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D5.1 – Scalability and manufacturability of single phase HX material

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Abstract	This report reviews the manufacturability and scalability of shell-and-tube and plate heat exchangers (HX) with GeoHex coatings	

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[1] Dissemination level security:

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CONTENTS

Summary and Scope

This report reviews the manufacturability and scalability of shell-and-tube and plate heat exchangers (HX) with GeoHex coatings. The following aspects are reviewed:

1. Current manufacturing routes for shell-and-tube and plate heat exchangers;
2. Manufacturability and scalability limitations for the GeoHex materials intended for heat exchangers;
3. The adaptability of current manufacturing routes to allow incorporation of GeoHex materials, and suggestions of alternate manufacturing routes when needed;
4. Final suggested manufacturing routes for shell-and-tube and plate heat exchangers.

In practice, single-phase and phase change heat exchangers have the same or very similar geometries and go through the same manufacturing processes. This applies to both plate heat exchangers and shell-and-tube heat exchangers. Therefore this deliverable will focus on shell-and-tube and plate heat exchangers, with no distinction necessary between single-phase and phase change conditions. This deliverable also reviews manufacturing considerations related to heat exchangers with GeoHex coatings and non-destructive testing to ensure coating integrity.

Air cooled condensers are specific phase-change heat exchangers, and will be discussed in Deliverable 5.2. Any manufacturing considerations specific to air cooled condensers with GeoHex materials will also be considered in that deliverable.

Objectives Met

The deliverable contributed towards the work package objectives:

1. To identify scalability and manufacturability issues within materials developed for single-phase heat transfer application in geothermal sector.
2. To propose an alternate route for manufacturing of HXs, if a conventional route does not support coating method.

1. INTRODUCTION

For GeoHex to maximise its impact, it is important to consider the final application at an early stage of the project. The objective is to consider how the coating methods fit into the current manufacturing routes of heat exchangers. Manufacturers are unlikely to radically change their existing manufacturing processes, which can be very costly, unless it gives their product added value or significant advantage over their competitors.

GeoHex utilises five different coating processes methods. Two of these methods, physical vapour deposition (PVD), and suspension plasma spray (SPS), are conventionally line of sight methods while the other three methods, electroless nickel plating (ENP), chemical vapour deposition (CVD) and hydrophobic coatings, are known to be non-line of sight. This difference in the coating processes is important for the manufacturing possibilities and routes of coated heat exchangers, especially for tubes and complex shapes. It is important to keep in mind the intended purpose of the coatings and if they are on the geothermal fluid side or working fluid side for organic Rankine cycle (ORC) power plants. This mostly applies when discussing shell-and-tube heat exchangers and some specific types of plate heat exchangers such as semi-welded plate heat exchangers. These types of heat exchangers have geometries and/or manufacturing processes that are different for the different fluid sides.

From a conversation with two heat exchanger manufacturers, Kelvion and Alfa Laval[1,2], we were informed that plate heat exchangers are nowhere made from carbon steel (and have not been for the last 30 years) and that there are no future prospects that the producers will divert towards this route unless carbon steel heat exchangers will somehow become more cost or economically effective. This is due to many factors such as longevity of manufacturing tools, corrosion resistance of stainless steel and manufacturing economics. It is therefore important for the coatings developed to be able to work both on stainless steel and carbon steel substrates, which is still very much used in plate-and-shell heat exchangers. The GeoHex coating development and testing programs have therefore been amended to include stainless and carbon steel substrates. The lowest alloyed steel Kelvion is using today is 304 while for their most demanding applications they use materials such as stainless steel 254SMO and titanium alloys. Both Kelvion and Alfa Laval mentioned that their greatest interest in coatings for heat exchangers lies in attributes which contribute to the reduction of scaling accumulation within heat exchangers. These same coatings must be wear resistant and durable.

2. PLATE HEAT EXCHANGERS

2.1 Overview

Plate heat exchangers consist of packs of thin plates to conduct heat between the hot and cold fluids. Portholes allow hot and cold fluid flow, which pass through every other channel allowing heat exchange to occur while the hot and cold streams do not mix. There are three main types of plate heat exchangers:

- Gasketed: In a gasketed plate heat exchanger, plates are stacked together and sealed around the edges with gaskets. Gaskets are placed around portholes on every other plate to allow channels with hot and cold fluid flow.
- Brazed: Brazed plate heat exchangers are joined by melting and flowing a filler metal into the joint. Heat exchanger plates are stacked together with filler metal before brazing in a furnace.
- Welded and semi-welded: Welds are used to seal the hot and cold passes in a fully welded plate heat exchanger, which are particularly used where an aggressive medium is involved. A semi-welded plate heat exchanger consists of welded channels that accommodate the aggressive medium and gasketed channels that accommodate the less aggressive medium.

In most applications, corrugated, embossed or stamped plates are used rather than flat plates, and plates are stacked in such manner that the pattern orientation changes, ensuring that there are numerous points of contact. This is illustrated schematically in Figure 1.

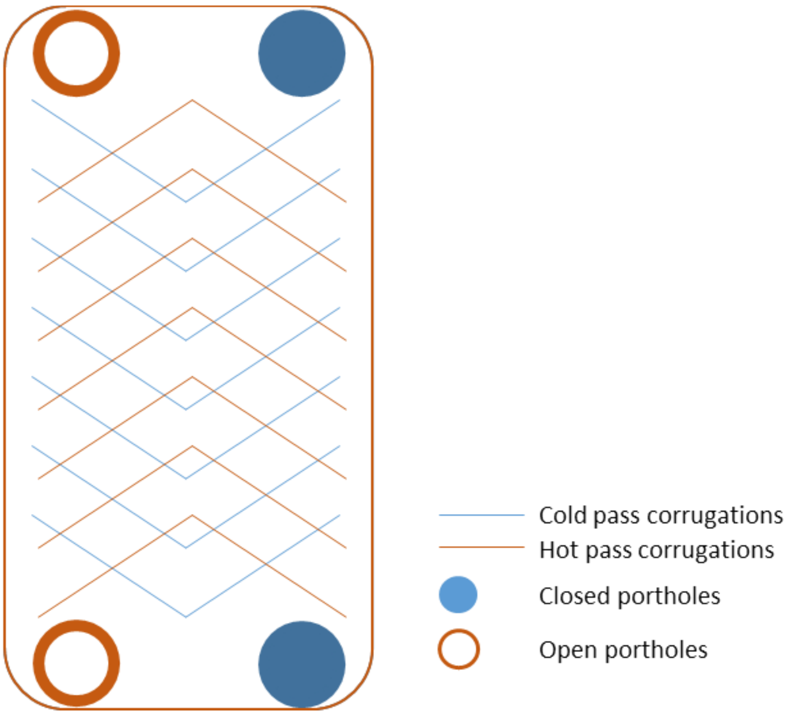

Figure 1: Schematic diagram of alternating chevron pattern orientations on successive plates of plate heat exchangers.

In addition to corrugated plates, gasket plate heat exchangers also include fixed and movable cover plates, along with tie bars and rods, which compress the heat exchanger plates in place. Gasketed plate heat exchangers allow the easy addition and removal of plates resulting in good flexibility of the system. They also allow higher heat transfer efficiency compared with shell-and-tube heat exchangers, meaning that the heat exchangers can be very compact. As the plates of gasketed heat exchangers are easy to take apart it provides ease in inspection and cleaning of the equipment.

