Numerical study of Electrical double layer development: Analysis of the charge genesis.

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Abstract. This work presents a numerical simulation of the Electric Double Layer (EDL) development process at a solid/liquid interface for adsorption and corrosion models. First, the study is conducted for static EDL development (without liquid flow) until it reaches a static equilibrium. Afterwards, the EDL is perturbed by a laminar liquid flow leading to flow electrification phenomena (dynamic study). The charge conservation equations of the liquid species have been implemented in an industrial code. A parametric study was performed to consider different chemical reaction scenarios and different models.

1. Introduction
In dielectric liquids, impurities are assumed to be at the origin of the Electric Double Layer (EDL) present at the solid-liquid interface. Due to a physicochemical phenomenon, which is still not well understood, these impurities react with the solid to electrically polarize the interface. One type of charge is accumulated in the solid surface if this one is a dielectric while the opposite charge is distributed in the liquid. Different models, adsorption or corrosion models, had been proposed to help understanding the phenomenon. Different numeric simulations were realized according to each of these two models [1-2]. Unfortunately, all the different simulations have not permitted to confront directly these two models. Using finite volume CFD tool Code-Saturne®, we have developed software that allows simulation, from the same entry data, of both the corrosion and the adsorption models. This paper is focused on a comparative study between the adsorption and the corrosion models on the dynamics of the EDL development versus time without liquid flow (static development) and with flow (dynamic development). The input data will be extracted from literature.

2. Physicochemical Adsorption and Corrosion Models
The two models suppose that in the liquid charge impurities are dissociated in two ionic species, positive and negative. Assuming that only one type of neutral impurity $A_L B_L$ is present in the liquid, the chemical reaction is given according to equation (1):

$$A_L B_L \underset{k_r^L}{\overset{k_d^L}{\rightleftharpoons}} A_L^+ + B_L^-$$

(1)

where k_d^L and k_r^L are the kinetic constants of the dissociation reaction. Initially, the liquid is electrically neutral when the contact with the solid medium occurs. Thus, liquid ionic species could

react with the solid according to the adsorption or corrosion models (figure 1). The two schemes suppose that the solid is polarized negatively and the liquid positively. This is the major situation observed in experiments.
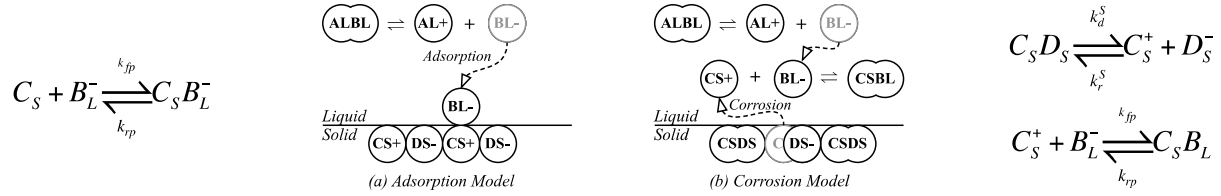

Figure 1. Physicochemical mechanism occurring at the solid-liquid interface for adsorption and corrosion models

All the chemical species (positive, negative and neutral) are transported in the liquid by diffusion, migration and convection (when the liquid flow is induced). The flux transport equations are coupled to the Poisson's equation and the Navier-Stokes equation. To compare the models of adsorption and corrosion, all equations were nondimensionalized according to the Buckingham's theorem. All the dimensionless values were marked with "*" symbol. The simulations carried out with these two models are analysed and compared in this work according to the dimensionless distance z* (z*=z/a with a is half-height) and dimensionless time t* (t*=t/τ_c with τ_c is the Maxwell). Simulations are decomposed into two steps:

• **Step 1 -Static development of the EDL:** without fluid motion, the system reaches an equilibrium depending on the different chemical kinetic constants. When the equilibrium is reached, the electrical current through the interface becomes negligible.

• **Step 2 - Dynamic development of the EDL:** from this static equilibrium, a Poiseuille flow is applied at the entry and the impact of the flow is studied.

