



# Spacial Chlorine Plasma PFR with Power Profile

CAPP-Plasma-2 (v1.0) December 15, 2007

## Summary

This application note presents an example of a Plasma Plug Flow Reactor with a specified power-versus-distance profile.

## Project Description

This feature might be used to model an experimental apparatus where the inductive coils providing the power are spaced unevenly. Alternatively, this could be used to model a system where there is a lower-power region where a probe is used that cannot operate in a high-plasma density region, or where a measurement window is located.

This example is for a plasma at a total pressure of one torr with pure chlorine gas flowing into the reactor at  $35 \text{ cm}^3/\text{s}$ . The electron energy equation is solved, and there is consideration of heat loss through the wall of the reactor. The area used for surface chemistry and heat loss corresponds to the physical walls of the tubular reactor.

The chemistry set is for a pure chlorine plasma without surface etching reactions that is based on work published by Meeks and coworkers.<sup>1, 2</sup>

The gas-phase chemistry in the chlorine plasma is relatively simple. The element list contains three elements: E (the electron), Cl and Si. Si does not actively participate in any chemical reactions, as it only appears in the surface input file, *surf.inp*, in the composition of surface species on the wall material, but it still needs to be included in the element list in the GAS-PHASE KINETICS input file. The gas-phase species list contains seven species:  $\text{Cl}_2$ , Cl,  $\text{Cl}^*$  (chlorine atoms in a metastable electronically excited state),  $\text{Cl}_2^+$ ,  $\text{Cl}^+$ ,  $\text{Cl}^-$  and E. The gas-phase reactions include electron collisions with  $\text{Cl}_2$  leading to vibrational and electronic excitation, dissociation, ionization, and dissociative attachment. Electron reactions with Cl include electronic excitation into a number of excited states, including  $\text{Cl}^*$  formation, and ionization. The gas-phase reaction mechanism also includes electron collisions with  $\text{Cl}^-$  leading to

<sup>1</sup>"Modeling of Plasma-Etch Processes Using Well Stirred Reactor Approximations and Including Complex Gas-Phase and Surface-Reactions", E. Meeks and J. W. Shon, *IEEE Transactions On Plasma Science*, **23**(#4):539-549 (1995).

<sup>2</sup>"Effects of Atomic Chlorine Wall Recombination: Comparison of a Plasma Chemistry Model With Experiment," E. Meeks, J. W. Shon, Y. Ra, P. Jones, *JVSTA* **13**(#6):2884-2889 (1995).

electron detachment, electron collisions with  $\text{Cl}^*$  leading to ionization, and gas-phase neutralization of  $\text{Cl}^-$  with  $\text{Cl}^+$  and  $\text{Cl}_2^+$  ions. All the reactions are irreversible, as is typical of non-thermal plasmas. In low-pressure plasmas, ionization and dissociation are balanced primarily by surface recombination reactions. The rates for the electron-impact reactions depend on the electron energy, rather than the neutral gas temperature.

The surface mechanism for reactions occurring on the reactor wall is also fairly simple. It only involves neutralization of  $\text{Cl}^+$  and  $\text{Cl}_2^+$  with electrons (subject to the Bohm criterion), de-excitation of  $\text{Cl}^*$  and radical recombination reactions for  $\text{Cl}$  to  $\text{Cl}_2$ . The neutralization and de-excitation reactions are non-site specific, but the recombination reactions are described in terms of open and  $\text{Cl}$ -covered sites. Although this example problem does not include surface etching reactions, surface recombination and neutralization reactions can be quite important in determining the overall composition of these kinds of low-pressure plasmas. All the surface reactions are irreversible. The thermodynamic properties for surface species, therefore, provide the elemental composition of the surface species, but the polynomial fitting parameters are considered placeholder values and are not used in the simulation.

## Project Setup

The CHEMKIN project file is called *plasma\_pfr\_cl\_power\_profile.ckprj*. The data files used for this sample are located in the CHEMKIN-installed directory *samples\plasma\_pfr\cl\_power\_profile*. This reactor diagram contains a gas inlet, a Plasma Plug Flow Reactor, and an outlet.

To specify the reactant gas mixture, go to the Species-specific Property tab of the C1\_Inlet1 panel. Although the input gas is actually pure  $\text{Cl}_2$ , in order to have the plasma “light” in the simulation, we have modified the inlet gas to include a small amount of electrons and ions in the inlet gas.