Gaskets are generally elastomers and therefore there are limitations in terms of temperature and pressure, 160°C and 25 atm[3]. However, plate heat exchangers with high-temperature gaskets and double-walled gaskets have been designed to allow operation up to 250°C and ~93 atm[4]. Apparently, this is less of a concern for brazed or welded heat exchangers despite the joints making the system less flexible. The narrow gaps between plates mean that pressure drops can be high and therefore pumping power and costs are increased. The narrow gaps between plates and pressure limitations also mean that plate heat exchangers are often unsuitable for phase change applications. However recent conversations with heat exchanger manufacturers have suggested that solutions can be implemented to allow plate heat exchangers to be used effectively in phase change applications. It is also understood that plate heat exchangers are normally preferred for ORC applications.

2.2 Plate heat exchanger manufacturing sequence

The manufacturing sequence of gasketed plate heat exchangers consists of stamping or embossing of plates to provide corrugations before the application of gaskets around the portholes and plate perimeters, which are either glued or clipped in place. The plates are then stacked together and compressed via cover plates and tie rods. Semi-welded or welded plate heat exchangers are generally welded together using tungsten inert gas (TIG) or laser welding with the joint configurations lap or butt welding generally used. Two plates are welded together to form a cassette for semi-welded heat exchangers before gaskets are applied to the non-welded passes and the cassettes are compressed together.

Generally, plate heat exchangers incorporate a double-walled or double gasket design to avoid mixing of fluids in the case of leakage. In a double-walled design, the hot and cold passes are separated by an empty cavity which is filled only if a leak occurs. In a double gasket design, there are double gaskets around each of the sealed port holes so that if there is a leak through the port hole gasket it flows into the empty cavity which is sealed by the secondary gasket. There are generally bleed ports in the secondary gasket to enable leak detection.

2.3 Gasket selection

Gaskets for plate heat exchangers are generally moulded elastomers and are selected based on fluid compatibility and operating temperature and pressure. Typical gasket materials and their maximum operating temperatures are summarised in Figure 2. Chemical compatibility of gasket materials with various fluids, including certain refrigerants, is generally available from the gasket suppliers, for example Shurjoint[5] and Gasket resources incorporated[6]. However, these resources did not include the specific refrigerants to be used in GeoHex, namely R134a and R1233zd. Refrigerants can pose a problem for gaskets, especially for high temperature service conditions. Plate heat exchanger manufacturers therefore often recommend semi-welded heat exchangers for usage in ORC applications, so that high-temperature refrigerants are sealed off by metal rather than gaskets. This solution is what Enogia implements currently in their geothermal ORC systems. Following conversations with heat exchanger manufacturers, gaskets used for plate heat exchangers in WP7 were selected as hydrogenated nitrile rubber (HNBR). This gasket material is suitable for the WP7 evaporator at up to 160°C and compatible with the selected refrigerants.

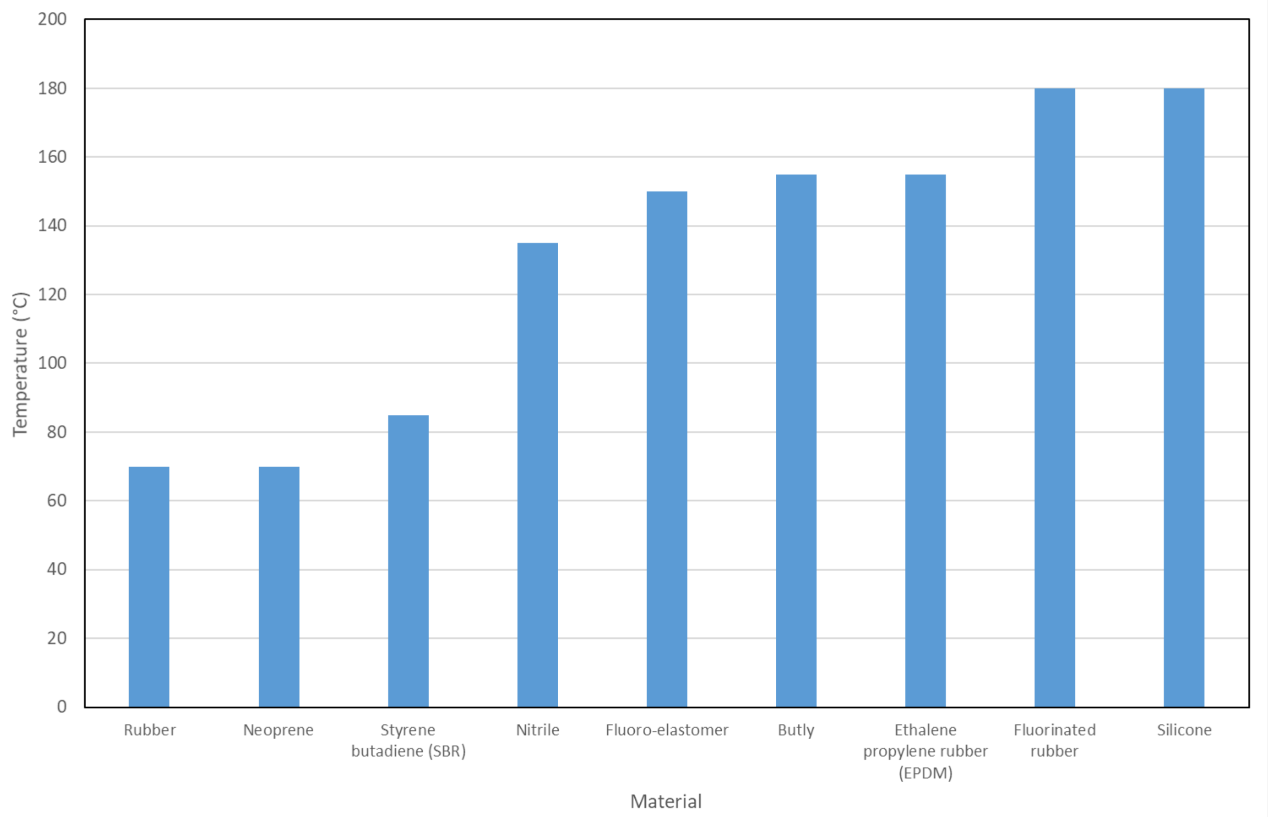

Figure 2: Maximum operating temperatures for various gasket materials.

