperature, it is necessary to test and understand these corrosion interactions at elevated temperature.

A corrosion test system has been designed and built for evaluating molten salt/material interactions to 700°C. The primary components of this system are several salt containment vessels that are constructed of 6” dia. x 24” long stainless steel, aluminum diffusion treated pipes with flat plate welded to one end and a flanged lid on the other. The vessels are designed to operate with a charge of 10 kg of molten salt and accommodate a “sample tree” on which corrosion test coupons may be suspended. The salt vessels are heated and insulated on the bottom half, roughly to the salt fill level, and cooled on the top half to protect the flange gasket and feedthrough ports. The samples trees have a stainless plate that reduces radiative heat transfer from the molten salt to the lid. Finite element analysis was performed to determine the pipe length and heating and cooling requirements to maintain molten salt at 700°C while limiting the lid gasket to 300°C or less.

The vessels are designed to have an oxygen atmosphere in the ullage region to mitigate nitrate decomposition. Oxygen systems for operation at 700°C require careful design including the sizing, routing, cleanliness, and material selection of components in order to reduce risk of fire. Additionally, the system is designed to run at 1-2 psig which requires specialized low pressure / high temperature components.

In this paper we present the design of the molten salt corrosion test system including details related to the containment vessels, oxygen handling system, and control software along with a discussion of the safety considerations necessary for these high temperature, high oxygen partial pressure tests.

INTRODUCTION

Renewable energy offers numerous advantages over conventional energy sources including the potential of reduced environmental impact and domestic production. For solar renewable energy to truly compete with coal and fossil fuels, however, it will be important to utilize systems that include energy storage to ensure dispatchability and reliability to meet utility load demands whenever they occur. Concentrating solar thermal systems have been demonstrated with thermal storage of many hours. The most widely used method of thermal storage is molten nitrate salt because of its relatively low cost, its environmental compatibility, and its high heat capacity, thermal conductivity, and an operational temperature range that closely matches today’s concentrating solar technology.

Current line focus (trough) systems charge the salt at temperature around 390°C. Molten salt tower point focus systems typically charge the salt at temperature approaching 585°C. The most commonly used salt for operation to 585°C is a nitrate salt composed of 60% sodium nitrate and 40% potassium nitrate. As the temperature approaches 600°C at atmospheric pressure with air as the ullage gas, the nitrate salt starts to dissociate and form nitrite compounds (1,2). As the temperature continues to increase, the percentage of nitrite continues to increase and the rate of corrosion of salt carrying materials (steels, stainless steels, etc.) continues. This process has been shown to be controlled to an extent by the use of oxygen as an ullage gas.

Operation of solar thermal plants with output temperatures between 600°C and 700°C is quite desirable because of the increase in power plant efficiency that should be achievable with these increased temperatures. Operation at temperature near 700°C also offers the opportunity to utilize alternative power cycles to the commonly used subcritical Rankine cycle.

In order to realize these higher output and storage temperatures, however, it will be necessary to understand the effects of the molten salt at these temperatures on potential materials for use as pipes, valves, heat exchangers, and storage vessels. This understanding is important because of the significant rise in the cost of pipe materials for high temperature and high corrosion resistance. Another concern is the grade of salt necessary for utilization in the solar plant. Of key importance is an understanding of the amount of chloride that is really allowable in a heat transfer system. Past research has studied the effects of salt impurities up to 570°C (3) but the work needs to be extended to higher temperatures. Current practice by component suppliers is to require high grade salts with almost no chloride, while a slightly lower grade salt would cause a significant reduction in the cost of the salt. The exact correlation between purity, corrosion, and temperature needs to be further explored in order to minimize the cost of the thermal storage system in a concentrating solar power plant.

To that end, Sandia National Laboratories has built a set of vessels for the testing of corrosion rates of materials suspended in molten salt at temperatures up to 700°C. The design of these test vessels required thermal analysis, careful selection of materials, and painstaking attention to detail in the oxygen system for use at these high temperatures.

SYSTEM DESIGN AND THERMAL ANALYSIS

The design of the molten salt corrosion test vessels (MSCTV) began with the identification of a set of design goals. The design goals included operation at temperature up to 700°C with continuous runtime of 3000 hours needed for corrosion testing. The vessels needed to have the ability to maintain an "oxygen blanket" in the ullage above the salt which required the design of a pressure system that would safely handle oxygen in a high temperature application with fire prevention of primary concern in every decision. Also, because of the oxygen system, the vessels are designed as pressure vessels and require a pressure safety design. The materials selected for the vessel and all pressure components must be adequate for the maximum temperature or must have protection from that temperature. And the vessel must be designed to minimize the corrosion of the vessel and pressure components both for the longevity of the test system and for the reduction of contaminants in the salt that would reduce the ability to correctly identify corrosion rates and corrosion products from the materials under test.

