



Materials selection for dew-point corrosion in geothermal fluids containing acid chloride



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ARTICLE INFO

Keywords:

Dew point corrosion
Stainless steels
Nickel alloys
Titanium alloys
Geothermal fluids
Acid chlorides
Stress corrosion cracking
Localized corrosion

ABSTRACT

The paper is aimed to the evaluation of the corrosion behavior of corrosion resisting alloys (CRAs) in geothermal fluids operating at the dew point.

Several test series were carried out in geothermal production sites of Tuscany (Italy) under continuous flow. The vapor was extracted directly from the main flow and it was conveyed in an experimental device designed to simulate dew point conditions.

Nine martensitic stainless steel, one precipitation hardening stainless steel with martensitic structure, two ferritic extra low interstitial (ELI) stainless steels, four duplex (austenitic-ferritic) stainless steel, five austenitic stainless steels, six nickel alloys/super austenitic stainless steels, four titanium alloys were tested.

The main forms of corrosion were general corrosion, localized corrosion (pitting and crevice) and stress corrosion cracking. Corrosion maps are presented as a function of PREN index, chromium, molybdenum and nickel content.

1. Introduction

The presence of acid chlorides in steam – mainly hydrogen chloride (HCl) and ammonium chloride (NH₄Cl) – promotes severe corrosion in geothermal power plants. In the vapor-dominated system of Larderello, risk of localized corrosion and stress corrosion cracking arises on corrosion resistant alloys (CRA) blades of the wet section of steam turbines. Furthermore, severe general corrosion can be noticed in cold zones of carbon steel pipelines conveying steam from wells to turbines (Hjartarson et al., 2012; Culivicchi et al., 2000; Allegrini and Benvenuti, 1970; Bracaloni et al., 1995).

At the dew point, that usually is in the range between 150 and 190 °C at the operational pressure of plants, the early stage of condensation promotes the formation of a layer of very aggressive saline solution with acid pH, ranging between 2 and 4. Very high chloride concentrations in the order of 20000 ppm were estimated, depending on the chloride content in the vapor phase. Relevant concentrations of ammonium ion and boric acid were also detected.

Nowadays, corrosion mitigation is mainly achieved through steam scrubbing systems and chloride abatement with alkaline sodium hydroxide solution (Hirtz et al., 1991; Marshall and Braithwaite, 2017; Paglianti et al., 1996; Simonson and Palmer, 1995; Viviani et al., 1995).

Besides an increase in operating costs, such treatment reduces the fluid temperature leading to relevant loss of power of about 0.5 MW on 15 MW turbine. Thus, the use of CRAs can be a suitable solution (Gallup and Farison, 1998).

Corrosion damages on turbine blades operating at dew point are mainly due to general corrosion of low-alloyed steels, localized corrosion (pitting and under deposit crevice attack), stress corrosion cracking and corrosion-erosion. In addition, rotor blade collapse under cyclic loading at frequency higher than 50 Hz can occur due to fatigue crack initiation and propagation from pitting and stress corrosion.

Materials selection guidelines for acid chloride service in geothermal turbines mainly recommend the use of stainless steels and nickel alloys with a high content of chromium and molybdenum, but they are very expensive. However, titanium alloys should also be taken into account due to both cost and performances. Thomas (2003) discussed their application for geothermal service as viable candidates to replace common stainless steels in very aggressive environments. In addition, several advantages in terms of decrease of the weight of components and axial loads on rotating blades can be evidenced.

Furthermore, the reduction of loads on rotor blades allows the use of alloy with mechanical strength below the level required for iron alloys and nickel alloys.

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Based on these considerations, extensive researches were made in the early 80s on two geothermal sites during different campaigns to perform an experimental evaluation of corrosion resistance of different alloys. The experimental tests were mainly performed in situ, under real dew point exposure conditions. Recently, Yang et al. (2013) still outlined that it is recommend to study dew point corrosion by in situ test method owing to the different mechanisms involved with respect to acid solutions.

Initially, the research was aimed to identify the best technical-economic solution for the construction of standardized turbines. The testing was then addressed to identify materials for blades operating in contact with geothermal vapor containing up to 10 ppm of acid chloride. The results of exposure tests are discussed and analyzed in order to attain suitable design criteria in terms of material selection of materials operating at the dew point in geothermal plants.

2. Experimental

2.1. Testing section and environmental conditions

The investigation was performed in sections specifically designed for corrosion testing in two geothermal sites. Table 1 describes the typical fluid compositions at testing sections inlet. Tests have been performed at the dew point, at about 150 °C and 5 bar pressure, with vapor quality above 0.9 for 30 days. Four similar testing devices were built. Two test sections were installed in the Geothermal Plant of San Martino during '80s and '90s, and the other two sections were placed at the Selva 4C well since 2000.

