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# Hydrophobic Coatings for Corrosion Control of Aluminum Heat Exchangers

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67676>

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## Abstract

The production of thin films (nanocoatings) is a technological field with many applications to elaborate materials with new properties to be used as corrosion protection of traditional metals. Hydrophobicity is an example of such properties. In this chapter, an example of two hydrophobic corrosion coatings for possible use over aluminum heat exchanger geothermal power plants is discussed. Material substrate preparation, synthesis of hydrophobic sol-gel nanocoating, characterization, and electrochemical evaluation as a function of time of immersion, which are compared to another commercial fluorinated compound, are presented. Good corrosion protection was found for both hydrophobic coatings for possible application in geothermal heat exchangers.

**Keywords:** hydrophobic, coatings, corrosion, aluminum, geothermal heat exchangers

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## 1. Introduction

The main problem of heat exchanger operation in contact with highly corrosive geothermal fluids is the deposition of fluid salts within heat exchanger tube walls, giving rise to corrosion problems. In combination with fluid pH and aggressive ions concentration such as chlorides, they reduce the lifetime operation of such equipment. Due to these facts and including mass transfer considerations, affordable protection of heat exchangers is a must from the effect of corrosive geothermal fluid. Various materials do exist and are used in heat exchangers in the

geothermal energy production industries such as steel, copper alloys, and aluminum, depending on cost-benefit decision making. Nevertheless, proposals do exist to coat these materials with polymeric-coating systems giving dubious practical results in the past. A possible alternative is the use of hydrophobic coatings, to increase the long-term aluminum corrosion resistance under severe natural saline conditions encountered in geothermal fluid fields.

### 1.1. Nanocoatings

The production of thin films (nano coatings) is a technological field with many applications to elaborate materials with new properties as well as protection of traditional metals, nowadays and in the foreseeable future. Different materials and coatings are combined to produce hybrid or composite materials with special characteristics and properties [1].

The coating thickness range is from tens of nanometers (nm) up to some microns ( $\mu\text{m}$ ) and in most *grand* scale applications, mono-layered coatings are used, but fabricating oxide-oxide, oxide-metal or other variable metals oxides combination multi-layers, properties may be improved. Therefore, film thickness control is critical [2, 3].

Coating can be classified due to their manufacturing material interactions, substrate nature, and according to its specific barrier applications in thermal, corrosion and oxidation, wear and diffusion types [4]. Coating nano-technology concentrates in obtaining thinner films with the same or enhanced protection when compared to conventional coating technologies.

### 1.2. Sol-gel coatings

Within the recent deposition technique alternatives, the sol-gel route technology is promising. In the last two decades, there is an increased widespread use of nanotechnology coatings through sol-gel methods, formed by way of organic-inorganic components, eliminating highly damaging and toxic solvents to the environment and the human itself. These coatings protect the metal surface from corrosion by different corrosion protection mechanisms [5].

Sol-gel synthesis route represents an alternative to generate components or compounds with controlled size, which was difficult to obtain in the past by conventional preparation techniques. This uniform procedure process results not only in particles agglutination but also in a range of products such as fibers, monolithic structures, thin films, or coatings in a wide variety of hybrid or composite materials. The adequate selection of precursor and reactants allows obtaining materials with tailor-made–designed properties, useful in a wide variety of technological applications such as optics, electronics, biology, medicine, etc. [6]. In general, the sol-gel route is the formation of a three-dimensional oxide resulting from hydrolysis and condensation reactions of the molecules from precursors present in a liquid medium under relatively low temperatures and no physical and/or chemical reactions with the substrates, these being advantageous for practical applications.

### 1.3. Hydrophobic coatings

Hydrophobic coatings reject an aqueous dissolution or electrolyte. These characteristics may be accomplished by means of encapsulated functionalized species present in the coating or by

changing the medium composition. Also, if the more external or outer-layer morphology or structure of the system is changed or modified, a hydro- or superhydrophobic system is promoted [7–10]. The strategies or methodologies contemplating a superficial change through encapsulation systems promised advantageous success; nevertheless, few developments really achieved an effective corrosion protection, since the effect decreases as a function of elapsed time of surface (coating) contact electrolyte [11–13].