The initial concentration of positive and negative ions n_0, (A_L^+, B_L^-) is estimated from the liquid conductivity ($5 \times 10^{-12} S.m^{-1}$). Thus, the different chemical reactions of ionized impurity in the liquid can be determined considering the space charge (assumed to be initially zero). The main difference between the two models remains in the fact that the corrosion model is based on three successive different chemical reactions while the adsorption model is only based on two reactions. Thus, the initial species concentrations of the solid and liquid, their properties, the chemical kinetics constants are assumed equal for the simulation in both corrosion and adsorption models; the initial data values are summarized in table 1. For both models, the solid reaction is specific. It consists of an adsorption reaction for the adsorption model ($C_S B_L^-$) while it is a corroding reaction for the corrosion model ($C_S D_S + C_S^- B_L^-$). To analyse the results and favour the comparison, we assumed that the chemical reaction between $C_S B_L^-$ and $C_S^- B_L^-$ are equal (k_{fp}, k_{rp}). Solid species are supposed not to limit all the different reactions. Other kinetics constants were chosen according to Touchard's approach [3].

3. Numerical results

3.1. Comparison between adsorption and corrosion models at the Static Equilibrium.

In the goal to compare the dynamics of the different simulation models, we imposed for both simulations the same space charge density at the wall for a fully developed EDL (ρ_{wd}). The major entry data are taken equal for the two models. Then the kinetic constants of the dissociation reaction of the wall corrosion k_d^S, is chosen to reach a value of ρ_{wd} equal to the value simulated with the adsorption model. Therefore dimensionless space charge density ρ_{wd}^* will be equal to 1 in both models. Figure 2 shows the dimensionless space charge distribution in the liquid for a fully developed EDL. Adsorption and corrosion simulations are well superimposed. A small distinction is observed away from the interface. The corrosion model admits the presence of two kinds of impurities and,

unlike the adsorption model. It seems that this difference leads to a different distribution of space charge density between both models. Another important difference is observed on figure 3, the dynamics time evolution of the space charge near the interface in the liquid (ρ_{wd}) is plotted. The corrosion model seems about 50% faster. As the corrosion model consists of more successive events, three chemical reactions instead of two in the adsorption model, it could be expected that the equilibrium state would be reached within a longer period of time. However, the opposite effect is observed. The presence of an additional positive charge, C_S^+, in supplement to the positive ions A_L^+, in the liquid, leads to a faster development of the space charge density in the liquid.

Table 1. Physical constants; Initial values of reaction rates.

Constant	Symbol	Value
Initial ions concentration	n_0	$1.582 \times 10^{-16} \, molecule.m^{-3}$
Initial neutral ions concentration	n_{0i}	$1.448 \times 10^{-18} \, molecule.m^{-3}$
Recombination rate in the liquid	k_d^L	$1.65 \times 10^{-17} \, m^3 s^{-1}$
Dissociation rate in the liquid	k_r^L	$2.85 \times 10^{-3} \, s^{-1}$
Recombination rate in the solid	$k_d^{L'}$	$9.05 \times 10^{-19} \, m^3 s^{-1}$
Dissociation rate in the solid	$k_r^{L'}$	$1.57 \times 10^{-4} \, s^{-1}$

Table 2. Chemical kinetic constants for Adsorption and Corrosion models

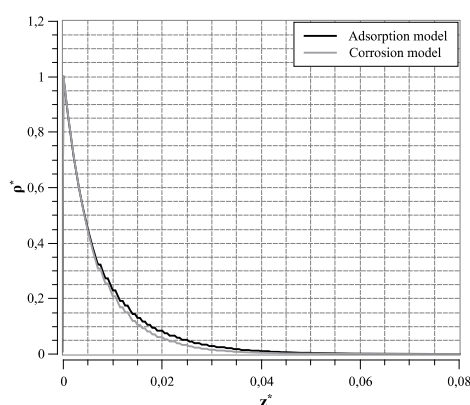| Constant	Adsorption model		Corrosion model	
	Liquid	Solid (interface)	Liquid	Solid (interface)
k_{fp}	No reaction	$1.28 \times 10^{-26} \, m^3 s^{-1}$	$2.324 \times 10^{-25} \, m^3 s^{-1}$	$1.28 \times 10^{-26} \, m^3 s^{-1}$
k_{rp}	No reaction	$1.28 \times 10^{-3} \, s^{-1}$	$2.324 \times 10^{-2} \, s^{-1}$	$1.28 \times 10^{-3} \, s^{-1}$
k_d^S	No reaction	No reaction	No reaction	$4.25 \times 10^{-11} \, s^{-1}$
k_r^S	No reaction	No reaction	No reaction	$2.81 \times 10^{-18} \, m^3 s^{-1}$

