Transport Of Cadmium Through Molten Salt To Argon Cover Gas In Electro Refiner

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Abstract : Electro refining is one of the important step in the Pyro processing of nuclear spent fuel with molten salt. The electro refiner is a process vessel consists of anode ,cathodes and stirrers and ultra –high pure argon gas is provided at the top for inert atmosphere and at the bottom , a cadmium layer is provided. As the vapour pressure of the cadmium is high at the operating temperature, the cadmium vapour transport through the molten salt and argon cover gas at the top of the electro refiner which may lead to the choking of components /mechanism. An axi-symmetric, 2-dimensional mathematical model in COMSOL Multiphysics® has been developed to study the transport of cadmium vapour through the salt solution and in argon gas.

Keywords: Cadmium vapours, molten salt, argon, diffusion, COMSOL.

INTRODUCTION

Reprocessing of spent fuel from the future metallic fuelled Fast Breeder Reactors (FBR'S) is proposed to be carried out by electrochemical process employing a molten LiCl-KCl salt as electrolyte. A pool of molten cadmium will be available at the bottom of the molten salt in the electro refiner. A 10 Kg engineering scale facility of electro refiner is being set up in IGCAR, Kalpakkam. A schematic of an electro refiner is shown in fig.1. Chopped spent fuel pins kept in a perforated basket acts as anode and a steel rod acts as cathode. Heavy metal from the anode basket gets electro-transported to the cathode. At the bottom of the High Temperature ElectroRefiner (HTER) a layer of liquid cadmium is provided which acts as sacrificial anode to dissolve the heavy metals falling to the bottom of the vessel. The salt is maintained at 500°C. The furnace is provided at the outer surface is the heat source for HTER. Argon gas above the salt surface maintains the inert atmosphere since LiCl-KCl is hygroscopic in nature. Since the vapour pressure of cadmium at 500°C is high (15 mmHg), the cadmium evaporates through the salt. This cadmium vapour diffuses through the salt surface and diffuses in to the argon cover gas space. Since top argon gas space is relatively colder than the salt region the cadmium vapours gets condensed and solidified at the cooler regions in the argon space, causing the equipment operation and handling problem.

DESCRIPTION OF HTER

In electro refining process, spent fuel will be used as anode and cadmium as cathode. The electrolyte salt will be kept at 500°C, which is sufficiently above the eutectic melting point (360°C). The electrolytic process will be carried out in a crucible containing salt over 50 mm layer of cadmium and ultra–pure argon as a covering gas. Since the melting point and boiling point of Cadmium is 321°C an 767°C respectively, the cadmium will present in the molten state in the bottom layer. A stirrer is provided in the salt region to achieve uniform distribution of electrochemical species in the electrolyte. In the argon cover gas radiation shields are provided to keep the top of HTER around 100°C, where 'O' rings are provided. In the argon gas region below the radiation shield, natural convection current is established due to the temperature difference at the salt interface and below the radiation shield. Since the vapour pressure of the cadmium at 500°C is high, the vapours of cadmium diffuses through the salt and argon gas and deposits at the cooler regions of the cover gas[1].

SCOPE OF THE WORK

In this paper, the transport of cadmium vapour from the salt surface to the argon cover gas region has been studied. From this analysis, the rate of cadmium transport in argon gas was estimated. This rate of transport will be useful for the design of a cadmium vapour trap.