To obtain a hydrophobic outcome, a “*Lotus leave*” effect must be generated, which is when the surface attains a roughness level that effectively repels any type of aqueous dissolution. To simulate this effect on coating surfaces, various types of species, such as potassium stearate or calcium hydroxide, porous silica or synthetic urea formaldehyde capsules, styrene-based copolymers such as methyl-methacrylate, were encapsulated and incorporated into coating systems, among others [7–14].

Sol-gel is a versatile method to produce super-hydrophobic surfaces. The literature reports [15] successive hydrolysis and condensation-polymerization reactions using ammonia as a catalyzer over aluminum substrate, generating films with high degree of hydrophobicity (contact angles  $\approx 150^\circ$ ). Good corrosion resistance for short periods of immersion was obtained. Incorporation of porous silica particles doped with 3-amino-propyl triethoxysilane compounds as hydrophobic agent generates transparent sol-gel coatings [16]. Also, sol-gel modifies the polymeric structure with diverse functionalized agents such as fluorinated compounds [17] and/or organic-inorganic precursors [15], or nano-fibers or nanotubes incorporation [18] promoting Lotus leaves-like nanostructures increasing corrosion resistance.

#### 1.4. Aluminum and alloys

Aluminum and alloys are widely used in the industrial, architectural, and marine environments due to technical and economic reasons, being the most extended metallic material used, after steel. Nevertheless, they are very reactive and the need for extra protection against corrosion is necessary for certain industrial applications, especially in chloride-containing environments. To achieve this goal, coating and surface modification technologies were speedily developed in recent times related to chemistry, electrochemistry, metallurgy, and other disciplines. Aluminum and alloy surface modification generally consists of surface roughness generation (etching), anodic oxidation, hybrid or composite coatings, etc. The chemically modified surface samples present super-hydrophobicity, increasing corrosion resistance of aluminum and its alloys. This result is attributed to the combined effect of nano/microstructures formed over the surface and low-energy surface material. Chemical etching improves the hydro- or superhydrophobic properties of aluminum and alloys.

#### 1.5. Corrosion in geothermal heat exchangers

In principle, the fluid extracted from the geothermal well is taken to a separator where the mixture, water vapor from the geothermal fluid, is separated. Vapor is sent to the turbine coupled to a generator, where mechanic energy is transformed into electrical energy. The turbine exit is coupled to a condenser helping to increase the cycle efficiency. Finally, the geothermal fluid is reinjected to the well to help recharging.

The main function of heat exchangers metallic tubes or plates is the heat transfer from a heated flow to the feeding water, and for that reason parameters like material thermal conductivity and thickness should be considered. Metallic corrosion promotes thinning of the tubes or plate walls, causing huge economic losses due to operation failures and plant shutdowns as well as malfunctioning of heat exchange processes. Incrustation is the undesirable material accumulation over the metallic elements, calcium carbonates being the most common precipitation, although silica and metallic sulfurous compounds are also common [19]. Both problems present a decrease in equipment performance and efficiency, since overall heat-exchange coefficient diminishes gradually promoting some component failure.

Geothermal environments present different composition with respect to the type of resources available, low or high enthalpy [19]. However, the composition solely does not depend on this; in low-enthalpy environments, the main forms of corrosion are generalized (overall) and localized (certain areas) corrosion. Localized corrosion is the most detrimental damage, since it cannot be predicted and is difficult to follow up its evolution and it can produce major damages. This type of corrosion includes galvanic, pitting, crevice; in general, three types of material incrustations may be encountered: silica and silicates, carbonates, and sulfates and sulfites [20]. Silica is in the form of amorphous silica, carbonate incrustations are in the form of low magnesium calcite and sulfates, while crystallized sulfite in many phases predominates as Pb, Zn, Fe, and Cu [20].

The pH control in geothermal water is a crucial factor to control corrosion and silica incrustations; to control the system, HCl or NaOH is added to the geothermal energy source, reactants being expensive. The alternative is to use protective coatings to help diminish incrustations within the tube walls.

The main problem during geothermal plant heat exchanger operation in contact with geothermal fluids is deposition of fluid salts over the tube walls originating multiple corrosion problems which in combination with the fluid pH and aggressive ions concentration (mainly chlorides) notably reduce the useful life of heat exchangers. Therefore, and taking into account heat transfer considerations, it is necessary to protect the heat exchanger metallic elements from the highly corrosive fluid. Different materials are used as heat exchangers in the geothermal industry like steel, copper alloys, or aluminum and proposals are being made to coat the metallic elements with different polymeric systems or schemes [21, 22].

