Development of an Advanced Electrochemical Sensor for Corrosion and Scaling Monitoring in Geothermal Power Plants

L. Freire, J. Sánchez, R. Castro and A. Fernández

AIMEN Technology Center, Relva 27A, 36410 O Porriño (Spain)

lorena.freire@aimen.es, julio.sanchez@aimen.es, ruben.castro@aimen.es, afernandez@aimen.es

Keywords: corrosion monitoring, impedance spectroscopy, electrochemistry, geothermal power plant, GECO Project, geothermal emission control

ABSTRACT

Corrosion and scaling are the major issues in the exploitation of geothermal sources. Geothermal fluids are very complex mixtures consisting of dissolved gases and high salinity solutions, which creates very aggressive environments. This aggressiveness is primarily due to the presence of high concentrations of carbon dioxide (CO_2), hydrogen sulfide (H_2S), chlorides and other chemical species in lower concentrations. Besides, the high temperature of the geothermal fluids increases corrosion rates promoting failures related to stress and fatigue corrosion. On the other hand, reinjection of cooled brine exiting the heat-exchanger favors corrosion and scaling onset, since the chemicals dissolved in geothermal waters may tend to precipitate promoting calcite, sulphate and/or silicate depositions on the casing. Corrosion and scaling phenomena are difficult to detect visually or monitor continuously. Standard techniques based on pH, temperature and pressure measurements, chemistry composition and fluid physical properties are habitually applied as indirect methods for corrosion rate control. Other traditional techniques such as mass loss probes or electrical resistance measurements have been introduced more recently for corrosion data registration. These methods, however, lack of enough robustness for accurate and reliable measuring and evaluating corrosion behavior of materials employed in geothermal systems. In this scenario, a novel system is proposed for online corrosion monitoring of materials due to the corrosive attack of geothermal fluids. The corrosion rate information early obtained will allow prediction of failures in the critical units of the plant through the correlation of process events to corrosion evolution. Thus, in the Geothermal Research Control (GECO) project, funded by the EU through the H2020, a dedicated electrochemical-based test system will be designed and developed for on-line and continuous monitoring of the corrosion/scaling rate of different materials exposed to the real plant conditions at different locations. This system will use non-standard methods based on Electrochemical Impedance Spectroscopy (EIS) for onsite and on-line monitoring of corrosion and scaling degradation. With this instrument, the corrosion of the inner side of the casing and geothermal pipes will be followed in real time in three demonstration plants sited in Iceland and Germany. The analysis of the impedance spectra by equivalent circuits can determine the contribution of each stage affecting to the corrosion process providing useful information about the corrosion mechanisms and the scaling growth.

1. INTRODUCTION

Geothermal power is cost effective, reliable, sustainable and environmentally friendly and UE recognize geothermal energy's essential role in the European energy transition towards net-zero greenhouse gas emissions in 2050. Recent estimates indicate that the global production capacity for geothermal electricity is at about 14GW (installed capacity in 2018) and is expected to rise to just over 17GW by 2023.

The economic feasibility of geothermal installations relies on continuous operation of the geothermal loop. However, exploitation of these power plants is usually accompanied by corrosion damages and formation of scale deposits in the pipelines and power equipment, leading to the efficiency reduction.

The overall economic losses connected with the formation of deposits and corrosion of metal at the plants comprise the costs for measures taken to remove the consequences and prevent the occurrence of the above-mentioned problems and the costs connected with underproduction of electricity due to failures and disconnection of equipment, forced outages, and degraded efficiency of the power station as a whole. These damages are caused by the geothermal fluids chemical interactions with the metallic surfaces. The scaling that accumulates on the inner surfaces of tubes and in heat exchangers causes an increase in the pressure losses within the primary loop of the geothermal plant and thus results in lower heat exchange capacity. This in turn requires an increase in pump energy consumption to pump around the brine and ultimately result in a loss of net power output. To restore the original conditions, the scale layers must be scoured off from the tubes which supposes a time-consuming process, with considerable down-time periods.

In this scenario, corrosion resistant components made of titanium alloy and high-alloyed stainless steels are commonly employed for dealing with these problems. However, if inexpensive carbon steel or low alloying stainless steel components could be used coated or non-coated, this would improve the power plant's economic factors by generating a considerable reduction in capital investment. Moreover, if the system could be monitored to know the material condition at real time, a decrease in the costs of operations and maintenance through optimized maintenance schedules would result. For new built plants this is an attractive option, but also existing geothermal plants can benefit.

