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Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics-Task V: Third Quarterly Report 03/01/2004-05/31/2004

Samir Moujaes
University of Nevada, Las Vegas, samir@me.unlv.edu

Yitung Chen
University of Nevada, Las Vegas, yitung.chen@unlv.edu

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UNLV-TRP University Participation Program

Principal Investigator: Samir Moujaes
Co-Principal Investigator: Yitung Chen

Purpose and Problem Statement

The Lead-Bismuth eutectic (LBE) has been determined from previous experimental studies by the Russians and the European scientific community to be a potential material that can be used as a spallation target and coolant for the TRP proposed application. Properly controlling the oxygen content in LBE can drastically reduce the LBE corrosion to structural steels. However, existing knowledge of material corrosion performance was obtained from point-wise testing with only very sparse experimental data. Scientists have noticed that the concentration of oxygen dissolved in the liquid alloy could control the corrosion rate of steels exposed to Pb or Pb-Bi. At high oxygen concentration, an oxide layer could be formed on the steel surface (lead oxides are less stable than iron oxide), which protects it from corrosion. At low oxygen concentration, there is no oxidation and corrosion occurs by dissolution of the steel components in the liquid metal. The surface of the oxide layer in contact with the bulk flow of liquid metal may also be eroded under a high fluid velocity. Then the surface of the metal will no longer be protected because a porous oxide layer will be formed.

The first subtask of this project involves using a CFD code (3-D simulation) such as STAR-CD to obtain averaged values of stream wise velocity, temperature, oxygen and corrosion product concentrations at a location deemed close to the walls of the LBE loop at more than one axial location along it. The oxygen and corrosion product inside the test loop will be simulated to participate in chemical reactions with the eutectic fluid as it diffuses through towards the walls. Details of the geometry of these loops will be obtained from scientists at LANL. These values will act as a set of starting boundary conditions to the second task.

The second subtask and the more important objective of this project is to use the information supplied by the first task as boundary conditions for the kinetic modeling of the corrosion process at the internal walls of the test loop. The outcome of the modeling will be fed back to the first subtask, and the steady state corrosion/precipitation in an oxygen controlled LBE system will be investigated through iterations. The information is hoped to shed some light on the likely locations for corrosion and precipitation along the axial length of parts of the test loop.

Personnel

Principal Investigator:

- Dr. Samir Moujaes (Mechanical Engineering)

Co-Principal Investigator:

- Dr. Yitung Chen (Mechanical Engineering)

Students:

- Mr. Narain Armbya, M.S. Graduate Student, (Mechanical Engineering)
- Mr. Guanjun Li, Ph.D. Graduate Student, (Mechanical Engineering)

National Laboratory Collaborator:

- Dr. Ning Li, Project Leader, Lead-Bismuth Material Test Loop, LANL
- Dr. Jinsuo Zhang, Post Doctoral Candidate, LANL

Administrative Issues:

We have met with Dr. Joe Smith from the Adapco Co. (providers of STAR_CD). He offered us some very helpful tips on how to setup our grid for the user supplied subroutine that the group is trying to develop for use in the chemical-kinetics simulation.One of our students Narain was out on vacation from May 15-June 21. Guanjun has been having a medical problem which till now has not been well diagnosed.

Technical progress:

Several CFD runs have been made by Narain to simulate flow in pipe fittings. These include sudden contraction, sudden expansion and a T-joint. Testing of a new turbulent model is also being made namely the k-e Chen model which will work a little better with high Re number flows and will be able to predict some of the peculiar flow features relevant to sudden expansions where eventually vortex generation is expected at the backward step (i.e. sudden expansion location) in that flow. It is important to try to predict that because it may have a bearing on the behavior of the chemical kinetics model when it is completed.

Guanjun continues to develop this user subroutine that will allow us eventually to simulate the corrosion/precipitation processes and predict their maximum/minimum location in a typical LBE loop.

Introduction:

Liquid lead-bismuth eutectic is considered as a prototype target and coolant for the Transmutation Research Project (TRP). It is an alloy of 45% lead and 55% bismuth with the melting temperature of 123.5^{o}C and boiling temperature of 1670^{o}C. Using liquid lead-bismuth eutectic (LBE) as coolant in nuclear systems has been studied for more than 50 years. LBE has many unique nuclear, thermo physical and chemical attributes that are attractive for nuclear coolant applications. This liquid's relatively low melting point and high boiling point in addition to good heat transfer properties make it a very good candidate for coolant. In addition, lead and bismuth can produce copious spallation neutrons when bombarded with energetic protons. This makes LBE one of the top candidates for a high-power spallation target in an Accelerator-driven Transmutation of Waste (ATW) system. Besides, the use of heavy liquid metal like LBE as a coolant for fast reactors offers several safety and economic advantages. These arise from the following basic material characteristics: chemical inertness with air and water, high atomic number, high boiling temperature and low vapor pressure at operating temperatures. Specifically, heavy-metal coolants do not react energetically with air and water; therefore, coolant fires are not possible and an intermediate heat transport loop is unnecessary. Also, the hard neutron spectrum achievable with these coolants enables the design of cores with minimal neutronic reactivity swing, small control requirements and long neutronic life time. The significantly lower reactivity associated with hypothetical voiding of the coolant, as compared to sodium, makes it possible to design lead or lead-bismuth-cooled cores with a negative coolant void coefficient, there by eliminating the possibility of severe accidents from consideration. Finally, lead or lead-bismuth coolants provide better shielding against gamma-rays and energetic neutrons, so that less shielding structures are needed. Liquid spallation source also eliminates some of the structural damage problems associated with the targets. Combining the target and coolant roles in one material allows for a simple target design.

One of the critical obstacles to the wide use of LBE as a nuclear coolant, though, is corrosion. The corrosion processes need to be controlled and reduced or they lead to severe safety problems. Unprotected steel undergoes severe attack by liquid lead and lead-bismuth alloy by dissolution of its components in the liquid metal. During the last years, not much was known about possibilities to improve the compatibility of steel with liquid Pb and Pb/Bi. Some compatibility tests with ferritic steels were reported which revealed corrosion attack can be minimized if an oxide layer exists on the steel surface. Scientists at IPPE, Obninsk, Russia, discovered that if an oxide film is allowed to form on the steel surface it prevents corrosion. This protective film consists mostly of steel components' oxides and it is based on Fe_3O_4. Formation and longevity of this protective film depends on oxygen concentration on the liquid metal. In order to use liquid lead-bismuth in AAA facility, we need to know how to control corrosion of structural materials.

