

Importance of Steel Alloying Elements in Geothermal Environment

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ABSTRACT

Steel and its alloys have been studied extensively where the inclusion of Ni and Cr have reportedly shown good corrosion resistance in high temperatures. Furthermore, Mo is known to provide pitting resistance. Geothermal environment has several corrosion initiators such as S, Cl, high temperature and pressure. In an S rich environment, the protective mechanism of the alloying elements differs. Mo is known to adsorb to S, reducing the diffusivity of the S into the bulk material, while Cr and Ni have antagonistic effects in presence of S. This paper seeks to confirm the importance of alloying elements in geothermal environment.

In the present work, EN 10028-2, S17400, S30403 and S31254 steel coupons were exposed in a geothermal wellhead at Hellisheiði powerplant, Iceland, for 3 months. Temperature and pressure in the wellhead were 198 °C and 13,9 Bar gauge, respectively. The corrosion rate during exposure was evaluated using weight loss measurements and microstructural analysis. The results demonstrated that non-alloyed steel had by far the highest material loss rate. These findings indicate a linear correlation between Ni content in alloy and a low corrosion rate in an S rich environment.

Key words: Corrosion, geothermal, steel, high temperature, alloys.

INTRODUCTION

Geothermal energy has established itself as an attractive alternative to traditional power generation processes where available. In geothermal powerplants hot geothermal water and steam are used to generate electricity. The geothermal fluid can contain highly corrosive chemical species such as: oxygen (very minimal due to reducing environment), hydrogen ion (pH), carbon dioxide, hydrogen sulphide species, ammonia, chloride ions, and sulphate ions¹. The steam and fluid are highly corrosive to the steel components where CO₂ corrosion is reported to cause metal dissolution and localized corrosion areas in the form of pitting. Meanwhile, H₂S is known to cause sulphide stress cracking which can occur at any temperature, hydrogen embrittlement, which occurs at low temperatures (normally during cooling of the steel), and stress corrosion cracking which is connected with synergy between chloride, H₂S and high temperatures². Furthermore, based on reported data from geothermal areas, an important source of corrosion is not only the geothermal fluid itself but in some cases biofilm produced by bacteria¹. Temperature and pressure affect the pH of the fluid resulting in changes in corrosiveness of the environment¹. The Pourbaix-diagram is shown in Figure 1A. for Ni, Fe and Cr in a S rich environment, the yellow box is the pH range that is operating in well HE-23, the well at Hellisheiði power plant in Iceland where testing was performed. From the Pourbaix-diagram it can be deduced that Ni and Fe will react with S while Cr will react with oxygen.

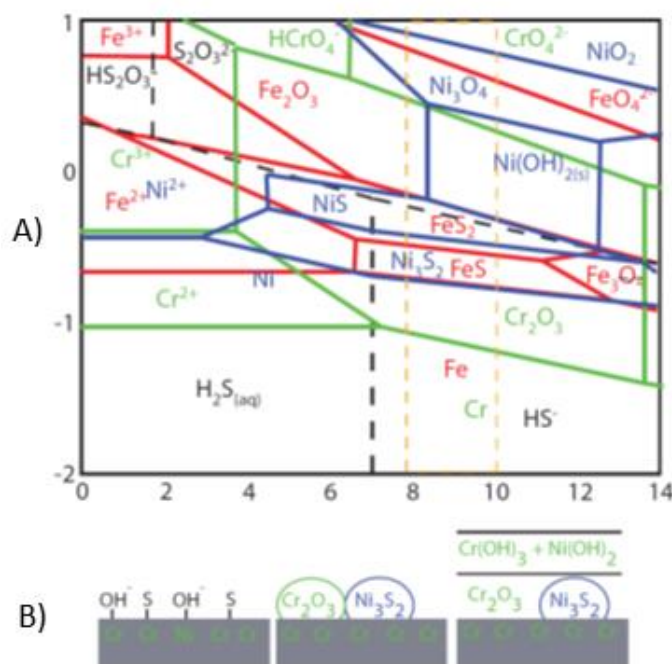


Figure 1: A) Pourbaix-Diagram of Ni, Cr and Fe, the yellow dotted line is the environment that is being tested in. B) antagonistic behaviour of the Cr oxide and Ni sulphide for forming protective layer.

Material performance testing is vital in order to identify the best material for a certain system. It has been reported that laboratory testing only partially represents the actual geothermal fluid but fails to reproduce the same results as field testing does in relation to mineral scaling and corrosion products³. In this paper, four different steel alloys were tested in a geothermal environment with the objective to understand the corrosion behaviour, their protective oxide layer formation and to confirm the importance of the alloying elements of steel alloys. The paper will focus on effects of the active alloying elements Cr, Ni and Mo in the Fe and their mechanisms for material protection in an S rich environment.