The goal of the GECO project (https://geco-h2020.eu/) is to advance the ability to provide cleaner and cost-effective non-carbon emitting energy across EU and the world. The aims of the project include a detailed and consistent monitoring program, geothermal analysis and comprehensive modelling that will allow to characterize the reactive and consequences of fluid flow in diverse field demo sites located in Iceland, Italy and Germany.

Freire and Sánchez et al.

As the laboratory testing cannot completely mimic all the complex processes that occur in real operation conditions, a detailed demonstration and monitoring development for evaluating the materials resistance at each demo site will be elaborated. Each site-specific plan will include tracer monitoring of the chemistry of fluids in the injection and monitoring wells and GECO will develop strategies to monitor possible corrosion of infrastructure like casing pipes due to injection of acidified brines. The monitoring plan will also include possible leakage effects during demonstration.

An innovative monitoring probe is introduced to be installed in the geothermal piping system for on-site and on-line corrosion monitoring using Electrochemical Impedance Spectroscopy (EIS) to determine the corrosion rate and the scaling degree of pipes under realistic circumstances. Two types of corrosion and scaling monitoring systems based on EIS will be designed and developed by AIMEN for testing in Iceland site (Hellisheidi and Nesjavellir) and Germany site (Bochum MULE). This involves designing two different cell configurations based on 2 and 3 electrodes for evaluating the corrosion resistance of selected materials and the identification of corrosion mechanisms, corrosion rate and scaling formation occurring in the internal wall of the well casing. Structural and electrical design of these corrosion probes will be realized together with the selection of materials and components to construct the monitoring systems according the specific geothermal characteristics at each site. The test will also allow the comparison between the behavior of different materials combinations under the exposure conditions and to establish a ranking of materials from the most resistant to the least.

This work focus on the preliminary design of the corrosion monitoring systems to be applied in the frame of GECO project.

2. EXPERIMENTAL

The corrosion monitoring systems provided by AIMEN are based on the principles of a conventional 3/2-electrode-configuration cell for electrochemical measurements. EIS will be performed on selected materials and the probe will respond in real time to changes in the corrosion rate of the materials exposed in the geothermal installation. A detailed description of the system design and operation will be presented in the following sections.

2.1 Design requirements

For the design of the electrochemical probe, the following requirements should be accomplished:

- 2/3-electrode cell: The system requires two or three electrodes: a reference electrode, a counter-electrode (these could be short-circuited to obtain more accurate measurements) and a working electrode (WE). This configuration is selected as optimum to perform reliable EIS measurements. Thus, the system will be composed by:
    - Working electrodes (WE): selected materials on which the electrochemical phenomena occur.
    - Counter-electrode or auxiliary electrode: it is a distributor of the external circuit current through the cell.
    - Reference electrode (RE): it serves as a reference to know the working potential because it is stable over time.
- Multi-material: Different combinations of coating/metals will be tested; therefore, it is necessary a probe incorporating several materials to be studied under the same conditions. This aspect is of paramount importance to establish a ranking of materials performance. Moreover, an insulating material must be selected to electrically isolate the electrodes.
- Dismountable: Materials need to be easily dismantled once the testing campaign has been completed. The materials will be analyzed by conventional characterization techniques after the exposure time, thus adhesives or any compound that could damage or react with the materials are not allowed since it would affect gravimetric measurements and visual inspection.
- Easy installation: The whole system (the probe and the data acquisition system) should be simple to install to avoid disruptions in the plant operation.
- Autonomous: Sensor operation should be unassisted since there are no personnel available at the plant to configure or collect data during its continuous operation. The measurements must be periodically scheduled and transmitted through wireless technology to an online server to be interpreted and analyzed by AIMEN.
- Working conditions: the design must withstand the harsh working conditions of the installation area and the geothermal fluid chemistry. These parameters are summarized in the following table:

Table 1. Conditions found in the demo sites

	Pressure	Temperature	Flow
Iceland site	8 bar	20 °C - 80 °C	60 L/s
Germany site	20 bar	13 °C	400 L/s

Based on those specified requirements, a conceptual design of the complete system is firstly made, including both the sensor geometry and the electrodes distribution, and the electronics for data acquisition, processing and transmission.