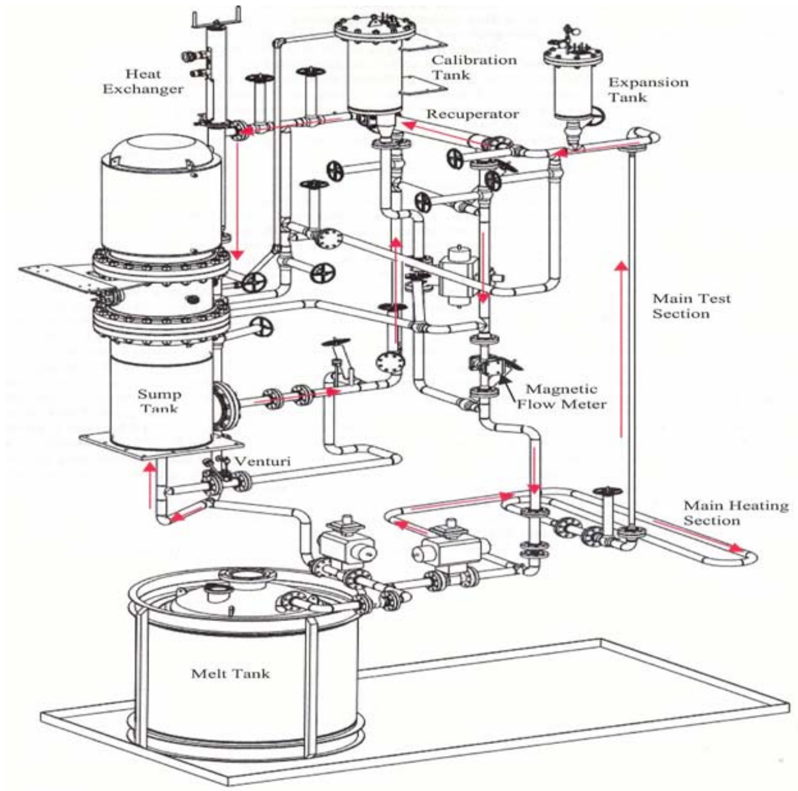

Figure – 1: Materials Test Loop

The active oxygen control technique exploits the fact that lead and bismuth are chemically less active than the major components of steels, such as Fe, Ni, and Cr. By carefully controlling the oxygen concentration in LBE, it is possible to maintain an iron and chrome oxide based film on the surfaces of structural steels, while keeping lead and bismuth from excessive oxidation that can lead to precipitation contamination. The oxide film, especially the compact portion rich in Cr, effectively separates the substrates from LBE. Once this oxide film is formed on the structure surface, the direct dissolution of structural materials becomes negligible because the diffusion rates of the alloying components are very small in the oxides. In this circumstance, the only effective means of transferring structural materials into LBE is through the reduction of the oxide film at the interface of the film and LBE. The Los Alamos National Laboratory's Accelerator-driven Transmutation of Waste (ATW) applications and the Department of Energy's TRP program have invested in developing LBE technology from spallation target and nuclear coolant applications since 1997. A Materials Test Loop (MTL) has been set up in Los Alamos. The MTL is a facility designed to test the safe operation of a medium-size, forced circulation LBE system with representative thermal hydraulic conditions (as spallation target and/or transmutation blanket systems), to perform corrosion tests, and to develop candidate materials with oxygen control (and related probes and control systems). Figure-1 shows the skeleton representation of the MTL.

It has been well known that fluid flow influences corrosion in many ways, including the increase of the diffusion of reactant species and the transport of potentially protective corrosion product forming ions away from surface. In the mass transfer controlled regime, the corrosion rate is determined by the mass transfer coefficient and the gradient between the corrosion product concentration at the solid-liquid interface and the concentration in the bulk flow. Corrosion rate is typically a function of local temperature and flow velocity. However, corrosion and precipitation rates and distributions can depend strongly on the global temperature distribution, limiting the applicability of many corrosion models.

The present study involves the estimation of corrosion in the liquid metal, by imposing an analytically developed concentration expression on the wall surfaces and thus benchmarking the CFD tool and performing a series of parametric studies on the loop model. The concentration and temperature diffusions due to different flow regimes have been studied. Regions of maximal corrosion and precipitation have been deduced from the simulations and the results have been compared with the analytical models. STAR-CD has been chosen as the CFD code for this purpose.

Numerical Simulation Technique:

The STAR-CD computer simulation code was chosen for the purpose of performing the Computational Fluid Dynamics (CFD) calculations for this project. STAR-CD is a commercially available code that is offered by ADAPCO Co. out of New York State. The code is a transient multidimensional simulator for Thermal hydraulics and chemical reactions occurring in the fluid flow itself.

STAR-CD is a general-purpose code that solves numerically a set of differential equations that describe the following conservation laws: mass conservation, momentum, energy and chemical species. The following equations are solved by this code:

Continuity Equation:

$$u_{i,i} = 0 \tag{1}$$

Momentum Equation:

$$\rho_0 [\frac{\partial u_i}{\partial t} + u_i u_{i,j}] = - P_{,i} + [\mu (u_{i,j} + u_{j,i})]_{,j} \tag{2}$$

Energy Equation:

$$\rho_o C_p (\frac{\partial T}{\partial t} + u_i T_{,i}) = (K^* T_{,i})_{,i} + \mu \Phi \tag{3}$$

Species Transport:

$$\rho (\frac{\partial C_n}{\partial t} + u_i C_{n,i}) = (\rho \alpha_n C_{n,i}) + q_{c_n} + R_n \tag{4}$$

Due to the Re number estimate for flow in a LBE loop a turbulent flow model should be used as a constitutive model for the momentum transport. It was decided that a k-ε model is to be used to account for that behavior. The model consists of adding two more non-linear (transport equations) partial differential equations to each unknown nodal location. The k denoted the turbulent kinetic energy $\overline{u_i u_i}$ and the ε is the viscous dissipation rate of the turbulent kinetic energy $\upsilon \overline{u_{i,j} u_{i,j}}$. The resulting equations are:

k – transport equation:

$$\rho_o(\frac{\partial k}{\partial t}+u_i u_{i,j})=(\mu_o+\frac{\mu_t}{\sigma_k}k_{,}j)_{,j}+\mu_t\Phi+\mu_t g_i(\frac{\beta_T}{\sigma_t}T_{,j})-\rho_o\varepsilon \qquad (5)$$

ε – transport equation:

$$\rho_o(\frac{\partial\varepsilon}{\partial t}+u_j\varepsilon_j)=(\mu_o+\frac{\mu_t}{\sigma_k})_{,j}+c_1\frac{\varepsilon}{k}\mu_t\Phi+c_1(1-c_3)\frac{\varepsilon}{k}g_i-\rho_o c_2\frac{\varepsilon^2}{k} \qquad (6)$$

Benchmark Study:

Benchmark is important in research, especially in numerical simulation. It provides the validation of the tools and the base for the further effort. Before used to carry out calculation for more complicated cases, the code was applied to a classic problem and compare outcome with widely accepted results. Incompressible flow in sudden expansions is one of the classical problems and suits our calculation domain perfectly. The other fittings considered are the t-joint and the sudden contraction.

The first section sheds light on the velocity profiles obtained from the sudden expansion model. The results are shown for the flow in the turbulent regime.

The second section sheds light on the velocity profiles obtained from the sudden contraction model. The results are shown for the flows both in the laminar and turbulent regimes.

The third section sheds light on the velocity profiles obtained from the t-joint model. The results are shown for the flows both in the laminar and turbulent regimes.

Sudden Expansion

A model of sudden expansion is created. The diameter at the inlet was selected as 0.0254m. The lengths of the inlet and outlet regions are taken as 10 diameters. The ratio of the inlet to outlet diameter is 1:2. The total number of the cells in the model is 225,000. The aspect ratio varies between 8 and 10 as specified by the CFD package. Runs were simulated for the Reynolds number of 200,000. The simulated results obtained are as shown.