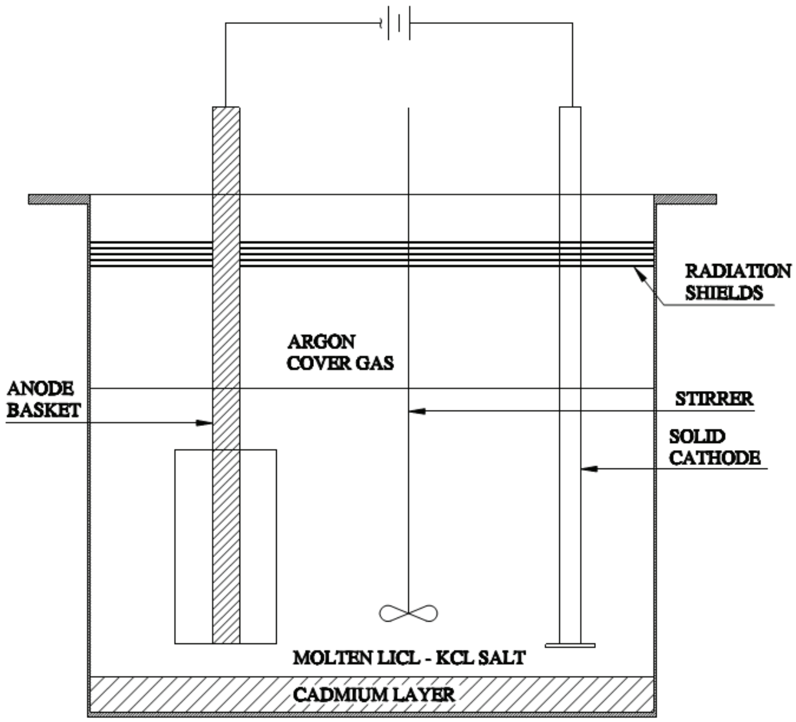

Fig.1: Schematic Sketch of the HTER

DESCRIPTION OF GEOMETRICAL MODEL

A 2-D axisymmetric model in cylindrical co-ordinates is considered. The bottom region is filled with eutectic LiCl-KCl salt mixture with stirrer to enhance the turbulence in the salt. The argon cover gas is above the salt surface. In this model the argon gas region below the first radiation shield only is considered for modelling, as the convection in the argon is comparatively negligible in the space between the radiation shields, it is neglected. The diameter of the cylindrical process vessel is 0.880 m .The height of the salt level is 0.320 m and the height of the argon region below the radiation shield is 0.389 m.

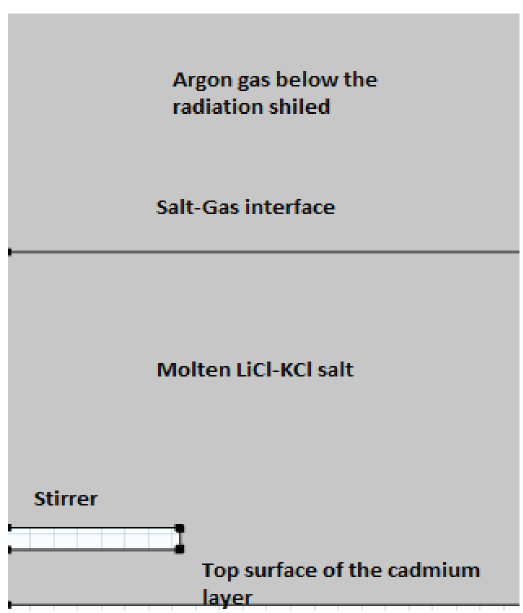

Fig.2: Axi symmetrical model of HTER

DESCRIPTION OF MATHEMATICAL MODEL

In this model the transport of cadmium in the salt region and argon gas region under transient condition is considered. The convection in the salt due to the stirrer is modelled using turbulent mixing in the salt and the temperature of salt is uniform at 500°C. The convection in the argon gas due to the temperature difference in the gas region is modelled using heat transfer in the argon cover gas region. The three main equation used in the analysis are continuity equation, momentum equation, and energy equation. The boundary condition imposed in this model are temperature, no slip , pressure point constraint in heat transfer module. The pressure, sliding wall, no slip wall boundary conditions are used in the turbulent flow module. The axial symmetry, no flux and concentration boundary conditions are used in the transport of mass module. The assumptions taken in the model are given below:

Assumptions

1. The non-symmetrical geometrical objects are not considered in this model.
2. All the penetrations and components in the argon space are neglected in the present study to reduce the complexity of the analysis in the argon space.
3. The radiation heat transfer in the argon space has not been considered, because temperature itself is defined as the boundary condition.
4. The argon cover gas below the radiation shield alone is considered for analysis, since the argon in between the radiation shields is almost stagnant.
5. The temperature in the salt is assumed to be uniform due to the turbulent mixing by the stirrer.
6. The velocity profile in the salt and argon is solved for steady state condition. This is considered as the initial condition for the cadmium transport under time dependent study.

