Corrosion Challenges & Material Testing in Superhot Geothermal Environments

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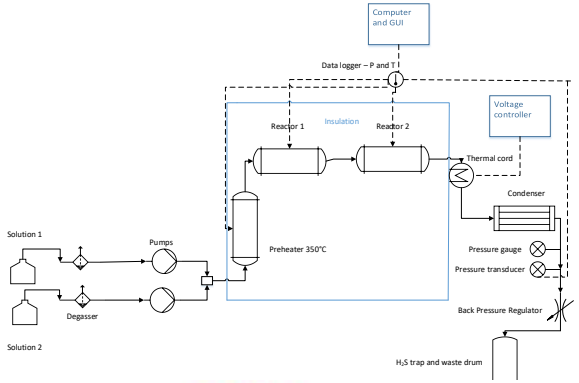
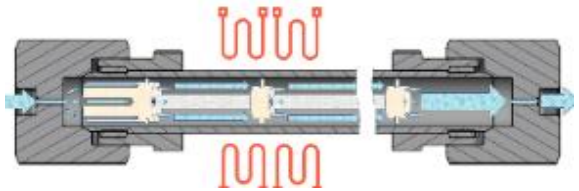
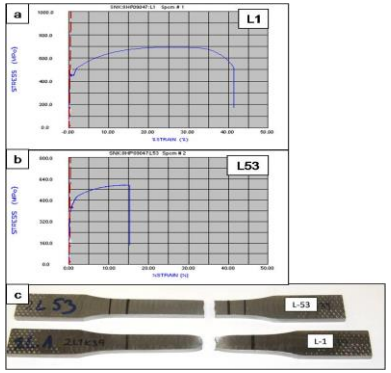
Corrosion Testing in-situ in Geothermal Environment

Corrosion Laboratory Testing HTHP FT Reactors & autoclave

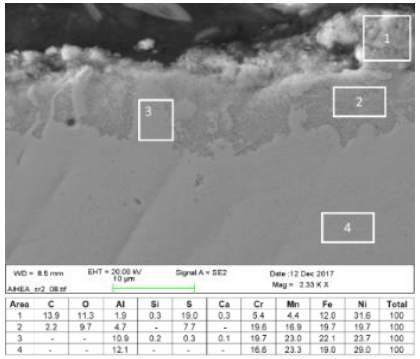




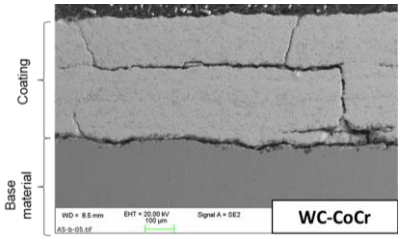
Mechanical Testing

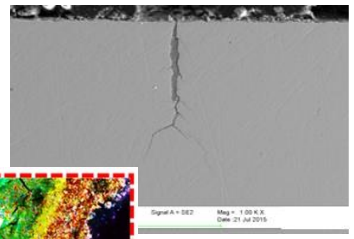


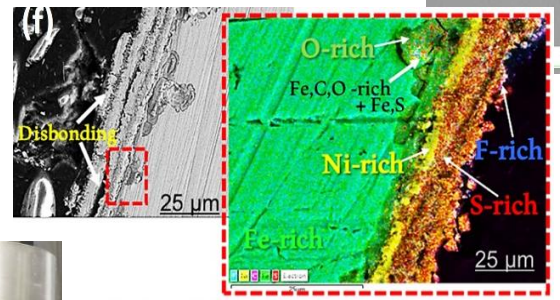
Microstructural & Chemical Analysis (SEM/EDS/EPMA)



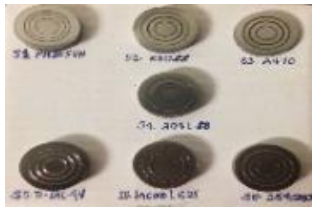
Area	C	O	Al	Si	S	Ca	Cr	Mn	Fe	Ni	Total
1	13.9	11.3	1.9	0.3	19.0	0.3	5.4	4.4	12.0	31.6	100
2	2.2	9.7	4.7	-	7.7	-	19.6	16.9	19.7	19.7	100
3	-	-	10.9	0.2	0.3	0.1	19.7	23.0	22.1	23.7	100
4	-	-	12.1	-	-	-	16.6	23.3	19.0	29.0	100

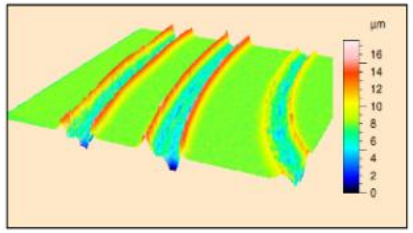




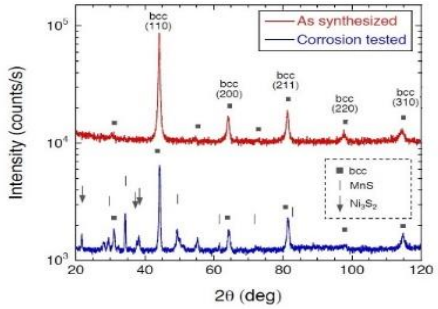


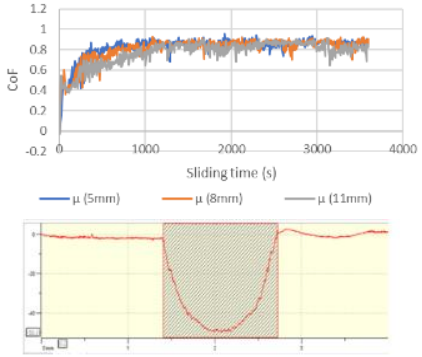
Tribological Testing





XRD analysis





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Superhot Geothermal Systems

Introduction

- Interest has increased substantially recently in utilizing geothermal energy from superhot or supercritical geothermal resources
- Most projects focus on drilling deeper than conventional geothermal wells (>3 km, >350°C) to obtain superhot geothermal fluid (h >2.086 MJ kg^{-1})
  - *Iceland Deep Drilling project* (IDDP) in Iceland, *GeoMex* project in Mexico, *Japan Beyond Brittle Project* (JBBP) in Japan, *Geothermal: The Next Generation project* in New-Zealand, *Newberry Deep Drilling Project* (NDDP) and *FORGE* project in the USA
- Goal to obtain higher power output per well with increased enthalpy of supercritical fluids that will enable increased productivity