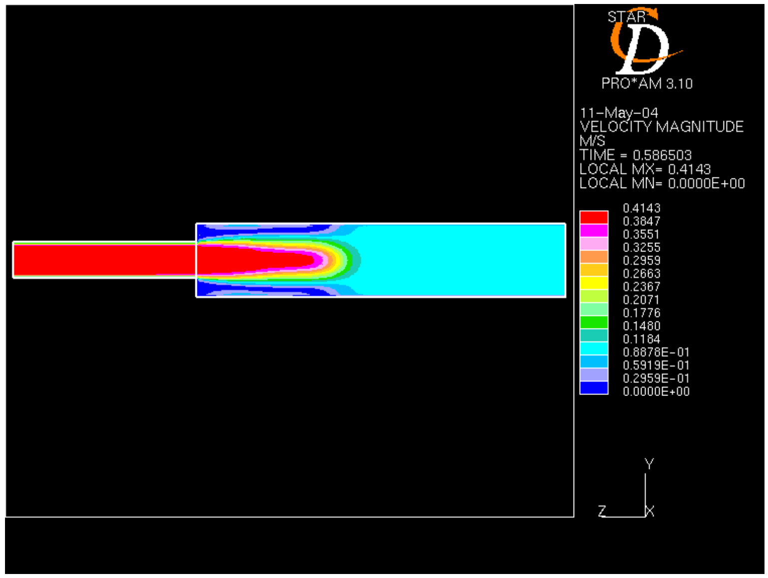

Figure - 2: Velocity plot for Re = 200,000

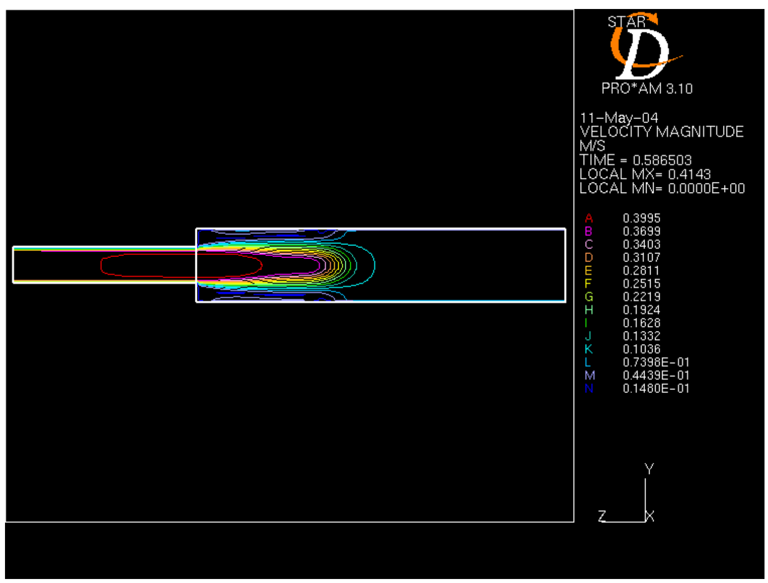

Figure - 3: Velocity lines for Re = 200,000

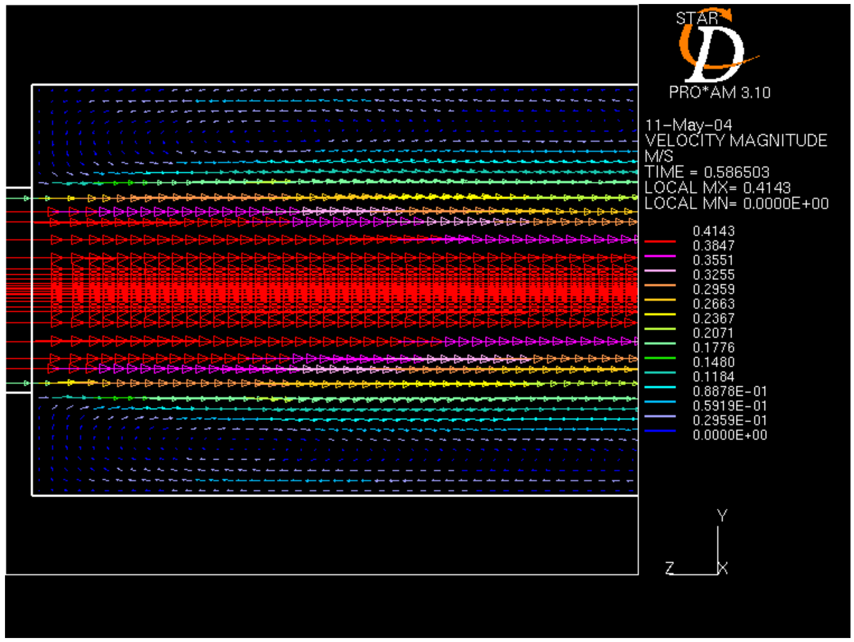

Figure - 4: Velocity vectors for Re = 200,000

Figure 4 shows the velocity vectors at the sudden expansion region. We can see some of the vectors reversing their direction.

The sudden expansion case was run in transient conditions. This was done to see the vortex shedding as the flow crosses the sudden expansion region. Figure 2 shows the development of vortices. But then they even out towards the outlet of the pipe. To overcome this the model is presently being tested under the K-epsilon-CHEN model

Sudden Contraction

The model, which had been created for the sudden expansion, is used here. But the inlet and outlet are changed accordingly. The simulated results obtained for both the laminar and the turbulent flows are as shown.

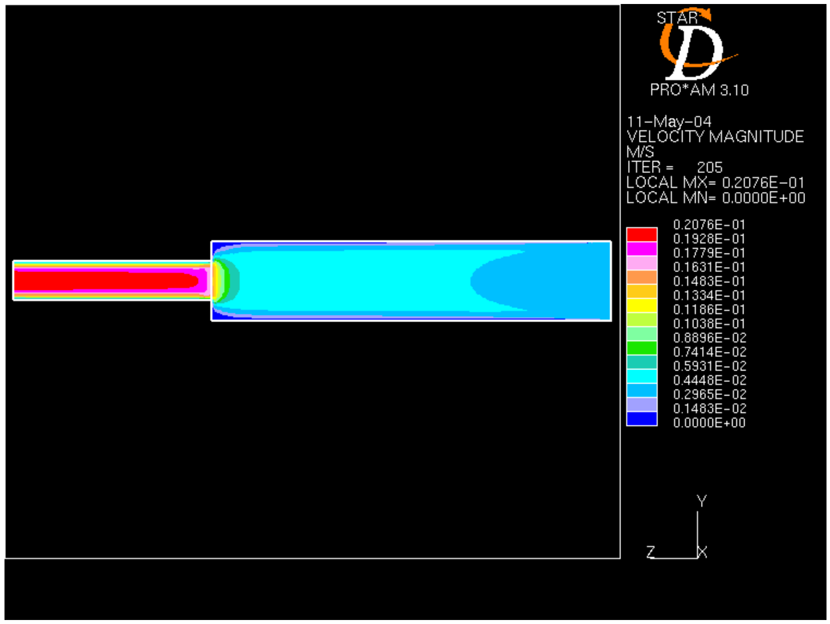

Figure - 5: Velocity plot for Re = 2000(laminar flow)

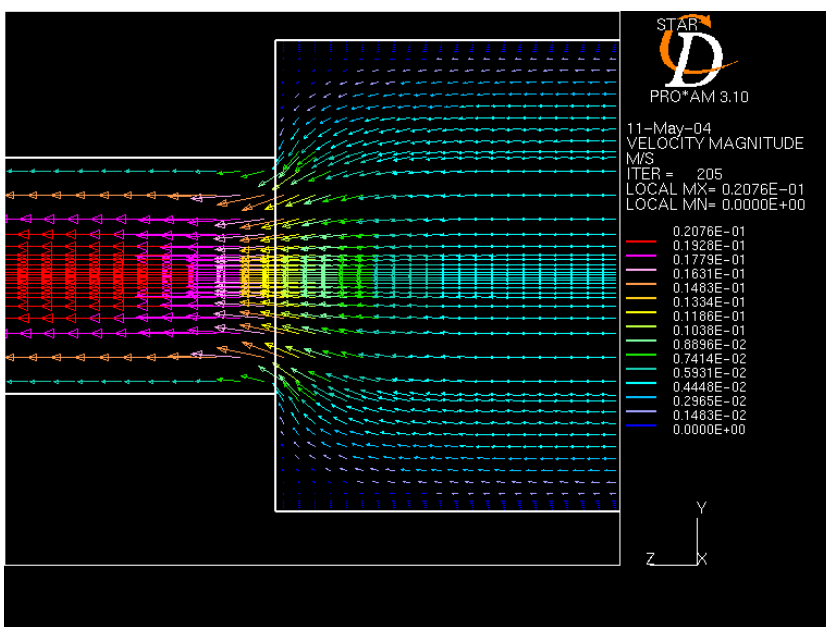

Figure - 6: Velocity vectors for Re = 2000(laminar flow)