Governing Equations

Continuity Equation

The conservation of mass law applies to a fluid passing through an infinitesimal fixed control volume yields the following equation of continuity:

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \mathrm{V}) \qquad (1)$$

where ρ is the fluid density and V is **the fluid velocity.**

For steady state and incompressible flow,

$$\nabla.\mathrm{V} = 0 \qquad (2)$$

For two dimensional cylindrical coordinate system, where u and v represents the r and z components of the velocity vector Eq. 2 becomes

$$\frac{1}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}}(\mathrm{ru}) + \frac{\partial}{\partial \mathrm{z}}(\mathrm{v}) = 0 \qquad (3)$$

Momentum Equation

Newton’s second law applied to a fluid passing through an infinitesimal, fixed control volume yields the following momentum equation:

$$\frac{\partial}{\partial t}(\rho \mathrm{V}) + [\nabla.\rho \mathrm{vv}] = -\nabla \mathrm{p} - [\nabla.\tau] + \rho \mathrm{g} \quad (4)$$

Where the τ is the stresses imposed by one fluid element on other fluid element. ∇p is the pressure gradient term. The last term in Eq. 4 is external force term generated due to gravity.

For steady state, incompressible and Newtonian flow Eq.4 is written in two dimensional cylindrical coordinate forms as:

$$\rho \mathrm{u}\frac{\partial \mathrm{u}}{\partial \mathrm{r}} + \rho \mathrm{v}\frac{\partial \mathrm{u}}{\partial \mathrm{z}} = -\frac{\partial \mathrm{p}}{\partial \mathrm{r}} + \mu\left[\frac{\partial}{\partial \mathrm{r}}\left(\frac{1}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}}(\mathrm{ru})\right) + \frac{\partial^2 \mathrm{u}}{\partial \mathrm{z}^2}\right] \qquad (5a)$$

$$\rho \mathrm{u}\frac{\partial \mathrm{v}}{\partial \mathrm{r}} + \rho \mathrm{v}\frac{\partial \mathrm{v}}{\partial \mathrm{z}} = -\frac{\partial \mathrm{p}}{\partial \mathrm{z}} + \mu\left[\frac{1}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}}\left(\frac{\partial}{\partial \mathrm{r}}(\mathrm{rv})\right) + \frac{\partial^2 \mathrm{v}}{\partial \mathrm{z}^2}\right] + \rho(\mathrm{T})\mathrm{g}_\mathrm{z} \qquad (5b)$$

In Eq. 5a & 5b all the properties of fluid such as dynamic viscosity (μ) and density (ρ) is constant and which value is determined from average temperature of fluid. The ρ (T) in Eq.5b is only the term which is not constant and varies with temperature. The ρ (T) depends on temperature variation in the fluid and coupled to the energy equation. The region falls under laminar region.

Energy Equation

For steady state, Newtonian, low viscous, constant density, constant thermal capacity and constant thermal conductivity fluid the two dimensional energy equation in cylindrical coordinate is written as:

$$\rho \mathrm{C_p u}\frac{\partial \mathrm{T}}{\partial \mathrm{r}} + \rho \mathrm{C_p v}\frac{\partial \mathrm{T}}{\partial \mathrm{z}} = \mathrm{k}\left[\frac{1}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r}\frac{\partial \mathrm{T}}{\partial \mathrm{r}}\right) + \frac{\partial^2 \mathrm{T}}{\partial \mathrm{z}^2}\right] \qquad (6)$$

where C_p and k are the heat capacity and thermal conductivity of the fluid. The value of Cp and k is assumed constant and which value is determined from average temperature of fluid. The radial velocity (u) and axial velocity (v) is determined from Eq. 5a & 5b.

Transport of species

For transient, newtonian fluid the transport of species equation as follows:

$$\frac{\partial c_i}{\partial t} - \nabla.(-D_i \nabla c_i) + u.\nabla c_i = R_i \qquad (7)$$

Di Diffusion Coefficient in m^2/s

C_i species concentration, mol/cm^3

U Velocity vector, m/s

R_i Species rate expression (mol/m^3.s)

MESHING

The fine triangular mesh is used in the entire domain. The boundary where there is momentum transfer taking place between the fluid and the wall is meshed with boundary layer mesh. The sketch of the mesh generated for the axis symmetrical model by COMSOL software is shown in fig.3 [2] .