## 2. Coatings

Examples of hydrophobic coatings were obtained from sol-gel, or dip-coating methods, over aluminum substrate. The hybrid-coating systems used were based on silane polymer solutions or compounds. Evaluation and characterization were done using electrochemical techniques and characterization through scanning electron microscope (SEM), water-drop contact angle, and thermal conductivity measurements.

## 2.1. Electrochemical etching

Commercial aluminum (see **Table 1**) rods were cut in cylinders 2 cm height to expose approximately 1 cm<sup>2</sup> area to the corrosive electrolytes, which after their electrical connection by means of a copper wire were encapsulated in an epoxy resin at room temperature. Before experiments, the electrodes' surface was prepared abrading with 600 grade emery paper and rinsed with distilled water, and after cleaning, the electrodes were degreased with acetone and finally dried in warm air flow. The purpose is twofold: to render the metal surface ready for coating application improving the coating adhesion and second to improve corrosion resistance of the metal surface. The electrochemical arrangement was a three-electrode cell using a graphite rod as a counter-electrode and a silver/silver chloride as a reference electrode.

The aluminum etching is as follows: the electrode was immersed in NaOH pH 11 solution for about 3 min. Afterwards, the electrodes were removed and cleaned again with de-ionized water, dried and immersed again, this time in a HCl pH 3 solution, promoting anodic dissolution, polarizing up to  $-100 \text{ mV}_{(\text{Ag}/\text{AgCl}_2)}$  potential and left constant at this potential for 30 min. The presence of chloride ions promotes the formation of micro-/nanopits or pores over the metal surface. The samples were ultrasonically cleaned with de-ionized water, dried, and ready for coating application.

**Figure 1** presents SEM micrographs (cross section) where micro/nanostructure can be observed over the aluminum surface, after electrochemical etching and anodic dissolution. Rough and convex irregular and attacked areas and pitted surface are clearly observed. These structures may be favoring the capacity to trap air bubbles supporting hydrophobicity with an appropriate surface roughness. The structure is irregular and disordered and micro/nanoparticles and pores can be observed.

In the presence of chloride ions, the surface structure promotes the appearance of a larger quantity of pits and nanopores at high potentials (above  $-100 \text{ mV}$ ). This is presented in general and a detailed view is seen in **Figure 2**, where a multitude of pits and pores over the anodized surface can be observed. The anodized compact film surface diminishes corrosive anions attacking the aluminum substrate [23].

## 2.2. Coatings

Then, the as-prepared samples were immersed in 5mM perfluoro ethyl trioxi silylne  $\{\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{-Si}(\text{OCH}_2\text{CH}_3)_3\}$  (PTES) solution obtained from Sigma Aldrich. The solution prepared was a mixture of de-ionized water and ethanol (volume ratio 1:1) at 60°C for 2 h [24]. The coating was applied through two-cycle dip coating technique. The first one was immersion for 1 min and then removed and was allowed to dry, and then a second 30-s immersion was done to seal the pores present on the coated sample.

Material composition (%)						
Aluminum	Mg	Fe	Mn	Zn	Cu	Si
	0.014	0.83	0.03	0.9	0.04	0.28