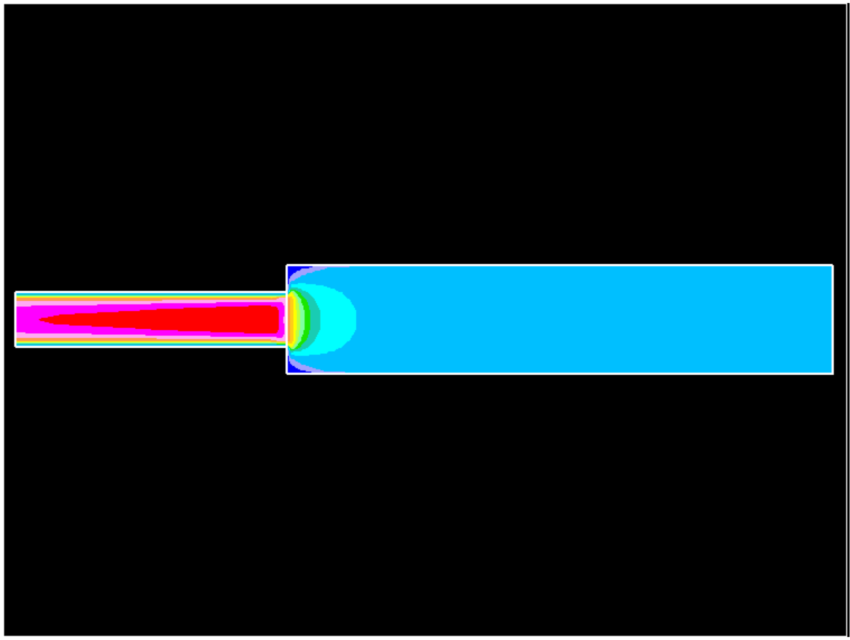

Figure - 7: Velocity magnitude for Re = 200,000(turbulent flow)

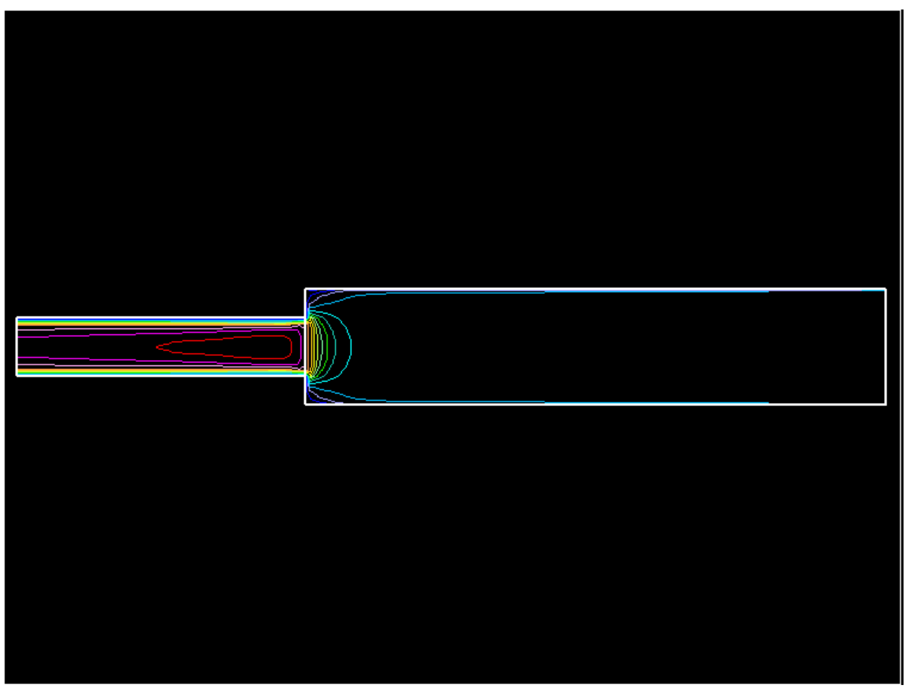

Figure - 8: Velocity lines for Re = 200,000(turbulent flow)

Figures 5, 6 and 7, 8 show the flow patterns occurring in the sudden contracting pipe at laminar and turbulent regimes respectively. Figure 9 shows the velocity vectors for the model at the contracting region at Re = 200,000. The concentration for this case was selected to be 0.01 and a temperature gradient is 50 degrees. Parametric studies, by varying the Reynolds numbers, concentration and temperature gradient are now being conducted.

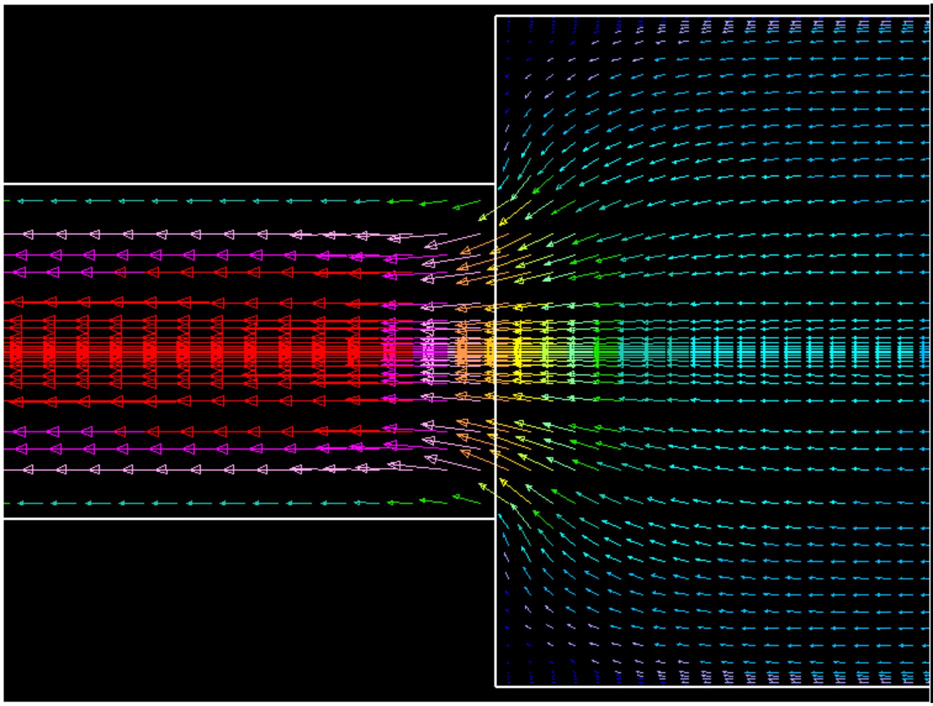

Figure - 9: Velocity Vectors for Re = 200,000(turbulent flow)

T-joint

The second loop fitting, which will be worked on is the tee-joint. The model is shown in Figure 10. This model was constructed using the modeling package **SOLIDWORKS**. It will then be meshed using **PRO-AM**. The simulated results obtained for both the laminar and the turbulent flows are as shown. A one-inlet, two-outlets model is considered. In this the first model has inlet at the side and the second model has the inlet in the middle.

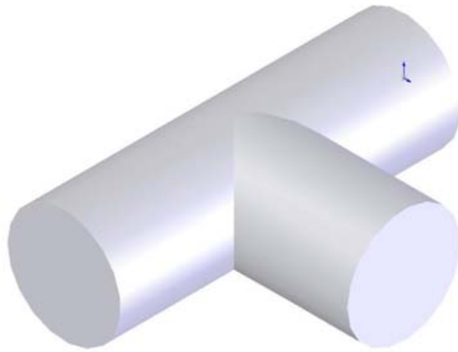

Figure – 10: A tee-joint.