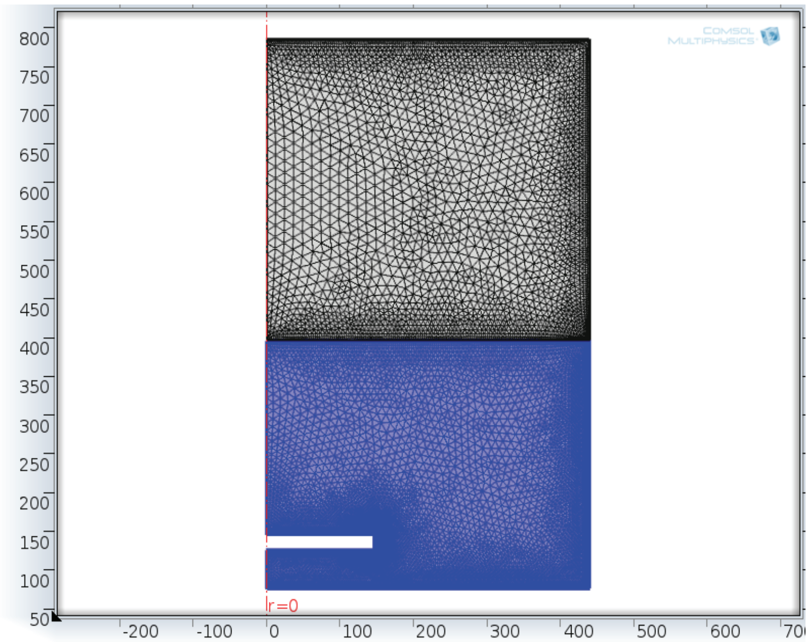

Fig.3: The meshing scheme for the electro refiner model

RESULTS AND DISCUSSION

i. Effect of stirrer speed in the salt phase

The effect of speed of the stirrer in the salt space was varied as 50, 90 and 120rpm.The concentration ratio as concentration at time to initial concentration vs time was plotted for the various stirrer speeds (Refer fig.4). From the graph, it is observed that within 5 hrs , the cadmium vapours achieves the equilibrium in the argon space .i.e. after 5 hrs, the concentration in salt and argon space is almost uniform.

ii. Velocity profiles in salt and argon gas spaces

The velocity profiles in the salt and argon gas spaces has been shown in fig.5.From the plot it is observed that the salt space region is in turbulent region and the argon gas region is in laminar region. The turbulence in the salt is created using the stirrer for the process requirement. The convection in the argon sets due to the temperature difference along the height of the vessel.

iii. The variation of concentration gradient of cadmium in argon gas space with time

The concentration gradient of cadmium vapours in argon space has been plotted in fig.6.From the figure it is clear that initially the cadmium vapour concentration is high in the salt phase. Since the turbulence in the salt is high enough transport of cadmium vapour in salt is dominated by convection .The transport of cadmium vapour in the argon gas space is carried out both naturally created convection as well as the diffusion since the diffusion coefficient of vapour in gas medium is nearly 10^4 to10^5 higher than in the liquid region.

