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Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics-Task V: First Quarterly Report 01/12/04-02/29/04

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Modeling Corrosion in Oxygen Controlled LBE Systems with Coupling of Chemical Kinetics and Hydrodynamics-Task V

Fourth Quarterly Report

01/12/03-02/29/04

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:

One of the desired solvers in the STAR-CD code is not linking. We are working with the Tech. support of ADAPCO to resolve that. Guanjun's computer is not booting up so we are letting Tech. support at UNLV look the computer over. Guanjun is a little bit under the weather and is seeing a physician for that.

Technical progress:

Based on the technical results that our previous student Kanthi had furnished, the students are helping out in calculating the average tangential magnitude of the velocity near the wall. The results it is hoped will show a monotonically increasing value of this magnitude which will offer an explanation for the increase of the concentration gradients at the wall that Kanthi provided from his thesis results. It is expected if these results are validated that a journal paper will be produced and presented for review in the Nuclear Science and Materials journal where Dr. Ning and Zhang have published before.

Narain is pursuing the completion of the 3-D model in two pipe fitting geometries i.e. a sudden expansion and a Tee section. These sections will be eventually placed in a LBE loop numerical simulation to find out how the concentration gradients develop inside these fittings.

Guanjun is working on completing his user provided subroutine which will be incorporated in the STAR-CD code. The subroutine will eventually allow us to include true reaction kinetics at the surface of the LBE for a particularly chosen reaction between lead and oxygen.

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°C and boiling temperature of 1670°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, thereby 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.

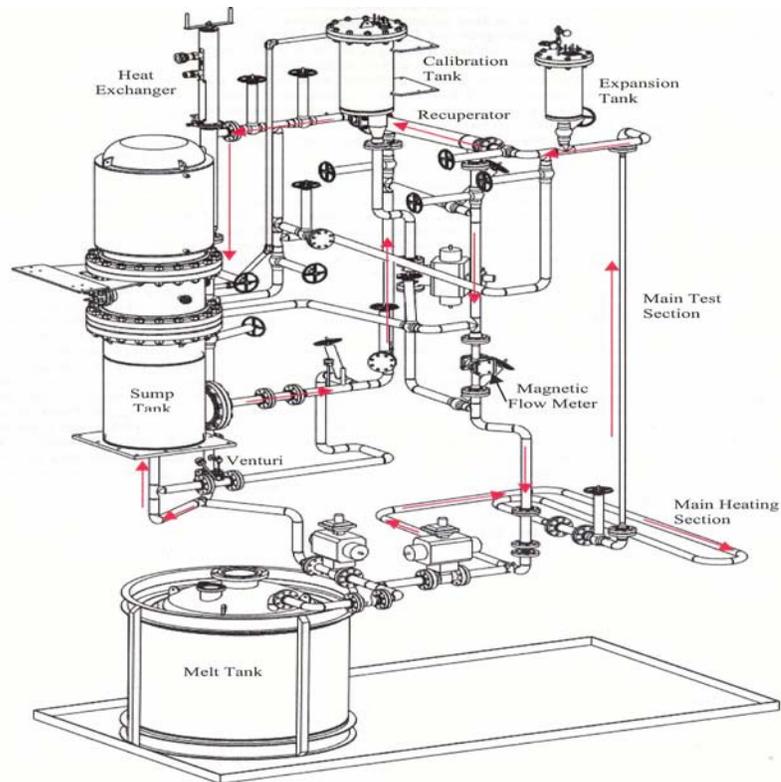


Figure – 1: Materials Test Loop

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:

$$u_{i,i} = 0 \quad (1)$$

Momentum Equation:

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

Energy Equation:

$$\rho_0 C_p \left(\frac{\partial T}{\partial t} + u_i T_{,i} \right) = (K * T_{,i})_{,i} + \mu \Phi \quad (3)$$

Species Transport:

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

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 $\overline{u_{i,j} u_{i,j}}$. The resulting equations are:

k – transport equation:

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

ε – transport equation:

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

Local Corrosion Modeling:

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.

This section sheds light on the velocity profiles obtained from the sudden expansion model. The results are shown for the flow in both the laminar regimes, which is followed by simulation results. Finally, the results are shown to be grid independent.

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 considered is less than 10 as specified by the CFD package. Runs were simulated for the Reynolds number of 100, 150, 200, 500, 1000 and 1500. The simulated results obtained are as shown.

Grid Independency:

Once the runs are simulated a check on grid independency is made. The cell layer next to the wall is selected and is refined to get 5 new cells in place of a single cell. Then this refined model is run for the same Reynolds numbers as mentioned above. Then a single cell at a particular distance (a distance of 4d is considered) from the sudden expansion region from both the models is isolated and the w-component of the velocity is compared. The matching of the two plots is a good indication of grid independency being established.

