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D1.2 – SOA Materials for Geothermal HX and limitation

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Abstract	This deliverable reports on the SOA of heat exchanger (HX) materials and its operational limitation regarding the handling of aggressive geothermal brine, HX types along with variants and using FMEA software perform heat exchanger failure analysis through failure mode effect analysis (FMEA)	

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Contents

1.	EXECUTIVE SUMMARY	5
1.1	OBJECTIVES MET	5
1.2	SCOPE	5
2.	ENVIRONMENTAL CONDITIONS	5
2.1	CONDITIONS AT THE HELLISHEIÐI GEOTHERMAL FIELD	5
2.2	PH.....	6
2.3	TEMPERATURE	6
2.4	FLUID VELOCITY:.....	6
2.5	HYDROGEN SULPHIDE (H ₂ S):.....	6
2.6	CARBON DIOXIDE.....	6
2.7	CHLORIDE:	6
2.8	OXYGEN:	6
2.9	AMMONIA (NH ₃):.....	6
3.	MATERIALS USED IN GEOTHERMAL HEAT EXCHANGERS.....	9
3.1	BACKGROUND.....	9
3.2	CARBON/LOW ALLOY STEEL	9
3.3	STAINLESS STEEL.....	9
3.4	TITANIUM AND ITS ALLOYS.....	10
3.5	COPPER BASED ALLOYS	10
3.6	NICKEL ALLOYS.....	10
4.	FAILURE MODES	10
4.1	UNIFORM CORROSION	10
4.2	PITTING CORROSION.....	10
4.3	CREVICE CORROSION	10
4.4	STRESS CORROSION CRACKING.....	10
4.5	EROSION-CORROSION.....	11
4.6	MICROBIOLOGICALLY INFLUENCED CORROSION	11
4.7	INTER-GRANULAR CORROSION.....	11
4.8	FATIGUE	11
4.9	CORROSION FATIGUE.....	11
4.10	SCALING AND FOULING	11
4.10.1	Fouling factors	11
4.10.2	Management, mitigation and cost implications	12
4.11	CORROSION RELATED TO WORKING FLUIDS	12
5.	ENVIRONMENTAL LIMITS	12
6.	FAILURE MODES AND EFFECTS ANALYSIS	14
7.	CONCLUSIONS	17
8.	REFERENCES	18



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Document:

Version:

Date: 5 March 2020

1. EXECUTIVE SUMMARY

The GeoHex project aims to develop coatings to enhance heat transfer, corrosion and scaling performance of heat exchangers (HX). The current document reviews current state of the art (SOA) materials used for heat exchangers, with a focus on HX materials used in geothermal environments. Section 2 details expected geothermal brine compositions and the effects of brine composition, as well as specific conditions, pH, temperature etc, on materials performance. Section 3 details specific materials used in geothermal heat exchangers, while Section 4 discusses failure modes that might occur in geothermal heat exchangers. Section 5 discusses environmental limits for materials under various geothermal conditions and Section 6 details a failure mode and effects analysis.

1.1 Objectives Met

The deliverable contributed towards the work package objectives:

- Identify SOA materials of heat exchangers for different geothermal power technologies across a wide range of geothermal condition such as temperature, enthalpy, corrosion and scaling potential.
- identify performance characteristics and operational limitations of SOA heat exchangers for geothermal applications.

1.2 Scope

This document reviews published data on the following aspects, relevant to Task 1.1 of the GeoHex program:

- SOA materials for geothermal heat exchangers, with consideration given to temperature and enthalpy, scaling and corrosion potential of geothermal fluids;
- Silica scaling and mitigation strategies
- Geometrical design to limit scaling;
- Cost implications related to water treatment for scaling avoidance.
- Materials compatibility with working fluids.
- Environmental limits and materials selection.
- Failure modes and effects analysis for geothermal heat exchangers.