A cylindrical body, divided in different segments simulating the pipe sections, with an internal diameter equal to the piping diameter is proposed. Using these dimensions, the fluid will pass through the installed probe without any load loss due to section changes. The segments, in form of rings, would be manufactured with the previous selected combinations coating/substrate materials, on which the electrochemical measurements will be performed to determine the corrosion rate under real conditions. These sections will form the WE of the electrochemical cells.

Taking as reference the configuration of a conventional three-electrode electrochemical cell, on both sides of the WE are distributed two CE with the same geometry and a RE. This disposition was selected to obtain a better distribution of the electric field over the WE.

These rings should be separated by an insulating material that has to withstand the operating conditions promoting a tight seal of the assembly. After manufacturing, the definitive monitoring probe should be tested at laboratory scale to check its behavior under high-pressure and high-temperature conditions to guarantee its integrity prior installation. Likewise, preliminary electrochemical tests were realized to validate the proper operation of the electrodes distribution.

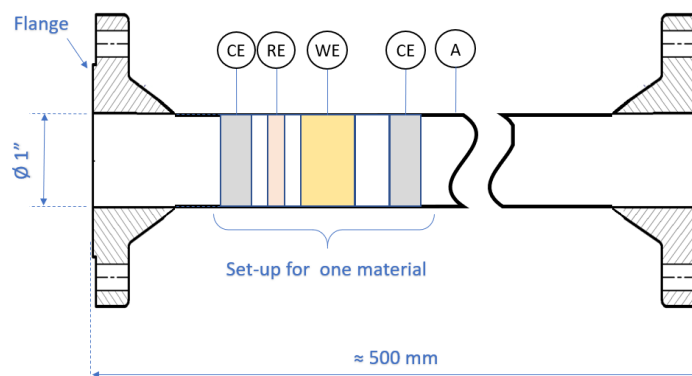An outline of the described preliminary design is shown in Figure 1.

Figure 1. Conceptual design of the corrosion monitoring probe for one material

Thus, the whole probe would be composed by several electrochemical cells (one for each selected materials combinations) placed sequentially and connected independently for being electrochemically assessed. All this set will be linked to the rest of the piping system by coupling flanges connected to a pipe test section. This testing section should facilitate the installation of the monitoring system in the geothermal plant without affecting the operation. The electrical connections of the electrodes will be taken to the outside part of the probe where a control unit equipped with a potentiostat will be installed. Moreover, to measure the cells individually, a multiplexer should be introduced.

The measurement procedure will be controlled by a specific software (developed in AIMEN) executed remotely on a PC. These measurements will be transmitted through a 3G modem and supervised periodically from AIMEN. A scheme of the exposed system is shown in Figure 2.
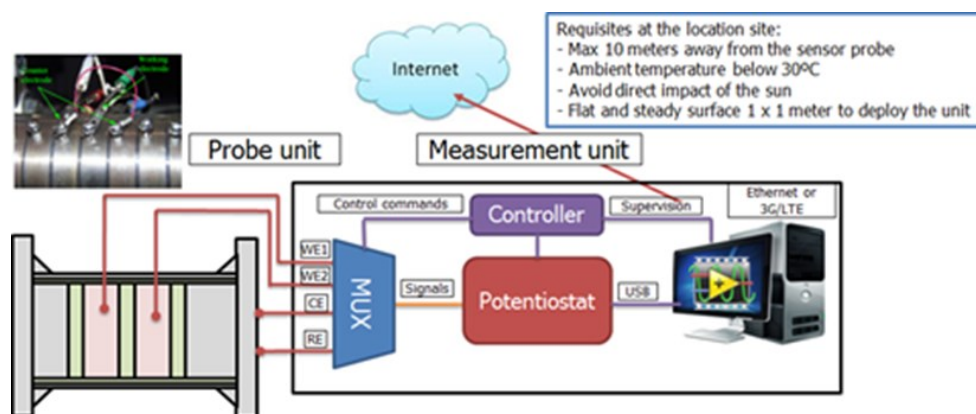

Figure 2. Scheme of the whole corrosion monitoring system equipment

2.2 Corrosion measurements. Electrochemical impedance Spectroscopy (EIS)

The main innovation of the corrosion monitoring system is related with the continuous updating of the corrosion/degradation state of the exposed materials in real time by using EIS measurements.