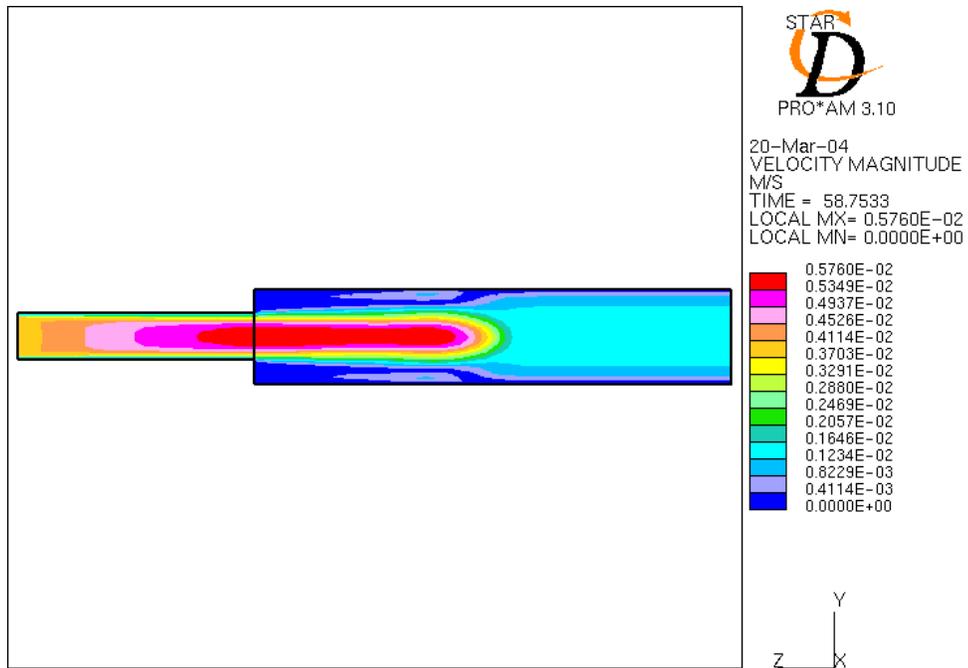


Figure - 2: Velocity plot for $Re = 100$

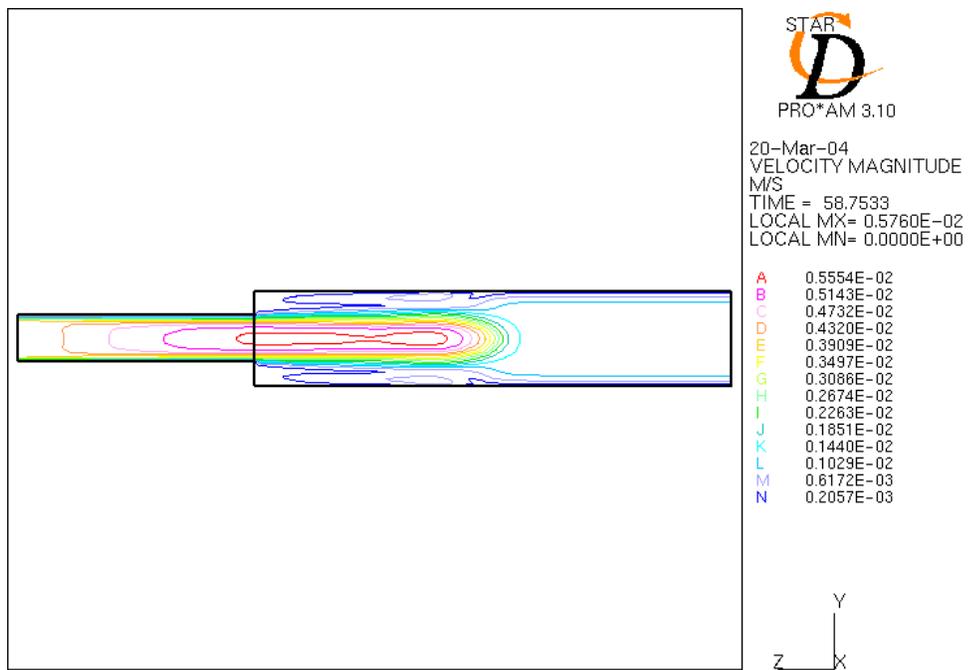


Figure - 3: Velocity lines for $Re = 100$

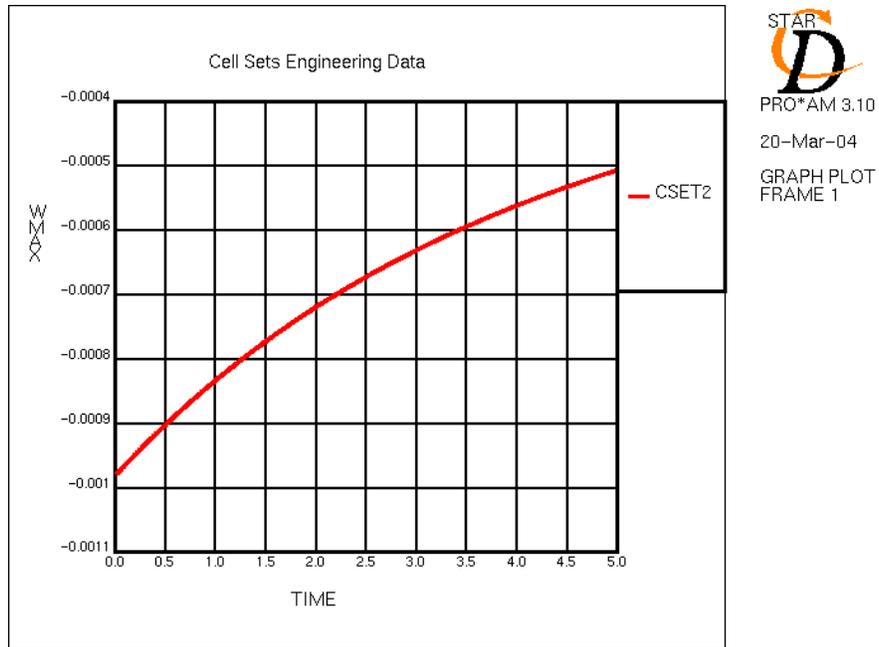


Figure - 4: W-component of the velocity for $Re = 100$

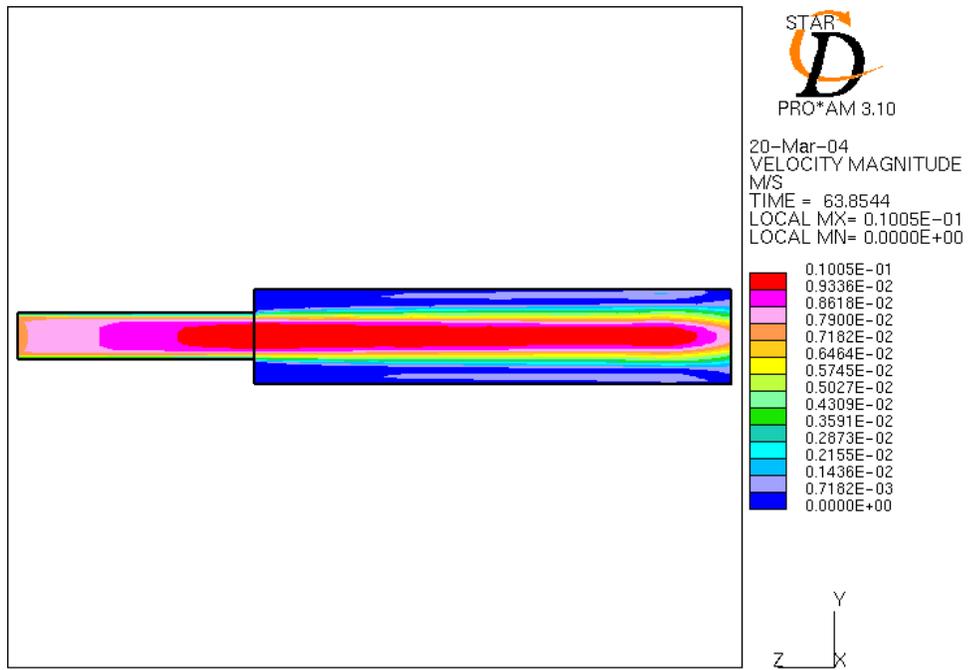


Figure - 5: Velocity plot for $Re = 200$

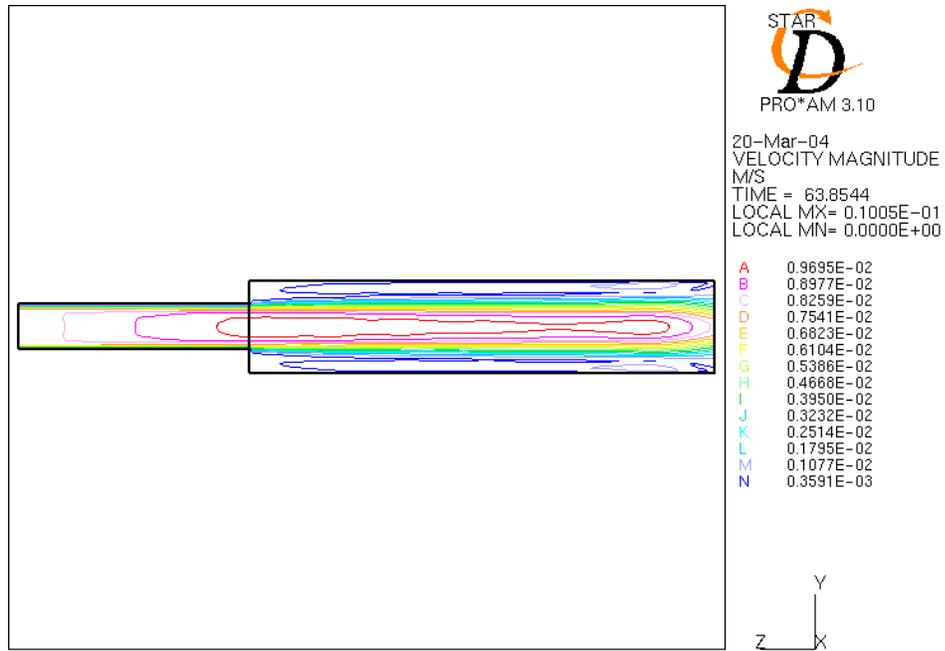


Figure - 6: Velocity lines for $Re = 200$