**Table 1.** Aluminum substrate composition.

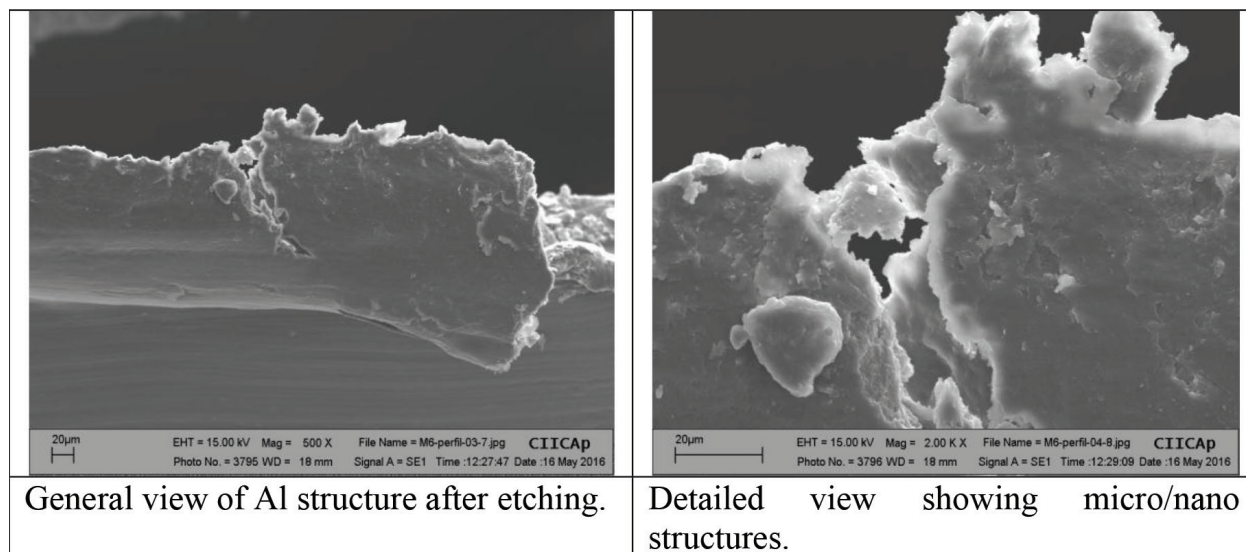


Figure 1. Micrograph after electrochemical aluminum etching in acid media.

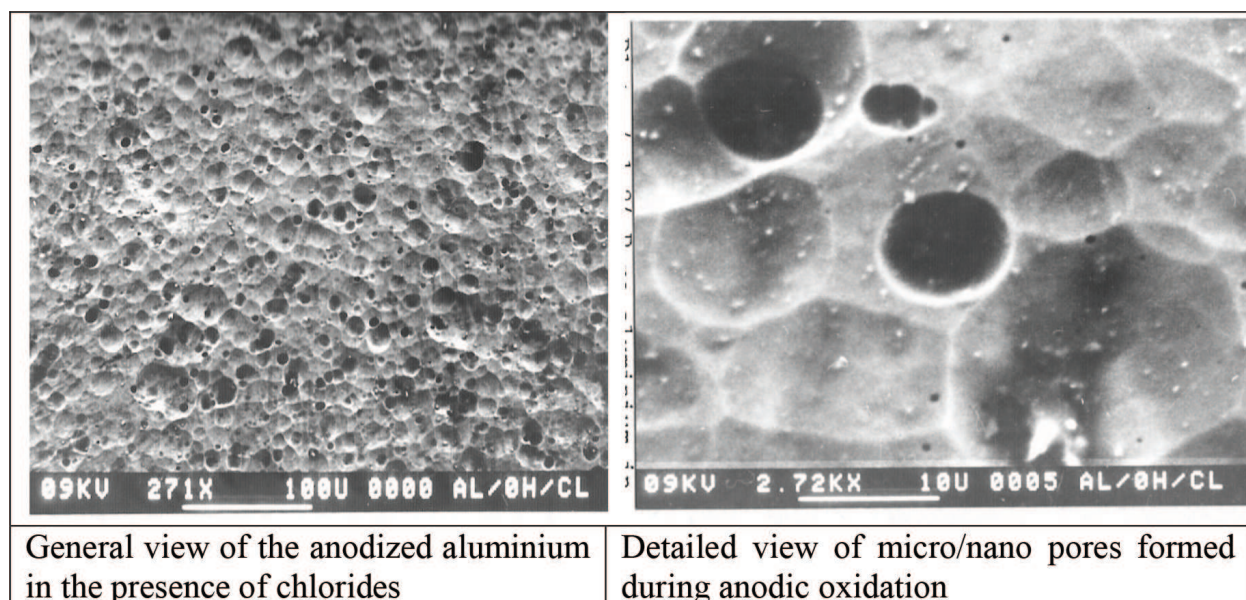


Figure 2. SEM micrograph showing pores over aluminum in acid media in the presence of chloride ions.

Another coating was prepared via sol-gel synthesis, combining one inorganic and another organic compound. The first one consists of a combination of zirconium tetra-n-propoxide with ethyl aceto-acetate using nitric acid pH 5, as a catalyzer for the reaction. The organic part was prepared mixing 3-glycyloxypropyltrimethoxysilane (GPTMS) with 2-propanol (SA nomenclature) also in the presence of HNO<sub>3</sub>. During the sol-gel synthesis, a commercial fluoride compound tetra deca-flouro hexane (TDFH) *Chemguard* from Sigma Aldrich (HA nomenclature) was incorporated in different weight proportions (10, 20, and 30%). The sol-gel coating was deposited using the spin-coating technique, at 2800 rpm for 28 s.