You can enter the problem type and reactor parameters such as pressure, temperatures, geometry, heat loss, and plasma power on the Reactor Physical Property tab of the C1\_Plasma PFR panel. The value for the electron temperature input here is used as the inlet electron temperature. You can set the plasma power profile by using the Profile tool or by selecting an existing profile file on the Reactor Physical Property tab of the C1\_ panel. This is an alternative to entering a constant value for the Plasma Power Deposition parameter. Enter the profile as a list of pairs of numbers, giving the power as a function of position. Values at intermediate points are straight-line interpolations of the two nearest specified values. Unphysically abrupt changes in the power profile can cause convergence problems in the simulation unless solver timesteps are set accordingly. Note that you must specify the power deposition for a plug-flow reactor profile in per-distance units, as it will be integrated over the channel distance.

As a simulation that marches forward from the inlet state, this sample problem has no “initial guess” for the gas composition, but Surface Fractions are provided on the Species-specific Data tab of the C1\_Plasma PFR panel. These site fractions provide initial estimates for the surface state of the channel inlet. An initial pseudo-steady calculation will be performed to determine consistent surface state based

on these estimates and the inlet gas composition, prior to the channel integration. The Sheath Loss parameter on the Material-specific Data tab of the C1\_ Plasma PFR panel describes the ion energy gained crossing the sheath.

## Project Results

*Figure 1* shows the profile of electrical power deposited into the plasma as a function of distance down the Plug Flow Reactor. As expected, the mole fractions of the electrons and atomic chlorine, shown in *Figure 2* and *Figure 3*, respectively, generally follow the plasma power profile, with differing degrees of non-linearity. This is consistent with the fact that the Cl is created in the plasma by electron-impact dissociation of molecular chlorine. The mole fractions for the  $\text{Cl}^+$  and  $\text{Cl}_2^+$  ions, shown in *Figure 4* also follow the plasma power profile.