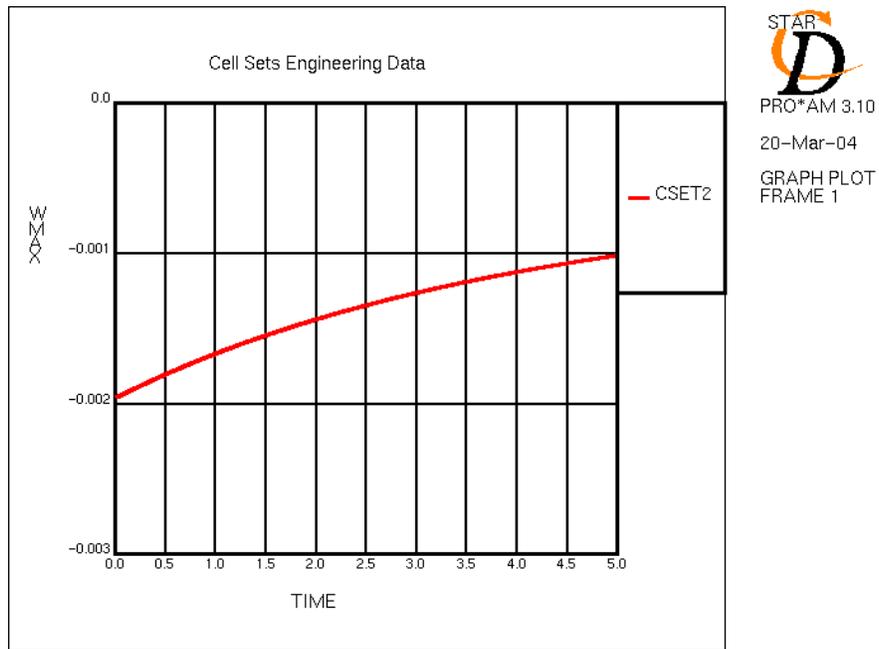


Figure - 7: W-component of the velocity for $Re = 200$

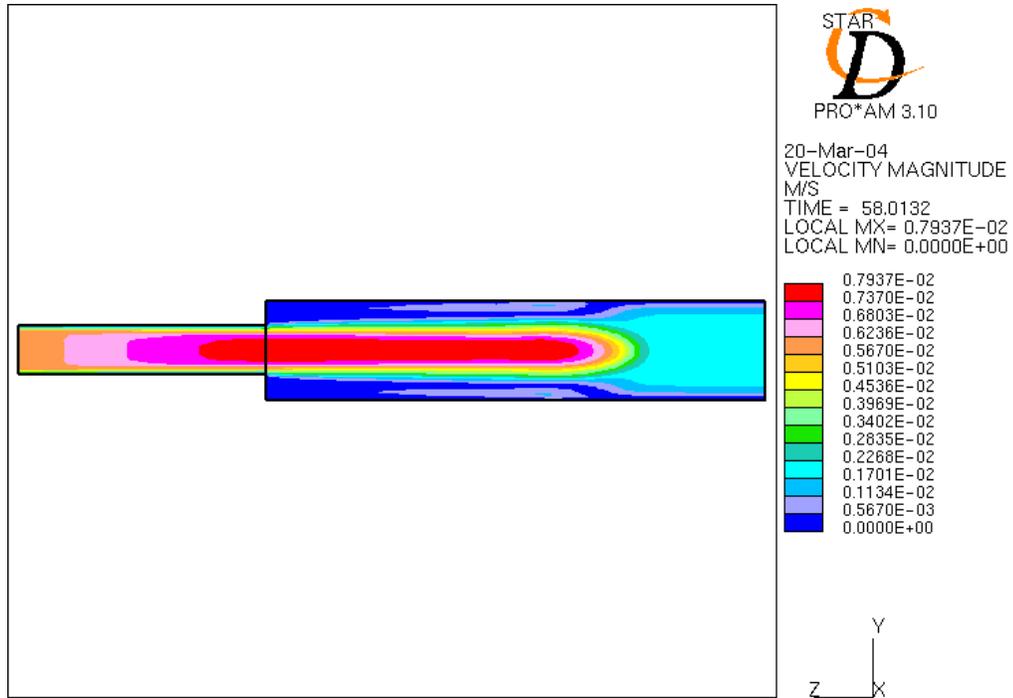


Figure - 8: Velocity plot for $Re = 150$

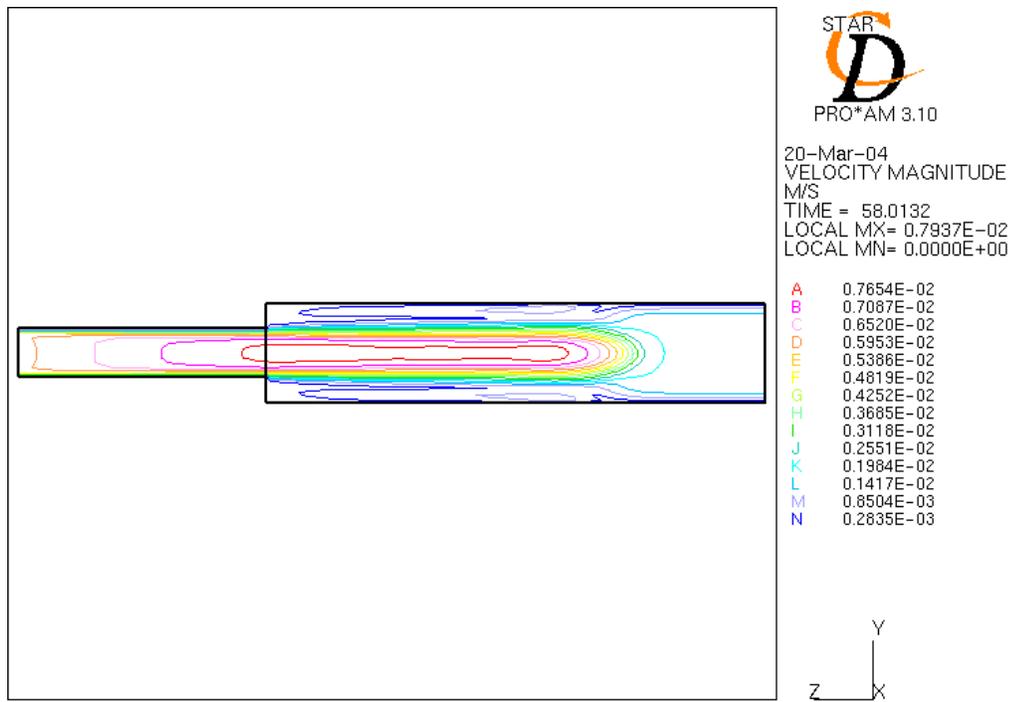
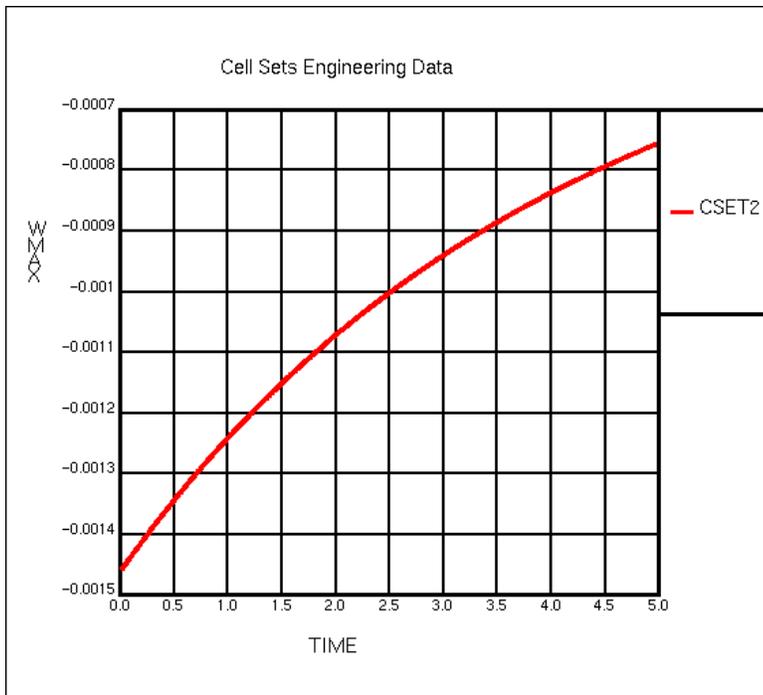


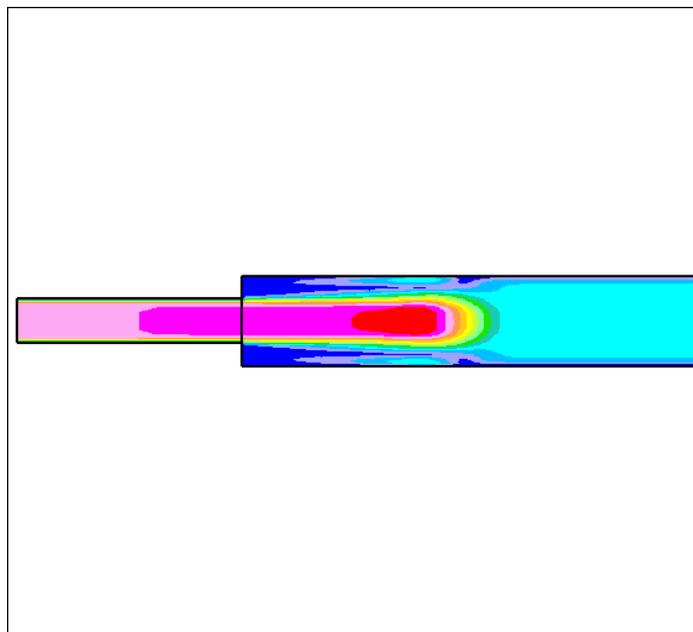
Figure - 9: Velocity lines for $Re = 150$



STAR

 PRO*AM 3.10
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 GRAPH PLOT
 FRAME 1