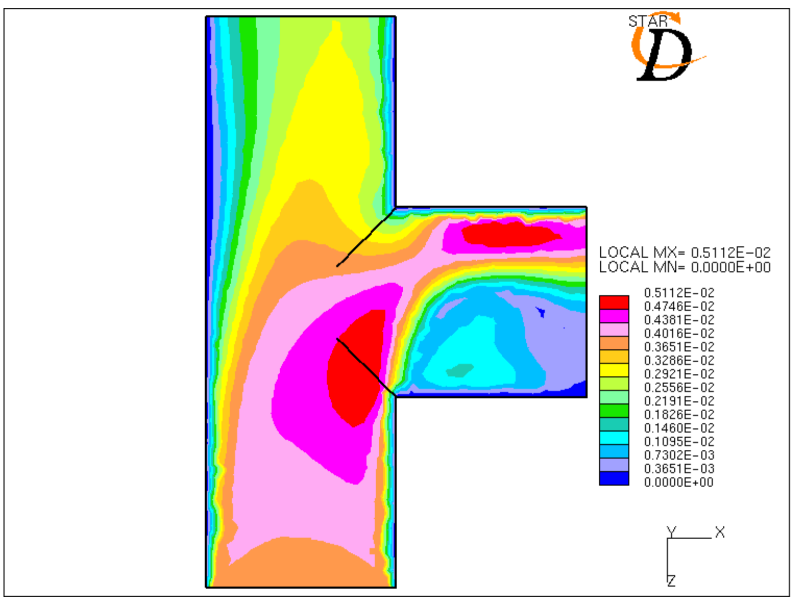

Figure - 11: Velocity magnitude for a side inlet(from bottom inlet) t-joint at Re = 2000(laminar flow)

In Figure 11 the inlet is from the side. The flow is halved as it nears the outlet region, i.e., an outflow of 50% from one outlet and 50% from the other. The development of flow reversal can be seen as the fluid enters the middle arm of the t-joint. This case is run at a Reynolds number of 2000.

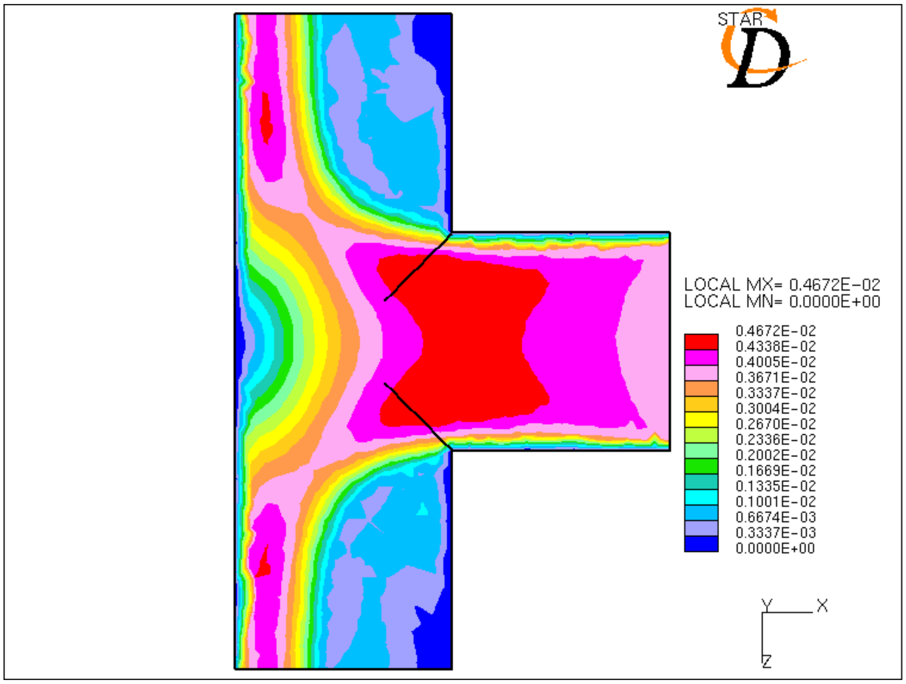

Figure - 12: Velocity magnitude for a middle inlet t-joint at Re = 2000(laminar flow)

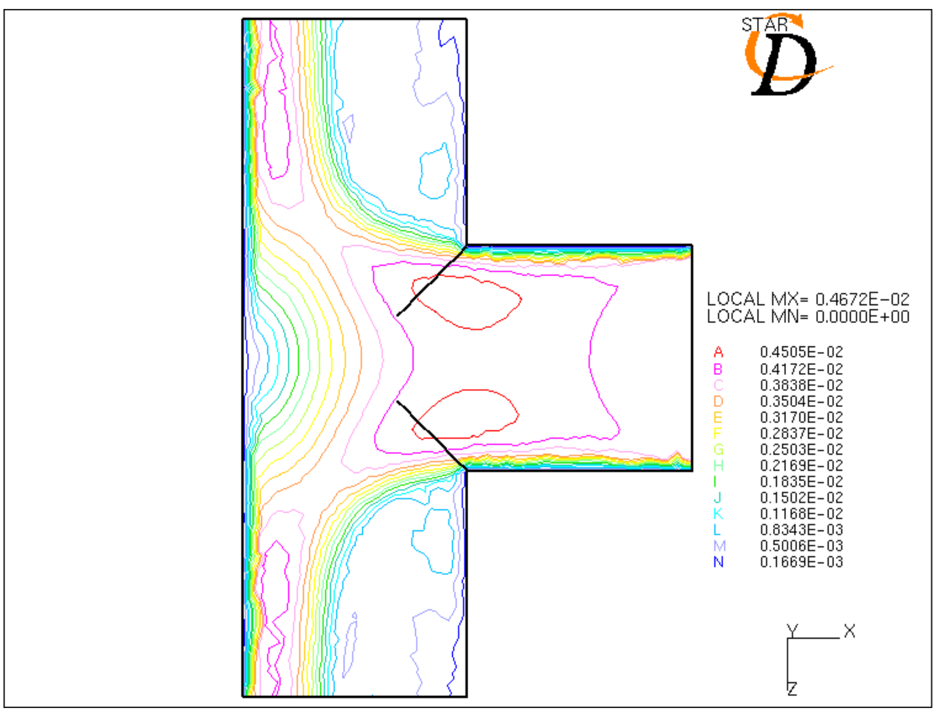

Figure - 13: Velocity lines for a middle inlet t-joint at Re = 2000(laminar flow)

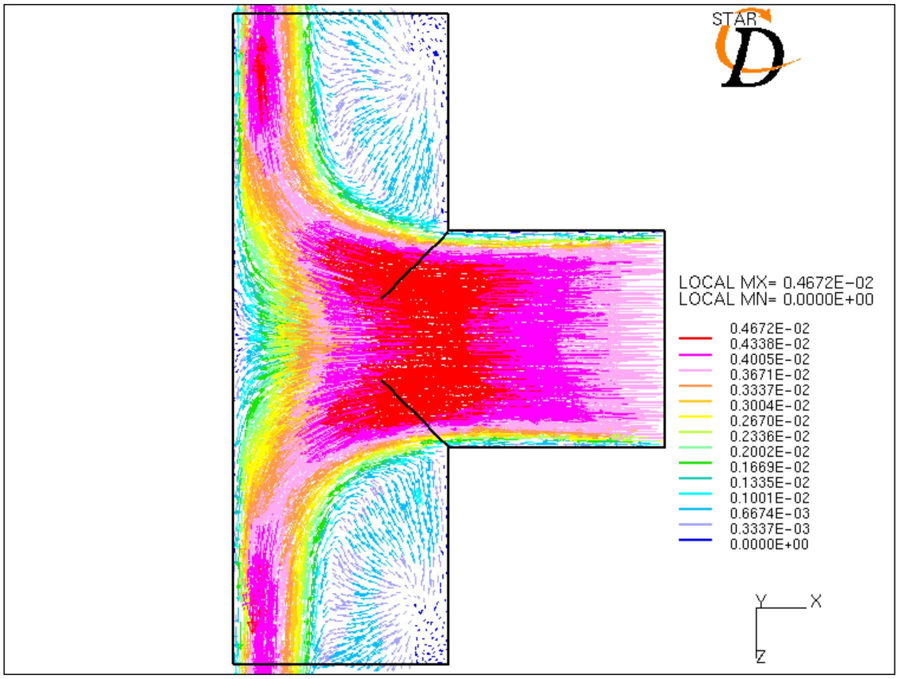

Figure - 14: Velocity vectors for a middle inlet t-joint at Re = 2000(laminar flow)