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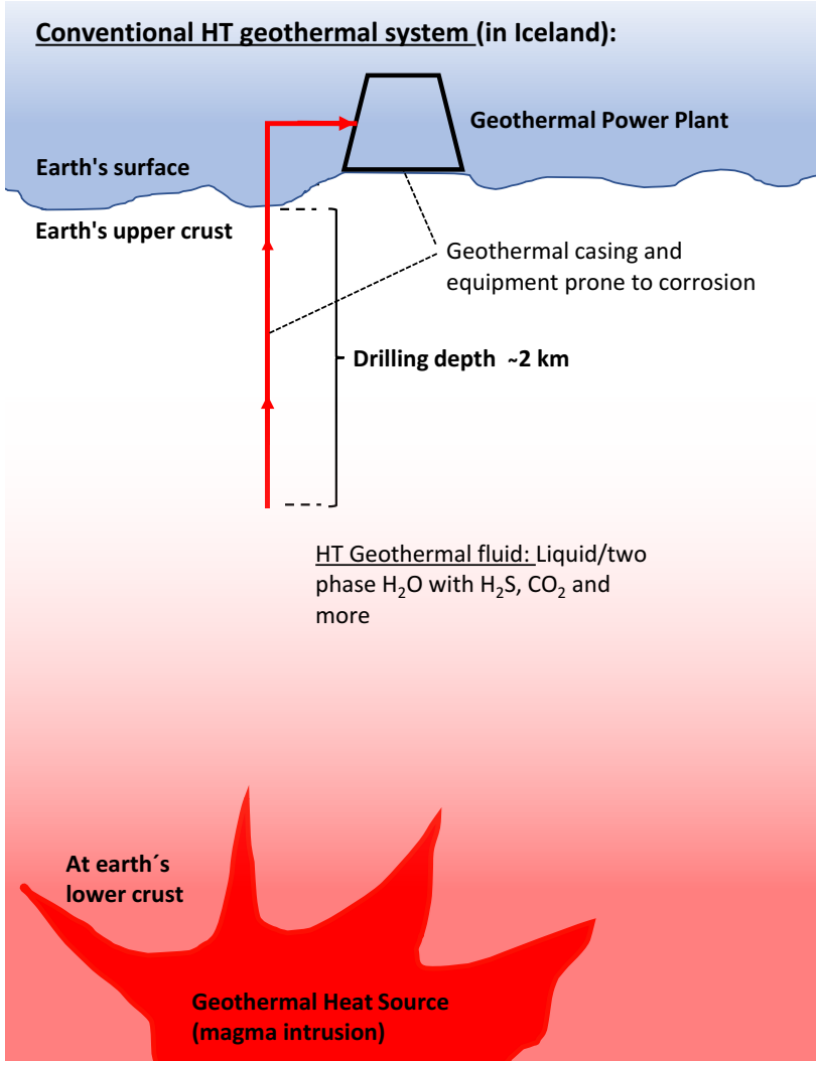
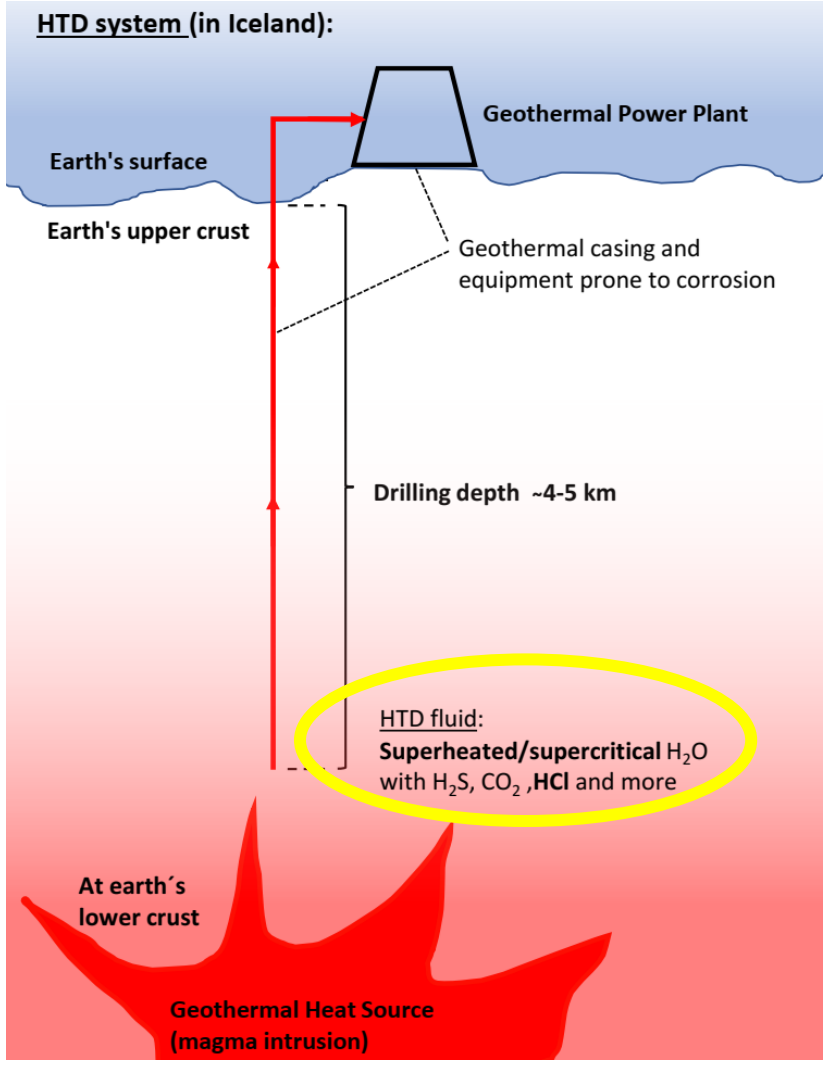
Conventional HT vs. SH Geothermal System

HT geothermal system



Increasing Temperature

Superhot geothermal system



Superhot and Supercritical Geothermal wells

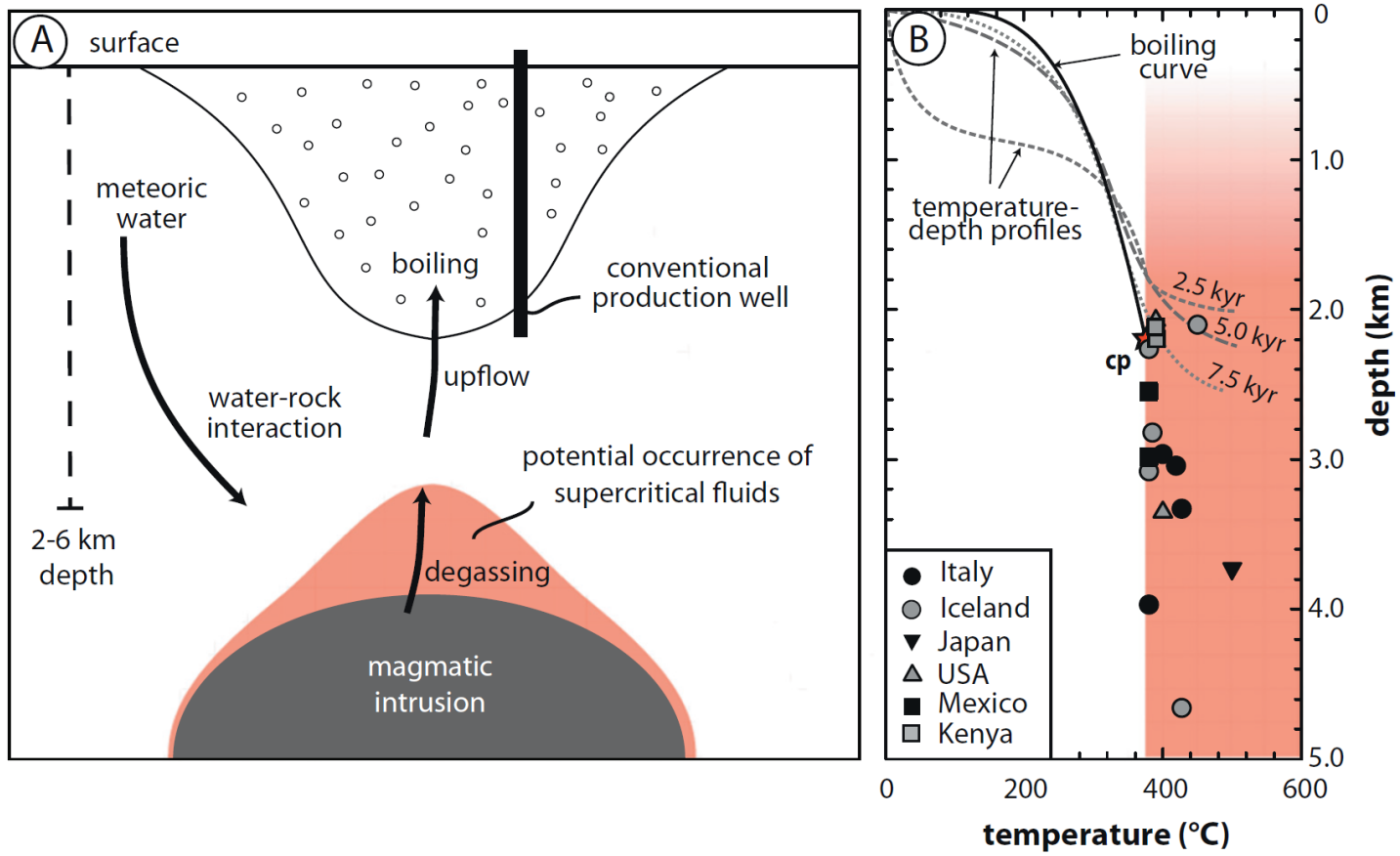


Fig. 1. Main characteristics of a volcanic geothermal system. (A) Conceptual model of a volcanic geothermal system showing fluid flow paths (black arrows) and the zone of heat convection where supercritical conditions may appear (red area) between the heat source (magmatic intrusion) and the circulating geothermal fluid. Depressurization boiling occurs near the surface (after Arnórsson et al., 2007; Scott et al., 2016). Conventional production wells do not commonly reach the supercritical zone. (B) The boiling curve of water. Dashed lines indicate temperature-depth profiles above magmatic intrusions at selected times (after Hayba and Ingebritsen, 1997). The red shaded area shows fluids having temperature exceeding the critical temperature of water (T_c > 374 °C). Wells with reported temperatures above the critical temperature of the water are also shown (see Reinsch et al., 2017).

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Superhot and Supercritical Geothermal wells

Comparison of predicted supercritical fluid composition from geochemical modeling and laboratory experiments and observed natural supercritical fluid composition.