EXPERIMENTAL PROCEDURE

The testing was done at ON at the Hellisheiði geothermal plant well HE-23, which has test conditions of 198 °C and 13,9 Bar gauge. The coupon samples were placed on a rack and into the geothermal wellhead shown in Figure 2A. The coupons were exposed for 3 months and evaluated afterwards. The chemical analysis of the environment is shown in Table 1.

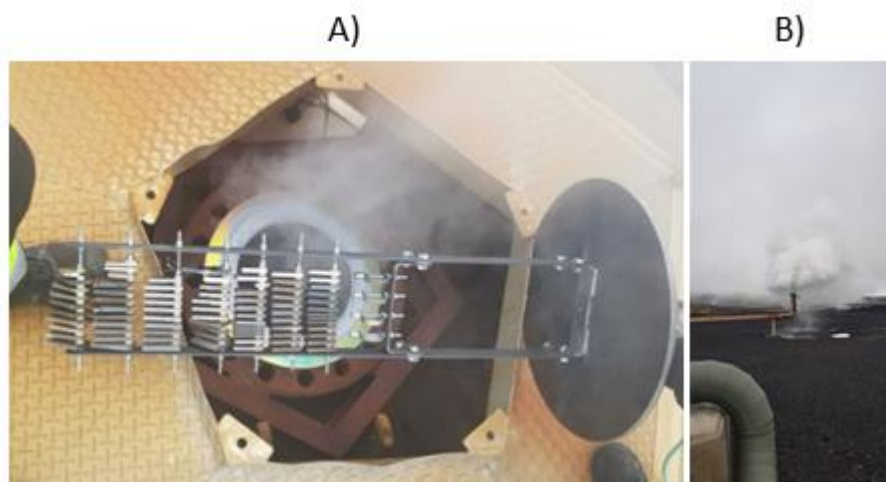


Figure 2: A) Shows the exposed sample on a sample holder and the inlet to the wellhead. B) shows the wellhead where the coupons were exposed to.

Table 1: Chemical analysis results from fluid sampled in well HE-23.

Condensed water analysis:	
Gas volume/cond.water mass [litre/kg]	0.886
Cl [mg/kg]	62.1
Na [mg/kg]	144
SO4 [mg/kg]	58.4
SO2 [mg/kg]	488
Gas - steam analysis:	
CO2 base [mg/kg]	15017
H2S base [mg/kg]	1363.4
Cl [mg/kg]	62.1
SO4 [mg/kg]	58.44
Liquid (w/electrodes and titration):	
CO2 water [mg/kg]	123
H2S water [mg/kg]	33.7

The evaluation methods were mass loss measurements and microstructure analysis. The mass loss measurements of the substrate were conducted according to standards ASTM G4-01, C.3.5 for Fe low in Cr and C.7.1. for stainless steel. The microstructure analysis was done with SEM/BES/EDX where the coupons were cut 12 mm from the lower end of the sample and mounted in Bakelite and baked for 3.5 min at 150°C. The coupons were then ground and the surface polished to 1 µm. The top surfaces were assessed from the centre of the samples. The materials selected for the testing and their active alloying elements are shown in Table 2.

Table 2: Amount of active alloying material in tested steels in wt% and their purpose of use.

Nr	Material	Ni	Cr	Mo	Cu	S	Purpose
1	EN 10028-2	≤0.30	≤0.30	≤0.08	≤0.30	0	Pipe & Casing
2	S17400	3.0-5.0	15-17.5	0	0.15-0.45	0.3	Valve stem & Turbine blades
3	S30403	8-12	18-20	0	0	0	Turbine diaphragm
4	S31254	18	20	6,1	0	0	Heat exchanger tube

RESULTS

Microstructural analysis

The interaction of a material with its surrounding defines its corrosive resistance of the material. In this section each material will be investigated separately with the focus on understanding the surface layer formation prior to and during wellhead exposure.

Sample 1 – EN 10028-2

EN 10028-2 is used in piping and casing. Its benefits are low cost and the good fabricability of the material. Carbon steel is considered having uniform corrosion in geothermal systems and thick walls are needed to account for thinning. When the coupon has been exposed in the wellhead for 3 months, there is a visible uneven distribution of corrosion products forming on the surface, seen in figure 3A. The corrosion products are black indicating FeS (Pyrrhotite), and reddish indicating Fe₂O₃. The irregularity of corrosion product might be due to preferential flow of the geothermal exposure. The corrosion products are of different size and are distributed unevenly over the area as seen in figure 3B. The corrosion products show a hexagonal shape which is typical for FeS (Pyrrhotite) product formed at high temperature (over 120°C) and high H₂S particle pressure. Pyrrhotite has a black colour and is the most stable of FeS products⁴. The EDX analysis of the corrosion products and surroundings showed 43%wt oxygen, 14%wt S and 39%wt Fe. Furthermore, there are areas on the surfaces that do not have defined structure as seen in figure 3C that could be deposits from the geothermal fluid. The images are taken in backscatter mode (BES) where the heavier elements are shown in lighter colour.