Conceptual Design

The conceptual design for the molten salt corrosion test vessels is based on two primary sources. The first is a set of existing corrosion test vessels at Sandia national Laboratories which are used for testing of molten salts up to 585°C. The second source is a design by ENEA (4) used for testing the gases and nitrites produced in molten salt to 560°C. With these two design bases, the concept of the MSCTV was developed to utilize 152.4mm nominal diameter (6" schedule 40) 316 stainless steel pipe for the vessel as shown in Fig. 1. A section of pipe 609mm (24") long was welded to a flat circular plate 12.7mm thick with the plate acting as both the bottom end cap of the vessel and the mounting flange for the support bolts. The support bolts are welded to a 610mm square stainless steel tray that acts as secondary containment to catch any salt leaks or spills and also as a large base to prevent the vessel from tipping over. The support bolts hold the vessel 50mm off of the tray and two 25mm layers of rigid insulation are placed between the tray and the vessel. The rigid insulation and the small conduction area of the support bolts is designed to reduce heat loss out of the bottom of the vessel. To further limit conduction and to protect the floor, the tray is sitting on 240mm of insulating refractory bricks. The pipe section is intended to be filled half full of salt (approximately 300mm) for materials testing.

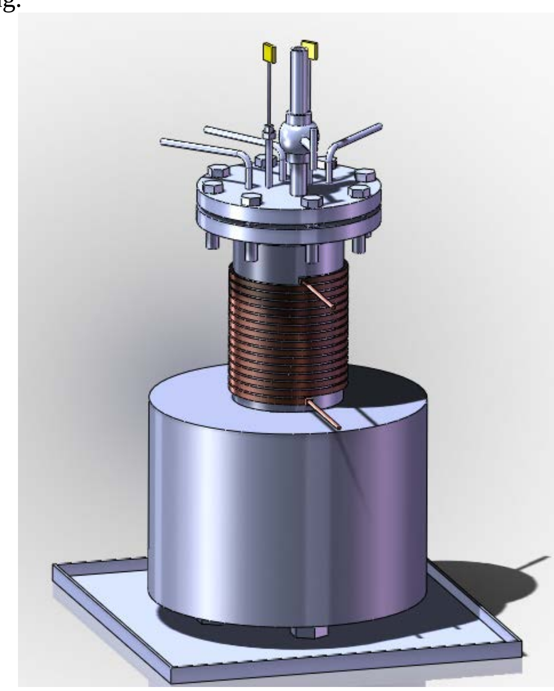

FIGURE 1. A MOLTEN SALT CORROSION TEST VESSEL DESIGN CONCEPT

The top of the vessel has a 150# slip-on weld flange welded to the pipe. This flange interfaces with a mica-stainless spiral-wound gasket (Flexitallic type CG) and a 25mm thick blind flange that serves as the lid of the vessel. The flange and gasket provide a means of securing the lid in a gas-tight configuration to maintain the purity of the oxygen ullage gas when used at temperatures over 600°C.

The pipe vessel is heated by two 25mm heater bands that are stainless steel with mineral insulation (Watlow Inc.) with a maximum output of 1000W. The bottom half of the pot is insulated with 3 layers of 50mm thick mineral insulation blanket (Thermal Ceramics Kaowool RT). Between each of the layers of insulation blanket, there is a wrap of aluminum foil to reduce infrared radiation, especially for operation above 600°C. The outside of the mineral insulation blankets is covered with a stainless steel sheet material. The top of the insulating blanket roll is also covered with this sheet material. The purpose of the stainless sheet is to prevent salt from spilling, leaking, or wicking into the insulation. Salt in the insulation ruins the insulating properties of the blanket and also can cause shorting of the electrical heater band so it is important to have this protective blanket in place. From a human safety perspective, this sheet also prevents the blanket from readily releasing fibers when the insulation bundle is bumped. After the ceramic blanket has been heated, the fibers released from the blanket material are of a size that may present a respiratory hazard so it is prudent to have a cover to significantly reduce the accidental release of these fibers.