Figure 14 shows the velocity vectors for a t-joint model with the inlet in the middle arm. Slight flow reversal can be seen at the opposite wall of the middle arm. This is because the velocity is low (0.004m/s)

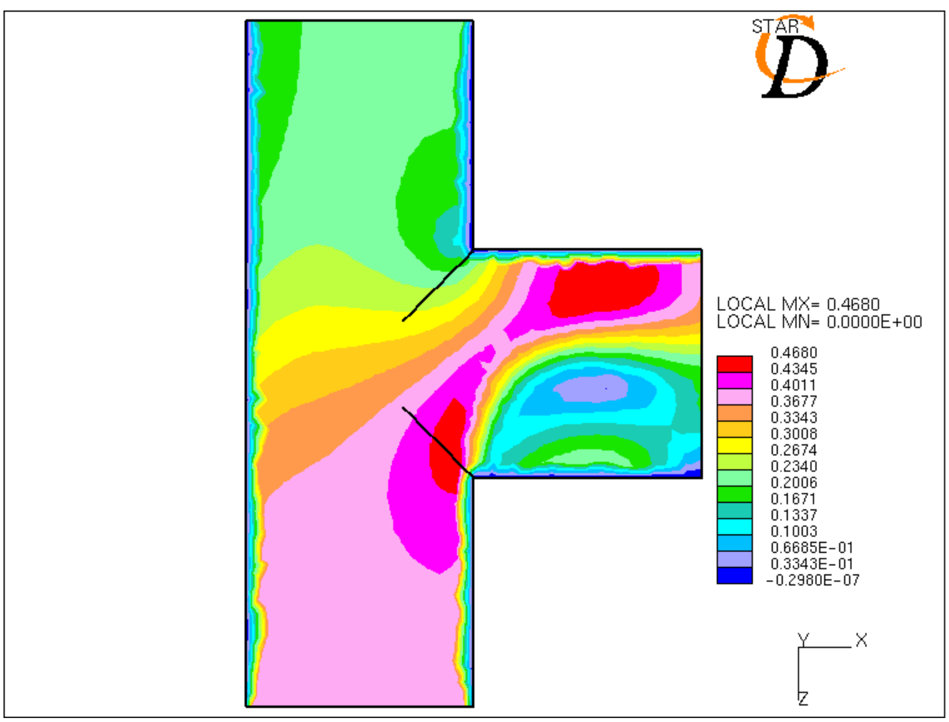

Figure - 15: Velocity magnitude for a side inlet(from bottom inlet) t-joint at Re = 200,000(turbulent flow)

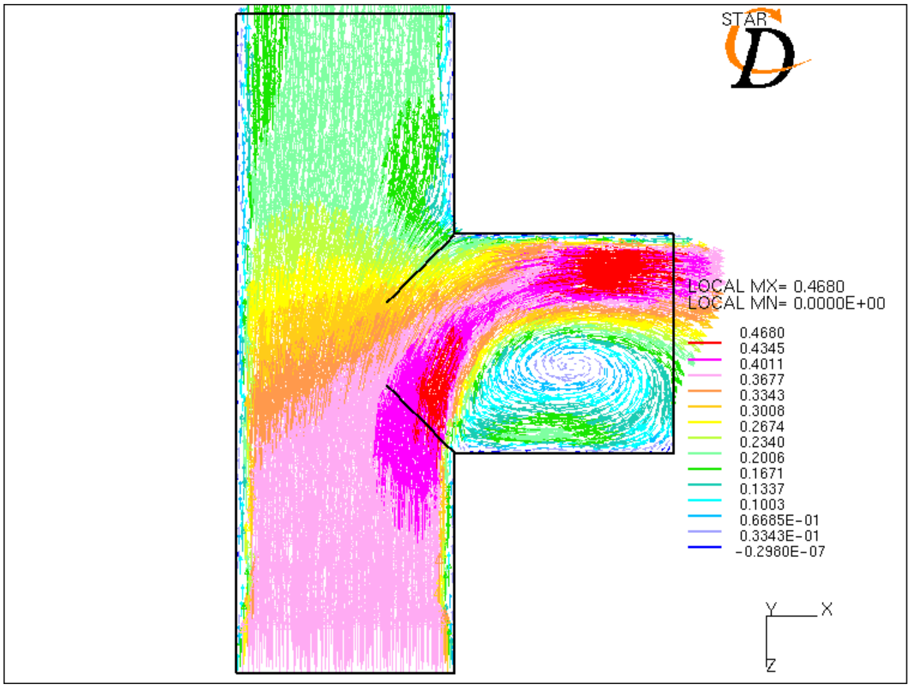

Figure - 16: Velocity vectors for a side inlet(from bottom inlet) t-joint at Re = 200,000(turbulent flow)

Figures 15 and 16 show the flow patterns at Reynolds number is 200,000. Here a prominent flow reversal of the fluid can be seen in the inner branch of the middle inlet. On the opposing wall of where the eddy current occurs, an area formed where the velocity magnitude increases. This is because of pressure drop.

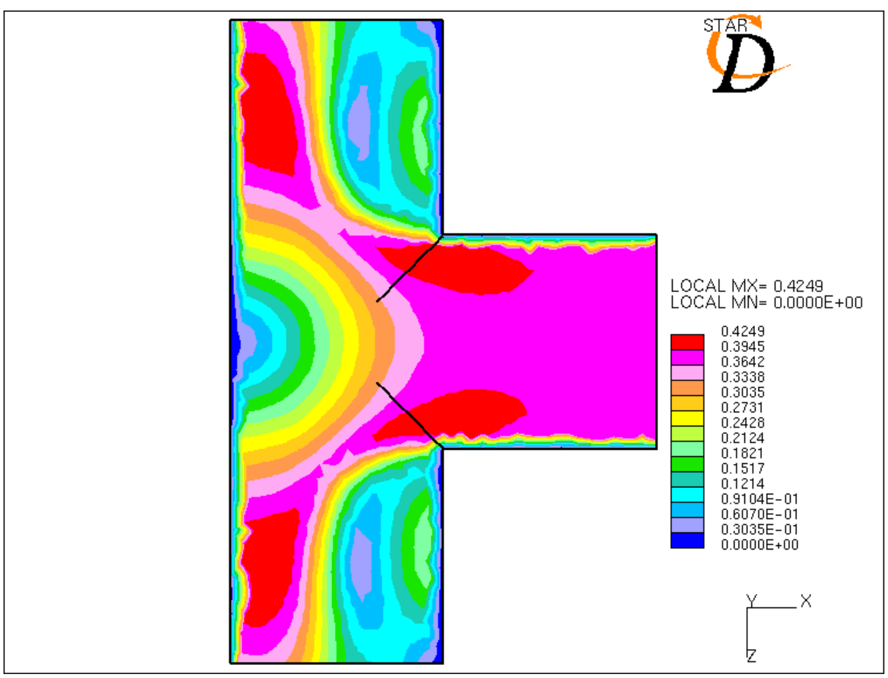

Figure - 17: Velocity magnitude for a middle inlet t-joint at Re = 200,000(turbulent flow)