A further deliverable, D1.1, will discuss heat exchanger types and structures. The final heat exchanger design, for the GeoHex program, will be considered in Work Package 5, and therefore considerations related to cost, service life, space, capacity and overall heat transfer coefficients, for different heat exchangers and working fluids, will be discussed in the deliverables of this work package. Parasitic loads will also be considered in Work Package 5 deliverables.

2. ENVIRONMENTAL CONDITIONS

2.1 Conditions at the Hellisheiði geothermal field

Separator water at the Hellisheiði power plant will be used for tests in WP2 and WP4 and is relevant to discussions regarding materials selection, in this report. The temperature of the fluid is between 120-170°C, and pressures between 2-10bar (Ragnarsdóttir, 2020; Kjartansson, 2010). Fluid compositions were previously measured and reported as part of the Geo-Coat program (Grant number 851917) and these data are reproduced in Table 1 (Haraldsdottir, 2018). A harmonised corrosivity index for geothermal fluids has been established (Nogara, 2018), Table 2, and according to this classification, the Hellisheiði geothermal fluid is Class IV, representing a moderately saline fluid, with near-neutral pH. The most aggressive geothermal fluids, such as at Salton Sea, USA, are highly saline, with salinity >100,000 ppm (Nogara, 2018). The following sections discuss the variables and corrosive species that affect the corrosion rate in a geothermal fluid.

Document:

Version:

Date: 5 March 2020

2.2 pH

The corrosion rates of stainless and carbon steels generally increase under more acidic conditions. The passivity, or formation of a protective passive film, on certain alloys, such as stainless steels, is also influenced by the pH level (Ellis, 1981). Low pH can cause the breakdown of passive films, resulting in uniform (if the breakdown occurs over the entire surface) or localised (if there is localised depassivation) corrosion.

2.3 Temperature

Temperature affects corrosion and corrosion related failure mechanisms in different ways. For instance, the risk of pitting and crevice corrosion is increased at higher temperatures, in aerated solutions, while the risk of sulphide stress cracking in C-Mn steels is highest at room temperature (Kane, 1998). Other factors also play a role, which often adds complexity, such as the formation of scales at different temperatures which might reduce the corrosion rate.

2.4 Fluid velocity:

Different types of corrosion can occur depending upon the fluid velocity. For instance, stagnant areas might develop, with low flow velocities resulting in crevice corrosion, while erosion, or erosion corrosion, can occur at high fluid velocities (Karlsdóttir, 2012). Fluid velocity also plays a part in the stability of the scales (if formed), and high velocities might hinder the attachment of the scale to the substrate.

2.5 Hydrogen Sulphide (H₂S):

H₂S is known to be responsible for sulphide stress cracking (SSC) at temperatures close to ambient, while sulphide scales can also be formed because of its presence, and the disruption of these scales can cause further corrosion. The temperature and H₂S concentration regimes, where such scales are formed, has been studied in detail. However, the complexity of the interplay between the different factors makes it challenging to predict the formation of scales.

2.6

2.6 Carbon dioxide

The form in which CO₂ exists depends on the pH. The speciation may result in dissolved carbon dioxide, bicarbonate ions and carbonate ions. Carbon dioxide is 100 times more soluble in water than oxygen at ambient (Chawla, 1993). The dissolution and subsequent formation of carbonic acid in water makes CO₂ an acid gas. Under ambient conditions, the amount of dissolved CO₂ is directly proportional to the acidity of the fluid and therefore high levels of CO₂ can cause corrosion.

2.7 Chloride:

The presence of chlorides can increase local and uniform corrosion as well as increasing susceptibility to stress corrosion cracking. Chlorides also destabilise oxide scales, which often protect the metal from corrosion. Hence, the presence of Cl⁻ ions may lead to depassivation and subsequent corrosion.

2.8 Oxygen:

Oxygen reduction is one of the main cathodic reactions in aqueous media. The addition of oxygen, even in parts per billion (ppb), can increase the likelihood corrosion, and a limit of 20ppb has been specified for low carbon steels (Kaya, 2005). Concentrations higher than 100ppb can cause stress corrosion cracking (SCC) in some austenitic stainless steels at elevated temperatures (Smith, 1983).