The purpose of having a long vessel and only filling it half full of molten salt is to use the upper half of the vessel for cooling to prevent damage to the flange gasket and oxygen system components. Only the bottom half of the vessel has heater bands and insulation to allow natural convection to cool the top of the vessel as can be seen in the section view presented in Fig. 2. The upper half of the pipe also has a copper coil wrapped around it through which chilled glycol can be circulated to further cool the vessel's top half. The top of the vessel must have its temperature low enough to prevent damage to the flange gasket and the gas system components, some of which have relatively low operating temperature ranges.

The blind flange which is used as a lid for the vessel has many holes penetrating it. Stainless steel tubing is welded into these holes and serves as feed-through ports for thermocouples measuring fluid and gas temperature, oxygen inlet and outlets, and a sample port used to collect samples of the salt for compositional analysis.

The lid also has a "parts tree" hanging into the salt bath. This tree is stainless steel tubing with orthogonal sets of threaded rod that are used to support material samples in the salt bath. The parts tree has a stainless steel circular plate fixed slightly above the half height position of the vessel. The purpose of this plate is to reduce the thermal radiation from the salt bath directly to the vessel lid and the top half of the pipe.

Thermal Analysis

In the design of the corrosion test vessels, it was necessary to protect some of the components from the 700°C temperatures found in the lower half of the pot. The flange gasket is limited to a maximum temperature of 300°C. Some of the oxygen system components have relatively low maximum temperature capabilities. When possible, these components were protected by distance, positioning them remotely from the test vessel with significant lengths of stainless tubing between the components and the salt vessel. For some components, however, positioning distantly was not a possibility. The lowest rated component on the salt pot itself is the 25mm ball valve for sampling the salt with a maximum temperature rating of 232°C. Because of the need to protect this valve and the flange gasket, a thermal finite element analysis was performed to determine the maximum temperature that these components would experience in both normal and abnormal operation.

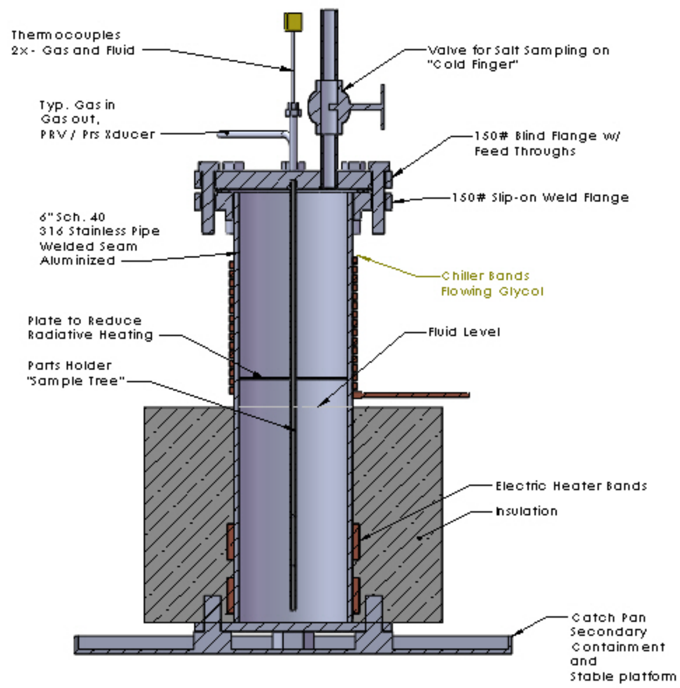

FIGURE 2. A SECTION VIEW OF THE VESSEL SHOWS THE HEATER BANDS, INSULATION AND PARTS TREE.

The thermal analysis modeling was done on an earlier configuration of the vessel as shown in Fig. 3. The thermal modeling used only the top half of the vessel because the primary concern was the cooling of the top of the vessel. The salt and vessel walls below the mid line of the vessel were assumed to be 700°C. In the modeling, the insulation extended further up the vessel walls than in the final design, but this gave a more conservative estimate of the ability to maintain the top components at acceptable levels. Four different analyses were performed and the conditions are shown in Table 1. These analyses include the most conservative case with no external radiation and no chiller bands to the most realistic which includes external radiation from the vessel and chiller bands. The analysis utilized half symmetry of the vessel and a large bounding box with ambient boundaries assumed to be at 40°C. For cases with the chiller band, the band was assumed to be 12mm thick with the outer surface maintained at 49°C to simulate a significant flow of coolant through the coil. The coil was positioned around the upper diameter of the vessel between the insulation and the slip-on weld flange.