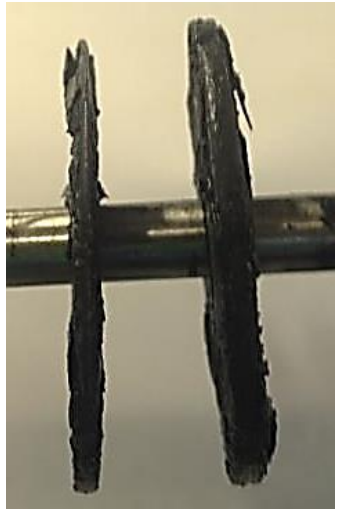
		low-NaCl fluids				NaCl-fluids					
		Experiments[a]	Modeling[a]	Krafla[b]	Menengai[c]	Experiments[a]	Modeling[a]	Kakkonda[d]	The Geysers[e]	Los Humeros[f]	Larderello[g]
				Iceland	Kenya			Japan	USA	Mexico	Italy
T	°C			440	~290			~500 °C	~400 °C	~400 °C	~430 °C
SiO_2	ppm	1.0–2.9	33–148	6.0	–	0.7–2.0	2.3–8.7		<1–4.1	22.0	–
B	ppm	0.3–1.4	0.24–1.5	1.41	–	1.4–2.9	1.4–3.3	~1700		958	~20–90
Na	ppm	1.0–1.6	45–130	0.51	–	2.9–9.3	0.05–3.7	~72,000	<0.1–0.15	0.58	–
K	ppm	0.2–0.4	1.6–21	0.12	–	0.08–0.3	0.01–1.8	~47,000	<0.5	0.36	–
Ca	ppm	0.04–0.1	0.00001–3.40	0.16	–	0.02–0.3	0.004–0.5	~21,000	<0.1–1.3	0.55	–
Mg	ppm	0.02–0.03	<0.00001	0.024	–	0.003–0.3	0.005–0.08	~40	0.005–0.05	0.04	–
Fe	ppm	0.1	0.004–0.025	5.25	–	0.02–3.2	0.02–0.09	~51,000	1	8.21	–
Al	ppm	0.05–0.08	0.00002–0.016	0.054	–	0.03–0.3	1.9–2.2				–
Cl	ppm	2.0–2.7	0.5–0.7	105	–	0.6–490	295–830	~270,000	<1–120	31	<0.01–120
CO_2	ppm	57–61	38–49	1637	27,000–80,000	26–185	23–420		~780–11,200	~32,000	~7000–115,000
SO_4	ppm	0.8–6.5	0.0001–79	32.7	–	1.2–14	37–163	~250	<0.01–10	45	
H_2S	ppm	10–40	54	630	1000–2700	5.5–32	20–54		~100–650	~3700	~90–1500

[a] This study.
[b] IDDP-1 fluid composition based on Heřmanská et al. (2019a) for IDDP-1.
[c] Based on Malimo (2013) and Montegrossi et al. (2015).
[d] Based on data reported by Kasai et al. (1998a). The data have been corrected for mixing with drilling fluid as proposed by Kasai et al. (1998a) taken the mixing ratio of the deep fluid to the non-thermal drilling water to be 69/31.
[e] Based on Truesdell et al. (1989) for vapor only well discharges except for CO_2 and H_2S that is based on the upper and lower quarter of gas data reported by Lowenstern and Janik (2005).
[f] Total discharge for H-43 as reported by Cruz and Tovar (2008) and Diez et al. (2015).
[g] Based on data reported by Ruggieri and Gianelli (1995), Truesdell and Nehring (1978) and Truesdell et al. (1989).

Matylda Heřmanská, Barbara I. Kleine, Andri Stefánsson "Geochemical constraints on supercritical fluids in geothermal systems" Journal of Volcanology and Geothermal Research 394 (2020) 106824

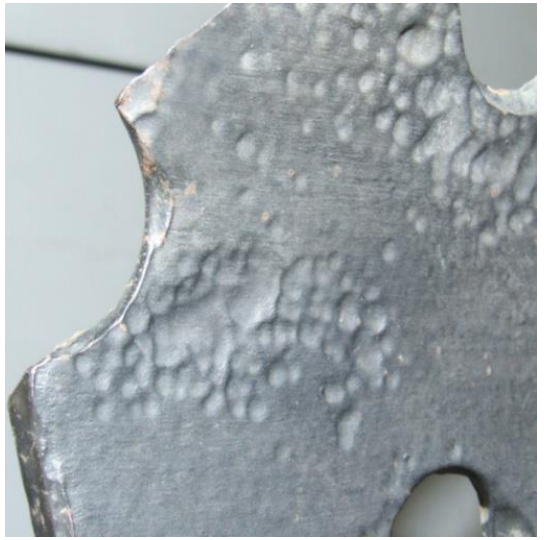
Corrosion in Geothermal Systems

- Materials in direct contact with geothermal fluid can be subjected to corrosion
- Corrosion aggressiveness of geothermal fluid depends on chemical composition and physical characteristics of the fluid and exploitation parameters
  - e.g., H_2S, CO_2, HCl, Cl^-
  - pH level, temperature, flow rate



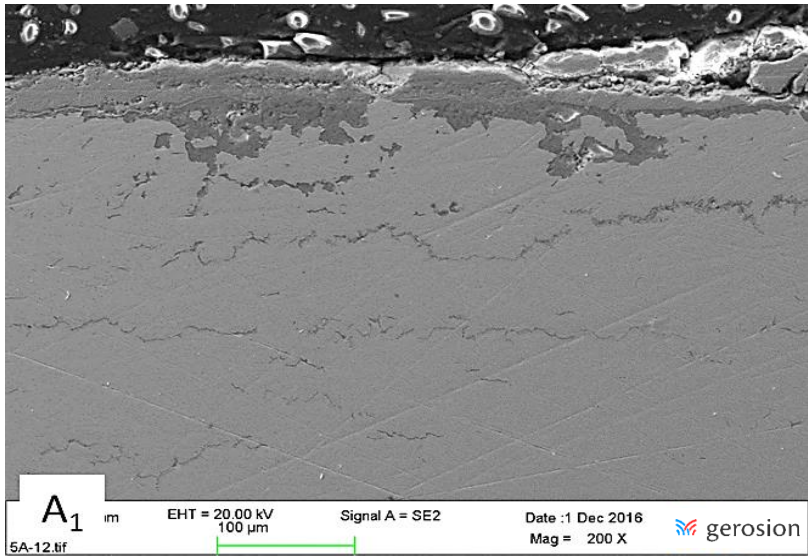
Corrosion in Superhot Geothermal Environment

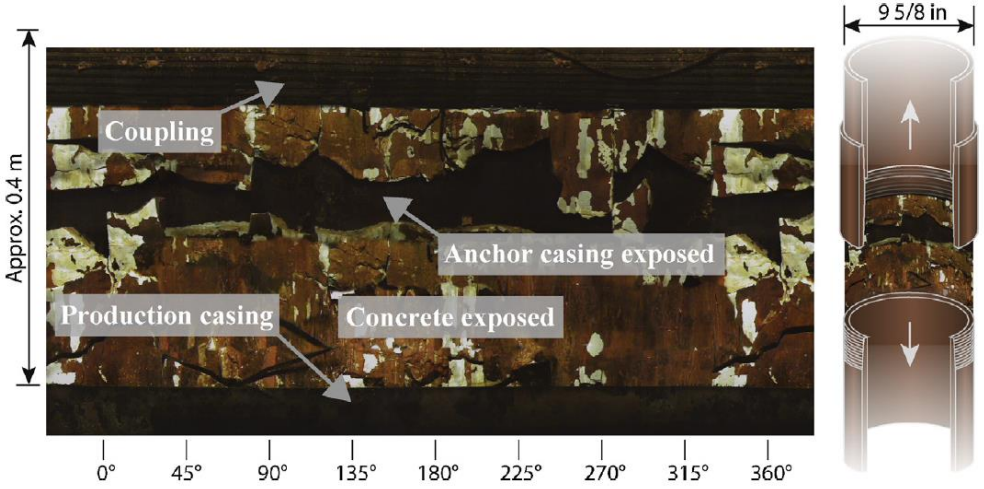
- In vapor dominated geothermal systems (T>300°C) hydrogen chloride (HCl) often present in wells with superheated geothermal steam
- Carbon-steel casings corrode at accelerated rates upon the condensation of the super-heated steam with HCl gas
- Only a few ppm of HCl is needed in the geothermal steam to cause severe corrosion failures
  - Geysers, Larderello, Tiwi, Krafla