Figure - 10: W-component of the velocity for Re = 150



Y
 X
 Z

Figure - 10: Velocity plot for Re = 500

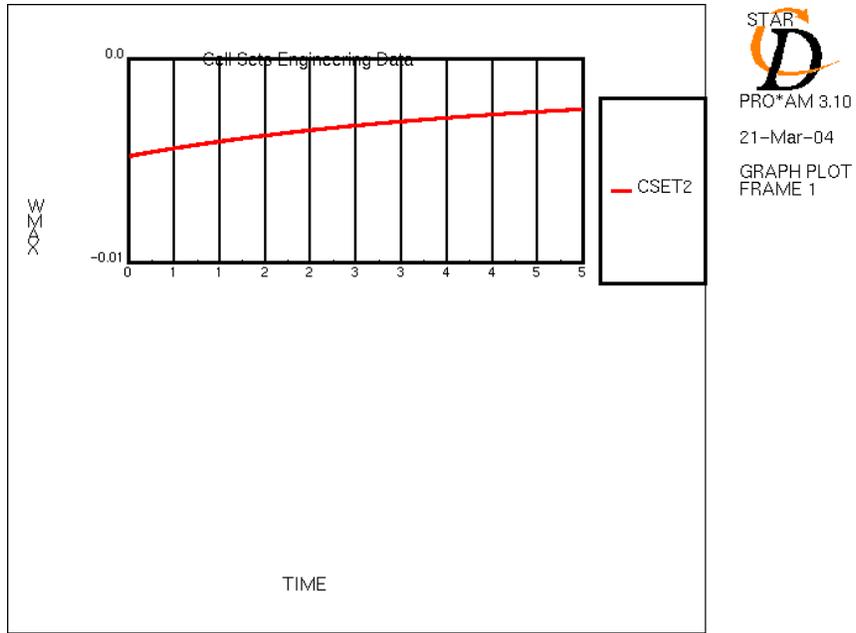


Figure - 11: W-component of the velocity for $Re = 500$

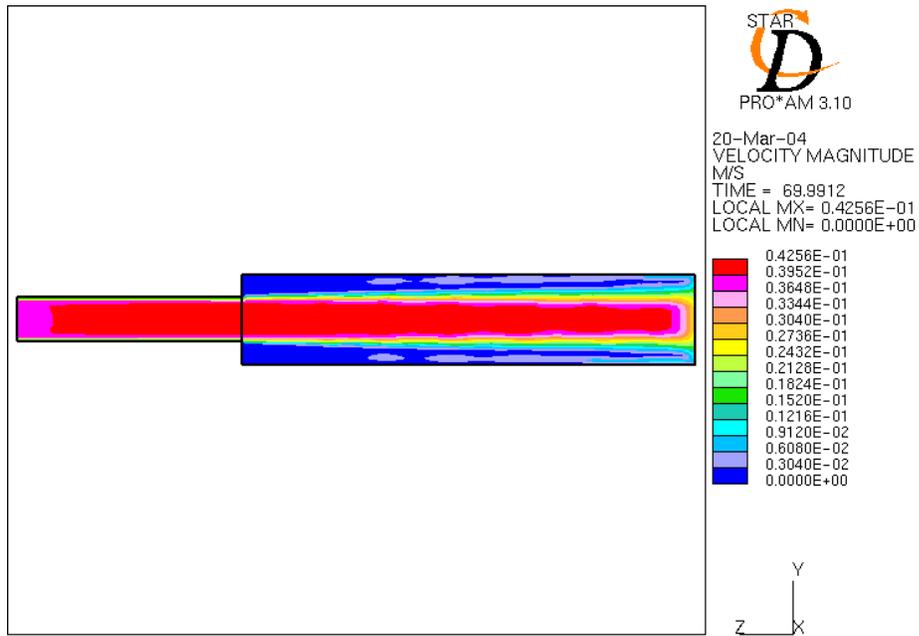


Figure - 12: Velocity plot for $Re = 1000$

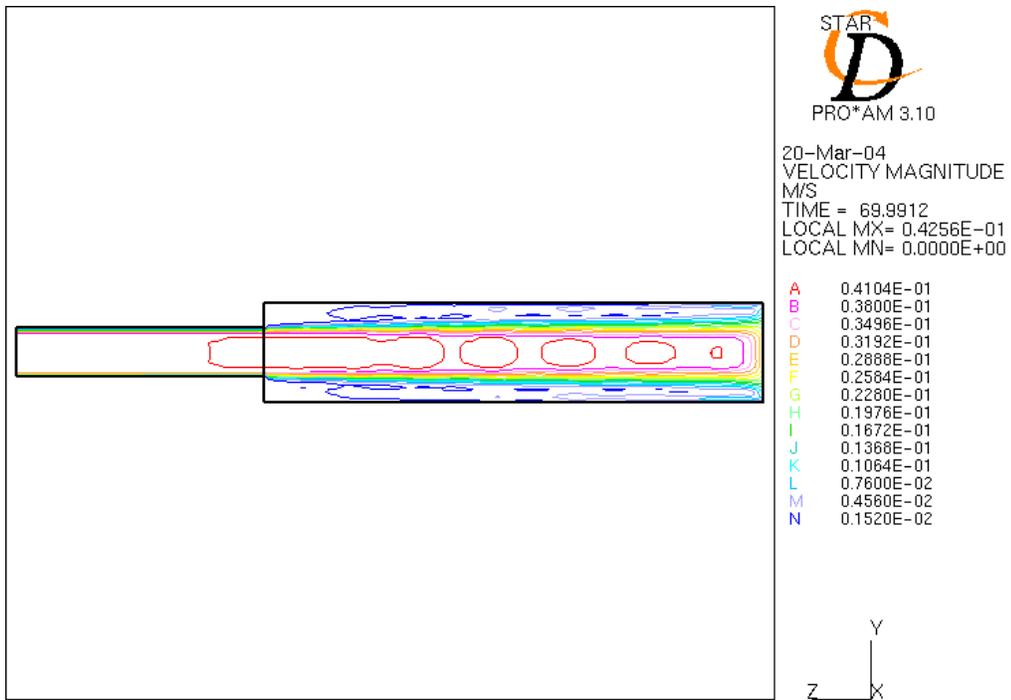


Figure - 13: Velocity lines for Re = 1000

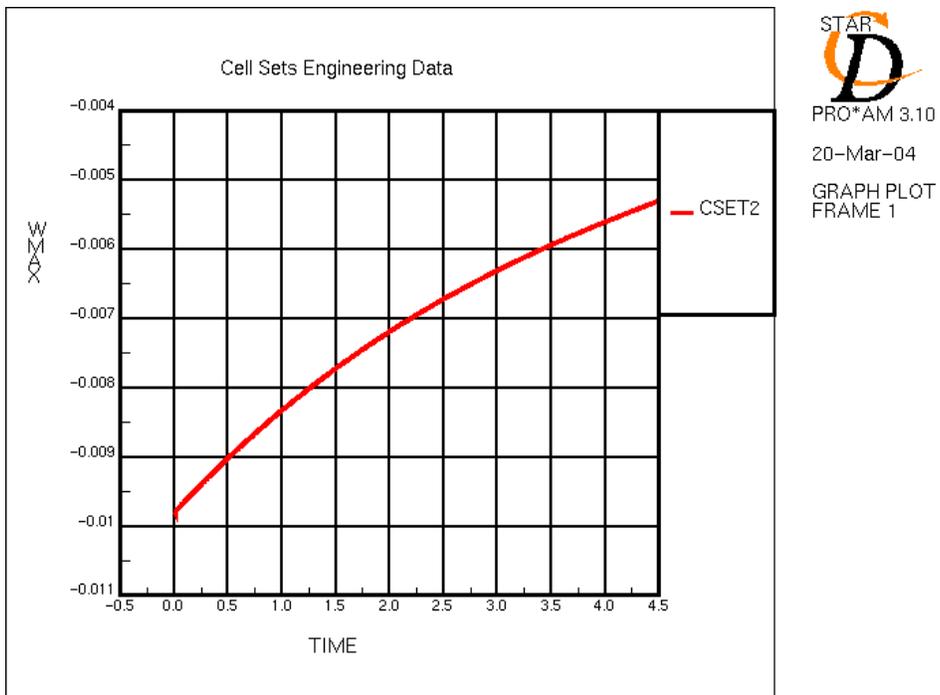


Figure - 14: W-component of the velocity for Re = 1000

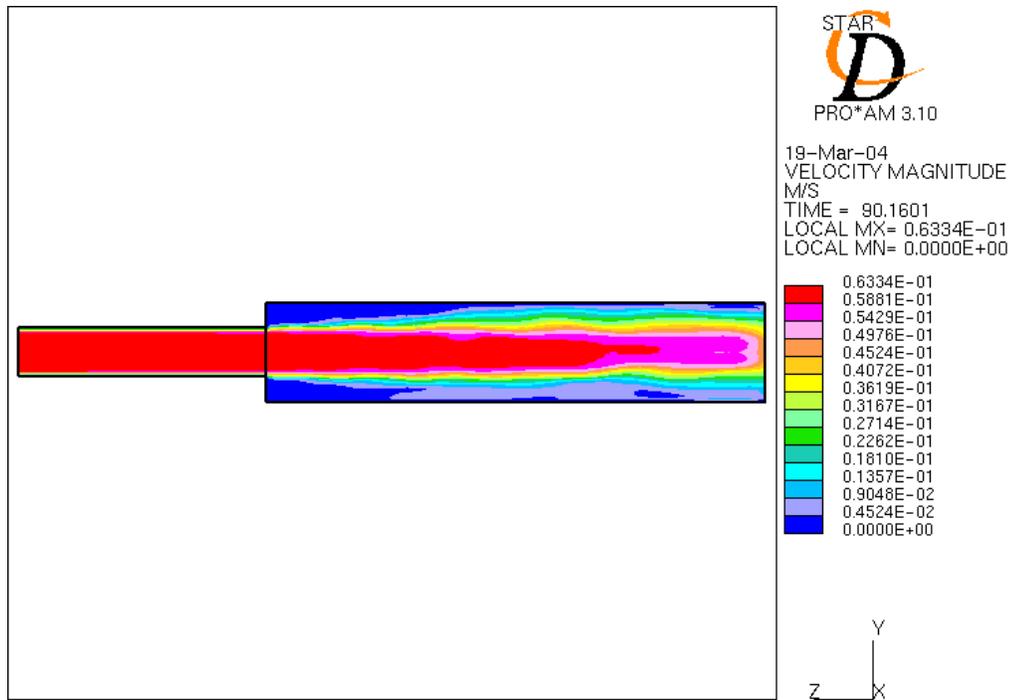


Figure - 15: Velocity plot for $Re = 1500$

The vortex shedding starts to occur at $Re = 1500$ for a 3-d model as shown in figure 13. For a 2-d axisymmetric case, the vortex shedding occurs at $Re = 150$ as shown in the figure 15.

