Simulation of soil remediation polluted by hydrocarbons using non - thermal atmospheric plasma.

Jeanne Rojo, Stephanie Ognier, and Simeon Cavadias*

Laboratoire de Génie des Procédés Plasmas et Traitements de Surfaces-(EA 3492,
Ecole Nationale Supérieure de Chimie de Paris - University Pierre et Marie Curie,
*11 rue Pierre & Marie Curie, 75231 Paris Cedex – France, simeon-cavadias@chimie-paristech.fr

Abstract:
A non-thermal plasma reactor used for soil remediation is simulated with the CFD code COMSOL®. The soil is treated by an electrical discharge produced in air between a high voltage electrode and the ground electrode. It is deposited as a thin layer on the ground electrode which is moving under the HV electrode. The pollutant “immobilized” in the soil reacts with active species, namely ozone which are created in the discharge by electron-molecule (O_2) and diffuses inside the soil. A 1D model is used for the calculation of electron concentration and energy. A 2D convection-diffusion associated with a kinetic model with 4 species (e, O, O_2 and O_3) and 2 reactions allow the calculation of the concentration of active species (O and O_3). Another 2D convection-diffusion model describes the interaction between O_3 and the organic pollutant inside the layer. Calculations show the feasibility of this simulation and the possibility to have more accurate results with use complex kinetic schemes including several species and reactions.

Keywords: electrical discharge, soil remediation, 2D reactor simulation

1. Introduction

A lot of techniques are developed to treat soils polluted by hydrocarbons pollutants such as incineration, thermal treatment, extraction, chemical oxidation, or bioremediation [1]. Some of these techniques are very energy consuming (incineration, thermal treatment…) and often need a subsequent treatment of the generated gases or liquids. Of all the decontamination methods, bioremediation appears to be the least damaging and most environmentally acceptable technique. However, some problems are encountered when dealing with this technique, for example slow degradation kinetics or even stopping of the biological reactions. To solve these issues, the combination of chemical oxidation with ozone and biodegradation appear as a promising way, but this technique suffers from two main drawbacks. Firstly, the energetic cost of ozonation techniques is high. Secondly some organic species present a poor reactivity with the ozone molecule. The issues encountered when treating polluted soils by ozonation could be solved by creating the electrical discharge directly in the contaminated soil [2]. An electrical discharge in air is obtained by imposing a high electric potential between two electrodes. A lot of species are created by the discharge in the inter-electrode gap: electrons, ions, radicals and excited species. The life-time of these species is short (generally below 1 ms) and they recombine rapidly. Therefore, the energetic efficiency could be increased by creating, the oxidant species by the discharge directly inside the soil.

In our process the soil is treated by an electrical discharge produced in air between the high voltage electrode and the ground electrode (fig.1).

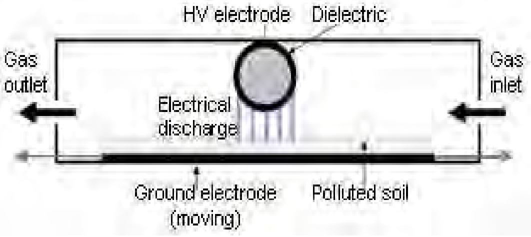

Fig.1: Experimental set-up for soil depollution

A soil polluted by kerosene (74 mg/kg) was treated in a dielectric barrier discharge reactor at atmospheric pressure using air as sweep gas flow. The soil is deposited as a thin layer on the ground electrode which is moved under the high voltage one. The removal percentages varied from 25 to 88% for treatment times ranging from 4 to 12 minutes. During the soil treatment experiments, analyses of the exhaust gas phase were also performed. They showed that CO, CO2, and total hydrocarbons represented less than 8 % of carbon balance, indicating that the transfer of organic contaminants from solid phase to gas phase was negligible. Further analyses of soils showed finally that the decrease of kerosene was accompanied by the formation of new oxygenated organic compounds in the soil in non negligible quantities, indicating that main mechanism could be the soft oxidation of kerosene constituents in the soil matrix. The high voltage electrode (~10 kV and 40kHz) is a rod of stainless steel covered by a glass tube as dielectric. At atmospheric pressure, the discharge is filamentary. It is constituted by numerous tiny luminous filaments which continuously start from the anode, cross the soil material layer and reach the cathode. The simulation of the reactor (fig. 2) is performed in three steps. In the first step is simulated, in 1D configuration, the ionization of oxygen by collisions e-O2 in the discharge region. To this end is resolved the Poisson equation and the equations for conservation of electrons and positive ions.

This leads to the calculation of electrons concentration, during each period (25µs) and the determination of an average electron concentration used in the kinetic model of the second step.

