# Thermal Modeling of Chlorination Reactor

Asif Ahmad Bhat*[1], B. Muralidharan[1], G.Padmakumar[1] and K.K.Rajan[1]
[1]Fast Reactor Technology Group
Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, India.
*Corresponding author: 207, PPES, FRTG, IGCAR, Kalpakkam, 603102; asifbhat@igcar.gov.in

**Abstract:** Chlorination reactor is used to dry molten LiCl-KCl eutectic salt before it is put to use in electrorefining operation [1]. Molten salt electrorefining is a pyrochemical method of separation of heavy elements from spent metallic nuclear fuel. It is a high temperature process which uses molten salt as supporting electrolyte for electro deposition of heavy metals. The LiCl component in the molten LiCl-KCl salt is more reactive towards $H_2O$. The LiCl-KCl eutectic salt likely forms hydroxides when moisture is introduced in the system.The salt is first vacuum dried and then reacted with $Cl_2$ in chlorination reactor to remove the left out moisture.To arrive at the adequate design of the reactor, temperature distribution needs to be accurately predicted inside the reactor. This paper describes the thermal modeling of chlorination reactor using COMSOL Multiphysics.

**Keywords:** chlorination reactor, chlorination, thermal analysis, multiphysics

## 1. Introduction

The chlorination reactor forms the central component of salt handling and purification system. In this system, molten LiCl –KCl salt is purified before being put to use for electrorefining operation.The purification of the salt is carried out by vacuum drying followed by bubbling the chlorine gas through the salt melt at around 500˚C.The salt handling and purification system consists of nitrogen atmosphere glove box, vacuum oven, chlorination reactor and storage and transfer vessels. The salt is mixed with the blender provided in the glove box and fed to the vacuum oven to remove superficial moisture. The vacuum drying is carried out at 125˚C for about 36 hours. The vacuum dried salt is subjected to intrinsic moisture removal in chlorination reactor. About 50 kg of the salt can be processed in the reactor.

The reactor consists of graphite crucible graphite liner, graphite lid and an outer vessel made of Inconel.The graphite liner is provided to prevent the corrosion of Inconel vessel. The reactor has provision for gas (nitrogen, argon and chlorine) s and outlets, powdered salt transfer line, molten salt, pressure gauges and thermo wells. Figure1 shows the layout of the chlorination reactor.The vessel is heated by an external resistance heating furnace under vacuum. Once the LiCl-KCl salt is transferred to the reactor vessel, the vessel is evacuated and purged with nitrogen. When the temperature of the salt reaches 200˚C, the atmosphere of the vessel is changed from vacuum to chlorine. The chlorine gas is bubbled through the melt for about an hour. The chlorination reaction as shown below takes place at 500˚C.

$$Cl_2 + LiOH \rightarrow LiCl + HOCl + HCl$$

The system is the bubbled ultra high pure argon gas followed by evacuation of the vessel. The chloride impurities thus resulted from hydroxide impurities and the un-reacted chlorine gas is neutralized in the sodium hydroxide scrubbing system. The purified moisture free salt from the chlorination reactor is transferred to storage vessel wherefrom it is fed to electrorefiner.

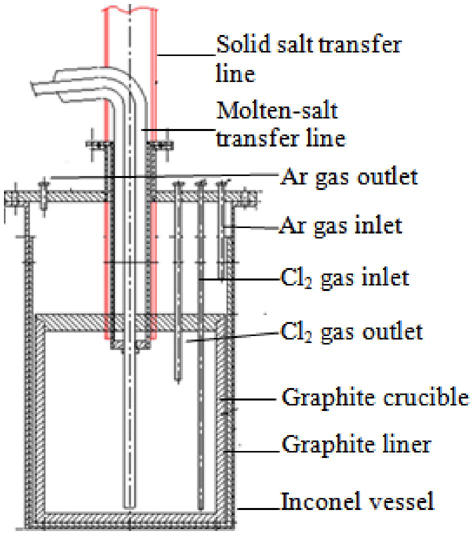

**Figure 1:** Schematic diagram of chlorination reactor.

The two dimensional axisymmetric model of chlorination reactor is considered in this computational analysis, using COMSOL Multiphysics.