### 2.2.1. Coating thickness

After substrate preparation and coating application, film thickness measurements were taken using a coating thickness tester. The average values obtained from five measurements are presented in **Table 2**.

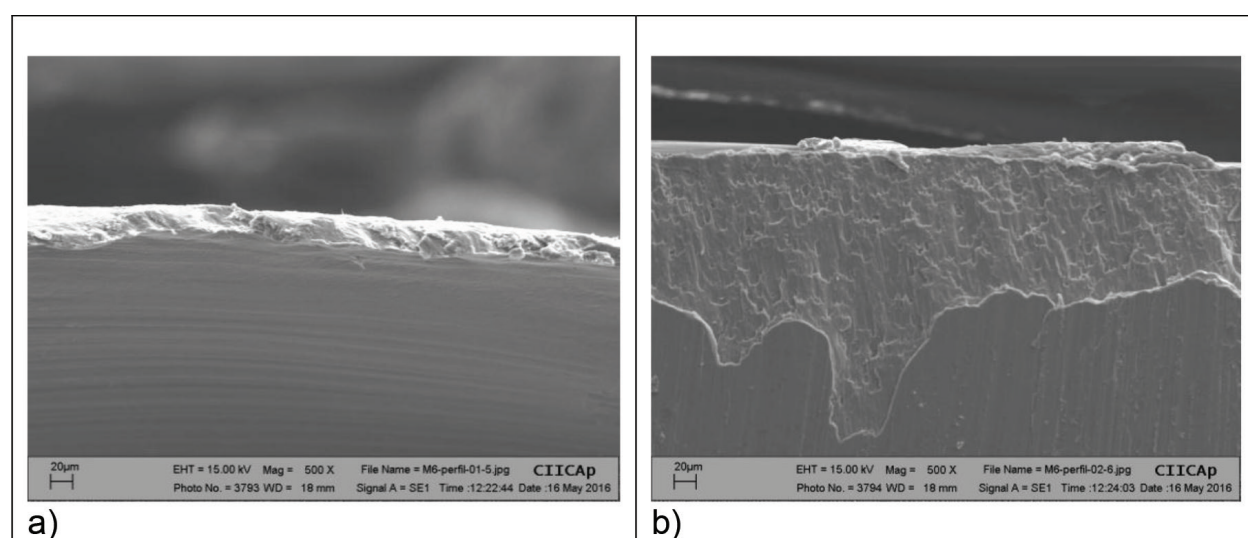
The highest thickness obtained and observed was the PTES coating, while the sol-gel coatings were 10 times thinner. From these coatings, the higher thickness obtained was the SA coating and the CH 30%, with the highest fluoride compound percentage incorporated. As an example, **Figure 3** presents the general and detailed view (cross section) of the aluminum PTES-coated sample, showing good adhesion conditions over the metal substrate.

### 2.2.2. Hydrophobicity

For each sample, the contact angle (right and left) was measured and the average was obtained. When a surface shows a contact angle greater than  $90^\circ$ , it represents a hydrophobic surface. The PTES- and CH 20%-coated samples clearly present hydrophobicity (see **Table 2**). The image is presented in **Figure 4**.

Coating	Thickness ( $\mu\text{m}$ )	Contact angle (degrees)
Blank	1.99	66.7
PTES	24.2	115
SA10%	2.27	70.3
CH 10%	2.02	82.6
CH 20%	2.02	118.9
CH 30%	2.36	95.8