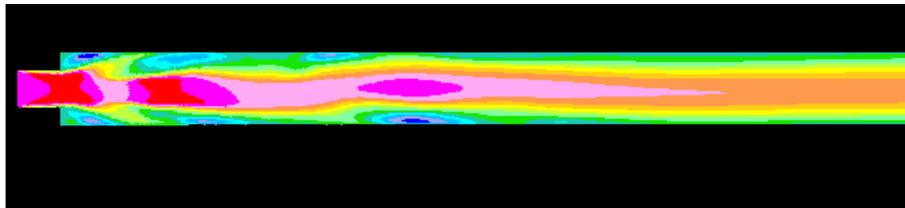


Figure - 16: Velocity plot for $Re = 1500$

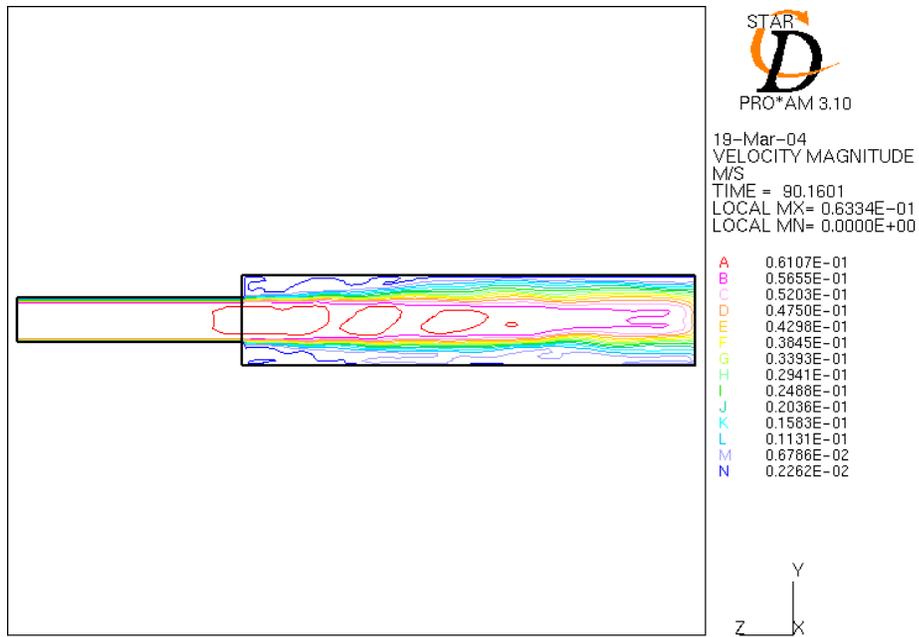


Figure - 17: Velocity plot for $Re = 1500$

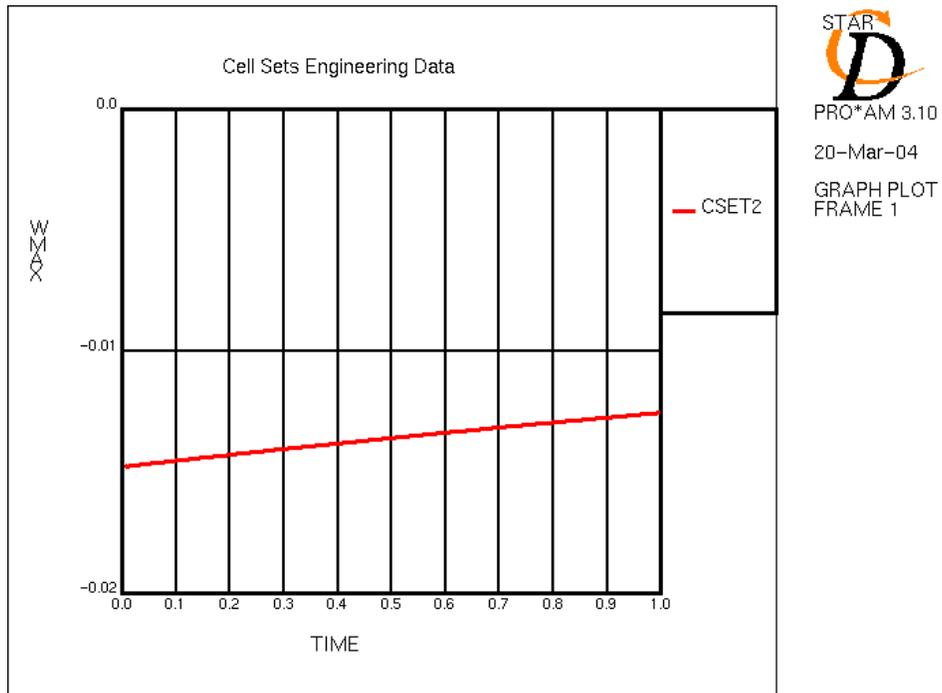


Figure - 18: W-component of the velocity for $Re = 1500$

Grid Independency Results

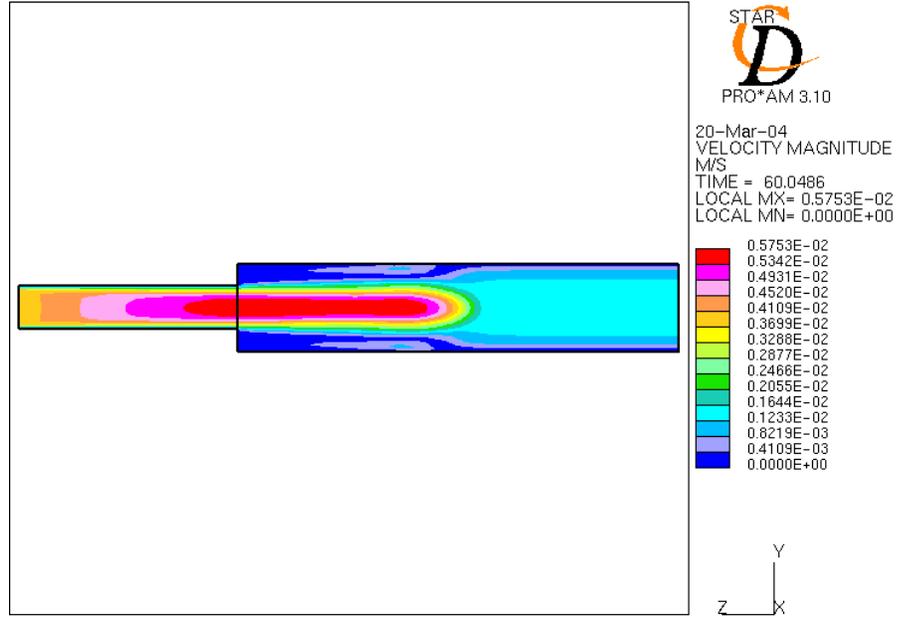


Figure - 19: Velocity plot for Re = 100

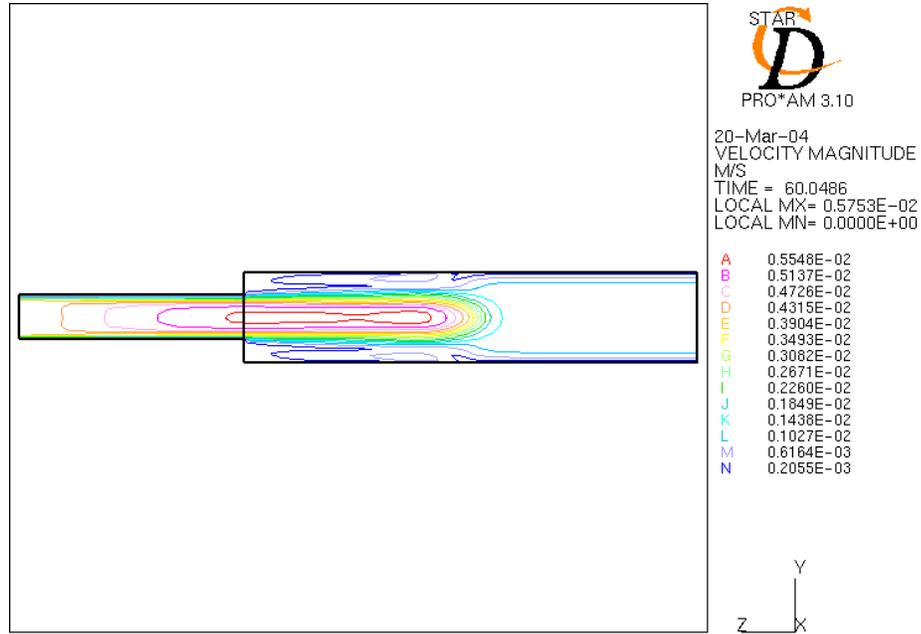


Figure - 20: Velocity lines for Re = 100