Figure 2. Dimensionless space charge density distribution in the liquid from the interface to the liquid bulk direction for the adsorption and corrosion simulations
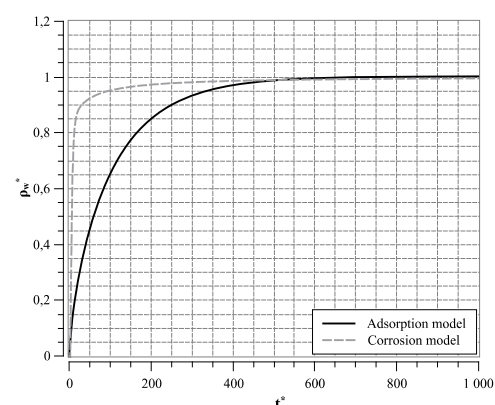
Figure 3. Dimensionless space charge density at the interface versus dimensionless time for the adsorption and corrosion simulations

3.2. Comparison between adsorption and corrosion models at the Dynamic Equilibrium.

Regardless of corrosion or adsorption models, the streaming current shows the same evolution at the different flow velocities (figure 4). However, at the beginning of the flow, the adsorption model leads to a peak current magnitude higher than corrosion model. A reverse behaviour is observed after a few seconds of flow. When the EDL is still fully developed at the exit of the duct, which is the case at the first few seconds of the flow or at low velocity (0.1 m.s^{-1}), the streaming current simulated with the adsorption model is usually higher than the one simulated with the corrosion model. When the EDL is partially developed at the exit of the duct, the analysis of the current simulation is quite different. It is important to consider the contact time between the solid and liquid relatively to the time required for the formation of the EDL. Static analyses have clearly shown that the dynamics of the EDL formation for the corrosion model is faster than for the adsorption model. For a given liquid flow velocity and solid length, the EDL space charge distribution developed by corrosion model is higher compared to the one developed by adsorption model and therefore the streaming current.
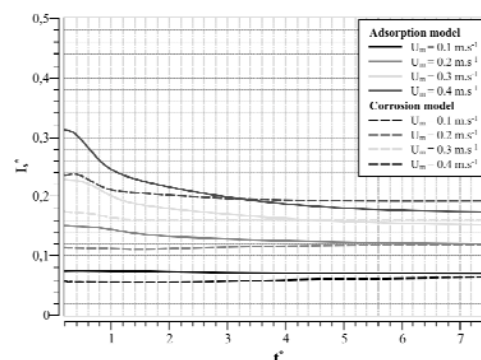

Figure 4. Dimensionless streaming current versus non-dimensional time for the adsorption and corrosion simulations

4. Conclusion

Two scenarios of the interface chemical reactions were simulated. All the numerical simulations are comparable to experimental results for the adsorption and corrosion models. What is notable is the fact that the electrical double layer development, and thus the streaming current, is dependent of the model used. For our entry data, the corrosion model was faster than the adsorption model. Nevertheless, a parametric study is needed to be able to understand the weight of each term and their dynamics. The comparative study is particularly interesting as, based on the experimental results and this numerical simulation, it would be possible to identify the chemical phenomena that control the electrical double layer.

5. Acknowledgments

6. References

[1]   El_Adawy, Paillat T, Bertrand Y, Moreau O and Touchard G 2010 Physicochemical analysis at the interface between conductive solid and dielectric liquid for flow electrification phenomenon *IEEE Trans. Indus. Appl.* **46**(4) 1593-1600

[2]   Cabaleiro J M, Paillat T, Moreau O and Touchard G 2009 Modeling of static development and dynamic behaviour of the electrical double layer at oil-pressboard interface *Electrostatics Joint Conference, USA*

[3]   Touchard G, Patzek W and Radke C J 1996 A physicochemical explanation for flow electrification in low-conductivity liquids in contact with a corroding wall *IEEE Trans. Indus. App.* **32**(5) 1051-1057