**Table 2.** Coating thickness measurements.



**Figure 3.** SEM micrograph showing PTES coating: (a) general and (b) detailed view.



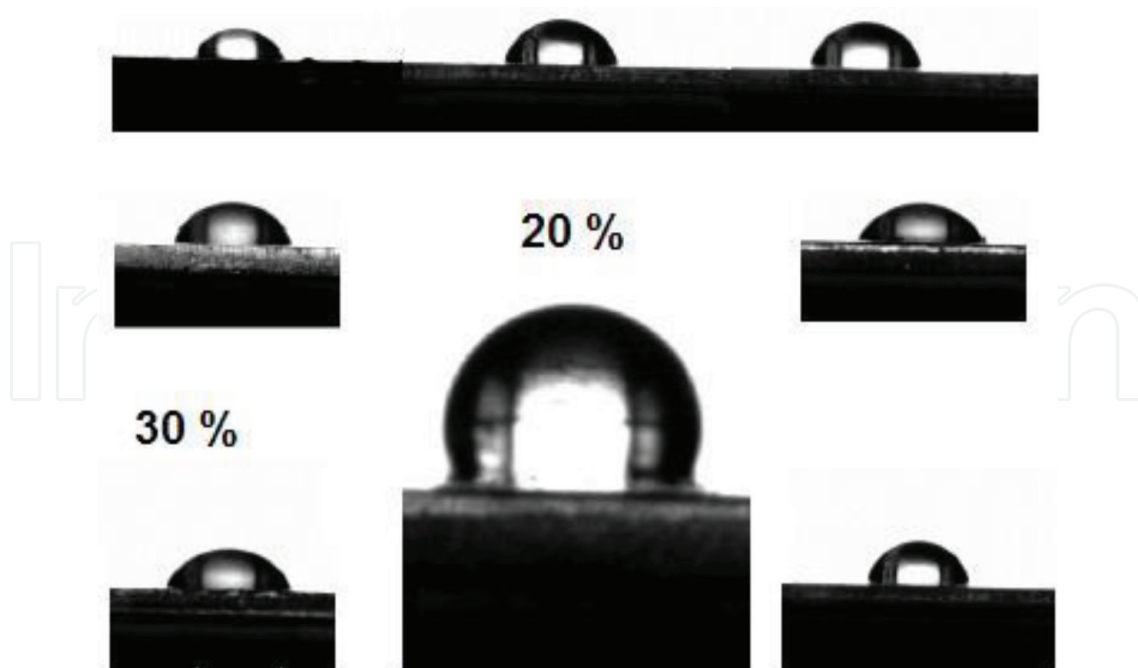


Figure 4. Contact angle of coating.

### 2.2.3. Thermal conductivity

One method to evaluate the thermal conductivity (heat transfer) of polymer coatings, which is important to use in heat exchangers, is the heat plate method to measure the temperature distribution of thermal conductivity. This is according to ISO 8302:1991 standard [25]. Its principle consists in generating a unidirectional heat flow through the samples, as flat plates