## 2. Use of COMSOL Multiphysics

### 2.1 Numerical model

The heating process in the chlorination reactor is a multiphysics problem. The reactor is heated by resistance heating furnace. This heat is transferred from outer inconel vessel to crucible contents by conduction through the physical contact of the components, by convection via the gas in the cover gas space and by radiation. The different physical fields i.e., fluid flow and heat transfer phenomena are coupled due to the inter-related nature of physical properties. Hence non-linear properties of the materials are considered to model the heating process in the reactor. The effect of forced convection water cooling on the flange temperature is also modeled. The chlorine bubbling and melting processes have not been modeled in this study.

### 2.2 Geometry

A simplified 2D axi-symmetric model of the chlorination reactor was setup in COMSOL. The model has the same dimensions as that of the reactor. The geometry was created and modified using Geometry tool of COMSOL. Materials were assigned to different domains of the model using COMSOL Material Library [5] and along with some user defined materials. Physics controlled extremely fine triangular mesh was used for the model using Mesh tool. Figure 2 shows the COMSOL model of the chlorination reactor

### 2.3 Main features of the model

To model heat transfer in chlorination reactor, it is possible to approximate it as a 2D axisymmetric geometry due to the cylindrical symmetry while ignoring the nozzle connections. The conjugate heat transfer interface which combines heat equation with turbulent flow, is used. The physics interface is used to model energy transport in single-phase flows at high Reynolds numbers. The physics interface is applicable for low Mach number (typically less than 0.3) flows. The Conjugate Heat Transfer interfaces solves for conservation of energy, mass and momentum in fluids and for conservation of energy in solids. Turbulence effects are modeled using the standard two-equation k-ε model with realizability constraints. Flow and heat transfer close to walls are modeled using wall functions.

The buoyancy driven flow in the cover gas is modeled by using volumetric force term. The model has different domains like argon, crucible, salt, vessel, shields etc. The fluid flow or momentum equation is solved only in argon space. To model convection in argon space between the shields; effective conductivity model [2, 3] is used. This model helps in capturing the convective heat transfer phenomena by changing the conductivity of argon to effective conductivity and as a result the model requires only energy equation to be solved in argon cover gas between the shields.

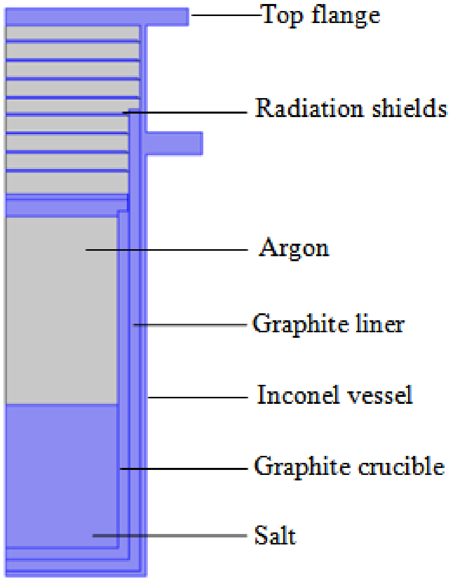

**Figure 2:** 2D-axisymmetric COMSOL Multiphysics model of chlorination reactor.

### 2.4 Governing equations and boundary conditions.

The heat transfer and fluid flow phenomena in the chlorination reactor model are governed by continuity, momentum and energy equations. These equations, for the model, are solved in COMSOL Multiphysics [5] using the formulations given below. The equations are based on assumptions of steady state, incompressible flow, Newtonian and low viscous fluids.