3. SHELL-AND-TUBE HEAT EXCHANGERS

3.1 Overview

Shell-and-tube heat exchangers consist of tubes mounted inside a shell, with one of the fluids flowing through the tubes and the other flowing through the shell, outside the tubes. The heat exchanger can be divided into three parts, the front and rear heads and the shell[7]. Tubes are supported in the shell section, in the middle of the heat exchanger, with tube sheets and baffles. Tube sheets are metal discs with holes drilled into them to allow the tubes to pass through. Tubes are fitted into the tube sheet by roller expansion or pneumatic or hydraulic pressure, and can be further strengthened by welding. Unlike tube sheets, baffles do not extend from edge to edge of the shell and therefore allow the shell side fluid to flow back and forth resulting in higher flow velocities and heat transfer rates[8]. Shell-and-tube heat exchangers can be classified based on their construction[9]:

- U-tube: A U-tube heat exchanger consists of tubes bent into a 'U-shape', and tube inlets and outlets attached to a single tube sheet.
    - This construction does not allow easy cleaning of the tubes as flexible equipment is required for mechanical cleaning of the bend region.
- Fixed tube sheet: Consists of straight tubes attached to tube sheets at either end of the heat exchanger, with both tube sheets welded to the shell. This construction is a low cost design, but the tube bundle cannot be removed and therefore cleaning of the outside of the tubes is difficult.
    - Expansion joints might be required in this construction to accommodate large gradients in temperature.

- Floating head: In this construction one of the tube sheets is welded to the shell, while the other is allowed to float.
  - Floating head heat exchangers are expensive because of the complicated construction, but allow removal of the tube bundle for easy cleaning of the insides and outsides of the tubes. The floating head can also allow accommodation of temperature differentials.

The choice of fluid for the shell and tube is based on the following general considerations[8]:

- It is cheaper to use corrosion resistant alloys in the tubes compared with the shell, therefore more corrosive fluids can be passed through the tubes in comparison with the shell.
- The tubes are easy to clean, therefore the fluids that are more prone to cause fouling should be passed through the tubes.
- Tubes are more capable of accommodating higher pressure fluids.
- Fluids requiring low pressure drops (drop in pressure between the input and output sides) should be placed in the shell, as the shell allows greater design flexibility, such as modification of tube pitch (distance between centres of tubes), baffle spacing etc.

The above considerations suggest that the more fouling and corrosive brine is flowed through the tube side and working fluid is flowed through the shell side. Deliverable 1.1 of the GeoHex project also stated that this was practised for geothermal heat exchangers[10].

3.2 Shell-and-tube heat exchanger manufacturing sequence

3.2.1 Overview

Common operations to produce shell-and-tube heat exchangers are described below[11].

3.2.2 Manufacture of the shell

The shell of a shell-and-tube heat exchanger is either a seamless or seam welded pipe. Larger heat exchangers might require the seam welding of several curved plates to build up the shell structure. After seam welding, the plates are generally checked for circularity and tested non-destructively via penetrant inspection, radiography or another suitable technique. After the inspection and repair of any defects in the longitudinal welds, shell sections can be welded circumferentially, possibly with the use of spider assemblies to ensure circular alignment[9], before further non-destructive testing to ensure weld integrity.

3.2.3 Attachment of nozzles

Holes are then drilled into the shell before nozzles are attached, which convey fluids into and out of the shell. The attachment of the nozzles can be via welding, brazing, threading or expansion of the connections. Reinforcing rings might also be welded to add strength to the nozzle opening.

3.2.4 Assembly of the tube bundle

Baffles and tube sheets are drilled deburred and checked for imperfections or defects, before tie bars are attached to tube sheets and the baffles are slid in place on the tie bars. Spacers are used to ensure the correct spacing of the baffles and the heat exchanger tubes are then pulled through the tube sheets and baffles.

For fixed tube sheet heat exchangers, one or both of the tube sheets is welded to the shell before insertion of the tubes, while for a floating head heat exchanger the tube assembly might be assembled outside of the shell before welding one tube sheet to the shell.

3.2.5 Tube-to-tube sheet attachment

Tubes can be attached to tube sheets via roller expansion or welding, however, roller expansion is more common.

3.2.6 Finished assembly and leak testing

The ends of the heat exchanger are bolted in place and the heat exchanger is finally leak and hydrostatically tested.

4. GEOHEX COATINGS

4.1 Thermal spray coatings

Nano-porous and Fe doped CuO, TiO_2, Fe_3O_4 and TiO_2/Al_2O_3 coatings produced with modified thermal spray are developed in Tasks 2.2 and 4.2. Thermal spray is a line of sight coating process and is performed at atmospheric pressure. The temperature of the flame used during the deposition process reaches 1000 K and the temperature of the coated surface can reach between 100-300°C depending on process parameters, and with coating thickness of 20-1000 μm.

4.2 Physical vapour deposition

PVD is a very versatile coating process which can be used to produce coated surfaces with an almost unlimited combination of coating substances and substrate materials. PVD is used to apply thin decorative coatings on plastic and metals, antireflection coatings onto optical lenses, to fabricate electronic devices and to coat titanium nitride onto cutting tools among many other applications. PVD is a line of sight coating process.
The PVD process is done in three steps: first the coating vapour is synthesised, afterwards the vapour is transported to the substrate and finally the vapour is condensed onto the substrate surface. Usually, the process is conducted inside a vacuum chamber. There are three variants of the PVD process: vacuum evaporation, sputtering and ion plating.
In vacuum evaporation, the source and substrate are placed in a vacuum chamber. The source is then heated up so that particles start evaporating. The evaporated particles move in a straight line towards the substrate as there are no other particles in the vacuum. As the particles impact the colder substrate target they solidify onto it. For vacuum evaporation the equipment is relatively low cost and simple but the deposition of compounds can be difficult and the coating adhesion is generally not as good as for other PVD processes.

Sputtering has better coating adhesion than vacuum evaporation and is able to coat compounds. On the other hand it has slower deposition rates and is more difficult to control than vacuum evaporation. In sputtering, the cathodic coating material has its surface bombarded by argon ions. This causes atoms from the coating material's surface to escape and then to travel to and deposit onto a substrate. In this version, the substrate and coating material are usually much closer to each other than in vacuum evaporation. Sputtering is generally performed in a vacuum chamber like the other two variations.

Ion plating is sometimes considered as the best version of the three, it generally provides excellent coverage and adhesion of the coating. It also has higher deposition rates than sputtering although the process control is the most complex of the three versions. The process works as follows, first the substrate is set up to be the cathode in the upper part of a vacuum chamber with the coating source material placed below the substrate. Argon gas is placed into the chamber and an electric field used to ionise the gas and establish a plasma. This causes sputtering of the substrate which cleans the surface of the substrate to a condition of atomic cleanliness. Afterwards, the source material is heated up so that vapour is produced which passes through the plasma and coats the substrate. This results in films of uniform thickness and very good adhesion. Ion plating can be used to apply coatings to parts of irregular geometries[12].

The amorphous coatings developed by Grein research in Tasks 2.4, 3.5, 4.4 and 4.5 are deposited using the DC magnetron sputtering variation of the PVD process. The coatings developed by Grein are composed of three chemicals: Si, Ta and a third material which is either Cr, Ti, Fe or Al. The amorphous metal coatings are produced by co-depositing metals where the coating atoms are trapped in an amorphous state. The surface smoothness is due to lack of grain boundaries which is highly beneficial for anti-corrosion, fouling and scaling surface properties. This is due to the rapid quenching that takes place when an atom interacts with the sample surface. The coating thickness that is achieved is under 20 µm. The substrate temperature might increase by 60-70°C. The substrate is preferably electrically grounded but might be biased to ~ 60-100 V. PVD will also be used to prepare catalysts for multi-walled carbon nanotubes (MWCNT), in Tasks 2.3 and 4.3.