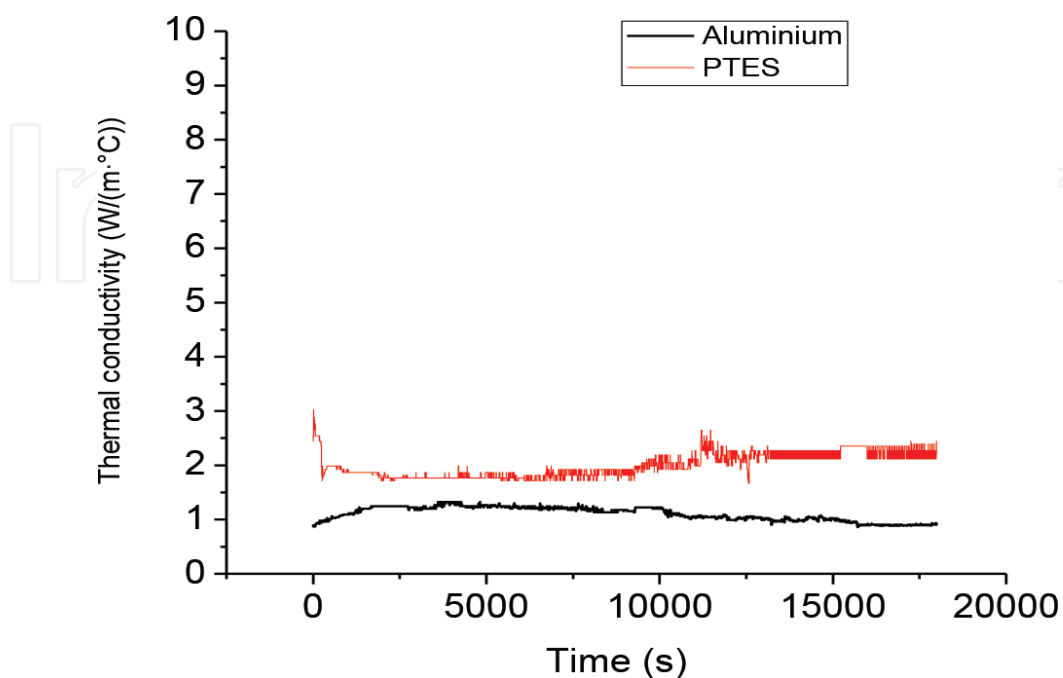


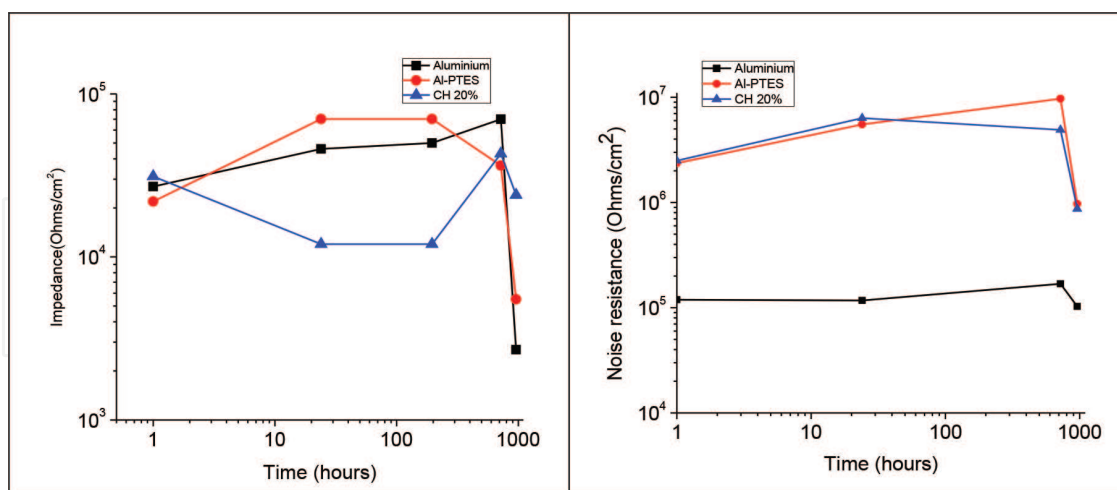
Figure 5. Thermal conductivity of bare aluminum and PTES-coated sample.

conducting heat. As an example, **Figure 5** presents the thermal conductivity as a function of time of PTES coating over the aluminum substrate and compared with the blank (bare metal) sample. The coating presents favorable thermal conductivity conditions when compared with aluminum.

### 3. Electrochemical evaluation

To evaluate the performance and efficiency of corrosion protection coatings, it is common to use electrochemical methods, electrochemical impedance spectroscopy (EIS) being widely applied. The working electrode was immersed in the test solution similar to a geothermal fluid containing 3580 ppm Na and 6693 Cl until a steady-state open-circuit potential ( $E_{oc}$ ) was measured. Electrochemical impedance spectroscopy measurements as a function of time were made using an ACM potentiostat, carried out at corrosion potential  $E_{oc}$  by using a small sinusoidal signal with an amplitude of  $\pm 10$  mV, in a frequency interval of 50 mHz to 20 KHz recording six points per decade. The EIS results were represented using Nyquist and Bode plots, and the effect of time of exposure of the aluminum and coated samples to the corrosion media was also evaluated. Also, electrochemical noise measurements (ENMs) were taken with a second electrode at the tip of a platinum wire and the reference electrode.

The parameters for electrochemical noise were a second Pt tip electrode 1 or 0.5 s per sample obtaining 1024 measurements. The electrolyte was (3580 ppm Na and 6693 ppm Cl) similar to a geothermal fluid (see **Figure 6**).



**Figure 6.** Electrochemical measurements as a function of time: EIS charge transfer resistance and electrochemical noise resistance.

From the electrochemical results obtained EIS charge transfer resistance and electrochemical noise resistance, a similar pattern is revealed. After 720-h immersion, a decrease was observed for both techniques, suggesting an increase in the corrosion rate for the coatings tested. A decrease of one order of magnitude was observed [26].

## 4. Conclusions

An example of hydrophobic coatings for geothermal heat exchangers was presented. The coating characterization was obtained and coating evaluation as a function of time was presented. Good coating behavior was obtained for both hydrophobic coatings tested.

## Acknowledgements

Rebecca Jaimes Ramírez acknowledges Programa de Becas Posdoctorales from DGAPA, Universidad Nacional Autónoma de México 2016-2017, and J. Uruchurtu thanks CONACYT for financial support during sabbatical stay.

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