Figure 1 Spatial Chlorine Plasma—Plasma Power vs. Distance

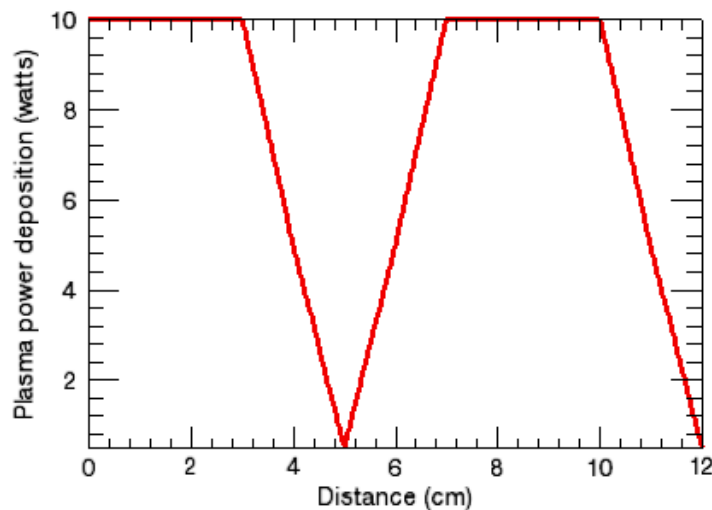


Figure 2 Spatial Chlorine Plasma—Electron Mole Fraction

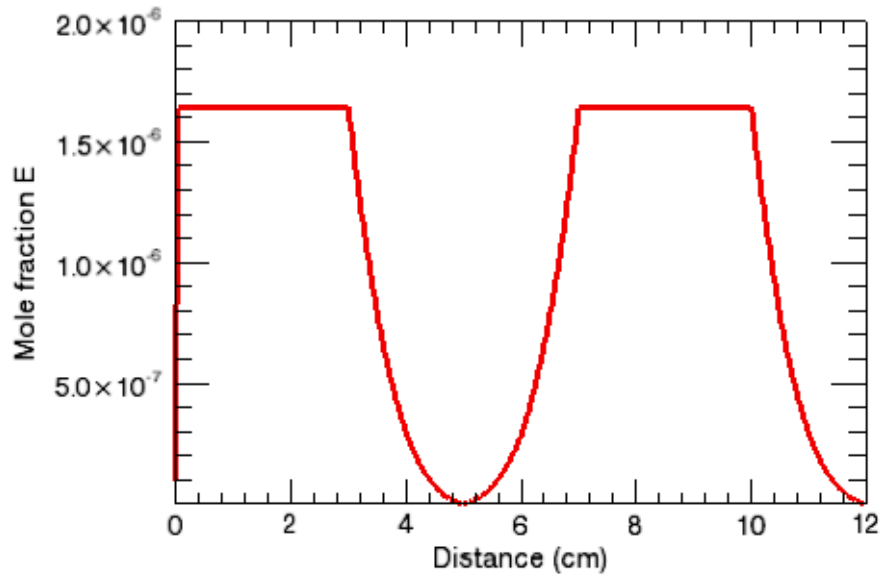


Figure 3 Spatial Chlorine Plasma—Cl Mole Fraction

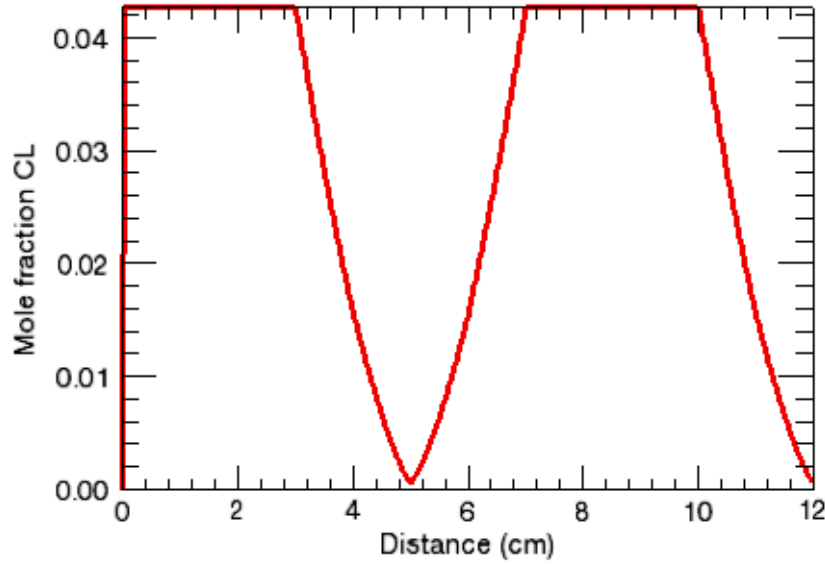
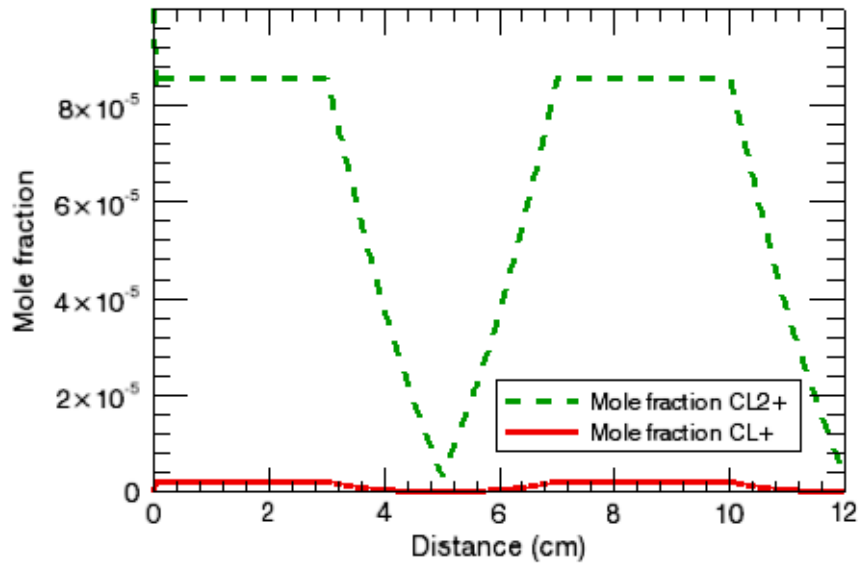


Figure 4 Spatial Chlorine Plasma—Cl<sup>+</sup> and Cl<sub>2</sub><sup>+</sup> Mole Fractions



The electron temperature rises somewhat in the lower-power regions of the reactor tube. This is consistent with the inverse trend between electron densities and electron temperatures seen at low power densities in the [Steady-State Chlorine Plasma example](#).