Fig. 1 shows the layout of the experimental device. Steam from the main vapor line is conveyed to the test section and temperature and pressure were adjusted by means of a laminating valve and a heat exchanger in order to achieve incipient condensation conditions into the testing chamber. A further back pressure valve installed at the output of the testing chamber stabilizes the temperature and pressure. A conical joint was installed at the inlet to avoid turbulence and homogenize the flow. Finally, the steam is discharged passing through demister and silencer.

The testing device was equipped with pressure and temperature sensors for environmental condition monitoring. The specimens were fixed into the chamber by means of metallic plate. Insulating gaskets were used in order to avoid galvanic coupling between different metals. The specimens were placed at different distances from the steam ingress. During all tests, two specimens of AISI 316 stainless steel were exposed for comparison purposes in order to verify that aggressive conditions were effectively achieved. In such conditions, AISI 316 stainless steel is susceptible to chloride stress corrosion cracking.

2.2. Specimens

Weight loss measurements were also performed on 100 × 20 mm specimens with an hole for mounting. The measurements were carried out by means of 0.1 mg precision scale, U-bend specimens (100 × 10 × 3 mm) were used to perform SCC tests (Fig. 2). The

Table 1
Composition of geothermal fluids.

Plants	S. Martino	Selva 4C
Not condensable gases (%)	2.13	4.97
pH	6.1	5.5
CO ₂ (%w)	87.75	91.19
H ₂ S (%w)	2.36	1.72
H ₃ BO ₃ (ppm)	501	1106
Cl ⁻ (ppm)	51.5	102
NH ₄ ⁺ (ppm)	56	69.7
Na ⁺ (ppm)	0.1	0.01

thickness was around 3 mm for most of the specimens. Slightly thicker specimens were used in function of metal sheet thickness availability. The surfaces were polished by means of emery paper up to 1000 grit and then they were degreased in acetone.

After exposure, the corrosion scale was removed by pickling in 5% hydrochloric acid with hexamethylenetetramine. The corrosion morphology was analyzed through micro and macro observations of the surfaces and on the metallographic sections of the U-bend specimens for detecting SCC.

2.3. Materials

Several materials were tested including martensitic, ferritic, austenitic and duplex stainless steels, nickel super alloys, and titanium alloys having different resistance to localized corrosion and chloride stress corrosion cracking. Table 2 summarizes their compositions. The stainless steels and nickel alloys have chromium contents between 12 and 27%, molybdenum up to 17% and nickel up to 74%. Furthermore, there are two traditional Ti6Al4V (grade 5) alloys, a low interstitial Ti Grade 29 ELI alloy with ruthenium and Ti 6246 alloy. The materials were tested in as received metallurgical conditions.

3. Results and discussion

3.1. Dew point solution

At the pressure of the vapor in the inlet section of the turbine, the mean value of the temperature at dew point is 190 °C. However, such temperature decreases to 150–160 °C due to the pressure drop inside the turbine.

The composition of the solutions at the dew point was estimated by means of ENEL proprietary software (LAVAG code) (Culivicchi et al., 2000) by using the thermochemical data of fluids of the Larderello plants.

The composition of the first droplet was calculated by considering the thermodynamic conditions of the fluid, the average chemical composition of steam, and the adiabatic transformation that occurs during steam expansion inside the turbine. Table 3 shows the chemical composition estimated for both the sites, San Martino and Selva 4C. The composition of the first droplet shows very low pH – between 3.8 and 3.9 – and very high chloride and boric acid contents. Hydrogen chloride and ammonium chloride mainly address the low pH values because the ammonia content in the vapor is not sufficient to maintain the pH of solution at neutral point. Ammonium chloride also raises the ebullition temperature allowing condensation at higher temperatures due to the increase of salinity. This phenomenon is almost negligible during isobaric cooling but is relatively important in the case of adiabatic expansion.

3.2. Corrosion forms

The main forms of corrosion identified during testing were general corrosion, pitting corrosion and stress corrosion cracking. In fact, tests were performed under static loading at flow rates not critical for erosion. Furthermore, no formation of deposits on the surface of specimens was noticed due to vapor flow and relatively short exposure time.

3.3. Weight loss

The corrosivity of the environment in terms of general corrosion is primarily related to the acid nature of the condensate that forms at dew point. Corrosion process occurs due to the cathodic process of hydrogen evolution and is favored by both acidity and chlorides, which make passivity film less stable and prevent its reformation on corrosion resistant alloys.

The resistance to this form of attack depends on the alloy

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