2.9 Ammonia (NH₃):

Pitting and SCC of certain copper based alloys can occur in environments with ammonia, and concentrations above 1-2ppm are thought to be problematic (Francis, 2016).

Document:

Version:

Date: 5 March 2020

Table 1 Composition and environmental parameters of Hellisheiði power plant separator water.

Location	T [°C]	P [bar]	pH	CO ₂ [mg/kg]	H ₂ S [mg/kg]	SiO ₂ [mg/kg]	Na +[mg/kg]	K+[mg/kg]	Ca ²⁺ [mg/kg]	Cl ⁻ [mg/kg]	SO ₄ ²⁻ [mg/kg]	Se [mg/kg]
Separator water after 2nd flash	119	2-10	9.2	20	30	735	203	38	0.85	186	21.5	16

Document:

Version:

Date: 5 March 2020

Table 2 Harmonised corrosivity index (Smith, 1983).

Geothermal Resource Class	Characteristics	
I	Resource type	Liquid-dominated
	Total key species (TKS)	>100,000ppm
	TKS chloride fraction	0.99
	pH (unflashed)	<5
	pH (flashed)	5-6
	Inlet Temperature (°C)	199
II	Resource type	Liquid-dominated
	Total key species (TKS)	1000-10,000ppm
	TKS chloride fraction	
	pH (unflashed)	<4.5
	pH (flashed)	<4.5
	Inlet Temperature (°C)	121-177
III	Resource type	Liquid-dominated
	Total key species (TKS)	10,000-20,000ppm
	TKS chloride fraction	45-99%
	pH (unflashed)	5-6
	pH (flashed)	>6
	Inlet Temperature (°C)	149-191
IV	Resource type	Liquid-dominated
	Total key species (TKS)	500-10,000ppm
	TKS chloride fraction	45-99%
	pH (unflashed)	>5
	pH (flashed)	>6
	Inlet Temperature (°C)	121-199

Document:

Version:

Date: 5 March 2020

3. MATERIALS USED IN GEOTHERMAL HEAT EXCHANGERS

3.1 Background

A number of factors are taken into consideration for the selection of geothermal heat exchanger materials. These include reliability of supply and cost effectiveness of the materials, mechanical and thermal properties, ease of maintenance, as well as corrosion performance, among other factors. The nature of working fluids, as well as the compositions of geothermal brines also play crucial roles in appropriate materials selection. The characteristics of commonly used materials for geothermal heat exchangers are detailed below, with a particular focus on performance in contact with geothermal fluids.

3.2 Carbon/low alloy steel

Carbon steel (CS) is an attractive choice in terms of cost, and heat exchangers that are manufactured using CS are approximately 2.5 times cheaper than AISI 316 stainless steel and over 3 times cheaper than 254 SMO (Couper, 2012). They cannot however be used in conditions where the pH of the brine is low or the working fluid is highly acidic (Lukawski, 2010). CS can also corrode in the presence of aerated water at ambient temperature. The rate of uniform corrosion of these materials is generally between 0.03-0.3mm/year when the chloride concentration is <2% and pH higher than 6 (Karlsdóttir, 2012). High strength low alloy (HSLA) steels are susceptible to SSC in environments containing H₂S, while SCC in other CSs can occur in environments with high levels of H₂S, HCl, low pH, and/or when the microstructure is coarse or residual stresses high.