4.3 Chemical vapour deposition

Chemical vapour deposition (CVD) will be used to deposit multi-walled carbon nanotube coatings developed by UPB in Tasks 2.3 and 4.3. These coatings have strong adhesion and co-adhesion with excellent thermal and chemical stability. The tensile strength is 63 GPa and the coating can be produced in single or multilayers.

CVD is executed in an enclosed reaction chamber where an interaction between a mixture of gases and heated surface of a substrate causes the formation of a solid coating onto the substrate through the chemical decomposition of some of the gas constituents. The process is generally used in applications where resistance to wear, corrosion, erosion and thermal shock are important. CVD does not need a vacuum during production CVD coating generally produces good bonding between the substrate and the coating and materials can be deposited at temperatures below their melting and sintering temperatures with the possibility to control the grain sizes of the material deposited. On the other hand, the harmful nature of the raw materials usually require a closed chamber and special pumping and disposal equipment. Some of the raw materials needed to create the chemical vapour are quite expensive and the utilisation of material is usually low.

CVD is suitable to deposit metal coatings including W, Mo, Ti, V and Ta. CVD is also excellent for depositing compounds such as Al_2O_3, SiO_2, TiC and TiN among others. Various reacting gases or vapours are metallic hydrides, chlorides, fluorides and carbonyls. These gases include the metal intended for deposition. Other gases are also used in some of the reactions.

CVD is done inside a reactor which includes a reactant supply system, deposition chamber and a disposal or recycle system. Deposition temperatures for the CVD process is in a broad range, often from 250°C to 1950°C. The CVD process can also be done in a low-pressure setting; the CVD process is then called low-pressure chemical vapour deposition (LPCVD). The deposition can also be done by reacting the ingredients in a plasma and then the process variation is called plasma-assisted chemical vapour deposition (PACVD)[12].

4.4 Electroless nickel coatings

Electroless nickel plating (ENP) is a subset of electroless coatings which use controlled chemical reduction catalysed by either the deposited alloy or metal substrate. An even layer of nickel-phosphorus alloy, sometimes with additional particles of PTFE or SiC for enhanced properties, is deposited on a substrate immersed in a solution with nickel salts and a reducing agent which contains phosphorus. Hypophosphite salt is often the choice of reducing agent. The name stems from a comparison with electroplating, which requires an electric current to achieve coating of a substrate. As the name suggests, ENP coating deposition does not require any electric current.

The electroless nickel plating process will be used to deposit Ni-P/Ni-P-PTFE coatings in Tasks 2.5 and 4.5. This process is non-line of sight and was initially developed for coating the inner walls of tubes[13]. Typical thicknesses of ENP coatings range from 10-50µm.

4.5 Hydrophobic coatings

GeoHex considered hydrophobic coatings, which were either sol-gel, fluorinated saline or polysilazane based. Nano-scale roughness was incorporated into these coatings using silica nanoparticles. The coatings were intended to be hydrophobic allowing dropwise condensation, as opposed to filmwise condensation, and thereby increasing heat transfer performance.

4.6 Hi-Mesh coatings

The bonding of mesh structures on to substrates can have the effect of encouraging sucking flow condensation. This mechanism of condensation enhancement relies on condensed droplets being drawn into the mesh enabling a liquid film running through the mesh. This leaves a large area of remaining surface area, on top of the mesh, to allow further droplet formation. GeoHex focussed on aluminium, copper, stainless steel and carbon steel meshes, bonded to substrates of the same material type.

5. MANUFACTURING OF HEAT EXCHANGERS WITH GEOHEX MATERIALS

5.1 Overview

Here, the manufacturing of heat exchangers with GeoHex coated surfaces is discussed and concerns for the manufacturing of certain heat exchanger and GeoHex coating combinations addressed. Section 5.3.3 details some alternative routes and geometries for small diameter tubes, when coated with line-of-sight methods.

5.2 Plate heat exchangers

5.2.1 Overview

Any of the GeoHex coatings could be easily utilised with gasketed plate heat exchangers; however, consideration of the manufacturing sequence is required for semi-welded or fully-welded plate heat exchangers.

5.2.2 Gasketed plate heat exchangers

Implementing the developed GeoHex solutions on a gasketed plate heat exchangers is a straightforward process for most coating processes. The plates of the heat exchanger are pressed into shape under a high-pressure mechanical process. The coatings would be damaged by the high-pressure process which shapes the plates into the correct form so it would be necessary to coat the plates after they have been pressed. This could be done either in series or batches, depending on the nature of the coating process. No post-processing of the coated plates such as welding or brazing is needed here. What needs to be kept in mind, and perhaps tested, are the contact points between the plates themselves and if the wear resistance of the coatings is good enough to withstand it, as mentioned in discussion with Alfa Laval. These parts of the plates are under high-pressure during operation which could wear out some coatings. This does not need to compromise the working of the coating as a substrate might be selected which is resistant to the operational environment. Poor integrity of the coating in a small area, i.e. at the contact points, is then potentially less of an issue. It is also noted that coating of areas where gaskets are placed might be detrimental to performance. Therefore, gasket locating grooves should be left uncoated.

5.2.3 Brazed plate heat exchangers

Brazing the heat exchanger plates together adds a process step which needs to be taken into account in regard to the coating of the heat exchanger plates. For some coatings, which resist the brazing temperatures and have wettability sufficient enough to produce a sound brazed joint, they would not require a change in the manufacturing process of the heat exchangers, apart from of course including the coating step. The SPS, amorphous and carbon nano-tube coatings should all be quite resistant to high temperatures although their wettability would need to be investigated further. If the low wettability (high contact angle), of the coatings proves to be an issue for the brazing of the heat exchangers, a mask could be introduced to the coating process. This mask would ensure that the brazed parts of the heat exchanger plates lie on the substrate itself but not on the coatings. Thus, the edges of the plates would remain uncoated before they are brazed together. Preferably, the material used to braze the heat exchanger would wet the substrate up to the coating, so to ensure that the substrate is fully covered. Alternatively, the wettability of the coatings could be modified locally prior to or during the brazing process with different methods depending on the coating.

The brazing process of the coated joints could be improved by for example applying a DC current to the surfaces to improve and control the wettability of the surfaces as investigated by Bobzin et al. [14]

In the case of ENP, brazed heat exchangers could, and should, be coated after the brazing process. The heat exchanger would be filled with the chemical fluid which deposits the ENP coatings onto the internal substrate of the heat exchanger. This would therefore be the last step in the manufacturing process of the coated brazed plate heat exchanger. The effect of the coating process on the brazing material would need to be investigated to make sure that the interaction does not cause any harm to the heat exchanger.

5.2.4 Diffusion Bonding

Diffusion bonding is an established technology for the production of compact plate and fin heat exchangers[15], and Hi-mesh structures/coatings will be joined to substrate materials using this process. However, as diffusion bonding generally takes place in a high vacuum furnace and involves various presses, there are size limitations to the components that can be diffusion bonded, with the largest furnaces allowing the accommodation of parts ~0.9 x 1.2m[16]. Diffusion bonding will be a suitable technique for the production of the GeoHex plate heat exchangers, by stacking the heat exchanger plates and meshes appropriately to produce the construction.

