

## Corrosion Testing of Graphene-Oxide-Polymer Coatings for Geothermal Drilling Applications

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### ABSTRACT

The Geo-Drill project aims to save time, increase service life of equipment and instrumentation, and reduce costs during drilling of geothermal wells by improving drilling methods with new materials and novel design of a down-the-hole (DTH) drill hammer. In the project polymer coatings (PTFE/PPS) with added graphene oxide (GO) nano-particles were corrosion tested at high temperature and pressure to evaluate the corrosion resistance in simulated geothermal drilling environment. The results from the corrosion testing of the PTFE/PPS-GO coatings in simulated geothermal drilling environment at two different conditions that can be encountered during drilling operation are reported here. One set of samples with various GO content was tested in moderately alkaline water, pH = 9, at 120 °C and 50 bar for 14 days; simulating normal drilling conditions. A second set of samples were tested at harsh conditions at 250 °C, 50 bar for a duration of 7 days in water (vapor and liquid phases) with CO<sub>2</sub> and H<sub>2</sub>S gasses added, which are conditions that can be encountered during geothermal well drilling if loss of circulation of the drilling fluid occurs with the subsequent ingress of corrosive gases into the well. To evaluate corrosion resistance, weight changes were measured, and microstructural and chemical composition analyses were performed with scanning electron microscope with an attached energy-dispersive X-ray spectroscopy equipment before and after testing.

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Key words: CO<sub>2</sub>/H<sub>2</sub>S Corrosion; High Temperature Corrosion; Geothermal Environment; Geo-Drill; Graphene-Oxide-Polymer coatings.

## INTRODUCTION

The high temperature and chemical composition of the geothermal fluid results in corrosion damage of drilling equipment, well casing and other components made of steel and iron alloys used in geothermal power production. This corrosive nature of the geothermal environment decreases the service life and increases the need for maintenance of geothermal power plants and geothermal wells. The main reasons for the corrosion of components are hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) present in geothermal system.<sup>1</sup> Geothermal fluids can also contain aggressive chloride [Cl<sup>-</sup>] and sulfate [SO<sub>4</sub><sup>2-</sup>] ions,<sup>2</sup> which might increase corrosion rate and facilitate pitting corrosion, crevice corrosion and other localized corrosion effects. The corrosion rate for carbon steel generally increases in acidic environments,<sup>1</sup> while in more alkaline environment the corrosion rate decreases due to formation of passive film on carbon steel in pH ranging from 9.5 to 14.<sup>3</sup>

In addition to corrosion, geothermal systems are subjected to material fatigue, wear, and erosion from the extremely harsh environment in terms of temperature, pressure, rock breaking, etc. Through improvement of drilling methods and equipment, the Geo-Drill project aims to save time, increase service life of equipment and instrumentation, and reduce costs during drilling of geothermal wells. To reduce corrosion damage of materials operating in the harsh geothermal environment, novel corrosion resistant coatings and materials for drilling applications have been developed, fabricated, and tested in the project at pressure, temperature, and chemical conditions equivalent to those of a geothermal well drilling operation. Graphene Oxide (GO)-PTFE based coatings were developed as part of this work. In the project, these coatings are intended to improve wear, erosion, and corrosion resistance of DTH hammer components to prolong their service life.<sup>4</sup>

Polyurethanes with addition of GO greatly enhances the anti-corrosive performance of polyvinylidene difluoride coatings.<sup>5</sup> The synthetic polymer PTFE (Polytetrafluoroethylene) is commonly used in many products due to its favorable properties like durability, chemical inertness, high capacity of insulating, dielectric properties, etc. The bi-dimensional material Graphene Oxide is produced by the strong oxidation of graphite, which introduces oxygen moieties in the structure. This makes the GO compatible with a wide range of matrices and increases the interlayer distance between flakes facilitating division into monolayer sheets. Adding small amounts of the GO improves the properties of PTFE because of the high aspect ratio of the GO. Nemati et al. observed that adding 15 vol% GO to PTFE decreases the wear rate from  $5.6 \times 10^{-8}$  to  $1.9 \times 10^{-9}$  mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. This study also demonstrated a reduction of the coefficient of friction in the micro-scale from 0.16 to 0.045 while this improvement was less in the macro-scale.<sup>6</sup>

This paper presents the results from corrosion testing of GO - PTFE coatings with various content of GO in simulated geothermal drilling environment at two different conditions that can be encountered during drilling operation: normal drilling conditions with moderately alkaline water as drilling fluid, pH = 9, at 120 °C and 50 bar for 14 days, and an unplanned shut-down (drill stuck in well) with leakage of geothermal fluid containing dissolved H<sub>2</sub>S and CO<sub>2</sub> into the well at 250 °C and 50 bar for one week. Microstructural and chemical composition analyses were performed with scanning electron microscope with an attached energy-dispersive X-ray spectroscopy equipment before and after testing to investigate the corrosion resistance of the GO - PTFE coatings in the test conditions. Weight changes were also measured to evaluate the stability at high temperatures and corrosion resistance.