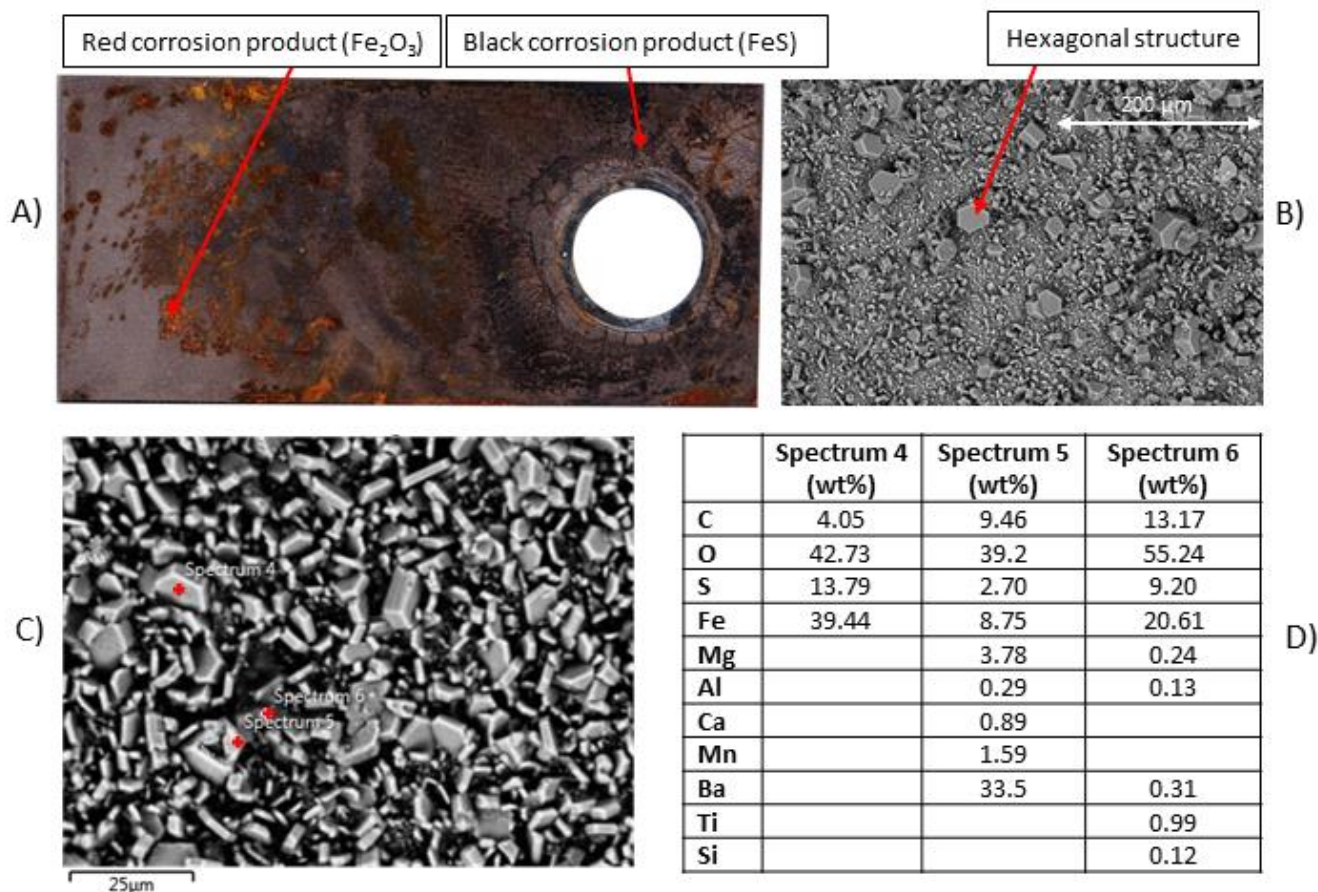


Figure 3: EN 10028-2 after 3 months exposure in geothermal well. A) Coupon after exposure where corrosion products are formed on the top surface. B) The surface under high magnification with corrosion products evident. C) Further magnification of the surface where the typical Fe hexagonal structure are evident. D) Chemical weight presentence of points shown in C).

The cross sections profiles are shown in Figure 4. The Figure 4D shows optical imaging of the steel's cross-section at low magnification where several pits can be seen. Figure 4E shows the profile in high magnification where pits are frequently formed under the corrosion product. The corrosion product can be seen to detach from the surface and mix into the geothermal deposition, where corrosion product are light grey and geothermal deposits is dark grey. Figure 4F steel shows the high magnification of the surface profile, where thin layers are seen on the steel surface.

The EDX profile analysis, presented in Figure 5, illustrates a thin Fe oxide layer of around $1.5 \mu\text{m}$ on the steel surface. This layer is below a thicker layer of Fe-S product of around $4 \mu\text{m}$ Fe, which is mixed with geothermal fluid deposits.