In the GeoHex project, hydrophobic coatings were applied to the mesh structures and discussion of the manufacturing considerations related the processes required to deposit hydrophobic coatings are detailed in Section 5.3.1. It is noted that these prior processes, namely anodization, etching and dip coating, were demonstrated on the internal surfaces of tubes. However, it is unclear how effective they would be for application to the internal surfaces of plate heat exchangers, which are much more tortuous than the tubes of shell and tube heat exchangers. It is likely that further work will be required to demonstrate the applicability of these techniques to plate heat exchangers. Considering that the mesh structures are only considered for condensers, which are either water or air cooled, the opposite side to that with the mesh structure is not expected to require a coating.

5.2.5 Fully-welded plate heat exchangers

Welding through coated structures can result in welding defects such as porosity and in deterioration of the coating close to the weld, as discussed in Section 5.4. Industry guidelines, therefore, suggest, for cases where parts are to be welded after coating, an area of 5-10 mm is left uncoated around where a weld is to be placed[17]. If plate heat exchangers are coated before welding, the uncoated regions adjacent to welds, would be inaccessible for repair coating with a line of sight processes as the gaps between plates are very narrow. Therefore, for fully-welded plate heat exchangers, the only practical means of coating are with non-line of sight processes, after the welding of the heat exchanger. It is noted that literature was not found addressing the coating of previously welded plate heat exchangers using the non-line-of-sight processes, CVD, electroless nickel or hydrophobic coatings, and therefore further development is likely to be required. In circumstances where corrosion is not a concern, it might also be suitable to leave uncoated regions of heat exchanger plates which might be the case where the coatings are used to enhance heat transfer or fouling performance.

5.2.6 Semi-welded plate heat exchangers

The coating of semi-welded heat exchangers allows more flexibility as the surfaces of the gasketed passages are accessible for coating. For the welded passages an uncoated region, where welds are to be placed, must be maintained, or non-line of sight process must be used to allow coatings after welding of the cassette, similarly to the case for fully-welded heat exchangers.

5.3 Shell-and-tube heat exchangers

5.3.1 Overview

For shell-and-tube heat exchangers, coatings will be deposited on the inner and outer surfaces of the heat exchanger tubes. Major developments will be required to coat the internal surfaces of the tubes with thermal spray or physical vapour deposition techniques as the technologies have only been demonstrated on pipes with large inner diameters (~70 mm). Coating of the internal surfaces of tubes with <20 mm diameter has been demonstrated for CVD, electroless nickel and hydrophobic coatings, and therefore these technologies are currently more viable for this purpose. Access is not a concern for coatings on the tube outer surfaces and therefore any of the coating processes can be utilised. Welding of the tube to tubesheet is generally achieved via a fillet weld, with schematics of some configurations shown in Figure 3a-c. Flush or protruding configurations might be recommended for GeoHex materials to protect the coating on the internal surfaces of the tube, which will be exposed to the corrosive brine. It is not thought that the working fluids on the shell side are corrosive and therefore an uncoated region might be left on the shell side so that the weld quality is not compromised by welding through the coating, Figure 3d and e. Tubes and tube sheets might also be joined via roller expansion, however care would be needed to ensure that the integrity of coatings was maintained after this process, which involves deformation of the parts.

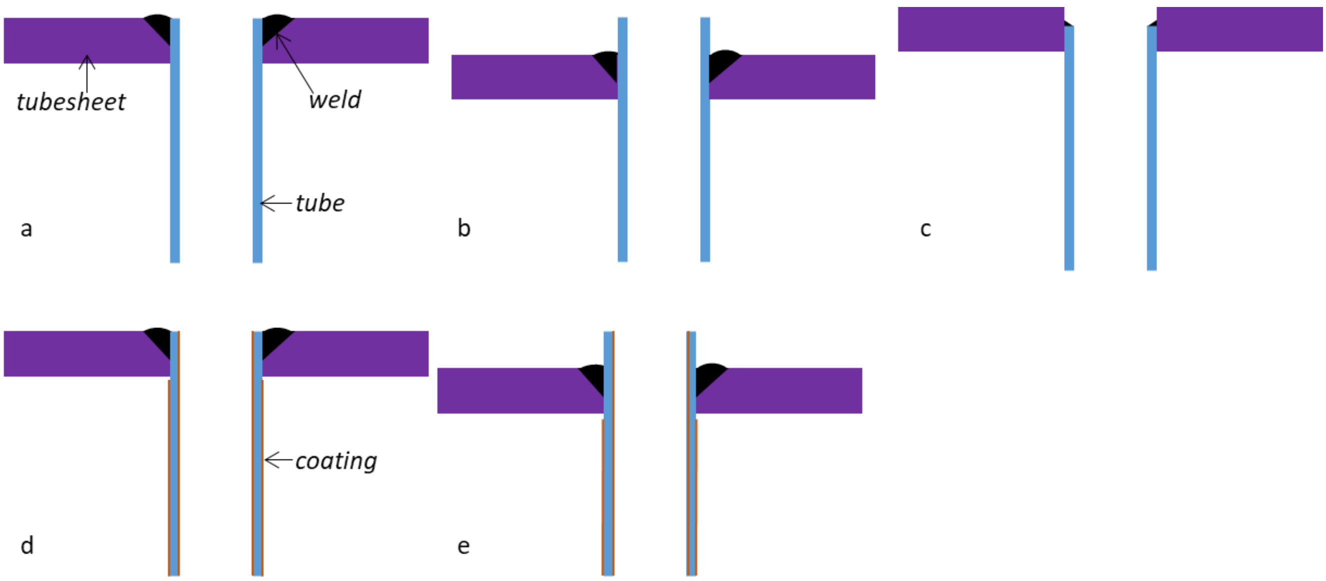

Figure 3: Weld configurations with a) Flush tube, b) protruding tube and c) recessed tube; Weld configurations for coated tubes: d) flush e) protruding.

Even though thermal spray is a line of sight process, thermal spray of WC-Co-Cr coatings, on the internal surface of pipes has been demonstrated using a compact high velocity oxy fuel (HVOF) torch[18]. Pipes of 200 mm length and 70, 90 and 110 mm diameter were internally coated, with stand-off distances of 30, 50 and 70 mm. The best mechanical properties were obtained for the 90 mm pipe/50 mm stand-off distance condition.

It was presumed that the deterioration in performance for the larger diameter pipe was related to the larger stand-off distance, rather than the pipe diameter, and therefore it might be suggested that a similar performance can be achieved for all pipes larger than 90mm, by maintaining a 50 mm stand-off distance. It was noted that even the best wear rate achieved for internally sprayed coatings was higher than for a conventionally sprayed coating, ~$3x10^{-7}$ relative to $1.42x10^{-8}$ mm^3/Nm. Therefore, more development work is required to obtain better mechanical properties.

Shell and tube heat exchanger designs were reviewed in Deliverable 1.1[10], and generally, tubes with diameters of ~20mm were determined to be used for shell-and-tube heat exchangers in geothermal service. Therefore, significant development is still required to coat the internal surface area of heat exchanger tubes and in the near future it is likely that modified thermal spray coating is only applicable to very accessible surfaces, i.e. outer diameters of tubes in shell-and-tube heat exchangers and the plates of gasketed plate heat exchangers, where surfaces are accessible.

