Laboratory HCl acid condensate testing of geothermal casing steels

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ABSTRACT

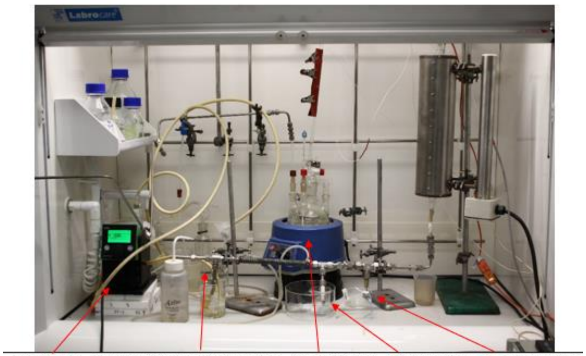
The geothermal steam discharged from superheated geothermal wells can contain a range of corrosive gases: mainly hydrogen sulphide (H_2S), carbon dioxide (CO_2) and ammonia. Occasionally hydrogen chloride (HCl) and boric acid may also be present. At the temperatures encountered in geothermal wells the superheated "dry" steam is rarely corrosive. However, dew point corrosion can be significant even with relatively low concentrations of HCl gas leading to corrosion of steam pipelines, wellheads and at times well casings. HCl contaminated dry steam reaching the turbine can lead to corrosion as well as Stress Corrosion Cracking of the turbine components. This paper is aimed to the evaluation of the corrosion behavior of K55 and new casing steels in an acid steam condensate derived from high temperature HCl gas contaminated steam condensing at atmospheric pressure and a temperature of the order of 97 °C. A Steam Condensate Test rig was developed for testing of the comparative resistance of the casing steels. This work used a miniature probe design. A three electrode system was used with Electrochemical Impedance Spectroscopy (EIS) to compare the performance of K55 alloy and the new casing steels, 17Cr and Cr13U. This paper will summarise the results from this study (a NEDO commissioned project) including measured corrosion rates and pH limits identified for examined casing steels in HCl contaminated steam condensate.

1. INTRODUCTION

Quest Integrity NZL Limited and Geothermal Energy Research and Development Co Ltd. (GERD) completed a joint program of work on a range of geothermal processes and materials performance aimed at improving the utilisation and efficiency of geothermal energy projects in Japan. As part of this work, the use of new casing steels for superheated steam in newly encountered dry steam wells having a risk of HCl gas production was investigated. Previous work by Giorgio et al., 2000 showed a dependence of corrosion rate on Cl concentration in the steam condensate (derived from HCl gas in the steam). That work was with carbon steel and was at a temperature of the order of 185 °C.

This paper describes the development of a test method for steam condensate corrosion rate determination with small electrode area, controlled condensation and refreshing of the flowing condensate with a stable operating temperature, at atmospheric pressure.

The laboratory Steam Condensate Test rig arrangement for testing of the comparative resistance of casing steels to acid steam condensate derived from high temperature HCl gas contaminated steam condensing at atmospheric pressure and a temperature of the order of 97 °C is shown in Figure 1 and Figure 2. Testing temperature was based on a temperature limit imposed by our use of glass steam piping and furnace tubing.



Overall steam condensate test arrangement

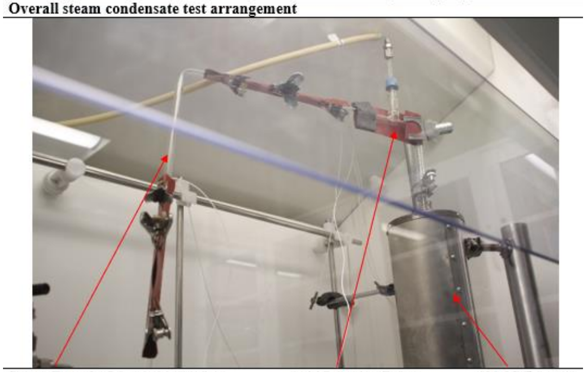


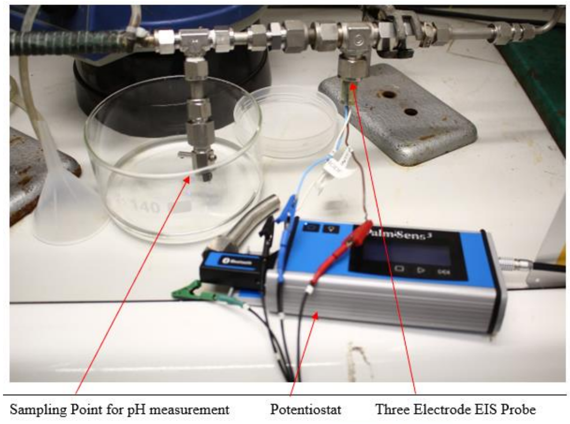
Figure 1: Acid steam condensates test arrangement.