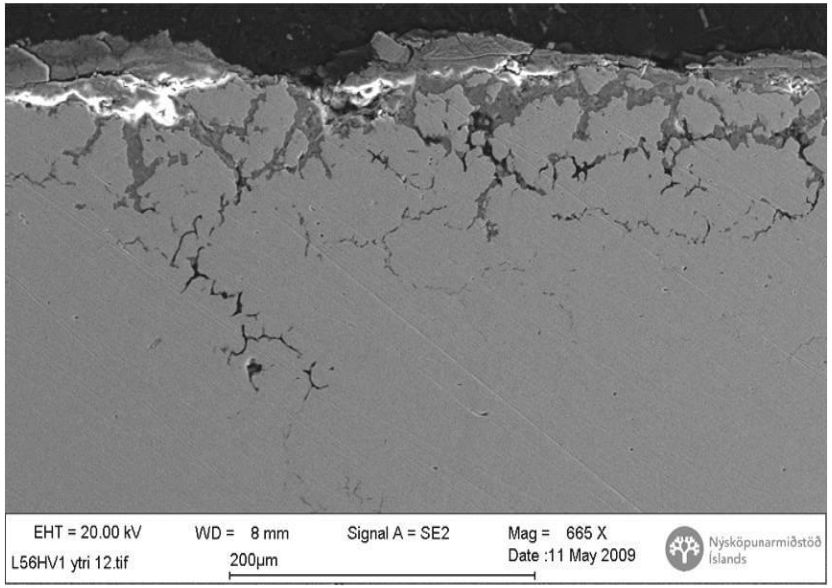


Material Challenges – Superhot Geothermal wells

- Corrosion problems
  - Acid condensate & hydrogen related damages (HE, HTHA)
- High thermally induced stresses and plastic strain causing casing and connection damage and rupture
- Poor cementing promoting casing collapses
- Erosion-Corrosion due to high flow rates







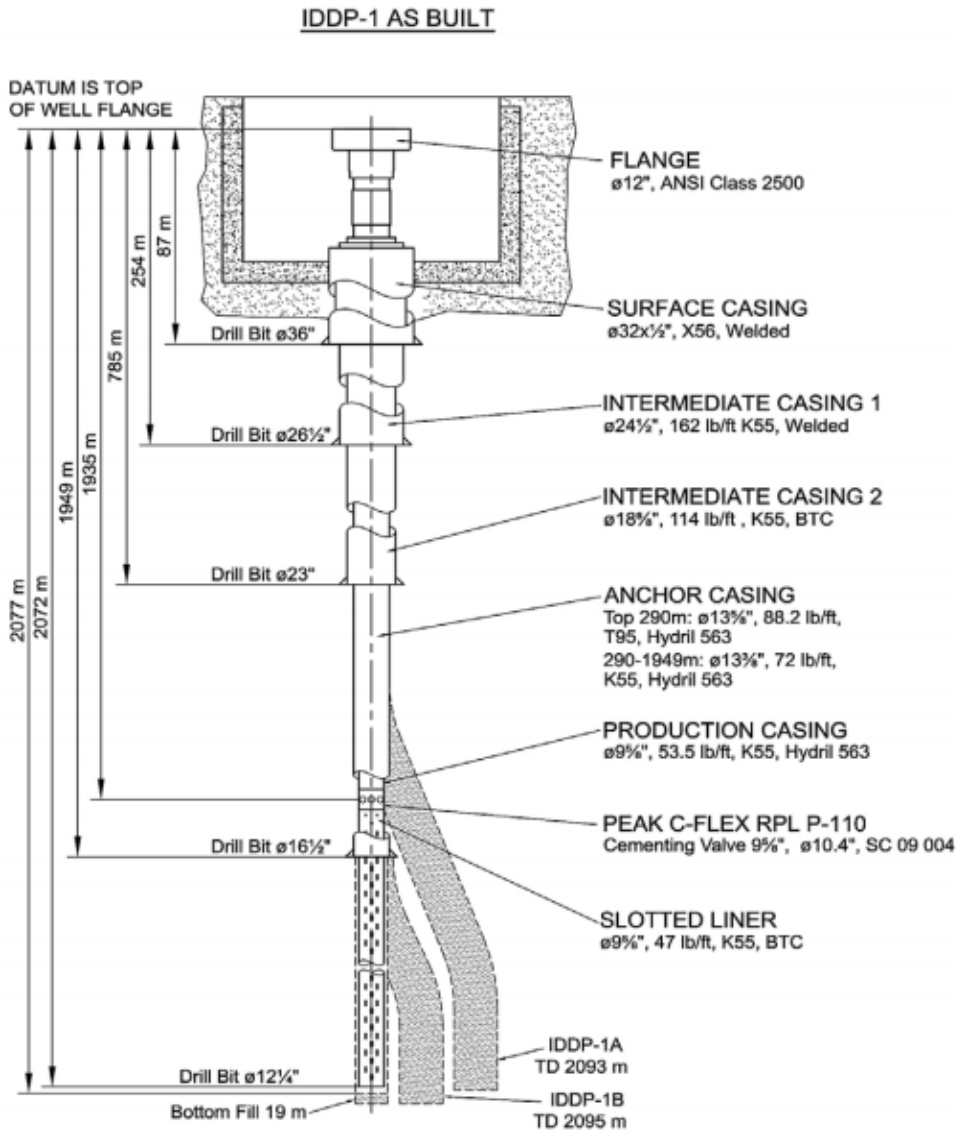
G.S. Kaldal. M.Þ. Jonsson. H. Palsson. S.N. Karlsdottir. “Structural modeling of the casings in the IDDP-1 well: Load history analysis.” *Geothermics*. 62 (2016)1-11

IDDP wells

IDDP-1 well

Hottest producing well in the world

- ***450°C and 140 bar at wellhead & HCl, HF, H_2S, CO_2 & pH ≈ 3***
- ***Dissolved silica and silica particles***



Thorhallsson, S., Palsson, B., Hólmgeirsson, S., Ingason, K., Matthíasson, M., Bóasson, H. Á., & Sverrisson, H. "Well design and drilling plans of the Iceland Deep Drilling Project (IDDP)". In Proceedings world geothermal congress, (2010).

IDDP-1 well

IDDP-1 During initial flow tests

...and then producing superheated steam!

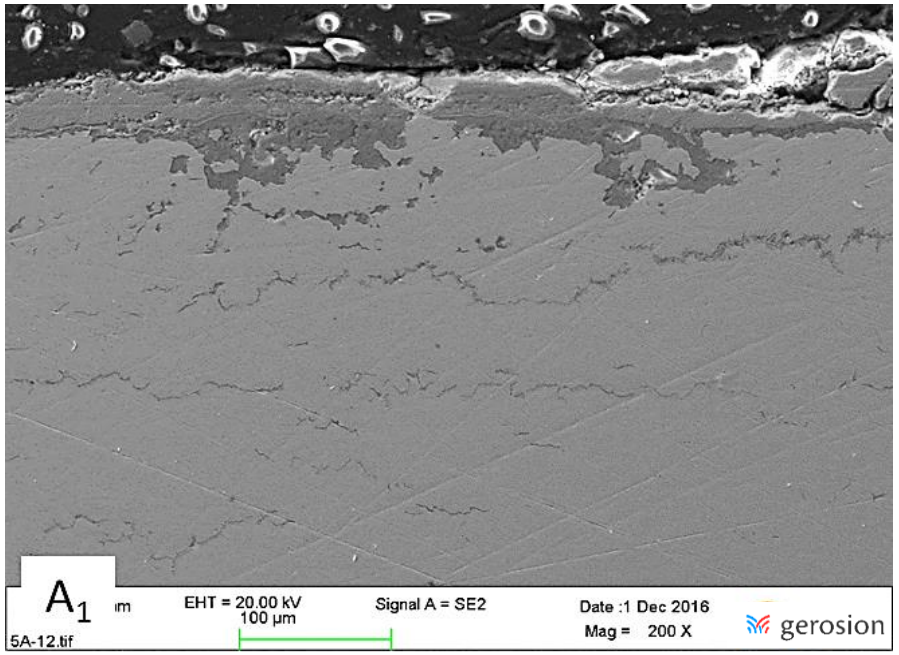
IDDP wells

IDDP-1

- Corrosion damages due to hydrogen effects due to the chemical composition of the steam (H_2S, HCl)
- Micro-cracks due to High Temperature Hydrogen Attack (HTHA)
- At high temperatures (above 200 °C) in hydrogen rich environment

$$8H^+ + C + Fe_3C = 2CH_4 + 3Fe$$

- CH_4 too large to diffuse away and excessive pressure develops within the metal structure causing rupture along the crystalline boundaries



IDDP wells

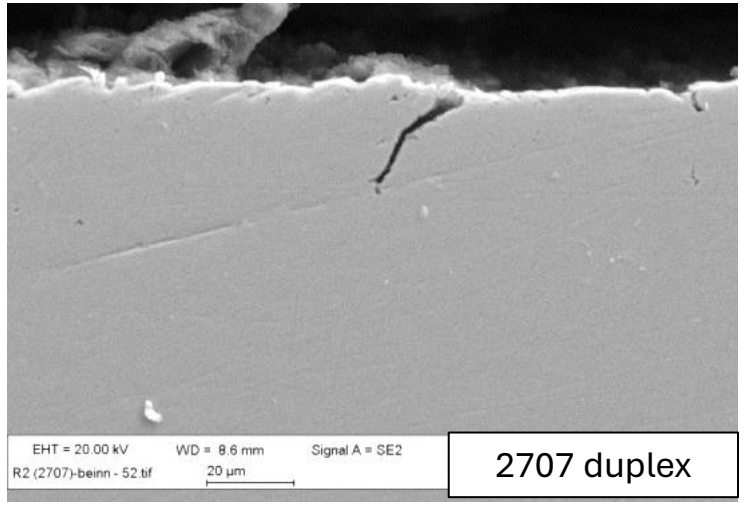
IDDP-2 – Casing damages

- Deepening of existing well in Reykjanes geothermal field (2017)
  - 4650 m depth, 427˚C and 340 bar at bottom
- Damage discovered (opening) in the casing at 2300m depth
  - decrease in strength of the cement/non-existence of the cement causing increased stress and failure
  - corrosion damages of cold-water injection drill string, likely also for perforated liner close to bottom