3.3 Stainless steel

Stainless steels are considered to be more corrosion resistant than CS, and are therefore an appropriate choice for heat exchangers dealing with chemically aggressive geothermal fluids (Lukawski, 2010). In conditions with high chloride or sulphide concentrations, however, stainless steels can undergo localised corrosion such as pitting and crevice corrosion, and stress corrosion cracking (SCC). A commonly used metric to rank stainless steels in terms of their corrosion resistance is pitting resistance equivalence number (PREN), which is normally defined as (Sedriks, 1996):

$$PREN = Cr + 3.3Mo + 16N$$

Where Cr, Mo and N are weight percent of Cr, Mo and N, respectively. The formula accounts for the beneficial effects of these 3 elements and also gives greater weight to the elements imparting greater corrosion resistance, namely Mo and N. Alloy 316 has higher corrosion resistance than 304 because of its increased molybdenum content (Smith, 1983). The susceptibility of the materials to these crevice and pitting corrosion increases with increase in temperature (Sedriks, 1996).

More highly alloyed stainless steels, such as 254 SMO are more resistant to corrosion, because of their higher chromium and molybdenum contents. A further advantage of 254 SMO is its high yield strength, which is approximately double that of austenitic 300 series stainless steels. Highly alloyed stainless steels are, however, more expensive than lower alloyed stainless steels (Kaya, 2005), and therefore the most suitable materials for geothermal heat exchangers are generally 304 or 316 stainless steels (Rafferty, 1989). Materials selection, of course, depends on the temperature and chloride content of the geothermal fluid (Couper, 2012).

Document:

Version:

Date: 5 March 2020

3.4 Titanium and its alloys

Titanium alloys are used in harsh geothermal environments, where stainless steels would not be suitable, such as well casings at Salton Sea, USA (Karlsdóttir, 2012). Titanium alloys are used in environments where the chloride concentration exceeds 5000ppm and the temperature is greater than 100°C (Sanada, 2000). Titanium is also susceptible to hydrogen embrittlement (Kaya, 2005), and unlike in stainless steels and nickel alloys, titanium alloys can form hydrides which can blister and spall.

3.5 Copper based alloys

Pitting and SCC of copper alloys can occur in the presence of sulphur and/or ammonia. However, cupronickels are resistant to corrosion in sea water and fresh water brines, if they do not contain significant amounts of hydrogen sulphide (Smith, 1983).

3.6 Nickel alloys

Nickel alloys are used in aggressive environments involving high temperatures (Kaya, 2005). Although the materials can be susceptible to hydrogen embrittlement and SCC, in the presence of H₂S and high temperatures, nickel alloys are much more resistant to these failure modes than stainless steels. Nickel alloys are susceptible to intergranular corrosion in high temperature oxidising chloride environments (Karlsdóttir, 2012), when the microstructure is compromised.

4. FAILURE MODES

4.1 Uniform corrosion

Uniform corrosion affects the entire exposed surface of the metal uniformly and with time results in the uniform reduction of metal thickness (Fontana, 1986; Jones, 1991). This form of corrosion is fairly predictable and the thickness loss must be accommodated in design.

4.2 Pitting corrosion

Pitting is a form of localised attack on the metal surface that results in the formation of holes or cavities, with the diameter of these holes (pits) equal to or less than their depth (Fontana, 1986; Jones, 1991). The growth of these pits may ultimately result in perforation. Stainless steels and nickel alloys are particularly prone to pitting, and pitting of these materials most commonly occurs in chloride containing environments. Temperature is a crucial factor for susceptibility to pitting and low alloy stainless steels (Alloy 304 and 316), have critical pitting temperatures not much higher than 0°C (Sedriks, 1996)

4.3 Crevice corrosion

Crevice corrosion is associated with narrow gaps, where there is differential aeration between the surfaces in the narrow gap and outside of it (Sedriks, 1996). This leads to the formation of a galvanic cell where the aerated region acts as a cathode and the region with lower oxygen as anode. The critical crevice temperatures of 304 and 316 stainless steels are also not such higher than 0°C.

4.4 Stress corrosion cracking

Stress corrosion cracking (SCC), occurs by the interaction of tensile stress, environment and a susceptible microstructure (Ahmad, 2006). Cracks propagate trans-granularly or inter-granularly and are generally branched. SCC is of most concern for austenitic stainless steels operating at moderate to high temperatures and chloride concentrations. SCC of copper based alloys can occur in the presence of ammonia, while sulphide stress cracking (SSC) is a special case of SCC involving the presence of H₂S.