PVD is a line of sight process and therefore similar manufacturability considerations are required to thermal spray coatings. PVD of the internal surfaces of tubes is perhaps more developed than the same using thermal spray, with the technique being at an advanced stage of development for coating the internal surfaces of long, 71 mm diameter tubes, with access points every 500 m[19,20]. Deposition of silver on the inner surfaces of 6 mm diameter and 60 mm long tubes, and platinum on the inner surfaces of 10 mm diameter and 120 mm long tubes have also been investigated, although adhesion property data for the coatings was not presented[21].

CVD is a non-line of sight process which might be very suitable for the coating of inner surfaces of heat exchanger tubes. Diamond-like carbon coatings have been deposited on the inner surfaces of 60 mm long and 10 mm diameter 304 stainless steel tubes[22], while carbon nanotubes have also been deposited on the inner surfaces of 600 mm long and 1.27mm diameter tubes[23].

The ENP coating process might be the most developed process for coating tubular components, with Ni-PTFE coatings applied on the internal surfaces of tubes used in the textile texturing process[24]. The chemical nature of the ENP coating process might cause the coating process not to interact with the stainless steel substrate in the same manner as for carbon steel, which it was originally developed for. A preliminary activation process of the stainless steel surface before coating, using, for example, UNICLEAN625[25], has been suggested. However, coating of stainless steel is at an early stage of development.

The coating of tube internals with hydrophobic coatings, which will be developed in Tasks 3.2 and 3.3 of GeoHex, has been demonstrated on tubes of shell-and-tube heat exchangers[26]. Degreasing, etching and anodising of the internals of long and narrow tubes, which is a pre-processing step before application of hydrophobic coatings, has also been demonstrated[27]. However, it is likely that further development work on the techniques to coat the internal surfaces of tubes are required before commercialisation.

TWI and ULEIC experience has suggested that coatings can be applied on the surface of tube internals via dipping or gravitational flow methods. In the case of the dipping approach, the tube can be immersed into coating solution for few seconds and pulled out with a constant speed. This approach was also used in[28]. In the case of the other method, the coating solution can be driven down through the tube by gravity (with pressure applied, if necessary). The curing will be undertaken based on the chemistry of the selected hydrophobic coating. Thus, it will be done via a combination of heating and ambient drying, or just by air drying, where applicable.

5.3.2 Alternatives for small diameter tubes

As previously addressed, the line-of-sight coating processes, PVD and thermal spray, are the two processes which have difficulties in effectively coating the internals of small diameter tubes. To address this, the geometries or manufacturing routes of such shell-and-tube heat exchangers would need to be modified, or the coating deposition technologies adapted to reach the technological state of being able to coat these small (<20 mm) diameters.

5.3.3 Alternative manufacturing routes for small diameter tubes

It is recommended to use seamless tubes in most shell-and-tube heat exchangers. Nevertheless, for lower-pressure applications, welded tubes can be a viable option. If the GeoHex coatings deposited using PVD and thermal spray are proven to be able to withstand it, there is an option to introduce the coatings into the last step of welded tube manufacturing (Figure 4). The coatings would need to withstand the mechanical wear of the rolling during the last tube forming step as well as well as the welding of the tubes together. Further investigation into the properties of the coatings, their resistance to mechanical wear and welding before this option can be proven viable.

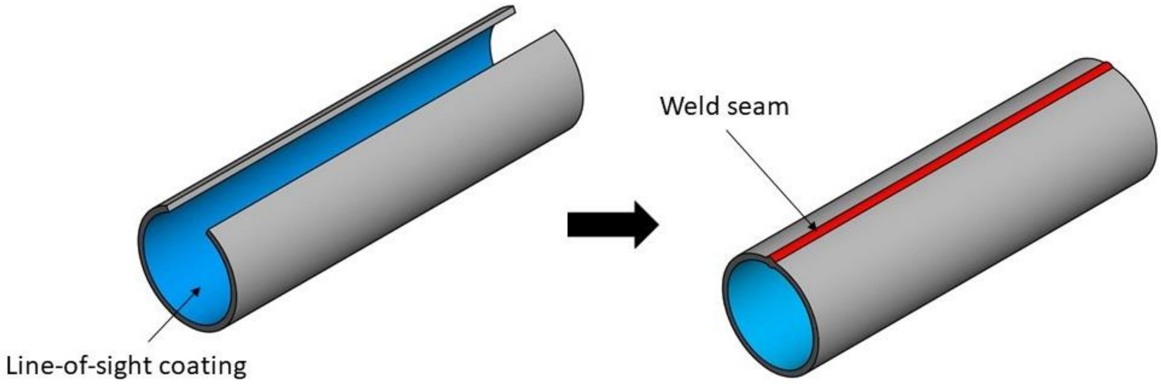

Figure 4: An alternative route of producing internally coated small diameter welded tubes coated with line-of-sight methods.

If the coating deposition methods can be modified to internally coat small diameter tubes of a certain length, which has been investigated and performed on diameters down to 10 mm although with tube lengths of 100 mm as detailed previously, another manufacturing alternative possibility is to weld together multiple internally coated tubes to form tubes of adequate length (Figure 5). Discussions between Zoe Minivielle at CEA and the company ACM, which will manufacture coated tubular heat exchangers for WP7 tests reveal that this alternative would not reduce the ability of the heat exchanger to service high pressure environments. However, again the coating would need to maintain integrity after welding.

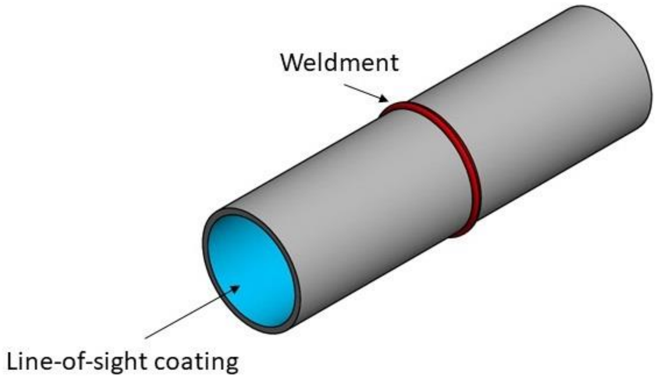

Figure 5: Another possibility of producing long small diameter pipes internally coated with line-of-sight methods.

5.3.4 Alternative geometries to small diameter tubes

In cases, where the benefits of using the line-of-sight GeoHex coatings for their scaling and corrosion resistance trump the heat exchange efficiency of using small diameter pipes the diameter of the tubes might simply be enlarged to suit the line-of-sight methods. The potential loss in heat exchange efficiency to compare with the benefits of applying the coatings would need to be investigated and examined in order for the market to implement this alternative. Additionally, it is noted that coating the internals of tubes, even for relatively large diameter tubes, e.g. 100mm, is not fully mature and development will be needed to ensure coating integrity. Another consideration is that the tube diameter has an influence on fluid velocity and therefore fouling, with more fouling expected with larger tube diameters and slower fluid velocity. Therefore, there is an additional cost-benefit consideration in that larger tubes enable anti-fouling coatings to be applied, but also increase the potential for fouling.