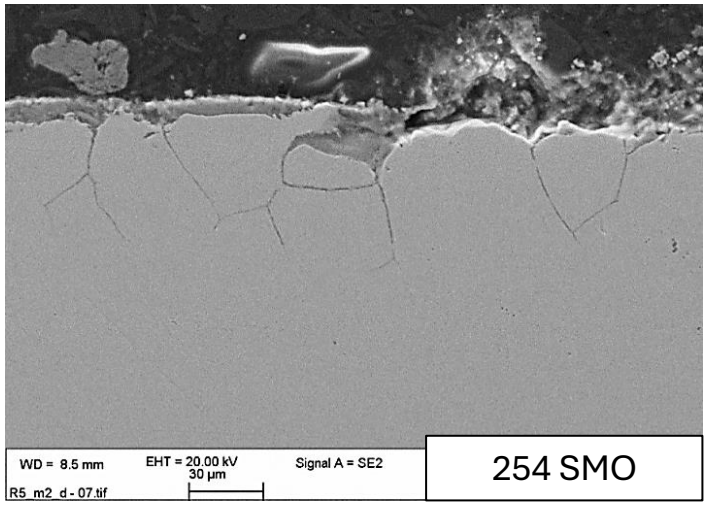
- Any fluid travelling up the IDDP-2 well likely disappears into the opening in the formation at this location and prevents pressure build up and discharge of the well

IDDP-1: In-situ corrosion tests

- Large amount of silica scaling covered the test samples and clogged pipes
- Stress Corrosion Cracking (SCC) of 254 SMO in heat-exchanger experiment
- SCC of low alloyed stainless steel (304 & 316)
- Overall best performance Ni and Ti alloys



2707 duplex



254 SMO

S.N. Karlsdottir, Thorbjornsson, I.O., Ragnarsdottir, K.R., Moller, A., Einarsson, A. “On-site erosion–corrosion testing in superheated geothermal steam.” Geothermics, [51], 170-181, (2014).
S.N. Karlsdottir, K.R. Ragnarsdottir, I.O. Thorbjornsson, A. Einarsson. *“Corrosion testing in superheated geothermal steam in Iceland,”* Geothermics, [53], 281-290, (2015).

HTHP Autoclave Corrosion Laboratory

Simulating Superhot Geothermal Environment

The HPHT corrosion laboratory

The autoclave (middle), gas filling station (right) and H_2S capture system (left)

The autoclave with the lid opened before installation of test samples in the sample holder

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HTHP Autoclave Corrosion Testing

- Up to 500°C and 300 bar
- Test duration: 7 days includes heating and cooling time

Test nº	Phases	Pressure	Temperature	CO_2 content	H_2S content	NaCl
1, 2, & 3	Liquid + Steam	165 bar	350 °C	5000 ppm	500 ppm	0.0025 mol/L
4	Superheated	148 bar	400 °C	20 000 ppm	500 ppm	0.0025 mol/L
5	Superheated	167 bar	450 °C	20 000 ppm	500 ppm	0.0025 mol/L
6	Superheated	167 bar	400 °C	20 000 ppm	500 ppm	0.0025 mol/L

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Metal Casing Materials

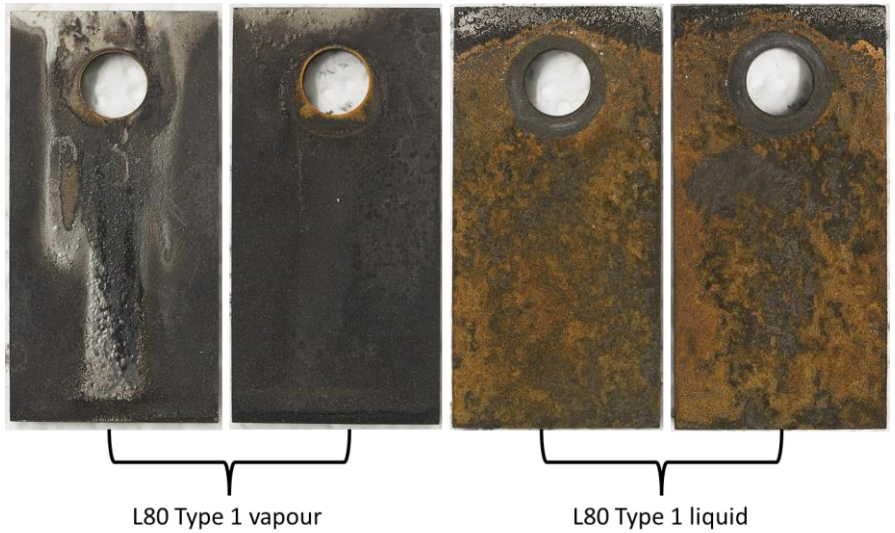
- Steel and CRA casing types tested in HTHP autoclave in superhot conditions (340/400/450°C, 165 bar)
- Evaluation of materials performance:
  - Corrosion damages (cracks, pits) with SEM/EDS
  - Corrosion rate (CR) calculations (mm/year)
  - Corrosion & scaling products (SEM/EDS/XRD)

Material	Grade/UNS Number
Carbon Steel	API L80
Stainless Steel	API L80-13Cr
Nickel alloy C276	N10276
Nickel alloy 2550	N06255
Titanium alloy Ti-475	Ti-0.4Ni-3.6Mo-0.75Zr

Results

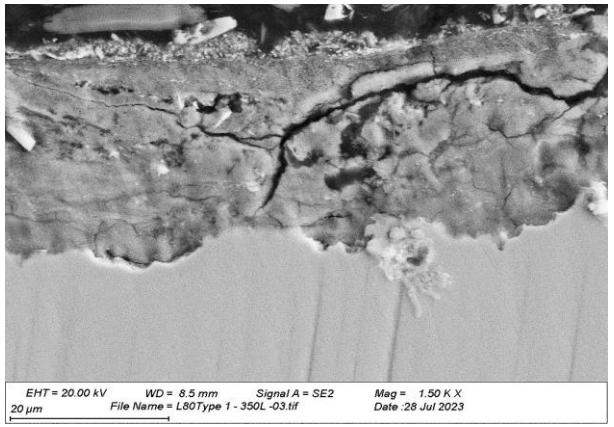
L80-Carbon Steel
Microstructural analysis

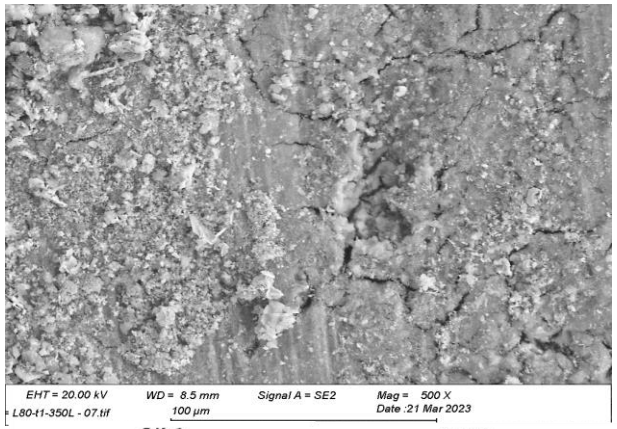
- Carbon steel prone to uniform and localized corrosion damage
- Iron oxide outer layer, sulphide rich sublayer and Cl rich pits

