

Project Proposal

**Development of a time dependant numerical model
for the quantification of AC corrosion phenomena**

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Executive Summary

1. Introduction

The phenomenon "a.c. corrosion" was investigated very detailed since the observation of the first corrosion damages induced by a.c. corrosion on cathodically protected pipelines in the year 1988 [1, 2]. Soon the a.c. current density was identified as a critical parameter [3-5]. Later the contribution of the d.c. current density to the corrosion rate was reported [7-10]. However, a profound understanding of the detailed mechanism was lacking for years. Only in recent investigations it was possible to develop a model capable of explaining the empirically obtained experimental data [11].

Based on this concept, the a.c. corrosion rate can be decreased to insignificantly low values, if the d.c. current density is limited. Preferably the value should be below 1 A/m^2 . This should be achievable if the on potential is in the range of -1.2 V CSE and the off potential is below -0.85 V CSE [11]. Under these conditions, the driving force for d.c. current flow is minimized, resulting in minimal possible d.c. current densities.

2. Problem

While the experimental observation can readily be explained by the qualitative model concepts its full potential can currently not yet exploited. Especially the consequences of the threshold values determined in laboratory investigations on the protection of a cathodically protected pipeline are not understood.

In order to assess if the AC corrosion model that results from experimental data is valid, a sound mathematical model that describes all phenomena that have been observed is required. In a second step, advanced numerical simulation tools that can solve this complex time-dependant model are required.

Elsyca has developed advanced numerical modelling tools for simulating local electrochemical processes in the millimeter range [12-15], d.c. current distribution on entire pipelines [16-17] with zoom options on local defects [18], and a.c. interference calculation tools [19-20]. The simulation software PIRoDE (Parameter Identification on a Rotating Disk Electrode) as describes in reference [12-15] has been developed to identify kinetic and mass transfer parameters for complex multi-ion electrolytes from steady-state and time-dependant experimental data. In the past however, PIRoDE has been used mainly for electroplating applications.

The aim of this fundamental research project is to combine the electrochemical modeling expertise of Elsyca with the field and experimental know-how of SGK in order to develop and validate a time dependant numerical model for the quantification of AC corrosion phenomena.

3. Project

The project is based on experimental work and the development of a numerical model and simulation tool that quantifies the physico-chemical processes at the steel/soil interface. Typically the work will proceed as follows:

1. Determination of experimental data as input for the simulation
2. Modification of the existing PIRoDE software towards AC corrosion
3. Experimental validation of the new software

The experimental work will be performed by SGK, while the extension of the PIRoDE software towards the goals of this project, including all simulation work will be done by Elsyca.

The state-of-art understanding of the physico-chemical processes taking place at a steel/soil interface needs to be translated in a coherent so-called Multi Ion Transport and Reaction model:

- Transport of ions and neutral species towards/away from the steel/soil interface (including OH^- , determining the local pH);
- Electrode reactions (iron/alloy metal oxidation, oxygen reduction, water reduction);
- Capacitive effect of the steel/soil interface.

The iron oxidation is to be considered as a 2 step process ($\text{Fe} \rightarrow \text{Fe II}$, $\text{Fe II} \rightarrow \text{Fe III}$), whereby the Fe II ions can form an oxide layer or other adsorbed state (corrosion product) on the steel surface and create a reversible redox couple Fe II/Fe III. Note that both the capacitive effect of the steel/soil interface and the Fe II/Fe III oxide redox system can accumulate charge during AC cycles without actually causing any corrosion. The transport of ions will intrinsically describe any change of spread resistance around the defect, whereas the electrode reaction speed (in case of iron oxidation) is directly related to the metal loss.

This model is to be translated into the proper mathematical conservation equations (mass and charge).

The resulting set of equations is to be **solved in real time** (so not in the frequency domain!), for any possible combined DC / AC on-potential signal. This will be done as said by adapting the PIRoDE software developed by Elsyca in the past is extended and adapted to enable simulating this DC / AC corrosion model.

The parameters of this model (reaction kinetics constants, ion diffusion constants and bulk concentrations, capacity value of steel / soil interface, ...) have to be defined based on comparison to and reverse engineering from well chosen laboratory experiments. A Design of Experiment (DoE) defines the complete set of experiments as required to fine tune all model parameters based on comparison the experimental results (observed transient current response, metal loss, ..).

Next, the validity of the DC / AC corrosion model is tested preliminary by running the model for some DC / AC on-potential signals that correspond to the signals used for some of the lab experiments, and by comparing the current response signal and metal loss.

The tasks involved in this work package are the following:

- Task 1: physico-chemical AC corrosion model building
- Task 2: extension of PIRoDE for enabling simulation of the AC corrosion model
- Task 3: definition of a DoE for the laboratory experiments
- Task 4: laboratory experiments
- Task 5: model parameter fitting
- Task 6: model validation
- Task 7: reporting

The outcome of this project will be a time dependant numerical model for the quantification of AC corrosion phenomena that is validated with well defined and controlled lab measurements. This will be a major breakthrough in the fundamental understanding of AC corrosion phenomena and will open the door for a more applied research project.

4. Consortium partners

The following European gas operators are proposed to be the members of the initial consortium: Gasunie (NL), Gaz de France (FR), E.On (GE) and Fluxys (BE).

The logo for Gasunie, featuring the word "gasunie" in a lowercase, grey, sans-serif font.The logos for E.ON and Ruhrgas. E.ON is in red, lowercase, italicized font. Ruhrgas is in red, uppercase, sans-serif font, separated from E.ON by a vertical line.The logo for Gaz de France, featuring a stylized blue and green flame icon above the text "Gaz de France" in green, lowercase, sans-serif font.The logo for Fluxys, featuring the word "FLUXYS" in bold, uppercase, sans-serif font, with a stylized orange and grey flame icon to the right. Below it is the tagline "EXCELLENCE IN GAS TRANSPORT" in small, uppercase, sans-serif font.