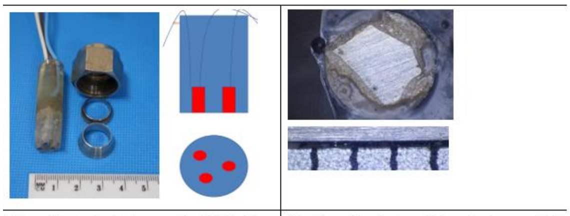
2. TEST RIG AND OPERATION

The test arrangement shown in Figure 1 and Figure 2 featured:

- A boiler to generate clean steam – nitrogen bubbling was used before boiling and while testing for deaeration and as an assist for steam raising. A heated glass steam feed tube to minimise condensing in the feed – use of glass allowed a visual check on the degree of condensation.

- A pump for addition of diluted HCl nitrogen deaerated acid to the steam feed tube just before the furnace.
- A downward slope after the acid feed was used to ensure the acid is transferred to the furnace.
- A glass wool holdup was inserted into the hot entry of the furnace to ensure that all of the injected acid was vaporised.
- A flexible exit from the furnace to a stainless steel test pipe section angled so as to flow over the face of the test electrodes.
- A bottom entry three electrode flush test sample with three small diameter electrodes set in a Casting Araldite.
- A sampling port for pH and conductivity testing. Note that this sampling port was able to take the full flow of generated condensate.
- A cooling coil to ensure total condensation.
- Fluid sampling point just after the EIS test point for pH and conductivity measurement.
- A vent and drain to atmosphere to allow removal of the added nitrogen gas and avoid steam pocket formation – each vent was fitted with a bubbler.





Three Electrode design used for EIS testing

Working Electrode with sealamt appplied over the edges before final polish (mm scale)

Figure 2: Testing of K55 casing material. A Palm-Sense potentiostat was used with a three electrode EIS arrangement. Made using rod material mounted in a casing Araldite with exposed ends polished flush.

3. CASING STEELS TESTED

The key chemical elements in the tested casing steels, K55, an existing TN95Cr13S and newly developed materials for both oil and gas and geothermal applications, TN125Cr13U and 17Cr are as given in Table 1, as previously reported by Yanigisawa et al., 2021 and Sato et al., 2021.

Table 1: The chemical composition of materials and Cr equivalent From Yanagisawa et al., 2021 and Sato et al., 2021

Material	Cr %	Mo %	Cr equivalent	
			min	max
TN95Cr13S	13 %	2.0 %	13.2	15.5
TN125Cr13U	13 %	3.0 %	13.5	16.2
17Cr	17 %	2.5 %	18.6	21.4
TenarisNKK Sample Code		Alloy Designation		Abbreviad Name
GN1-3		API K55		K55
GN4-3		TN110Cr13S		Cr13S
GN13		TN125Cr13U		Cr13U
GN14		TN125Cr17		Cr17 and 17Cr

4. K55 AND NEW CASING STEELS CORROSION RATE MEASUREMENTS

The three electrode test sample arrangement and setup are illustrated in Figure 2:

- AISI 316 stainless steel in Swagelok^{TM} materials were used for the condensate contact components with a Test cell located in a 316 T.
- A Palm-Sens portable potentistat was used for the corrosion rate measurements.
- The pH range was obtained by injection of pH 2.0 HCl acid into the flowing steam phase which was then heated to 400 °C before being allowed to condense. The condensate pH ranged from that obtained with clean steam (pH 6.1 at 25 °C) to the maximum acidity achievable with pH 2.0 feed acid (pH 2.2 at 25 °C).
- A measure of the steam condensate conductivity indicated a low conductivity was occurring, even for the acidified condensate as the amount of chloride added was small. The work was therefore completed using the Electrochemical Impedance Spectroscopy (EIS) method, with a small electrode area.

- The use of sealant around the edges of the EIS working electrode ensured no contribution from crevice corrosion.
- A Palm-Sens portable potentiostat was used for the EIS measurements, using a frequency range from 50,000 Hz to 5 Hz with higher corrosion rates requiring measurements to 1 Hz as summarised for the K55 casing steel in Figure 3.
- In this work, all of the EIS results have been normalised to a lower frequency of 1 Hz by extrapolation of results obtained at and above 5 Hz to the preferred frequency of 1 Hz.
- Lower frequencies would require extra time and were not considered warranted for this work.
- All of the reported EIS data has been compensated for solution resistance by subtracting the solution resistance, Rs, from the circuit resistance, Rct, to give a true polarisation resistance, Rp.
- For the EIS work, the three electrode probes were coated with acrylic polish to fill the crevice between the electrodes and the casting araldite and then the dried acrylic was polished using 500 grit wet paper, just enough to remove the acrylic and expose the full face of all three electrodes with a controlled surface finish.