Tubes in shell-and-tube heat exchangers do have varying diameters, and generally range from diameters of 12.7 mm to 50.8 mm, although 19.05 mm and 25.4 mm are most common. The line-of-sight coatings could prove to provide attractive benefits to shell-and-tube heat exchangers with 50.8 mm standard tube diameter sizes, given future advances in the deposition process.

5.4 Welding and brazing of previously coated structures

Welding and brazing are two similar joining methods which both use high heat input to join together different parts permanently. Welding is generally considered to join metals by melting the base materials together, usually adding a third melted material into the so-called weld pool, called filler metal. Brazing, on the other hand, does not melt the base material but joins materials by using a filler metal with a lower melting temperature than the base material. An important parameter of brazing is the wettability of the surfaces being brazed together. High wettability, which also means low contact angle, of the melted filler metal on the surfaces is necessary to achieve good joints when brazing.

Welding and brazing are both used for the manufacturing of heat exchangers. Welding is widely used in shell-and-tube heat exchangers and in various types of plate heat exchangers, such as in semi-welded heat exchangers, where laser welding is used to join two plates together into modules, or “sandwiches”, which form the welded passes of the heat exchanger, as shown in Figure 6. The sandwiches are then placed into the heat exchanger setup with gaskets in between, to form the non-welded passes. This heat exchanger setup is often used when transferring heat between two different media, one of which is not suitable for usage with gaskets. Brazed plate heat exchangers are very common and are considered to be one of the cheapest options when it comes to heat exchangers. They do not use gaskets but instead, the plates are permanently joined and sealed using brazing.

Figure 6: A laser welded module "sandwich” heat exchanger plate within a semi-welded heat exchanger being disassembled.

Welding of coated materials adds additional factors that need to be considered when joining materials. If the coating and substrate materials are analogous, joining two coated structures together through welding might not necessarily compromise the weld joints. This of course is case-dependent and relies on a filler wire that is compatible with both the coating and the substrate. In the Geo-Coat project[29] we joined two parts of carbon steel pipe, S235JR, coated with laser metal deposited high entropy alloy. The filler wire chosen was an Inconel 625 filler wire and the welding method was tungsten inert gas welding. During the initial optical inspection, the weld seemed to form a strong joint between the two pipe sections. The joined pipe was subsequently sent to corrosion exposure testing. The testing just recently finished, therefore the analysis of the joint integrity is not available in this deliverable. Many of the GeoHex coatings are oxide coatings, rather than metallic, which might result in additional complications compared with those in GeoCoat.

A large part of the literature on the welding of coated steel focuses on zinc, or aluminium-zinc, coated steels. This is due to the popularity of zinc and Al-Zn galvanised steels in various industries. Welding of coated steels can, depending on the coating, be considered to have similar issues as the welding of dissimilar metals i.e. the formation of intermetallic compounds that form inside the weld joint where the different metals meet under high temperatures. These intermetallic compounds are usually brittle and often compromise the joint strength of the joined materials. It is generally considered best practice to try to reduce the thickness of the intermetallic compound layer between the dissimilar materials. This thickness is influenced by various welding parameters, most notably heat input[30]. For zinc-coated steels the welding issues faced are not the same as for metal coatings closer in properties to the substrate. The vaporisation temperature of zinc is lower than the melting temperature of steel. Under butt-weld or other joint configuration where the zinc vapour has an easy way to escape from the coating this does not normally introduce instability to the welding process. On the other hand, in the lap weld configuration as used in the manufacturing of semi-welded plate heat exchangers, the zinc vapours do not have an easy way of escaping from the melted metal around them and may compromise the welding process and the weld joint.

Yang et al. investigated the cold metal transfer welding of aluminium alloy 6061-T6 to zinc-coated steel with lap joints. They managed to control the thickness of the intermetallic layer between the dissimilar material to below 10 µm although the erratic zinc vapour produced during the welding led to an unstable welding process, although it could be somewhat controlled by increasing the gap distance between the base materials to allow the vapour to escape more easily from the weld zone. It was hypothesised that the presence of zinc on the steel surface could suppress the formation of brittle Al-Fe compounds in the intermetallic layer[31].

Kim et al. investigated the laser welding of Al-Si coated advanced high-strength steel in a butt weld joint configuration. They found that for the coated metals the fracture location in tensile shear testing was along the fusion line in the weldment due to stress concentration and brittle intermetallic compounds[32].

Zhang et al. showed that a modified metal inert gas CMT welding-brazing method can produce sound aluminium-zinc coated steel lap joints. The CMT method can considerably reduce the heat input into the welding/brazing joint, strengthening the joint by reducing the amount of brittle intermetallic compounds formed[33].

Milberg and Trautmann produced defect-free zinc-coated steel lap joints using bifocal hybrid laser welding. They discovered that using a small gap of a few tenths of a millimetre allows for the zinc vapour to escape and not introduce instabilities to the welding process or weakness to the weld joint[34].

It could be said in general that it is considered a better practice to coat welded structures rather than to weld coated structures. For non-line of sight coating processes such as ENP, this is an advantage for the process. The heat exchangers can be welded together and coated afterwards using the ENP coating method without closed off surfaces posing a problem for the process. For line of sight methods, this might be impossible in some cases, for example with welded plate heat exchangers. In those cases, it is necessary to coat the surfaces of the heat exchanger before welding/brazing and a coating holiday must be maintained close to where the weld will later be placed.

6. NON-DESTRUCTIVE EXAMINATION TECHNIQUES APPLICABLE TO GOEHEX MATERIALS

6.1 Techniques for inspection of the structure

GeoHex heat exchangers will rely on their coatings to ensure structural integrity and therefore it is imperative that the coatings are of adequate quality when manufactured, while the coatings will also need to maintain their effectiveness so that they protect the underlying structure for the lifetime of the heat exchanger. Non-destructive examination (NDE) might be used to check the quality of the coating after manufacture, while it will also play a crucial role in assessing the integrity of the coating and structure more generally throughout its lifetime. The normal procedures involved in the inspection of heat exchangers include:

- **Visual examination:** This is the simple process of looking at the examined part to identify flaws and defects. The technique of-course requires access to the examined surfaces, while boroscopes, magnifying glasses or digital imaging systems might also be utilised.
- **Liquid penetrant inspection:** This is a technique to detect surface breaking cracks and involves the use of a low viscosity fluid to give a visible indication of a flaw;
- **Magnetic particle inspection:** Involves magnetic particles being drawn into cracks/discontinuities before a magnetic field is used to reveal flaws;
- **Leak testing:** A number of methods can be used for leak testing, with pressure change leak testing perhaps the most relevant for heat exchangers which are closed systems and where there is a necessity to inspect inaccessible surfaces.
- **Radiography:** Where radiation, commonly X-rays, are passed through the component to detect differences in density, which are indicative of flaws. Radiography will be possible only with appropriate access, which will depend on the size and geometry of the component.
- **Ultrasonic testing:** involves the use of high frequency sound to detect flaws.
- **Eddy current testing:** An AC current is passed through an electrically conductive coil, generating a magnetic field, and eddy currents are generated when the coil is brought close to the sample surface. The eddy currents in the sample generate an opposing magnetic field. Near surface defects in the sample affect the magnitude of the eddy current and therefore also affect the current and voltage in the coil. These changes are monitored to allow detection of thickness loss or defects. Only surface breaking flaws can be detected in ferromagnetic materials, while some sub-surface detection can be achieved in non-magnetic materials.
- **Thermography:** Temperature variations are monitored using an infrared camera, with variations possibly indicating thickness loss or scale build-up. Samples can be heated conductively, using for example a hot plate, or using infrared radiation. Static thermography utilises a static heat source, while flash thermography utilises a brief pulse of radiation to heat the surface, with the thermal radiation from the sample measured as a function of time.
- **Thickness measurements:** Remaining wall thickness measurements are important when assessing corrosion damage. Ultrasonic methods can be used, where reflections from wall surfaces are measured, while pulsed eddy currents can also be used.