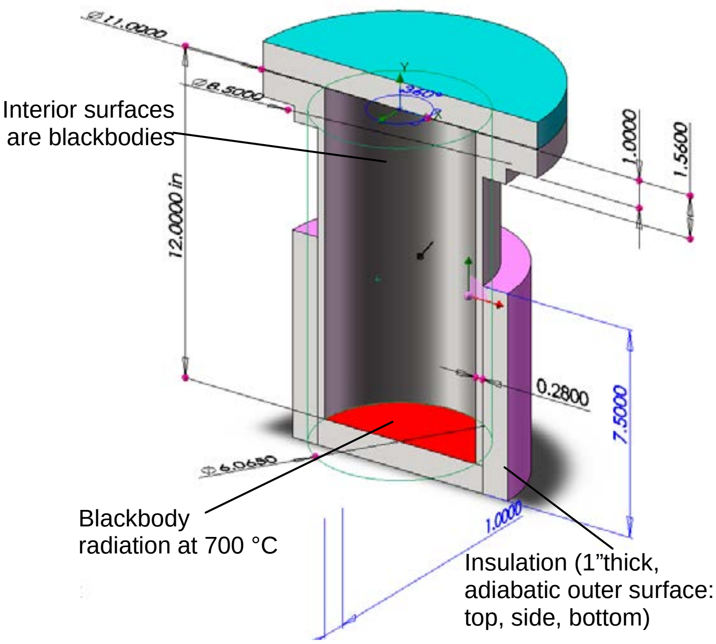

FIGURE 3. THE MODEL USED IN THE THERMAL ANALYSIS INCLUDES ONLY THE TOP HALF OF THE VESSEL WITH THE BOTTOM HALF ASSUMED TO BE ISOTHERMAL AT 700°C.

TABLE 1. FOUR SETS OF CONDITIONS WERE USED IN THE THERMAL ANALYSIS FROM THE MOST CONSERVATIVE #1 TO THE MOST REALISTIC #4.

Analysis	Int. Radiation	Ext. Rad.	Chiller Band
#1	X	-	-
#2	X	X	-
#3	X	-	X
#4	X	X	X

The analysis was performed in Solidworks Flow Simulation using 316 Stainless steel for the material of the vessel and all components. Figure 4 shows the graphical result of analysis case #1. Evident in the figure is the convective flow created by the warm surfaces of the top and sides of the vessel. Table 2 shows the results of all four analysis cases and displays the performance metrics of the temperature at the bottom of the lid, and the heat losses through the various mechanisms. The most important result is that the temperature at the bottom of the lid is below the 300°C maximum temperature limit of the flange gasket. This indicates that even with the chiller band not operating, the gasket would still remain at an acceptable temperature. The chiller band is still part of the design to provide extra margin for the components, but knowing that the vessel is safe even in the event of a loss of chilled fluid is comforting.

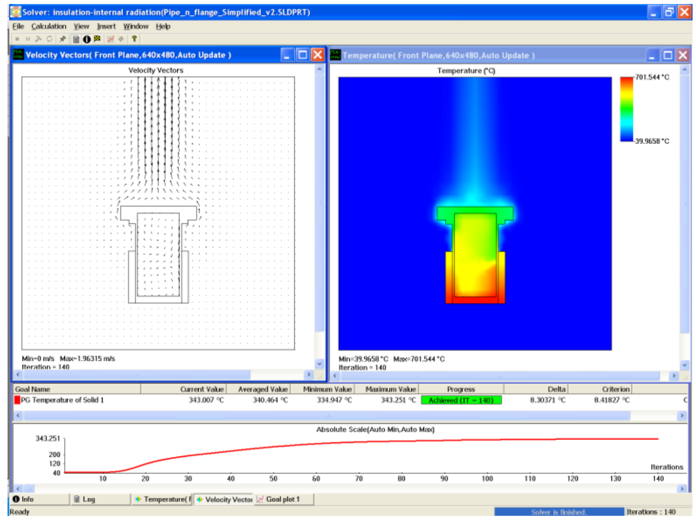

FIGURE 4 . AN IMAGE FROM ANALYSIS CASE #1 WITH NO EXTERNAL RADIATION AND NO CHILLER BAND SHOWS THE CONVECTIVE FLOW CREATED BY THE HOT LID AND WALLS OF THE VESSEL.