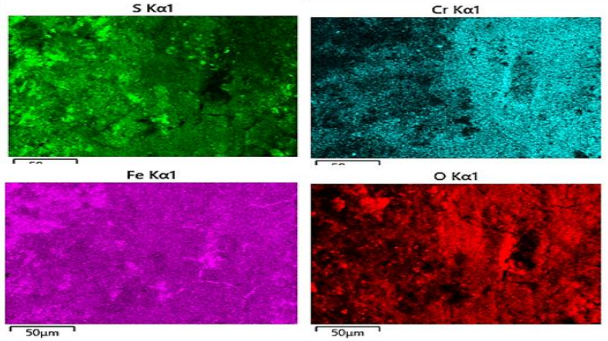


350°C, 165 bar

Liquid



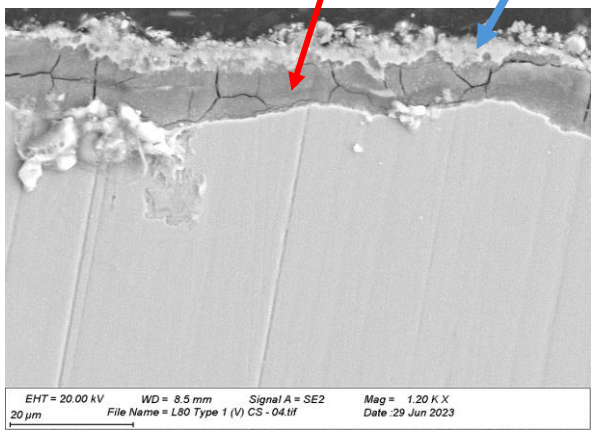


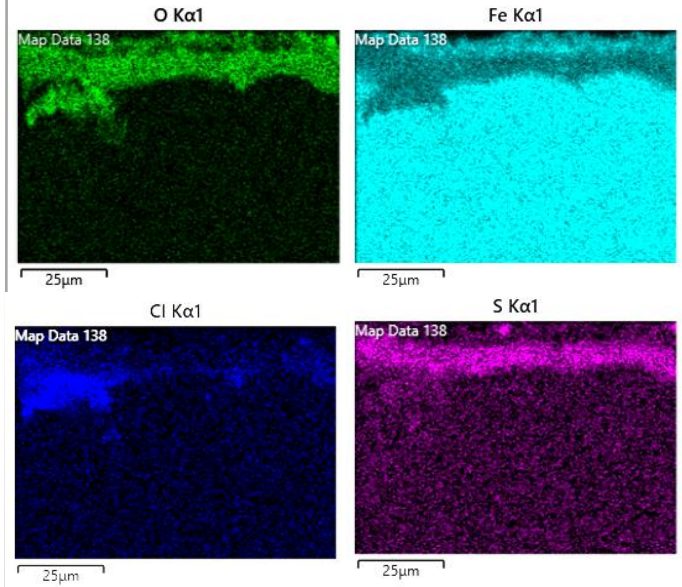


Vapor

S-rich

O-rich

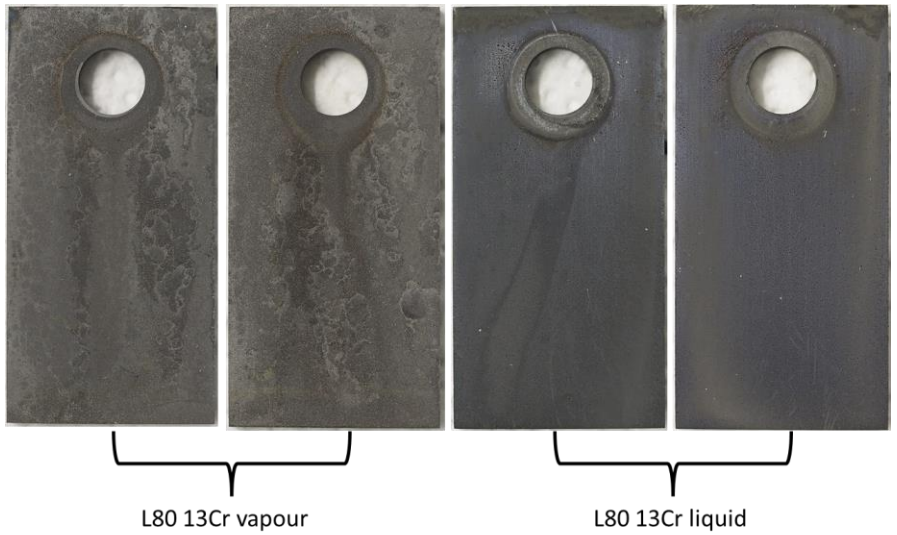




Results

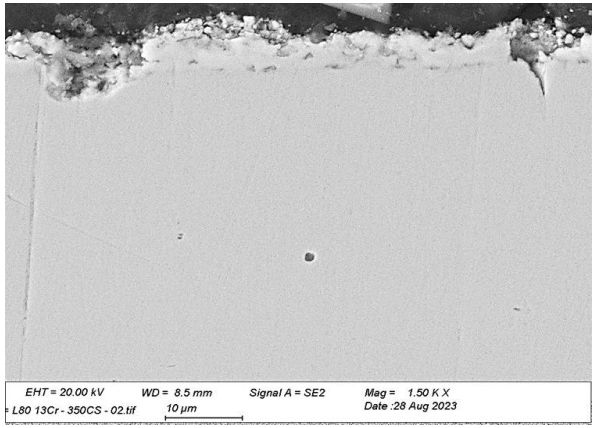
L80-13Cr Stainless steel Microstructural analysis

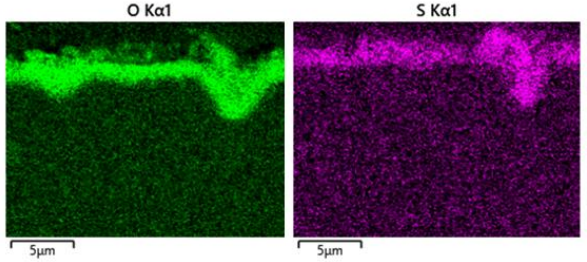
- Pits and uniform corrosion
- Iron oxide rich layer with iron sulfide particles

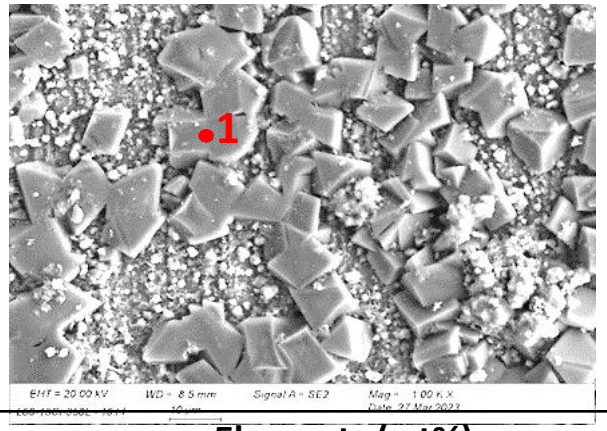


350°C, 165 bar

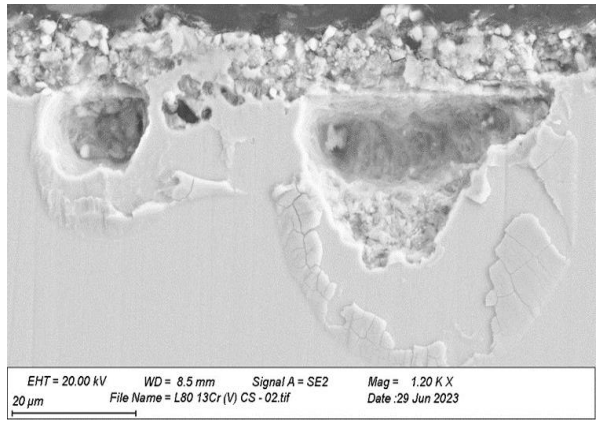
Liquid

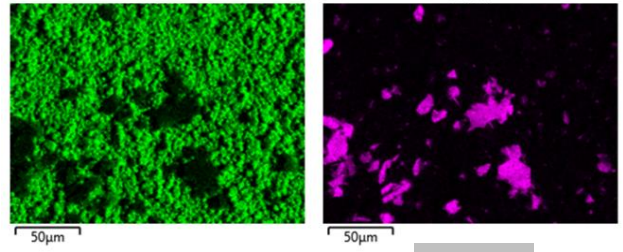


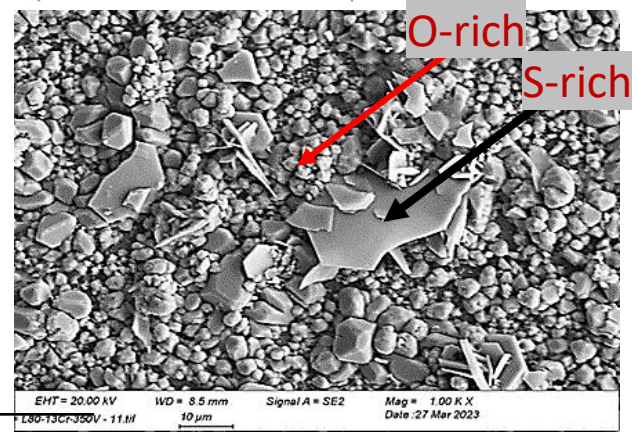




Vapor





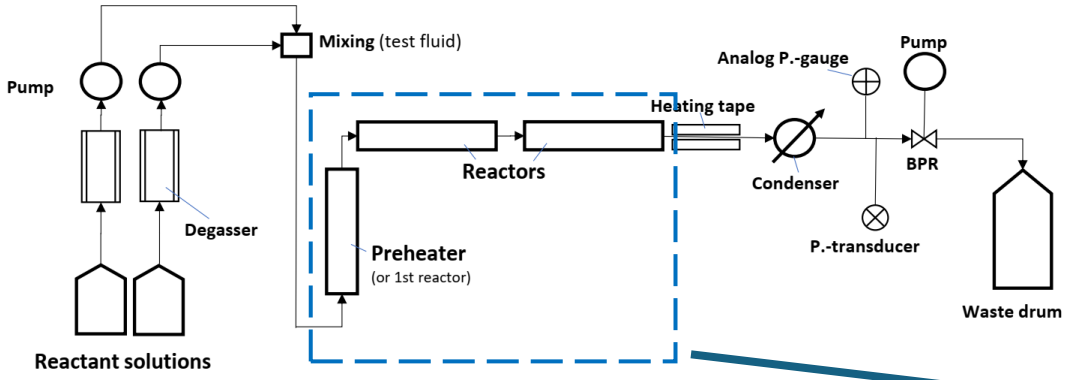


Elements (wt%)