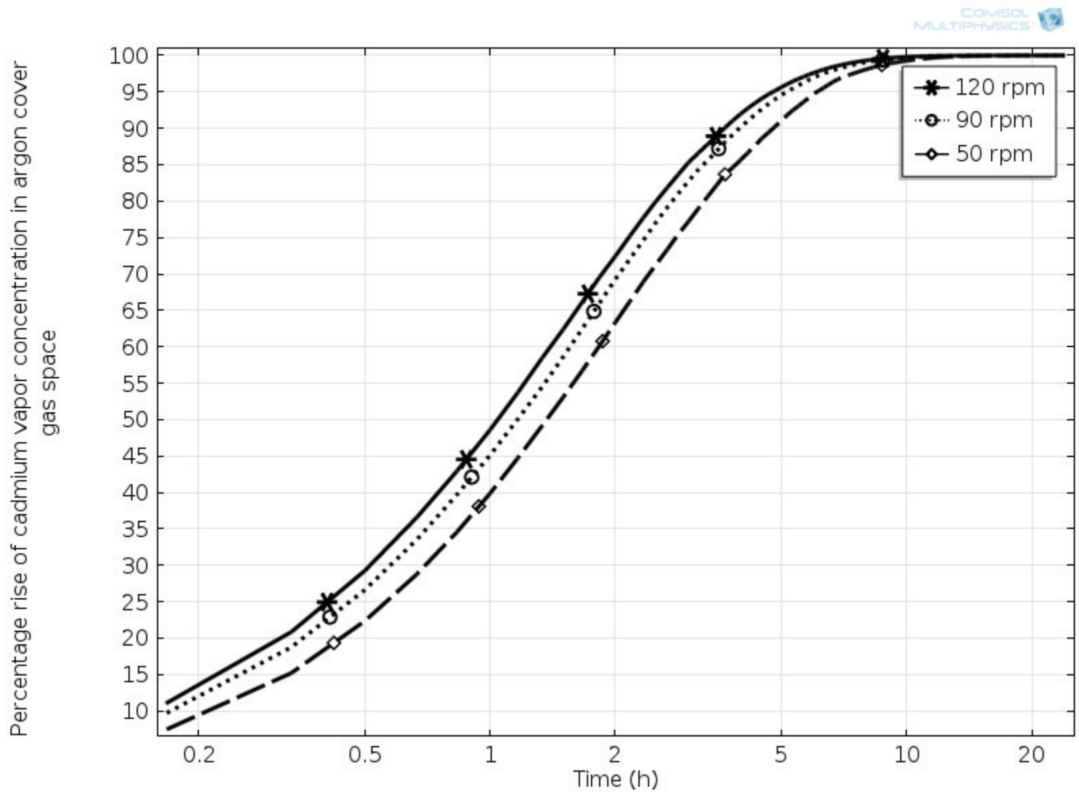

Fig.4: The percentage rise of cadmium concentration in argon for different speed of stirrer in the salt space.

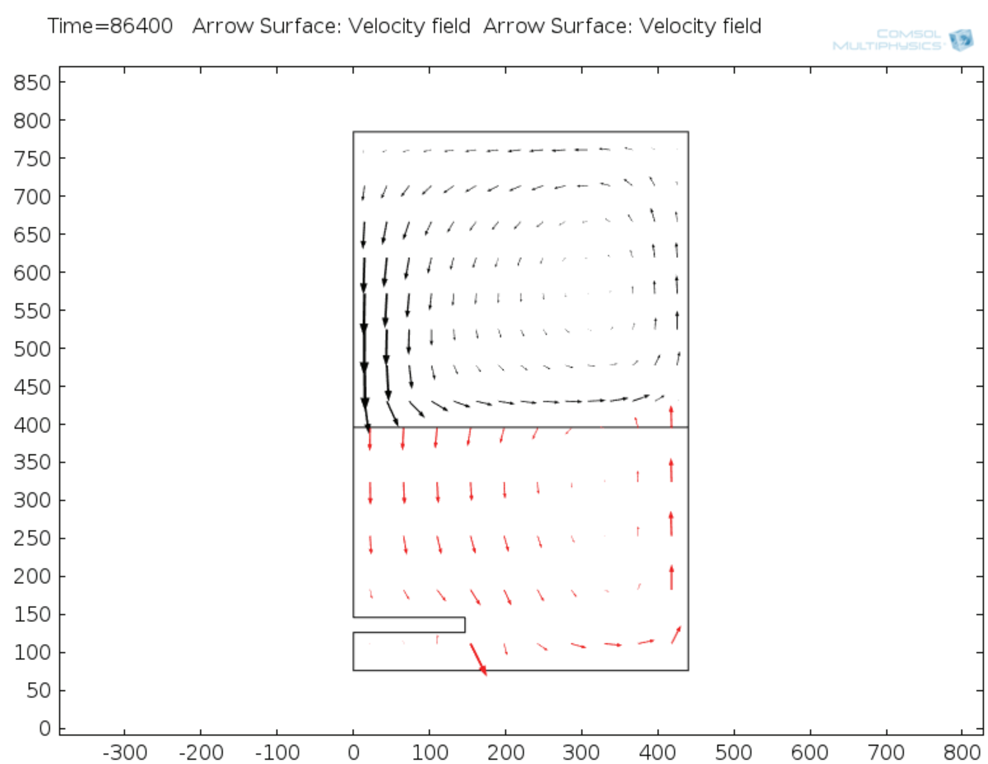

Fig.5: The velocity profiles in the salt space and in the argon gas space in the HTER under steady state condition.