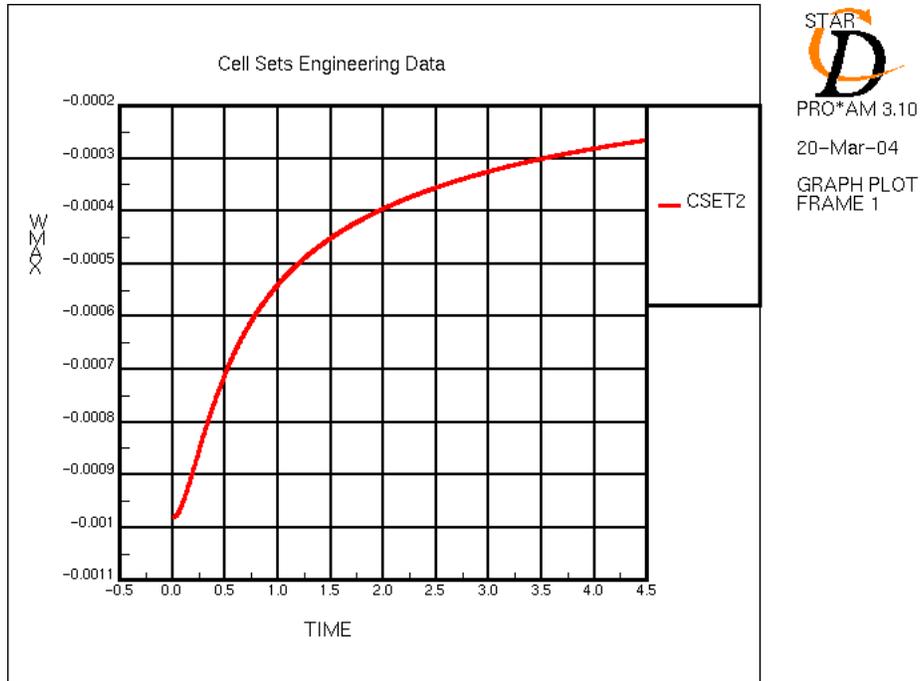


Figure - 21: W-component of the velocity for $Re = 100$. This curve is almost similar to that in figure 4

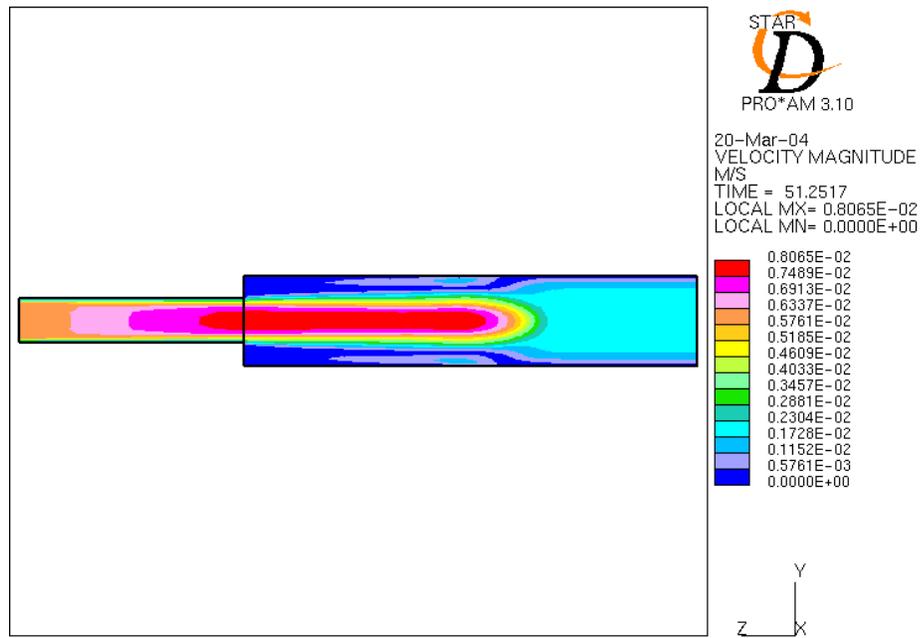


Figure - 22: Velocity plot for $Re = 150$

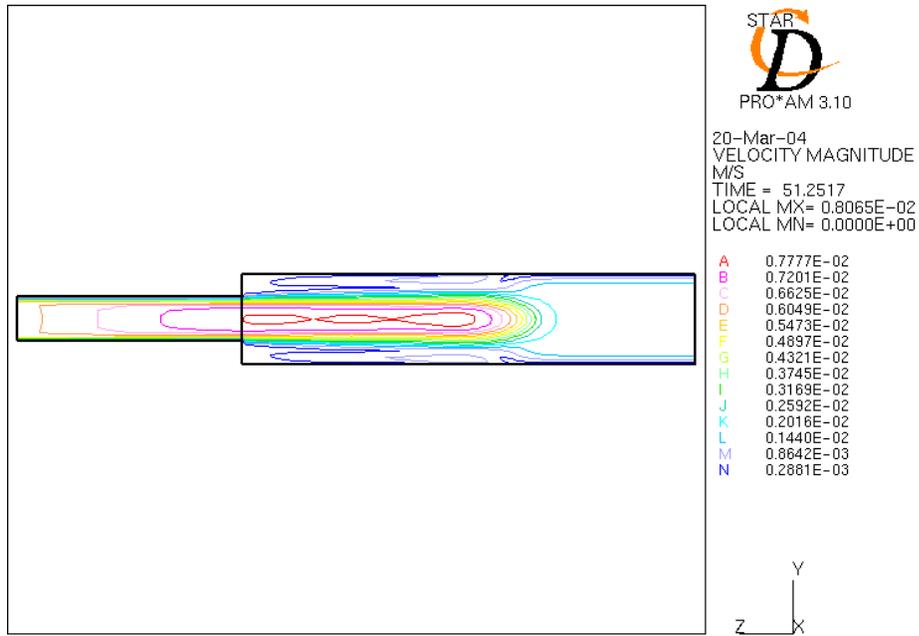


Figure - 23: Velocity lines for $Re = 150$

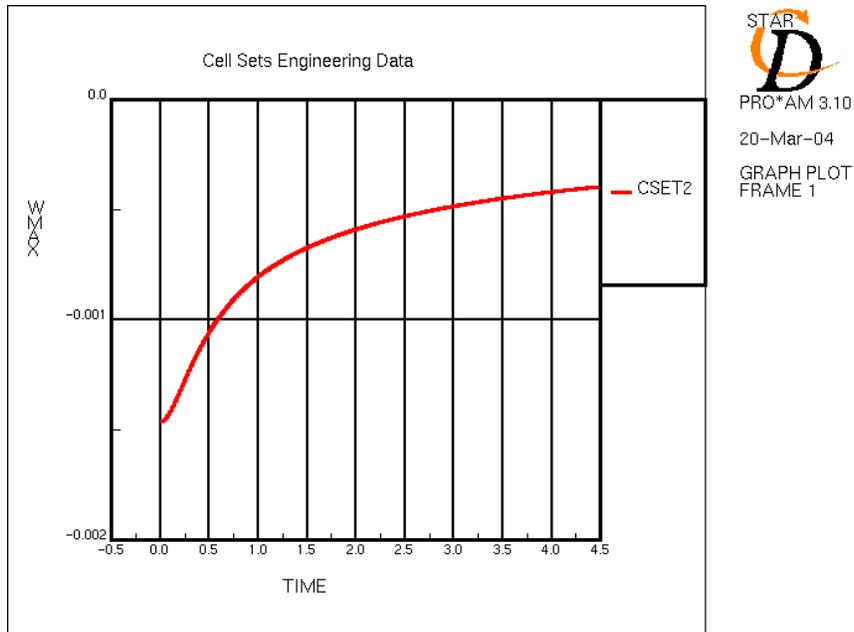


Figure - 24: W-component of the velocity for $Re = 150$. This curve is almost similar to that in figure 10