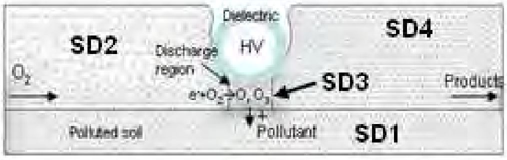

Fig.2: Simulated reactor for plasma polluted soil interaction

Electrons, produced in the discharge zone, then react with oxygen, in a time interval of some nanoseconds to tenths of milliseconds, forming the active species O and O3 that diffuse inside the soil and react with the pollutant. This process is simulated in the second step by using COMSOL®. The flow field above the soil is calculated with ns model. For the calculation of flow field in the polluted soil is used a Brinkman model *chns*. The calculation of electron concentration is performed using the code PLASIMO® in a 1D model. The concentrations of active species were obtained by the convection - diffusion model *chcd* in the second step. Finally the interaction of ozone with the pollutant was calculated with the convection - diffusion model *chcd* in the third step.

2. Modelling of the flow field flow

The 2D model used for the simulation of the non-reactive flow, subdomains, boundaries and mesh are shown in fig. 2. Oxygen enters in the left side of the reactor, passes through the space between the electrode high voltage and the wall of the reactor. Oxygen is used as sweep gas flow. It is introduced at atmospheric pressure and room temperature in the plasma reactor at 1 L.min^{-1}. The 3 mm thick thin of contaminated soil by organic compounds homogeneously sprayed on ground electrode is considered as a porous media with porosity 0.3 and a permeability of 100 Darcy's. The flow in this porous media is calculated using a Brinkman model *chns*.

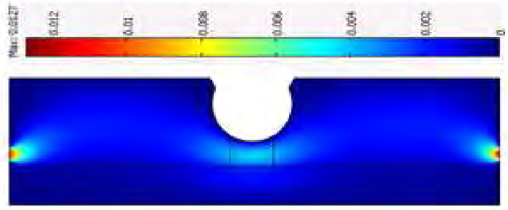

Fig.3 Velocity field in the reactor

The velocity field (fig.3) shows the highest velocity in the interélectrode region. In the bed of contaminated soil the velocity is zero with exception of the space under the electrical discharge region where is low.

3. 1D electron density modelling

The electron density is an important parameter in DBD reactors as electrons are simultaneously reactants and energy carriers, initiate and perform activation, dissociation or ionization reactions at ambient temperature. Their concentration depends on the electrode gap, the nature of the gas or the dielectric, thus their density must be calculated continuously as for the other species (O, O_3). The simulated domain is between the two electrodes with three subdomains: glass dielectric in the HV electrode side, the gas phase and the soil considered as a dielectric. Calculations of electron density and energy, are performed by solving, in a 1D configuration (fig.4), a system of 4 non linear equations, including the equation of Poisson for the electric potential and the 2 equations of conservation for the two species (e^-, and O_2^+) corresponding to the ionization of oxygen $e + O_2 \rightarrow O_2^+ + 2e$ and the equations of electron energy conservation. In our case electrons are created by oxygen ionization reaction only, move under the action of the field and are lost in the two dielectrics. These calculations were performed with the code PLASIMO®[3].

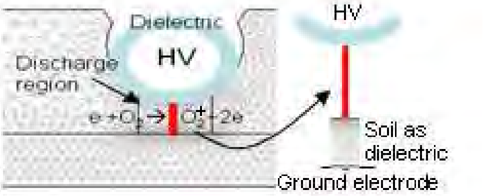

Fig.4:1D simulated domain for the electrical discharge.

A high alternative voltage (40 kHz) of 16 kV peak to peak (U_{pkpk}) is considered. Calculations are performed for several cycles of 25µs (period corresponding to the frequency of 40 kHz).

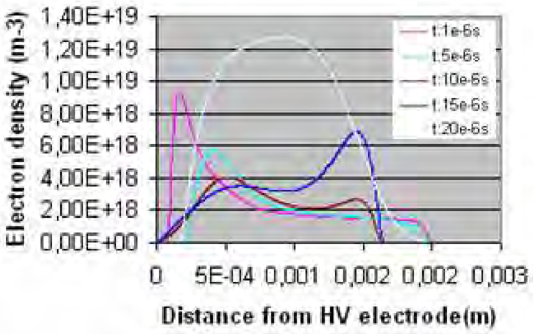

Fig.5: Electron density in the interélectrode distance.

The results (fig.5) show for electron density, a maximum of 1.3e19 m^{-3}. So for the calculations of the production of active species in the reactor an average electron density of 1e19 m^{-3} is considered.