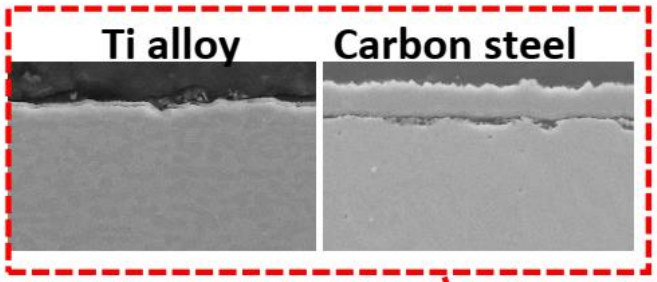
Location	C	O	Cr	Mn	Fe
1	13.93	38.06	1.04	9.37	37.06

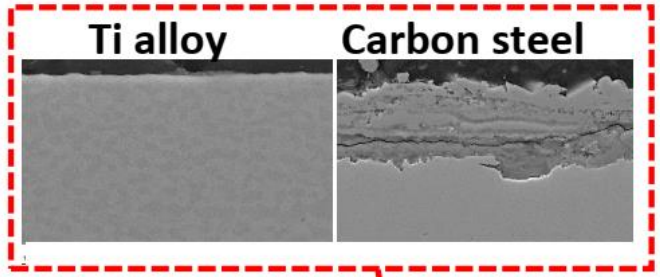
Corrosion Research: Testing in SH geothermal steam