Document:

Version:

Date: 5 March 2020

4.5 Erosion-corrosion

Erosion-corrosion involves the simultaneous corrosion and wear of materials, as a result of a fast flowing corrosive fluid. High flow rates cause wear of the material surfaces, resulting in bare surfaces which are prone to corrosive attack. Troughs, surface grooves and waves on the material surface are distinctive features of this sort of degradation (Volkan, 2014).

4.6 Microbiologically influenced corrosion

Microbiologically influenced corrosion (MIC) is the degradation of materials with the involvement of microorganisms. Certain microorganisms are sulfate reducing and produce H₂S gas, which is corrosive, as described above, while crevice corrosion can also occur, because of the crevice formed between the microorganism and the metal surface (Nogara, 2018).

4.7 Inter-granular corrosion

Intergranular corrosion can affect stainless steels and nickel alloys that have been through inappropriate heating and cooling cycles, as a result of welding or heat treatment. Precipitation at grain boundaries can cause the depletion of certain elements, that impart corrosion resistance, adjacent to the grain boundaries, leaving the grain boundary regions vulnerable to corrosive attack.

4.8 Fatigue

Fatigue is the failure of a material because of cyclic loads, and can also occur in cases where the applied stresses are lower than the static yield strength. Fatigue normally initiates at stress concentrations in structures, such as weld toes or sharp transitions in geometry.

4.9 Corrosion fatigue

Corrosion fatigue can occur when a component is subjected to a cyclic stress in a corrosive environment. The cyclic loading might be associated with start-ups and shutdowns or vibrations, among other factors.

4.10 Scaling and fouling

4.10.1 Fouling factors

Scaling is one of the primary failure modes in geothermal systems and results from the deposition of silicates, carbonates and sulphide compounds on the surfaces of equipment. Corrosion products can also result in scaling of heat exchanger equipment. The deposition of scale increases thermal resistance, and therefore degrades heat exchanger performance, but also can increase pressure drop and reduce flow rates. As decreased flow result in decreased power output, there is a requirement for frequent cleaning of the heat exchanger equipment. Silica scaling is particularly problematic in binary plants, for instance those utilising organic Rankine cycles, as they operate at lower temperatures, and the solubility of silicates increases with temperature (Gallup, 2011). Carbonate (calcite, CaCO₃) and anhydrite (CaSO₄) have retrograde solubility, and are not expected to deposit in heat exchangers (Zarrouk, 2014).

The loss in performance related to fouling can be defined by:

$$R_f = \frac{1}{U_f} - \frac{1}{U_c}$$

Were U_f and U_c are heat transfer coefficients of fouled and clean heat exchangers, respectively. Fouling factor data, for a number of different geothermal conditions and three different materials, were reported by Ellis (1983), and a correlation between material and fouling factor was not evident from these data. The three materials considered were CS, titanium and 90/10 cupronickel. In contrast, scaling rates for stainless steel heat exchanger tubes were demonstrated to be lower than those of CS (Hernandez-Galan, 1989).

Document:

Version:

Date: 5 March 2020

4.10.2 Management, mitigation and cost implications

Management of fouling is considered to be easier for plate heat exchangers, compared with shell-and-tube heat exchangers as plate heat exchangers are more easily disassembled (Rafferty, 1989). Narrower tubes, in shell-and-tube heat exchangers, are preferred for heat transfer performance, but hinder cleaning (Farhami, 2011). A similar balance between ease of cleaning and heat transfer performance would be expected for plate heat exchangers.