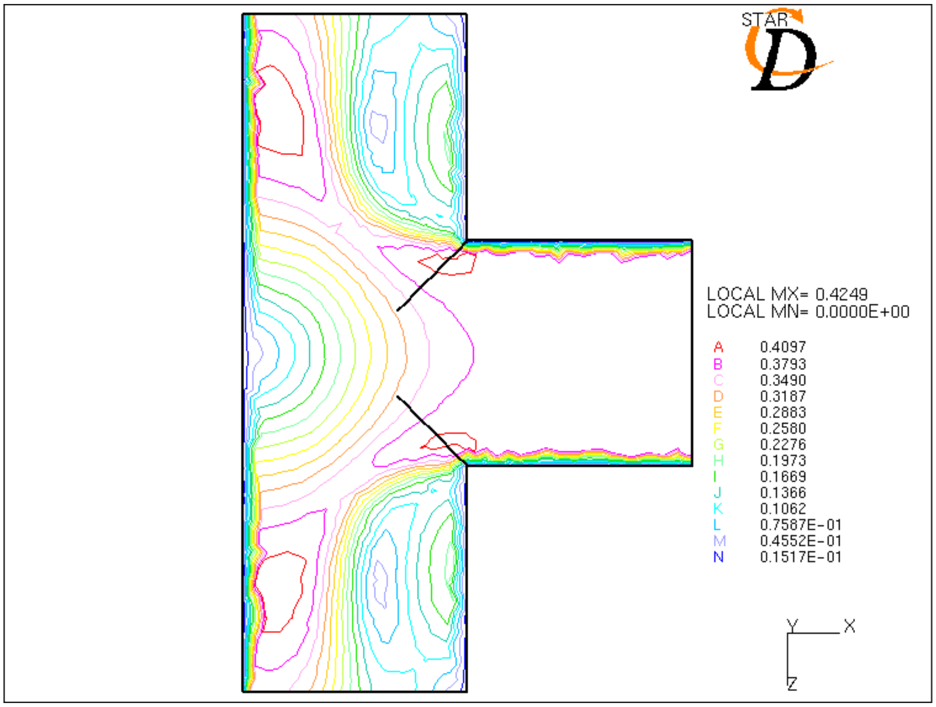

Figure - 18: Velocity lines for a middle inlet t-joint at Re = 200,000(turbulent flow)

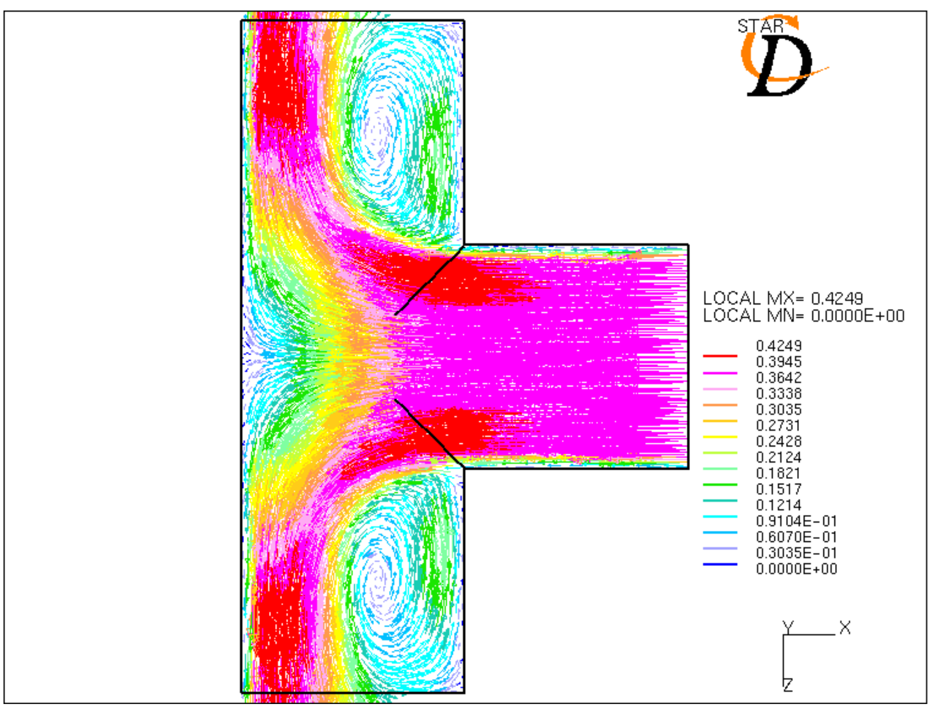

Figure - 19: Velocity vectors for a middle inlet t-joint at Re = 200,000(turbulent flow)

Figures 17, 18 and 19 show the flow patterns when the inlet is through the middle arm. the velocity vectors are larger in magnitude at the outer wall just after going through the tee intersection on both sides. These bigger velocity vectors then move toward the outlets. The cause of the bigger velocity vectors at these locations seems to be the pressure drop at these locations and there is no back flow or increased pressure areas between these locations and the outlets to slow down the flow. Directly above these areas of bigger velocity magnitude, two areas of smaller velocity magnitude can be seen coinciding with the two areas of lower pressure. Figure 19 displays the formation of two eddy currents at these locations where the flow actually forms a circular pattern.

Study of Surface Chemical Reactions

The CFD domain, material, fluid zones, boundary conditions, each species' inlet concentration, temperature, etc., have been defined. Specifically, a very simple straight pipe (0.0508 m * 0.25 m) 3-d CFD model has been built to serve as benchmark case. A fluid zone with a thickness of 2.54 mm (the green area in Figure 20) is used to monitor the concentration change of Fe. The outer surface of this fluid zone is defined as wall boundary condition. It is defined as adiabatic boundary condition and its material is set to be Fe. The bulk fluid inside the piping is also modeled as a fluid zone (the red area in Figure 21). In addition, a layer of baffle cells between the monitoring fluid cell zone and bulk fluid cell zones was created. Both sides of the baffle have been defined as adiabatic boundary conditions at this time. They might be changed to diffusion boundary conditions if fluid condition changes.

One end of piping is defined as a 'inlet' boundary condition while the other end is defined as 'outlet' boundary condition. The velocity of inlet is set to be 0.5 m/s which is close to real condition. The bulk fluid material (so called background material) is set to be Lead-Bismuth eutectic.

A chemical reaction subroutine dealing with surface chemistry has been developed (see Appendix) and been incorporated into the CFD model. The subroutine includes the specific reactions (in this case, $3Fe + 2O_2 = Fe_3O_4$ and $Fe_3O_4 + 4\,Pb = 3\,Fe + 4PbO$) which occur at LBE surface, chemical reaction rate calculation, the species' molecular weights, the initial species' concentration, temperature, iterations, etc. Arrhenius Equation is used to calculate the reactant reaction rate. But some coefficients need to be validated by experimental result if they are available for our specific reactions.

Several run with and without subroutine connected have been made. Figure 21 shows velocity profile inside the piping without subroutine connected . It is obvious that this is a laminar flow. The fluid condition inside the pipe will significantly affect the species' diffusion, hence the corrosion process of the piping wall.