Electrochemical Impedance Spectroscopy is a sophisticated electrochemical technique extensively used in laboratory testing of protective coatings or materials corrosion performance (Hack et al., 1991; Waters et al., 2010). EIS measurements are also being made in the field on materials in service in different industrial environments. In the field, EIS is a method to monitor the coating/material condition, rate of deterioration, remaining life, etc. (Shreepathi et al., 2011; Calderón-Gutiérrez et al., 2014), information that is valuable in planning maintenance programs.

EIS is a non-destructive technique and so can provide time-dependent quantitative information about the electrode processes and complex interfaces and extract characteristics of materials including high resistance materials (paintings, oxide coatings, etc.). ISO 16773:2016 gives the guidelines for optimizing the collection of EIS data with focus on high impedance systems. The standard deals with instrumental setup, data validation, performing EIS measurement and experimental results, but does not give guidelines for data interpretation.

Freire and Sánchez et al.

EIS method consists in measuring the response of an electrode to a sinusoidal potential modulation at different frequencies. At low frequency range, the system will remain excited for a long time, exciting and relaxing all the partial steps involved in the process, including the slower ones. On the contrary, as the frequency increases, only response from the faster process (having short relaxation time) will be observed. Having this in mind and considering that ion migration process through the electrolyte is a fast process, they will be visible in the high frequency range, providing an estimation of the conductivity of the medium (> 10kHz). On the other hand, the corrosion processes of the material, involving oxidation-reduction reactions, are slower processes that will be distinguishable in the lower frequency range (1kHz-1mHz). Thus, it is essential to define the frequency range to be explored so that all the processes involved can be studied.

The main advantage of EIS lies in its high sensitivity, detecting changes in the material/coating long before any visible damage occurs.

One popular format for evaluating EIS data, consists of plotting the imaginary impedance component (Zim) against the real impedance component (ZRe) at each excitation frequency. This is called the Nyquist plot. Further spectra analysis allows formulation of a hypothesis on the electrical behaviour of the system and establishment of an equivalent circuit model. EIS data is commonly analysed by fitting it to an equivalent electrical circuit model consisting of passive elements that do not generate current or potential such as resistors, capacitors and inductors. The different impedance parameters involved in the selected EIS model were obtained by a regression procedure based on a simplex strategy.

Literature proposes different models of equivalent circuits to interpret the impedance data (Orazem et al., 2008, Freire et al., 2010; Freire et al., 2011) however, to be useful, the elements in the model should have a physical meaning in the electrochemistry of the system. Thus, this technique is relatively easy to apply, but the data extracted from it are not, in most cases, directly interpretable, and require a deep prior knowledge of the real system.

As a simpler way to assess the protective character of the coatings or the corrosion resistance of the materials, the impedance modulus (|Z|) at low frequencies, as the polarization resistance (Rp), is employed as a quantitative parameter to determine materials corrosion performance. Rp is the transition resistance between the electrodes and the electrolyte and can be used to compare the corrosion resistance of different systems exposed under the same conditions. There is a good linear relationship between average corrosion current and the polarization resistance, therefore, higher Rp implies higher corrosion resistance and, in consequence, better barrier properties for the coating. Rp can be estimated from the diameter of the semicircle of the Nyquist diagram as shown in Figure 3. Thus, the larger the diameter of the semicircle the higher the resistance Rp, and hence, the lower the corrosion rate (Aguilar et al., 1990).
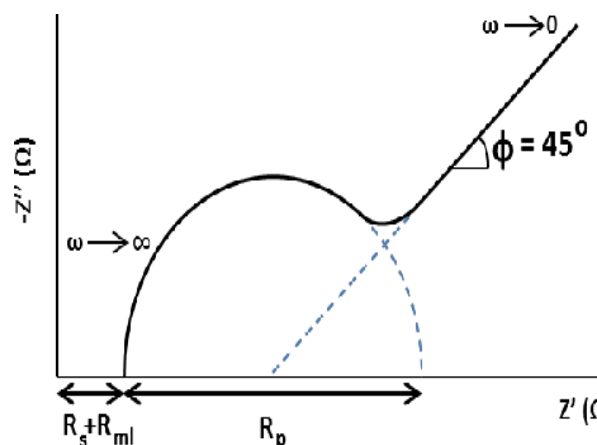

Figure 3. Conventional Nyquist plot for impedance measurements and Rp determination. *Source: Lagunas et al., 2014*

In GECO cases study, the following criterion will be applied (Bierwagen et al.,2000): $Rp >10^8 \Omega cm^2$ provide excellent protection without noticeable penetration of electrolyte or high corrosion resistance. Rp between $10^7 \Omega cm^2$ and $10^8 \Omega cm^2$ provide good protection with minimal electrolyte absorption into the coating or good corrosion resistance. $Rp >10^6$-$10^7 \Omega cm^2$, the electrolyte penetrates the coating and creates a path to the surface of the metal substrate, there is not active corrosion yet and the degree of protection or metal corrosion resistance is ranked as doubtful. $Rp<10^6 \Omega cm^2$, the coating is deemed as non-protective, the electrolyte penetrates the coating and there is active corrosion process on the substrate.