*Continuity Equation*

$$\frac{1}{r}\frac{\partial}{\partial r}(ru)+\frac{\partial}{\partial z}(v)=0 \qquad 1$$

*Momentum Equation*

$$\rho u\frac{\partial u}{\partial r}+\ \rho v\frac{\partial u}{\partial z} = -k\frac{\partial p}{\partial r}+\mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}(ru)\right)+\frac{\partial^2 u}{\partial z^2}\right] \qquad 2a$$

$$\rho u\frac{\partial v}{\partial r}+\ \rho v\frac{\partial v}{\partial z} = -k\frac{\partial p}{\partial z}+\mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}(rv)\right)+\frac{\partial^2 v}{\partial z^2}\right] +\ \rho(T)g_z \qquad 2b$$

*Energy Equation*

$$\rho c_p u\frac{\partial T}{\partial r}+\ \rho c_p v\frac{\partial T}{\partial z} = k\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\partial^2 T}{\partial z^2}\right] \qquad 3$$

Where $\rho$ is the fluid density, u & v represent r & z components of velocity, μ is dynamic viscosity $c_p$ is the heat capacity k is thermal conductivity of the fluid and T is the absolute temperature. All the physical properties are constant. The ρ(T) in Eq. 2b is only the term which is not constant and varies with temperature. The ρ(T) depends on temperature variation in the fluid and is coupled to the energy equation. The k-ε model is used to model the flow falling under turbulent regime.

All the equations are solved in fluid computational domains of the model while only energy equation is solved in solid domains [5]. The boundary conditions imposed for fluid flow are no slip and pressure point constraint. For the heat transfer boundary conditions, all the initial temperatures are set to 30˚C. All the inside free surfaces in the model are allowed to participate in surface to surface radiation. Dirichlet boundary condition is imposed for furnace wall heating. The other outer vessel wall surfaces are allowed to participate in surface to ambient radiation and convective cooling using suitable values of heat transfer coefficients [4]. Water cooling on the vessel wall near the top flange is given as convective cooling boundary condition. The heat transfer coefficient is calculated using Dittus-Boelter correlation by assuming cooling water to be at the temperature of 30˚C and channel dimensions of 0.06 m height and 0.035m width.

## 3. Numerical Results

The chlorination reactor model is solved for steady state velocity field and temperature distribution simultaneously. The study is carried out with furnace temperature i.e. the surface temperature of outer vessel of the reactor of 600˚C and with eight number of inconel radiation shields placed in cover gasspace between the crucible lid and the top flange of the reactor. Figure 3 and Figure 4 show the three dimensional and two dimensional temperature distributions in the reactor. The average temperature in the salt region is around 500˚C. The temperature gradually decreases in the salt region followed by a rapid decrease in the cover gas region between the salt surface to the crucible lid. The temperature again gradually decreases in the radiation shield region.