Heat exchangers can be cleaned by water blasting, while polyphenylenesulfide and phenolic-based coatings have been demonstrated to provide corrosion and fouling resistance (Gawlik, 2000). Scaling can also be controlled by control of pH, with sodium hydroxide and hydrofluoric and sulphuric acid solutions being utilised (Zarrouk, 2014). A pH of 5-6 is thought to reduce scaling, when acidifying brines, and therefore the corrosion risk, related to this process, is considered to be limited (Gallup, 2011). The addition of reducing agents, such as sodium formate, to the acid solution is also thought to inhibit scaling as well as corrosion (Gallup, 2011).

Specific published data on costs and cost advantages of heat exchangers utilising chemical treatments, compared with those without such treatments, were not found. Although it has been reported that the frequent cleaning of production wells, in a geothermal flash plant, resulted in costs of \$500,000/year, while the cost of water treatment was \$70,000/year (Mouche, 2003).

4.11 Corrosion related to working fluids

Binary cycle working fluids are generally considered to be non-corrosive to all common engineering alloys, however problems have been reported in cases where the working fluid has been contaminated. There is a much greater propensity for contamination in power plants utilising direct contact heat exchangers (Smith, 1983), but contamination of working fluids is likely to be minimal for plants using organic Rankine cycles, with plate or shell-and-tube heat exchangers.

5. ENVIRONMENTAL LIMITS

Literature searches were undertaken to suggest environmental limits for various materials, and these limits are included in Table 3. The limits in Table 3, as well as the compositions and conditions of geothermal brines, can be used to guide materials selection. The partial pressure of H₂S for separator water after the second flash, according to Table 1, is 30mg/kg, corresponding to a partial pressure of 0.004psi, and ISO 15156-2:2015 suggests that no precautions are normally required for the selection of steels under these conditions. It is noted that ISO 15156 is a Standard for oil and gas production equipment, operating in conditions with low levels of oxygen. Therefore, precautions need not be taken only in conditions where there is limited/no aeration. Localised corrosion of certain copper alloys might, however, be expected under these conditions, precluding them from use.

Document:

Version:

Date: 5 March 2020

Table 3 Environmental limits for certain materials.

Materials	Failure mode	pH	Cl content	Temperature	H ₂ S	Oxygen level	Flow rate	REFERENCE
Carbon and low alloy steels	Uniform/localised corrosion	>6	<2%	-	-	-	-	Karlsdóttir, 2012
Carbon and low alloy steels	SSC	>5	-	≥190°C	-	-	-	Karlsdóttir, 2012
Carbon and low alloy steels	Uniform corrosion	>5	-	<250°C	-	-	-	Nogara, 2018
Carbon and low alloy steels	Corrosion	-	-	-	-	<ppb	-	Smith, 1983
	MIC	<5 and >9		>40°C	-	-	-	Nogara, 2018
304 Stainless steels	Localised corrosion	-	<210ppm	<140°C	-	-	-	Smith, 1983
316 Stainless steels	Localised corrosion	-	<510ppm	<140°C	-	-	-	Smith, 1983
Titanium	Localised corrosion	-	<5000ppm	<100°C	-	-	-	Karlsdóttir, 2012
Copper alloys	Localised corrosion	-	-	-	<7 ppb	-	-	Smith, 1983
Copper alloys	Erosion-corrosion	-	-	-	-	-	<6.1-39 ft/sec	Smith, 1983
Austenitic stainless steels	-	Any	Any	<60°C	100kPa	-	-	ISO 15156-3:2015
254SMO	-	Any	Any	<60°C	100kPa	-	-	ISO 15156-3:2015
Alloy 718	-	Any	Any	<232°C	200kPa	-	-	ISO 15156-3:2015
Titanium Alloys	-	Any	Any	Any	Any	-	-	ISO 15156-3:2015
Carbon and low alloy steels	-	-	-	-	<0.05psi	-	-	ISO 15156-2:2015

-: Indicates no data.