The K55 corrosion test completed using a stock acid solution of pH 2.0 and using the EIS method with the final arrangement as shown in Figure 1 and Figure 2. At this concentration of injection acid, the pH proved more difficult to control in the range of 6 to 3 than initial tests using pH 3 HCl acid for injection, however the pH 2 acid was used for all subsequent testing. The K55 and TN110Cr13S EIS measured corrosion rate results are summarised in Figure 3 and results for TN125Cr13U and TN125Cr17 casing steels are summarised in Figure 4.

The pH limits for casing steels in HCl contaminated steam condensate at 97 °C can be inferred from Figure 3 and Figure 4 as follows:

- K55 lower limit at pH 4.0.
- TN110Cr13S lower limit at pH 3.5.
- TN125Cr13U lower limit at pH 3.5.
- TN125Cr17 lower limit at pH 2.0.

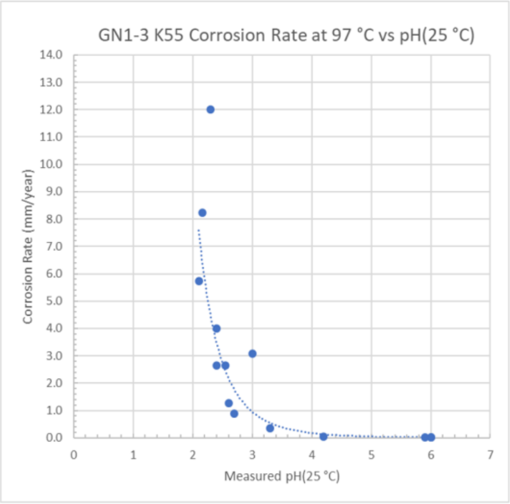
5. COMPARISON WITH FIELD EXPERIENCE

It is useful to compare the lower temperature laboratory test results with published field corrosion rates in acid steam condensate. Laradello data from Giorgio et al, 2000 have been summarised as a function of chloride in the steam condensate as described by an equation,

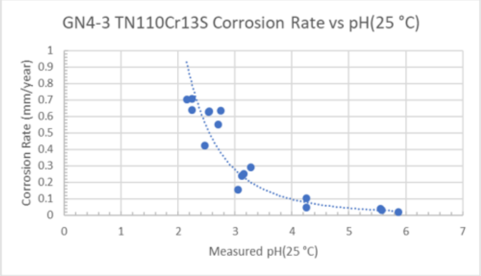
$$CR(\text{mm/year}) = 0.35^{*}\ [\text{Cl mg/kg}]$$

The corrosion rate (CR) in the field test was approximately three times the rate in the lower temperature laboratory test. The results have been plotted in Figure 5 for comparison with results obtained in this work.

The test results for Geysers, from Gallup and Farrison, 1998, in wellhead applications were of the order of four to fifteen times higher than those of carbon steel at similar pH and higher temperature than in the laboratory tests of K55, suggesting a higher corrosion rate of the order of 10 times in the field application at higher temperatures. The new alloys having higher Cr equivalent than a typical 410 alloy also showed a similar 10 times lower corrosion rate in the laboratory tests at similar pH, see Table 2.

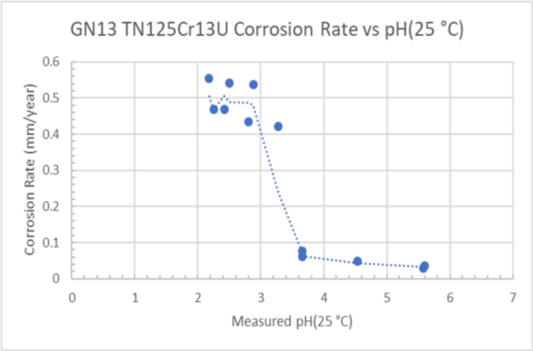


EIS Measured Corrosion Rate for K55 Casing Steel. Power law trendline shown.

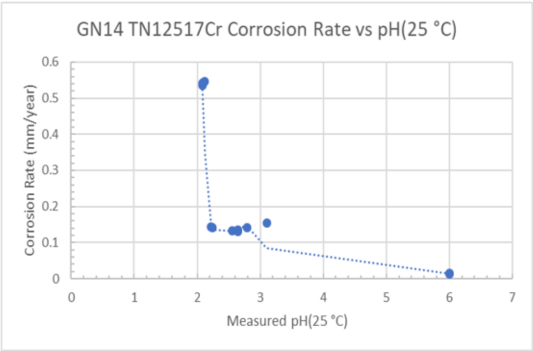


EIS Measured Corrosion Rate for TN110Cr13S Casing Steel. Power law trendline shown.