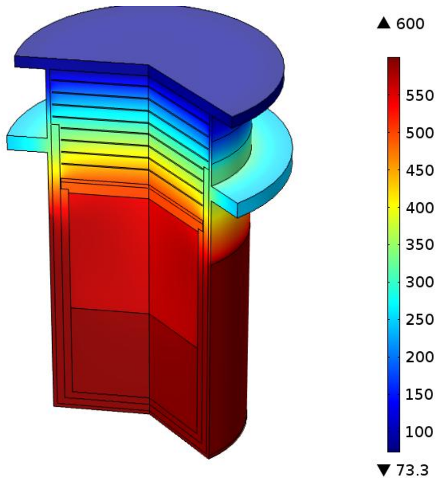

**Figure 3:** 3D Temperature distribution in the chlorination reactor

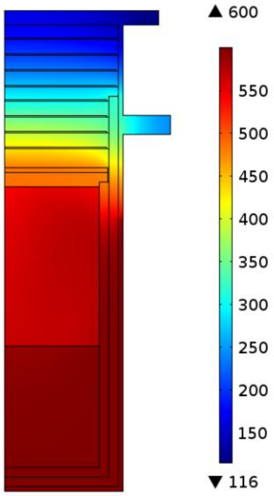

**Figure 4:** 2D-Temperature distribution in chlorination reactor.

The velocity field in the cover/argon gas region occupied between the sat surface and the crucible lid is also modeled using the boundary and domain conditions as mentioned above. Figure 5 shows the stream line and arrow plot of the velocity field. As seen from the plot, convection loop is formed in the argon space. The maximum velocity is towards the entre of the reactor. The velocity field is further generated for the case of vessel wall cooling. Figure 6 shows the shows the stream line and arrow plot of the velocity field obtained in this case. It is seen that the two convection loops are formed in the cover gas space.

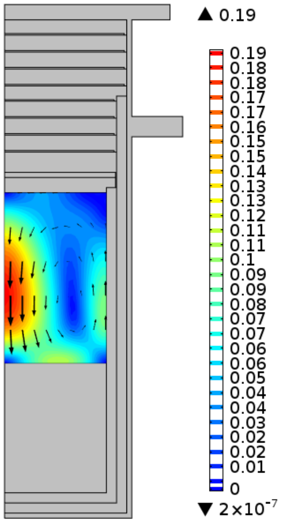

**Figure 5:** Velocity distribution in the cover gas (Natural convection case).

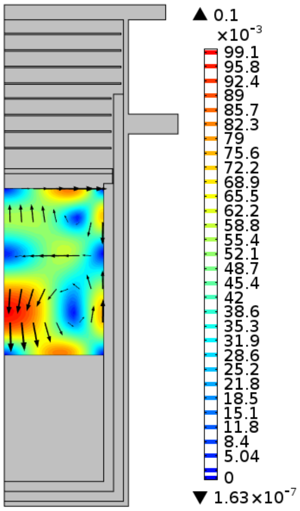

**Figure 6:** Velocity distribution in the cover gas (Forced convection case)

Figure 7 shows the temperature on the top portion of outer vessel along the height, both with and without water cooling, obtained from the study. The top flange temperature in case of natural convection heat loss is in the range of 80-100˚C. There is 50 % reduction in the flange temperature when water cooling is used. However, the temperature profile is steep in the top vessel portion. It can be inferred from the results that the temperatures in the top flange are within acceptable limits for the case of natural convection cooling and that the water cooling may lead to structural integrity problems of the vessel.

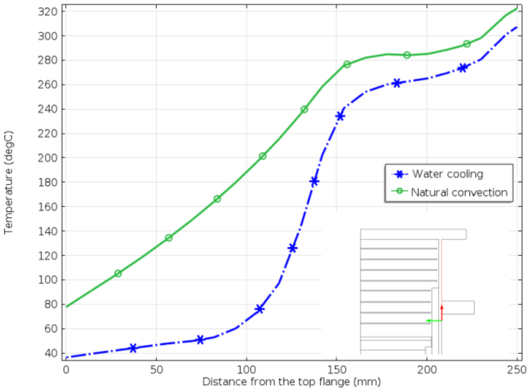

**Figure 7:** Temperature profile in top portion of outer vessel.

## 4. Conclusions

This paper presents the solution of heating problem in the chlorination reactor using COMSOL. Based on the assumption that heating is invariant in one dimension, a 2D-axisymmetric model of chlorination reactor was setup in COMSOL Multiphysics and the steady state solution, for various conditions was generated. The results of this study have shown that furnace temperature of 600 ˚C is sufficient to maintain the salt phase at temperature of about 500 ˚C. The water cooling, if attempted for the vessel, will change temperature distribution in the reactor and result in steep thermal gradients in the vessel wall hence calling for thermal stress analysis of the components.The radiation shields provided and with natural convection cooling of the vessel wall, the top flange temperature is reasonable to allow smooth operation of the reactor. The numerical analysis of chlorination reactor, using COMSOL Multiphysics, serves as a valuable tool for the thermal and mechanical, design of the chlorination reactor.

## 5. References

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