TABLE 2 . THE RESULTS OF ALL 4 THERMAL ANALYSIS CASES SHOW THAT IN ALL BUT CASE 1, THE TEMPERATURE AT THE BOTTOM OF THE LID IS WITHIN THE DESIRED RANGE.

Metric	Analysis Case			
	1	2	3	4
Lid Temp (°C)	340	180	78	74
Total Convective Heat Loss (W)	474	204	21	18
Total Radiative Heat Loss (W)	N/A	447	N/A	30
Heat Loss to Chiller Band (W)	N/A	N/A	595	575
Total Heat Loss (W)	474	651	616	623

Pressure Analysis

The system is designed to operate just above ambient pressure so that the ullage gas will be maintained at a high partial pressure of oxygen. The salt vessel and all attached stainless tubing and components were analyzed for their pressure capacity. The operating temperature of 700°C causes a significant loss of tensile strength in 300 series stainless steel, and it is important to evaluate the 316 stainless used at the correct temperature. The ASME Boiler and Pressure Vessel Code was used for the material properties and calculation methods. The results of the pressure calculations for the vessel are shown in Table 3. As seen in the table, the bottom end plate is the limiting portion of the vessel and this is primarily due to the butt weld used between the pipe and the plate. A better choice of weld would give a higher working pressure.

TABLE 3. THE MAXIMUM ALLOWABLE WORKING PRESSURE FOR THE VESSEL

Analysis	Maximum Allowable Working Pressure
Flat End Plate	147kPa / 21psig
Cylindrical Vessel	1110kPa /161psig
Flange Bolts	2165kPa /314psig

The initial design operating pressure was 2.3kPa (0.33psig) and there are check valves that can be used as pressure relief valves for this level of pressure. Unfortunately, these check valves have a relatively higher reseating pressure of 20.6kPa (3 psig). Additionally, these valves have high variability in operation pressure up to 20.6kPa. Because of this, though the intended operation pressure is 2.3kPa, the pressure for calculation purposes must be 20.6kPa to accommodate the variability in release pressure. In order to better deal with this uncertainty, a backpressure regulator was selected as the primary means of setting backpressure in the system. A pressure schematic is shown in Figure 5 where every number identifies a unique pressure component or fitting. Because of this significant number of fittings, the pressure design process was extensive.

An important aspect of the pressure design was to plan for the presence of high purity oxygen in a 700°C environment. It is important to incorporate the guidance of standards and guidelines for the design of oxygen systems (5,6,7). These guides give best practices to be followed to mitigate the risk of fire. Each step of the design must include consideration of cleanliness, minimization of dead legs in the flow path, proper selection of materials in all valves, regulators, components, and safety equipment, proper electrical grounding, low flow rates and slow acting valves to prevent pressure wave ignition. The system also cannot have hoses so the design must have disconnects to allow for removal of the vessel lid from the pressure system. Additionally, the system was designed with electronics outside of the test cells to the extent possible to isolate electrical energy from the potential oxygen environment.

The final pressure safety measure is the inclusion of a sophisticated control system that monitors multiple temperature points, oxygen and coolant flows, heat band current, and that has the ability to remove power from the system and to stop the flow of oxygen when measured parameters leave the design space.

FABRICATION, INSTALLATION AND STARTUP

The pipe sections were welded to the flat base plates and then all components that would be in contact with the salt were sent out for aluminization. The aluminization process provides an oxidized layer on the surface of the stainless steel giving the stainless increased corrosion resistance at elevated temperatures. The purpose of this process was to prevent the salt vessel from corroding into the salt mixture. This permits the salt mixture to be tested to determine the elements that have been reacted out of the materials under test.

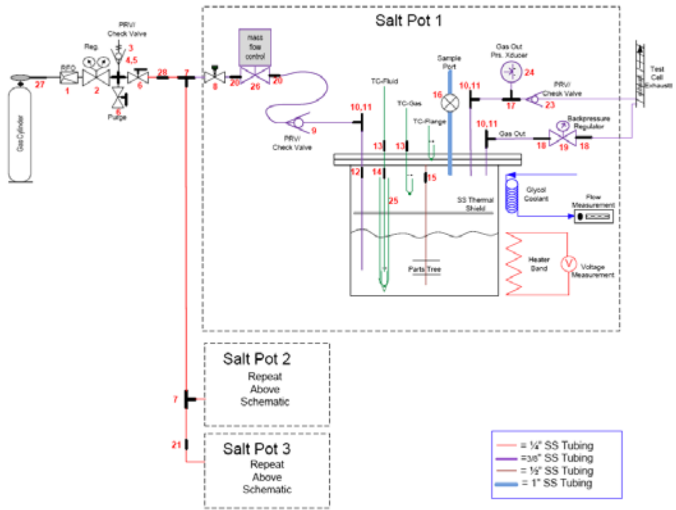

FIGURE 5 . THE PRESSURE SCHEMATIC SHOWS THE COMPLEXITY OF THE SYSTEM. EACH NUMBER ON THE FIGURE REPRESNETS A UNIQUE PRESSURE FITTING.