Document:

Version:

Date: 5 March 2020

6. FAILURE MODES AND EFFECTS ANALYSIS

A failure mode and effects analysis (FMEA) has been completed using the data available from literature. FMEAs for geothermal plants, in general, have been conducted (Haraldsdóttir, 2020; Feili, 2013), and the identified aspects, pertinent to geothermal heat exchangers, are included in Table 4. A risk priority number (RPN), included in Table 4, was defined as:

$$RPN = S * O * D$$

Where S is severity, rated between 1-10, O the likelihood of occurrence, rated between 1-10, and D the likelihood of detection, rated between 1-6.

An FMEA has also been reported for a heat exchanger of a hot water system (Vyas, 2017). Based on the reviewed data an FMEA has been suggested for the heat exchangers used in the GeoHex project, Table 5. It is noted that the current RPN data are quite subjective as operator data were not available, although published data were used for guidance. Therefore, the FMEA will be reviewed throughout the project and will be supplemented with occurrence, severity and detectability data, if these data become available. As experiential data on occurrence, severity and detectability were not available, it was sufficient to undertake the FMEA with a simple table, as opposed to dedicated software.

Document:

Version:

Date: 5 March 2020

Table 4 Literature FMEA data pertinent to geothermal heat exchangers.

Failure	Effect	Cause	RPN	Reference
Fouling of condenser tubes	Poor cooling, loss of efficiency	Corrosion of tubes	40	Feili, 2013
Blocking of nozzles	Poor cooling, loss of efficiency	Scaling/corrosion	192	Feili, 2013
Cooling pipes	Hindered flow	Scaling	48	Haraldsdóttir, 2020
Condenser tubes	Leaks	Corrosion of tubes	72	Haraldsdóttir, 2020
Condenser tube supports	Material reduction	Corrosion	12	Haraldsdóttir, 2020

Document:

Version:

Date: 5 March 2020

Table 5 FMEA of a heat exchanger for a hot water system.

Failure	Effect	Cause	S	O	D	RPN	Mitigation	Notes
Fouling of preheater, evaporator, superheater	Loss of efficiency	scaling/corrosion	4	8	2	64	Fluid treatment	Detectable with pressure drop
Leaking of preheater, evaporator, superheater	Replacement of HX	Corrosion/stress corrosion/erosion	6	2	2	24	More appropriate materials selection	
	Contamination of working fluid (if undetected)							
	Loss of efficiency							
Leaking of heat exchangers	Replacement of HX	Fatigue	6	2	2	24	Changes in design to remove stress concentrations Changes to heating and cooling cycles to limit risk of thermal fatigue	
	Contamination of working fluid (if undetected)							
	Loss of efficiency							
Deformation of heat exchangers	Loss of efficiency/fracture	Overloading	7	2	4	56	Control of temperature/pressure	

Document:

Version:

Date: 5 March 2020

7. CONCLUSIONS

This document has reviewed the SOA of materials for geothermal heat exchangers, with consideration given to the corrosivity of the particular geothermal environment. Scaling and its mitigation has also been considered as well as failure modes and their effects. The following conclusions were drawn from the review:

- SOA materials for geothermal heat exchangers include carbon steel, stainless steel, titanium alloys, copper alloys and nickel alloys (Section 3)
- Silica scaling can be controlled with water treatment and a pH, of the treated brine, of 5-6 is thought to be effective. Risk of corrosion with such a pH is thought to be minimal (Section 4.10.2).
- Scaling removal via water blasting is thought to be more effective for larger heat exchanger openings (Section 4.10.2).
- The cost of cleaning, for scaled heat exchangers, is thought to be higher than costs related to water treatments (Section 4.10.2).
- Materials compatibility with working fluids is not a concern for heat exchangers without direct contact (Section 4.11).
- Separator water after the second flash, at the Hellisheiði, would not be considered to be corrosive to steels, if the level of aeration was low (Section 5).
- An FMEA for the GeoHex heat exchangers was conducted and risks were generally determined to be fairly low. Mitigations were identified to further reduce risk, and these included appropriate maintenance, including water treatment and operational control, as well as considerations in design (Section 6).

Document:

Version:

Date: 5 March 2020

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