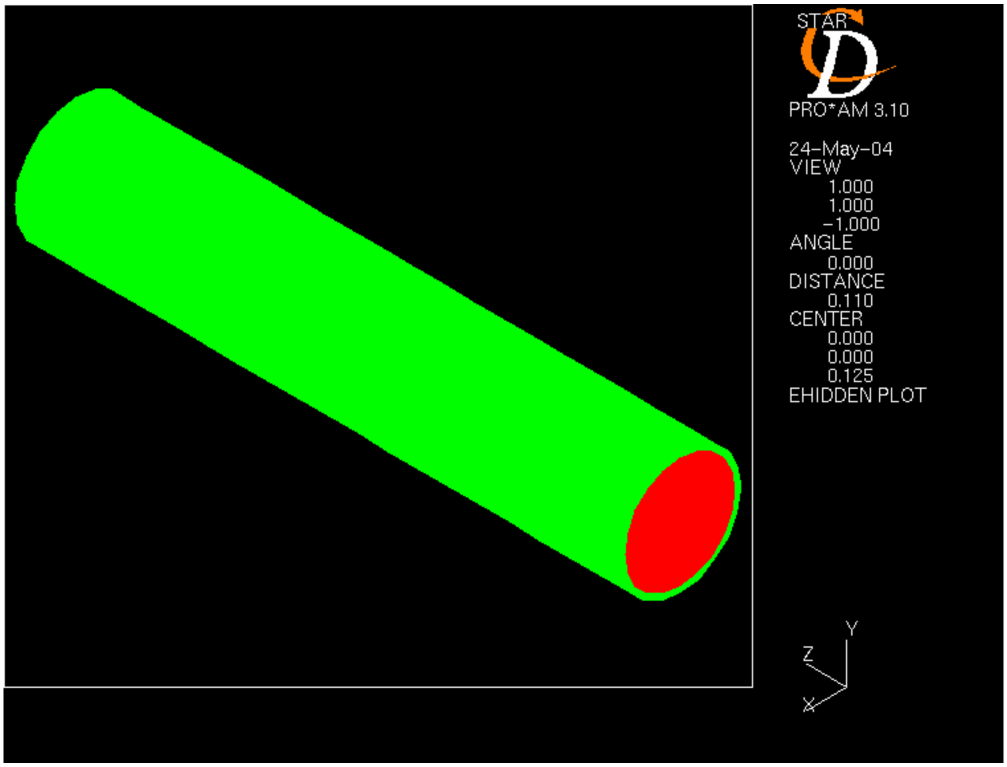

Figure 20 The 3-D CFD model (0.0508 m * 0.25 m straight pipe)

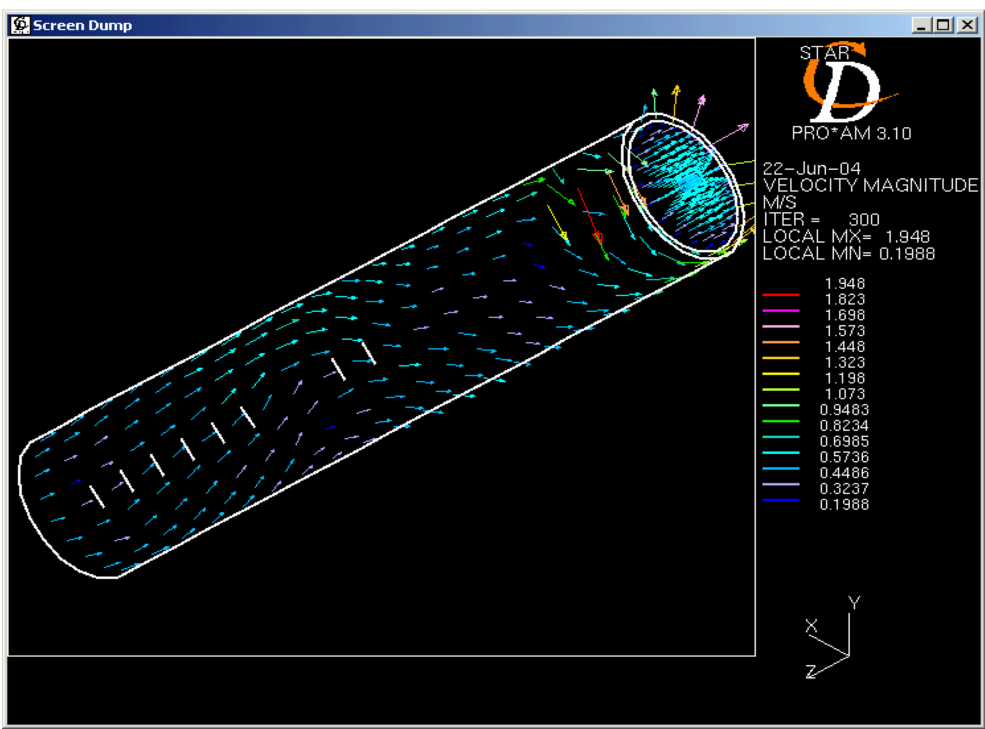

Figure 21 The velocity vector inside the pipe

- Appendix (part of subroutine)
  - LBE surface chemical reaction subroutine
  - C** ******
  - SUBROUTINE REACFN(RATE)
  - C CHEMICAL REACTION RATE
  - C** *******
  - C--*
  - C STAR RELEASE 3.150
  - C--*
  - INCLUDE 'comdb.inc'
  -
  - COMMON/USR001/INTFLG(100)
  -
  - INCLUDE 'usrdat.inc'
  - COMMON/USREAI/IR,NR
  - COMMON/USREAR/TAUL,TAUG,AEBM,BEBM,AMFU,AMFB,ARCK,BETCK,EACT,
  - * RTCKF,AMRC(3),RTCKR(3)
  - common /speed03/ wmfuu,wmoxi,stoxi,tauml
  - DIMENSION SCALAR(50), HFORM(50)
  - EQUIVALENCE(UDAT12(001), ICTID)
  - EQUIVALENCE(UDAT03(001), CON)
  - EQUIVALENCE(UDAT04(001), CP)
  - EQUIVALENCE(UDAT04(002), DEN)
  - EQUIVALENCE(UDAT04(003), ED)
  - EQUIVALENCE(UDAT04(006), P)
  - EQUIVALENCE(UDAT04(008), TE)
  - EQUIVALENCE(UDAT04(009), SCALAR(01))
  - EQUIVALENCE(UDAT04(059), U)
  - EQUIVALENCE(UDAT04(060), V)
  - EQUIVALENCE(UDAT04(061), W)
  - EQUIVALENCE(UDAT04(062), VISM)
  - EQUIVALENCE(UDAT04(063), VIST)
  - EQUIVALENCE(UDAT04(007), T)
  - EQUIVALENCE(UDAT04(067), X)
  - EQUIVALENCE(UDAT04(068), Y)
  - EQUIVALENCE(UDAT04(069), Z)
  - EQUIVALENCE(UDAT09(001), IS)
  - EQUIVALENCE(UDAT10(101), HFORM(01))
  - C--
  - C For a specified material “imat” (i.e., surface cells where
  - C reaction takes place) and for a specific reaction “IR”, set the

```
•  C  necessary parameters (i.e., initial concentrations, temperature, etc.)
•  C------------------------------------------------------------------
•       if(imat.eq.1) then
•         If(IR.EQ.1) then
•           iFe3O4=1
•           iPbO=2
•           iO2=3
•           iFe=4
•           iPb=5
•           wFe3O4=232
•           wPbo=223
•           wO2=32
•           wFe=56
•           wPb=207
•           sum=0
•  C------------------------------------------------------------------
•  C  collect all the scalars for the reaction rate
•  C------------------------------------------------------------------
•           Sum = scalar(Fe3O4)/wFe3O4 + scalar(PbO)/wPbO +
•      &          scalar(O2)/wO2
•      &         + scalar(Fe)/wFe + scalar(Pb)/wPb
•
•           wmix=1./sum
•
•           T1=T
•           s1=scalar(iFe3O4)
•           if(s1.lt.0) s1=0
•  C------------------------------------------------------------------
•  C  Calculate the reaction rate, some constants such as 2.5e7, 25000,
•     1.987, T1,0.75 need to be traced and changed in LBE case
•  C------------------------------------------------------------------
•           rate=2.5e7*exp(-25000./(1.987*T1))
•           rate=rate*(den*scalar(iFe3o4)*wmix/wFe3O4)**.75
•
•         endif
•       endif
•
•       Return
•       End
```

REFERENCES

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