Of the above techniques leak testing is possibly not relevant to the assessment of coated heat exchangers as the underlying structure and welds/gaskets, as opposed to the coating, are responsible for leak tightness. All of the other techniques might be relevant to gasketed plate heat exchangers which can be dismantled to allow access to the surfaces of each of the individual plates. If the dismantling is carried out, most inspection methods including the volumetric methods such as Radiography and Ultrasonics can be applied. One of the major limitations of both Radiography and Ultrasonic Testing is access, i.e. the ability to place probes in appropriate positions to facilitate testing.

For semi-welded heat exchangers, the gasketed passes will also be accessible, so inspection will not be impaired. The welded passes will be adjacent to gasketed passes and therefore ultrasonic testing might be undertaken, from the gasketed side, to measure wall thickness and identify defects in the welded pass. Double wall single image radiography might also be undertaken but the technique lacks sensitivity compared with the more conventional single wall single image technique, while the defect location is also much more difficult to identify. Liquid penetrant and magnetic particle inspection, as well as visual examination and thermography, are not appropriate to assess the welded passes because of the lack of access to view them. It is noted that penetrant and magnetic particle inspection would require additional cleaning, following testing, which could be time consuming for samples with complex geometry.

These conventional techniques, which assess the structure as a whole, rather than the integrity of the coating, are nonetheless important as the detection of defects, or loss of wall thickness might indicate that the coating is compromised. This strategy is very blunt however, as damage to the structure might be very rapid once the coating is compromised and therefore there is a significant risk that failure might occur between inspection intervals. There are very limited inspection methods for fully welded heat exchangers, although some research has been undertaken into the use of embedded sensors to monitor strain while heat exchangers are in operation[35,36].

For shell-and-tube heat exchangers, the internal surfaces of the heat exchanger tubes are generally in contact with the more aggressive fluids and therefore would be more important for inspection. A common method of inspecting the internal surfaces of tubes is by pulling an ultrasonic probe, which is mounted on a rotating test head, through the tubes which are flooded with water. The trade name for this system is the internal rotary inspection system (IRIS). Guided wave ultrasonic testing can also be used to inspect the tubes, with small probes being developed so that they can be placed inside the tubes[37]. This can be important if the outsides of the tubes are inaccessible.

In terms of eddy current testing of heat exchanger tubes, the heat exchanger methods could include a multiplex/simultaneous injection instrument or a tubing/surface array instrument, including probing that combines bobbin and array features, which allow articulation of the probes facilitating testing of any part of the circumference of the tube with different target zones/areas depending on bobbin or array. Remote field testing (RFT) can also be used, allowing users to get the data in any testing radius without the need for bobbin or array features. RFT is only applicable to ferromagnetic tubes, such as carbon steel, and ferritic stainless steel[38].

6.2 Techniques for inspection of coatings

Coating thickness can be measured in a number of ways as discussed below:

- Ultrasonic methods can be utilised on thicker coatings[39] where the echo from the front face and the coating/substrate interface can be differentiated, however, more generally this technique is utilised to measure coatings on non-metallic substrates.
- Eddy current testing is more suited to the determination of coating thickness for non-conductive coatings on a conductive substrate, particularly where the coating has low electrical conductivity. Coating thicknesses between 20-300 µm were characterised using high frequency eddy current testing[40]. The calibration phase of the eddy current equipment is key to the inspection of the components; special calibration samples with the specific coating and appropriate thicknesses must be manufactured prior to the inspection to facilitate the calibration phase.
- Magnetic pull-off testing can be utilised for the case of a non-ferromagnetic substrate on a ferrous substrate. This test uses the principle that pull-off loads will be lower with increase in coating thickness.

Techniques to determine the level of adhesion between coating and substrate have been reviewed by Maxwell, 2007[41]. For coatings thinner than 50 µm, as will be the case for all of the GeoHex coatings the following techniques were applicable:

- Static and flash thermography; access must be considered as the area being inspected will need to be heated and imaged without either the heating source or camera being blocked.
- Acoustic emission: utilises sensors placed in-situ to listen for bursts of sound indicative of coating damage. This technique would not be practical for the assessment of heat exchangers, as sensors would need to be placed in the heat exchanger internals. Access will be an issue for acoustic emission to place and to remove the sensors after the inspection.
- Laser surface acoustic wave: Utilises laser pulses to cause rapid localised heating, before monitoring the resultant emitted surface acoustic waves. Similar to the other techniques, access will be an issue as some parts of the samples will not be accessible to the laser tool.
- Terahertz pulsed imaging: involves the use of ultra-fast lasers which illuminate the sample and are reflected by the coating-substrate interface. Discontinuities and their locations are determined using the output signal and the delay between the pulse being emitted and the signal being received. Due to the size of the equipment, this technique would be applicable only to some accessible parts of the sample.

All of the above techniques are reliant on the coated surface being accessible and no references were found related to the non-destructive inspection of coatings on inaccessible surfaces. Therefore it might be recommended that destructive testing is undertaken on representative coated samples to demonstrate adequate coating properties as well as fitness for service, in a manufacturing setting. Coating procedure specifications might also be produced, specifying the range of parameters that can be used to produce coatings.

7. SCALABILITY OF HEAT EXCHANGERS WITH GEOHEX COATINGS

7.1 Scalability of coating and joining processes

All of the joining technologies discussed in this report are already used in production and therefore it is not thought that any scalability challenges will be associated with them for the construction of GeoHex heat exchangers. Similarly, the technologies used for coating delivery are also widely used for production, however the particular coatings will of-course be optimised for application to geothermal heat exchangers. Therefore, aside from the technical challenge associated with production of the high performance coatings, which is in the scope of GeoHex, it is not thought that any additional scalability challenges will be encountered.

7.2 Scalability of non-destructive testing processes

It is not envisaged that scalability challenges will be presented considering most of them are used in production.

8. SUMMARY

This report reviews the manufacturability and scalability of phase change heat exchangers (HX) with GeoHex coatings. Some possible manufacturing routes related to coated heat exchangers were identified and applicable non-destructive testing methods were reviewed. Certain coating and heat exchanger geometries which needed special attention in terms of manufacturing were identified and solutions to foreseen issues detailed and discussed.

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