4. 2D model for active species formation

In this model formation of actives species like atomic oxygen (O) is initiated by electron-molecule collision in the discharge region. Then oxygen atoms can react with molecular oxygen to form ozone. Both species can diffuse and react with the pollutant that is immobilized in the fixed bed layer. The kinetic model for the formation of active species includes 4 species (e, O, O_2, O_3) and 3 reactions.

	Chemical Reactions	Rate Constants (cm^3/s)or(cm^6/s)
1	$e+O_2 \rightarrow 2O+e$	1.95e-9
2	$O+ O_2+O_2 \rightarrow O_3+O_2$	6.4e-34*exp(510/300) [4]
3	$O+O_3 \rightarrow 2O_2$	2.5e-8*exp(-2300/300) [4]

The first reaction takes place essentially in the discharge region (fig.4). However due to the diffusion (in x direction) and the mobility (in y direction) there is a none zero concentration in the other domains, so this reaction 1 can also take place. The second reaction ozone formation and the third one (ozone destruction) can take place in all domains.

The concentration field is calculated by using the convection-diffusion *chcd* model. In order to obtain the average electron density of 10^{14} cm^{-3}, calculated previously with the 1D DBD model, a constant production source term of electrons before their sink term due to the e- + O_2 reaction 1, is introduced in the subdomain settings of the discharge region. Molecular oxygen concentration in the inlet is 54 mol/m^{-3}. All calculations in this model where performed in stationary regime *without interaction of active species with the pollutant.*

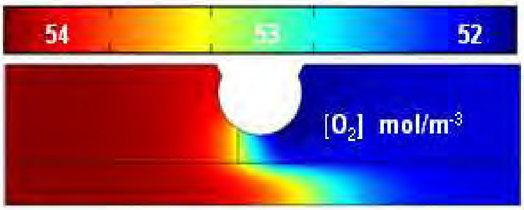

Fig. 6: Concentration field for molecular oxygen

Calculations for molecular (fig.6) oxygen concentration show its consumption in the discharge region. Atomic oxygen is formed in the discharge (fig.7) by electron collisions and then is consumed by the second reaction for ozone production.

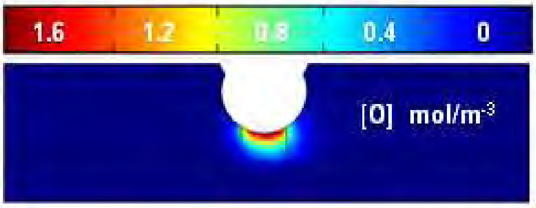

Fig. 7: Concentration field for atomic oxygen

Finally ozone is produced (fig.8) by the second reaction and consumed by the third one.

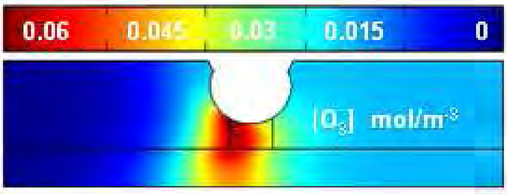

Fig. 8: Concentration field for ozone

As 2 reactions are considered in this model, the results are semi-qualitative. It is possible to obtain more accurate results by adding more species and reactions. However these results allow us to continue with the simulation of the interaction between active species and especially ozone and an organic pollutant absorbed in a porous material.

5. 2D interaction active species-pollutant modelling

For this simulation a second convection-diffusion model (chcd) is introduced for the calculation of the pollutant concentration in the contaminated soil (SD1). In order to "immobilize" this pollutant in this pollutant in the contaminated soil a very low diffusion coefficient (1e-8 m^2/s) is considered in this subdomain. Furthermore in order to prevent the transport of the pollutant in the gas phase the diffusion coefficient introduced in the subdomains SD2, SD3 and SD4 is much lower (1e-10 m^2/s). For the kinetic model are considered 2 species (O_3, pollutant) and just 1 reaction:

pollutant+O_3→products

with k= 1.2e-12 cm^3/molec.s

In order to limit the number of equations to resolve, the products are not taken into consideration. As in the reactor the soil moves from the left to the right under the HV electrode this model should be treated in transient mode. The initial concentration of the pollutant that varies from 1 to 5mol/m^{-3}, could be introduced by two ways, either as uniform concentration in all the subdomain SD1, either as boundary limit concentration in the ground electrode. This last solution provides a gradient along the axis y (fig.9). In the transient solution the time step is 0.1s and the treatment last 10s and are simultaneously resolved all the equations of conservation of species. For the flow field the stationary mode solution is kept.

The results (fig.9) show a decrease of the pollutant concentration below the electrical discharge region. This depletion of the pollutant under the electrode is total after about 4 seconds.