Figure 3: EIS Corrosion Rate results for K55 and TN110Cr13S casing steels. Solution resistance compensated data.



EIS Measured Corrosion Rate for TN125Cr13U Casing Steel. Moving average trendline shown.



EIS Measured Corrosion Rate for TN125Cr17 Casing Steel. Moving average trendline shown.

Figure 4: EIS Corrosion Rate results for TN125Cr13U and TN125Cr17 casing steels. Solution resistance compensated data.

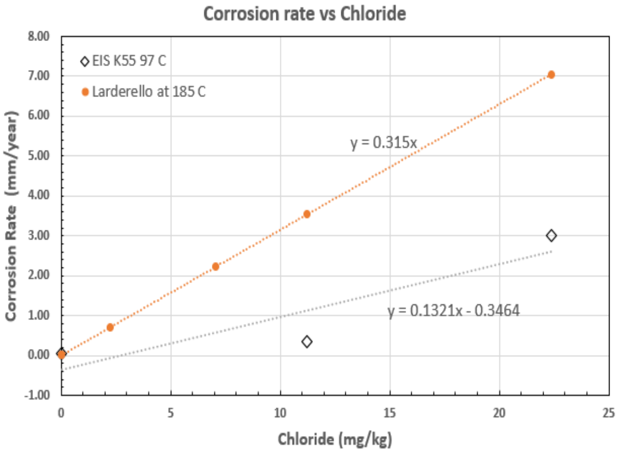


Figure 5: Comparison of acid steam condensate corrosion rates for K55 in laboratory testing using EIS (this work) and for Carbon Steel field testing (Giorgio et al., 2000).

Table 2: Corrosion rates for materials exposed in Geysers wells producing HCl gas contaminated steam vs CR(EIS) of casing steels.

Material	Geysers Liner Well A (Top of Liner)	Geysers well B (coupons)	Geysers Well C (coupons)	This work pH 3 at 97 °C
	CR (Pitting)	CR (Pitting)	CR (Pitting)	CR (EIS)
K55	7.6 (300)	1.8 (3.0)	0.5 (0)	0.05
9Cr 1Mo	3.8 (150)	2 (4)	0.2 (2.2)	n/a
410 St.St.	n/a	0.5 (12)	0.3 (1.5)	n/a
Cr13S (variation to 410)	n/a	n/a	n/a	0.08
Cr13U (variation to 410)	n/a	n/a	n/a	0.08
316L (useful comparison with 17 Cr)	n/a	0.1 (1)	<0.1 (1.5)	n/a
17Cr	n/a	n/a	n/a	0.08

Notes: CR and CR(EIS) = Uniform corrosion in mm/year (some pitting was expected to have occurred but was not quantified). Data from Gallup and Farrison, 1998 (Localised Corrosion (Pitting) reported in mm/year).

Note that if the laboratory results at pH 2 were used, the difference for carbon steel/K55 would be much less.

6. CONCLUSION

The following conclusions have been drawn:

The pH limits identified for casing steels in HCl contaminated steam condensate at 97 °C were:

- K55 lower limit at pH 4.0.
- TN110Cr13S lower limit at pH 3.5.
- TN125Cr13U lower limit at pH 3.5.
- TN125Cr17 lower limit at pH 2.0.

The corrosion rates measured in the laboratory can be compared to those obtained in field tests at the same pH (based on steam condensate chloride content):

- K55 corrosion rates were lower in the 97 °C laboratory test than in the 180 °C field tests at Larderello at similar pH (based on chloride in steam condensate).

- TN110Cr13S, TN125Cr13U and TN125Cr17 alloys showed similar corrosion rates in the laboratory tests to comparable alloys tested in Geysers contaminated steam at 180 °C in field tests although the comparable alloys experienced pitting corrosion in the field tests.

ACKNOWLEDGEMENTS

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REFERENCES

Gallup D.L. and Farrison, J.R.: Testing of Materials in Corrosive Wells at The Geysers Geothermal Field, Proceedings 20th Geothermal Workshop (1998)

Giorgio, M. et al.: Corrosion Rates in The Dew-Point Zone of Superheated Steam, Proceedings World Geothermal Congress, Tohoku, Japan (2000).

Sato, M. et al.: Laboratory Corrosion Testing of Casing Steels in Acidic Brine and the Field Testing at Kakkonda Geothermal Field, Proceedings World Geothermal Congress 2020+1, Reykjavik, Iceland, (2021)

Yanagisawa, N. et al. : Corrosion Rate Estimation Of Cr Casing Steels At High Temperature Acid Conditions, Proceedings 43rd New Zealand Geothermal Workshop, Wellington, New Zealand (2021).