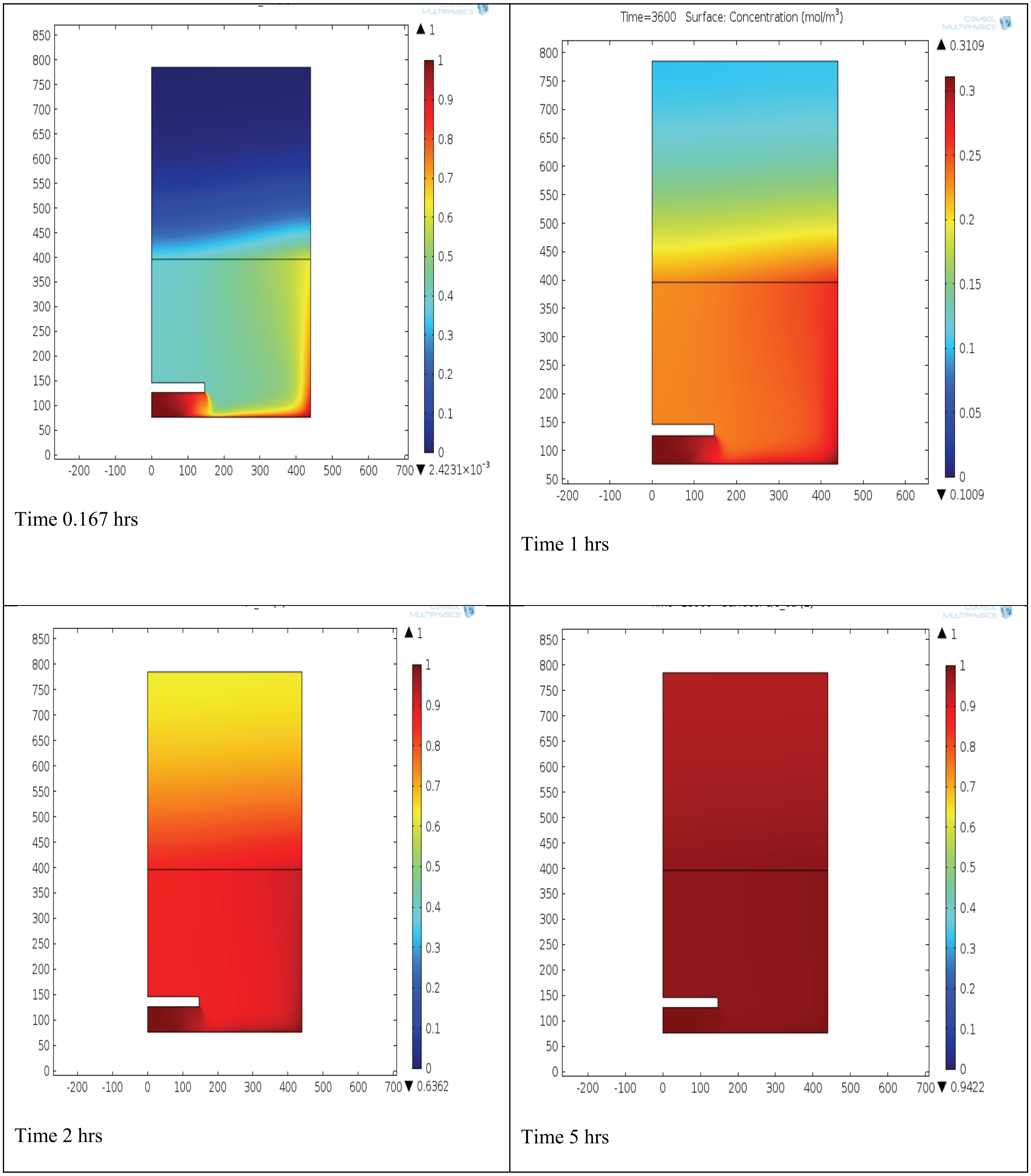

Fig.6: The cadmium concentration profiles in the salt space and in the argon gas space in the HTER under transient condition.

iv. Determination of rate of cadmium transport in the argon cover gas in the unsteady state condition.