Figure 5 Spatial Chlorine Plasma—Electron Temperature

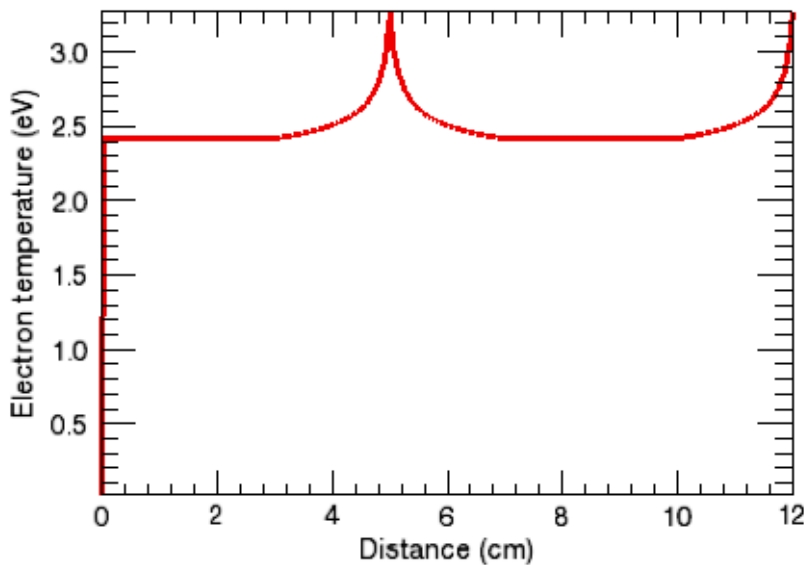
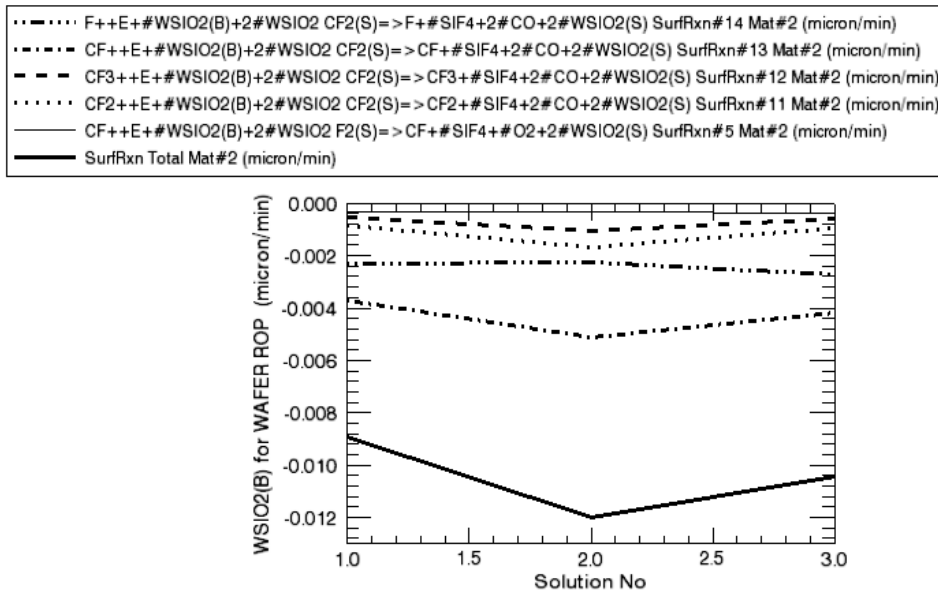


Figure 6



## About Reaction Design

Reaction Design helps transportation manufacturers and energy companies rapidly achieve their Clean Technology goals by automating the analysis of chemical processes via simulation and modeling solutions. Reaction Design is the exclusive developer and distributor of CHEMKIN, the *de facto* standard for modeling gas-phase and surface chemistry that provides engineers ultra-fast access to reliable answers that save time and money in the development process. Reaction Design also offers the KINetics software module, which brings detailed kinetics modeling to other engineering applications, such as Computational Fluid Dynamics (CFD) programs. Reaction Design’s world-class engineers, chemists and programmers have expertise that spans multi-scale engineering from the molecule to the plant. Reaction Design serves more than 350 customers in the commercial, government and academic markets.

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