The Molten Salt Corrosion Test Vessels have been installed in individual test cells. Each test cell has ventilation and an outside air exchange. All electronics which could be placed outside of the room have been, especially the power electronics for operation of the heater bands. The floor of the test cell was first lined with a layer of refractory bricks, and then a square stand of 3 layers of furnace bricks was built to hold the salt pot and to further insulate the floor from the hot salt vessel. The salt vessels were assembled to the catch-pan stands and electrical connections were made. The vessels were then insulated and measurement channels were wired for thermocouples, flow switches, and flow controllers. A salt vessel is shown if Fig. 6 before the addition of insulation and outer stainless steel sheathing.

Initial startup of the system showed the ability to reach 540°C, but the winter cooling combined with lower than expected voltage to the heater bands required the addition of a second heater band to achieve higher temperatures. The system has been charged with an initial 10kg of salt which has been used for system testing and also to collect any residual materials left on the surfaces of the vessel from the manufacturing process.

TESTING

Startup testing of the salt vessels has shown the ability of the vessels to reach 700°C and to maintain the flange and oxygen equipment at acceptable temperatures. Figure 7 shows a plot of the fluid temperature as the vessel heats the fluid from 585°C to 700°C and then maintains the salt temperature at

700°C for 2 hours. The Figure shows that even at these elevated salt temperatures, the oxygen in the ullage region reaches a maximum temperature of 150°C and the flange temperature reaches a maximum of 54°C. This ability to keep the flange and ullage temperature low shows the adequacy of the design especially in light of the test being run with the lowest flowrate of coolant possible. During this test, none of the oxygen components reached temperature over 22°C while the stainless steel sheathing on the outside top of the insulation reached 40°C which reduces risk of injury to the user. The salt vessel right at the top of the insulation did reach 331°C so it is still imperative that the user wear thermal insulating gloves and be aware of the potential for high temperature, but this region is very small and isolated.

FIGURE 6. A MOLTEN SALT CORROSION TEST VESSEL SHOWN IN THE TEST CELL BEFORE INSULATING.

CONCLUSIONS

A set of salt vessels was created for testing of corrosion in molten nitrate salts at temperature up to 700°C. The design of the vessels allows the salt to reach the desired temperature while protecting the flange gasket and the oxygen components from the excessive heat. The design also includes the ability to use oxygen in the ullage space to reduce the rate of nitrate formation in the molten salt. The oxygen system design and fabrication was completed with specific attention directed toward preventing fire by following design best practices.

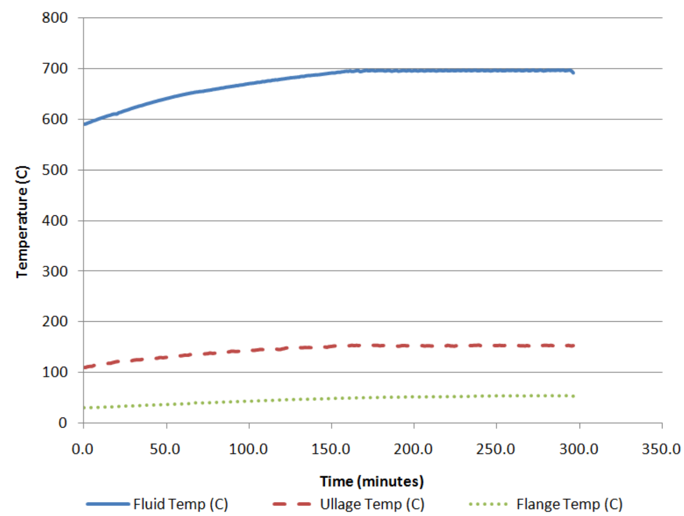

FIGURE 7. PLOT OF VESSEL HEATING UP FROM 585°C TO 700°C AND THE FLANGE AND ULLAGE GAS TEMPERATURE DURING THIS PROCESS

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