EIS measurements will be obtained by using a potentiostat PGSTAT20 AUTOLAB from Ecochemie®. Impedance will be measured in the frequency range between 100kHz and 0.1Hz (5 points per decade) with a selected AC potential perturbation which will be dependent of the testing materials resistivity. It is expected that EIS measurements be daily executed and registered every 8 hours in order to follow the behaviour of the materials exposed under real conditions in the well during a period of one year.

Additionally, visual examination of the WE sections and microscopical studies will allow at determining the type of corrosion process taking place on these materials Therefore, a triple approach methodology will be applied to evaluate the performance of GECO sites' selected materials and establish a final ranking of materials corrosion resistance: in-situ EIS measurements using a dedicated corrosion monitoring equipment for online and continuous monitoring of the degradation rate of the materials, on-site visual inspection and detailed laboratory assessment of the tested section at the end of the exposure period time.

3. CONCLUSIONS

The GECO project proposes a detailed and consistent monitoring program to provide cleaner and cost-effective non-carbon emitting geothermal plants.

A dedicated corrosion monitoring equipment for online and continuous monitoring of materials degradation for geothermal plants will be designed, developed and installed by AIMEN Technologic Center in the demo sites located in Iceland (Hellisheidi and Nesjavellir) and Germany (Bochum MULE) to run under high temperature and pressure conditions during one year.

Electrochemical Impedance Spectroscopy (EIS) measurements will be registered and evaluated in real time to compare the corrosion performance of the selected materials and anticipate potential damages in the infrastructures. Following the impedance measurements allows detecting how the outages or plant malfunctions can affect the corrosion processes on the piping materials anticipating leakages due to pipe damages and, in consequence, avoiding long non-operational periods and high repair costs.

ACKNOWLEDGEMENTS

REFERENCES

Aguilar, A., Sagüés, A., Powers, R. Corrosion Rates of Steel in Concrete. ASTM-STP 1065, American Society for Testing and Materials, 66-85, 1990

Bierwagen GP, L. He, J. Li, L. Ellingson, D. Tallman, Studies of new accelerated evaluation method for coating corrosion resistance-thermal cyclic testing. Prog. Org. Coat. 39, 67-78, 2000

Calderon-Gutierreza JA, Bedoya-Lora FE. Barrier property and lifetime prediction by EIS of a high-performance organic coating. DYNA, 81(183), 97, 2014

Freire, L., Carmezim, MJ, Ferreira, MGS, Montemor, MF. The passive behaviour of AISI 316 in alkaline media and the effect of pH: A combined electrochemical and analytical study. Electrochimica Acta, 55(21), 6174–6181, 2010

Freire, L., Carmezim, MJ, Ferreira, MGS, Montemor, MF. The electrochemical behaviour of stainless steel AISI 304 in alkaline solutions with different pH in the presence of chlorides. Electrochimica Acta, 56(14), 5280–5289, 2011

Hack HP, Scully JR. Defect area determination of organic coated steels in seawater using the break point frequency. J Electrochem Soc 138(1),33, 1991

Inman, On-line corrosion monitoring in geothermal steam pipes. Geothermics 27,2, 167-182 (1998)

Orazem ME, Tribollet B, Electrochemical impedance Spectroscopy, Willey 155-162, 2008

Renewables. International Energy Agency Report, 2018. https://www.iea.org/topics/renewables/geothermal/

Shreepathi S, Guin AK, Naik SM, Vattipalli MR. Service life prediction of organic coatings: EIS vs actual service life. Journal of coatings technology and research. 8(2), 191-200, 2011

Waters SA, Tsaprailis H, Kovacs III W, Tuggle JR, Garfias-Mesias LF. Characterization of internal and external coatings used on steel pipelines. Paper 10038 presented at NACE Corrosion Conference 2010