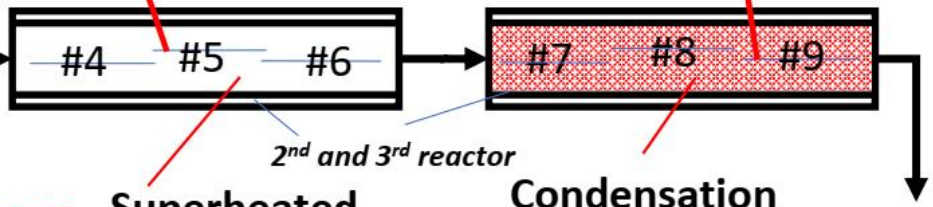
350°C, ~ 13 bar



Ti-745 (Ti-0.4Ni-3.6Mo-0.75Zr),

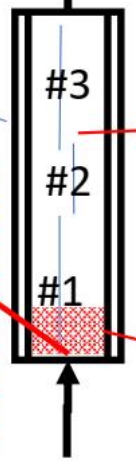






Preheater/1st reactor

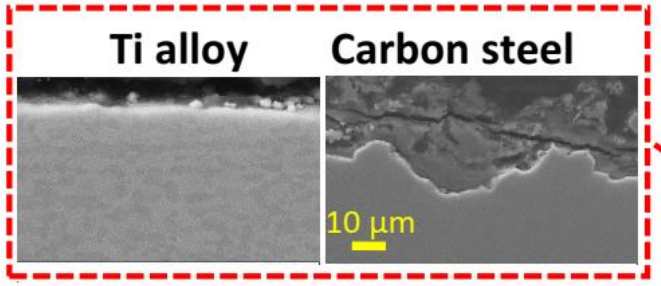
2nd and 3rd reactor



Superheated state

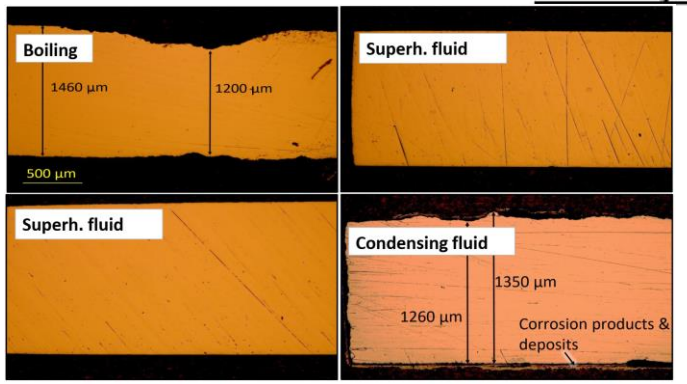
Condensation state

Outlet flow



Boiling state

Inlet flow

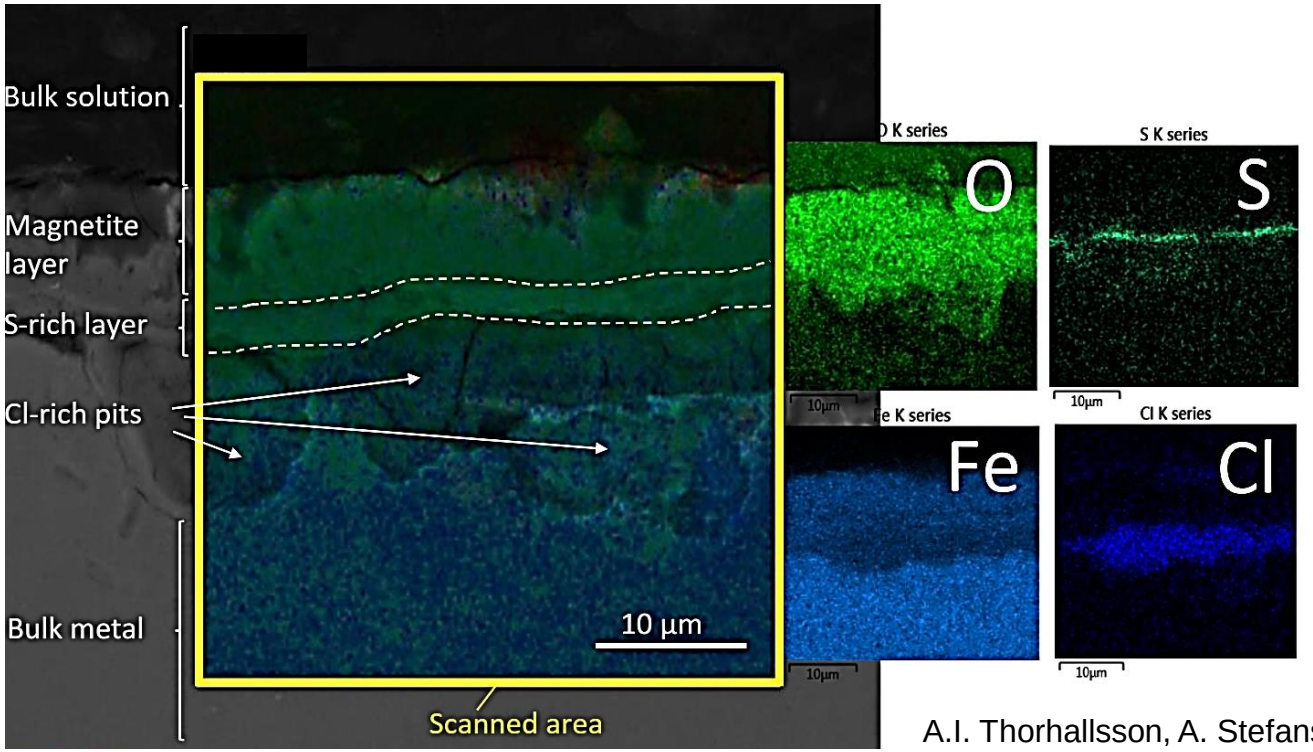


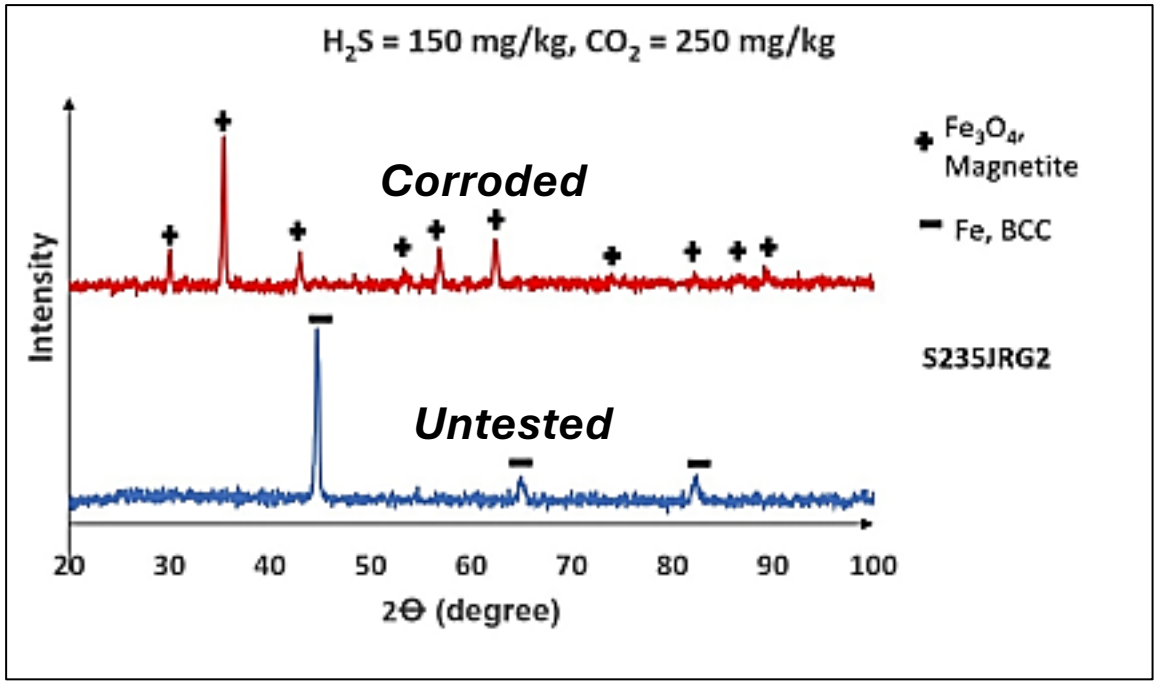
A.I. Thorhallsson, S.N. Karlsdottir, Corrosion Behaviour of Titanium Alloy and Carbon Steel in a High-Temperature, Single and Mixed-Phase, Simulated Geothermal Environment Containing H_2S, CO_2 and HCl, Corros. Mater. Degrad. 2 (2021) 190–209. https://doi.org/10.3390/cmd2020011.

Corrosion Research: Testing in SH geothermal steam

- Carbon steel prone to localized corrosion damage, not the CRAs
- Magnetite (Fe_3O_4) superficial layer, sulphide rich sublayer and Cl rich pits

Carbon steel corrosion tested – cross-section

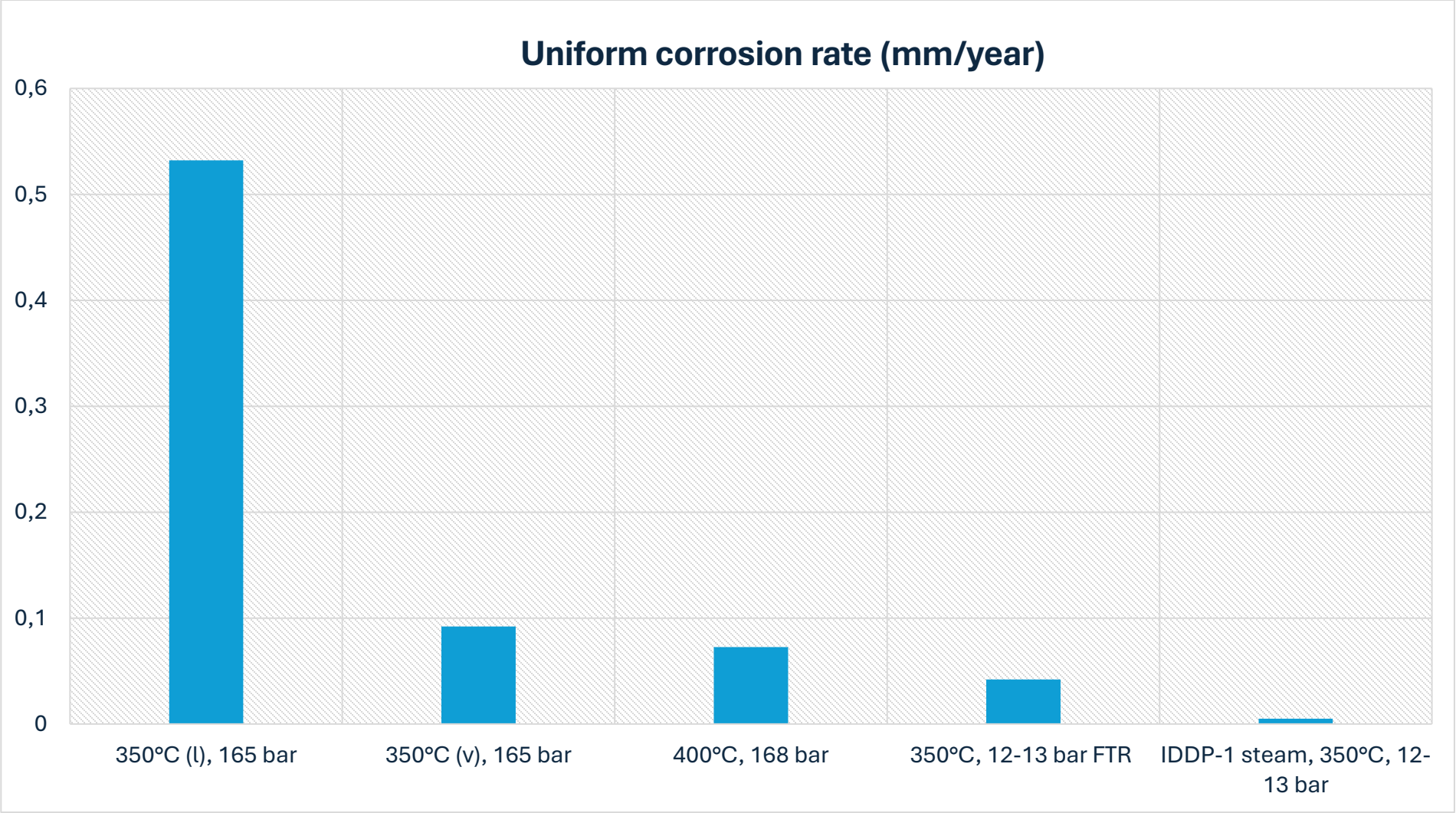




Carbon steel – XRD analysis

A.I. Thorhallsson, A. Stefansson, D. Kovalov, S.N. Karlsdottir, Corrosion testing of materials in the simulated superheated geothermal environment, Corros. Sci. 168 (2020) 108584.

Discussion – CR of CS in SHG environment



A.I. Thorhallsson, A. Stefansson, D. Kovalov, S.N. Karlsdottir, Corrosion testing of materials in the simulated superheated geothermal environment, Corros. Sci. 168 (2020) 108584.
S.N. Karlsdottir, et al. Corrosion Testing of Carbon Steel and 13Cr Casing Materials in Simulated Superhot Deep Geothermal Well Environment, New Orleans, USA, AMPP-2024-20903, (2024).
S.N. Karlsdottir, K.R. Ragnarsdottir, I.O. Thorbjornsson, A. Einarsson. "Corrosion testing in superheated geothermal steam in Iceland," Geothermics, [53], 281-290, (2015).

Summary – SoA & Lessons learned

- CS casing material is vulnerable to thermal cycling that can lead to fracture of the casing
- CS casing materials lose strength (yield and tensile strength) at elevated temperatures thus less stress and strains needed for failure
- CS susceptible to various corrosion forms (HE, SSC, HTHA)
- CRA with resistance against thermal cycling effects are needed to achieve structural integrity of superhot well
- Potential candidates could include the newly developed titanium alloy Ti-745 (Ti-0.4Ni-3.6Mo-0.75Zr), the nickel alloys SM2245 and SM2550

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Conclusion

- Material challenges exist in construction and utilizing superhot geothermal wells
- CR of L80-carbon steel casing > 0.5 mm/year in liquid phase and close to 0.1 mm/year in vapor for 350°C but lower at higher temperature and same pressure
- Carbon steel prone to localized corrosion damage, difference in structure of corrosion layer in vapor vs. liquid phase
- Corrosion effect negligible on the tested Ti-475 alloy and SM2550
- Both potential candidates for superhot geothermal wells with good corrosion resistant in the simulated geothermal well environment

Acknowledgements

Icelandic Research Centre for Research (RANNÍS) for funding the project within the Technology Development Fund (TDF) that this work was done within called “Material Research and Modelling for High Temperature and Deep Geothermal Wells,” no. 2113356-0611.

Nippon Steel for collaboration and supplying L80-CS, 13Cr and SM2550 casing materials

Timet for collaboration and supplying Ti-475 casing material

Thank you for your attention