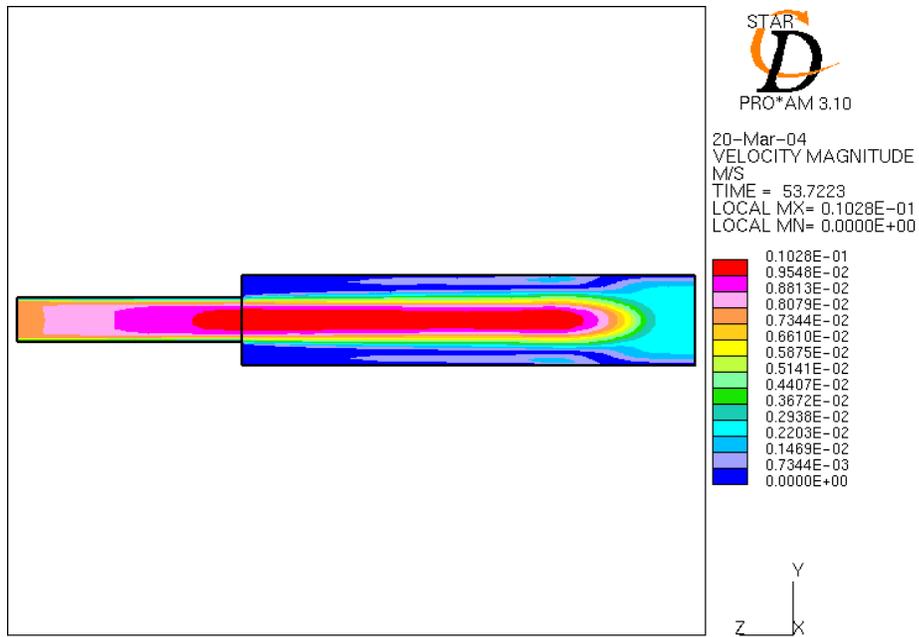


Figure - 25: Velocity plots for $Re = 200$

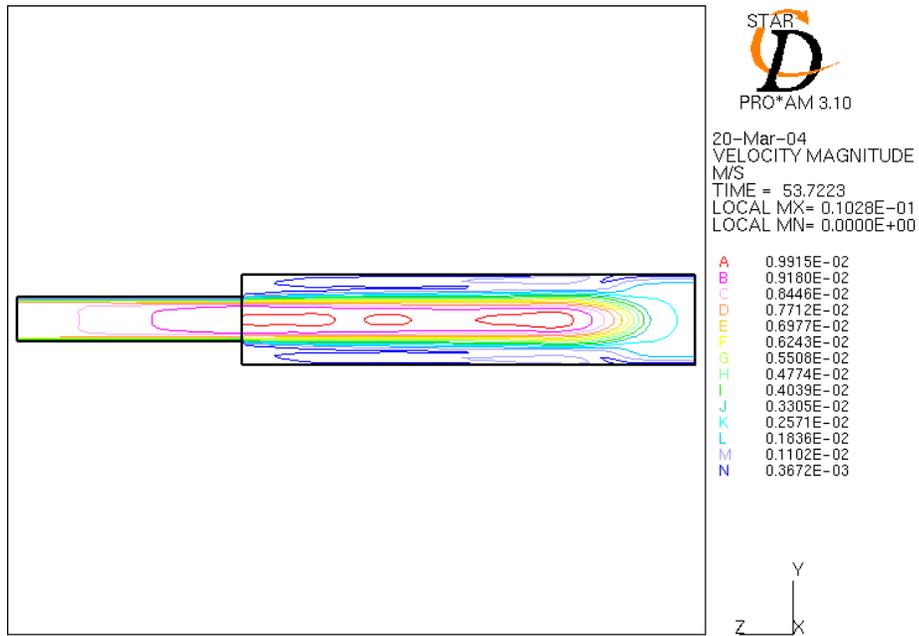


Figure - 26: Velocity lines for $Re = 200$

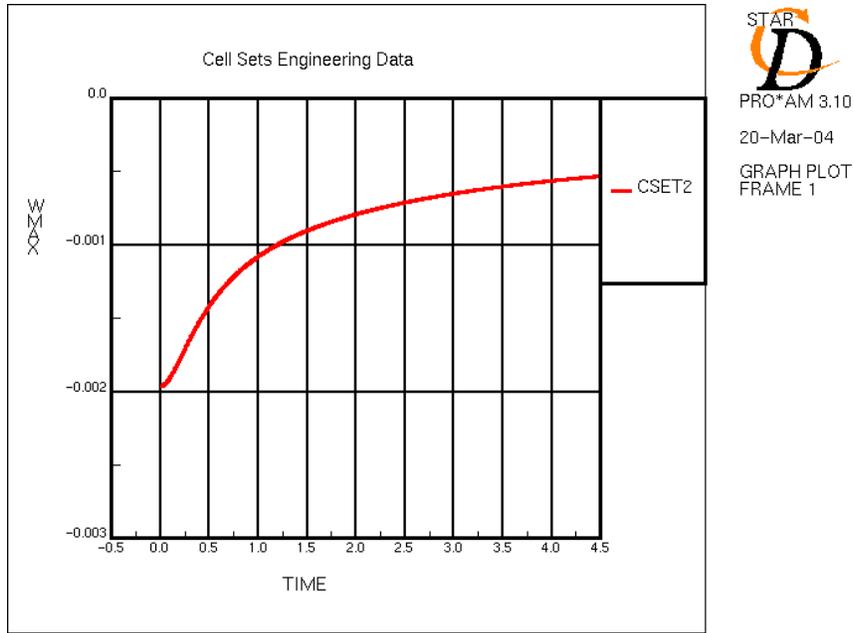


Figure - 27: W-component of the velocity for $Re = 200$. This curve is almost similar to that in figure 7