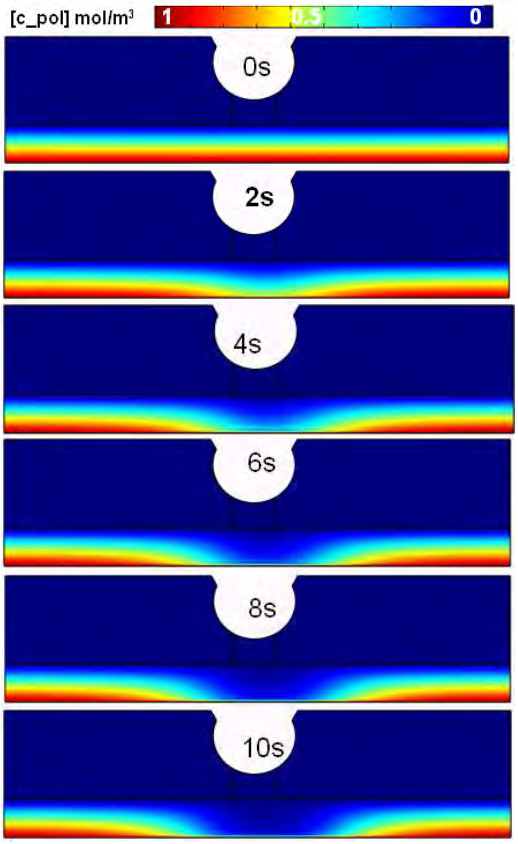

Fig. 9: Concentration of the pollutant in the soil as a function of treatment time.

Taking into account the time treatment and the width of the treated zone it is possible to calculate the velocity of the displacement of the polluted soil for a complete depletion.

This depletion will depend on the thickness of polluted soil, the initial concentration and the concentration of active species that means the electron concentration and the electrical characteristics of the discharge. So these results (calculations) show the feasibility of this simulation. However to go much further it is necessary to take into consideration more species, reactions and parameters.

5. Discussion

In this simulation the process operates at room temperature but in a DBD a part of the energy is dissipated as heat in the discharge region. However as the power induced in the discharge is some tenths of watts and the heat produced increases the temperature of the fixed bed locally of about 50°C. This local increase of temperature may induce the diffusion of the pollutant in the gas phase. The introduction of a heat transfer model is suitable for the simulation this process and can improve the accuracy of the simulation. In this case diffusion coefficient of the pollutant should be temperature dependant. This implies one more equation (of energy) to resolve. The kinetic model for active species formation used in this simulation is simplistic. Instead of oxygen must be used air. Also in this model the products of degradation of the pollutant are not taken into account. Among those, there are oxidized species which remain fixed on the solid, or species which can diffuse into the gas phase.

In this case several species must be added that implies additional equations to resolve. Improvement can be made in the electric model. Indeed, for the calculation of the electron concentration we have considered only the ionization of oxygen but not the attachment or recombination that consume electrons and can change their average. Another important point is the role of electrons inside the bed bed. In this case under the action of external electric field the bed particles are polarized and create an intense local electric field. This can accelerate the electrons that make collisions with molecules within the fixed bed, resulting additional formation of active species. Taking into account all these processes can greatly enhance the accuracy of the global depollution process.

5. Conclusion

A process for depollution of the soil contaminated with kerosene, treated by an electrical discharge, is simulated using COMSOL® code. Calculation of flow field is very accurate. The use of simplistic kinetic model for the formation of active species and their interaction with the pollutant gives semi qualitative results. These results (calculations) show the feasibility of this simulation. Obtaining more accurate and representative results depends on the performance of the computer as it is necessary to use complex kinetic schemes including several species and reactions.

8. References

[1] Pichtel J., Fundamentals of Site Remediation, *For Metal- and Hydrocarbon-Contaminated Soils*, Government Institutes, Rockville, Maryland (2000).

[2] Redolfi, M. Makhloufi, C. Ognier, S. and Cavadias, S.
Oxidation of kerosene components in a soil matrix by a dielectric barrier discharge reactor.
Process Safety and Environmental Protection, Vol: 88, 3, p. 207-213, (2010)

[3] van Dijk J, Peerenboom K, Jimenez M, Mihailova D and van der Mullen J.
The plasma modelling toolkit plasimo
J. Phys. D: Appl. Phys. 42 194012, 2009
http://plasimo.phys.tue.nl/

[4] Hamson R. F. and Garvin D. (eds)
Chemical, Kinetic and Photochemical Data for Modelling Atmospheric Chemistry.
NBSIR 74-430 (Washington DC: NBS) (1975)