4. Budget and time schedule

The total budget for this research project is 120,000 EUR and will be executed by SGK and Elsyca in a time period of 7 months. Each partner will contribute to an amount of 30,000 EUR and a description of the milestones and budget allocation is given in the following table.

The start date of the project is July 1st, 2009.

Tasks	Milestone	Timing	Budget
1-2	Physico-chemical model parameters report to the consortium partners	2 months	30,000 EUR
3-4-5	Meeting of consortium partners for DoE presentation of the laboratory experiments	3 months	60,000 EUR
6-7	Report on model validation and application extensions	2 months	30,000 EUR

5. References

1. G. Heim, G. Peez, "Wechselstrombeeinflussung einer kathodisch geschützten Erdgashochdruckleitung", *3R International* **27**, 345 (1988).
2. B. Meier, "Kontrollarbeiten an der Erdgasleitung Rhonetal", *GWA* 69, 193 (1988).
3. M. Büchler, C.-V. Voûte, H.-G. Schöneich, "Evaluation of the effect of cathodic protection levels on the a.c. corrosion on pipelines", *Eurocorr Conference Proceedings*, (2007).
4. M. Büchler, C.-H. Voûte, H.-G. Schöneich, "Diskussion des Wechselstromkorrosionsmechanismus auf kathodisch geschützten Leitungen: Die Auswirkung des kathodischen Schutzniveaus", *3R International*, 344 (2008).
5. G. Heim, G. Peez, "Wechselstrombeeinflussung von erdverlegten kathodisch geschützten Erdgas-Hochdruckleitungen", *gwf*, 133 (1992).
6. D. Funk, W. Prinz, H. G. Schöneich, "Untersuchungen zur Wechselstromkorrosion an kathodisch geschützten Leitungen", *3R International*, 31 (1992).
7. M. Büchler, C.-H. Voûte, F. Stalder, "Characteristics of potential measurements in the field of ac corrosion", in *CEOCOR 6th international Congress*, CEOCOR, c/o C.I.B.E., Brussels, Belgium, (2003).
8. M. Büchler, F. Stalder, H.-G. Schöneich, "A new electrochemical method for the detection of ac-corrosion", in *CEOCOR 7th international Congress*, . Editor. CEOCOR, c/o C.I.B.E., Brussels, Belgium, (2004).

9. M. Büchler, F. Stalder, H.-G. Schöneich, "Eine neue elektrochemische Methode für die Ermittlung von Wechselstromkorrosion", *3R International* 44, 396 (2005).
10. M. Büchler, "Wechselstromkorrosion an kathodisch geschützten Rohrleitungen", *GWA*, 617 (2006).
11. M. Büchler, C.-H. Voûte, H.-G. Schöneich, "Effect of cathodic protection levels and defect geometry on the a.c. corrosion on pipelines", in *CEOCOR international Congress*, . Editor. CEOCOR, c/o C.I.B.E., Brussels, Belgium, (2007).
12. L. Bortels, B. Van den Bossche, J. Deconinck, S. Vandeputte, A. Hubin, "Analytical solution for the steady-state diffusion and migration involving multiple reacting ions. Application to the identification of Butler-Volmer kinetic parameters for the ferri/ferrocyanide redox couple", *J. Electroanal. Chem.*, 429 (1997) 139-155.
13. B. Van den Bossche, L. Bortels, J. Deconinck, S. Vandeputte, A. Hubin, "Quasi-one-dimensional steady-state analysis of multi-ion electrochemical systems at a rotating disc electrode controlled by diffusion, migration, convection and homogeneous reactions", *J. Electroanal. Chem.*, 397 (1995) 35-44.
14. C. Dan, B. Van den Bossche, Leslie Bortels, Gert Nelissen, Johan Deconinck, "Numerical simulation of transient current responses in diluted electrochemical ionic systems", *Journal of Electroanalytical Chemistry* 505 (2001) 12–23.
15. B. Van den Bossche, G. Floridor, J. Deconinck, P. Van Den Winkel, A. Hubin, "Steady-state and pulsed current multi-ion simulations for a thallium electrodeposition process", *Journal of Electroanalytical Chemistry* 531 (2002) 61-70.
16. L. Bortels, J. Deconinck, "Numerical Simulation of the Cathodic Protection of Pipeline Networks under Various Stray Current Interferences", Chapter in book "Modelling of Cathodic Protection Systems", WIT Press.
17. M. Purcar, B. Van den Bossche, L. Bortels, J. Deconinck, P. Wesselius, "Numerical 3D Simulation of a CP system for a Buried Pipe Segment Surrounded by a Load Relieving U-shaped Vault", *Corrosion* 59 (2003), pp. 1019–1028.
18. L. Bortels, A. Dorochenko, B. Van den Bossche, G. Weyns, J. Deconinck, "Three-Dimensional Boundary Element Method and Finite Element Method Simulations applied to Stray Current Interference Problems. A Unique Coupling Mechanism that takes the best of both Methods", *Corrosion* 63 (2007) , pp 561-576.
19. L. Bortels, L., J. Deconinck, C. Munteanu, V. Topa, "A general applicable model for AC predictive and mitigation techniques for pipeline networks influenced by HV power lines", *IEEE Transactions on Power Delivery*, Volume 21, Issue 1, Jan. 2006.
20. L. Bortels, "Manage pipeline integrity by predicting and mitigating HVAC interference", *ICC*, Las Vegas, Nevada, 2008.