## EXPERIMENTAL PROCEDURE

### Experimental setup

Figure 1 shows the recently installed laboratory capable of conducting high-pressure and high-temperature experiments with geothermal fluids at the University of Iceland. The laboratory was designed and constructed by Cormet Oy, Finland. It is equipped with gas detection and alarm systems to ensure safe operation for experiments with  $\text{H}_2\text{S}$  and  $\text{CO}_2$  gas. A 3 L autoclave made of C-276 Hastelloy\* and rated for pressures up to 300 bar and temperatures up to 500 °C is the key equipment in this laboratory (Figure 2). A custom-made stirrer impeller connected to a magnetic stirrer is installed in the autoclave lid. During an experiment, test samples are installed between the vertical supports of the custom-made sample holder, which is also attached to the lid. After installation of the samples and before starting an experiment, the lid, which is controlled by an electrical lifting mechanism, is lowered, and connected with 9 bolts to the autoclave vessel. Gauge pressure is measured with a Keller\* pressure transmitter and temperature is measured with a Pt100 temperature sensor in the vessel. Heating elements around the autoclave vessel control the temperature and insulation of the lid ensure low heat loss to the surroundings during experiments (Figure 3). The autoclave can be pressurized from the bottom gas inlet line with  $\text{N}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . Figure 3, right part of the photo, shows the gas filling panel with Brooks\* mass flow controllers that are used to fill a programmed quantity of each of the three gas components during the filling procedure. During depressurization, the gas is drained through gas draining line in the top and flows through three 20 L plastic containers (Figure 3, left part of the photo), filled with alkaline water solution containing dissolved zinc acetate and NaOH with pH =13.5. Zinc acetate reacts with  $\text{H}_2\text{S}$  gas from the autoclave and form solid  $\text{ZnS}$  that precipitates out of the solution and accumulates in the bottom of the plastic containers. There is also a valve for draining of liquid from the bottom of the autoclave.



**Figure 1: The corrosion laboratory constructed in a 40-foot high-cube container by Cormet Oy, Finland, shipped to Iceland, and installed at the campus of the University of Iceland.**

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\* Trade name.

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**Figure 2: The autoclave with the lid opened before installation of test samples.**



**Figure 3: Experimental setup with filling panel (right) and H<sub>2</sub>S capture system (left).**

## Materials

Graphenea SA provided the carbon steel (CS) substrates of 50 x 25 x 3 mm coupons (Figures 4, a and b) coated with PTFE-PPS coatings mixed with different weight fractions of graphene oxide (GO). This study reports the results from testing of the following three coatings: CS coated with PTFE-PPS coating with no GO added (0wt% GO coating), CS coated with PTFE-PPS and 0.5wt.% GO, and CS coated with PTFE-PPS and 2.5wt.% GO. The graphene oxide is produced by Graphenea SA using a modified Hummers method:<sup>7</sup> Graphite powder was dispersed and cooled down in H<sub>2</sub>SO<sub>4</sub>. KMnO<sub>4</sub> was then added to the mixture. After stirring for 1h, the mixture was heated up to 30°C and kept at this temperature. The mixture was cooled down and distilled water was slowly added to the slurry. Finally, H<sub>2</sub>O<sub>2</sub> was added, and this dispersion was purified by cleaning with distilled water obtaining the GO slurry (water dispersion). Commercial PTFE-PPS coating was used as a reference for this study. In the preparation of the PTFE-PPS / GO mixtures, the required amount of GO slurry was added to the PTFE-PPS and dispersed with a Dispermat<sup>†</sup> system at velocities from 600 to 1000 rpm during 15-30 min. The CS substrates were spray-coated with the PTFE-PPS / GO mixtures and cured at 400 °C for 10 min. Adhesion test of the Xylan-0wt% coating has been studied in the research project by other consortium member such as with a cross-cut test according to UNI EN ISO 2409 and gave good results, but the results are not included here since the focus of this study is on corrosion tests.

## Experimental procedure

The insides of the autoclave vessel were cleaned with acetone, ethanol, and DI-water before an experiment. After weighing, the coupon samples (Figures 4, a and b) were installed between the vertical sample holder supports (Figure 4 c). For the test simulation normal drilling conditions with moderately alkaline water as drilling fluid, 2 L of tap water with pH = 9, was filled in the autoclave vessel before closing of the lid. In general, the tap water in Iceland is moderately alkaline according to measurements.<sup>8</sup> Samples were only installed in the lower part of the sample holder in this test in order that all samples would be submerged in water after closing of the lid. For the test simulating an unplanned shut-down with leakage of geothermal fluid, 1.5 L of deionized water with 0.60 g of NaOH and 0.44 g of NaCl dissolved in the water was filled into the vessel before closing of the lid. The NaOH and NaCl added to the water resulted in a stable neutral pH after filling H<sub>2</sub>S, CO<sub>2</sub> and N<sub>2</sub> and heating to 250 °C. Table 1 reports the

<sup>†</sup> Trade name.

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