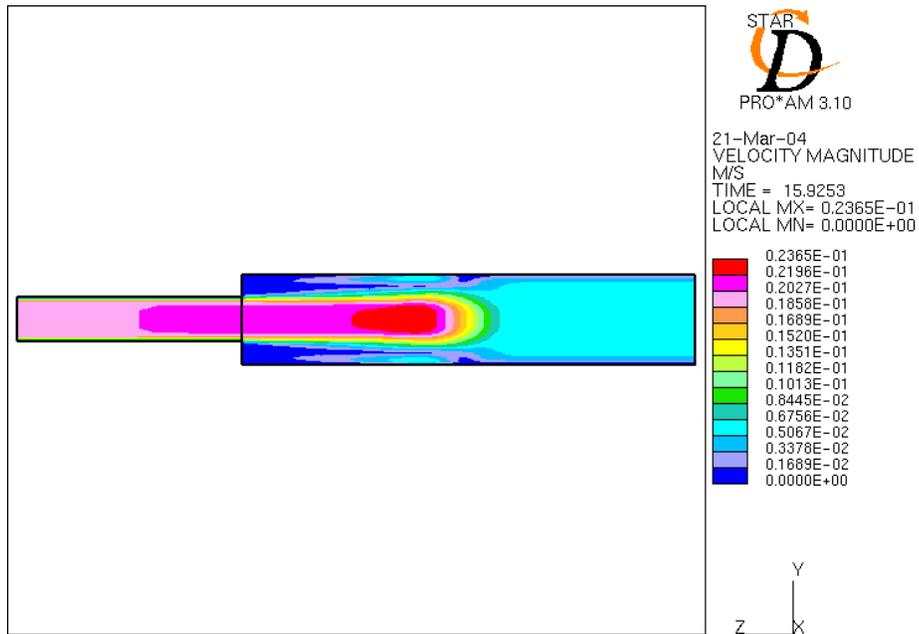


Figure - 28: Velocity plot for $Re = 500$

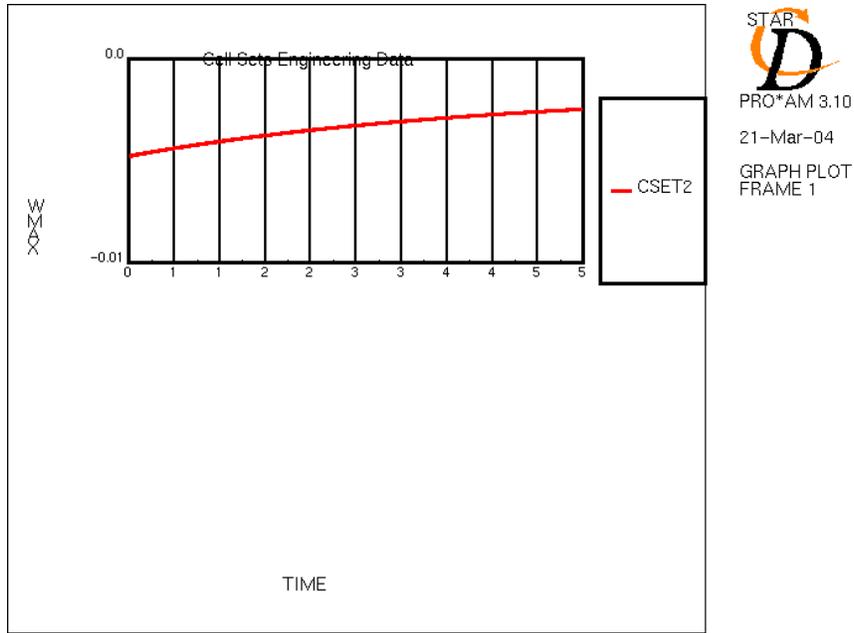


Figure - 29: W-component of the velocity for $Re = 500$. This curve is almost similar to that in figure 11

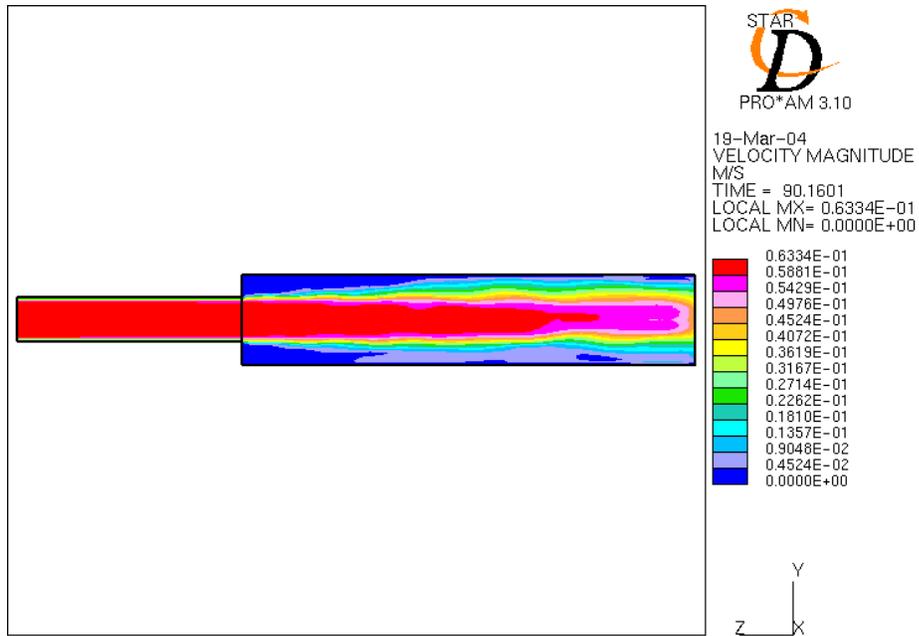


Figure - 30: Velocity plot for $Re = 1500$

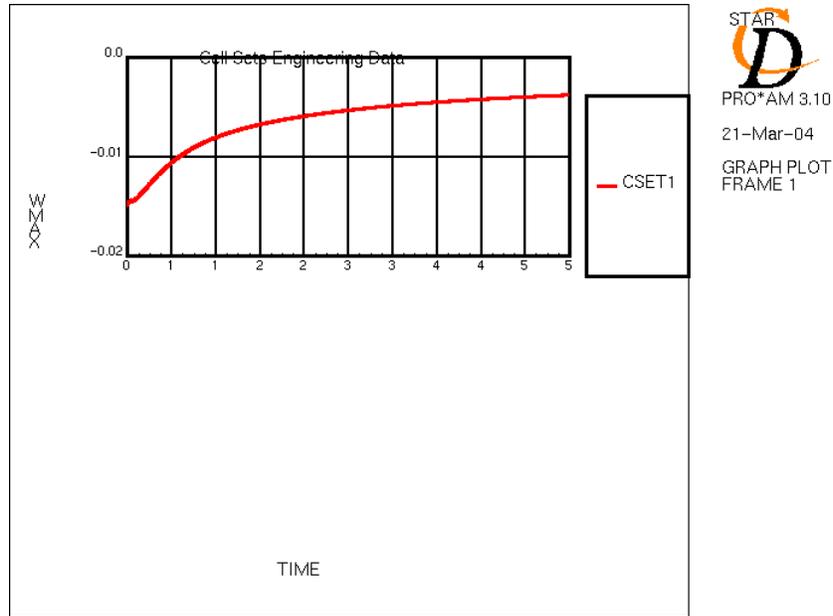


Figure - 31: W-component of the velocity for $Re = 1500$. This curve is almost similar to that in figure 18

These plots and graphs show that grid independency has been established.

The second loop fitting, which will be worked on is the tee-joint. The model is shown in figure 32. This model was constructed using the modeling package SOLIDWORKS. It will then be meshed using PRO-AM.

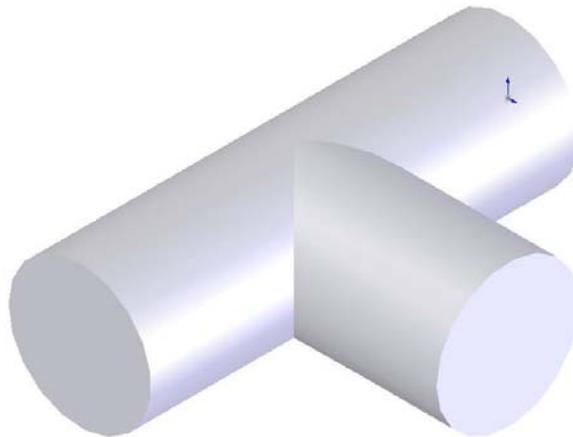


Figure – 32: A tee-joint.

Chemical Reaction Study in Oxygen Controlled LBE Loop Systems

Some hydraulic studies regarding how diffusion, mass transfer and convection affect corrosion and precipitation rate of steel in oxygen controlled non-isothermal LBE loop piping system under various temperatures have been done. In these studies, it was assumed that chemical reactions are much slower than the characteristic time of diffusion/convection and hence, they contribute little to the mass transfer in LBE bulk fluids.

A chemical reaction model will possibly be developed to estimate the contribution of chemical reactions to the corrosion rate of steel in oxygen controlled non –isothermal LBE flow loop by using a CFD code STAR-CD. Since STAR-CD provides for the solution of conservation equations for chemical species and energy, it can add the net mass production and /or depletion rate of additional species (due to chemical reactions) into the convection-diffusion mass transport equation. This will be done by using the standard or subroutine feature of STAR-CD if they are applicable in the LBE loop system.

Generally, chemical reactions can be grouped as homogenous reactions and heterogeneous reactions. Homogenous reactions occur within the bulk of the fluid. For heterogeneous reactions, the reactions take place only at surface. In LBE loop system, the major chemical reactions, which might affect the loop steel corrosion and precipitation rate, include a oxidation reaction between Fe and oxygen which forms the protective film Fe₃O₄ at the inner wall surface, as well as a reduction reaction between the film Fe₃O₄ and Pb. Both reactions are heterogeneous reaction since they occur at surface. The surface chemical reactions are currently implemented via user-supplied subroutines. Due to the fact that Fe is more active than Pb, the reduction reaction can only occur when the Fe surface concentration is extremely low at the interface between film and the LBE bulk.

In addition to the surface chemical reactions mentioned above, if there are homogeneous reactions (e.g. a reaction between Pb and O₂, etc.), which occur in the LBE bulk fluid, the standard chemical reaction feature of STAR-CD could be used by applying the eddy break-up model, chemical kinetic model or a combination of these two models to calculate the reaction rates. Both homogeneous reactions and surface reactions need to be considered to evaluate the corrosion rate accurately in LBE loop system.

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