Rate of transport of cadmium vapour in argon gas space $= Q_{total} / t_{equ}$

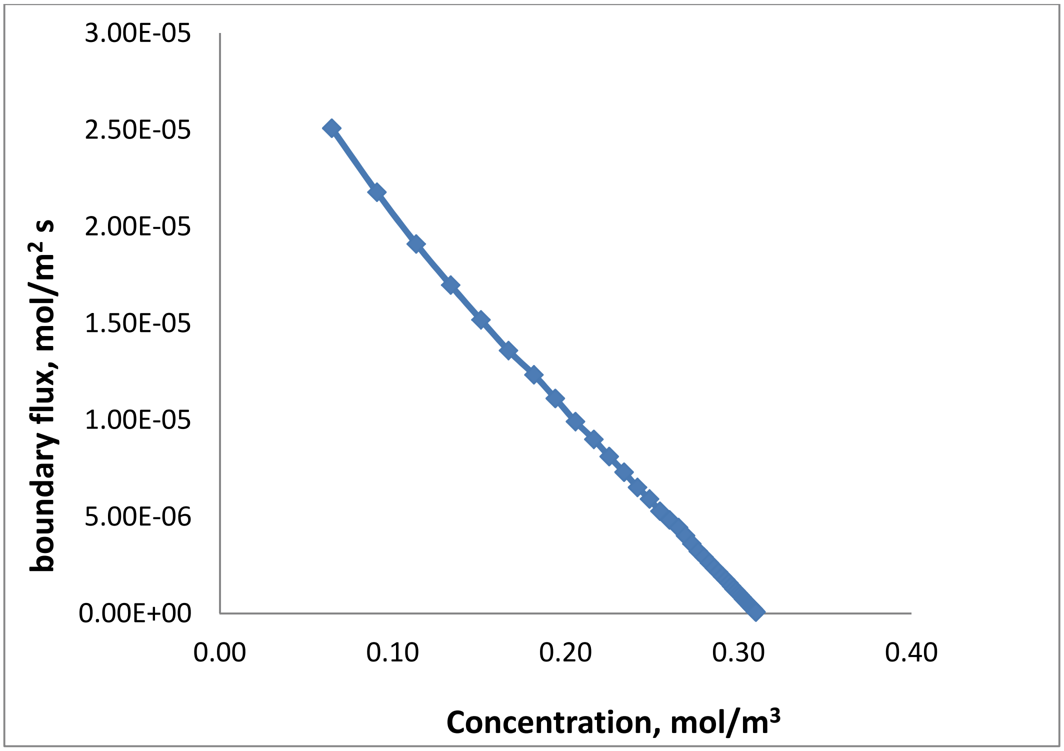

Fig.7: The mass flux of cadmium vs concentration of cadmium under transient condition

Q_{total}------------Total amount of cadmium, g

t_{equ}-------------Equilibration

Mass flux of cadmium = Rate of transport of cadmium in argon space /Surface area of argon space.

From analysis the mass flux of cadmium vapour in argon space is 5.483×10^{-6} mol/m2.s and the approximate rate of cadmium vapour to argon gas space is 0.012 g/hr. So, this high rate of cadmium tarnsport requires the cadmium vapour trap in the argon gas region.

CONCLUSION

A detailed mass and thermal analysis were carried out for transport of cadmium vapours through molten salt to argon gas space for the unsteady state condition in HTER. From the analysis, the turbulence due to the stirrer in the molten salt will increase the transport of cadmium vapour to argon gas. Similarly the larger temperature difference along the height of the argon gas will enhance convection which in turn increase the transport rate of cadmium vapours.The mass flux of cadmium vapour to argon is 5.483×10^{-6}.g/s.m^2 and the approximate rate of cadmium vapour to argon gas space is 0.012g/hr. So, the cadmium vapour trap is necessary in the argon gas region.

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